United States
Environmental Protection
Agency

Office of Research and
Development
Washington DC 20460

EPA/600/R-95/012
April 1995

EPA

21st Annual RREL Research Symposium

Abstract Proceedings

Margins for all text pages--
same as originals.

EPA/600/R-95/012
April 1995

21st ANNUAL RREL RESEARCH SYMPOSIUM

ABSTRACT PROCEEDINGS

Coordinated by:

Science Applications International Corporation
Lower Gwynedd, PA 19002

Contract No. 68-C2-0148
Work Assignment No. 3-7

Work Assignment Manager:

Emma Lou George
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
Cincinnati, OH 45268

RISK REDUCTION ENGINEERING LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

Printed on Recycled Paper

NOTICE

The abstracts presented in these Proceedings (with the exception of those from the Hazardous Substance Research Centers and National Institute of Environmental Health Sciences) have been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Today's rapidly developing technologies and industrial practices frequently carry with them the increased generation of materials, that if improperly dealt with, can threaten both public health and the environment. The U. S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of EPA with respect to drinking water, wastewater, pollution prevention, solid and hazardous waste, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between researchers and users.

These Abstract Proceedings from the 1995 Symposium provide the results of projects recently completed by RREL and current information on projects presently underway. Those wishing additional information on these projects are urged to contact the author or the EPA Project Officer.

RREL sponsors a symposium each year in order to assure that the results of its research efforts are rapidly transmitted to the user community.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

The 21st Annual Risk Reduction Engineering Laboratory (RREL) Research Symposium was held in Cincinnati, Ohio, April 4-6, 1995. The purpose of this Symposium was to present the latest significant research findings from ongoing and recently completed projects funded by the U.S. Environmental Protection Agency Risk Reduction Engineering Laboratory.

These Proceedings are organized into two sections. Part One contains extended abstracts of the paper presentations. Part Two contains abstracts of the poster displays. Subjects include pollution prevention demonstrations and life cycle analysis; remediation technologies from the SITE Program, RREL technologies, and oil spills remediation technologies; drinking water and wastewater technologies; municipal solid waste technologies; and hazardous waste technologies.

CONTENTS

PART ONE - PAPER PRESENTATIONS

A Practical Approach to Choosing a Substitute Solvent
Garry Howell, U.S. EPA, RREL 1

Onsite Recycling of Electric Arc Furnace Dust: The Jorgensen Steel Facility
Ivars Licis, U.S. EPA, RREL 5

A Replacement Solvent Cleaner/Degreaser Study at Duffy Electric and Machine Company
Johnny Springer, U.S. EPA, RREL 9

Evaluation of Supercritical Carbon Dioxide Spray Technology to Reduce Solvents in a Wood Finishing Process
Paul Randall, U.S. EPA, RREL 14

Demonstration of Alternatives for Vapor Degreasers
Dean Menke, University of Tennessee 19

Research Support to the Pollution Prevention Program of the U. S. Postal Service
Terri Hoagland, U.S. EPA, RREL 24

Life Cycle Design Framework and Demonstration Projects
Gregory Keoleian, University of Michigan 27

Industrial Assessment Database for Energy Efficiency and P2
Peter Polomski, Rutgers University 29

Applications of Supercritical Fluid Technology to Pollution Prevention and Waste Minimization
Ronald Turner, U.S. EPA, RREL 35

Development of High-Rate Trickle Bed Biofilter
Richard Brenner, U.S. EPA, RREL 38

Integrated System for Treating Soil Contaminated with Wood Treating Wastes
Carolyn Acheson, U.S. EPA, RREL 45

Development of a Multi-Level Protocol for Determination of Biodegradation Kinetics and Bioavailability of Organic Compounds to Enhance In-Situ Bioremediation
Henry Tabak, U.S. EPA, RREL 49

Design and Testing of an Experimental In-Vessel Composting System
Carl Potter, U.S. EPA, RREL 56

Evaluation of Abiotic Fate Mechanisms in Soil Slurry Bioreactor Treatment
John Glaser, U.S. EPA, RREL 61

Biotransformation of Sulfur and Nitrogen Oxides in Stack Gases
Rakesh Govind, University of Cincinnati 64

Anaerobic Biodegradation of Pesticides and TNT: SITE Emerging Technology Demonstration
Wendy Davis-Hoover, U.S. EPA, RREL 71

Iron Enhanced Abiotic Degradation of Chlorinated Hydrocarbons
Chien Chen, U.S. EPA, RREL 74

Testing the Sonotech Pulse Combustor in a Pilot-Scale Rotary Kiln Incinerator
Marta Richards, U.S. EPA, RREL 79

The Relative Effectiveness of Mineral-Based Sorbents for Metal Capture in a Bench-Scale Incinerator
Gregory Carroll, U.S. EPA, RREL 84

Research on the Low-Temperature Decontamination of Soil
John Rindt, University of North Dakota 89

A Summary of Two Recycling Technology Evaluations Completed Under the MITE Program
Lynnann Hitchens, U.S. EPA, RREL 94

Full-Scale Leachate-Recirculating MSW Landfill Bioreactor Assessments
David Carson, U.S. EPA, RREL 98

Removal of Mercury from Stack Gases by Activated Carbon
Radisav Vidic, University of Pittsburgh 103

Application of Ambersorb 563 Adsorbent Technology for Treatment of Chlorinated Organics in Groundwater
Russell Frye, Roy F. Weston, Inc. 108

Geosafe In Situ Vitrification SITE Demonstration
James Hansen, Geosafe Corporation 113

Unterdruck-Verdampfer Brunnen (UVB): An In Situ System for Remediation of Contaminated Aquifers
Michelle Simon, U.S. EPA, RREL 120

SITE Demonstration of Terra-Kleen Response Group's Mobile Sovent Extraction Process
Mark Meckes, U.S. EPA, RREL 125

Electrokinetic Remediation: Technology Status
Yalcin Acar, Louisiana State University 129

SITE Demonstration of Bioremediation of Cyanide at the Summitville Colorado Site
Leslie Thompson, Pintail Systems, Inc. 134

Reductive Photo-Dechlorination (RPD) Process for Safe Conversion of Hazardous Chlorocarbon Waste Streams
Moshe Lavid, ENERGIA, Inc. 140

Treatment of Hazardous Landfill Leachate by the Rochem DTM Membrane Separation Technology
Douglas Grosse, U.S. EPA, RREL 145

SITE Demonstration of the SVVS Technology
Paul dePercin, U.S. EPA, RREL 149

Use of Sulfate-Reducing Bacteria in Acid Mine Drainage Treatment
Thomas Powers, U.S. EPA, RREL 153

Buffing, Burnishing, and Stripping of Vinyl Asbestos Floor Tile
Bruce Hollett, U.S. EPA, RREL 159

Contaminants and Remedial Options at Pesticides Sites - A Technical Resource Document
Richard Koustas, U.S. EPA, RREL 162

Contaminants and Remedial Options at Selected Metals Contaminated Sites - A Technical Resource Document
Michael Royer, U.S. EPA, RREL 166

Overview of Technical Resource Document for Solvent Contaminants and Remedial Options at Superfund Sites
Uwe Frank, U.S. EPA, RREL 172

SITE Demonstration of the Dynaphore/Forager Sponge Technology to Remove Dissolved Metals from Contaminated Groundwater
Carolyn Esposito, U.S. EPA, RREL 177

Case Studies of the High Voltage Electron Beam Technology for Wastewater Treatment
Mary Stinson, U.S. EPA, RREL 181

SITE Demonstration of the ZenoGem™ Technology to Treat High Strength Wastewaters
Daniel Sullivan, U.S. EPA, RREL 186

Recovery of Monomers from Recycled Plastics
Laura Sharp, University of North Dakota 189

Two-Phase Ozonation of Chlorinated Organics
Dibakar Bhattacharyya, University of Kentucky 194

Evaluation of Base-Catalyzed Decomposition (BCD) Process for New York/New Jersey Harbor Sediment Decontamination
Dennis Timberlake, U.S. EPA, RREL 199

Electrokinetic Soil Remediation: Impact of Aqueous Phase Properties on Soil Surface Charge and Electroosmotic Efficiency
Leland Vane, U.S. EPA, RREL 203

Base Catalyzed Decomposition - New Hydrogen Donors and Reaction Activators/Catalysts
Fred Kawahara, U.S. EPA, RREL 207

Swirl Technology - Proper Design, Application, and Evaluation
Richard Field, U.S. EPA, RREL 211

A Multi-Chambered Stormwater Treatment Train for the Treatment of Stormwater
Robert Pitt, University of Alabama at Birmingham 217

Groundwater Contamination from Stormwater Infiltration
Tom O'Connor, U.S. EPA, RREL (Storm & Combined Sewer) 222

Colloidal Contaminants in Urban Runoff
Mark Wiesner, Rice University 227

Modelling Air Emissions from Contaminated Dredged Materials
Louis Thibodeaux, Louisiana State University 232

Bioremediation of Contaminated Sediments
Joseph Hughes, Rice University 236

Pollutant Fluxes to Aquatic Systems via Bed-Sediment Processes
K.T. Valsaraj, Louisiana State University 243

Accelerating Research and Development of Innovative Technologies
Norma Lewis and Randy Parker, U.S. EPA, RREL 247

Supercritical Extraction of Polychlorinated Biphenyls from Soils and Sediments: Remediation and Possible Risks
Lawrence Tavlarides, Syracuse University 248

By-Products from Supercritical Water Oxidation: Pathways, Kinetics and Mechanisms
Phillip Savage, University of Michigan 254

Oxidation and Hydrolysis of Acetic Acid and Methylene Chloride in Supercritical Water as a Means of Remediation
Philip Marrone, Massachusetts Institute of Technology 258

Soil Lead Remediation: Is Removal the Only Option?
James Ryan, U.S. EPA, RREL 260

Review of Mathematical Modeling for Evaluation of SVE Applications
James Mercer, GeoTrans, Inc 265

Representative Sampling and Analysis of Heterogeneous Soils
Ann Leitzinger, U.S. EPA, RREL 272

Bioremediation of Trinitrotolulene by a Ruminal Microorganism
Kenneth Williamson, Oregon State University 278

Full-Scale In-Situ Bioremediation of Trichloroethylene in Groundwater: Preliminary Modeling Studies
Mark Goltz, Stanford University 283

A Microbiological Surrogate for Evaluating Treatment Efficiency
Eugene Rice, U.S. EPA, RREL 288

Evaluation of Membrane Performance and Fouling by Pyrolysis- GC/MS
Thomas Speth, U.S. EPA, RREL 293

Biofiltration for Control of Volatile Organic Compounds (VOCS)
Dolloff Bishop, U.S. EPA, RREL 298

Potential Cryptosporidium Surrogates and Evaluation of Compressible Oocysts
Sylvana Li, U.S. EPA, RREL 305

Remote Monitoring and Control of Small Drinking Water Package Plant Systems
John Teuschler, U.S. EPA, RREL 309

Control of Copper Corrosion of Household Plumbing Materials
Michael Schock, U.S. EPA, RREL 312

Hydraulic Fractures As Subsurface Electrodes: Early Work on the Lasagna Process
Larry Murdoch, University of Cincinnati 318

Hydraulic Fractures as Anaerobic Biological Treatment Zones
Wendy Davis-Hoover, U.S. EPA, RREL 323

Advances in TCE-Degrading Thermophilic, Mesophilic, and Alkaline-Resistant Organisms
Steven Vesper, University of Cincinnati 325

Integrated Pneumatic Fracturing and Bioremediation for the In-Situ Treatment of Contaminated Soil
David Kosson, Rutgers University 329

Fundamental Criteria for the Better Design of Secondary Combustion Chambers
Guido Sacchi, MIT 333

Kinetics of Metal Leaching from Heavy Metal Contaminated Soils
John Van Benschoten, SUNY - Buffalo 338

Intrinsic Bioremediation of Chlorinated Solvents at the St. Joseph, MI Aquifer-Lake Michigan Interface
Peter Adriaens, University of Michigan 344

Monitoring and Control of Pseudomonas sP. Strain KC for In-Situ Bioaugmentation of Carbon Tetrachloride Contaminated Sites
Craig Criddle, Michigan State University 349

Remediating Munitions Contaminated Soils
Pat Shea, University of Nebraska 354

Risk Reduction Through Waste Minimizing Process Synthesis
L.T. Fan, Kansas State University 359

Prepared Bed Reactor for Full Scale Remediation of Soil Contaminated with Wood Preserving Wastes: Field Bioremediation Evaluation
Ronald Sims, Utah State University 364

PART TWO - POSTER DISPLAYS

The EPANET Water Quality Model
Lewis Rossman, U.S. EPA, RREL 368

Removal of Alkanes from Drinking Water Using Membrane Technologies
Carol Fronk, U.S. EPA, RREL 369

An Evaluation of Drinking Water Samples Treated with Alternative Disinfectants
Kathleen Patterson, U.S. EPA, RREL 370

A Measurement Method for Pollution Prevention Progress
Dave Stephan, U.S. EPA, RREL 371

Pollution Prevention Possibilities for Small and Medium-Sized Industries: The Waste Reduction Innovative Technologies Evaluation (WRITE) Project Summary
Ivars Licis, U.S. EPA, RREL 372

Pollution Prevention Research and Outreach
Ruth Corn, U.S. EPA, RREL 373

Computer Supported Information System for Measuring Pollution Prevention Progress
Rada Olbina, U.S. EPA, RREL 374

QA of Fortune
Kim McClellan, U.S. EPA, RREL 375

Treatability Data Base, Version 5.0
Glenn Shaul, U.S. EPA, RREL 376

Mine Waste Technology Program
Thomas Powers, U.S. EPA, RREL 377

Comparison of Reactor Designs for Biological Ex-Situ Soil Treatment
Carl Potter, U.S. EPA, RREL 378

Integrated Pneumatic Fracturing/Bioremediation for the In-Situ Treatment of Contaminated Soil
Uwe Frank, U.S. EPA, RREL 379

Results of a SITE Demonstration of the COGNIS-TERRAMET® Lead Extraction Process to Remove Heavy Metals from Soil
Michael Royer, U.S. EPA, RREL 380

RREL Site Remediation Technical Support Program
Benjamin Blaney, U.S. EPA, RREL 381

Location of Leaks in Pipelines Using Acoustical Principles
Anthony Tafuri and Robert Hillger, U.S. EPA, RREL 382

Alternative Treatment Technology Information Center Computer Database System
Daniel Sullivan, U.S. EPA, RREL 383

Clean Technology Demonstrations for the 33/50 Chemicals
Diana Kirk, U.S. EPA, RREL 384

Pollutant Element Foms within Sludges Generated by Treatment of Two Acid Mine Waters with Lime, Inorganic Sulfide and Sulfate Reducing Bacteria
Bill Chatham, Montana Tech 385

ACKNOWLEDGMENTS

The 21st Annual RREL Research Symposium was planned in partial fulfillment of Contract No. 68-C2-0148, Work Assignment No. 3-7 by Science Applications International Corporation (SAIC) under sponsorship of the U.S. Environmental Protection Agency. Emma Lou George of the Risk Reduction Engineering Laboratory (RREL) was the Work Assignment Manager responsible for coordinating this project. The conference program and activities were planned by a committee consisting of the following individuals: Emma Lou George, Daniel Sullivan, Lou Garcia, Franklin Alvarez, Randy Parker, and Walter Feige of RREL and Lisa Kulujian of SAIC.

A PRACTICAL APPROACH TO CHOOSING A SUBSTITUTE SOLVENT

S. Garry Howell and Johnny Springer
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 W. Martin Luther King Drive
Cincinnati, OH 45268

E. Thomas Marquis
Austin Laboratories Huntsman Corporation
7114 N. Lamar Blvd.
Austin, TX 78752

INTRODUCTION

Organic solvents have a multitude of uses in industrial processes, and, although there is some progress being made in replacing them with aqueous systems, many applications still require them. Many cleaning operations which require merely removal of light soils and easily emulsified oil or grease have been changed to aqueous systems with excellent results. Other applications, such as paint removal, cleaning of easily corrodible metal surfaces, removing polymer coatings, or baked on carbon, still may require application of an aggressive solvent. This paper will focus on coating removal, or paint stripping, and consider several instances where substitutes were chosen, and attempt to explain why (or why not) these substitutes performed well.

A major use of organic solvents is in the formulation of solvent coatings such as paints, enamels, varnishes, and lacquers. This is an extremely broad and specialized field, and will not be covered in this brief discussion. Instead, we will discuss the other end of the spectrum, that is, removing coatings which have reached the end of their useful life. The techniques for choosing solvents for coating removers can follow almost the same rules used to formulate them, except that while the resins used to formulate a coating are soluble in the proper solvent mixes, many coatings cure or crosslink after application and become insoluble, and merely swell or soften. Indeed, complete dissolution of the coating to be removed is undesirable, since a softened coating may be removed in large pieces, instead of as a viscous solution.

A brief outline of progress in solvent selection indicates that the earliest discovery that solvent mixtures were more effective than pure solvents was made by paint and varnish formulators. As knowledge advanced, the Edisonian approach of trial and error was replaced by reasoning; if one had a clue about the chemical structure of both the resins being dissolved, and of a group of available solvents, then trial and error could be reduced. Others postulated that physico-chemical parameters of both the solvents and resins or other solutes could be measured and described mathematically using solution theory. Modern solution theory relies heavily on work done 40 or more years ago by Hildebrand[1] and expanded upon by Hansen[2]. Hansen proposed that there were three contributors to the solubility parameter as developed by Hildebrand which he designated S_d, S_p, and S_h, each contributing in its own way to the overall solubility of a compound, and that a close numerical match (about 1 or 2 Hildebrand(H)) is required for mutual solubility of two compounds. S_d quantifies the dispersion or van der Waals intermolecular forces; these are the primary forces at work in hydrocarbons. S_p is a polar component common to acids, alcohols, etc. S_h is the hydrogen bonding parameter which designates the bond between hydrogen and two unshared electrons of another molecule. There are several tables of these values available, notably the Solvent Properties chart listing over 200 solvents prepared by Dr. Tom Marquis and published by Texaco Chemical Company, (now Huntsman Corporation). Huntsman Corporation has also developed a computer program which will calculate the solubility parameter of mixtures of solvents. Others have both tables and computer solvent selection programs available today[3], although some programs concentrate more on such factors as evaporation rate, smog formation, and flash points.

RREL and the U.S. Air Force recently funded an extensive assessment of pollution prevention opportunities at Tinker Air Force Base (TAFB), Oklahoma. Among the processes evaluated by the contractor, Battelle, were a number of depainting and degreasing operations where either toxic, flammable, or ozone depleting solvents were used. One of these was a depainting operation where aircraft radomes were depainted by showering them with methyl ethyl ketone (MEK).

The radomes to be depainted at TAFB had three coats of paint; an epoxy primer, a urethane rain erosion layer, then a low visibility topcoat. When time came to overhaul an aircraft, the radomes were removed, the coatings were scored, and the radome placed under a shower of MEK until the coating bubbled and could be squegeed off; the operation typically takes 1 1/2 to 3 hours. Because of the flammability, volatility, and toxicity of MEK, the shower was enclosed in a large closed booth with forced ventilation. During the process, MEK vapors were discharged to the atmosphere, and about 50,000 pounds were lost in 1992. One of the coauthors, Mr. Johnny Springer, was Project Officer on a task to determine if mixture of solvents would perform almost as well as MEK, be less volatile, have a higher flash point, and be less toxic. After looking through a table of solubility parameters, it appeared that a low volatility, non toxic solvent such as propylene carbonate (PC) blended with others to match the S_o, might make a candidate replacement solvent. Dr. Marquis agreed to try to develop a substitute mixture having the requisite characteristics, as he thought a single solvent would not be effective. Development of these formulations and some guidance on developing new ones are the subject of this paper.

METHODOLOGY

Using the Hildebrand solubility parameter of MEK as a rough starting point, Dr. Marquis made up several blends of solvents for laboratory testing. All of the blends contained propylene carbonate and N-methyl pyrrolidone (NMP) and at least one other solvent. The combinations were not chosen on their removal efficiency alone; vapor pressure (a large contributor to evaporation rate), flash point, and toxicity were also considered. Small sections of a condemned B-52 radome were immersed in the solvent blends in open beakers and compared to MEK, however it was noted that the volatile MEK evaporated rapidly, which was overcome by enclosing those beakers in polyethylene bags. Table 1 lists the time required for the paint to completely Bubble so that it could be easily wiped off. MEK took up to 12 times as long to bubble the coatings in this test as the mixtures did. This did not compare to the experience of the operators of the depainting operation at TAFB; their experience with the shower head arrangement indicated that complete removal of the paint usually occurred in less than three hours.

TABLE 1

Solvent	S_d	S_p	S_h	Strip Time Hours	Composition by Weight (%) PC NMP DBE
MEK Dry	7.8	4.4	2.5	24	
Blend 1	8.9	5.6	3.5	4	33.33% each
Blend 2	8.9	5.7	3.5	2	25 50 25
Blend 3	8.5	3.8	4.2	4	15 15 40 DPM 15 MIAK 15

MEK - methyl ethyl ketone; PC - propylene carbonate; NMP - N-methyl-2-pyrrolidone;DBE - Dibasic esters (Du Pont) (mixture of dimethyl esters of succinic, glutaric, and adipic acids);DPM - Dipropylene glycol monomethyl ether;MIAK - Methyl isoamyl ketone

Looking at the solubility parameters of the blends indicates that they were all fairly similar to those of MEK, and therefore should not differ too greatly in solvent activity. Questioning of the engineer in charge of the TAFB operation revealed that the removal time with MEK decreased after the first run or so, and that he suspected water absorbtion from the air could be the reason. From this information, the contract laboratory reasoned that enclosing the beakers was a mistake, and found that open beakers of MEK performed better. They then found that adding 12.5% of water to the MEK yielded bubbling times of 30 minutes. This contradiction of conventional wisdom was not apparent at first, since one would think that water would detract from, rather than augment, removal efficiency. An explanation of this was sought by reevaluation of the MEK solubility parameters, especially S_h. Looking again at Table 1, S_h of MEK is 2.5, only 1 Hildebrand (H) lower than Blend 2, the best of the three tested. In general a match within 1 H is considered adequate for solvent matching, but knowing the effect of water, the strongest hydrogen bonder, on the process, the effect on this parameter was calculated.

Solvent blend 2 in Table 1 is clearly the best paint stripper of the three blended solvents. Its hydrogen bonding parameter is 3.5 compared to 2.5 for MEK, and S_p at 5.7 is clearly higher than MEKs 4.4 H. It is then quite likely that an important part of this blends effectiveness is the hydrogen bonding ability of one or more of its components. NMP is hygroscopic, that is, it readily absorbs water out of the air. Blend 2, having 50% NMP, quite likely absorbed water during the time it was in the beaker with the radome section. The calculated S_h of both MEK and NMP are increasing as water is added, and at 12.5% water, MEKs S_h is about 4.3H; Blend 2 only requires 4% water reach 4.3H. This may partially explain why MEK/water is an effective stripper for this particular coating.

Solvent blends 1 and 3 are apparently affected by S_p and a third factor, dielectric constant, closely related to it. An attempt to incorporate this factor into an overall equation is underway, and will be the subject of a subsequent paper.

What's happening? Why does Blend 2 work almost as well as MEK/water? Why doesn't plain water remove the coating? While there is no trite answer to the questions, an effective remover/stripper must have the following characteristics:

A. Ability to diffuse into the film. Only one of the components of a blend may do this alone, but it may carry the others with it, as diffusion implies solubility, which means that polymer chains are separated[4] by solvent.

B. The proper solvent power to move coating molecules apart so that the film is softened and/or swelled. In this, and in (A.) above, the solvent must have at least one parameter which matches the coating film. For example, a styrene/butadiene rubber will hardly be affected by MEK but will swell considerably in hydrocarbons such as toluene. This is easily determined by experimentation, but also by looking at the solvent properties chart, and a list of polymer solubility parameters[5,6]. In this case, should the solvent be too effective and make the surface sticky, adding a poor or moderately hydrogen bonding solvent could produce a good swelling or removal agent.

C. Adhesion of a coating to a substrate can occur in several ways. In the case of the radome example above, it was apparently largely through hydrogen bonding, and increasing the hydrogen bonding parameter of the solvent with the addition of water allowed water to occupy sites at the polymer/substrate interface, weakening the polymer/substrate bond. Conversely, using toluene to remove a hydrocarbon coating may work, but if not crosslinked, the coating might dissolve completely, making a viscous solution almost as difficult to remove as the coating. This might be overcome by adding another component which is a moderate hydrogen bonder which would keep the resin from going completely into solution.

D. When the coating polymer is polar, as polyurethanes are known to be, a solvent of high

dielectric constant may aid in separating charged areas, thus making space for other solvents to soften the film.

If a table of polymer solubility parameters includes the one you wish to strip, so much the better, but if not, a practical technique for developing a stripper/ remover would be to find one that does the job, however volatile, toxic, or odoriferous it may be, and try to find its solubility parameters in the literature. From this point, one may develop a solvent blend which closely matches these parameters.

We are continuing work on finding solvent substitutes; our next task, which is to the reporting stage, is finding a blend which eliminates NMP, as it has recently come under suspicion of being a mutagen. Findings from the MEK/NMP/PC study above will help in this task. Our next planned project is to find a substitute for the phenol/methylene chloride stripper used on complete aircraft. This might prove to be much more difficult than stripping a relatively small, smooth surfaced radome. There are problems of corrosion, volume of solvent, and overall cost, since active solvents are more expensive.

REFERENCES

1. Hildebrand, J.H., Scott R.L. The Solubility of Non Electrolytes Reinhold, New York, 1950.

2. Hansen, H.J. J. Paint Technol. (1967) 40, 197.

3. In addition to Texaco-Huntsman, Dow Chemical Co., Shell, Arco, BP, Eastman, and EXXON have computer programs for choosing solvents.

4. Hildebrand reasoned that the energy required to separate two molecules could be measured by the heat of vaporization. While this measurement is feasible for small molecules, polymers usually decompose before they vaporize, so their solubility parameters are measured indirectly, by finding solvents which will dissolve or soften them. The solubility parameters of the solvents are then used to estimate that of the polymer.

5. Brandrup, J., Immergut E.H. Polymer Handbook Wiley Interscience, New York 1989 p. VIII 519.

6. Barton, A.F.M. CRC Handbook of Solubility and Other Cohesion Parameters CRC Press Boca Raton, FL 1983.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Ms. Ann Hooper and colleagues of F.W. Envirosponse and to Carlos Nazario of Tinker Air Force Base for their observations which led to this paper.
Thanks also Dr. William B. Jensen of the University of Cincinnati for much valuable insight on the aspects of hydrogen bonding/acid-base interactions.

ONSITE RECYCLING OF ELECTRIC ARC FURNACE DUST: THE JORGENSEN STEEL FACILITY

Ivars J. Licis
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 West Martin Luther King Drive
Cincinnati, OH 45268
(513) 569-7718

Robert C. Bermark
Washington State Department of Ecology
PO Box 47600
Olympia, WA 98504-7600
(360) 407-6812

INTRODUCTION

The steel-making industry produces a large amount of Electric Arc Furnace (EAF) dust as part of normal production. This waste is listed as K061, defined as "emission control dust/sludge from the primary production of steel in electric arc furnaces" under 40 CFR 261.32. A glass making technology called Ek Glassification™ (hereafter called "the Process") has been developed by Roger B. Ek and Associates, Inc. (hereafter called "the Developer") to recycle EAF dust and convert it, along with other byproducts of the steel-making industry, into marketable commodities.

This Process was evaluated under the Waste Reduction Innovative Technology Evaluation (WRITE) Program. The project was designed and conducted in cooperation with the Washington State Department of Environmental Quality, the Process Developer and the host test site, the Earle M. Jorgensen (EMJ) Steel Company of Seattle, Washington. Test personnel for EPA were supplied by SAIC Inc., on contract to EPA.

The overall objectives of the project were to conduct a pilot scale evaluation of the Process, investigate if toxic metals are leached from the products (such as colored glass and glass-ceramics; ceramic glazes, colorants, and fillers; roofing granules and sand-blasting grit; and materials for Portland cement production). Three glass recipes (Glass I, II, and III) were designed by the developer for potential use at EMJ. The EPA portion was focused on determining the toxic metals concentrations of the Glass II recipe, evaluating the P2 impact of using this Process in comparison to traditional methods of waste treatment and disposal, and assessing the economics of both.

METHODOLOGY

For this project, a portable pilot-scale process furnace was utilized. The furnace was located in the steel-melting area of the EMJ plant so that fugitive emissions could be collected with the steel plant's dust collection system and routed to the baghouse. Natural gas burners were used for the initial melting of the glass and to heat the furnace to its operating temperature of approximately 2,500°F. The furnace was also equipped with molybdenum metal electrodes, which could be used for partial or complete electric heating of the furnace. For this test, the electrodes were also tested to provide criteria for designing a full scale system, including requirements for the electric power supply.

EMJ supplied samples of feed materials for the test. Chemical analyses were performed on the feed materials to serve as a basis for mixing the three recipes. The feed materials used for the production of the glass included EAF dust, spent steel slags, spent refractories, mill scale, and grinding swarf. Approximate batch size was 300 lbs.

The Developer's test program consisted of the sampling and analysis of all three glass recipes, and process monitoring throughout the test.

The Glass II recipe was sampled and analyzed as part of the EPA testing activities. This recipe was used to prepare glaze, iron silicate for Portland cement production and sandblasting grit.

Glass was dispensed either into molds to form castable products or into a granulator (water quench) to form granular products. Once ladling or pouring was complete, the furnace was refilled with glass batch and the process was repeated.

Samples obtained were split for analysis by both EPA's laboratory (NET Pacific, Inc.) and the Developer's laboratory (Sound Analytical Services, Inc.) and placed in 1-L glass jars. The primary granular, and a composite of the castable samples were subjected to the TCLP in accordance with SW-846 Method 1311 and subsequently analyzed for eight RCRA metals plus zinc. The TCLP analyses performed on Glasses I and III by the Developer's laboratory were reported to be within TCLP limits.

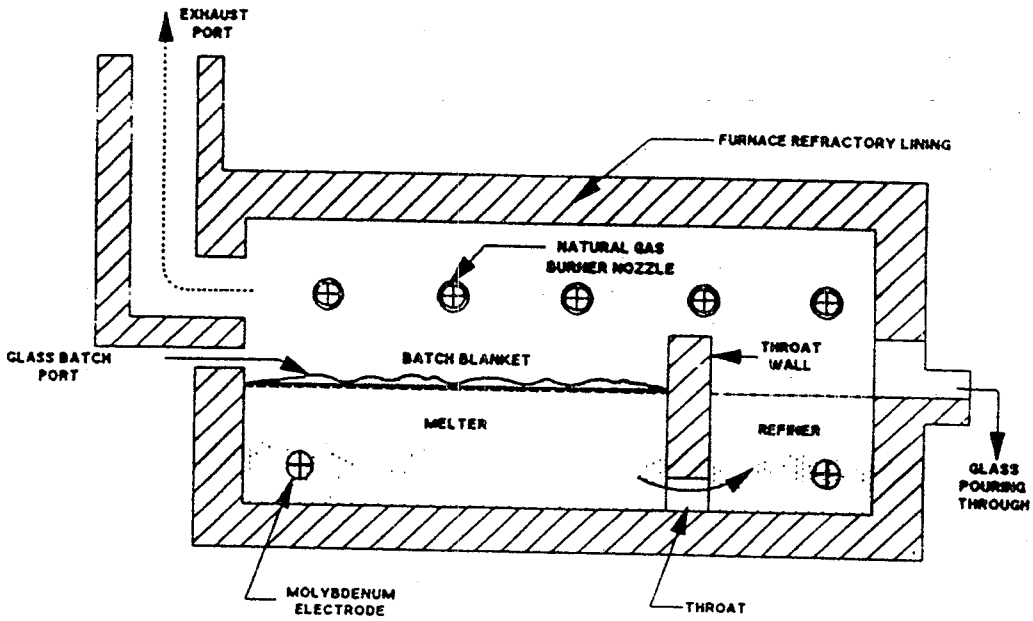


Figure 1. Ek Glassification™ Test Furnace for EAF Dust

RESULTS

Results from analyzing leachability characteristics for are shown in Table 1. The leachable metals concentrations, in both the castable and granular samples were within the TCLP limits for all compounds analyzed. Barium, chromium, lead, and zinc were the only compounds detected in either of the EPA samples. Comparison of these data to those obtained by the Developer produced similar results (for the granular product only).

TABLE 1. TCLP RESULTS AND COMPARISON TO REGULATORY LIMITS FOR SAMPLES FROM EMJ

EPA HW No.[1]	Contaminant	EPA Castable Sample[2] (mg/L)	EPA Granular Sample[2] (mg/L)	Developer Granular Sample (mg/L)	Regulatory Level[3] (mg/L)
D004	Arsenic	<0.0025	<0.0025	<0.2	5.0
D005	Barium	0.043	0.025	<0.1	100.0
D006	Cadmium	<0.0035	<0.0035	<0.1	1.0
D007	Chromium	0.050	0.13	0.1	5.0
D008	Lead	0.067	0.120	<0.1	5.0
D009	Mercury	<0.000086	<0.000086	<0.002	0.2
D010	Selenium	<0.001	<0.001	<0.3	1.0
D011	Silver	<0.0092	<0.0092	<0.1	5.0
----	Zinc	0.95	0.60	0.6	NR

1 Hazardous Waste Number
2 Average of duplicate samples
3 Regulatory levels taken from 40 CFR ch. 1 (7-1-90 Edition), Section 261.24, Table 1
NR Not Regulated

The major P2 impact of implementing this Process is the double effect of precluding the treatment and burial of the EAF dust in a hazardous landfill while negating the requirement of mining and processing virgin material for the purpose of making identical products. For this limited evaluation, the pollution involved in making glass products the traditional way, vs. recycling, the relative energy consumption, resource depletion, etc. were not quantified.

The recycling of other, non-hazardous wastes into the Process, is an added benefit.

The economic estimates indicate that a profitable operation is possible. Industrial product prices ranged from $2/ton (Portland cement materials) to $650/ton (glass ceramics/ architectural tiles feedstocks) based on 1991 information. Assuming that the average price of products sold is in the middle of the price range, and based on the Developer's projection of operating costs, in a ten-year period, the Process could produce a gross profit of $63,195,000. Avoiding disposal costs (at around $200/ton) could save another $43,040,000, for a total of $106 million. The capital costs for this facility would be $10,500,000 Additional benefits could be reduced liability, and avoidance of administrative costs for permits and managing of

hazardous waste under the old system. The actual savings realized will depend heavily on the types and amounts of products sold.

Air emissions and process wastewater were not analyzed for this test. For full scale applications these may need to be investigated under actual operating conditions.

Stack gas sampling data were previously gathered during earlier, pilot-scale tests at the Oregon Steel Mill (OSM). Although these data suggest acceptable air emissions, the data do not satisfy EPA stack testing protocols and standards. Prior to this project, on the basis of historical and glassmaking data from other sources, the Developer was allowed to proceed in building a full-scale facility at OSM by the Oregon Department of Environmental Quality.

The full report and project summary, titled "Recycling of Electric Arc Furnace Dust: Jorgensen Steel Facility", by Trevor W. Jackson, et al., are being published as EPA reports.

CONCLUSIONS:

The glass product types which were prepared by the Process and tested as part of this study resulted in relatively non-leachable glasses. The concentrations measured were lower than those allowed under RCRA regulations for TCLP.

- The Process utilizes both listed and non-hazardous foundry wastes to replace constituents that would otherwise be mined and processed from virgin sources as additives for glass-making. Ideally this results in both a conservation of resources and reduction of hazardous and non-hazardous wastes for disposal.

- This project did not focus on investigating compliance issues in terms of air emissions and waste water generated during batch charging, melting, quenching and drying of the three glass products. Although there is historical evidence for glassmaking, for a rigorous evaluation of species and concentrations, this type of testing would need to be evaluated at full scale under actual operating procedures/conditions.

A REPLACEMENT SOLVENT CLEANER/DEGREASER STUDY AT DUFFY ELECTRIC AND MACHINE COMPANY

Johnny Springer, Jr.
Waste Minimization, Destruction
and Disposal Research Division
Risk Reduction Engineering Laboratory
Cincinnati, Ohio 45268
(513) 569-7542

Bruce Sass
Battelle
505 King Avenue
Columbus, Ohio 43201-2693
(614) 424-6315

INTRODUCTION

Duffy Electric & Machine Company repairs and rebuilds electric motors. The company overhauls large electric motors (AC and DC with greater than 15 hp output). The company also overhauls small electric motors. The process involves gross cleaning of electromechanical devices to achieve a level of cleanliness that facilitates inspection, repair, and testing.

The cleaning system used in this study is comprised of a cleaning unit and a rinse unit. The cleaning unit is the IBR Series 400 parts washer, made by Inter Basic Resources, Inc., of Grass Lake, Michigan. The unit features an 11-inch-diameter impeller blade with 100-rpm rotation mounted at the inside bottom of an immersion tank. Cleaning fluid is circulated through a 50-µm filter at 5 gallons per minute, at 1 foot of head pressure to create turbulence in the cleaning fluid. Parts are cleaned as the fluid impinges on them. A 100-VAC electric motor powers the unit. The motor turns the impeller blade and runs the pump that circulates the fluid. The immersion well is 16 in x 19 in x 11.5 in and it holds approximately 14.5 gallons. Safety switches shut off the air motors if the loading door is open. The cleaning tank contains an insertion heater. The ester bath is heated to approximately 130°F. Light scrubbing is used to dislodge heavy grease and other difficult-to-remove contaminants.

The IBR alcohol rinser consists of a chamber that encloses a manifold sprayer. The tube-shape manifold is fitted with an array of nozzles to spray isopropyl alcohol (IPA) onto the parts from a variety of angles; the nozzles project a flat spray. Pneumatic pumps power the unit. The power supply is a high-pressure air line (110 to 120 psig) connected to the shop's air compressor. Alcohol drawn from a 5-gallon drum by an internal pump is sprayed inward toward the center of the manifold, which moves up and down at about 4 cycles per minute while spraying to better reach all of the part surfaces. While IPA is being delivered, runoff is caught by a pan at the bottom of the unit, flows to a drain, and is pumped by a smaller air motor back into the 5-gallon drum. When the IPA spray is deactivated after 5 minutes, the drain pump operates for another minute. Cabinet air is then purged by forcing air into the chamber through a venturi and exhausting through a hose to the outside of the building. The IPA rinser operates at ambient temperature.

The cleaner used in this study, Petroferm BIOACT™ 285, was selected because it is representative of its class of material. BIOACT™ is a mixture of high molecular-weight aliphatic esters and can be categorized as a semi-aqueous fluid. The cleaner is meant to be used without dilution and must be rinsed with alcohol, such as IPA, rather than with water. The alcohol is a technical grade that is at least 98% IPA, with the remainder being water. The IPA rinse is completely miscible with the ester solvent. The IPA evaporates rapidly due to its high vapor pressure (3 mm Hg @ 68°F).

METHODOLOGY

The product quality evaluation involved analytical testing to ensure that the new technology provides an acceptably cleaned product. Cleaning effectiveness was evaluated to show whether the new process cleans electric motor parts to an acceptable level of cleanliness (judged visually by an experienced technician at Duffy).

A more quantitative approach also was used to monitor cleaning effectiveness. Two similar motors were selected from the shop's inventory, each was disassembled and a rotor, housing with stator, and end cover were saved. The two sets of motor parts were contaminated with an oil/carbon mixture, representative of the soils found on actual motor parts. The soiled parts were heated in a 105°C oven for 16 to 24 hours (MIL-C-85570B) and then cleaned at regular intervals using the cleaning system. Cleaning performance was determined by measuring residual soluble surface material on the parts being cleaned in the cleaning system.

The parts were cleaned using the IBR cleaning system, then visually inspected by a Battelle technician and by Duffy staff. Then the parts were cleaned by agitation in a 1-L bath of hexane. Parts were classified as Set A or Set B. Afterward, the hexane was evaporated onto platinum weigh dishes to determine nonvolatile matter according to ASTM D 1353, i.e., the amount of residue remaining after cleaning.

Certain parameters for monitoring the condition of the cleaner and alcohol also were checked, including appearance, color, nonvolatile matter (alcohol only), specific gravity, and pH of a water extract of the ester cleaner.

One of the product quality parameters was designed to show possible adverse effects of the cleaner and IPA on wire insulation materials. Tests were conducted to evaluate whether the elastomers are compatible with BIOACT™ 285. Swell ratio (by weight and thickness change, ASTM method D 2765) was measured in small (approximately 2-inch-square) coupons of the elastomers Buna-N, Hypalon M, silicone, and neoprene. These materials are used for electrical insulation on the wire leads of older electric motors.

Waste volume was determined by measuring the volumes of spent cleaner and IPA after completion of testing. After cleaning about 108 parts over a twelve week period, the testing was terminated and the cleaner and alcohol were disposed of.

The economic evaluation compared the costs of the new cleaning system with what is currently used in the shop. A return on investment and payback period for installation of a new ester cleaning system were not calculated because at this shop the ester-based cleaning system cost more to use on an annual basis.

RESULTS

The data in Table 1 show that the residual soil levels on both sets of motor parts varied consistently over the course of the study. Except for the first measurement (day 8), residue measurements from day 37 to day 86 are within 1 to 2g per set of motor parts. The higher values on day 8 are believed to be due to removal of debris from the motors or to incomplete cleaning, because these results are not consistent with the remainder of the cleaning runs. Higher residue measurements at 71 and 79 days are believed to be caused by soil-loading of the ester cleaner.

The check of appearance and color was used to assess how soiled the cleaner and alcohol had become. By the 7th week of the study, or after washing 30 parts, the cleaner and rinse were very darkly colored. After 100 parts were cleaned, they appeared highly contaminated. Specific gravity is useful to track how much soil loading the cleaner and alcohol experience. Both solutions showed a

small, monotonic increase in specific gravity over time. The main contaminants expected to be present in the cleaner are oils and suspended solids; in the alcohol, the main contaminant is dragout cleaner.

The pH of the cleaning solution was measured for solution acidity or alkalinity changes over time. This test was done to determine whether exposure to moisture over time caused any acid increase in the ester cleaner. Acidity was determined by extracting samples of the cleaner with water (ASTM D 2110). The pH dropped rapidly, reaching a steady state of about 5.04 in the seventh week. In all cases, the materials in the compatibility tests experienced a net decrease in weight and thickness, which is probably caused by removal of process oils, colorants, stabilizers, and other additives. The loss of these constituents could have a negative effect on the performance of the elastomers.

In evaluating waste reduction/pollution prevention potential, the new cleaner achieves waste reduction through the elimination of solvent air emissions and potential discharge of wastewater to the environment because it is a nonaqueous process. However, the spent liquid must be disposed of. Contaminants in the ester cleaner primarily are oil, grease, and shop dirt. Therefore, the cleaner itself is assumed to present little environmental or health hazard during use.

Annual solvent usages were calculated to be 51.4 gal of cleaner and 55.2 gal of IPA. These values represent a worst-case estimate for the cleaner because it was not fully spent at the time the study was concluded. However, the cleaning performance was determined to be degrading. The annual volumes of waste liquids were calculated to be 39.0 gal of cleaner and 39.1 gal of IPA.

The petroleum solvent formerly used by Duffy Electric Company had been supplied at a rate of 360 gal per year. Industry estimates indicate that about half of the amount of petroleum solvents supplied is recovered. The remainder is lost due to dragout, evaporation, and spillage during transfers. About 180 gal of spent solvent can be collected for distillation and later reuse, and another 180 gal is unrecoverable. In contrast, the alternative cleaning system generates 106.6 gal of solvent (total) per year, of which 16.1 gal of IPA is unrecoverable due to evaporation, and 78.1 gal of liquid waste is produced.

Table 2 gives the annual operating costs of both the existing petroleum solvent cleaner and the alternative ester-based cleaning system. The major operating cost of the new cleaning system is the cost of the ester cleaner and IPA rinse. If a heating element is used, energy usage also needs to be considered. Disposal costs may vary depending on the system currently in use. At this shop a contractor retrieves the used petroleum solvent for recycling and supplies the shop with a clean recycled product for use.

CONCLUSIONS

The ester-based cleaner used at Duffy Electric performed adequately for cleaning parts when used in conjunction with a heater or with manual scrubbing for final touch-up cleaning. Soiled parts were cleaned in the ester system to determine the amount of residue remaining after cleaning to determine the life of the cleaner and to observe the rate of degradation. In general, parts removed from the alcohol rinse were visibly dry and residue-free upon removal.

The economics of the ester cleaner are not advantageous when compared to the recycled petroleum solvent used at Duffy Electric. Because the same contractor handles the supply and recovery of the petroleum solvent, its cost is relatively low. Currently, the ester cleaner is not recycled by a contractor, although the potential for recycling does exist. When the economics of the ester cleaning system are compared to those of other existing systems such as the use of chlorinated solvents, the results will differ. The ester cleaning system is likely to be less expensive than chlorinated solvent use.

The pollution prevention aspects of the ester-based cleaning system must be looked at on a case-by-case basis. In the shop that participated in this study, Safety-Kleen is contracted to provide a

recycled petroleum solvent and to perform recycling on the spent product, so the solid waste generated is minimal. Currently, the ester cleaning waste and the alcohol rinse are sent to hazardous waste disposal sites, and therefore the pollution prevention benefits for this shop in using an ester cleaner are limited to reduced waste toxicity and decreased VOC emissions. With further commercialization of the product, recycling may become more common and the benefits more apparent. In shops that use chlorinated solvents, which are usually more regulated, the pollution prevention benefits of an ester cleaner become more obvious.

Air emissions also need further study when evaluating the benefits of an ester- and alcohol based cleaning system. Industrial suppliers of petroleum solvents estimate that approximately 50% is unrecoverable. The petroleum distillate solvent contains an unknown amount of toluene, ethylbenzene, and other hazardous air pollutants. Certain chlorinated solvents result in evaporation of high percentages of these compounds. Many such compounds are included in the 33/50 Program list and are regulated as hazardous air pollutants (HAPs) under the Clean Air Act. The ester-based cleaner itself does not result in any significant evaporation. Although the alcohol rinse has a high evaporation rate, its constituents are not as hazardous as those found in petroleum solvents or chlorinated solvents.

Health hazards, although not specifically studied in this testing, are important to weigh when considering the ester-based cleaning system. The ester cleaner does not have the defatting properties common in other cleaners that lead to skin irritations and dermatitis.

TABLE 1. TOTAL SOLIDS RESIDUE ON PARTS

				Weight of Solids (g/part set)		
Sample ID	Motor Part	Sample Date	Days of Study	Primary	Duplicate	Average
H2	A	6/17/93	8	3.22	3.27	3.25
H3	B	6/17/93	8	3.05	3.29	3.17
H4	A	7/16/93	37	1.99	1.76	1.87
H5	B	7/16/93	37	1.44	1.24	1.34
H6	A	7/27/93	48	1.83	2.06	1.94
H7	B	7/27/93	48	1.33	1.55	1.44
H8	A	8/6/93	58	1.24	1.01	1.13
H9	B	8/6/93	58	1.62	1.66	1.64
H10	A	8/19/93	71	2.60	1.98	2.29
H11	B	8/19/93	71	1.50	1.30	1.40
H12	A	8/27/93	79	2.79	3.42	3.11
H13	B	8/27/93	79	2.73	2.81	2.77

TABLE 2. ANNUAL OPERATING COSTS

New Cleaning System	
Ester: 51.4 gal @ $20.00 per gal	$1,028
Isopropyl Alcohol: 55.2 gal @ $3.00 per gal	$166
Disposal: 78.1 gal @ $2.50 per gal	$195
Total[a]	$1,389
Existing Petroleum Solvent System	
Solvent purchase and disposal	$1,070
Total[b]	$1,070

[a] Total does not include labor, energy, and small maintenance costs.
[b] Total does not include cost of drying the parts, should faster drying be necessary.

EVALUATION OF SUPERCRITICAL CARBON DIOXIDE SPRAY TECHNOLOGY TO REDUCE SOLVENTS IN A WOOD FINISHING PROCESS

Paul M. Randall
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
26 West Martin Luther King Drive
Cincinnati, Ohio 45268
(513) 569-7673

INTRODUCTION

The purpose of this evaluation was to provide an objective evaluation of the use of supercritical carbon dioxide (CO_2) as an alternative technology for spray applied in wood finishing processes using reduced solvent formulations. Union Carbide has pioneered this technology under the UNICARB™ trademark. In the UNICARB™ process, the solvent-like properties of supercritical CO_2 are employed to replace a portion of the organic solvent in the conventional coating formulation. The supercritical CO_2 acts as a diluent solvent to thin the viscous coating just prior to application so that the coating can be atomized and applied with a modified spray gun. According to Union Carbide, 30 to 80 percent of the organic solvent in a coating formulation can be replaced with the supercritical fluid.

This evaluation addressed the issues of product quality, pollution prevention potential, and process economics. The testing was conducted at the Pennsylvania House Furniture Company in White Deer, PA. The White Deer facility produces cherry and oak chairs, stools, dining room tables, and four poster beds. At the time of the evaluation, the White Deer plant had been using the UNICARB™ process to apply nitrocellulose lacquer finish on their chair line for over a year with good results. Testing was done to quantify and qualify these results.

METHODOLOGY

In this technology evaluation, three issues were examined:

- Product Quality: to show that a coating applied by this technology meets company standards for a quality finish.
- Pollution Prevention Potential: to demonstrate that use of spray application technology for solvent replacement in coatings reduces volatile organic compounds (VOCs) released during finishing operations.
- Economics: to document the cost to install and operate this pollution prevention technology on an existing spray coating finish line.

In the product quality evaluation, the objective was to determine whether nitrocellulose lacquer applied by the UNICARB™ process provided a wood finish of equal or better quality than does the conventional nitrocellulose formulation and spray technique previously used by Pennsylvania House. At Pennsylvania House, the appearance and quality of the final finish are judged through visual examination by inspectors on the coating line. Special attention is given to gloss, smoothness, and lack of surface defects such as blisters or pinholes. In this project, product quality was evaluated through independent evaluations performed by Pennsylvania House staff and coatings experts at Battelle. Nine chair-back splats(three sample sets) were prepared by Pennsylvania House staff on the chair finishing line. All panels were finished by the same production methods that typically are used on the chair line.

The pollution prevention potential of the UNICARB™ process is based on reducing emissions of organic solvents without adding to other wastestreams. In this project, VOC emissions from the coating formulation and spray booth wastes(including solvent laden filters and nitrocellulose dust) were evaluated. In the UNICARB™ process, most of the fast- and medium-drying solvents are removed from the formulation, and the slow-drying solvents are adjusted slightly for better film formation. Supercritical CO_2 is used to replace the fast- and medium-drying solvents. Thus, the supercritical CO_2 spray process was expected to reduce VOC emissions from the chair-finishing line at the Pennsylvania House plant.

The objective of the economic analysis was to determine the payback period for the switch to the supercritical spray process from the conventional system. This was accomplished by comparing the operating costs of the UNICARB™ process to the conventional finishing process. The initial investment by Pennsylvania House in capital equipment and installation costs was considered, as were operating costs, which include materials, waste disposal, labor, and utilities. A return on investment (ROI) and payback period for the conversion was calculated.

For further details, a Quality Assurance Project Plan (QAPP) was prepared (USEPA & Battelle, 1993) which described the approach and scientific rationale.

RESULTS

The results of the product quality assessment indicated that the nitrocellulose lacquer finish applied by the supercritical CO_2 process is of equal or better quality than the finish obtained by conventional methods. Product quality verification was supported by coating experts, who typically will be more critical of the more subtle aspects of the coating finish, and by non-expert examinations. Both groups indicate that the UNICARB™ process will provide a finish with acceptable consumer appeal. Thus, it is concluded that the use of this process for the application of nitrocellulose lacquer finishes on the chair line at Pennsylvania House in no way compromises the quality of the finished product. These results are supported by the fact that Pennsylvania House has not seen an increase in returns since the inception of the UNICARB™ process. Further, the number of chairs that have to be reworked in the plant to remove finish defects before shipping has decreased, indicating that the production efficiency has remained the same or increased slightly since the UNICARB™ process was implemented.

Pennsylvania House records indicate that it takes approximately 16 oz of the conventional formulation to apply the two coats needed to achieve the desired quality in the finished product. The UNICARB™ process required about 7 oz of the reduced solvent formulation per furniture unit to achieve the same quality. There are two reasons that a smaller volume of coating is required when the UNICARB process is used: the higher solids content of the UNICARB™ formulation means more resin is transferred to the substrate per volume of formulation sprayed; and the increased viscosity of the film deposited by the UNICARB™ process inhibits film buildup by soaking into the wood substrate.

Data on the volatile content of the conventional nitrocellulose coating and the UNICARB™ coating were obtained from the coatings formulator (Lilly) and from direct determination of percent volatile/percent solids content of samples collected. VOC contents were determined by methods outlined in ASTM D2369. Liquid samples of both the conventional nitrocellulose coating and the nitrocellulose coating modified for the UNICARB™ process were collected for laboratory analysis. Coating formulation samples were taken from drums of coating material received by Pennsylvania House from Lilly. The supplier, lot number, and date were recorded in the laboratory record book for each field sample. At the White Deer facility, drums of coating are temperature equilibrated in the paint room for at least 24 hours before mixing and dispensing to the spray guns. Three samples were pumped into glass jars with Teflon® lid liners from a drum of conventional solvent-based nitrocellulose and three from a drum of the nitrocellulose coating reformulated for the UNICARB™ process. Sample containers were sealed to prevent evaporation during shipping.

The Material Safety Data Sheets (MSDS) for each of the formulations indicate the UNICARB™ coating is formulated using 16.7 percent less solvents (on an absolute basis) than the conventional formulation. Only 9.67 percent of the UNICARB™ formulation is comprised of Hazardous Air Pollutants(HAP) materials compared to 30.46 percent for the conventional formulation. On a per-gallon-of-coating-sprayed basis, this would result in a relative decrease in VOC emissions of 22.81 percent, with a 68.25% decrease in HAPs using the UNICARB™ formulation and 5.9 lb/gal for the conventional system.

In order to determine the reduction in VOC emissions on an annual basis, the number of gal of each formulation sprayed per year (Q) was estimated using the following equation:

$$Q = PV \times DOP \times OZ/16 \times 1/D$$

where PV is the daily production volume, DOP is the days of operation per year, OZ is the amount of coating sprayed per unit, and D is the density of the coating formulation. An average production rate of 250 chairs a day was assumed, with 200 production days a year. Pennsylvania House operates one shift a day. Density is reported on the MSDSs as 8.0 lb/gal for the UNICARB™ formulation and 7.7 lb/gal for the conventional formulation. The total volume of each coating sprayed per unit has been established at 7 oz for the one-coat UNICARB™ process and 16 oz for the two coats of conventional formulation. Under these assumptions, 2734.4 gal of UNICARB™ formulation are needed compared to the 6495.5 gal of the conventional formulation needed to finish the same number of units.

Using the VOC content reported on the MSDSs, this corresponds to an annual VOC emission reduction of 67.5 percent when the newer process is used. Even if the VOC content of the formulations were the same, an annual reduction in VOC emissions of 57.9 percent would be achieved because of the decreased amount of formulation needed per unit using the UNICARB™ process to achieve the same quality of finish.

Supercritical CO_2 is used in the UNICARB™ process to decrease VOC emissions. The reduced solvent formulation used by Pennsylvania House requires approximately 2.43 lb of CO_2 for every gal of coating concentrate sprayed with the UNICARB™ process. The amount of CO_2 released annually into the atmosphere can be determined based on annual usage of the UNICARB™ formulation. This has been determined previously to be 2734.4 gal for an annual production of 50,000 units. Using this as a basis, the annual emission of CO_2 from the finishing process is expected to be 6645 lbs (2.43 lb/gal x 2734.4 gal).

Carbon dioxide is not being produced through use of the UNICARB™ process. It is simply being used as a substitute solvent to thin and aid in the spray atomization process. The CO_2 used in this technology is supplied by various distributors of CO_2 which obtain and sometimes purify CO_2 generated as a by-product of other chemical processes. Thus, CO_2 used in processes such as supercritical CO_2 spray application of coatings does not actually contribute to the emission of CO_2 into the atmosphere.

Coating overspray at Pennsylvania House is collected on dry filters that are compressed and stored in 55-gal drums for disposal by landfill. One drum, at a disposal cost of $150/55 gal drum, can hold about 200 compacted filters and solid debris. Waste products generated will include dry and solvent-laden filters and nitrocellulose dust, both loose and trapped in the filters. No liquid waste was generated. Because Pennsylvania House does not separate waste by production lines, no physical data were available for the solid wastestream analysis. However, discussions with Pennsylvania House management and staff consistently indicated that the solid and liquid wastestreams were unaffected by the conversion to the supercritical CO_2 technology.

The chair-finishing process is the same except for the application of the nitrocellulose lacquer finish. Using the old process, two booths were in operation which required cleaning and maintenance.

With the UNICARB™ process, only one booth is needed. The transfer efficiency of the modified UNICARB™ spray gun and the air-assisted spray gun are both approximately 50% based on Union Carbide records. However, due to the increased solids content of the UNICARB™ formulation, more solid waste is generated from the overspray by the UNICARB™ process. The 28 dry filters in each of the two spray booths needed for the conventional two-coat finishing process were changed once per week for a total disposal rate of 56 filters/week. The 28 dry filters in the one spray booth required for UNICARB™ finishing are changed twice per week for a total of 56 filters/week. Dry paint and dust from the booths is packed in the disposal drums with the filters, but no increase or decrease in the total volume of these products was noted. In conclusion, no change was observed by Pennsylvania House in the volume of solid waste generated by converting to the supercritical CO_2 spray process on the chair line.

The results of the pollution prevention analysis clearly indicate that a reduction in VOC emissions occurred with use of the UNICARB™ process. The only new by-product of the process introduced into the wastestream is CO_2, but market information clearly indicates that the CO_2 sold commercially is itself a by-product of other production processes. Thus, the emission of CO_2 from the UNICARB™ process is not considered a detriment to the environment. Although the higher solids UNICARB™ formulation made it necessary to clean the spray booth more often, the difference in waste generation was offset by the fact that only one spray booth is needed with the UNICARB™ process.

The initial investment for the UNICARB™ process was $ 58,000, of which $ 46,000 was for equipment purchase and $ 12,000 for installation of the equipment. The operating costs were based on production of 50,000 chairs per year. The UNICARB™ process costs of $ 45,546 included $ 35,848 for the coatings formulation and $ 9,698 for the CO_2 equipment rental and concentrate. The conventional formulation cost was $ 46,883. By converting from a two-coat process to the one-coat UNICARB™ process, Pennsylvania House was able to decrease its utility costs by $ 11,000 because there was one less booth to operate and labor costs by $ 46,000 because one less finisher and one less sander were needed. No change was assumed for line waste handling and disposal costs or for finishing line maintenance.

The economic evaluation demonstrated a positive return on investment after the first year with a total payback period within 3 years if gas utility savings are included, and 5 years if gas utilities are not included.

This analysis reflects the economics of the actual operation is use on the chair line at the time of this evaluation. Implementing the UNICARB finishing process on the chair line at Pennsylvania House resulted in substantial annual savings in both utilities and labor. Cost savings could be realized from a decrease in raw materials costs, but these savings are offset by the leasing fees for the CO_2 tank and pump at Pennsylvania House. Additional savings could be realized by decreasing the size of the existing ovens to reflect the change to a one-coat system.

CONCLUSIONS

This evaluation of supercritical CO_2 spray technology for application of solvent-borne coating focused on three aspects: product quality, pollution prevention potential, and process economics.

The quality of the one-coat nitrocellulose lacquer finish applied at Pennsylvania House Furniture Company by supercritical CO_2 spray technology was demonstrated to be equal to or better than the quality of the two-coat finish applied by conventional air-assisted airless spray in this evaluation. In production, the furniture finish passes or fails on the basis of subjective evaluation of the total appearance by Pennsylvania House experts and ultimately by the customers. Quality of the supercritical CO_2 finish was supported by subjective evaluations by Pennsylvania House staff, coatings experts in the Battelle Coatings Group, and a group of non-experts, as well as by Pennsylvania House's records on customer acceptance and rates of in-plant defect corrections spanning more than one years's produc-

tion line use of the supercritical CO_2 spray technology support.

Release of volatile organic compounds during the finish process was reduced at Pennsylvania House by the supercritical CO_2 spray technology. The CO_2 used in this process is recovered from the wastestream of other industrial processes so it is not an additional contributor to global warming. Overall CO_2 may be decreased because many organic solvents that can add CO_2 to the wastestream are eliminated from the coating formulation. An annual reduction in VOC emissions in the range of 57% to 67% was demonstrated. Much of this reduction occurred because supercritical CO_2 is used at Pennsylvania House to apply a one-coat finish. The conventional finish process required two coats of nitrocellulose lacquer. Solid waste remained the same.

Capital investment costs incurred by Pennsylvania House will be recovered in the first 5 years of operation. Most of the economic benefit gained from conversion to the supercritical CO_2 process can be attributed to the reduction in labor and operating costs on the chair line at the White Deer plant.

This technology is one approach to reducing VOC emissions in the application of solvent-borne coatings. Product quality can be maintained and operating costs can be decreased. Capital costs will vary with each implementation but a favorable payback period can be anticipated, in light of the findings of this evaluation.

This technology evaluation focused on a single product type and coating formulation wood furniture industry. However, this specific supercritical CO_2 spray technology seems adaptable to a number of solvent-borne coating formulations and products.

REFERENCES

Battelle Memorial Institute, Quality Assurance Project Plan for Evaluation of Supercritical Carbon Dioxide Technology to Reduce Solvent in Spray Coating Applications, May 13, 1993.

Heater, K.J. and Parsons, A.B., Olfenbuttel, R.F., Evaluation of Supercritical Carbon Dioxide Technology to reduce solvent in spray coating applications," EPA/600/R-94/063, U.S. Environmental Protection Agency, Cincinnati, Ohio, April 1994.

FOR MORE INFORMATION

Paul M. Randall
U.S. Environmental Protection Agency
Pollution Prevention Research Branch
26 West Martin Luther King Drive
Cincinnati, Ohio 45268
Telephone: 513-569-7673
Fax: 513-569-7111
Email: Randall.Paul@epamail.epa.gov

DEMONSTRATION OF ALTERNATIVES FOR VAPOR DEGREASERS

Dean Menke - Center for Clean Products
Rupy Sawhney - Department of Industrial Engineering
University of Tennessee
327 South Stadium Hall
Knoxville, Tennessee 37996-0710
(615) 974-8979

INTRODUCTION

The "Cleaner Technology Demonstrations for the 33/50 Chemicals" is a cooperative agreement project between the Center for Clean Products and Clean Technologies and the U.S. EPA. Though originally designed to support the 33/50 Program, the results of this RREL-funded research will have a broad range of applications within industry and offer pollution prevention benefits beyond the 33/50 goals. The overall objective of this project is to evaluate substitutes of the 33/50 chemicals in order to encourage reductions in their use and release within specified priority use clusters. Priority use clusters, identified in the "Product Side of Pollution Prevention: Evaluating Safe Substitutes for the 33/50 Chemicals" report, are products and/or processes that consume a significant fraction of the 33/50 chemicals (1). The first evaluation, presented here, focused on the metal and parts degreasing priority use cluster and specifically substitutes for solvent degreasing processes that eliminate the use of the chlorinated degreasing solvent dichloromethane, tetrachloroethylene, 1,1,1-trichloroethane, and trichloroethylene.

In this study the Center for Clean Products worked directly with an industry partner to demonstrate substitute feasibility and to gain actual industrial information. Calsonic Manufacturing Corporation (CMC) is aggressively pursuing less polluting alternatives to solvent degreasing and agreed to participate as the Center's industrial partner to demonstrate solvent degreasing substitutes. CMC manufactures automotive parts included heaters, blowers, cooling units, motor fans, radiators, auxiliary oil coolers, and exhaust systems. Over the past four years, CMC had evaluated and implemented a number of environmental improvements to completely eliminate 1,1,1-trichloroethane (TCA) from their degreasing processes. This research focused on two of these improvements; an aqueous wash system which replaced five vapor degreasers of the radiator manufacturing line, and a no-clean processing alternative (i.e. application of an evaporative lubricant which does not require cleaning for subsequent processing) which eliminated two vapor degreasers of the condenser manufacturing line.

METHODOLOGY

The technical, environmental, economic, and national impact evaluations performed for the aqueous wash system and no-clean alternatives employed at the CMC facility had the following specific objectives:

1. technical evaluation
   - evaluated the substitutes' effects on process and product performance as compared to the solvent degreasing processes
2. environmental evaluation
   - evaluated the releases and off-site transfers of the 33/50 chemicals in the production process compared to the substitutes' chemical releases and transfers
3. economic evaluation
   - evaluated the costs, traditional and nontraditional, of the substitutes as compared to the 33/50 chemicals
4. national impact evaluation
   - evaluated and compared the overall life-cycle national environmental impacts of replacing the 33/50 chemicals with the substitutes

Data required to perform the technical, environmental, and economic evaluations were collected from CMC through data request tables, site visits, and interviews with CMC employees. Data request tables, completed by CMC employees and during site visits, allowed for the collection of process information including capital costs, operating and maintenance costs, utilities consumption, and production data. Questions concerning generation rates and disposal costs of waste (hazardous and non-hazardous) and wastewater accompanied the data request tables, as well as questions concerning permitting requirements. Tables and questions were directed at operations both before and after the process changes.

Site visits and interviews allowed Center staff to become familiar with the day-to-day operations of each CMC manufacturing line of interest. This information was used to extend the traditional economic evaluation by using activity-based cost accounting. Activity-based cost accounting specifically identifying the frequencies, durations, costs, and possible chemical emissions for every activity required to operate and maintain the solvent degreasers and alternative systems. Direct manufacturing activities, as well as indirect support activities (e.g. paper work, waste management, supervision) were identified and included in the evaluation.

These evaluations of CMC, supplemented by on-line databases and literature sources, were used to estimate the national environmental impacts that could occur if entire industrial sectors replaced solvent degreasing systems with the alternatives.

RESULTS

For this study, process and product performance were used as the two parameters to evaluate the technical feasibility of the alternative cleaning systems. As part of a continuous manufacturing line, the cleaning process (or no-clean alternative) has the potential to influence both of these parameters. Process performance was defined as the rate of production. Product performance was based on the part reject rate per unit of production which was determined from the leak test records of every unit manufactured. The production and part reject rates when the solvent degreasing processes were on-line were used as the baseline for comparisons with the alternative processes.

Production rates and part reject rates were both established through historical records and employee interviews. Evaluation of this data revealed that the production rate of either process line (radiator or condenser) was not affected by the change to the alternative system. Neither was the part reject rate of the condenser line, both before and after the process change to the no-clean alternative. The part reject rate for the radiator line, however, did significantly decrease after the aqueous wash system was installed. By implementing the aqueous wash system, and through the efforts of a Radiator Task Force established by CMC, the leak detection rate of the radiator line was decreased nearly 77 percent.

Though the alternative processes eliminated TCA releases and transfers from the radiator and condenser process lines, other chemical releases and transfers resulted from their implementation. Therefore, it was necessary to evaluate multiple medias (land, air, and water), as well as hazardous and nonhazardous wastestreams, to capture the full impact of the changes to the alternative processes.

Air releases and off-site transfers, reported to the 1992 Toxic Release Inventory (TRI), were the predominant releases and transfers of TCA from CMC's manufacturing facility. Table 1, below, summarizes these releases and transfers, and shows how they decreased over the past four years. TRI only requires facilities to report total releases and transfers of a chemical, not process-by-process releases or transfers. Therefore, specifically identifying the contribution to the overall reductions from either the radiator or condenser process lines was not possible. However, chemical use records for these process line, and employee interviews establish the following estimates:

1. the radiator process line, consuming 250,400 lb. of TCA for solvent degreasing in 1990, released 115,000 lb./yr. in 1990, 86,800 lb./yr. in 1991, and 0 lb./yr. in 1992; and
2. the condenser process line, consuming 88,550 lb. of TCA for solvent degreasing in 1992, released 75,500 lb./yr. in 1992, and 0 lb./yr. in 1994.

The implementation of these alternatives eliminated this consumption of TCA and the releases and

transfers associated with its use.

The implementation of the aqueous wash system for the radiator line, however, generated an 8,400 gallon/day water wastestream. Treated at an on-site pretreatment facility, this wastewater represents a significant waste management change. A nonhazardous, oily wastestream, skimmed from the surface of the aqueous wash reservoirs, was also a newly generated wastestream of the aqueous wash system. The no-clean alternative, by applying an evaporative lubricant to eliminate the need for parts cleaning, generated a new source of volatile organic compound (VOC) emissions to air. Based on lubricant consumption records, and assuming 100 percent evaporation, approximately 4,000 pounds/year (1.7 pounds/day) of volatile organics are emitted to the air from this alternative process.

TABLE 1. CMC TRI-REPORTED RELEASES AND TRANSFERS OF TCA

Year	TCA Air Emissions (lb./yr.)	Percent Change	TCA Off-Site Transfers (lb./yr.)	Percent Change
1990	425,756	-	233,530	-
1991	194,622	-54.3	338,525	45.0
1992	176,239	-9.4	206,345	-39.0
1993	89,446	-49.8	194,975	-5.5
1994*	66,800	-25.3	109,000	-44.1

* Values estimated from eleven months of TCA purchase records and trends of previous years

The traditional economic evaluation, results of which are presented in Table 2, indicated return on investments in as little 0.3 years (CMC-determined RI for the condenser line). The activity-based costs accounting economic evaluation had not been complete at the time of this abstract publication. However, initial review of the activities recorded during site visits to CMC identified significant differences in the required activities between the solvent degreasing processes and those of the alternative systems. These differences centered around two operations; one being the activities required to manage toxic chemicals and toxic waste; the other was the costs associated with the treatment of the aqueous system's wastewater. These results will be available by the time of the presentation, and copies of the methodology and results will be available.

TABLE 2 - COMPARISON OF SPECIFIC TRADITIONAL COSTS

Costs	Radiator		Condenser	
	Degreasers	Aqueous System	Degreasers	Evap. Lube.
Capital Investment	not avail.	$463,595	not avail.	$44,000
Chemical Costs	$182,490	$21,400	$67,040	$4,720
Waste Disposal	$20,000	$12,430	$13,735	$0

Chemical releases and transfers occur through out their life cycles; from their production, use, and disposal. Significant changes in these emissions can occur if entire industrial sectors were to implement alternatives to solvent degreasing similar to those of CMC. Therefore, a life-cycle, multi-media approach

to the national environmental impact evaluation was used to capture the overall environmental impacts of the alternatives.

Production facility releases and transfers of the chlorinated degreasing chemicals, in TRI reporting year 1992, totaled 1,286,823 lb. An estimated 34 percent of the chlorinated solvents produced in the U.S. were used in solvent degreasing applications in 1992 (2). Using a life-cycle approach, some fraction of the production emissions may be attributed to solvent degreasing; 34 percent to the production releases, establishing the potential upper boundary, equalled 440,000 lb. The EPA estimates that 24,500 solvent degreasers were operational in 1992 within the US (3). These solvent degreasers consumed approximately 440 million pounds of chlorinated solvents. Based on this information, the EPA also established a 1992 air emission baseline from these 24,500 solvent degreasers at 283.5 million pounds (4). Eliminating the use of chlorinated chemicals in solvent degreasing processes would greatly reduce or eliminate these emissions, both associated production releases and transfers, as well as the use and disposal releases and transfers. Phase-out regulations for TCA will reduce the use and releases/transfers of TCA regardless of the degree of which these alternatives are implemented.

The alternatives to solvent degreasing also have their life cycle environmental releases and transfers associated with them. Aqueous detergents may include in their formulations surfactants, saponifiers, chelators, corrosion inhibitors, and stabilizers. Specific examples from each of these additive classes were analyzed. Disposal of the water wastestreams may have significant effects on publicly owned treatment works (POTW). The POTW infrastructure of the nation was evaluated, and the potential impact the aqueous wash systems have on the infrastructure was established. A similar life-cycle approach was used to evaluate the mineral-spirits-based evaporative lubricants.

CONCLUSIONS

A significant number of studies are being conducted, or have been completed, which evaluate the effectiveness of cleaning alternatives. These studies primarily focus on one of the four evaluations performed in this study; little integration of all potential issues is attempted. This cooperative agreement with EPA expands the existing knowledge of alternatives to solvent degreasing by integrating technical, environmental, and economic issues, as well as addressing the life-cycle attributes of the alternatives on a nation scale.

The technical feasibility of CMC's process changes has proven to be positive. Significant reductions in toxic chemical releases and transfers were a result of the process changes, while other wastestreams were generated which required different management schemes. The traditional economic evaluation of this study did not reveal any unique conclusions. However, the activity-based cost accounting method did identify the costs associated with managing toxic chemicals and wastes, costs normally absorbed by the company as overhead. Finally, the national impact evaluation identified the importance of a life-cycle approach to evaluate pollution prevention projects. Though the alternatives evaluated in this research eliminate chlorinated chemical emissions, there are new wastestreams and wastestream constituents that must be addressed.

REFERENCES

1. Product Side of Pollution Prevention: Evaluating Safe Substitutes of the 33/50 Chemicals, EPA/600/R-94/178, U.S. Environmental Protection Agency, Office of Research and Development, September 1994

2. Product Side of Pollution Prevention: Evaluating Safe Substitutes of the 33/50 Chemicals, EPA/600/R-94/178, U.S. Environmental Protection Agency, Office of Research and Development, September 1994

3. National Emission Standards for Hazardous Air Pollutants: Halogenated Solvent Cleaning - Background Information Document, EPA-453/R-93-054, U.S. Environmental Protection Agency,

Office of Air Quality, November 1993.

4. National Emission Standards for Hazardous Air Pollutants: Halogenated Solvent Cleaning - Background Information Document, EPA-453/R-93-054, U.S. Environmental Protection Agency, Office of Air Quality, November 1993.

FOR MORE INFORMATION: Diana Kirk
Risk Reduction Engineering Laboratory
26 W. Martin Luther King Drive, MS-466
Cincinnati, Ohio 45268
(513) 569-7674

RESEARCH SUPPORT TO THE POLLUTION PREVENTION PROGRAM OF THE US POSTAL SERVICE

N. Theresa T. Hoagland
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
Pollution Prevention Research Branch
26 W. Martin Luther King Drive
Cincinnati, OH 45268
(513) 569-7783

INTRODUCTION

The USPEA Risk Reduction Engineering Laboratory's (RREL) Pollution Prevention Research Program focuses on the question "How should consumer, government and industrial products and processes be designed, manufactured, used, and/or performed so that their manufacture, use, disposal, or performance will have a minimal effect on the environment." Research projects addressing this issue are divided into five areas: (1) Clean Technology Projects; (2) Clean Products Projects; (3) Longer Term P2 Research; (4) P2 Assessments; and (5) Cooperative P2 Projects with Other Federal Agencies.

Under the general heading of Cooperative P2 Projects with Other Federal Agencies, a specific research program exists at RREL, which is referred to as the WREAFS Program (Waste Reduction Evaluations At Federal Sites). Many of the projects with the Departments of Defense (DOD) and Energy (DOE), are funded under the Strategic Environmental Research and Development Program (SERDP). The primary components of the WREAFS program are: (1) opportunity assessments; (2) research, development and demonstration; and (3) technology transfer.

Most of the WREAFS projects involve Pollution Prevention Opportunity Assessments (PPOA) and have been conducted in conjunction with DOD facilities; however, several "civilian" agencies are now beginning to participate in the program, as well. One major player which is emerging as a leader in addressing P2 on an agency-wide basis is the US Postal Service (USPS). Like most agencies, the USPS' operations entail many industrial-type processes that are common to the private sector industrial complex.

METHODOLOGY

The PPOAs were conducted by an assessment team that was composed of personnel from EPA, USPS, and SAIC, under contract with EPA. The assessments followed the procedures described in the EPA Report, *Facility Pollution Prevention Guide* (EPA/600/R-92/088), which identifies the four major phases of an assessment: (1) Planning and Organization, which includes organization and goal setting; (2) Assessment, which includes a careful review of a facility's operations and waste streams and the identification and screening of potential options to reduce waste; (3) Feasibility Analysis, including an evaluation of the technical and economic feasibility of the options selected and subsequent ranking of options; and (4) Implementation, which involves procurement, installation, implementation, and evaluation.

Many of the pollution prevention opportunities identified during WREAFS projects involve low-cost changes to equipment and procedures that can often be implemented by the facility without extensive engineering evaluations. Other pollution prevention opportunities identified require further study before full implementation can be realized. Typically, opportunities requiring further evaluation are those that have the potential to affect the process and/or require the use of new procedures or equipment. In such cases, it may be necessary to conduct demonstration projects.

Depending on the nature and state of development of the pollution prevention option selected for demonstration and evaluation, these projects may include: (1) process design, (2) detailed design and specification, (3) system procurement, (4) installation and start-up, (5) monitoring, and (6) reporting. Some projects may require bench-scale and/or pilot testing prior to, or as a part of, the demonstration project. Other projects may utilize full-scale equipment directly on the production line.

RESULTS

An example of the PPOA process as applied by the US Postal Service is the assessment conducted at a USPS facility complex in Buffalo, NY. The complex encompasses 25 acres with a vehicle maintenance facility (VMF) and general mail facility (GMF). At the VMF, a staff of automotive technicians maintain a fleet of 1,200 vehicles, which range from light delivery vehicles to 18-wheel tractor trailers. In a year, approximately 2,500 to 3,000 maintenance and repair jobs are performed and 500 vehicles completely painted with USPS colors at this facility alone, which is only one of 350 such facilities nationwide.

The GMF consists of a three-story building and a one-story 276,000 square foot mail processing floor (another building on the site houses the Computerized Forwarding System and the Undeliverable Bulk Business Mail (UBBM) operation). Dock positions for more than 50 trucks are located here and the building is occupied 24 hours every day by up to 1,515 full-time employees. The facility receives nearly two million pieces of mail each day for processing; nearly three million pieces are sent out daily for delivery. The Buffalo GMF processes all mail from the eastern seaboard destined for Canada, and as such serves as a concentration center for mail transportation equipment.

These industrial-type facilities generate industrial-type pollution. The GMF generates approximately 537 tons of waste per year, at an annual solid waste disposal cost of approximately $42,000. The wastes are comprised of 253 tons of old corrugated cardboard, two tons of computer paper, 46 tons of mixed office paper, 30 tons of metals, 13 tons of plastic film, 192 tons of "undetermined wastes," and an undetermined amount of machinery maintenance wastes (oil, grease and parts-cleaning solvent). Typical wastes that were produced by the VMF include about 4,100 gallons of waste petroleum naphtha generated annually during brake and engine parts cleaning operations and about 300 antifreeze were disposed of as hazardous waste.

As an example of the PPOA findings and recommendations:

Paint wastes comprise approximately 16 percent of all hazardous wastes generated by the VMF and are responsible for half of the hazardous waste management costs. The three primary PPOA recommendations for reduction of paint related wastes are described below.

- *Investigate water-based or high-solids paints* - Investigations at the VMF indicate that water-based primers may be substituted for conventional ones without affecting performance. Water-based top coatings, however, have been shown to exhibit insufficient durability. One solution currently under evaluation at the VMF involves the use of a waterborne primer with an acrylic enamel top coat.

- *Conversion to HVLP paint application systems* - HVLP spray guns operate at a much lower pressure than conventional spray guns, resulting in considerably lower paint waste due to bounce-back. Two HVLP spray guns were purchased for the VMF and have resulted in improved-quality paint jobs and savings in paint usage. Because the equipment was installed only recently, the VMF has not been able to provide accurate data on the incurred savings. The VMF's conservative estimate is a twenty percent reduction in paint usage per vehicle, with an associated reduction in VOC emissions. These figures are based on a four-month test period.

- *Install a paint-gun washer station* - At present, paint guns are washed in an open solvent tank. The PPOA recommended using specially designed enclosed paint-gun washing stations which reduce VOC emissions by 75 to 90 percent. The VMF has plans to purchase a paint-gun washer station during FY94.

CONCLUSION

Many of the recommendations made in the PPOA have been successfully implemented at the Buffalo facility. Approximately 624 tons of solid waste were disposed of by the GMF in 1992, incurring disposal costs of $42,120. In fiscal year 1993, waste generation was reduced to approximately 244 tons. Additional cost reductions are expected as further plans are implemented.

Aerosol chemical use has been eliminated in all postal facilities in the western New York District. Portable sprayers are used to dispense maintenance products, which are purchased in bulk five gallon containers. As a result, significant reductions have been achieved in waste aerosol cans and packaging. In 1992, over 2,400 aerosol paint cans were used at the VMF.

In the past, approximately 4,100 gallons of waste petroleum naphtha were generated annually during brake and engine parts cleaning operations at the VMF. This represented about one third of the total hazardous waste costs. The VMF has recently converted to an aqueous cleaner for cleaning brakes, which will eliminate over 2,000 pounds of hazardous waste annually. In addition, a longer-lasting solvent for cleaning automotive parts is in use which should also result in a substantial reduction in hazardous waste generation.

The Buffalo PPOA was just the beginning. PPOAs are, or have been conducted at other representative USPS facilities throughout the United States. These facilities include: a forensic laboratory; an engineering and research development laboratory; a stamp distribution center; a bulk mail center; an area supply center; and customer service centers. Results of these assessments and P2 plans will be shared with other Federal agencies and the private sector as they are received.

LIFE CYCLE DESIGN FRAMEWORK AND DEMONSTRATION PROJECTS

Gregory A. Keoleian
National Pollution Prevention Center
University of Michigan
Dana Building 430 E. University
Ann Arbor, Michigan 48109-1115
(313) 764-1412

Mary Ann Curran
Project Officer
Pollution Prevention Research Branch
Risk Reduction Engineering Laboratory
Office of Research and Development
US Environmental Protection Agency
Cincinnati, OH 45268

The life cycle design project was sponsored by the US Environmental Protection Agency's Pollution Prevention Research Program and was organized into two phases: Phase I - development of the life cycle design framework (published in Life Cycle Design Guidance Manual (EPA/600/R-92/226)) and Phase II - two demonstration projects and refinement of the framework (published in Life Cycle Design Demonstration Projects: Profiles of AT&T and AlliedSignal (in press))

Life cycle design is a proactive approach for integrating pollution prevention and resource conservation strategies into the development of more ecologically and economically sustainable products. The specific goal of life cycle design is to minimize the aggregate risks and impacts associated with a product life cycle, which encompasses raw materials acquisition through materials processing, manufacture and assembly, use and service, retirement, disposal, and the ultimate fate of residuals. Environmental impacts include resource and energy depletion and ecological and human health effects resulting from environmental releases and wastes. The following key elements of the life cycle design framework are outlined: a firm's environmental management system, needs analysis and project initiation, specification of design requirements, selection and synthesis of design strategies for minimizing environmental burden, and evaluation of design alternatives using environmental analysis tools.

Environmental issues can not be addressed in isolation of other design criteria. Multicriteria requirements matrices were developed as a key tool for systematically identifying and evaluating performance, cost, legal, and cultural requirements in addition to environmental criteria. Balancing these criteria in successful designs requires the participation of members of a cross-functional design teams. Industrial designers, process engineers, corporate executives, product development managers, production workers, environmental health and safety staff, purchasers, accountants, marketers, and legal staff each play a critical role in developing cleaner products.

Life cycle design is influenced by a complex set of factors. Design teams are challenged by external factors that affect the design process such as government regulations, market demand, public and scientific understanding of environmental risk, and existing infrastructure. Within a corporation successful application of life cycle design depends on a firm's environmental management system, which includes environmental policies and goals, environmental performance measures, organizational design, education programs and other factors.

In the Life Cycle Design Demonstration Projects, both AT&T Bell Labs and AlliedSignal, Filters and Spark Plugs applied life cycle design to the development of cleaner products. AT&T focused on achieving greater material and energy efficiency, a higher degree of recyclability, and fewer toxic constituents and releases in their design of a business telephone terminal. AlliedSignal developed design criteria to guide the improvement of future engine oil filters. the AlliedSignal team considered a cartridge filter with a reusable housing and a single-use, spin-on design. Both AT&T and AlliedSignal concluded that multicriteria requirements matrices are a useful tool for organizing, identifying, and evaluating the complex set of life cycle issues affecting the design of a product system. Major accomplishments and difficulties in implementing life cycle design are highlighted for each project.

The University of Michigan Research Team, in cooperation with the US EPA, is currently investigating life cycle design of automobile powertrains, automotive coatings, beverage packaging, and photovoltaics.

Industrial Assessment Database for Energy Efficiency and P2

Michael Muller and Peter Polomski
Office of Industrial Productivity and Energy Assessment

Introduction

The Energy Analysis and Diagnostic Center / Industrial Assessment Center (EADC/IAC) Program, in existence since 1976, is a federally funded service provided to small to medium sized manufacturing firms. The program is funded out of the Office of Industrial Technology of the U.S. Department of Energy with support from the Pollution Prevention Research Branch of the U.S. Environmental Protection Agency. Over 5000 energy assessments have been performed by teams made up of faculty and students from engineering schools at universities throughout the United States. Normally the teams perform a one day site visit at a manufacturing plant which follows an extensive pre-assessment data gathering function. Following the site visit, the assessment team prepares a written report for the industrial client which includes information about the plant's resource use, processes, waste handling, and other operations. In addition, several assessment recommendations (ARs) are written up with sufficient engineering design to provide for anticipated savings, implementation costs and simple payback for each AR. Nearly 50% of the more than 35,000 recommendations have been reported implemented by the industrial clients.

The program has been highly successful since its inception with four schools. With 30 universities now active Centers, combined assessments encompassing both energy conservation and waste minimization began on a limited basis during the 1994 program year. Expansion of this effort to all participating schools is planned for 1996.

Program benefits are not limited to the manufacturers served, students educated and faculty enriched but also extend to the community at large through data generated by the program. Since 1980, the data has been compiled from the assessments performed under this program and since FY 93 has been made available to the public via internet links to the Office of Industrial Productivity and Energy Assessment (OIPEA) at Rutgers University. For FY 95, a major revision to the database and the accompanying Assessment Recommendation Coding (ARC) scheme was undertaken to bring the structure in line with the combined nature of the program.

The EADC/IAC Program Database

The EADC/IAC Program Database has evolved from a flat compendium of data issued annually to a fully relational dataset updated daily. Data provided from the EADC/IAC reports is uploaded in spreadsheet "boilerplates" via the internet to OIPEA where it is processed through various translation algorithms and ultimately appended to the database. Responsibility for the accuracy of the data rests with the uploading Center but consistency checks are included within the translation schemes.

The database consists of two separate datasets: the Assessment Database [ASSESSxxx.DBF] contains information pertaining to each individual assessment and the Recommendation Database [RECCxxx.DBF] where information pertinent to each recommendation arising from the site visit is logged (Table 1). The database relation exists via a derived common identifier field consisting of the EADC/IAC name and report number which together comprise the ID field in the assessment and a portion of the SUPERID field in the recommendation database. To speed data transfer, most derived fields such as the ID field in the recommendation data set have been left to the user.

TABLE 1. FIELDS IN THE EADC/IAC DATABASES

ASSESSMENT		RECOMMENDATION	
Field Name	Description	Field Name	Description
id	Unique identifying number given to all records based on EADC/IAC Name & Report # .	superid	The unique identifying number given to all records based on EADC/IAC Name, Report # & Recc #.
eadc/iac	The identifier assigned to each EADC /IAC.	ar_number	The recommendation number sequentially as it appears in the report
repnum	The number assigned by the EADC/IAC to the visit & report.	appcode	Application for recommendation (see ARC Manual).
visitdate	The date of the assessment.	arctype	Recommendation type (see ARC Manual).
sic	The Std. Industrial Code for the plant's principle product.	arc	The code representing the specific recommendation made (see ARC Manual).
sales	The annual sales in dollars for the site reported by the client.	impdate	Client reported date of implementation of this Assessment Recommendation.
employees	The total number of employees on the site.	impstatus	Client reported implementation status of this Assessment Recommendation.
plant_area	The total amount in square feet of area used for production and office support purposes.	impcost	Client reported implementation cost. This cost may be estimated.
products	Principle products of the plant (in words).	impconser	Client reported amount of energy conserved upon implementation of the Assessment Recommendation.
resources	The total number of resources tracked at the plant.	impsaved	Client reported amount of money saved upon implementation of the Assessment Recommendation.
produnits	The units of production for the principle product (coded).	psourccode	The Primary Resource [coded]. This resource may not necessarily be the most important resource involved in the Assessment Recommendation, but is usually chosen based on greatest usage before conservation measures are suggested (logic follows for secondary & tertiary).
prodlevel	The client reported total number of units produced annually.	pconserved	The amount of primary resource conserved.
prodhours	Client reported annual production hours.	psaved	The primary resource's dollar savings for this Assessment Recommendation.
numars	The total number of ARs recommended in this report.	ssourccode	The Secondary Resource involved in this Assessment Recommendation.
--------	The annual usage and cost of energy taken from actual bills.	sconserved	The amount of secondary resource conserved
nrgcosttot	Total energy cost for this client.	ssaved	The secondary resource's dollar savings.

--------	The annual production and cost of waste.		tsourccode	The Tertiary Resource involved in this Assessment Recommendation.
wstcosttot	Total waste cost for the client.		tconserved	The amount of Tertiary resource conserved.
comments	General comments about the assessment.		tsaved	The Tertiary resource's dollar savings.
fy	The fiscal year in which the assessment was performed.		rebate	Indicative of whether the Assessment Recommendation included a rebate.
			incremntal	Indicates if the AR is to be implemented on an incremental basis- included in the database for the first two years only.
			descript	Description in words of the AR.

Resource Stream Tracking in the Database

Program expansion into the waste reduction / pollution prevention arena necessitated a revamping in the way resources are thought of in the database. Spirited debate centered around which database modifications would expand the presented information without sacrificing understanding of the issues. Ultimately it became clear that any suggestions or considerations for change must represent a clear and unmistakable improvement over past practice. The judgments made often became a compromise between two or more equally valid points of view with the simpler argument holding sway.

Perhaps the easiest decision centered on the number of resource streams to track ("track or tracking" refer to information inclusion in the Assessment Database in terms of cost and usage and in the Recommendation Database where savings and reductions appear). Waste reduction recommendations tend to involve energy, resources, and waste. An increase from two to three streams allows recognition of tertiary detail which in the past would have been buried in the recommendation calculations. Recommendations have been calculated that involve more than three streams (even six or more!) but good database management precludes carrying so many as this burdens the database with a large number of empty fields acting merely as place holders.

The stream definition question focused debate on tracking issues important enough for inclusion without becoming bogged down in minutiae. Previously, the only items tracked involved energy sources, additional income, material costs and operating costs. Stream types now define four primary areas of interest:

- ◇ Energy
- ◇ Waste Reduction
- ◇ Resource Costs
- ◇ Production

The energy streams remain unaffected. Waste minimization and pollution prevention plays require the obvious consideration of liquid and solid waste (hazardous and non-hazardous) and gaseous waste in the waste reduction category. Water disposal is differentiated from other liquids conceding the importance of this shrinking resource. Resource costs break out detail from the old material and operating cost fields. Material is broken into primary raw material and ancillary material cost. Personnel changes and administrative costs cover the operating cost category. Water consumption costs become germane to many waste reduction recommendations as to warrant inclusion as a distinct heading. The production streams track one primary product and one byproduct only.

Waste Reduction Assessment Recommendation Coding

Concurrent with the inclusion of waste reduction efforts in the industrial assessment is the addition of a new coding scheme for the assessment recommendations. Older coding consisted primarily of Energy Conservation Opportunities (ECOs) and the need arose for a coding system for recommendations involving enhancements in energy efficiency, waste minimization and manufacturing productivity. Most recommendations can be collected into groups that focus either on the same system or on the same general strategy for enhancement. Attempts were made to develop a coding scheme which would be consistent along either one of those lines, but neither approach proved satisfactory. The resulting organization of recommendations has been done in an "expert system" fashion. Therefore, the code has been assembled to best collect recommendations which would be considered together by an experienced professional. For example, recommendations for energy savings for air compressors (a system) are grouped. In a similar fashion, waste heat recovery (a strategy) recommendations are collected together.

A coding system like this will change frequently as new technologies and strategies reach the manufacturing floor. The ARC consists of a code as follows:

X.YYYY.Z

The first number, "X" is the recommendation type. Examples are 2 for energy savings, 3 for waste reduction etc. The second four numbers, "Y1Y2Y3Y4", detail the strategy being employed. The final number, "Z" is the application of the strategy, indicating whether the recommendation impacts the process, the building and grounds, or other application (Table 2).

Database Strengths and Weaknesses

The EADC/IAC Program Database is a unique representation of over 15 years of manufacturing site visits by engineering faculty. Updated daily, the database reflects the latest in industrial assessment techniques, energy and waste costs for small to medium size industrial plants throughout the U.S., recommended / implementation costs and savings for a large number of recommendations involving a variety of resource streams, and other useful data. The database has been used successfully around the world for pre-assessment preparation, utility Demand Side Management planning, government policy recommendations, in conjunction with case studies to gain insights into the investment criteria required for successful recommendations, and many other applications.

The database must still be viewed for what it is: a collection of information generated by human beings. There can be errors made in almost any step of the data collection process. There are biases in the data and disagreements over what constitutes an acceptable technology. Earlier datasets do not provide the level of detail found after FY 94. Electricity data does not break out demand, etc. This should be remembered during any and all analysis of the data.

Database Location

The database access location for downloading purposes is the OIPEA Home Page on the World Wide Web (W3) at: "http://OIPEA-WWW.rutgers.edu".

FOR MORE INFORMATION

Michael R. Muller
Director, Office of Industrial Productivity and Energy Assessment
Rutgers, The State University of New Jersey
Piscataway, NJ 08855-1179
(908) 445-3655

TABLE 2. WASTE MINIMIZATION / POLLUTION PREVENTION ARC GROUPS

Major Group (Y1)	Sub Group (Y2)	Heading (Y3)
Operations	Procedures	Process Specific
		Material Application
		Stripping
		Scheduling
		Desulfurization/Slag Mgmnt
		Reduction / Elimination
		Product Specifications
		Byproduct Use
	WasteStream Contamination	Dragout Reduction
		Rinsing Strategies
		Miscellaneous
	CAD/CAM	General
Equipment	General	Fault Tolerance
		Painting Operations
		Process Specific Upgrades
		Tank Design
		Automation
		System Monitoring
Treatment / Minimization	General	Neutralization
		Removal of Contaminants
		Material Concentration
Water Use	General	Close Cycle Water Use
		Reduction
		Water Quality
		Chlorination

Recycling	Liquid Waste	Oil
		Ink
		White Water
	Solid Waste	Sand
		Metals
Waste Disposal	General	Sludge Maintenance
		Miscellaneous
Maintenance	Cleaning / Degreasing	Mechanical Cleaning
		Reduction of Cleaning
		Rag Use
		Preventive Maintenance
	Spillage	Operations
		Hardware
	Other	Leak Reduction
		Miscellaneous
Raw Materials	Solvents	Use Reduction
		Emission Reduction
		Material Replacement
		Solvent Recovery
	Other Solutions	Water-Based Substitutes
		Other Substitutes
	Solids	General

APPLICATIONS OF SUPERCRITICAL FLUID TECHNOLOGY TO POLLUTION PREVENTION AND WASTE MINIMIZATION

Ronald J Turner
U.S. Environmental Protection Agency
Office of Research and Development
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268

INTRODUCTION

Many commonly used solvents and extractants are hazardous materials. In the past, careless disposal of these materials resulted in widespread contamination of groundwaters as proven by the large number of Superfund sites having this kind of contamination. Lack of adequate worker protection also resulted in a significant health risk in the workplace from contact with the liquid and vapor forms of the solvents.

One approach to the prevention of pollution and the reduction of worker exposure from conventional solvents is the use of less hazardous substitutes. One of the more novel substitutes is carbon dioxide. Although carbon dioxide is a gas at ordinary conditions, it can be liquified by application of pressure. In its supercritical state, it exhibits good solvent properties. Separation of the carbon dioxide from the extracted materials can be accomplished by pressure reduction, adsorption onto activated carbon, or with a membrane process, e.g., decaffeination of coffee.

Supercritical fluid extraction has been studied extensively on a laboratory scale to remove organic compounds from hazardous mixtures and contaminated waters. Few such systems have been employed commercially. One used liquified propane/butane to demonstrate extraction of organics from sediment at New Bedford Harbor, Massachusetts, under the EPA's Superfund Innovative Technology Evaluation program. However, supercritical carbon dioxide (SCCO2) may be the preferred choice for industrial extractions where relatively low temperatures are required.

Carbon dioxide is a non-polar solvent which is relatively non-toxic, non-flammable, with a critical temperature of only 31 degrees C and a critical pressure of 73 atmospheres. Extraction with SCCO2 offers several advantages over conventional solvent extraction, including minimization of organic liquid waste generation. Its solvent strength and low viscosity dependence on temperature and pressure makes SCCO2 attractive for replacement or recovery of organic compounds from liquid and solid materials. The use of SCCO2 in a remediation process allows rapid extraction of toxics and relatively easy solute concentration and recovery. Brady et.al.(1) successfully extracted PCBs, DDT and toxaphene from two types of contaminated soil using SCCO2. They observed that over 90 percent of the PCBs could be extracted in less than one minute. The SCCO2 extraction of naphthalene, anthracene, hexachlorobenzene and phenol from soil has also been reported.

The EPA is supporting a competitive university-based supercritical carbon dioxide research program administered by the Risk Reduction Engineering Laboratory, Cincinnati. The goal of this program is to develop and demonstrate current and new uses of SCCO2 in industrial processes as pollution prevention and waste minimization alternatives to chlorinated and other hazardous solvents. The degree to which this goal is accomplished will be determined by the acceptance of the SCCO2 processes for commercialization. A major factor limiting the commercial applications of supercritical fluid technology is the lack of reliable data for the design of the extraction or synthesis units.

This paper presents a brief overview of the university and federal laboratory collaborative efforts focusing on processes using supercritical carbon dioxide as a substitute for hazardous solvents. The SCCO2 technology applications under this program include extraction of natural pharmaceutical materials, phase-transfer catalysis, solvent replacement in chemical synthesis, temperature-solubility

relationships, and separation of organic materials from soils and slurries. A paper on the extraction of heavy metals with SCCO2 was presented by Ataai et.al. at the 87th National Meeting, A&WMA (2). This work is also supported by the EPA.

OVERVIEW OF THE SUPERCRITICAL CARBON DIOXIDE RESEARCH PROGRAM

Selective Oxidation in Supercritical Fluids (Department of Energy, Los Alamos National Laboratory)

This research partnership will develop new, environmentally-friendly, selective catalytic oxidation routes to the production of oxygenated hydrocarbons, using supercritical carbon dioxide as the reaction medium in place of hazardous process solvents. This should reduce by-product wastes and improve downstream separation of products/catalysts. For example, a new class of heterogeneous oxidation catalysts, titanium silicates, catalyze a number of useful reactions including epoxidation, alcohol oxidation, aromatic hydroxylation, and ammoxidation. Titanium silicates and analogs will be examined in both supercritical carbon dioxide and water/carbon dioxide mixtures using a number of substrates (alkenes, arenes, alcohols). The reactivity of olefins with several palladium catalysts in supercritical carbon dioxide/water mixtures will also be investigated, as there is considerable industry interest in new routes to polymer intermediates or precursors.

Supercritical Fluids for Phase-Transfer Catalysis (Georgia Institute of Technology)

This research, under C.A. Eckert, will study the replacement of toxic and hazardous fluids with supercritical carbon dioxide to design "cleaner" manufacturing processes. This includes catalyst solubility studies and determinations of reaction kinetics. Phase-transfer catalysis in supercritical fluids will be demonstrated, providing opportunities for faster heterogeneous reaction rates at milder conditions, tailored to achieve a variety of process goals. In correspondence with the EPA, Dr. Eckert cited an example of a successful phase-transfer catalysis reaction in a supercritical fluid which produced benzyl bromide from a quaternary ammonium bromide salt and benzyl chloride. This reaction is representative of an industrially important class of processes. A major chemical company is collaborating with Dr. Eckert to identify specific reactions where phase-transfer catalysis can be used for pollution prevention. This partnering will improve commercialization opportunities.

Environmentally Benign Pharmaceutical Processing (Georgia Institute of Technology)

This study will employ supercritical carbon dioxide in a separation process, replacing alcohols and chlorinated solvents to extract compounds of therapeutic value from natural organic materials. This activity is being conducted under Dr. A.S. Teja, and includes study of solubility, extraction, and analytical characteristics of taxol and taxol-related compounds. The present separation method uses exhaustive ethanol extraction, partitioning between water and chloroform, followed by successive chromatographic separations and crystallization from aqueous methanol. Dr. Teja proposes to combine supercritical extraction with high pressure adsorption and other techniques to yield a novel hybrid separation process. His initial studies indicate that the hybrid process will eliminate the use of chlorinated solvents and reduce the use of alcoholic solvents by 85%. This process could potentially be used for the production of a large class of taxol-like pharmaceuticals.

Supercritical Carbon Dioxide Extraction at Elevated Temperatures (University of North Dakota)

The goal of this study is to provide fundamental solubility data for a variety of semivolatile organic compounds, including polycyclic aromatics, and to determine the effect of temperature on CO2 extraction efficiencies of both polar and non-polar organic compounds. Solubility is expected to increase dramatically with elevated temperatures (i.e., above typical 50 to 100 degrees C) for many components thought to be insoluble, extending the usefulness of SCCO2 for industrial processing and extractive clean-up. The results of the investigations by Dr. Steven Hawthorne should apply to the supercritical carbon dioxide extraction of organic contaminants from soils, sediments, spent sorbents,

contaminated catalysts, and industrial waste sludges. The data generated in this study will also be used to predict solubility of organics in SCCO2, and will support the development of processes to replace hazardous organic solvents with SCCO2.

The Use of Supercritical Fluids for Waste Minimization (Louisiana State University)

This research will evaluate the practicality of SCCO2 to reclaim industrial organic materials by a non-destructive extraction process. Drs. K.M. Dooley and F.C. Knopf will utilize LSU's bench-and pilot-scale units to find the best conditions for specific extractions, and to implement new operating strategies for supercritical fluid extractions applicable to process streams. A countercurrent bubble column mode which can be directly scaled up to industrial practice will be operated on difficult-to-extract materials. The types of compounds to be tested include aqueous streams of alcohols, nitriles, and nitroaromatics; soils contaminated with polynuclear aromatics; and slurries of soils containing the above classes of compounds.

COMMERCIALIZATION OF SUPERCRITICAL CARBON DIOXIDE

Industrial chemists and engineers should begin to consider the potential uses of supercritical fluids as less hazardous solvents in chemical separation/synthesis applications. The successful commercial application of supercritical carbon dioxide technology for pollution prevention and waste minimization in organic solvent-using operations will help U.S. companies become more competitive by improving their manufacturing process efficiencies, reducing waste and associated disposal costs, and enhancing environmental compliance.

The EPA will assist its partners in this program with technical transfer of reports, presentations, and publications. Formation of partnerships between the technology developers and industry will also aid commercialization. Another possibility under consideration is a future EPA workshop to highlight the results of the supercritical fluid research under the EPA program with the inclusion of similar efforts conducted under private or other public sponsorship.

REFERENCES

1. Brady, B.O., Dooley, K.M., Knopf, E.C., and Gambrell, R.P., Ind. Eng. Chem. Res., 26,26 (1987).

2. Beckman, E.J., Ataai, M.M., Extraction of Mercury, Arsenic, and Lead from Soils Using Supercritical Carbon Dioxide and Novel, CO2-Philic Chelating Agents, 87th Annual Meeting, A&WMA, Cincinnati, Ohio (1994).

DEVELOPMENT OF HIGH-RATE TRICKLE BED BIOFILTER

Francis L. Smith, George A. Sorial, Makram T. Suidan, and Pratim Biswas
Department of Civil and Environmental Engineering
University of Cincinnati
Cincinnati, OH 45221-0071

Richard C. Brenner
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

INTRODUCTION

Since enactment of the 1990 amendments to the Clean Air Act, the control and removal of volatile organic compounds (VOCs) from contaminated air streams have become a major public concern (1). Consequently, considerable interest has evolved in developing more economical technologies for cleaning contaminated air streams, especially dilute air streams. Biofiltration has emerged as a practical air pollution control (APC) technology for VOC removal. In fact, biofiltration can be a cost-effective alternative to the more traditional technologies, such as carbon adsorption and incineration, for removal of low levels of VOCs in large air streams (2). Such cost effectiveness is the consequence of a combination of low energy requirements and microbial oxidation of the VOCs at ambient conditions.

Preliminary investigations (3) were performed on three media: a proprietary compost mixture; a synthetic, monolithic, straight-channeled (channelized) medium; and a synthetic, randomly packed, pelletized medium. These media were selected to offer a wide range of microbial environments and attachment surfaces and different air/water contacting geometries. The results of this preliminary work demonstrated that 95+% VOC removal efficiency could be sustained by all three media at a toluene loading of 0.725 kg COD/m^3-d, but at different empty bed contact times (EBCTs). For the pelletized medium, this performance could be achieved at an EBCT of 1 min, for the channelized medium at 4 min, and for the compost medium at 8 min. Both synthetic media developed headloss over time, with the pelletized medium showing a pressure drop in excess of several feet of water after sustained, continuous operation. These results left open the question of which medium could provide the optimum combination of high VOC elimination efficiency at high loading with minimum pressure drop.

This paper discusses the continuing research being performed for development of biofiltration as an efficient, reliable, and cost-effective VOC APC technology. The objectives of the recent research were to conclude the evaluation of the three media and to develop workable strategies for the removal and control of excess biomass from the (ultimately) selected pelletized attachment medium.

METHODOLOGY

The biofilter apparatus used in this study consisted of three, independent, parallel biofilter trains, each containing 4 ft of attachment medium: biofilters "A", "B", and "C". A detailed schematic and equipment description is given elsewhere (4). Biofilter "A" was filled with a proprietary compost mixture, "B" with a Corning Celcor® channelized medium, and "C" with a Manville Celite® pelletized medium. Biofilters "A" and "B" were square and had an inner side length of 5.75 in., and biofilter "C" was round with an inside diameter of 5.75 in. The air supplied to each biofilter was highly purified for complete removal of oil, water, CO_2, VOCs, and particulates. After purification, the air flow for each

biofilter was split off, the VOCs were injected into it, and then it was humidified and fed to the biofilters. The air feed was mass flow controlled, and the VOCs were metered by syringe pumps. The flow direction of the air and nutrients inside each biofilter was downward. Each biofilter was insulated and independently temperature controlled.

Buffered nutrient solutions were fed to biofilters "B" and "C". A detailed description of the nutrient composition is given elsewhere (4). Each of these biofilters independently received a nutrient solution containing all the necessary macro- and micro-nutrients with a sodium bicarbonate buffer. The nutrients required in biofilter "A" were included as part of the original compost mixture.

RESULTS

Biofilter "A": This biofilter run on the compost medium was made to evaluate the effect of temperature, and then loading, on toluene removal efficiency. Figures 1a and 1b summarize the biofilter performance. The biofilter was started up and, after some operational difficulties, stabilized by day 10 at 52°F, 50 ppmv toluene, 2 min EBCT, and a removal efficiency of about 58%. On day 17, the temperature was raised to 60°F, resulting in a rise in efficiency to about 75%, which decreased after day 24 into the 60's, and after day 32 into the 50's. On day 41, the temperature was increased to 70°F, resulting in a gradual increase in efficiency to about 75% by day 47. On day 53, the temperature was increased to 80°F, resulting in an increase in efficiency into the low 80's. On day 61, the temperature was increased to 90°F, resulting in a further increase in efficiency to the mid 90's (Figure 1a). After day 77, the feed was increased slowly to about 95 ppmv toluene, resulting in a drop in efficiency to about 88%. Further increases in the feed concentration to a maximum of 180 ppmv toluene on day 139 resulted in a further decline in efficiency to about 58% (Figure 1b). The run was terminated on day 215.

Biofilter "B": This biofilter run was made on the synthetic channelized medium to evaluate the effect of temperature, and then nutrient feed rate, on removal efficiency. The biomass in the channels of the medium remaining from the previous run was removed by hydroblasting the eight 6-in. high medium blocks from top and bottom. The corners of these square blocks were filled with grout to provide a "round" active block. This last step was taken to match a round block cross section with the round pattern of the nutrient delivery spray nozzle. Figure 2 shows the biofilter performance as a function of time. The biofilter was started up at 52°F, 50 ppmv toluene, and 2 min EBCT. By day 36, the removal efficiency had drifted over a range from about 62% to 80%. On day 36, the nutrient feed rate was increased from 30 to 60 L/day while keeping the mass loading of the nutrients constant. The increased nutrient flow rate effectively doubled the wetting cycle from 20 sec/min to 40 sec/min. An immediate increase in efficiency to 99% was observed, which then quickly dropped and ranged by day 50 between about 30% and 70%. On day 50, the nutrient feed rate was increased to 90 L/day (increasing the wetting cycle to 60 sec/min), but the efficiency dropped from 69% and ranged by day 67 from about 22% to 65%. On day 67, the temperature was raised from 52°F to 60°F and the efficiency increased to 66%. By day 75, the efficiency was 87% and this level was maintained to day 83. After day 83, the temperature was raised further, in 10°F steps, to 90°F but the efficiency did not improve. In fact, for the rest of the run, at 90°F and 60 L/day, the efficiency ranged between about 58% and 83%. The run was terminated on day 152.

Biofilter "C": The first biofilter run on the synthetic pelletized medium was made to evaluate the effect of pressure drop, and then temperature, on toluene removal efficiency. The biofilter was charged with pellets used in the previous run. These pellets were washed by hand in hot water (150°F) until the accumulated surface biomass had been removed and the pellets were free flowing. Figure 3 presents the biofilter performance as a function of time. The biofilter was started up at 52°F, 50 ppmv toluene, and 2 minutes EBCT. By day 21, the removal efficiency was 99% and, by day 27, it had reached 100% and remained at this level until day 50. From day 51 to day 57, the EBCT was gradually reduced to 1 minute, causing the efficiency to drop to 84%. Subsequently, the toluene removal efficiency rapidly increased to the low 90's and remained in that range until day 81. On day

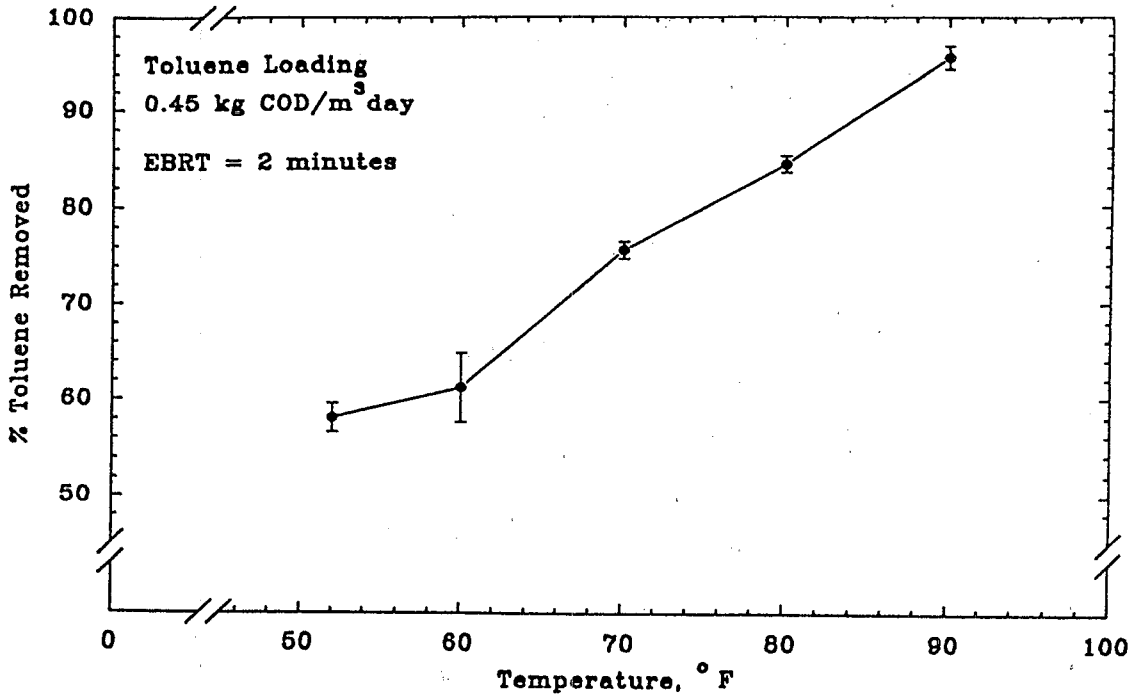


Figure 1a. Effect of Temperature on the Performance of the Compost Biofilter

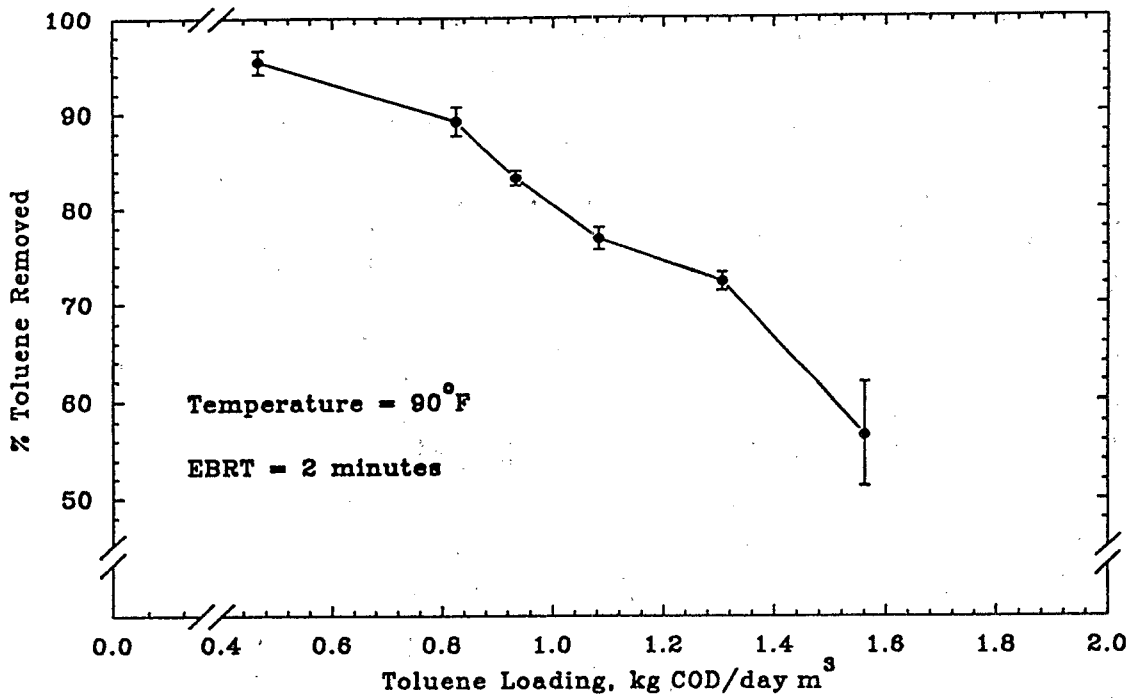


Figure 1b. Effect of Toluene Loading on the Performance of the Compost Biofilter

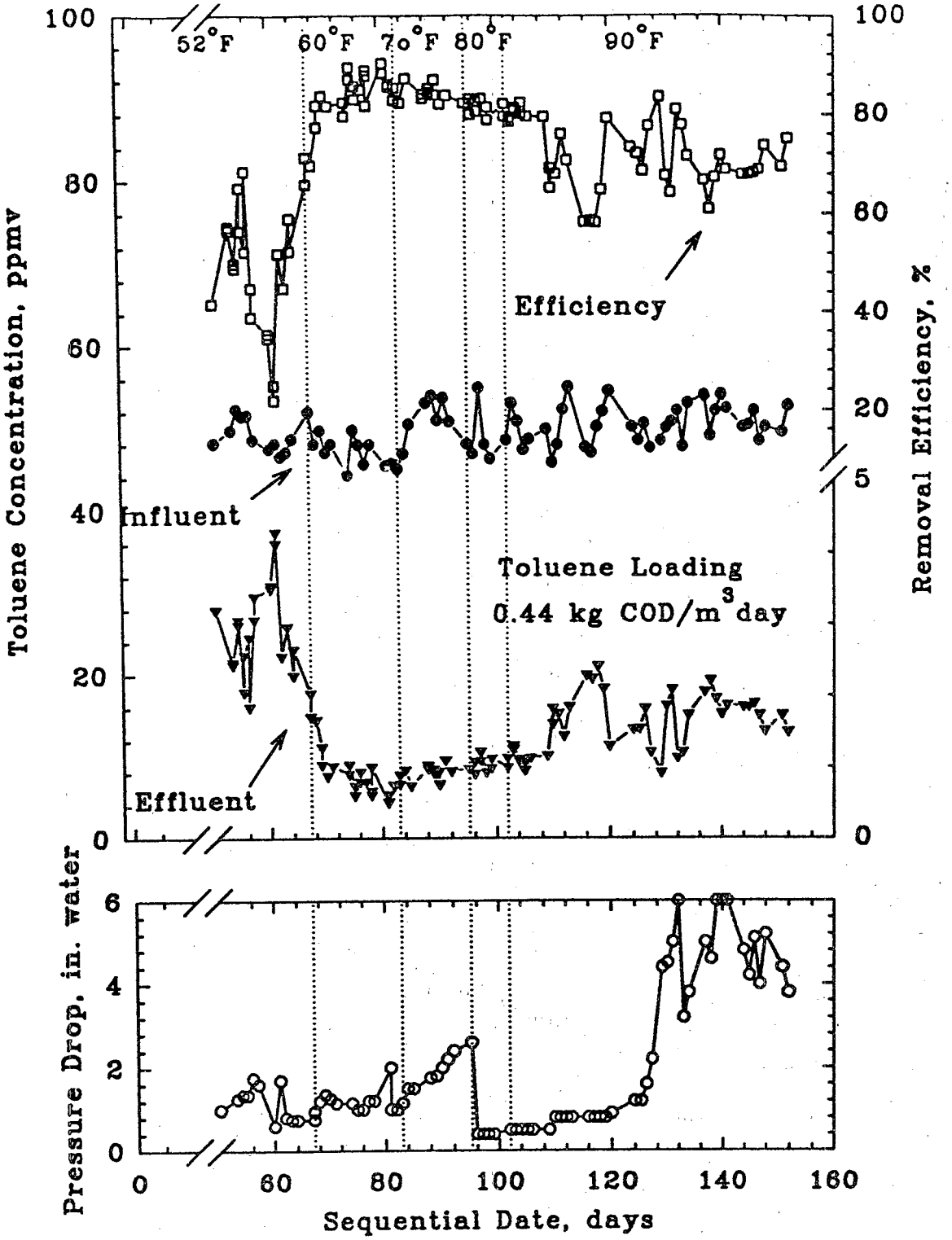


Figure 2. Performance of Channelized Biofilter with Respect to Toluene Removal at an EBRT of 2 Minutes

82, the temperature was raised to 60°F and the efficiency steadily rose until complete biodegradation of the toluene was reached on day 89. This essentially 100% efficiency in toluene removal was maintained through day 97. During the period between day 54 and day 97, pressure drop across the system increased from 0.2 to 5.5 in. water. From day 97 to day 111, the efficiency dropped steadily from 100% to 86% while the pressure drop increased from 5.5 to 6.0 in. water. On day 112, the temperature was increased to 70°F and the efficiency rebounded by day 113 to a peak value of 97%, after which it dropped to 85% by day 188. On day 119, the temperature was raised to 80°F and the efficiency rose to about 89% by day 120. During the period from day 112 to 120, the pressure drop increased from 6 to 18 in. water. By day 128, the efficiency had steadily dropped from 89% to 77% as the pressure drop increased from 18 to 27 in. water. This pattern of a steady loss of efficiency with a coincident increase in pressure drop suggested the development of short circuiting within the biofilter medium due to biomass accumulation, which resulted in a significant reduction in actual contact time.The first run was terminated on day 128.

The second biofilter run on this medium was conducted to evaluate routine biomass control by backwashing. The biofilter was charged with a 50:50 mixture of fresh pellets and pellets from the previous run. The used pellets were thoroughly washed by hand in tepid water (90°F) until the accumulated surface biomass had been removed and the pellets were free flowing. Figure 4 shows the biofilter performance as a function of time. The filter was started up at 90°F, 50 ppmv toluene, and 2 min EBCT. By day 4, the removal efficiency was 100%. (Note: this second run, started up with pellets washed in tepid water, contrasts with the slower start-up in the first run, where the pellets were washed with hot water.) On day 8, the feed was increased to 250 ppmv toluene and the efficiency dropped to 97%, ranged between 92% and 98% until day 25, when it again reached 99%. Subsequently, the efficiency dropped as low as 86% before regaining 99% on day 81, after which the efficiency was nearly always 99+%. Initially, backwashing was performed once per week by using 100 L of fresh water at a rate of 6 gpm. After day 28, the frequency was increased to twice per week and, after day 38, the volume was increased to 200 L. These changes were made because measurable pressure drop was observed between backwashings. On day 73, the backwash rate was increased to 15 gpm in order to induce full fluidization. Although the pressure drop increase was minimal, the efficiency did not improve, suggesting some form of channelizing within the bed. Therefore, on day 80, the length of the backwash period was increased to 1 hour by recirculating the backwash water. After this final adjustment, the toluene removal efficiency, as mentioned above, achieved and sustained 99+%. During this latter period, the total volume of water used per backwash was optimized to 120 L. Of this volume, 70 L were used for the 1-hour backwash recycle, while the remaining 50 L were used to flush the released solids from the reactor.

CONCLUSIONS

A marked improvement in toluene removal efficiency with increasing temperature was demonstrated in this study for the compost mixture, the channelized medium, and the pelletized medium. The direct consequence of this finding is that much less medium would be needed for a biofilter operating at 90°F than at 52°F, resulting in a proportional reduction in capital cost. The economic tradeoff with the cost of heating the incoming air should usually favor operation at these warmer conditions.

The modest performance of the compost mixture with respect to increased loading complimented our earlier findings with respect to decreasing EBRT (3). Unfortunately, implicit limitations of the experimental apparatus may have resulted in reduced performance. Specifically, the manufacturer recommended using a width-to-depth ratio of 1/1, rather than 1/8. They also stated that from their experience the only effective means of controlling bed moisture content was to weigh the entire biofilter. This was impossible with the heavy stainless steel unit used here, which was bolted to a support frame. Several moisture measurement and control strategies were attempted, but it was never possible to be certain that the bed moisture content was consistently at the reported optimum range, i.e., between about 50% and 60% (5,6). The sometimes erratic performance may

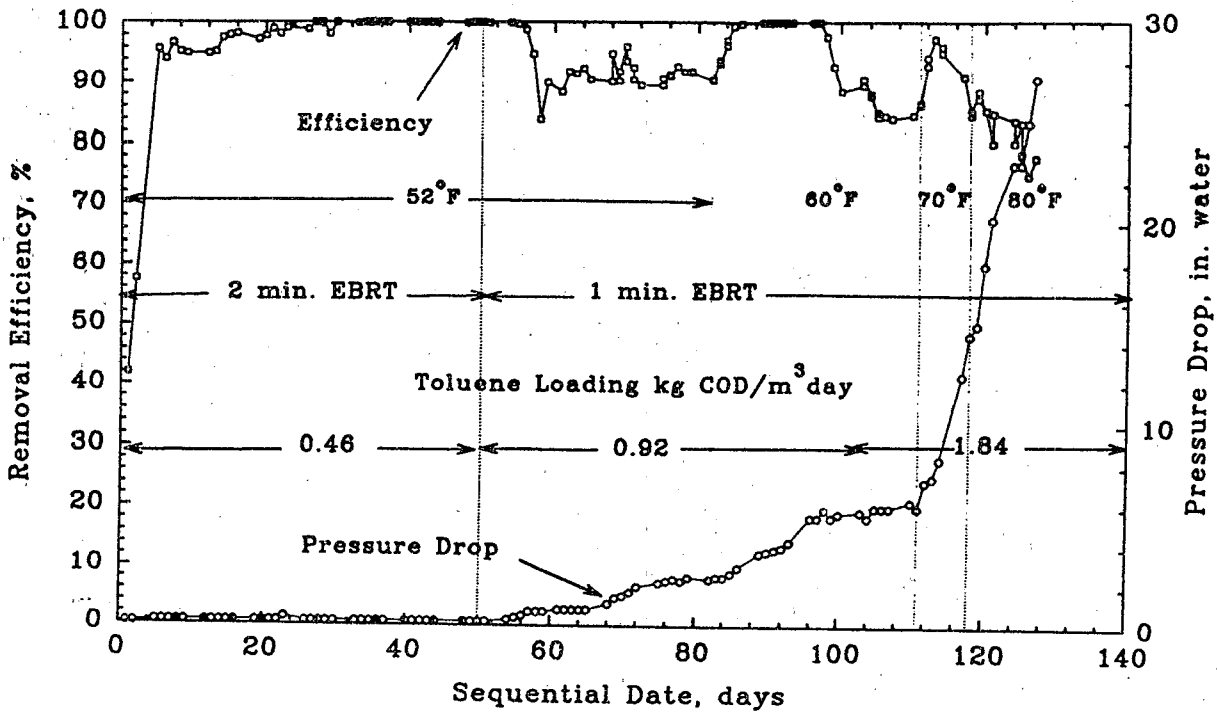


Figure 3. Performance of Pelletized Biofilter with Respect to Toluene Removal at 1 and 2 Minutes EBRT without Backwashing

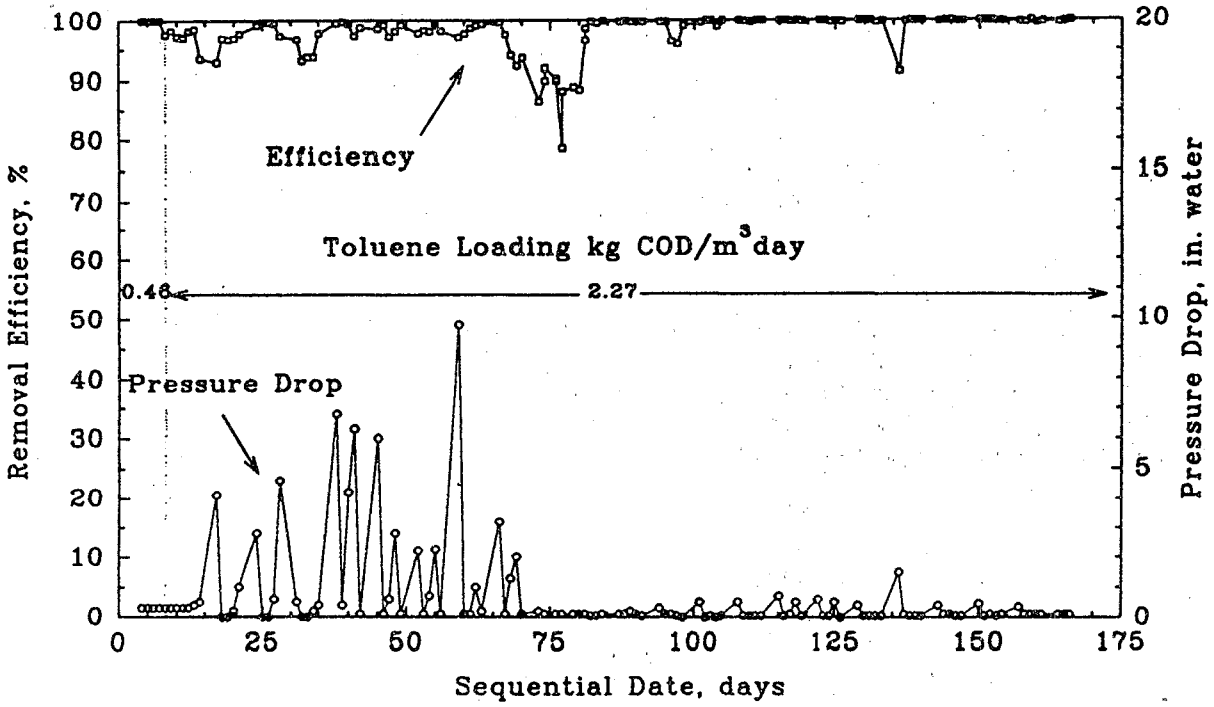


Figure 4. Performance of Pelletized Biofilter with Respect to Toluene Removal at 2 Minutes EBRT with Backwashing

have been influenced by variations in bed moisture content. However, it can be seen that the best removal efficiencies achieved by the compost mixture were better than exhibited by the channelized media but worse than exhibited by the pelletized media.

The performance of the channelized medium also confirmed our earlier findings that this medium is distinctly inferior to the pelletized medium (3). The best performance was achieved during the use of new medium blocks. After biomass accumulation within the channels and subsequent removal by hosing, the performance never regained the previous, still modest, levels. Attempts to adjust nutrient flow as a means of testing the effect of the duration of the wetting in the nutrient application cycle did not overcome the previously demonstrated efficiency limitations. The more erratic performance of this medium after removal of the biomass suggests that this medium may be unsuitable for sustained efficiency after periodic cycles of biomass removal. This erratic performance, due to suspected random uneven plugging of channels by biomass, coupled with its relatively low overall removal efficiency, difficulty in biomass removal, and intrinsicly high medium cost suggests that this medium may not be a viable option for this application.

The pelletized medium exhibited the best and most consistent performance of the three media tested. It rapidly achieved high removal efficiencies at high toluene loadings. As the first run demonstrated, however, an excessive accumulation of biomass, shown by a rise in the pressure drop across the medium, results in a substantial loss in efficiency, followed by a very rapid rise in pressure drop. This suggested that efficient, sustained performance might be achieved through early and periodic control of biomass accumulation by backwashing. In the second run, the implementation of a suitable backwashing strategy for biomass control was achieved by using full medium fluidization. This strategy permitted sustained operation of the biofilter at high loadings with efficiencies consistently at 99+%.

REFERENCES

1. Lee, B. Highlights of the Clean Air Act Amendments of 1990. J.Air Waste Manage. Assoc. 41(1):16, 1991.
2. Ottengraf, S.P.P. Exhaust Gas Purification. In: H.J. Rehn and G. Reed (eds.), Biotechnology. Vol. 8. VCH Verlagsgesellschaft. Weinham, 1986.
3. Sorial, G.A., Smith, F.L., Smith, P.J., Suidan, M.T., Biswas, P., and Brenner, R.C. Evaluation of Biofilter Media for Treatment of Air Streams Containing VOCs. In: Proceedings of the Water Environment Federation 66th Annual Conference and Exposition, Paper No. AC93-070-002. Anaheim, California, 1993. pp. 429-439.
4. Sorial, G.A., Smith, F.L., Smith, P.J., Suidan, M.T., Biswas, P., and Brenner, R.C. Development of Aerobic Biofilter Design Criteria for Treating VOCs, Paper No. 93-TP-52A.04. Paper presented at 86th Annual Meeting and Exhibition of Air and Waste Management Association, Denver, Colorado, June 13-18, 1993.
5. Bohn, H.L. Biofiltration: Design Principles and Pitfalls, Paper No. 93-TP-52A.01. Paper presented at the 86th Annual Meeting and Exhibition of Air and Waste Management Association, Denver, Colorado, June 13-18, 1993.
6. Van Lith, C., David, S.L., and March, R. Design Criteria for Biofilters. Trans. Inst. Chem. Eng. 68B:127-132, 1990.

FOR MORE INFORMATION

Richard C. Brenner
Risk Reduction Engineering Section
U.S. Environmental Protection Agency
26 W. Martin Luther King Drive
Cincinnati, OH 45268
513/569-7657

INTEGRATED SYSTEM FOR TREATING SOIL CONTAMINATED WITH WOOD TREATING WASTES

Carolyn M. Acheson and Richard C. Brenner
U. S. EPA Risk Reduction Engineering Laboratory, Cincinnati, OH 45268

Amid P. Khodadoust, Gregory W. Wilson, Karen M. Miller, and Makram T. Suidan
University of Cincinnati, Department of Civil and Environmental Engineering
Cincinnati, OH 45221-0071

INTRODUCTION

Approximately 20% of the hazardous waste sites undergoing bioremediation are contaminated with wood treating wastes, primarily compounds such as pentachlorophenol (PCP), creosote, polycyclic aromatic hydrocarbons (PAHs), and other hydrocarbons (1). A process that combines soil washing with sequential anaerobic and aerobic biotreatment is being integrated to remediate soil contaminated with these wood treating wastes. By extracting the target compound from the soil, soil washing facilitates degradation by mobilizing the target compound and expanding the range of feasible remediation technologies. Additional flexibility is possible since soil washing can be conducted in an *in-situ* or *ex-situ* format. In this process, the wash solution is initially bioremediated in an anaerobic environment. Mineralization of the target compound is completed aerobically. Based on preliminary results, the integrated process could meet the target cleanup level for PCP in approximately 45% of the bioremediation sites (1).

Process development began by independently evaluating soil washing and target compound degradation. PCP contaminated soils were the initial focus, but this work is currently being extended to include soils contaminated with both PCP and PAHs. In addition, based on promising results from the soil washing and degradation evaluations, these individual unit operations are being integrated to form a complete process to remediate soils contaminated with wood treating wastes. This complete process incorporates soil washing, soil wash solution recycling, and biodegradation of the target compounds and is outlined in Figure 1.

RESULTS

Soil Washing

An ethanol and water mixture (mass fractions with soil: 0.02 soil, 0.49 ethanol, 0.49 water) has been selected as the soil washing solution. Compared to other ethanol-water mixtures, this mixture achieves the highest removal efficiency, 65% to 100% depending on soil size, contaminated age, and soil washing format. Comparing ethanol-water soil washing to the analytical procedures of soil sonication and soxhlet extraction, soil washing removes between 93% and 114% of the PCP removed by these analytical methods (2). With the equimass mixture of ethanol and water, essentially complete extraction is achieved in a 30 minute contact time. The ability of the ethanol-water mixture to remove PAHs from soil is being evaluated using naphthalene, acenaphthalene, pyrene, and benzo(b)fluoranthene as model compounds.

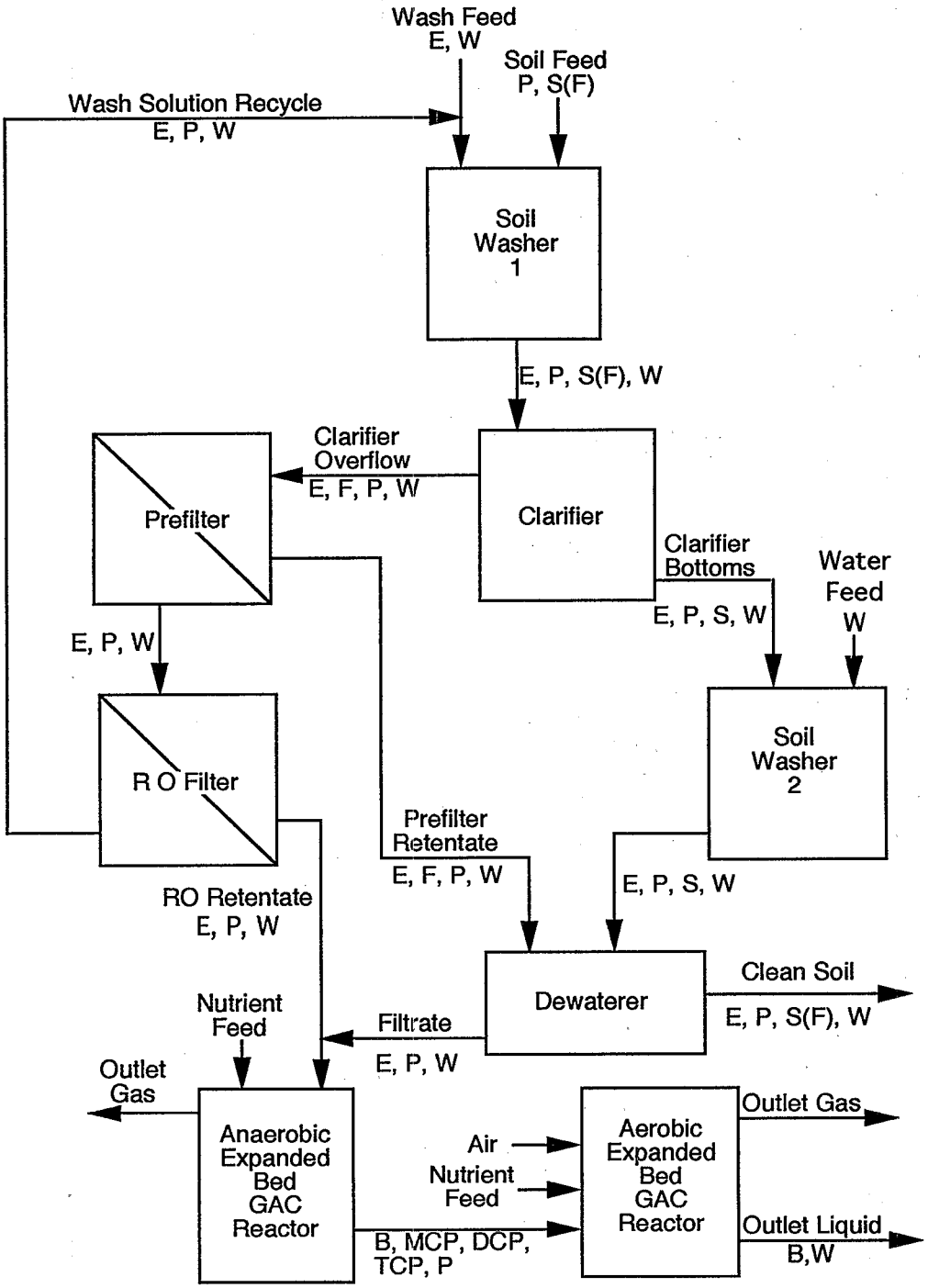


Figure 1. Integrated Process for Remediating Soil Contaminated with Wood Treating Wastes. The diagram details the flow of the following components: Biomass (B), Ethanol (E), Soil Fines (F), PCP (P), Soil (S), and Water (W).

Recycling Wash Solution

To reduce costs and the volume of PCP bearing liquid, the soil wash liquid will be concentrated and the removed ethanol and water will be recycled to the first soil washing unit. Reverse osmosis (RO) has been selected as the wash solution recycle operation to avoid the high energy costs of distillation. The feasibility of reverse osmosis will be determined in large part by the amount of wash solution which can be recycled and the economics of this process step.

Biodegradation

The retentate from the wash solution recycle process, the more concentrated wash solution, will be fed to an anaerobic expanded-bed granular activated carbon (GAC) reactor. The expanded-bed GAC reactor consists of a 96.5 cm Plexiglas tube with an internal diameter of 10.2 cm and an influent and effluent header. The reactor volume is 10 L including the recycle loop. Two of these reactors have been operated for over 40 months to evaluate variables such as PCP loading and retention time. When operated at retention times of 1.2 and 2.3 hours, greater than 99.97% of the influent PCP (0.6 g/day) is dechlorinated to monochlorophenol (MCP). The outlet stream from the reactor operating with the 2.3 hour retention time contains: 0.55 mmol MCP/L, 0.02 mmol dichlorophenol (DCP)/L, 0.005 mmol phenol/L, 0.0008 mmol PCP/L, and 0.00035 mmol trichlorophenol (TCP)/L. Inhibition of the microbial cultures in these reactors, presumably by elevated levels of MCP, was alleviated by decreasing the PCP feed rate to the current level of 0.6 g/day. Ethanol is also included in the reactor feed stream at a level of 33.3 g/day; however, the ethanol feed in the integrated process will be determined by the wash solution recycle process unit.

The outlet stream from the anaerobic expanded-bed GAC reactor will be fed to an aerobic expanded-bed GAC reactor. Under aerobic conditions, the remaining chlorinated compounds should be mineralized (3). Since analysis of the anaerobic reactor is nearly complete, characterization and optimization of the aerobic reactor will begin shortly.

In addition, experiments to characterize an anaerobic expanded-bed GAC reactor fed PCP and the four model PAHs have begun. An 11 L slurry-type reactor is also being evaluated. These reactors are also feed ethanol as a primary substrate.

CONCLUSIONS

A process integrating soil washing and sequential anaerobic-aerobic biodegradation may be an effective method of remediating wood treating wastes. The process meets the target cleanup level in 45% of the PCP bioremediation sites, or less than 35 mg PCP/kg soil. Soil washing with a mixture of ethanol and water removes PCP at levels comparable to those achieved through the analytical techniques of soil sonication and soxhlet extraction. Following soil washing, some of the soil washing solution will be recycled. The concentrated PCP bearing liquid is fed to an anaerobic expanded-bed GAC reactor where 99.97% of the PCP is reduced to MCP. The outlet from the anaerobic reactor feeds an aerobic expanded-bed reactor that should mineralize the remaining chlorinated phenols.

Current efforts are directed towards adapting the process to soils contaminated with both PCP and PAHs, evaluating reverse osmosis as a means of recycling the soil washing solution, and integrating the process.

REFERENCES

1. Bioremediation in the Field No. 11. EPA/540/N-94/501, U. S. Environmental Protection Agency, 1994. 63 pp.

2. Khodadoust, A. P.; Wagner, J. A.; Suidan, M. T.; Safferman, S. I. Solvent Washing of Aged PCP-Contaminated Soils. Paper presented in 1993 at the Water Environment Federation, Anaheim, California. October, 1993.

3. Rochkind, M. L. and Blackburn, J. W. Microbial Decomposition of Chlorinated Aromatic Compounds. EPA/600/2-86/090, U. S. Environmental Protection Agency, Cincinnati, Ohio, 1986. 269 pp.

FOR MORE INFORMATION

Carolyn M. Acheson
Risk Reduction Engineering Laboratory
U. S. Environmental Protection Agency
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268
(513) 569-7190

DEVELOPMENT OF A MULTI-LEVEL PROTOCOL FOR DETERMINATION OF BIODEGRADATION KINETICS AND BIOAVAILABILITY OF ORGANIC COMPOUNDS TO ENHANCE IN-SITU BIOREMEDIATION

Henry H. Tabak
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 West Martin Luther King Drive
Cincinnati, Ohio 45268

Rakesh Govind, C. Fu, X. Yan, S. Pfanstiel, and C. Gao
Department of Chemical Engineering
University of Cincinnati
Cincinnati, Ohio 45221-0171

INTRODUCTION

Knowledge of biodegradation kinetics in soil is needed to understand the efficacy of *in-situ* and *ex-situ* bioremediation technologies. Laboratory studies to determine biodegradation rates can be used as screening tests to determine the rate and extent of bioremediation that might be attained during remediation, and to provide design criteria. (Graves et al, 1991; (1) Tabak et al, 1992; (2) Govind et al, 1993; (3) Tabak et al, 1994, 1995) (4,5) Traditionally, *in-situ* biodegradation kinetics have been determined using soil microcosms (6,7) which are difficult to model mathematically. Laboratory studies involving soil slurry reactors have been reported by Bachmann et al. (8) Kaplan and Kaplan (9), Milhelcic and Luthy (10) and Brunner et al. (11). Currently there is no systematic methodology to quantitatively determine biodegradation kinetics of contaminants in compacted soil systems.

Biodegradation in soil is a fairly complex process which involves diffusion of contaminants in the porous soil matrix, adsorption to the soil surface, biodegradation in the biofilms existing on the soil particle surface and in the large pores as well as in the bound and free water phase after desorption from the soil surface. In soil slurry reactors, biodegradation of contaminant occurs both in the liquid phase by soil microorganisms desorbed from the soil matrix and by the biofilms immobilized on the soil particle surface. In compacted soil systems, biodegradation occurs in the free and bound water phase primarily by the soil immobilized microorganisms and the contribution of water suspended microbiota is small due to low water content. In this paper a systematic protocol based on three types of bioreactors and one representative contaminant, phenol, has been developed to determine the biokinetic parameters of the suspended and immobilized microbiota and the transport parameters of contaminant and oxygen in the soil matrix.

EXPERIMENTAL PROCEDURES AND MATERIALS

In this study, three types of bioreactors, shown in Figure 1, to determine the biokinetic parameters of the suspended and immobilized microbiota were: (1) slurry bioreactor, where soil at 5% slurry concentration is vigorously mixed with the contaminant, dissolved in water with nutrients; (2) wafer reactor, where a thin wafer of soil is spiked with contaminant and nutrients dissolved in water, to obtain a 50% total soil moisture content; and (3) porous glass tube reactor, where sieved soil with contaminant is packed in a porous glass tube with moisture content identical to the wafer reactor.

In the soil slurry reactor there are no limitations of oxygen, which freely diffuses into the well-stirred slurry, nutrients, which are initially dissolved in the aqueous phase and water. Hence, the biodegradation rate in soil slurry reactors depends on the intrinsic biokinetic rate, microorganism concentration in the soil matrix and inherent diffusivity of the contaminant. In the soil wafer reactor, oxygen diffuses freely through the thin soil matrix, and hence biodegradation rate is controlled by the water content in addition to the other intrinsic parameters, as in

the case of the soil slurry reactor. In the porous tube reactor, biodegradation rate is controlled by the water content and oxygen diffusivity and other intrinsic biokinetic parameters. The porous tube reactor provides a better estimate of biodegradation rates for *in-situ* bioremediation than the soil wafer and soil slurry reactors.

Biodegradation rates of phenol in the three soil reactor systems were determined by electrolytic respirometry (Voith Respirometer) used to continuously measure the cumulative oxygen uptake and to simultaneously monitor the carbon dioxide evolution. Appropriate concentrations of phenol stock solution in distilled deionized (DD) water were added to the reactor system containing Organization for Economic Co-operation and Development (OECD) nutrient solution composed of inorganic salts, trace salts, vitamin solution and/or yeast extract solution and different soil concentrations. Stock solution containing OECD nutrients with no phenol were used for control reactor flasks. In addition, radiolabelled contaminant was used to confirm the oxygen uptake from the contaminant rather than due to normal soil respiration.

The soil was characterized to determine soil moisture content, clay, sand and silt content, percent organic matter, soil pH, cation exchange capacity, bulk density, and nutrients in soil. The soil selected for the study was uncontaminated silt loam soil with the following characteristics: soil moisture 17%, organic matter 2.9%, classification silt loam, cation exchange capacity 6.5, soil pH 6.1, bulk density 1,06, nutrients in soil (ppm) phosphorus 17, potassium 90, magnesium 80, calcium 1100 and sodium 17. Table 1 summarizes the soil characterization data. The Brunauer, Emmett and Teller (BET) specific surface area was 20.27 m^2/g, BET void volume was 01029 cm^3/g and the BET average pore diameter was 58Å. The soil porosity was 6.53%. Soil particle size distribution was determined using outline by Day (1965) (12). Soil porosity, pore size distribution, pore volume and surface area was determined by nitrogen adsorption using Micrometrics ASAP 200.

Abiotic adsorption and desorption kinetics of the contaminant into the soil matrix and oxygen uptake data obtained for the soil slurry, soil wafer and porous tube reactors are used in conjunction with detailed mathematical models to derive the intrinsic biokinetic and transport parameters. To determine the adsorption and desorption characteristics, the soil was air dried and passed through 2 mm sieve. Abiotic adsorption and desorption equilibria were quantified using the Freundlich isotherm equation. A systematic protocol for conducting the abiotic adsorption and desorption kinetics was initially developed using soil slurry systems.

Soil Slurry Experiments

To simulate biodegradation of substrate in soil slurry bioreactors (1) 20 g of soil was mixed with 250 mL of DD water containing OECD nutrients and phenol at different concentration levels; (2) 10 mL of KOH solution (pH 9.5) was injected in carbon dioxide trap; (3) Reactor vessel was closed and cumulative continuous oxygen uptake measurements were made using respirometer. Reactor vessels were stirred continuously with teflon coated stirring bars. (4) KOH solution was withdrawn from CO_2 trap and the amount of CO_2 evolved, was quantified by measuring the change in pH of KOH solutions. (5) In radiorespirometric studies both gaseous and aqueous 14 CO_2 and radiolabelled intermediates were analyzed by Packard scintillation counting apparatus.

Soil Wafer Experiments

To more closely simulate the actual biodegradation of phenol in intact soils, soil wafer studies were developed for respirometer experimentation. The wafer system consisted of a thin layer (or wafer) of soil with a known moisture content. Procedures for the wafer experiments were as follows: (1) 20.0 g of soil and measured amount of water, approximately 20 to 30 mL in volume were placed in reaction flask, well mixed to give uniform initial biomass concentration, and the entire flask was weighed; (2) the flask(s) were placed in fume hood overnight and re-weighed. The weighing procedure was repeated until weight of flask indicated that the soil contained the desired moisture content; (3) the soil wafer was contaminated with 2.5 to 10.0 mL of experimental stock solution, depending on the desired concentration, using a syringe. Steps 3 thru 5 for the slurry experiments were followed without stirring the soil wafer.

Microporous Tube Experiments

Microporous tube reactors were developed for use in electrolytic respirometer to study the effects of oxygen diffusivity. The porous glass tubes used were purchased from Corning (Corning, NY) and were made from vycor glass with pores averaging 40 Angstroms in diameter. This pore size was selected because it was found to be optimum for containing the soil and water within the tube and allow free flow of oxygen into the soil. The porous glass tube pore sizes exceeding 40 A° were found not to effect the oxygen uptake results. The experimental procedure was as follows: (1) the microporous glass tubes were placed in the laboratory oven set at 200°C and left overnight to evaporate any water or contaminant in the pores or on the surface of the tubes; (2) the tubes were removed from oven and allowed to cool for several hours to room temperature. The tubes were placed in a beaker containing DD water to initially saturate the pores in the glass; (3) the tubes were removed from the water and filled with 20.0 g of soil, plugging both ends with glass wool; (4) the soil was contaminated evenly in the tube with 1.25 to 5.0 mL of experimental stock solution by inserting a syringe through the plugs at either end and mixing the soil around with the syringe as much as possible while injecting the solution; (5) two tubes were placed into each flask and procedures according to steps 3 through 5 for the slurry experiments were followed.

Adsorption and Desorption Experiments

For adsorption experiments, 50 g soil sample were placed in a 250 mL glass bottle. Various concentrations of each compound, namely 10, 25, 50, 100 and 150 mg/L were used. The volumes of the total solution added to each bottle were 250 mL in order to maintain a minimum head space. The head space was important, as it not only affected the degree of mixing during stirring but also controlled loss of phenol due to volatilization. Blanks containing only the phenol solution allowed the measurement of volatilization losses. In order to prevent phenol degradation in solution, 1 mL $HgCl_2$ saturated solution was added to each bottle. All adsorption experiments were conducted in a fume hood, so that the temperature of adsorption could be controlled at 24°C.

The mixture in the bottle was stirred using a magnetic stirrer for 96 hours. The samples at 2, 4, 6, 8, 12, 24, 36, 48, 72, and 96 hours from the beginning of the adsorption experiment were filtered using 0.45 μm silver membrane and placed in a 50 mL sample vial for extraction. The extraction method was based on U.S. EPA Method 604 & 610.

The GC used was a HP-5890A model equipped with a flame ionization detector. The following conditions were used throughout this study; initial oven temperature 60°C, initial hold time 5 minutes oven temperature rate 8°C/min., final oven temperature 280°C, final hold time 5 minutes, injector temperature 225°C, detector temperature 310°C, makeup gas (nitrogen) flowrate, 35 mL/min, detector gas flowrate 32 mL/min. hydrogen and 435 mL/min. air, carrier gas (helium) 2 mL/min., column HP-5 methyl silicon gum and 5m x 1.53mm x 2,54mm film thickness, and software: HP Chemstation.

After adsorption equilibrium was attained, the solution in a 250 mL glass bottle was mixed with 250 mL distilled deionized water in a large 500 mL glass bottle to start the desorption experiment. All the conditions for the desorption experiment were the same as for adsorption experiment. Samples for quantifying desorption were treated the same way as for adsorption studies, although the time taken to achieve desorption equilibrium was significantly longer.

RESULTS AND DISCUSSION

The Freundlich isotherm adsorption parameters (Ka and 1/n) and desorption parameters (Kd and 1/n) as well as the values for porosity of adsorbent (ϵ) and density of adsorbent (ρ) are listed in Table 2. Phenol adsorption equilibrium isotherm was highly non-linear compared to the desorption equilibrium isotherm and the extent of adsorption was significantly higher than the desorption extent. This suggested that significant amounts of phenol remained irreversibly bound to the soil matrix.

Figure 2 shows the oxygen uptake data for the slurry, wafer and porous tube reactors for 100mg/L phenol concentration. Clearly, the oxygen uptake curve for the slurry reactor reaches a higher plateau than the curves for the soil wafer and porous tube reactors, indicating that more phenol is being degraded in the slurry reactor. The soil wafer reactor degrades more phenol than the porous tube reactor. Furthermore, the slurry reactor data attain a plateau value faster than the wafer and porous tube oxygen uptake data. This shows that biodegradation rates in soil slurry reactors are the highest since there are no limitations of oxygen, nutrients and water and biodegradation occurs both in the liquid phase by the suspended microorganisms and by the soil immobilized biofilms. In the soil wafer reactor, there is no oxygen limitation and the biodegradation rate is governed by the contaminant desorption and subsequent degradation in the free and bound water phase by the soil immobilized biofilms. Since the water content of the soil in the wafer reactor is significantly less than in the slurry reactor, the biodegradation rate is also lower than in the slurry reactor. In the porous tube reactor, in addition to the limited water content in the soil, as in the case of the soil wafer reactor, oxygen diffusion in the soil matrix is also limited. This limits phenol degradation only in the outer region of the tube and phenol present in the interior of the tube does not biodegrade due to unavailability of oxygen.

This demonstrates, that *in-situ* bioremediation rates are significantly lower than biodegradation rates achievable in soil slurry reactors due to limited water content and oxygen diffusivity. Furthermore, nutrient limitations may further limit bioremediation rates in contaminated soil sites. While bioventing approaches may maximize availability of oxygen, delivery of water and nutrients are still major limitations for maximizing *in-situ* bioremediation rates.

Detailed mathematical models were developed for analyzing the oxygen uptake data from the soil slurry, wafer and porous tube reactors. It was found that in the soil slurry reactor, significant degradation of contaminant occurs in the aqueous phase by the suspended soil microorganisms rather than by the soil immobilized biofilms. Biodegradation rates in soil wafer and porous tube reactors increase linearly with contaminant concentration and active microbiota concentration. 81% of the phenol added initially was biodegraded in the soil wafer reactor and 64% degraded in the porous tube reactor. As shown in Figure 2, the mathematical model fitted the experimental data quite well. The soil slurry reactor data were used to derive the biokinetic parameters for the suspended and immobilized microorganisms. These parameters when used with the appropriate amount of free water, were used to fit the wafer reactor data. The wafer reactor data were used to obtain additional information with no oxygen limitations and the porous tube reactor data provided quantitative estimation of oxygen diffusivity in the soil matrix. The porous tube reactor data was used to derive the oxygen diffusivity in the soil phase.

Determining the oxygen profile in the porous tube soil using the model showed that the radial oxygen concentration decreases rapidly attaining a zero value at a radial distance of 0.25R from the tube center, where R is the radius of the porous tube. This again confirmed that there were oxygen limitations in the porous tube reactor due to limited oxygen diffusion in the soil matrix.

In the soil slurry reactor there are no limitations of oxygen, which freely diffuses into the well-stirred slurry. Hence, the biodegradation rate in soil slurry reactors depends on the intrinsic biokinetic rate, microorganism concentration in the soil matrix and inherent diffusivity of the contaminant. In the soil wafer reactor, oxygen diffuses freely through the thin soil matrix, and hence biodegradation rate is controlled by the water content in addition to other intrinsic parameters, as in the case of the soil slurry reactor. In the porous tube reactor, biodegradation rate is controlled by the water content in addition to other intrinsic parameters, as in the case of the soil slurry reactor. In the porous tube reactor, biodegradation rate is controlled by the water content and oxygen diffusivity and other intrinsic biokinetic parameters. The porous tube reactor provides a better estimate of biodegradation rates for *in-situ* bioremediation than the soil wafer and soil slurry reactors.

Experiments with uniformly labeled C^{14} phenol and measurement of carbon dioxide evolution by absorbing the KOH solution and scintillation counting showed that the net oxygen uptake (actual uptake minus the oxygen uptake in the control flask) was solely due to phenol degradation. This verified our initial assumption that the net

cumulative oxygen uptake in each type of soil reactor could be used to derive the biokinetic and transport parameters.

DESCRIPTION OF PROTOCOL

The overall protocol for evaluating soil biodegradation kinetics involves the following steps: (l) Measure cumulative oxygen uptake in soil slurry reactors. The slurry reactor model is used to obtain the aqueous and soil phase Monod biokinetic parameters. (2) Measure cumulative oxygen uptake in soil wafer reactor. Use the biokinetic parameters determined from the slurry model and detailed wafer model to determine diffusivity of contaminant in soil matrix. (3) Measure cumulative oxygen uptake in porous tube reactor. Use the parameters determined from soil slurry and wafer models to calculate oxygen diffusivity in the slurry reactor which was also the highest when compared to the other reactors. The soil slurry reactor oxygen consumption attains a plateau value in about 1 day, while the wafer and tube reactor's cumulative oxygen uptake attains a plateau value in about 3.5 days.

The oxygen uptake data for the soil slurry, wafer and tube reactors were analyzed using a detailed mathematical model to determine the best-fit values for the model parameters. The slurry reactor was used to determine the biokinetic parameters for the suspended and soil immobilized microbiota in soil from porous tube reactor model. (4) Measure radiolabelled carbon dioxide evolution using uniformly labeled compound in soil slurry, wafer and porous tube reactors to verify that oxygen uptake was due to compound mineralization. The biokinetic parameters, compound and oxygen diffusivity in soil determined using the protocol can be used to model kinetics of *in-situ* bioremediation.

REFERENCES

1. Graves, D.A., C.A. Lang and M.E. Leavitt. 1991. "Respirometric Analysis of the Biodegradation of Organic Contaminants in Soil and Water." Applied Biochem. Biotech. 28/29: 813-826.

2. Tabak, H.H., C. Gao, L. Lai, X. Yan, S. Pfanstiel, I.S. Kim, and R. Govind. 1992. "Methodology for Testing Biodegradability and Biodegradation Kinetics of Toxic Organics in Soil." Gas, Oil, Coal and Environmental Biotechnology, V, IGT, Chicago, Illinois. (Eds.) C. Akin, R. Markushewski and J. Smith.

3. Govind, R., X. Yan, L. Lai, S. Pfanstiel, C. Gao, and H.H. Tabak. 1993. "Development of Methodology to Determine the Bioavailability and Biodegradation Kinetics of Toxic Organic Pollutant Compounds in Soil." In R.E. Hinchee, D.B. Anderson, F.B. Metting, Jr. and G.D. Sayles (Eds.) Applied Biotechnology for Site Remediation, pp. 229-239, Lewis Publishers, Boca Raton, FL.

4. Tabak, H.H., C. Gao, L. Lai, X. Yan, S. Pfanstiel, I.S. Kim, and R. Govind. 1994. "Determination of Bioavailability and Biodegradation Kinetics of Phenol and Alkyl Phenols in Soil." ACS Symposium Series 554 "Emerging Technologies in Hazardous Waste Management IV. (Eds.) D. William Tedder and F.G. Pohland.

5. Tabak, H.H., C. Gao, L. Lai, X. Yan, S. Pfanstiel, C. Fu, and R. Govind. 1995. "Determination of Bioavailability and Biodegradation Kinetics of Polycyclic Aromatic Hydrocarbons in Soils." ACS Symposium Series. "Emerging Technologies in Hazardous Waste Management V. (Eds) D. William Tedder and F.G. Pohland.

6. Chang, F. 1985. "Microbial Biodegradation of Crude Petroleum and Model Hydrocarbons in Simulated Deep Soil Environment." ASM Abstracts. 85th ASM Annual Meeting, Las Vegas, NV., March 3-7, 1985. Q-50, 266.

7. Michaels, G.B., J.P. Laplante and D.J. Schneck, 1988. "Biodegradation of Hydrocarbons by Indigenous Microbial Populations in an Arid Soil Ecosystem." ASM Abstracts. 88th ASM Annual Meeting, Miami Beach, FL. May 8-13, 1988 Q-136, 305.

8. Bachman, A., P. Walet, P. Wunen, W. de Bruin, J.L.M. Huntiens, W. Roelofsen, and A.J.B. Zehnder. 1988. "Biodegradation of Alpha- and Beta-Hexachlorocyclohexane in a Soil Slurry under Different Redox Conditions." Appl. Environ. Microbiol. - 54, No. 1, 143-149.

9. Kaplan, D.L. and A.M. Kaplan. 1985. "Biodegradation of N-Nitrosodimethylamine in Aqueous and Soil Systems." Appl. Environ. Microbiol. 50, No. 4, 1077-1086.

10. Mihelcic, J.R. and R.G. Luthy. 1988. "Microbial Degradation of Acenaphthene and Naphthalene under Denitrification Conditions in Soil-Water Systems." Appl. Environ. Microbiol. 54, No. 5, 1188-1198.

11. Brunner, W., F.H. Sutherland and D.D. Focht. 1985. "Enhanced Biodegradation of Polychlorinated Biphenyls in Soil by Analog Enrichment and Bacterial Inoculum." J. Environ. Qual. 14, No. 3, 324-328.

12. Day, P.R. 1965. "Particle Fractionation and Particle Size Analysis." In: C.A. Black (Ed) Methods of Soil Analysis, 43, American Society of Agronomy, Madison, WI.

FOR MORE INFORMATION CONTACT:

Henry H. Tabak
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 West Martin Luther King Drive
Cincinnati, OH 45268
Phone: 513/569-7681

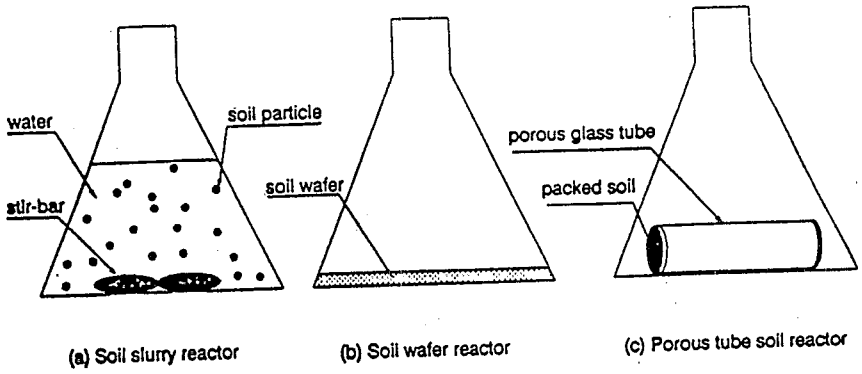


FIGURE 1 Schematic of Soil Slurry, Soil Wafer and Soil Porous Tube Respirometric Reactors

TABLE 1 Soil Characterization Data

Particle size	
Clay (< 2 um)	24%
Silt (2-44 um)	58%
Sand (> 44 um)	18%
Classification	Silt Loam
Organic Matter	2.9%
Cation Exchange Capacity	6.5
Soil pH	6.1
Bulk density	1.06
1/3 bar moisture	30.7%
15 bar moisture	14.8%
Nutrients in soil (ppm)	
Phosphorus	17 (h)
Potasium	90 (m)
Magnesium	80 (l)
Calcium	1100 (m)
Sodium	17 (v)

Note: h = high; m = medium; l = low; v = very low

TABLE 2 Adsorption/Desorption Soil Equilibrium and Soil Porosity and Density Parameters

K_a	1/n	K_d	1/n'	ϵ	ρ(g/L)	R(mm)
0.0105	0.84	0.01259	0.77*	0.06525	2250	0.334

* Only for the slurry model

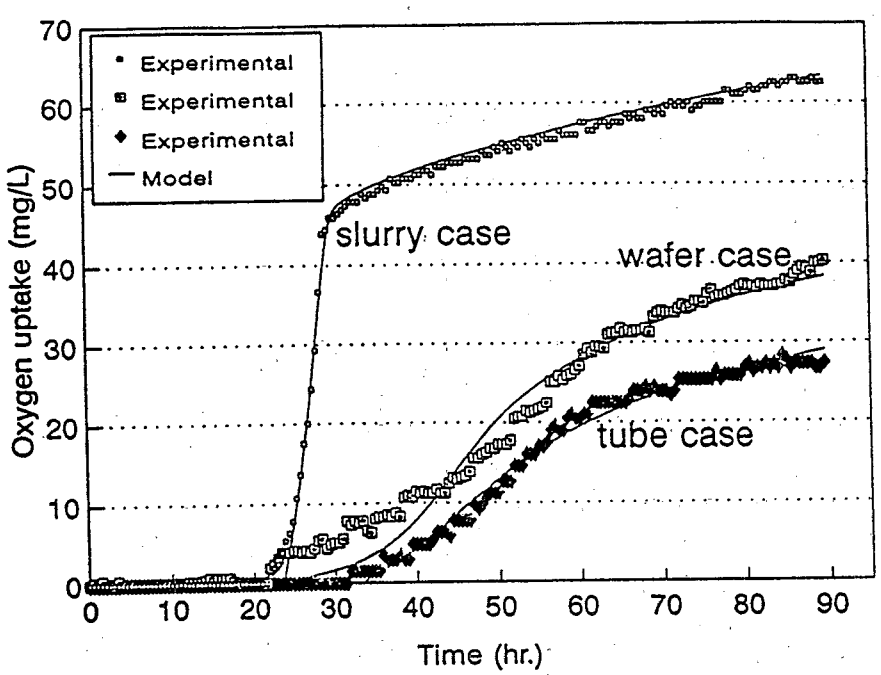


FIGURE 2 Oxygen Uptake Curves for Soil Slurry, Wafer and Porous Tube Reactors for Phenol. The line indicates the Fit by the Mathematical Model Developed for each Reactor Type

DESIGN AND TESTING OF AN EXPERIMENTAL IN-VESSEL COMPOSTING SYSTEM

Carl L. Potter and John A. Glaser
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
Cincinnati, OH 45268

Majid A. Dosani, Srinivas Krishnan, Timothy A. Deets, and E. Radha Krishnan
IT Corporation
11499 Chester Road
Cincinnati, OH 45246

INTRODUCTION

Composting has received much attention as a potential technology for treating solid waste. Most of that attention has been focused on treatment of municipal solid waste, sewage sludge, yard trimmings, and agricultural wastes. More recently, composting has been investigated as a remediation technology for hazardous wastes. Laboratory and field-scale work has been conducted to determine the fate of pesticides, hydrocarbons, and explosives in the composting environment (Ziegenfuss *et al.*, 1991).

In the composting of non-hazardous materials, the objectives are to stabilize and oxidize organic materials, reduce the volume of waste, reduce the moisture content of waste, and destroy pathogens. Composting of hazardous waste includes the same objectives plus detoxification of hazardous substances into innocuous end-products.

Optimal application of biotechnology to large-scale compost systems is based on a working understanding of processes and mechanisms involved in composting of organic material. Currently, commercial compost operations are operated as black-box systems where optimization is largely achieved through trial and error. Large-scale treatment of hazardous waste will require optimal controls to meet the specified end points.

Some proponents of compost treatment have claimed significant success in destruction of hazardous wastes without strong data to support their claims. Disappearance of parent compounds has been used to claim that microorganisms successfully degraded waste chemicals. However, some toxic chemicals could potentially adsorb to, or react with, humic substances in the compost and become undetectable by chemical analysis. Such toxicants might later desorb from humus and migrate to the biosphere. This emphasizes the need for well controlled studies to rigorously document degradation rates and identify metabolic products of hazardous chemicals, metabolically active microbial species, and mechanisms of hazardous chemical transformation in compost systems.

We have designed and tested closed bench-scale compost reactors to evaluate composting processes using contaminated soils. Identification of suitable co-compost and bulking agents, appropriate ratios of soil to organic components and effective aeration strategies and rates have been selected as major factors requiring investigation.

This research program is designed to develop a thorough engineering analysis and optimization of composting as a process to treat soil contaminated with hazardous waste. Bench-scale composters serve as diagnostic tools to predict treatment effectiveness of larger systems. Fully enclosed, insulated reactors permit reliable data collection on microbial population dynamics and fate of toxic chemicals during soil composting.

The goal of the compost study is to evaluate the potential use of compost systems in remediation of soils contaminated with hazardous chemicals. In pursuit of this goal, we have developed bench-scale composters to model large-scale systems. We are currently studying the ability of compost microorganisms to biodegrade polynuclear aromatic hydrocarbons (PAHs) in in-vessel reactors located at the U.S. EPA Test & Evaluation (T&E) Facility in Cincinnati, OH. Soils contaminated with PAHs have been obtained from the Reilly Tar Pit Superfund site in St. Louis Park, MN for use in these studies.

BACKGROUND

Optimum conditions for composting may vary depending on a number of factors, but generally aerobic conditions with 45° - 55°C temperature, 40% - 60% moisture, and a carbon to nitrogen ratio of 20:1 to 30:1 have been considered best. Mesophilic composting (35° to 55°C) might prove to be the most effective for destruction of wastes. However, it may not always be practical to maintain temperature below 55°C from an economic standpoint if it requires too much energy to maintain lower temperature.

Composting differs from other *ex-situ* soil treatment systems in that bulking agents are added to the compost mixture to increase porosity. This allows air to flow through the contaminated soil and maintain aerobic conditions. Microbial metabolism of substrate generates heat raising the temperature. Temperature changes in the pile bring about changes in the microbial ecology. Some microbes will fare better at one temperature, while others will take over as the temperature rises or falls.

The conventional aerobic compost process passes through four major microbiological phases identified by temperature: mesophilic (30° - 45°C); thermophilic (45° - 75°C); cooling; and maturation. The greatest microbial diversity has been observed in the mesophilic stage.

The early stage of composting, where the temperature rises rapidly, is called the active stage of composting. In an active compost pile, temperature can easily exceed 55°C, and temperatures as high as 70°C have been reported. Compost temperature above 55°C becomes lethal to most bacteria. Microbes found in the thermophilic stage have been spore forming bacteria (Bacillus spp.) (Nakasaki, et al., 1985) and thermophilic fungi (Strom, 1985; Fogarty and Tuovinen, 1991).

As aerobic microbes are killed during the thermophilic stage, aerobic activity (heat production) slows and temperature declines back into the mesophilic range below 45°. Microbial recolonization during the cooling phase brings the appearance of mesophilic bacteria and fungi whose spores withstood the high temperatures of the thermophilic stage.

A maturation, or curing, phase is the final compost stage. By this stage, most digestible organic matter has been consumed by the microbial population, and the composted material is considered stable. Fungi and Actinomycetes may dominate the eco-system during the curing stage.

REACTOR DESIGN

Prototype composter evaluation at the U.S. EPA T&E facility has proceeded through several different designs. The performance of each design was evaluated by conducting a treatability experiment using PAH-contaminated St. Louis Park soil. For our design criteria, one particular prototype offered considerable versatility. This design was used to build stainless steel reactor units.

Ten 55-gal, insulated, stainless steel composters have been fabricated to perform closely monitored treatability studies. These fully enclosed, computer monitored, bench-scale reactors hold about 1/4 cu. yd total compost mixture.

The reactor units stand upright with air flowing vertically through the compost mixture. Enclosed units permit online analysis of oxygen, carbon dioxide, and methane at inlet and exit locations. A data capture system accumulates these data and transmits them to the central computer that monitors and controls each reactor. XAD traps in the exit line of each composter permit trapping of volatile organic compounds (VOCs) for analysis.

The bottom of each reactor consists of 2 in. gravel contained above a conical collection system for periodic sampling of any leachate leaving the reaction mixture. Mass balance studies on soil contaminants are possible by direct sampling of the reaction mixture at different depths through bung holes in the lid, together with capture of VOCs and leachate leaving the reactor.

Periodic determination of compost moisture content in each reactor unit permits adjustment of total moisture content in the compost matrix to 40% to 50%. Moisture condensers inside compost units promote recycling of moisture. Otherwise, with typical air flows, each unit could lose significant amounts of water daily. If moisture falls below 40%, a water distribution system inside the reactor may be used to facilitate water addition to the reaction mixture without opening the reactor.

Cylindrical reactor design permits mixing of reactor contents by rolling each unit on a drum roller at desired intervals. Mixing can be used to break up anaerobic pockets and to avoid packing of the compost mixture. All reactors are mixed simultaneously by placing them on rollers over a modified conveyor belt that forces the reactors to turn in unison. Baffles inside reactors promote mixing of the compost during rolling.

An insulated space between the reactor core and the outer shell reduces heat loss from the reactor during aerobic activity. Heating coils in this space provides the option of warming the reactor to accelerate composting during startup. Each composter houses five thermocouples connected to a central computer for online temperature measurements. Thermocouples reside at four equally spaced locations within the compost mixture and a fifth thermocouple tracks ambient temperature outside the reaction vessel.

One operational scheme permits temperature control by introduction of ambient air through a computer controlled valving system. If the mean temperature of the middle two reactor thermocouples exceeds a predetermined high value, the computer switches that unit to high air flow (20 L/min) to cool the reaction mixture. After the high-temperature unit cools to a specified low temperature, the computer switches the unit back to low air flow (5 L/min) to reduce further heat loss from the reaction mixture.

CURRENT RESEARCH

Current studies focus on defining acceptable operating conditions and process characteristics in order to establish suitable parameters for treatment effectiveness. Parameters of interest include aeration, moisture dynamics, heat production, and physical and chemical properties of the compost mixture.

Aeration studies evaluate porosity (air flow) in the compost system, and attempt to discover relationships between free air space, forced air flow, and composting rate. Aeration studies also investigate roles of anaerobic and aerobic metabolism in chemical degradation. Anaerobic pockets may benefit the process by initiating degradation of

recalcitrant compounds, especially highly chlorinated compounds, via reductive metabolism. After an initial reductive step, aerobic biodegradation of toxicants may proceed more readily. The research program will attempt to identify optimal aeration rates and pile mixing frequency for the most effective combination of anaerobic/aerobic conditions for biodegradation of recalcitrant substrates. These studies will investigate whether forced anaerobiosis and inoculation with a facultative anaerobe prior to development of aerobic compost conditions enhances biodegradation of toxic wastes.

Moisture dynamics studies evaluate rates of change in moisture content for different regions of the compost reactor. Moisture may be lost through evaporation and convection. Changes in moisture content are attributable to factors such as aeration rate, temperature, and compost composition (e.g., soil type and co-compost material).

Heat production may be highly variable throughout the compost reactor. We have devised a method to continually monitor temperature changes (heat production) at various reactor locations. Bench-top composters are insulated to control heat loss, thereby mimicking a large scale compost pile where heat is lost by ventilation and water evaporation more than by conduction.

A preliminary study was performed on PAH-contaminated soil mixed with 1% by weight fresh cow manure and 50% by volume ground corn cobs. Reactor core temperature ranged from 20°C to 60°C when moisture content was below 52%. However, when moisture content exceeded 57%, temperature remained below 30°C, suggesting that aerobic metabolic activity was inhibited at moisture content 57% under these conditions.

Critical properties of the compost mixture include density (g/cc), pH changes in various reactor locations, pressure drop across the pile if it is actively aerated, solids fraction, moisture content, and concentrations of organic compounds. These investigations focus on potential to enhance biodegradation by manipulation of physical and biological parameters that influence the process. These studies will also investigate whether recycling mature compost material into fresh compost enhances biodegradation of contaminants.

Early microbiological studies have focused on enumerating total microorganisms and determining the presence of PAH degraders. Current studies focus on characterizing changes in biological activity during the four stages of composting and identifying microbial species responsible for significant biodegradation of PAHs during each compost stage. Reappearance of fungi and other mesophiles (e.g. Actinomycetes) during the cooling stage is also of interest.

FUTURE RESEARCH

Future investigations will include treatability studies on pentachlorophenol and other soil contaminants. Research on technical developments necessary to improve composting applications for degradation of hazardous waste will remain as a primary objective. To judge the abilities of microorganisms to degrade hazardous wastes in soil under various compost conditions, emphasis will be placed on determining mass balance of contaminants and degradation products in compost, and identifying microbial species responsible for biodegradation of contaminants.

REFERENCES

Fogarty, A.M and Tuovinen, O.H. 1991. Microbiological degradation of pesticides in yard waste composting. Microbiol. Rev. June 1991:225-233.

Nakasaki, K., Sasaki, M, Shoda, M., and Kubota, H. 1985. Change in microbial numbers during thermophilic composting of sewage sludge with reference to CO_2 evolution rate. Appl. Environ. Microbiol. 49(1):37-41.

Strom, P.F. 1985. Identification of thermophilic bacteria in solid-waste composting. Appl. Environ. Microbiol. 50(4):906-913.

Ziegenfuss, P. Scott and Williams Richard, T. 1991. Hazardous materials composting. J. Haz. Mater. 28, 91-99.

FOR MORE INFORMATION

Carl L. Potter, U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, Telephone (513) 569-7231, FAX (513) 569-7105.

EVALUATION OF ABIOTIC FATE MECHANISMS IN SOIL SLURRY BIOREACTOR TREATMENT

John A. Glaser and Paul T. McCauley
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
26 W. Martin Luther King Dr.
Cincinnati, Ohio 45268

Majid A. Dosani, Jennifer S. Platt, and E. Radha Krishnan
IT Corporation
11499 Chester Rd.
Cincinnati, Ohio 45246

INTRODUCTION

Biological treatment of contaminated soil slurries may offer a viable technology for soil bioremediation. Slurry bioreactor treatment of soils, however, has not sufficiently progressed to be a durable, reliable, and cost-effective treatment option.[1]

Critical to the evaluation of slurry bioreactors is a better description of pollutant mass transfer during the treatment phase. Losses attributable to abiotic means are generally overlooked in field application of the technology. Discussions with EPA regional personnel and inspection of active soil slurry bioreactor operations have identified operational problems such as foaming which could result in possible abiotic loss.[2] Field bioslurry operations have adopted various approaches to reduce foaming: 1.) the addition of defoaming agents, 2.) the reduction of rotational speed of the agitator, and 3.) the reduction of gas flow through the bioreactor system. The foaming phenomena is viewed as a nuisance rather than a potential beneficial removal mechanism. In the case where the pollutants have a specific gravity less than water, once desorbed from the slurried soil, they would rise to the surface as in a flotation process. Our hypothesis was that foam formation could be related to this pollutant release process. If this analysis has merit, it is possible that the operational strategy used in the field is counterproductive since a separated contaminant phase is re-entrained with a partially cleaned soil material.

We have conducted two bench-scale slurry bioreactor treatability studies, at the U.S. EPA Testing & Evaluation Facility in Cincinnati, Ohio, which were designed to investigate some of the operating factors leading to foam formation and identify the most advantageous means to deal with foaming. The initial study has been previously presented as a general treatability study for treatment of creosote contamination in a soil.[3] During this study, foaming became a major problem for operation. The foaming conditions were mitigated by use of defoamer and, in the more extreme cases, through reduction of the mixer rotational speed and gas flow. A subsequent study which was devoted specifically to investigating the causes and conditions of foaming using a different batch of soil from the same site as the earlier study showed little foaming at the very beginning of the study.

METHODOLOGY

Treatability Study[3]

A soil from St. Louis Park, Minnesota was contaminated with polynuclear aromatic hydrocarbons (PAHs) and used to evaluate the performance of bench scale slurry reactors. The bench-scale bioslurry reactor was fabricated from a 8-L glass conventional resin kettle with a four-port cover fitted with standard taper joints. The reactor vessel was fabricated to have three sample ports located at 5, 10, and 15 cm vertically from dead center of the reactor bottom. The ports in the reactor cover permitted introduction of the stirring shaft, influent and effluent gas lines, and a thermocouple temperature probe

into the reactor. Operational slurry volume was 6 L, representing (75%) of the total reactor volume.

Ten bench-scale reactors were used to assess the effect of engineering variables on the degradation of PAH constituents over a 10-week treatment period.

Experimental Design

Experimental variables selected for this study were solids loading, rotational speed of the mixing impeller, and dispersant. Soil solids concentrations of 10% and 30% (dry weight basis) were tested. Two mixing speeds were evaluated. A high mixing rate was selected for complete off-bottom suspension. A low mixing rate was arbitrarily set at 200 rpm lower than the high mixing rate. Effective high mixing rates were found to be 650 rpm and 900 rpm for 10% and 30% soil solids, respectively. The dispersant (Westvaco, Reax 100M) was added to test its ability to minimize foam production.

Two separate reactors were operated under abiotic conditions to serve as bio-inactive control reactors. Formaldehyde was used as a biocide in these reactors and maintained at 2% residual concentration.

The following monitoring and operating conditions were held constant for the reactors:

Dissolved Oxygen (>2 mg/L)
pH (range of 6-9)
Ambient Temperature (recorded daily)
Treatment Duration (10 weeks)
Nutrients (C:N:P ratio = 100:10:1)
Antifoam (as needed to control foam)

Foam Study

To evaluate the conditions and causes of foam formation, a subsequent study was designed. This investigation used the monitoring conditions specified for the treatability study and was conducted using six bench-scale slurry reactors. Each reactor was loaded at 30% solids with an initial volume of 6 L. The study design employed two reactors which were permitted to develop foam, two reactors in which the foam formation was suppressed through the use of defoamer; and two reactors where formaldehyde was used to suppress biological activity.

RESULTS

The high solids control reactor showed the greatest amount of foaming in the treatability study. This is a surprising event since our expectation was that foaming was related to the formation of biosurfactants by the microbiota. The addition of formaldehyde to the control reactor was the only other explanation for the foam formation observed. The other reactors had foaming problems but this reactor was very noticeable in contrast to the others. Higher solids loading was also observed to contribute to foam formation.

In contrast with the initial treatability study, the designed foaming study showed little foam formation. There was a small amount of foaming on the first day of operation. There were a few differences in the physical characteristics of the soil and the operation of the bioslurry reactor between the two studies which may have contributed to decreased foam formation in the designed foam study. Although soil from the same site was used for both the treatability study and foam study, the batch of soil used for the foam study was coarser (<1/4") which may have resulted in lower PAH concentrations in the foaming study and lead to decreased foam formation. Furthermore, the air flow rate used for all six reactors in the foam study (1 ft^3/min) was approximately 20 percent of that used in the treatability study (5 ft^3/min) which could have also contributed to decreased foam formation.

CONCLUSIONS

The lack of foam formation in the one study devoted to its analysis was a set back to our initial goal. We will continue to investigate foam formation and appropriate controls for soil slurry bioreactors. The unpredictable nature of foaming events must be better understood to provide dependable operating conditions required for field scale bioslurry applications.

REFERENCES

1. U.S. EPA, Engineering Bulletin: Slurry Biodegradation, EPA/540/2-90/016 Cincinnati, Ohio.

2. Jerger, D.E., Erickson, S.A., and Rigger, R.D. "Full-Scale Slurry Phase Biological Treatment of Wood Preserving Wastes at a Superfund Site." 1994 Draft Manuscript.

3. Glaser, J.A., Dosani, M.A., McCauley, P.T., Platt, J.S., Opatken, E.J., and Krishnan, E.R. Soil Slurry Bioreactors: Bench Scale Studies. In: Twentieth Annual RREL Research Symposium: Abstract Proceedings. EPA 600/R-94-011. United States Environmental Protection Agency, Cincinnati, Ohio, 1994. p. 127.

FOR MORE INFORMATION:

John A. Glaser
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268
(513) 569-7568 (Voice)
(513) 569-7105 (FAX)

BIOTRANSFORMATION OF SULFUR AND NITROGEN OXIDES IN STACK GASES

Rakesh Govind, Rama Puligadda
Department of Chemical Engineering
University of Cincinnati
Cincinnati, OH 45221

and

Dolloff F. Bishop
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26W. Martin Luther King Drive
Cincinnati, OH 45268

INTRODUCTION

The Nation's large supply of high sulfur coal and increasingly stringent emission regulation led to priority development of advanced innovative processes for treating pollutants in flue gases from coal combustion. The principal pollutants in flue gases, sulfur oxides (SO_2,SO_3) and nitrogen oxides (NO_x) cause acid rain. Thus, the Department of Energy's Clean Coal Program is funding projects to commercialize technologies that minimize emission of sulfur and nitrogen oxides at power plants. The emerging technologies should be applicable to coal-fired combustors in the electric utility, industrial and commercial sectors. The technologies should also achieve high degrees of reliability and have low operating and capital costs. The status of flue gas cleanup technology is summarized in the folowing sections.

Flue gas cleanup technology provides emission control of sulfur dioxide, nitrogen oxides, and particulate matter (PM) in combustion of coal using two generic categories of processes: One category, dry sorbent injection, uses dry sorbents such as limestone injected directly into the combustion zone or downstream of a coal- fired boiler, to capture sulfur dioxide insitu. In this strategy, a low-NO_x combustion environment is usually maintained to aid capture. The second category, post combustion gas cleanup, uses sorbents in a slurry, aqueous liquor, or dry powder injected into the combustion gas leaving coal-fired boilers to effect post combustion capture of SO_2. Processes in both categories employ various approaches to control emission of particulate matter (PM).

In the last 10 to 20 years, a wide variety of dry sorbent injection and post combustion gas cleanup systems (1-12) have evolved. A representative system for dry sorbent injection is the Limestone Injection Multistage Burner (LIMB) used at utility power- generating stations in existing pulverized coal-fired (PC) boilers firing run-of-mine (ROM) coal. The boilers are equipped with conventional particulate matter (PM) controls (typically an electrostatic precipitator). The LIMB system injects dry alkali metal limestone or hydrated lime into the furnace operating with low-NO_x combustion environment achieved through modifications of the burner assembly or combustion operating conditions. LIMB is an emerging technology undergoing research and development at the bench, pilot, prototype, and demonstration plant levels. The thrust of ongoing research is to identify factors that govern performance to optimize removal efficiency.

Numerous activities by both private and public sectors to improve emission control systems are summarized as follows:

1. Research for control of particulate matter (PM) is focussed on performance improvement and optimization. Due to concern for health risks from trace element and inhalable particulate matter, emphasis is placed on the removal of submicron-sized particles.

2. Research in existing flue gas desulfurization (FGD) systems is focused on the use of organic acids or magnesium salts to enhance SO_2 removal efficiency and reagent utilization. Results indicate that a removal efficiency of 95 % can be achieved at reduced operating costs.
3. Research in existing and new FGD systems is to reduce fresh water consumption and clean-up of waste water discharges since these requirements may improve siting and operational problems at coal power plants.
4. A promising low-cost FGD option for SO_2 control is dry injection of sorbent in flue gas before the fabric filter. This process has been demonstrated by the Electric Power Research Institute (EPRI) at full-scale and is applicable to both new and existing low-sulfur coal power plants. Additional research is proceeding on high-sulfur coal applications for use with electrostatic precipitators, for improved waste fixation and disposal, for system optimization and for use of lower-cost alternate reagents.
5. Advanced limestone/gypsum FGD processes are being developed for application which produce marketable gypsum by forced oxidation of the spent slurry.
6. For post-combustion control of NO_x, selective catalytic and selective non-catalytic reduction systems are the most advanced. Pilot- scale systems of these two technologies have been successfully tested on coal-fired power plants. However, these processes are more expensive than modification of burners for low NO_x emission. Major improvements are needed in the process control subsystems, extension of catalyst life, elimination of ammonia leakage, and reduction in overall cost.

Long term research efforts are focused on advanced SO_2 control, combined SO_2/ NO_x control and PM removal. The primary emphasis in advanced SO_2 control technologies is placed on reagent regeneration and saleable product processes to eliminate or minimize solid waste disposal problems.

Biological desulfurization of coal is a pretreatment method that attempts to remove both pyritic and organic sulfur in coal before combustion. In the past, several laboratory studies have been reported to remove sulfur from coal using microorganisms (13-18). Two main microorganisms that have been studied are *Thiobacillus ferroxidans*, a mesophilic (10^oC-37^oC) bacterium isolated from acid mine drainage, and *Sulfolobus acidocaldarius*, a thermophillic (55^oC-80^oC) bacterium. Both organisms aerobically oxidize pyritic sulfur, primarily FeS_2, and organic sulfur to soluble sulfates. Atlantic Research Corporation, Virginia (19) developed a unique microorganism (CBI) capable of removing a portion of the organic sulfur from coal. CBI primarily attacked thiophenic sulfur in coal, removing the sulfur as a water soluble sulfate. In laboratory batch and bench-scale continuous systems, CBI removed up to 47% of the organic sulfur. The sulfur removal depended on coal type, particle size and surface properties. Attia and Elzeky (20) used *thiobacillus ferrooxidans* bacteria to selectively modify the pyrite surface chemical behavior to improve pyrite sedimentation in the flotation of coal. They studied the effects of variables (bacterial conditioning time, concentration of bacterial cells, pH, temperature and nutrient solution) on the flotation behavior of pyrite and coal suspensions. Their results indicated that about 40% reduction in the pyrite content of coal was achieved with bacterial pre-conditioning of less than 15 minutes, while coal flotation was unaffected.

METHODOLOGY

Current sulfur and nitrogen oxide control approaches for contaminated gas streams such as stack gases have limitations and are relatively expensive. Practical methods for removal of carbon dioxide are not available. In this paper, the controlled use of biotransformation to remove these oxide pollutants from contaminated gases involves complex biooxidation and bioreduction of the oxides in appropriate bioreactors, ultimately to elemental sulfur, nitrogen gas and biomass. Two separate bioreactor experiments were conducted to investigate the application of biological reactors for removal of sulfur dioxide, nitrogen oxides and carbon dioxide from stack gases.

Biofilter Studies

An experimental biofilter was operated for 5 months to study biological removal of sulfur dioxide, nitrogen oxides and carbon dioxide from stack gases. A 2-inch diameter stainless-steel tube was used to construct the biofilter and ceramic straight-passage monolith with 100 cells/square inch, obtained from Corning Glass, Inc.,

NY, was used as the support media. The height of the biofilter was 3 feet. Stack gas, with flowrate that was varied in the range 1-2 liters/minute, was introduced at the top of the biofilter. The recycled OECD nutrients (21) were also trickled down the biofilter cocurrent with the flow of the stack gas. 30 mg of *Thiobacillus* (obtained from ATCC culture bank and grown in specialized culture reactors) was suspended in 0.5 liters of OECD nutrients and recirculated through the biofilter to seed the ceramic media with the desired organisms. About 16 gms of the culture was attached after 2 hours of recirculation of the suspended culture through the biofilter.

Stack gas, with the following composition: Carbon dioxide (41.56%), Nitrogen (50%), Oxygen (8%), Sulfur dioxide (0.4%), nitrogen oxides (0.04%), was introduced at the top of the biofilter at an initial flowrate of 1 liter/minute, which resulted in a 2-minute gas phase empty-bed residence time. OECD nutrients with the following composition: (21): KH_2PO_4 (85 mg/L)), K_2HPO_4 (217.5 mg/L)), $Na_2HPO_4.2H_2O$ (334 mg/L), NH_4Cl (25 mg/L), $MgSO_4.7H_2O$ (22.5 mg/L), $CaCl_2$ (27.5 mg/L) and $FeCl_3.6H_2O$ (0.25 mg/L), $MnSO_4.H_2O$ (0.0399 mg/L), H_3BO_3 (0.0572 mg/L), $ZnSO_4.7H_2O$ (0.0428 mg/L), $(NH_4)_6Mo_7O_{24}$ (0.0347 mg/L), $FeCl_3$.EDTA (0.1 mg/L), and yeast extract (0.15 mg/L) were also introduced at the top of the biofilter at a flowrate of 4 liters/day. The biofilter was operated at ambient temperature of 25°C.

Suspended Culture Bioreactor

A bioreactor experiment was conducted to evaluate SO_2/NO_x removal from stack gases by suspended culture bacteria. The design and operating conditions for the bioreactor have been summarized in Table 1. Stack gas, consisting of carbon dioxide, nitrogen, sulfur dioxide, nitrogen oxides and oxygen was bubbled at a rate of 1.5 liters per minute through the bioreactor. The bioreactor, a 4-inch diameter glass column, 3 feet tall, was filled with 2 feet of deionized distilled water and 20 gms of activated sludge as seed. There was no further addition of activated sludge to the reactor. The reactor was mixed by the incoming stack gas flow. The reactor detention time was 4 minutes for the gas stream. The reactor detention time has not been optimized.

The incoming gas stream and the exiting gas stream compositions (refer to Table 1) were analyzed by a sulfur dioxide and nitrogen oxides Beckman Analyzer. OECD nutrient media was batch fed daily to the reactor (0.2 liters) and an equivalent amount of liquid was withdrawn (Table 1) from the reactor. The exit gas was also analyzed using a gas chromatograph.

RESULTS

Biofilter Studies

Complete removal of sulfur and nitrogen oxides was observed in this experiment. No oxygen or hydrogen sulfide was present in the exit gas stream. The carbon dioxide composition was reduced to 32.4%, from an initial feed gas composition of 41.56%. The composition of nitrate in the exit liquid stream was 12 ppm and sulfate composition was 10 ppm. Free sulfur was obtained from the liquid stream. The amount of free sulfur, quantitated by filtering and weighing, closely agreed with the complete conversion of sulfur dioxide to sulfur.

The biofilter consisted of two distinct zones: (1) oxidation zone, in which the sulfur dioxide and nitrogen oxides were converted abiotically and biologically to sulfate and nitrate in the liquid phase; and (2) reduction zone, in which the sulfate and nitrate were converted to hydrogen sulfide, sulfur and nitrogen gas. The hydrogen sulfide formed also reacted with sulfur dioxide in the gas phase to form sulfur, which exited with the nutrient liquid flow.

The following are the possible reactions occuring in the oxidation and reduction zones:

Oxidation zone: Biological reactions

$$1/2\,O_2 + H_2O + SO_2 \xrightarrow{\text{Bacteria}} SO_4^{=} + 2H^+$$

$$1/2\,O_2 + H_2O + NO \xrightarrow{\text{Bacteria}} NO_3^- + 2H^+$$

$$1/2\ O_2 + H_2O + 2NO_2 \xrightarrow{\text{Bacteria}} 2NO_3^- + 2H^+$$

Sulfur dioxide is also oxidized to sulfate abiotically.

Reduction zone: Biological reactions

$$SO_4^{2-} + \text{organic source} \xrightarrow{\text{Bacteria}} H_2S + \text{alkalinity}$$

$$NO_3^- + \text{organic source} \xrightarrow{\text{Bacteria}} 1/2\ N_2 + \text{alkalinity}$$

$$SO_4^{=} + \text{organic source} \xrightarrow{\text{Bacteria}} S^0 + \text{alkalinity}$$

With nutrient recycle, the alkalinity (HCO_3^-) produced in the bioreduction zone neutralizes the acidity produced due to the formation of sulfate and nitrate in the oxidation zone. Waste activated sludge was continuously added to the biofilter and primarily served as the organic source for the bioconversion of sulfate to hydrogen sulfide. The steady-state pH of the exit nutrient stream was 9.2. The majority of the carbon dioxide in the gas stream was absorbed by the bicarbonate to form carbonate. The H_2S produced in the reduction zone combined with sulfur dioxide (SO_2) in the gas phase to form free elemental sulfur.

$$2H_2S + SO_2 \longrightarrow 3S^0 + 2H_2O$$

The major problem encountered in this experiment was the senstivity of the exit gas composition to inlet stack gas flowrate. If the stack gas flowrate was abruptly changed even by a small amount, the conversion of sulfur dioxide would immediately drop and then again achieve 100% conversion after a period of 2-3 hours. For example, at a stack gas flowrate of 1.2 liters/minute, immediately after being changed from a steady-state flow of 1 liter/minute, the conversion of sulfur dioxide immediately dropped from a steady-state value of 100% to 85%; i.e., 15% of the incoming sulfur dioxide was observed in the exit gas stream. Nitrogen oxides were also observed in the exit gas stream, although their composition was very low due to low inlet composition. However, if the biofilter was operated for about 3 hours at a steady-state stack gas flowrate of 1.2 liters/minute, then the sulfur dioxide and nitrogen oxide conversion again reached a steady-state value of 100%.

The instability of the biofilter process to changes in stack gas flowrate was mainly due to disruption of the oxidation-reduction zones, due to penetration of oxygen, present in stack gas, into the reduction zone. However, after the reactor had been operated for some time, usually a few hours, bacterial growth responded to restore the balance of the oxidation-reduction zones, thereby again attaining complete conversion of the sulfur and nitrogen oxides to sulfur and nitrogen gas.

Suspended Culture Bioreactor

After acclimation, complete removal of sulfur dioxide, nitrogen oxides and oxygen was observed in the bioreactor for a period of two months. 30% of incoming carbon dioxide was removed in the bioreactor. The reactor pH remained at near neutral values. The chemoautotrophic sulfate reducing bacteria also use carbon dioxide from the stack gas to support biomass development. Thus CO_2 conversion to biomass and alkalinity (HCO_3^-) also occurs in the process. Chemoautotrophic bacteria function over a wide range of temperature from normal ambient to high temperatures nearing the boiling point of water. Temperature optimization of the processes have not been attempted. About 25% of the sulfur (SO_2) entering the reactor was released as H_2S in the exit gas. The carbon dioxide in the exit liquid was determined by acidification and measurement of CO_2 evolution. The bulk of the carbon dioxide removed from the stack gas was converted to carbonate in the liquid phase. The biomass produced by chemoautotrophic sulfate reducing bacteria supplied some of the organic material needed for sulfate reduction. Waste activated sludge was added to the reactor and primarily served as the organic source for sulfate reduction.

Analysis of the 0.2 liter aqueous stream from the bioreactor revealed that the nitrate/nitrite composition during the two month study varied between 50-120 ppm, the sulfate concentration was steady at 180 ppm. Qualitatively, particulate sulfur was present in the biomass.

The naturally adapted organisms and the water in the bioreactor support the following complex reactions:

Dissolution and Oxidation in Water:

$$SO_2 + H_2O \Longrightarrow H_2SO_3$$
$$2SO_2 + 2H_2O + 1/2O_2 \text{ ------> } H_2SO_4 + H_2SO_3$$
$$H_2SO_3 + 1/2O_2 \text{ ----> } H_2SO_4$$
$$2NO + O_2 \text{ -----> } 2NO_2$$
$$2NO_2 + H_2O \text{ -----> } HNO_2 + HNO_3$$
$$CO_2 + H_2O \Longrightarrow H_2CO_3$$

Bioreduction:

$$CH_3COO^- + SO_4^{2-} \xrightarrow{\text{Bacteria}} H_2O + CO_2 + HCO_3^- + S^{2-}$$
$$3CH_3COO^- + 4SO_3^{2-} \xrightarrow{\text{Bacteria}} 3H_2O + 3CO_2 + 3HCO_3^- + 4S^{2-}$$

$$2H^+ + S^{2-} \text{ ----------> } H_2S$$

$$SO_4^{2-} + 2H^+ + 3H_2S \text{ ----------> } 4S + 4H_2O$$

Nitrite and nitrate ions are also biologically reduced to nitrogen gas. The alkalinity (HCO_3^-) produced by the reduction neutralizes the acids produced in the oxidation reactions and by the dissolution of the gases in the water of the bioreactor. The steady-state pH in the bioreactor was 9.0.

Sulfur, biomass, sulfate and nitrate ions are removed from the reactor in the effluent aqueous stream. The small residuals of soluble sulfate and nitrate ions may be separated from the particulate sulfur and biomass in the stream. With or without separation, the soluble sulfate and nitrate ions may be reduced in a second reactor using waste organic sources, such as sewage sludge.

CONCLUSIONS

Biological conversion of sulfur dioxide and nitrogen oxides in stack gases is possible using either immobilized biofilms or suspended culture reactors. Complete conversion of sulfur and nitrogen oxides are achieved in the reactors with the final products being sulfur and nitrogen gas, respectively. Detailed reactions explaining the experimental data have been presented in this paper. Biotransformation of stack gas contaminants offers an alternative approach to manage combustion of high sulfur coal, without requiring landfilling or disposal of sludge.

REFERENCES

1. McCrea, D.H., Forney, A.H., and Myers, J.G., Recovery of Sulfur from Flue gas Using a Copper Oxide Absorbent. J.Of Air Pollution Control Association, Vol. 20. No. 12. 819, Dec. 1970.

2. Strakey, J.P., Bauer, E.R., and Haynes, W.P., Removal of SO_2 and NO_x from flue gad in Fluidized bed copper oxide process. Presented at the Sixth National Conference on Energy and Environment, Pittsburgh, Pa., May 21- 24, 1979.

3. Demski, R.J., Gasoir, S.J., Bauer, E.R., Jr., Yeh, J.T., Strakey, J.P., and Joubert, J.I., Simultaneous removal of SO_2 and NO_x from flue gas employing a fluidized bed copper oxide process. Presented at the 1092 Summer National Meeting of the AIChE, Cleveland, Ohio, August 29- September 1, 1982.

4. Yeh, J.T., Demski, R.J., Strakey, J.P., and Joubert, J.I., PETC Fluidized bed copper oxide process for combined SO_2 /NO_x removal from flue gas. Presented at the 1984 Winter National meeting of the AIChE, Atlanta, Ga., March 11- 14, 1984.

5. Drummond, C.J., Yeh, J.T.,Joubert, J.I., and Ratafia- Brown, J.A., The design of a dry, regenerative fluidized bed copper oxide process for the removal of sulfur dioxide and nitrogen oxides from coal fired boilers. Presented at the 78th Annual Meeting and Exhibition of the Air Pollution Association, Detroit, Michigan, June 16 -21, 1985,

6. McArdle, J.C., Leshick, D.G., and Williamson, R.R., Sorbent Life Cycle Testing of the Fluidized bed copper oxide process, Presented at the 1987 Spring National Meeting of the AIChE, Houston, Texas, March 29- April 2, 1987.

7. Tseng, H.P., Haslbeck, J.L., and Neal, L.G., Evaluation of the NOXSO combined NO_x/SO_2 flue gas treatment process. Report to the U.S. Department of Energy , Contract No. DE-AC22-FE6-0148, September 30, 1983.

8. Haslbeck, J.L., and Neal, L.G., Technical evaluation of the NOXSO combined NO_x/SO_2 flue gas treatment process. Presented at the 1985 Spring National Meeting of the AIChE, Houston, Texas, March 24-28, 1985.

9. Yeh, J.T., Drummond, C.J., Haslbeck, J.L., and Neal, L.G., The NOXSO process : Simultaneous removal of SO_2 and NO_x from flue gas. Presented at the 1987 Spring National Meeting of the AIChE , Houston, Texas, March 29- April 2, 1987.

10. Markussen, J.M., Yeh, J.T., and Drummond, C.J., Enhanced removal of nitrogen oxides in a spray dryer using a lime slurry containing sodium hydroxide. Presented at the 1986 Spring National Meeting of the AIChE, New Orleans, April 6-10, 1986.

11. Walker, R.J., Drummond, C.J., and Ekmann, J.M., Evaluation of Advanced separation techniques for application to flue gas cleanup process for the simultaneous removal of sulfur dioxide and nitrogen oxides, DE/PETC/TR-85/7 (DE85013006), June 1985.

12. Joubert, J.I., Drummond, C.J., Development of advanced flue gas emissions control technologies at the Pittsburgh Energy Technology Center, in "Coal Combustion", ed by J. Feng, Hemisphere Pub. Corp. N.Y. P. 853, 1988.

13. Kargi, F., and Robinson, J.M., Microbial Desulfurization of coal by Thermophilic Microorganism Sulfolobus Acidocaldarius, Biotechnology and Bioengineering, 24, p. 2115. (1982).

14. Kargi, F., Microbiological coal desulfurization, Enzyme Microb. Technol. 4. Jan. p. 13. (1982).

15. Kos, C.A., Poorter, R.P.E., Bos, P., and Kuenen, J.G., Geochemistry of sulfides in coal and microbial leaching experiments, Int. Conf. on coal science , Dusseldorf, p.842. (1981).

16. Dugan, P.R., Apel, W.A., Microbial desulfurization of coal, in : Metallurgical Application of Bacterial Leaching and Related Phenomena, L.E. Muer, A.E. Torma, and J.A. Brierly (BOS). Academic Press. N.Y., p. 223. (1978).

17. Detz, C.M., and Barvinchak, G., Microbial desulfurization of coal, Min. Congr. J. 65. p.75. (1979).

18. Isbister, J.D., and Kbylinski, E.A., microbial desulfurization of coal, in : Processing and Utilization of High Sulfur Coal, ed. by Y. A. Attia, Elsevier, N.Y., p. 627, (1985).

19. Murphy, J., Riestenbery, E, Mohler, R, Marek, D., Beck, B., and Skidmore, D., Coal desulfurization by microbial processing. in : Processing and Utilization of High Sulfur Coal, ed. by Y.A. Attia Elsevier, N.Y., p. 643. (1985).

20. Attia, Y.A., Elzeky, M.A., Biosurface modification in the separation of pyrite from coal by froth flotation. in : Processing and Utilization of High Sulfur Coals, ed. by Yosry. A. Attia, Elsevier, N.Y. p. 673. (1985).

21. OECD Guidelines for Testing of Chemicals, EEC Directive 79/831, Annex V, Part C: Methods for Determination of Ecotoxicity, 5.2 Degradation. Biotic Degradation. Manometric Respirometry. Method DGXI, Revision 5, 1983.

FOR MORE INFORMATION:

Rakesh Govind
Department of Chemical Engineering
University of Cincinnati
Cincinnati, OH 45221
Phone: 513/556-2666

Table 1. Design and Operating Conditions of the Suspended Culture Bioreactor

Diameter of reactor	4 inches	
Height of liquid in reactor	24 inches	
Amount of activated sludge added at start of experiment	20 gms	
Gas phase retention time	4 minutes	
Inlet Gas flowrate	1.5 liters per minute	
Outlet Gas flowrate	1.2 liter per day	
Inlet Gas Composition:	Carbon dioxide	41.56%
	Nitrogen	50.00%
	Oxygen	8.00%
	Sulfur dioxide	0.40%
	Nitrogen oxides	0.04%
Exit gas composition:	Carbon dioxide	36.4%
	Nitrogen	62.6%
	Moisture	0.88%
	Hydrogen sulfide	0.12%
	Sulfur oxides	0.00%
	Nitrogen oxides	0.00%
Reactor temperature and pH	$27^{o}C$; 9.0	
Amount of nutrient media fed daily to reactor	0.2 liters (OECD composition)	
Amount of reactor liquid withdrawn daily	0.2 liters	
Exit liquid composition (average) nitrate/nitrite	100 ppm	
sulfate	180 ppm	
free sulfur	present	

ANAEROBIC BIODEGRADATION OF PESTICIDES AND TNT: SITE EMERGING TECHNOLOGY DEMONSTRATION

Wendy Jo Davis-Hoover
Risk Reduction Engineering Laboratory (RREL)
5595 Center Hill Ave.
Cincinnati, Ohio 45224
513-569-7206; fax 513-569-7879

Trevor Jackson
SAIC
Idaho Falls, Idaho
208-528-2131; fax 208-528-2197

INTRODUCTION

J. R. Simplot, Inc. is a multiconglomerate whose initial interest was in the production of potatoes in the Pacific Northwest. This has lead them into the agricultural chemical business including pesticides. Dinoseb (a carcinogenic herbicide used to kill the foliage of potato plants allowing for easer harvesting) was used by them and after its ban in the U.S., J. R. Simplot realized the only acceptable way to dispose of dinoseb contaminated soils was to incinerate them at considerable cost. Thus J.R.Simplot became interested in developing a disposal solution that would be less cost prohibitive and as effective as incineration.

J. R. Simplot submitted a proposal and was accepted into the SITE Emerging Technology Program to optimize the anaerobic biodegradation of nitroaeromatics (dinoseb) contaminated soils with the addition of water, pH buffers, and potato waste as a source of starch. This work ultimately resulted in a good understanding of the biological and chemical process of destruction (optimum conditions of 35 and 37 degrees C, and pH of approximately 7, leads to destruction in 14 days) of both dinoseb and TNT and in several peer reviewed publications (1-7).

METHODOLOGY

The process was then tested by the SITE Demonstration Program at a small field scale at much less than optimum conditions at Ellensburg, Washington in the cold summer of 1993 on soil contaminated with an average of 27.3 milligrams of dinoseb per kilogram (mg/kg) of soil. The process was also evaluated at the previously functioning Weldon Spring Ordnance Works near St. Louis in the even colder fall/winter of 1993/94 on soil contaminated with an average of 1510 mg of TNT/kg of soil.

Sixty one samples were randomly collected from the excavated one half inch screened contaminated soil and analyzed for dinoseb by HPLC using a method developed for this evaluation. The 39 cubic yards of contaminated soil was moved into a truck-trailer sized reactor while 2-5 percent of the weight was added as potato waste. Dinoseb-free water was added at a 1 L/ kg of contaminated soil ratio. The pH was buffered to about 7.1 and an inoculum of previously treated soil (5 gallon bucket) was added. Two mixers were used with the dinoseb bioreactor to keep the soils and liquids mixed but not to add oxygen. The process is initiated by allowing the aerobic organisms to consume the potato waste and thus utilize the oxygen. The anaerobic conditions that result allow the anaerobic organisms to degrade the dinoseb and any byproducts. A negative control of excavated, screened, and dinoseb-contained soil was kept at the site and analyzed before and after the testing for dinoseb. After treatment, 41 randomly generated areas of the bioreactor were sampled, and the sediments, and eluent from these samples were analyzed for dinoseb and any known byproducts along with a toxicity screen which showed the presence of other pesticides.

The TNT contaminated soils were treated in the same manner except the soils had a higher clay count and thus the mixers were ineffective. To obtain the soil/water interface, the bioreactor was therefore lanced every 7-14 days. As the ambient temperature dropped significantly at this site, heaters were added to keep the bioreactor from freezing. TNT levels were determined by EPA method 8330 at time zero, 5 months and 9 months. Toxicity tests were analyzed on time zero and at 5 months.

RESULTS

No dinoseb was detected in any samples after only 23 days of remediation even though the temperature was as low as 18 degrees C. The concentrations of nitroaniline, parathion, malathion, and 4,4'-DDT were also found to be decreased in this process in just 23 days.

The winter conditions in St. Louis threatened to freeze the bioreactor so heaters were added to bring the temperature up from 4 degrees C. Sampling at roughly 5 months showed a 95 percent reduction in the concentration of TNT, and significant reductions in toxicity were measured by root elongation, early seedlings, and earthworm reproduction tests. After sitting for another 4 months the TNT contamination in the soil was reduced by 99.4 (95 % C.I. is 98.3-99.9) percent.

CONCLUSIONS

This process has shown substantial removal of dinoseb, TNT, their known byproducts, and toxicity in general (as measured by several methods) at costs that are significantly less than soil incineration even at non-optimized conditions. Testing has also shown that nitroaniline, parathion, Malathion, and 4,4'-DDT levels can also be reduced using this technology. Although the soil is excavated and thus disrupted it is left in better condition with this process than with incineration. Thus it appears to be a viable alternative to soil incineration for these contaminants. More complete information on these demonstrations can be found in their Innovative Technology Evaluation Reports (8, 9) and Technology Evaluation Reports (10, 11).

REFERENCES

1. Kaake, R., Roberts, D., Stevens, T., Crawford, R., and Crawford D. Bioremediation of Soils Contaminated with the Herbicide 2-sec-Butyl-4,6-Dinitrophenol (Dinoseb). Applied and Environmental Microbiology, May 1992, p. 1683-1689.

2. Spiker, J., Crawford, D., and Crawford, R. Influence of 2,4,6-Trinitrotoluene (TNT) Concentration on the Degradation of TNT in Explosive-Contaminated Soils by the White Rot Fungus Phanerochaete Chrysosporium. Applied and Environmental Microbiology, Sept. 1992, p. 3199-3202.

3. Funk, S., Roberts, D., Crawford, D., and Crawford, R. Initial-Phase Optimization for Bioremediation of Munition Compound-Contaminated Soils. Applied and Environmental Microbiology, July 1993, p. 2171-2177.

4. Kaake, R., Crawford, D., and Crawford, R. Optimization of Anaerobic Bioremediation Process for Soil Contaminated With the Nitroaromatic Herbicide Dinoseb (2-Sec-Butyl-4,6-Dinitrophenol). In: Applied Biotechnology for Site Remediation. Lewis Publishers, Boca Raton, Ann Arbor, London, Tokyo.

5. Roberts, D., Kaake, R., Funk, S., Crawford D., and Crawford, R. Anaerobic Remediation of Dinoseb from Contaminated Soil - An On-site Demonstration. In: Applied Biochemistry and Biotechnology, Vol. 39/40, 1993.

6. Daniel, B., Korus, R., and Crawford, D. Anaerobic Bioremediation of Munitions-Contaminated Soil. In Press, October 1993.

7. Funk, S., Crawford, D., Roberts, D., and Crawford, R. Two-Stage Bioremediation of TNT Contaminated Soil. In Press, October 1993.

8. U.S. Environmental Protection Agency. Ex-Situ Bioremediation Technology for Treatment of Dinoseb-Contaminated Soils. Innovative Technology Evaluation Report. U.S. EPA, Cincinnati, Ohio, 1995.

9. U.S. Environmental Protection Agency. Ex-Situ Bioremediation Technology for Treatment of TNT-Contaminated Soils. Innovative Technology Evaluation Report. U.S. EPA, Cincinnati, Ohio, 1995.

10. U.S. Environmental Protection Agency. Ex-Situ Bioremediation Technology for Treatment of Dinoseb-Contaminated Soils. Technology Evaluation Report. U.S. EPA, Cincinnati, Ohio, 1995.

11. U.S. Environmental Protection Agency. Ex-Situ Bioremediation Technology for Treatment of TNT-Contaminated Soils. Technology Evaluation Report. U.S. EPA, Cincinnati, Ohio, 1995.

FOR MORE INFORMATION

Wendy Jo Davis-Hoover
RREL
5595 Center Hill Ave.
Cincinnati, Ohio 45224
513-569-7206; fax 513-569-7879

For report requests call 513-569-7794

IRON ENHANCED ABIOTIC DEGRADATION OF CHLORINATED HYDROCARBONS

Chien T. Chen
U.S.EPA, Releases Control Branch
2890 Woodbridge Avenue, Edison, NJ 08837-3679
(908) 906-6985

INTRODUCTION

Since the 1970s, several researchers have investigated the ability of certain zero-valent metals or alloys to enhance the degradation of halogenated organic compounds in contaminated water. Iron, zinc, aluminum, brass, copper, and stainless steel have been studied at various times with varying degrees of success. Gillham and O'Hannesin have recently made a literature review and conducted tests on 14 halogenated aliphatic compounds using zero-valent iron as an enhancing agent (1). The results showed that rapid dehalogenation occurred on all of the compounds tested except dichloromethane. Based on these test results, EnviroMetal Technologies, Inc. proposed to remediate groundwater contaminated with chlorinated organic compounds using this technology.

The EPA Superfund Innovative Technology Evaluation (SITE) program has accepted this technology for demonstration. This demonstration project will include two processes, above ground reactor and in situ permeable wall. The demonstration on the above ground reactor is being conducted at a site in Wayne, New Jersey. The main contaminants at this site are tetrachloroethene (PCE) and trichloroethene (TCE). The in situ permeable wall process will be conducted at a site in upstate New York. This site is a shallow sand aquifer containing TCE, dichloroethenes, and 1,1,1-trichloroethane.

METHODOLOGY

Before the site demonstration, laboratory experiments were conducted on the contaminated groundwater to evaluate the efficiency of the process , under simulate site conditions. The procedures of this and the two demonstration processes are described below.

Column tests were undertaken in the laboratory to simulate the dynamic conditions of groundwater. The columns were constructed of plexiglass with a length of 50 cm and an internal diameter of 6.5 cm. Seven sampling ports were positioned at distances of 2.5, 5, 10, 15, 20, 30, 40 and 50 cm from the inlet end. The columns also allowed for collection of samples from the influent and effluent solutions. A total of three column experiments were set up, one control and two reactive columns. The control column was packed with 100% silica sand. One reactive column was packed with a mixture of 50% (by weight) granular iron and 50% (by weight) silica sand, while the other reactive column was packed with 100% granular iron. The mass of iron to volume of solution ratio for the 50% iron column was 3.4 g : 1 ml and for the 100% iron column was 8 g : 1 ml.

The above ground reactor was constructed of fiberglass with a height of 9 feet and an internal diameter of 8 feet. The reactor was packed from the bottom to the top with: 6" of pea gravel, 66" of granular iron, 24" of groundwater and 12" of air. The total weight of iron was 18003 kg with a porosity of about 0.4. The pore volume was calculated to be about 3400 L. Five sampling ports were positioned at distances of 21, 36, 48, 66 and 84 inches from the inlet end (top of the water level). The influent and effluent solutions were also collected. During the demonstration, groundwater was extracted from the site by passive recovery techniques, using tiles placed in the bottom of collection trenches (about 14 ft below the ground surface).

Groundwater flowed through the collection trenches to a sump, where it was pumped to the above ground reactor at a rate of 1.9 L per minute. This would let the water to have the residence time in the reacting medium of about 26 hours during which the TCE and PCE in the contaminated water would be completely dechlorinated according to the half lives of those two compounds obtained in the column test.

The in situ permeable reactive wall will be constructed by filling a trench with iron and inert materials. Groundwater will move naturally through the wall. The contaminants are expected to be dechlorinated after passing the reactive wall.

RESULTS

Column Tests

Tables 1-3 show the concentrations of PCE and TCE at different sampling positions with various pore volumes of the groundwater passing through the three columns. The results show that (1) for the control column containing only silica sand, the concentrations of PCE and TCE remained relatively constant over the entire length of the column, with the influent concentration very similar to the effluent concentration; (2) for the 50% iron/sand column, the observed decline in concentration with distance reflects that both PCE and TCE were degraded gradually along the column, at a distance between 15 and 20 cm from the influent, both compounds had degraded to below the detection limit (2.5 ug/L for PCE and 3.0 ug/L for TCE); (3) for the column with 100% granular iron, rapid declines in concentrations of PCE and TCE were observed, at a distance between 2 and 10 cm from the influent, both compounds had degraded to below the detection limit. The production of small amounts of 1,1-dichloroethene (1,1-DCE), cis-1,2-dichloroethene (cDCE), and vinyl chloride (VC) were observed in both reacting columns. However, 1,1-DCE disappeared rapidly in both columns, cDCE and VC were eventually dechlorinated in the 100% iron column. They were not completely removed in the 50% iron/sand column.

TABLE 1
CONTROL COLUMN (100% SILICA SAND)

		Distance Along Column (cm)								
		Influent 0	2.5	5	10	15	20	30	40	Effluent 50
	Pore Volume	Organic Concentration (ug/L)								
PCE	1.03	12394	12272	11863	2914	9997	10718	8896	2858	7709
	2.15	11031	9978	9798	8709	8050	9932	10947	11504	10061
	5.00	8305	8867	9640	9241	9213	9349	9012	10196	8841
TCE	1.03	508	465	490	319	444	404	400	242	234
	2.15	432	442	334	317	384	415	423	437	387
	5.00	298	273	305	291	293	304	287	330	273

Flow Velocity = 44 cm/day (1.44 ft/day)
Porocity = 0.39

TABLE 2
REACTIVE COLUMN I (50/50 Iron/Silica Sand)

		Distance Along Column (cm)								
		Influent 0	2.5	5	10	15	20	30	40	Effluent 50
	Pore Volume	Organic Concentration (ug/L)								
PCE	1.25	11882	73	0.7	0	0	0	0	0	0
	6.73	9327	5317	2790	0	0	0	0	0	0
	11.28	9438	7037	3781	0	0	0	0	0	0
	15.73	9434	6646	3712	47	0	0	0	0	0
	21.67	8934	4188	2480	249	0	0	0	0	0
	24.95	4593	3073	1851	285	0	0	0	0	0
	31.00	4360	1630	2000	388	0	0	0	0	0
	33.86	5062	3114	1681	302	0	0	0	0	0
	38.81	4846	2842	1805	486	1	0	0	0	0
	40.92	4316	2406	1314	379	3	0	0	0	0
TCE	1.25	462	133	0	0	0	0	0	0	0
	6.73	312	704	748	0	0	0	0	0	0
	11.28	379	589	636	90	0	0	0	0	0
	15.73	390	564	656	127	0	0	0	0	0
	21.67	361	495	397	143	0	0	0	0	0
	24.95	1160	730	500	132	0	0	0	0	0
	31.00	1042	374	516	157	4	0	0	0	0
	33.86	986	621	365	108	4	0	0	0	1.5
	38.81	1136	534	324	141	12	0	0	0	0
	40.92	938	400	213	105	12	0	0	0	0

Flow Velocity = 55 cm/day (1.8 ft/day)
Porocity = 0.34

The test results show that the degradations of both PCE and TCE follow first order kinetics. Therefore the half lives of these two compounds in the two reactive columns were calculated according to the equation:

$$t_{1/2} = 0.693/k \qquad (1)$$

where $t_{1/2}$ is the half life (the time at which the initial concentration, C_0, declines by one-half), k is the first order rate constant which is calculated according to the following equation:

$$\ln (C/C_0) = -kt \qquad (2)$$

where C is the concentration in solution at time t. From the experimental results, the half lives of PCE and TCE in the reaction columns are calculated to be as follow:

(1) For 50% iron/sand column - PCE:0.67 hrs, TCE:1.10 hrs
(2) For 100% iron column - PCE:0.42 hrs, TCE:0.52 hrs

Demonstration Using Above Ground Reactor

The sampling was started after about 3 pore volumes of water had passed through the reactor. The water samples were collected about once per week. So far, four sets of samples have been collected and analyzed. The results are shown in Table 4. In the first three sets of samples, all PCE and TCE were completely dechlorinated after passing through 12" of iron. No chlorinated hydrocarbons were observed (detection limit for all the probable products was 1.0 ug/L). In the fourth set of samples, the concentration of PCE was very high (13000 ug/L), so it did not completely disappear until the solution passed through about 24" of the reactive iron. The quantities of TCE increased first and then disappeared after the solution had passed through 24" of iron.

TABLE 3
REACTIVE COLUMN II (100% Grandular Iron)

	Distance Along Column (cm)	Influent 0	2.5	5	10	15	20	30	40	Effluent 50
	Pore Volume	Organic Concentration (ug/L)								
PCE	1.01	11963	0	0	0	0	0	0	0	0
	4.47	8227	1	0	0	0	0	0	0	0
	8.73	9602	462	0	0	0	0	0	0	0
	13.88	9847	1532	0	0	0	0	0	0	0
	19.25	7610	1136	6	0	0	0	0	0	0
	21.79	4535	923	14	0	0	0	0	0	0
	27.19	4476	1109	59	0	0	0	0	0	0
	29.62	5190	865	57	0	0	0	0	0	0
	33.02	4241	682	67	0	0	0	0	0	0
	34.85	4407	926	96	0	0	0	0	0	0
TCE	1.01	452	0	0	0	0	0	0	0	0
	4.47	282	6	0	0	0	0	0	0	0
	8.73	336	391.7	0	0	0	0	0	0	0
	13.88	384	541	10	0	0	0	0	0	0
	19.25	321	349	29	0	0	0	0	0	0
	21.79	1222	356	26	0	0	0	0	0	0
	27.19	1069	380	54	0	0	0	0	0	0
	29.62	1005	298	36	0	0	0	0	0	0
	33.02	1020	169	35	0	0	0	0	0	0
	34.85	998	262	46	0	0	0	0	0	0

Flow Velocity = 47 cm/day (1.54 ft/day)
Porocity = 0.40

TABLE 4
ABOVE GROUND REACTOR

		From the Influent (inch)							
		0	0	21#	36	48	66	84	96*
	Pore Volume	Concentration (ug/L)							
PCE	2.4		6200	6100	0	0	0	0	0
	8.8		9800	Nd**	Nd	Nd	Nd	Nd	0
	14.4		9700	Nd	Nd	Nd	Nd	Nd	0
	25.6		13000	8700	4200	0	0	0	0
TCE	2.4		110	0	0	0	0	0	0
	8.8		69	Nd	Nd	Nd	Nd	Nd	0
	14.4		130	Nd	Nd	Nd	Nd	Nd	0
	25.6		110	93	330	0	0	0	0

The reaction with iron started at 24" from influent port
* This is the effluent solution
** Not determined

The production of cDCE was observed between 0 and 12" below the iron surface. It was 92, 18 and 0 ug/L respectively at 12", 24" and 42" below the iron surface respectively. Small quantity of vinyl chloride (4.9 ug/L) was observed at 24" which disappeared at 42". At this sampling point, 1.5 ug/L of methylene chloride was observed which degraded to below 1.0 ug/L below the iron surface. The reaction process appeared to follow sequential dechlorination from PCE to TCE to cDCE and then to vinyl chloride and methylene chloride. However, all the chlorinated compounds were completely dechlorinated at the end if there was enough reactive iron.

CONCLUSIONS

The results from the column tests show that the 100% iron column can dechlorinate PCE and TCE much faster than the 50% iron/sand column. Also, the former column can completely dechlorinate the by-products but not the later column. Therefore the 100% iron column was used in the pilot scale experiment. The results obtained thus far showed that PCE, TCE and their chlorinated products can be completely dechlorinated in the above ground reactor.

The potential limiting factors of this technology such as: the possible formation of precipitates that might clog the treatment reactor's pore space and/or coat the iron surface and thus limiting water flow or reducing the reactivity of iron; the consumption of iron by its reaction with the chlorinated compounds to produce soluble iron compounds; and the increasing pH over time and thus impeding the reaction rate, are being studied. The approximate capital as well as the short and long term operating and maintenance costs are being evaluated.

The above ground reactor may replace the air stripper and activated carbon as methods of remediating halogenated organic compounds. The in situ permeable wall may permit passive treatment for a long period of time and thus eliminating the disposal or treatment of the pumped groundwater.

Acknowledgments

The author wishes to acknowledge S. Krishnamurthy of the United States Environmental Protection Agency (EPA) for his helpful discussion and critical review. He also wishes to thank Kim Lisa Kreiton of PRC Environmental Management, Inc (PRC) for her efforts in collecting and calculating the data in the above ground reactor demonstration and William Matulewicz of Rhode Engineering for his providing of the column test results. This research work was funded by EPA under Contract No. 68-CO-0047 to PRC.

REFERENCES

1. Gillham, R.W., and O'Hannesin, S.F. Enhanced Degradation of Halogenated Aliphatic by Zero-Valent Iron, Ground Water 32, 958-967, 1994.

2. Superfund Innovative Technology Evaluation Program, Technology Profiles, Seventh Edition, EPA/540/R-94/526, Office of Research and Development, Washington, DC, 1994, 174-175.

TESTING THE SONOTECH PULSE COMBUSTOR IN A PILOT-SCALE ROTARY KILN INCINERATOR

Marta K. Richards
United States Environmental Protection Agency
Office of Research and Development, Risk Reduction Engineering Laboratory
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268
513/569-7692

Larry R. Waterland
Acurex Environmental Corporation
Incineration Research Facility
Jefferson, Arkansas 72079
501/541-0004

Kenneth G. Partymiller
PRC Environmental Management, Inc.
5326 Paris Pike
Georgetown, Kentucky 40324
502/867-1397

INTRODUCTION

This is a report on an incinerator performance test of an innovative soundwave-based combustion burner system that was patented, designed, and fabricated by its developer - Sonotech, Inc., of Atlanta, Georgia. The Superfund Innovative Technology Evaluation (SITE) program Demonstration of the Sonotech, Inc., tunable-pulse combustion burner technology was conducted in the fall of 1994 at USEPA's Incineration Research Facility (IRF) in Jefferson, Arkansas. Sonotech claims the technology will provide benefits when applied in a variety of combustion processes. The burner system incorporates a natural-gas-fired burner, the pulse frequency of which can be tuned to induce large amplitude sonic pulsations inside a combustion process unit, such as an incinerator. Sonotech claims these pulsations will increase the efficiency of a combustion process by promoting better mixing of the combustion gases. In the SITE Demonstration of its technology, Sonotech's technicians retrofitted a pulse combustion burner in the government's pilot-scale rotary kiln incineration system (RKS) housed at the IRF.

Sonotech claims their burner significantly improves the performance of the incineration process by increasing the rates of mixing (i.e.,momentum) and mass and heat transfers within an incinerator. These, in turn, increase the incineration rate, reduce the amount of air required for incineration, reduce the severity of puffs, and reduce pollutant emissions. The developer claims these improvements reduce capital investment and operating costs in a wide variety of incineration systems and improve their performance.

TEST OBJECTIVES

The general test program objective was to develop test data to allow objective and quantitative evaluation of the Sonotech claims for their pulse combustion technology. For the Primary Test Program Objectives, we investigated whether the Sonotech technology, when applied to the IRF RKS and compared to conventional, non-pulsating combustion, results in:

- Increased incinerator capacity or productivity
- Increased principal organic hazardous constituent (POHC) destruction and removal efficiency (DRE)
- Decreased flue gas carbon monoxide (CO) emissions
- Decreased flue gas nitrogen oxides (NO_x) emissions
- Decreased flue gas soot emissions
- Decreased combustion air requirements
- Decreased auxiliary fuel requirements

Test data were also developed for the Secondary Test Program Objectives, which were to allow evaluating whether the application of the Sonotech technology, when compared to conventional, non-pulsating combustion:

- Reduced the magnitude of transient puffs of CO and total unburned hydrocarbon (TUHC)
- Allowed reduced incineration costs
- Caused significant changes in:
  - Distribution of hazardous constituent trace metals among the incineration system discharge streams (kiln bottom ash, scrubber liquor, baghouse flyash, and baghouse exit flue gas)
  - The mobility of the toxicity characteristic leaching procedure (TCLP) trace metals from kiln bottom ash, scrubber liquor, and baghouse flyash

The last secondary objective does not relate to any Sonotech claim, however, fates of metals and their leachabilities are of general interest to the EPA IRF research program.

TESTING PROTOCOL

The waste feed for all tests was a mixture of contaminated materials from two manufactured gas plant (MGP) Superfund sites. One site was the Peoples Natural Gas Company (coal gasification) site in Dubuque, Iowa, and the other was an oil gasification site in the Southeast U.S. The final waste feed was composed of coal and sludge from the Peoples site mixed with the contaminated soil borings and tar from the oil gasification site.

The final composite feed contained polynuclear aromatic hydrocarbons (PAHs) and other semivolatile organic compounds (SVOCs), benzene and other volatile organic compounds (VOCs), metals, and other contaminants. It was determined that, to guarantee meaningful calculation of DREs of specified POHCs, spiking of the waste feed with benzene and naphthalene was necessary. The spiked composite feed contained 13,500 mg naphthalene/kg feed and 9000mg benzene/kg feed.

Twelve field incineration test runs were conducted. Four incinerator system operating conditions - each in triplicate - addressed the Demonstration objectives. The four conditions were:

- Condition 1: Conventional combustion at baseline/typical operation
- Condition 2: Conventional combustion at its maximum feedrate
- Condition 3: Sonotech combustion at the same feedrate as Condition 2
- Condition 4: Sonotech combustion at its maximum feedrate

This testing program would allow comparison of Sonotech performance with conventional combustion and permit evaluation of the developer performance claims.

Table 1 shows the samples that were taken and the analyses that were performed.

TABLE 1. SAMPLING AND ANALYTICAL TEST PROGRAM

Samples \ Analyses	SVOCs	VOCs	Metals	PCDDs/PCDFs	TOC	TCLP
Feed	X	X	X			X
Kiln Ash	X	X	X			X
Scrubber Liquor	X	X	X			X
Baghouse Ash	X	X	X			X
AB Exit Particulate	X				X	
BH Exit Flue Gas	X	X	X			
AB Exit Flue Gas	X	X	X	X		

Note: SVOCs = Semivolatile Organic Compounds
VOCs = Volatile Organic Compounds
PCDDs/PCDFs = Polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
TOC = Total Organic Carbon
TCLP = Toxicity Characteristic Leaching Procedure of metals
AB = Afterburner
BH = Baghouse

To determine if performance satisfied the test objectives, continuous emission monitors (CEMs) constantly measured the oxygen (O_2), CO, carbon dioxide (CO_2), NO_x, and TUHC levels in the flue gas streams.

The test matrix was designed to give data that allowed evaluation of the vendor claims as follows. Test condition 1 provided emissions, POHC DRE, metals partitioning, and metals leachability data corresponding to baseline, typical, well-controlled incinerator operation. Test condition 2 provided the same kinds of data for operation corresponding to maximum feedrate possible under conventional incinerator operation, which is borderline acceptable operation approaching noncompliance with typical permit limits. Test condition 3 provided similar data corresponding to test condition 2, except with the Sonotech unit running, while test condition 4 corresponds to the maximum feedrate possible with the Sonotech pulse combustor operating.

RESULTS

Preliminary results of the test program related to the primary test objectives are reported here. Test condition 3 data are used to evaluate the last six primary objectives by comparing results with the those obtained under test conditions 1 and 2 data. Comparing test condition 4 data to those from test conditions 1, 2, and 3 allowed evaluation of the first primary objective. The numerical-average results are shown in Table 2.

TABLE 2. OPERATING DATA AND RESULTS BY TEST CONDITION

Parameter	Test Conditions*			
	Conventional Combustion		Pulse Combustion	
	1:	2:	3:	4:
Waste feedrate, lb/hr	61.0	72.8	73.6	82.4
Kiln Gas temperature, °F	1,720	1,730	1,700	1,700
Afterburner gas temperature, °F	2,000	2,000	2,000	2,000
Afterburner exit O_2, %	9.33	9.27	8.73	8.51
Heat input, kBtu/hr				
Waste	517	617	639	699
Auxiliary fuel	1,670	1,540	1,580	1,490
Total	2,190	2,160	2,220	2,190
Combustion air, dscf/hr	37,300	36,800	35,700	35,200
Afterburner exit CO, ppm @ 7% O_2	15.2	20.3	14.5	17.9
Afterburner exit NO_x, ppm @ 7% O_2	90.0	81.7	78.1	72.4
Afterburner exit soot emission rate (TOC in particulate, %)	<1.0	$\leq$2.4	$\leq$1.0	$\leq$2.1

* Each Data Point is the Numerical Average of 3 Tests
1: Baseline Feedrate
2: Maximum Feedrate with Conventional Combustion
3: Condition-2 Feedrate
4: Maximum Feedrate with Pulse Combustion

1. Incinerator capacity and productivity, shown in Table 2 - measured in terms of tested waste feedrate, showed an increase with pulse combustion of 20%, comparing test condition 3 with test condition 1 and an increase of 13%, comparing test condition 4 to condition 2. In addition, when comparing test condition 4 to test condition 1, the empirical data show that increasing the feedrate while using the pulse combustor resulted in a productivity increase of about 35% with similar resulting CO, NO_x, soot, VOC, and SVOC emission levels.

2. POHC DRE evaluations were inconclusive. Measured at the afterburner exit, benzene DREs for all 12 test runs were greater than 99.994% with a slight improvement in the third decimal place for the Sonotech burner. Naphthalene DREs were greater than, or equal to, 99.999% for all test conditions.

3. The average afterburner exit CO emissions decreased marginally with the operation of the Sonotech combustor.

4. NO_x emissions were low in all tests, but the average NO_x emissions with the pulse combustor in operation were slightly lower than those from conventional combustion.

5. Average soot emissions, measured by TOC analyses of the afterburner exit flue gas particulate and comparing soot emission rates, were lower with pulse combustion than conventional combustion at equivalent feedrates.

6. Combustion air requirements, determined from stoichiometric calculations, showed small decreases with pulse combustion.

7. Fuel requirements for all four test conditions were statistically similar.

For the secondary test program objectives:

1. The frequency of transient puffs of CO decreased with the pulse combustor in operation.

2. The average normalized distribution of the trace metals did not vary significantly from test to test.

3. The effect of the Sonotech combustor on incinerator residue toxicity characteristics, as measured by the TCLP, was inconclusive due to very low levels of metals in the kiln ash and, therefore, the leachate.

CONCLUSIONS

The most important difference measured with the Sonotech combustor in operation was the ability to increase the capacity of the EPA RKS. This increased capacity resulted in the same or slightly reduced CO, NO_x, and soot emissions. Additionally, the benzene and naphthalene DREs were equal or marginally improved with the Sonotech burner in operation. The increase in incinerator capacity was also realized without increasing fuel or air consumption to the system.

FOR MORE INFORMATION:

Marta K. Richards
United States Environmental Protection Agency
Office of Research and Development, Risk Reduction Engineering Laboratory
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268
513/569-7692

THE RELATIVE EFFECTIVENESS OF MINERAL-BASED SORBENTS FOR METAL CAPTURE IN A BENCH-SCALE INCINERATOR

Gregory J. Carroll
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
Cincinnati, OH 45268
513/569-7948

Shyam Venkatesh
Acurex Environmental Corporation
c/o NCTR, Bldg. 45
Jefferson, AR 72079
501/541-0004

INTRODUCTION

Given the concern over the emission of hazardous constituent trace metals from incinerators, there is currently considerable interest in the potential use of mineral-based sorbents for capturing and retaining those metals in the incinerator "ash" discharges (fly ash and bottom ash).

Most of the research completed to date has focussed on quantifying the effectiveness of various proposed sorbents for capturing vaporized metals from the flue gas. In such applications, it is theorized that vaporized metals will react with the sorbent particles at elevated incinerator temperatures or heterogeneously condense onto the sorbents as the flue gas cools. In the absence of available condensation sites, vaporized metals will primarily undergo homogeneous condensation, forming a fine fume. Thus, the goal with flue-gas sorbents is to make particles available with which the metals can react or upon which the metals can condense. Metals bound to larger sorbent particles will be more effectively collected by air pollution control systems (APCSs) than metals presented as a fine fume. Studies completed to date suggest that chemical reaction between the metal and the sorbent dominates over physical adsorption, offering the additional advantage of reduced potential for metal leaching from collected particulate.

Other researchers have studied the incorporation of sorbents into the solid feed. This approach seeks to capture and bind the metals in the incinerator bottom ash, preventing them from exiting with the combustion gases. Research completed to date suggests that for this approach to be effective, the metal should become volatile in the incinerator environment and chemically react with the sorbent material.

The subject test program was designed to further investigate this second approach by screening several minerals for their suitability as sorbent materials for capturing metals in the solid bed and preventing their release to the flue gas. In addition to capturing the metals, an ideal sorbent would retain them in the ash when disposed, so that extraction of the ash by the toxicity characteristic leaching procedure (TCLP) would yield a leachate with metals concentrations below respective regulatory levels. Accordingly, the objective of this screening program was to evaluate several candidate sorbents with respect to: [1] the degree to which they facilitate retention of trace metals in the ash/solid bed discharged from an incinerator; and [2] the degree to which they retain trace metals in the solid bed when subjected to TCLP extraction.(1)

METHODOLOGY

Test Equipment

The screening tests comprising this program were conducted in the bench-scale thermal

treatability unit (TTU) at the U.S. EPA Incineration Research Facility (IRF). The TTU is a small commercial pathological incinerator that has been modified to allow: continuous test material feed and treated material (e.g., ash) removal; variable treatment temperature control; and expanded process operation monitoring.

The combustor portion of the TTU consists of three chambers. The charge chamber is designed to accept the solid material feed stream and corresponds to the primary combustion chamber (or kiln portion) of a waste incinerator. The retention chamber, which directly follows the charge chamber, is designed to effect further organic constituent destruction and corresponds to the secondary combustion chamber (or afterburner) of a waste incinerator. The breaching chamber serves as a second-stage afterburner. Volumes of the charge chamber, retention chamber, and breaching chamber are 0.82 m^3 (29 ft^3), 0.67 m^3 (23.5 ft^3), and 0.10 m^3 (3.5 ft^3), respectively. Each of the three chambers is fired with natural-gas-fueled burners.

Test Program

The test program consisted of 50 tests, including two duplicates of one test condition. Test variables were sorbent material type, solid bed temperature, feed chlorine content, and metal form in the feed.

Six sorbents were evaluated. The first five (silica, diatomaceous earth, kaolinite, bauxite, and alumina) were selected based on the most promising results from other researchers and make up a sorbent-material spectrum ranging from pure silica to pure alumina. The attapulgite clay used in past IRF trace metals studies was tested as the sixth sorbent.

The approximate mineral content of diatomaceous earth, kaolinite, and bauxite are given in Table 1. Silica is presumed to be pure SiO_2; alumina is presumed to be pure Al_2O_3; and the attapulgite clay is a hydrated magnesium aluminum silicate [$(Mg,Al)_5Si_8O_{22}(OH)_4 \cdot 4H_2O$] containing some dolomite [$Ca,Mg(CO_3)_2$], calcite [$CaCO_3$], and silica.

Three solid bed temperatures were tested: 540°C, 700°C, and 870°C (1000°F, 1300°F, and 1600°F). Two feed chlorine contents were tested: 0% and 4% by weight. Polyvinyl chloride powder was added to the mixtures as the chlorine source.

TABLE 1. APPROXIMATE SORBENT MINERAL COMPOSITION

	Diatomaceous earth	Kaolinite	Bauxite
SiO_2	90.4	52	11
Al_2O_3	6.5	45	84
Fe_2O_3	2.3	1	5
TiO_2	--	2	--
CaO	0.2	--	--
MgO	0.3	--	--
Other oxides	0.3	--	--

Sorbent impact on the retention of the following trace metals was evaluated in the program: arsenic, cadmium, chromium, lead, and nickel. Two forms of incorporating the metals into the feed mixtures were evaluated. Past trace metals tests at the IRF have used aqueous metal spike solutions containing soluble nitrate salts of the metals (with the exception of arsenic which has been added as

As_2O_3). For continuity, this form was one of the two used in the tests.

The second form of metal spiking was a metal compound "dispersion". The dispersion consisted of metal compound powders suspended in a liquid carrier analogous to pigments dispersed in paint or ink. Chromium, cadmium and lead were present as metal oxides in the dispersion, while arsenic and nickel were introduced as sulfides and carbonates, respectively. Because of a difficulty achieving homogenous feed mixtures with the metal compound dispersion, the discussion of results in this abstract is limited to the 36 tests in which the aqueous metal spike solution was used.

For each test, weighed amounts of the appropriate mixtures of sorbent, PVC (for tests with chlorine-containing feed), and metal spiking formulations were added to a TTU quartz tray. Charge depth was held constant at nominally 2 cm, corresponding to a charge volume in the tray of approximately 300 cm^3. Target feed metal concentrations were also constant as follows: arsenic (200 mg/kg); cadmium (50 mg/kg); chromium (150 mg/kg); lead (250 mg/kg); and nickel (150 mg/kg). Charge mass ranged from 50 g to 320 g, depending on sorbent bulk density.

Tray residence time in the TTU was approximately 20 minutes at the target solid bed temperature. Based on the results of other research, no further reaction between the sorbent and metals was expected after the first 10 minutes at target temperature.

Sampling and Analysis

For each test, TTU gas temperatures and solid bed temperatures were measured. Samples of unspiked sorbent, metal spiking solution, TTU feed, and TTU discharge were collected for metal analyses. Additionally, one TTU feed sample from each of the sorbent/metal formulation combinations and TTU discharge samples from every test were subjected to TCLP extraction, and the resulting leachates analyzed for trace metals.(2) Quality assurance samples were prepared as well.

Aqueous liquid samples were digested using EPA Method 3010.(3) Solid samples were digested using a microwave-assisted HNO_3/HF procedure.(4) Analyses of each of the latter digestates for arsenic were by Method 7060 [GFAA].(3) All other digestates analyses were by Method 6010 [ICAP].(3)

RESULTS

Feed Samples

Despite the use of a rigorous digestion method, analyses of feed samples often yielded concentrations below those expected (based on prepared metal spike solutions). Of the five metals, cadmium and lead exhibited the largest difference between target and measured concentrations. On average, metal concentrations in the attapulgite clay and kaolinite were below target more so than the other matrices.

Since the same preparation and analysis methods were applied to both the feed and treated material samples, it is assumed that any sampling or analysis bias should manifest itself in both sample types (i.e., the feed and treated material associated with a particular sorbent). Therefore, comparisons between the feed samples and treated material were based on measured (as opposed to prepared) feed concentrations.

Retention of Metals in Ash

Metal volatility was judged by examining treated material (ash) concentrations relative to feed concentrations (adjusted for loss of mass during treatment); the greater the reduction in concentration, the greater the volatility. On average, there was little difference among the sorbents for limiting the

volatility for chromium and nickel. With no chlorine in the feed, there was also little difference between the sorbents for cadmium. With 4% chlorine present in the feed, cadmium appeared to be less volatile from kaolinite, relative to the other sorbents. Finally, for the tests both with and without chlorine in the feed, arsenic appeared to be less volatile from the attapulgite clay and lead less volatile from kaolinite, compared to the other sorbents.

In addition to the overall differences noted above, changes in temperature affected the retention of metals in several of the sorbents when chlorine was present in the feed. Arsenic volatility in the silica, diatomaceous earth, and alumina matrices increased with increasing temperature, while the reverse occurred in the attapulgite clay. Cadmium volatility in diatomaceous earth, alumina, and bauxite increased with increasing temperature. Chromium volatility was relatively constant across the temperature range. Lead volatility increased with increasing temperature for the alumina and bauxite matrices. Nickel volatility in the attapulgite clay decreased with temperature.

In cases where chromium appeared to impact metal behavior (independent of temperature), it consistently increased the volatility of the metal. Such increases were seen for arsenic in bauxite; cadmium in silica and attapulgite clay; and lead in silica. Chromium and nickel volatility did not appear to be impacted by chlorine in any of the matrices.

Resistance to Leaching by TCLP

"Fractional leachability" represents the ratio of the TCLP-extracted metal to the total metal measured in the sample. In nearly every case, leachabilities from treated samples were less than the corresponding feed samples. Attapulgite clay, bauxite, kaolinite, and alumina were better for limiting arsenic leachability during tests with and without chlorine in the feed. With no chlorine in the feed, all of the sorbents had similar leachabilities for cadmium and lead. With feed chlorine, attapulgite clay, kaolinite, and diatomaceous earth were better for limiting cadmium and lead leachability, as was bauxite for cadmium leachability. With one exception, all of the sorbents had similar chromium leachability; chromium was very easily leached from the treated attapulgite clay samples. Nickel leachability did not differ significantly among the sorbents for the tests with chlorine in the feed. With no chlorine in the feed, alumina, attapulgite clay, bauxite, and kaolinite were better at limiting nickel leachability.

Increases in temperature consistently led to decreased leachability of cadmium from each of the sorbents and of arsenic, chromium, lead, and nickel from diatomaceous earth. Arsenic leachability from the other sorbents was not affected by temperature. When chlorine was not present in the feed, chromium leachability from silica and alumina decreased with increasing temperature, as did lead leachability from kaolinite and nickel leachability from silica. With chlorine in the feed, lead leachability from silica, and nickel leachability from silica, alumina and bauxite decreased as temperature rose.(5)

CONCLUSIONS

Given the screening nature of these tests, and considering the analytical problems encountered with many of the feed samples, the results of the tests should be used with caution. Nevertheless, a number of preliminary conclusions may be made. Combining the two sorbent criteria of limited metal volatilization and reduced leaching by TCLP, kaolinite and attapulgite clay appear to be the most promising sorbents for arsenic; kaolinite for cadmium; kaolinite, diatomaceous earth, and attapulgite clay for lead. With few exceptions, the sorbents showed comparable performance for the other matrix/metal combinations; chromium leachability appeared to increase in the attapulgite clay matrix with increased temperature.(5)

REFERENCES

1. Acurex Environmental Corp. Quality Assurance Project Plan for Evaluating the Effectiveness of Additives as Sorbents for Metal Capture Using the Thermal Treatability

Unit. Contract No. 68-C9-0038, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1993.

2. Method 1311 Toxicity Characteristic Leaching Procedure (TCLP). 40 CFR Part 261, Appendix II.

3. Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, 3rd Edition, Revision 1, U.S. Environmental Protection Agency, 1992.

4. Methodology for the Determination of Metals Emissions in Exhaust Gases from Hazardous Waste Incineration and Similar Combustion Processes. 40 CFR Part 266, Appendix IX.

5. Acurex Environmental Corp. Evaluation of the Effectiveness of Additives as Sorbents for Metal Capture Using a Thermal Treatability Unit - Draft Report. Contract No. 68-C9-0038, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1994.

FOR MORE INFORMATION

Gregory J. Carroll
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory (ML 481)
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268
513/569-7948

RESEARCH ON THE LOW-TEMPERATURE DECONTAMINATION OF SOIL

Melanie D. Hetland and John R. Rindt
University of North Dakota Energy & Environmental Research Center
PO Box 9018
Grand Forks, ND 58202-9018
(701) 777-5000

INTRODUCTION

Decontamination of organically contaminated soil requires at least two processes: 1) separation of the contaminants from the soil and 2) destruction or stabilization and recovery of the organic contaminants. Techniques used to convert the organic contaminants must produce environmentally acceptable products. A process is seen as more favorable if the inorganic portion remaining after destruction of the organic contaminants retains a "natural" state, since ideally the residual should be returned to the original ecological system.

Low-temperature plasma (LTP) processing has the potential to offer decontamination equivalent to incineration with decreased production of harmful by-products and without changing the morphology of the inorganic matrix. Low-temperature plasmas are formed by electric discharge (rather than thermal means) at conditions that do not result in thermal equilibrium. It is possible with an LTP system for typical plasma reactions to occur at nearly ambient bulk temperatures.

The purpose of this project is to perform the appropriate engineering evaluations needed to scale up an LTP soil decontamination process developed at the Energy & Environmental Research Center (EERC). The LTP process under development uses oxygen plasma, resulting in oxidation of the contaminant species. Previous research at the EERC proved that the technique successfully separates organic contaminants from soil. The success of this previous research indicated that the use of LTP as a decontamination technique should be investigated further, with possible scaleup to real-world application.

METHODOLOGY

A program plan consisting of four phases was developed to enable the design and construction of a real-world-scale prototype unit. The Phase 1 work included operation of the existing EERC LTP unit with integrated gas analysis to verify that the fate of all organic species placed in the reactor could be determined. Phase 2 consists of gathering the engineering information needed for prototype design, while Phase 3 consists of the design, fabrication, and shakedown testing of the prototype. The design, fabrication, and integrated shakedown testing of any add-on equipment necessary for decontamination using the prototype constitute the Phase 4 work effort. This paper summarizes the testing performed during the Phase 1 carbon fate study.

The Phase 1 testing was performed on the EERC bench-scale LTP system. The system consists of a radio frequency (rf) generator, a reactor center, a vacuum system, a feed gas system, and an elaborate product gas collection system. The rf generator and the reactor center were manufactured by the International Plasma Corporation. The quartz reaction chamber is 8 inches long and 4 inches in diameter and has been modified to contain the hardware necessary for agitation during operation. A pair of rotating aluminum trays was used to agitate the sample during operation. The trays each have a lip on one longitudinal edge and are aligned so that, when turning on the rotary coupling, the sample falls from one tray to the other through the plasma. A vacuum pulls the plasma-producing gas through the chamber, while the rf energy is transmitted across the electrodes surrounding the sides of the reaction chamber.

The product gas collection system was designed and fabricated for use in all phases of the project. The system consists of a bypass loop, two product gas collection bags or bladders contained in two vessels, and three syringes that are used to transfer the gas from the collection bags to the analytical system. An on-line gas chromatograph (GC) was available for analysis of the product gas stream during the Phase 1 testing.

A statistically designed experimental matrix was used to gather data concerning the fate of the carbon species. The matrix was designed to vary five independent variables: oxygen flow rate, reactor pressure, rf power, reaction time, and percent carbon in sample. The statistical analysis of the data will indicate which operating parameters affect contaminant removal and destruction efficiencies and how these efficiencies are affected. The matrix was designed so that the test points would be performed in random order to minimize skewing of data that can occur when one variable is held constant for several tests in a row. Tests were performed in blocks to determine whether significant changes occurred in the system over the course of the testing.

All tests were performed using decolorizing carbon as the contaminant source and washed, 60- to 100-mesh sand as the inert matrix. Pure oxygen was used as the plasma-producing gas. The use of carbon and pure oxygen limited the various products of incomplete combustion (PICs) that could be produced, thereby greatly simplifying the product gas analysis. Both the feed and product solid samples were analyzed for carbon, hydrogen, nitrogen, sulfur, and ash content. Feed and product gas samples were analyzed using gas chromatography.

RESULTS

The purpose of this study was not to maximize contaminant removal and destruction efficiencies, but rather to lay the foundation for the testing that will take place during the remaining phases. The goals of the Phase 1 testing included verification that:

- Mass balance closures of ±5% are possible.
- The analytical scheme that is in place is capable of accurate results.
- The fate of the contaminant species can be accurately tracked.
- PICs can be identified and quantified with the existing product gas collection system and the on-line GC.

A mass balance closure criterion of ±5% was chosen as a project quality assurance objective because data gathered from tests with worse mass balances would not accurately represent the tests. Therefore, as a first step, a mass balance was calculated for each test, and those tests not meeting the criterion were repeated. A total of seven tests were repeated based upon initial mass balance calculations. A change in the mass balance calculation was made to account for minor contamination by air, resulting in only two tests that did not meet the mass balance closure criterion. The results of the Phase 1 testing are summarized in Table 1. Table 1 clearly shows that mass balances meeting the criteria were easily obtained. The average mass balance was 100.46%.

Quality assurance (QA) check samples were randomly submitted to verify that the analytical results accurately described the samples. Analyses of both the solid and gaseous products agreed with the calculated values well within the error range of the analytical instrumentation. Average differences between the calculated values and the analyzed values for the solid samples were +0.05 wt% carbon, −0.004 wt% hydrogen, −0.002 wt% nitrogen, +0.084 wt% sulfur, and −0.20 wt% ash. Instrument error is ±1.0 wt% for ash and ±0.5 wt% for the other components. The gas analysis checks were equally accurate, with average

TABLE 1. SUMMARY OF DATA GATHERED DURING PHASE 1 CARBON FATE STUDY*

Test No.	Reaction Time (min)	Reactor Pressure (torr)	RF Power (W)	O_2 Flow Rate (gmol/hr)	Carbon in Feed (wt%)	Mass Balance (%)	Carbon Balance (%)	Removal Efficiency (%)	Destruction Efficiency (%)
P560	16.5	1.75	75	2.2	6.6	95.5	134.0	19.3	85.7
P562	16.5	1.75	125	2.8	6.6	99.8	137.7	15.2	88.0
P564	45.5	3.25	75	1.8	6.6	100.2	143.0	36.0	92.7
P565	31	2.5	100	2.1	5.6	98.7	144.8	48.8	93.0
P566	16.5	1.75	75	2.4	6.4	100.0	130.2	4.9	96.0
P567	16.5	3.25	75	2.1	6.6	101.6	130.7	22.5	96.9
P568	45.5	1.75	75	1.6	4.3	100.8	126.2	64.1	82.9
P569	16.5	3.25	125	2.3	6.9	98.4	127.9	21.7	83.4
P572	31	2.5	100	2.3	5.4	98.8	147.9	37.9	81.7
P575	16.5	1.75	125	1.7	4.3	101.6	133.2	27.7	94.2
P576	16.5	3.25	125	2.3	4.2	100.0	136.6	29.0	97.0
P577	31	2.5	100	1.8	5.5	102.4	104.8	35.4	96.5
P580	45.5	3.25	75	2.6	4.3	102.8	120.2	57.3	89.0
P583	31	2.5	100	3.0	5.4	102.4	125.0	54.4	76.4
P584	31	2.5	100	2.2	5.4	100.6	135.5	39.9	89.2
P585	2	2.5	100	0.6	5.5	99.9	118.5	4.1	†
P588	31	1	100	2.4	5.4	100.0	104.7	55.6	92.1
P589	31	2.5	50	2.0	5.5	101.4	117.2	23.0	97.3
P590	31	2.5	100	2.0	5.5	100.9	92.0	45.4	97.1
P591	31	2.5	100	2.1	7.8	99.5	107.5	33.1	95.2
P593	31	2.5	150	2.2	5.4	102.4	128.5	47.2	82.4
P594	31	2.5	100	2.3	5.4	99.7	116.8	39.2	88.8
P595	31	4	100	2.3	5.4	101.1	144.1	39.9	81.4
P596	31	2.5	100	1.5	5.4	103.4	128.3	40.5	82.1
P638	16.5	3.25	75	1.6	4.4	100.5	149.5	38.2	87.2
P639	45.5	1.75	125	1.5	6.5	95.2	132.0	62.1	80.8
P640	45.5	3.25	125	1.6	4.3	101.3	112.1	56.7	90.9
P641	45.5	1.75	75	2.0	6.6	99.7	114.1	54.3	78.8
P642	45.5	1.75	125	2.2	4.2	100.4	108.1	76.2	83.5
P644	31	2.5	100	1.8	3.0	102.7	129.9	47.7	95.9
P645	60	2.5	100	2.1	5.4	98.9	127.9	67.3	85.7
P647	45.5	3.25	125	2.2	6.6	103.9	136.7	57.0	84.9

* All tests were performed using decolorizing carbon as the contaminant and SiO_2 as the inert matrix.
† Short residence time resulted in too small a gas sample to permit this calculation.

differences less than 1 mol% for all components. Instrument error for the GC is ±2 mol%. The GC detection of water in the calibration gas is an analytical anomaly, the cause of which has yet to be defined but should diminish as the project progresses to larger-scale equipment and samples.

The results summarized in Table 1 show that it is possible to accurately track the fate of the carbon species in the LTP system. Carbon balances were calculated for each of the tests and range from 92.0% to 149.5%. The mean carbon balance of 126.4% is close to the median value of 128.3%, indicating that the values are tightly grouped and therefore representative. Although these balances appear to be somewhat high when considering that a perfect balance would be 100%, all are within analytical instrumentation error of 100%.

The product gas composition was calculated for each test and is summarized in Table 2. By far the most prevalent species found was oxygen. This is logical since excess oxygen was provided for reaction. Carbon dioxide (the primary product of the reaction of oxygen and carbon), carbon monoxide (the expected PIC), water vapor, and hydrogen were also found to be present. The GC was calibrated to detect hydrogen sulfide and various hydrocarbon gases, but as none were detected these results were not included in the table. A minute amount of methane was detected in the product of the test having the largest contaminant loading in the feed sample.

The reproducibility of LTP processing can be seen by comparing the product gas composition of Tests P572, P584, and P594. These tests were performed at nominally the same operating conditions and contaminant loadings. As Table 2 shows, the product gas compositions of these tests are nearly identical, indicating that the results are reproducible.

Contaminant removal and destruction efficiencies were calculated for each of the tests, even though it was not the goal of the Phase 1 testing to maximize these efficiencies. These values are presented in Table 1. Removal efficiencies ranged from about 4% to about 76%, while destruction efficiencies for the removed contaminants ranged from about 76% to about 97%. These encouraging results imply that, when operating conditions are optimized, it should be possible to meet the project goals of removal of at least 99 wt% of the contaminants and destruction of 99.99 wt% of the removed contaminants.

The statistical analysis has not yet been completed. It is expected that the statistical results will indicate which operating conditions should produce the highest contaminant removal and destruction efficiencies. Such information will be used in upcoming project phases.

CONCLUSIONS

Several conclusions can be drawn from the results:

- It is possible to obtain mass balance closures of ±5 wt% with the existing LTP system.
- The analytical scheme currently in place accurately analyzes both solid and gaseous products.
- The fate of the contaminant species can be tracked in detail.
- The gaseous products of all tests consisted primarily of excess oxygen, carbon dioxide, and carbon monoxide.
- The tests are very reproducible.

In general, it can be said that both the mechanical and analytical aspects of the LTP system met or exceeded expected performance standards based upon previous research at the EERC.

TABLE 2. PRODUCT GAS SLATES FOR PHASE 1 TESTS

Test No.	O_2 (mol%)	CO_2 (mol%)	H_2 (mol%)	H_2O (mol%)	CO (mol%)	CH_4 (mol%)
P560	71.2	19.1	1.0	2.4	6.3	0.00
P562	77.2	16.4	0.8	2.1	3.5	0.00
P564	89.9	7.6	0.8	1.3	0.4	0.00
P565	85.2	11.2	0.7	1.7	1.3	0.00
P566	87.9	9.5	0.3	1.7	0.6	0.00
P567	91.5	6.3	0.5	1.4	0.3	0.00
P568	88.1	8.2	0.6	2.4	0.8	0.00
P569	70.3	20.4	1.4	1.6	6.3	0.00
P572	75.8	15.3	0.9	2.6	5.4	0.00
P575	81.4	14.7	0.7	1.9	1.4	0.00
P576	88.2	9.4	0.5	1.4	0.5	0.00
P577	91.5	7.5	0.6	0.0	0.4	0.00
P580	86.3	9.7	0.7	1.1	2.2	0.00
P583	80.0	13.5	0.5	0.9	5.1	0.00
P584	79.3	16.3	0.7	0.6	3.1	0.00
P585	99.6	0.0	0.0	0.4	0.0	0.00
P588	84.3	12.6	0.7	0.8	1.7	0.00
P589	92.9	5.6	0.4	0.9	0.2	0.00
P590	85.3	12.8	0.4	0.8	0.6	0.00
P591	80.0	16.2	0.4	2.1	1.3	0.02
P593	70.3	20.9	0.9	0.9	7.0	0.00
P594	78.5	16.4	0.5	1.4	3.2	0.00
P595	71.9	19.6	0.5	1.0	7.1	0.00
P596	68.5	22.0	1.2	0.8	7.5	0.00
P638	83.2	10.9	0.7	2.7	2.4	0.00
P639	70.4	18.9	0.6	3.2	7.0	0.00
P640	79.7	13.2	0.5	4.7	2.0	0.00
P641	93.0	3.9	0.5	2.3	0.2	0.00
P642	74.6	14.9	0.6	2.9	7.0	0.00
P644	83.6	10.5	0.4	4.8	0.7	0.00
P645	83.6	10.5	0.4	4.8	0.7	0.00
P647	73.9	17.6	0.7	2.9	4.9	0.00

FOR MORE INFORMATION

For more information, please contact:

Dr. C.C. Lee, Technical Project Manager
U.S. EPA – Risk Reduction Engineering Laboratory
26 West Martin Luther King Drive
Cincinnati, OH 45268
(513) 769-7520

A SUMMARY OF TWO RECYCLING TECHNOLOGY EVALUATIONS COMPLETED UNDER THE MITE PROGRAM

Lynnann Hitchens
Risk Reduction Engineering Laboratory
5995 Center Hill Road
Cincinnati, Ohio 45224
(513) 569-7672

INTRODUCTION

Through the Municipal Solid Waste Innovative Technology Evaluation (MITE) Program, EPA has evaluated a number of promising innovative technologies for municipal solid waste (MSW) recycling. These technologies have varied from collection and processing methods to evaluations of products made from post-consumer material. The MITE program was conceived with the purpose of providing objective, third-party evaluations on environmental performance and costs of innovative municipal solid waste management technologies and this program is administered for EPA by the Solid Waste Association of North America (SWANA), representing the public sector solid waste management needs. The technologies are selected via an annual solicitation and review by an Advisory Group made up of recycling coordinators and solid waste managers.

Once the technologies are selected and the evaluation is performed, the results are published in a report that is distributed to the information users or the general public. The benefit for technology developers in participating is that they receive objective, published information to assist them in the commercialization and marketing of their technology.

One unique point separating this innovative environmental technology evaluation program from others is that it is often the public sector (the municipality, county, or solid waste district) advancing MSW technology through research and development, and partnerships with private companies and trade organizations. A significant number of applicants to the MITE program have been cities or non-profit groups. This is the case with the two evaluations profiled below.

This summary will address two evaluations focusing on the collection of municipal solid waste and designs that foster cost-effective recycling and source reduction.

METHODOLOGY

The first project profiled is a weight-based municipal solid waste collection system. The second project is an evaluation of three co-collection systems for solid waste and recyclables.

Weight-Based Collection Pilot in Farmington, Minnesota

The City of Farmington, Minnesota applied to the MITE program for an evaluation of their proposed pilot for a weight-based MSW collection system. The purpose of this collection system is to charge waste generators according to the weight of the solid waste placed at the curb for disposal. The more waste generated, the higher the disposal costs would be. There is an economic incentive in generating less waste for disposal and Farmington theorized that this type of system would increase the amount of material set out for recycling, a service for which there is no charge, and also foster source

reduction at the residential level.

In order to implement this type of collection system with a minimum additional collection cost, the City attempted to retrofit a side loading collection vehicle to provide weight information for billing purposes. This vehicle was already in service, providing fully automated solid waste collection. The retrofit had three main components: the first consisted of load cells mounted to the vehicle's gripper mechanism. These load cells would weigh each refuse container during pick-up. The second component of the retrofit was the use of a Trovan radio-frequency identification (RFID) transponder attached to each refuse container. The transponder released coded information containing the address of the container when placed in proximity of the antenna, mounted on the refuse collection vehicle. These two components were tied into the third item, an on-board computer, which translates the information into an address identification and container weight. Thus, the weight of the refuse is correlated to an address for billing purposes.

It was agreed that Farmington would obtain the vehicle retrofit and pilot test it prior to the MITE evaluation. Unfortunately, there were many difficulties encountered in the development of this system. It was discovered that the load cells were not durable enough for Farmington's collection needs. There was also a problem with the accuracy of the weight measurements. The National Institute of Standards and Technology (NIST) has established national weights and measure requirements for on-board weighing systems. These systems have to meet Class III requirements, or an allowed tolerance level of accuracy of one pound for the first 500 pounds, two pounds for 501 to 2,000 pounds, and three pounds for 2,001 to 4,00 pounds.

Through pilot testing it was determined that approximately 90 percent of all weights recorded on the truck were within two pounds of accuracy. However, since full residential containers weighed less than 500 pounds, the project was not consistently conforming to Class III standards. Accuracy testing was performed by weighing the refuse containers first with a certified digital scale, then weighing the containers with the on-board system.[1]

There were also other factors affecting the accuracy of the load cells. Considerations such as the slope of the road surface, excessive wind speed, and shifting weight due to liquids in the container caused unpredictable errors in measurements. Because of noncompliance with the Class III standard, billing was never permitted by the Minnesota State Department of Weights and Measures.

Based on EPA's assessment of this pilot, there are a number of recommendations that can be made to municipalities and others attempting to conduct a weight-based collection pilot. Most important is to establish performance specifications for system development. These allow more control that design specifications. A second recommendation is to involve crew and staff in the development and implementation of the system. This will allow a smoother transition during implementation. It is also important to provide adequate training to staff and education to the waste generators.

The pilot, though not fully successful and not able to be fully tested, was a valuable learning experience for Farmington and other municipalities and companies. In 1994, a number of private firms, both here and in Canada made significant progress in the development of truck mounted systems for weight-based collection for solid waste. In fact, a number of systems have applied to, and are expected to receive NIST certification for their equipment, and allow public marketing of the systems. There is no doubt that the research and development done by the City of Farmington contributed to this rapid development.

---

1 Evaluation of the Weight-Based Collection Project in Farmington, Minnesota: A MITE Program Evaluation. EPA/600/R-94-164.

Co-Collection of Solid Waste and Recyclables

At the present time, the majority of community recycling programs that use of curbside collection utilize a separate vehicle in which to collect recyclables. These vehicles vary in design, depending on the overall recycling system. If the recycling program makes use of a Materials Recovery Facility, or MRF, to separate recyclables for market, the recyclables are often collected commingled in a single compartment collection vehicle. If the program makes use of a curb sorting system, the collection vehicle can take on a number of multi-compartment designs, depending on the amount and type of recyclables included in the recycling program.

It has been shown in numerous cost studies that collection costs are a significant portion of the total solid waste management cost. It has also been concluded in a number of instances that the "add-on" of the curbside recycling collection -- separate facilities, crews, and collection vehicles -- may not be the most efficient solid waste management system design. Simply speaking, all solid waste services should be considered in an integrated manner, looking at long term program needs. In an attempt to minimize collection costs, several communities across the United States are changing to a "co-collection" system, where the solid waste and recyclables are collected simultaneously in the same vehicle.

There are several co-collection system designs. The first and simplest system uses a collection vehicle (perhaps already in use for MSW only) with a single compartment. Recyclables and waste are separately bagged by the waste generators, picked by concurrently, and placed in the same vehicle. The bags of recyclables are separated from the bagged waste at a centralized facility. The second system is the use of a vehicle with separate compartments, the number depending on the number of items that are collected and the amount of curb-side sorting that occurs. The third unique system uses a dual compartment refuse container designed and manufactured for use specifically with a dual compartment automated collection vehicle.

Three separate systems will be evaluated in this project. They include a co-collection vehicle manufactured by Oshkosh Truck Corporation as utilized by Durham, North Carolina; the Western Curbside Collector co-collection truck manufactured by May Manufacturing Company, as utilized by Loveland, Colorado; and Ruckstell California Sales, Inc. co-collection refuse container system as utilized by Visalia, California.

One component of the evaluation consists of on-route data collection by the vehicle crew. Crew training and all data management will be done by RW Beck and Associates. RW Beck will also perform a sort of the recyclable stream for both the pre-existing two truck system and the co-collection system to evaluate any changes in quality of recyclables. Information to be collected includes times on and off route, time between stops, unloading and break time, the number of pick-ups, estimated distance between stops, pounds collected, driver distance, and crew number. A number of different routes will be evaluated over the two week data collection effort.

The information collected will be used for an economic analysis and a comparison of the quality of the recyclables. Costs per household will be calculated for each of the systems and they will be compared to the more traditional two vehicle systems for refuse and recyclable collection. There will also be an attempt made to identify key factors that determine system cost effectiveness and efficiency.[2]

The co-collection system evaluations are presently underway and it is expected that draft results will be available by May 1995.

---

2 Co-Collection System Evaluation, Draft Scope of Services. RW Beck and Assoc. 10/94.

CONCLUSIONS

US EPA's MITE Program, in cooperation with its partner, the Solid Waste Association of North America (SWANA), seeks to perform objective assessments of innovative technologies for solid waste management systems. Through these efforts, information on environmental effectiveness and costs on these technologies is spread to the user community, in the hopes that it will foster environmentally and economically sound municipal solid waste management.

REFERENCES

1. RW Beck and Associates. Draft Scope of Work: Co-Collection System Evaluation, October 24, 1994.

2. SCS, Engineers. Evaluation of the Weigh-Based Collection Project in Farmington, Minnesota: A MITE Program Evaluation. EPA/600-R-94/164, U.S. Environmental Protection Agency, Cincinnati, Ohio 1994. 17 pp.

3. Steuteville, R. Early Results with Co-Collection. Biocycle. February 1993.

For more information contact: Lynnann Hitchens, Risk Reduction Engineering Laboratory, 5995 Center Hill Road, Cincinnati, Ohio 45224, (513) 569-7672.

FULL-SCALE LEACHATE-RECIRCULATING MSW LANDFILL BIOREACTOR ASSESSMENTS

David A. Carson
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory (ML-CHL)
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268-3001 USA

INTRODUCTION

The integrated waste management hierarchy philosophy continues to develop as a useful tool to solve solid waste issues in an environmentally responsible manner. Recent statistics indicate that approximately two thirds of municipal solid waste in the United States is disposed in landfills. EPA research has continued to develop and refine the variety of technologies, materials, and operational techniques to further reduce risk from this most often used form of waste disposal.

Current landfill operational technique involves the preparation of a waste containment facility, the filling of the waste unit, installation of the final cover, and the maintenance of the unit. The goals being to isolate the waste from people, and to minimize infiltration of water, thus minimizing releases of moisture and decompositional gases into the environment. This method of operation has proven to be reasonably effective in waste disposal, effectively minimizing risk by collecting the liquid that percolates through the waste, called leachates, at the bottom of the landfill, and controlling landfill gas with collection systems. Effective gas collection often results in utilization of the gas for other purposes.

Concerns over the longevity of containment systems components present questions that cannot be answered without substantial performance data. Landfills, as currently operated, serve to entomb dry waste. Therefore, the facility must be maintained in perpetuity, consuming funds and ultimately driving up waste collection costs. Further, there is a concern about rare but possible environmental impacts from leakage through lining or cover components and possible catastrophic failures of the landfill system.

This presentation will describe a new form of solid waste landfill operation, it is a technique that involves controlled natural processes to break down landfilled waste, and further minimize risk to human health and the environment.

A landfill operated in an active manner will encourage and control natural decomposition of landfilled waste. This can be accomplished by collecting leachate, and reinjecting it into the landfilled waste mass. Keeping the waste mass moist will lead to a largely anaerobic system with the capacity to rapidly stabilize the landfilled waste mass via physical, chemical and biological methods. The system has proven the ability to breakdown portions of the waste mass, and to degrade toxic materials at the laboratory scale.

METHODOLOGY

Experiments are designed to compare similar landfill cells as each is operated in a different manner, either wet or dry. The experiments are time consuming and require long-term commitment to research. The projects are also very costly because of their magnitude. To gather data and analyze results, U.S. EPA embarked on a research program to study this operational technique for MSW landfills in the early 1980s. Bench-scale laboratory research on the anaerobic bioreactor in MSW landfills was conducted with the assistance of The Georgia Institute of Technology (1). Researchers found that by simply reinjecting common MSW landfill leachate under controlled sequences that the following benefits could potentially be realized at full scale:

- expansion of landfill capacity through volume reductions induced by biological decomposition of MSW in the landfill, reducing the actual number of landfills that must be sited

- improved quality and quantity of recoverable landfill gases (methane and carbon dioxide) through controlled biological reactions

- toxicity reduction of the MSW mass through biological decomposition and immobilization in the waste mass resulting in lower pollutant concentration in leachate

- reduced post-closure monitoring time due to toxicity reduction

Building upon this fundamental research, EPA sponsored further research to take this operational technique to the field in the form of pilot-scale landfill test cells (2). Anticipating the opportunity to build on this research, full-scale landfills were sought and selected to prove the technology at full-scale. One landfill was selected near Gainesville, Florida, and another landfill project is in the construction phase near Rochester, New York.

Table 1. U.S. EPA Landfill Bioreactor Projects in 1994

Location	Scale	Description	Status	Ref
Georgia	Lab	Model Landfill Lysimeters	Completed '93	1
Delaware	Pilot	Test Cells 2 each, 1 acre each, wet vs. dry	Covered	2
Florida	Full	Active Fill - 6 acres	Filling	3
New York	Full	Active Fill - 10 acres	Filling	4
Ohio	Full	Remediation of Existing Landfill	Planning	5

In addition to these activities, EPA is tracking related projects in the United States, and around the world. EPA is also pursuing the application of this technology in a remedial manner at an unlined, uncontrolled landfill.

Leachate-Recirculation Process

Prototype methods which have been utilized to date include surface spraying, surface ponds, vertical injection wells with and without wicks, and horizontal surface infiltration devices. Generally, additional costs for leachate recirculation materials are relatively low. For proper execution of a leachate recirculation system at a modern MSW landfill, the following components are generally considered to be necessary:

- a composite lining system comprised of a single or double composite compacted soil and a geomembrane, with leachate handling system.

- MSW placed at a density determined to accommodate leachate recirculation

- daily cover that does not significantly affect the continuous passage of moisture through the landfill from top to bottom (this rules out many traditional MSW landfill daily cover practices)

- a leachate reintroduction system that is concealed within the landfill enclosure, that only uses native landfill leachate

- an active gas collection system as part of a comprehensive landfill cap design

- a landfill cover capable of providing modern landfill cap functionality, that can maintain integrity as the leachate recirculation process causes landfill volumes to decrease,

- a trained landfill operator who understands the daily operational requirements of a leachate-recirculating landfill

Many of these issues remain as engineering challenges that need to be resolved in full-scale implementation.

The leachate-recirculation process is fundamentally simple, requiring relatively minor changes over the current designs. However, the number of variables involved to demonstrate control over the reactions in these studies are numerous, and every attempt is made during experimental design to control the number of variables. Operator training is critical, and outputs from these projects are aimed at operator control. As a matter of practicality, experiments to evaluate materials that may be added to the landfill during filling to enhance degradation have been relegated to future experimentation. Possible additions include waste pre-processing, microbiological additives, waste sludge, gases, or the control of temperature of the waste mass.

Concurrent with EPA research, other research projects are underway in the USA and around the world. There are new projects being initiated in California, Florida and New Hampshire, and underway around the world in Canada, Germany, Denmark, Italy, Sweden, Japan, and United Kingdom. The collective database formed in the study of these landfills will supply enough information to assess the performance of this operational technique in the field.

Landfilling in the Future

As landfills continue to evolve as sophisticated waste disposal and decomposition facilities, there are new goals anticipated for the future. Foreseen is a waste management park that will involve centrally located management of a variety of waste streams, of which a landfill will provide a necessary service. Waste water, sludges, composted waste and green waste, MSW materials recovery facilities, incinerators, and recycling facilities require inputs and outputs that can be integrated resulting in more efficient processing of MSW.

The landfill could produce an output of low to medium grade compost that could be used for soil amendments in roadways and earth works. Gas from the landfill could be used to generate electricity or power collection vehicles. The landfills could be arranged in a turntable-type arrangement so that cell #1 of the landfill can be constructed, filled, covered, and placed under leachate recirculation, then on to cell #2, where the process is repeated, and so on. When all cells are complete, the operator returns to cell #1, where the contents could be mined (7), with recyclables and compost removed, the bottom lining inspected and replaced when necessary, and the entire process again. While this technique will likely not eliminate the need to site new landfills, it will significantly increase the useful life of landfills when constructed to operate as bioreactors.

RESULTS

The status of active EPA sponsored projects are described here. The effort has benefitted from the active participation of major waste management companies in the USA, and from the collaborative research efforts of EPA's colleagues, and their participation is gratefully acknowledged. Results to date are derived from the following projects:

Laboratory Lysimeter Studies

Completed in 1993, the research performed at the Georgia Institute of Technology and University of Pittsburgh showed leachate recirculation offers rapid and complete stabilization of the landfilled waste masses. The system proved resiliency to toxic loadings that caused retardation but not defeat of the stabilization process. The study showed that landfills are capable of biological and physicochemical

reactions to attenuate waste constituents via reduction, precipitation, and matrix capture for heavy metals, and biotic and abiotic transformation, and sorption for organic materials. The study also showed that the performance of the bioreactor landfill can be monitored with leachate and gas parameters during significant phases of the reaction. The study concluded that the bioreactor landfill design is viable, and offers a significant improvement over traditional landfill operation (1).

Pilot-Scale Landfill Test Cells - Delaware

Two 1-acre pilot-scale landfill test cells are currently operated by the Delaware Solid Waste Authority in Sandtown, Delaware. Two identical cells were constructed, one operated traditionally (dry) and the other employing leachate-recirculation. The cells have been operating for approximately 1.5 years, and although the data is being analyzed, preliminary results have shown that the trends described in the early laboratory research are repeated in the field (2).

Full-Scale Landfill Project - Alachua County, Florida

The first of two full-scale landfill projects was selected near Gainesville, Florida. The landfill is operated by the City with assistance from The University of Florida, engineering firms, and others. The landfill is approximately half full, and leachate recirculation systems are being installed as filling progresses. A nearby landfill at that site has performed this technique in a less sophisticated manner, utilizing surface infiltration ponds in previous years with success (3).

Full-Scale Landfill Project - Monroe County, New York

The second full-scale landfill project is in the construction phase near Rochester, New York. EPA is assisting the New York State Energy Research and Development Authority (NYSERDA) in their efforts to study how this landfill operational technique may achieve complementary goals of environmental protection, and the potential for enhanced energy production through gas recovery (4).

Remediation Project - Ohio

An unlined landfill is under study in Cincinnati, Ohio for application of leachate recirculation as an alternative to pumping and treating groundwater at an uncontrolled pre-regulatory landfill. The project is significantly more complicated due to the absence of a bottom liner, but researchers are convinced that groundwater can be controlled and barriers can be constructed to accommodate leachate recirculation at the site (5). A feasibility study is in final draft status, and the project will soon enter its second phase to complete pre-construction details.

Comprehensive Study - University of Central Florida

A comprehensive evaluation of active landfill bioreactor projects is underway at the University of Central Florida (6). Researchers there are compiling data from these projects, other American projects, and data from projects from around the world by site visitation and interactions with specialty groups like the International Energy Agency's Landfill Gas Expert Working Group. Specific projects aim to assess moisture distribution of the leachate into the waste mass through computer models. This will assist designers in the configuration of the injection system, and may lead to guidance on placed waste densities that will accommodate leachate recirculation. A conference is planned for the autumn of 1994.

CONCLUSIONS

Landfills are currently designed and operated to serve as containment systems. While originally designed to entomb waste, the modern landfill has evolved into a more technically advanced containment system, with sophisticated controls and operational techniques. The landfill of the future will be protective of human health and the environment, will degrade the waste mass in the landfill, and will be reusable,

allowing the waste to be excavated for the cell to be inspected and refilled as part of an integrated waste management park.

REFERENCES

1. United States Environmental Protection Agency. 1993. *Behavior and Assimilation of Organic and Inorganic Priority Pollutants Codisposed with Municipal Refuse, Volumes 1 and 2.* EPA/600/R-93/137a and b (NTIS PB93-222198 and 93-222206). Risk Reduction Engineering Laboratory, Cincinnati, Ohio.

2. Vasuki, N.C. 1993. "Practical Experiences with Landfill Leachate Recirculation in Pilot and Field Scale Units, *Proceedings: 31st Annual International Solid Waste Exposition, Solid Waste Association of North America*, San Jose, California, August 3.

3. Townsend, T., and W. L. Miller. 1993. Alachua County Southwest Landfill Bioreactor Project, *Proceedings: Madison Waste Conference*, Madison, Wisconsin, September.

4. Babcock, J., and Reis, J. 1993. "Monroe County's Leachate Recirculation Project," Modern Double Lined Landfill Management Seminar, New York State Department of Environmental Conservation, Saratoga Springs, NY, March 2-4.

5. United States Environmental Protection Agency. 1993. *Leachate Recirculation for Remedial Action at MSW Landfills, DRAFT FINAL REPORT.* Risk Reduction Engineering Laboratory, Cincinnati, Ohio.

6. Reinhart, D. R., and Carson, D. A. 1993. "Full-Scale Application of Landfill Bioreactor Technology," *Proceedings: 31st Annual Solid Waste Exposition of the Solid Waste Association of North America*, San Jose, CA (August 2-5, 1993).

7. United States Environmental Protection Agency. 1993. *Evaluation of the Collier County, Florida Landfill Mining Demonstration.* EPA/600/R-93/163. Risk Reduction Engineering Laboratory, Cincinnati, Ohio.

FOR MORE INFORMATION

Please contact David Carson, U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory (ML-CHL), 26 W. Martin Luther King Drive, Cincinnati, Ohio, 45268-3001, USA, at (513) 569-7527.

REMOVAL OF MERCURY FROM STACK GASES BY ACTIVATED CARBON

Radisav D. Vidic
University of Pittsburgh
943 Benedum Hall
Pittsburgh, PA 15261
412-624-1307

INTRODUCTION

On combustion, the trace elements in the incinerator feed stream are partitioned between the bottom ash (slag) stream, and a flue gas stream containing suspended fly ash and vapors of volatile elements or compounds. A further partitioning of the flue gas stream takes place in the particulate emission control devices that efficiently remove larger fly ash particles but are less efficient for vapors and finer particles. Ash from the bottom of the combustion chamber and ash removed by the particulate control devices are flushed with water to ash ponds, where elements may be leached from the ash and enter the aquatic environment in runoff. Small particles and vapors are discharged to atmosphere through exhaust stacks and enter the terrestrial and aquatic environments by wet or dry deposition.

Environmental control agencies, researchers, and general public have become increasingly concerned with the mobilization of trace elements to the environment from solid and hazardous waste incinerators. Mercury is the trace element of particular concern since, during combustion, most of the mercury present in the influent stream is transferred into the vapor phase due to its high volatility. There is a considerable evidence in the literature that currently used pollution abatement technologies (flue gas clean-up and particulate control devices) are not capable of controlling gas phase mercury emissions.

Once discharged to the atmosphere, mercury persists in the environment and creates long term contamination problem. Furthermore, well documented food chain transport and bioaccumulation of mercury, together with high toxicity to mammals and severe health problems caused by the ingestion of mercury even at low levels, require strict control of mercury emissions from solid and hazardous waste incinerators.

Activated carbon adsorption is a unit process that offers great promise for achieving high quality air emissions with respect to mercury and other trace elements that might be present in gases emitted from solid and hazardous waste incinerators. This study is designed to evaluate the rate of vapor-phase mercury removal by virgin and sulfur impregnated activated carbons under various process conditions. The specific process conditions that will be evaluated for their effect on the rate and mechanism of mercury uptake include temperature, moisture content, oxygen partial pressure, and presence of other compounds and trace elements in the vapor-phase. Accurate description of the kinetics of mercury removal by activated carbon is an essential component in establishing design procedures that would ensure successful application of this efficient technology for mercury control.

METHODOLOGY

Experimental set-up that is used in this study is shown in Figure 1. Carrier gas used in the experiments is first passed through a drier and a 0.22 μm nylon filter to remove impurities and is then split into two streams. One stream goes through a regulating valve, mass flow controller, gas moisturizer

(if needed), and into a mixing chamber. The other gas stream goes through a regulating valve, mass flow controller and a mercury generator. Hydrogen chloride can also be added to this gas stream.

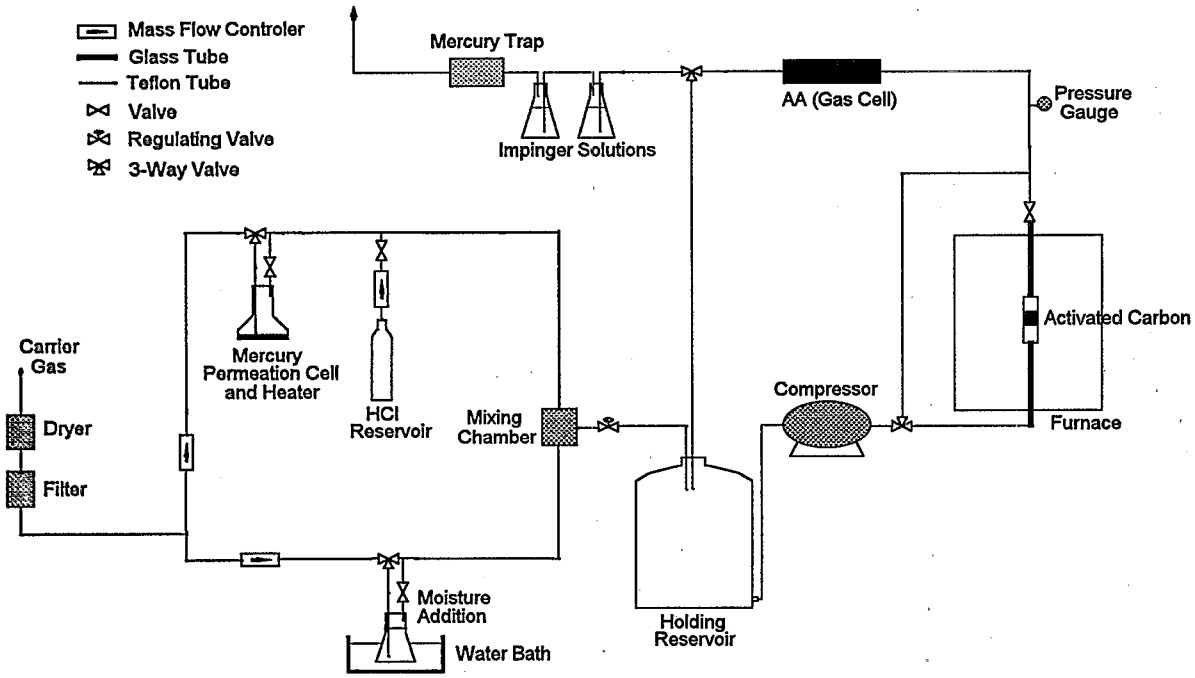


Figure 1. Schematic Representation of Experimental System

Mercury is added to the gas stream by passing the gas around a permeation cell that contains mercury and is submerged into a constant-temperature water bath. Desired mercury concentrations in the vapor phase is accomplished by adjusting the temperature of the water bath. HCl is added to the gas stream by injecting a known flowrate of a gas which contains a known concentration of hydrogen chloride in nitrogen. After the mixing chamber, the mercury laden gas stream passes through a holding reservoir that is placed into the system to increase the total system volume and improve the accuracy of experimental results. During the preparation phase, which precedes each measurement of mercury uptake by activated carbon, the gas stream is directed around the activated carbon bed until a steady-state conditions with respect to gas composition are achieved.

Gas stream then passes through a quartz cell placed in a light path of an atomic absorption spectrophotometer (AAS) which enables direct and continuous measurement of elemental mercury in the vapor phase. Finally, the gas stream is passed through appropriate impinger solutions to facilitate measurements of other forms of mercury in the gas phase as well as other trace compounds that might be present in the gas stream. Impinger solutions are placed in 250 mL gas washing bottles. The collection of a particular compound from the gas phase into an impinger solution is performed for a period of 60 minutes after which the fresh solution will be placed on line. The mercury trap at the exit from the system is a GAC column charged with 100 g of sulfur impregnated activated carbon (HGR) .

Once the composition of the gas stream is stabilized at predetermined levels, the regulating valve is closed to prevent any infusion of mercury into the holding reservoir and the gas stream exiting the AAS is directed back into the holding reservoir thereby, forming a completely closed system. The compressor in the system is operated at a very high flow rate (up to 3 cfm) to ensure complete mixing in

the system throughout the experiment. The flow of the gas is then directed to a differential (short) activated carbon bed positioned inside the furnace and the uptake of mercury by activated carbon is monitored with time.

Elemental mercury in the gas stream is measured continuously at a wavelength of 253.7 nm using a quartz gas cell placed in the AAS system which is first calibrated according to the procedure described by Shendrikar *et al.* (1) while the total mercury is determined by directing a gas through a 200 mL impinger solution containing 1.5% $KMnO_4$ and 10% H_2SO_4 that collects all mercury species from the gas phase. The total mercury concentration in the impinger solution is then analyzed using a cold vapor atomic absorption spectrophotometric method (2).

The proposed research objectives will be accomplished through the following activities:

1) Evaluate the effect of temperature and mercury concentration in the gas phase on the rate of mercury adsorption by virgin and sulfur impregnated activated carbons for a wide range of mercury concentrations (100 - 1000 $\mu g/m^3$) and temperatures (80-200 °C) that are representative of gaseous emissions from incineration plants. Activated carbons selected for this part of the study are bituminous-coal based virgin activated carbon designed for vapor-phase applications (BPL) and sulfur impregnated activated carbon (HGR) (Calgon Carbon Corporation, Pittsburgh, PA).

2) Evaluate the effect of activated carbon particle size on the rate of mercury uptake from the gas phase. Smaller particle sizes would provide easier access of mercury to the surface active sites where adsorption occurs, thereby improving the kinetics of adsorption. However, injecting smaller GAC particle sizes would facilitate faster build-up of pressure drop at the fabric filter which is used to control particulate emissions. Consequently, the frequency of fabric filter cleaning would increase leading to lower run times. Therefore, it is necessary to determine an optimal particle size that would satisfy these opposing requirements. The intention of this task of the study is to determine the extent of the improvement in adsorption kinetics with the reduction in activated carbon particle size. Activated carbon particle sizes that will be used in such experiments include 30x40, 60x80, and 170x230 U.S. Standard Mesh sizes. These kinetic experiments will be performed at 140 °C using an influent mercury concentration of 500 $\mu g/m^3$ as representative of incinerator flue gas conditions. Once the optimum activated carbon particle size is established during this phase of the study, it will be used in the rest of the experiments outlined below.

3) Determine the effect of environmental conditions on the rate mercury uptake by activated carbon. The key environmental conditions that need to be evaluated include moisture content and oxygen partial pressure in the gas stream. Effects of moisture on the adsorption kinetics will be evaluated using dry and moisture saturated nitrogen as a carrier gas. Dry nitrogen and dry air will be used as carrier gases in the experiments designed to evaluate the effect of oxygen partial pressure on the adsorption kinetics. All the kinetic experiments included in this task of the study will be conducted at three different temperatures (80, 140, and 200 °C) using an influent mercury concentration of 500 $\mu g/m^3$. All possible combinations of moisture content and oxygen partial pressure in the gas stream will be employed to study the effect of temperature on chemical interactions between mercury, oxygen, and moisture, and the related impact on the rate of mercury uptake by activated carbon.

4) Evaluate the effect of the presence of halogen compounds (most notably chlorine, Cl) in the gas stream on the kinetics of mercury uptake by activated carbons. Cl can react with elemental mercury and change its oxidation state and therefore, influence the affinity of mercury towards the carbon surface. This task of the study includes kinetic experiments at three different temperatures (80, 140 and 200 °C) using different ratios of mercury and chlorine concentrations in the influent stream. Typical chlorine in-stack vapor-phase concentrations for incineration plants range from 400 to 1000 $\mu L/L$ as hydrogen chloride, HCl (3). Two different HCl concentrations will be tested in this study, namely 400 and 1000 $\mu L/L$ while the concentration of mercury in both cases will be 500 $\mu g/m^3$.

RESULTS

An experimental system capable of producing constant concentrations of vapor-phase mercury was successfully constructed and tested at the outset of this study. Furthermore, an AAS was calibrated by trapping a carrier gas containing different concentrations of vapor-phase mercury in the impinger solutions. It was discovered that mercury adsorbs to glass walls of the impinger bottles and the problem was solved by rinsing the glassware with concentrated nitrohydrochloric acid. The calibration curve generated from these experiments is shown in Figure 2.

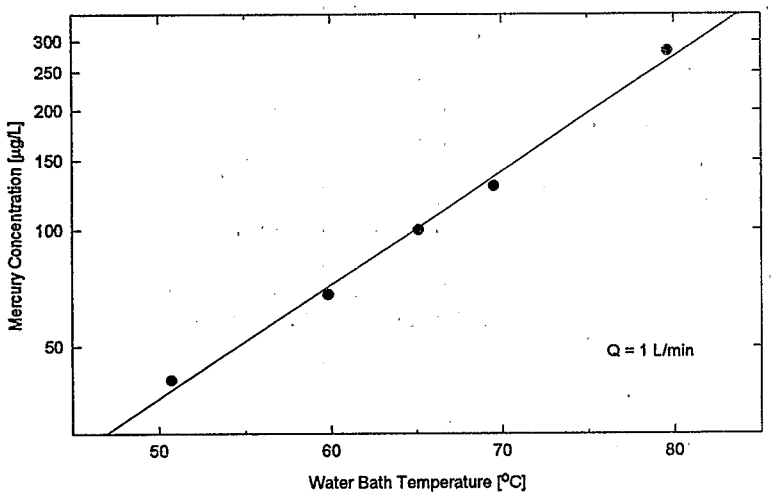


Figure 2. Vapor-Phase Mercury Concentration as a Function of Water Bath Temperature

Following the calibration of the instrument, the influence of mercury concentration and ambient temperature on the adsorptive capacity of virgin GAC was evaluated using the fixed-bed breakthrough experiments conducted with 100 mg of GAC and a carrier gas flow rate of 1 L/min. The results of these experiments are summarized in Figure 3.

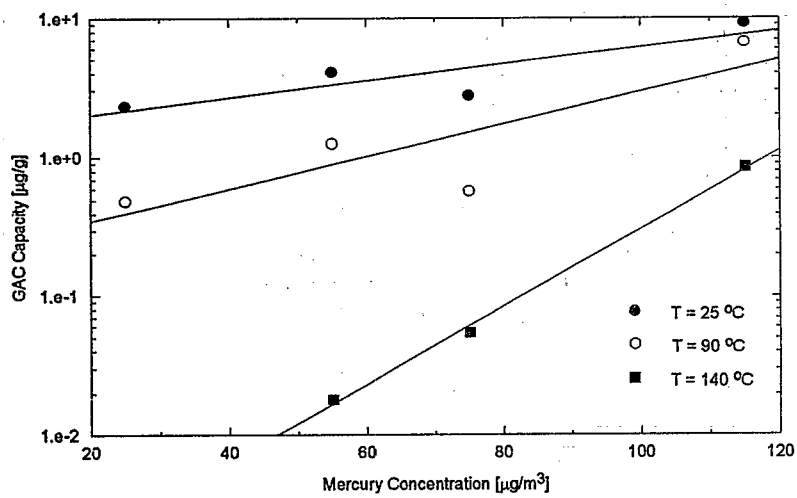


Figure 3. Effect of Temperature and Mercury Concentration on Virgin GAC Adsorptive Capacity

CONCLUSIONS

As is apparent from Figure 3, the increase in mercury concentration leads to an increase in virgin GAC adsorptive capacity for vapor-phase mercury. However, higher temperatures significantly reduce the ability of virgin activated carbon to remove mercury from the stack gases. Both of these trends were expected since the adsorption process is an exothermic reaction that is driven by the concentration of adsorbate in the fluid phase.

What is also apparent from Figure 3 is that the virgin GAC has very low capacity for the removal of vapor-phase mercury under the conditions that are prevalent in the incineration plant stacks (high temperatures). Furthermore, the presence of other trace inorganic and organic compounds in the stack gas would further diminish its capacity for the retention of mercury due to competitive adsorption. Therefore, it appears that sulfur impregnated carbon would be better suited for the control of mercury emissions from solid and hazardous waste incinerators for the following reasons: a) the capacity of sulfur impregnated GAC is several orders of magnitude above the capacity of virgin GAC; and b) the entire adsorptive capacity of sulfur impregnated GAC can be used exclusively for vapor-phase mercury since this carbon can not adsorb any other trace organic or inorganic compounds in the stack gas.

Next goal in this study is to evaluate the effects of temperature and mercury concentration on the ability of sulfur impregnated activated carbon to remove mercury from the gas phase (similar to those presented in Figure 3 for virgin GAC) followed by the evaluation of the rates of vapor-phase mercury uptake by both carbons. Based on the results of these experimental studies, a mathematical model that accounts for both diffusion rate and the rate of reaction between sulfur and vapor-phase mercury will be develop to assist in predicting the performance of these activated carbons in the control of mercury emissions from solid and hazardous waste incinerators.

REFERENCES

1. Shendrikar, A.D., Damle, A., and Gutknecht, F. Collection Efficiency Evaluation of Mercury-Trapping Media for the SASS Train Impinger Solution. EPA-600 S7-84-089, U.S. EPA, Washington, DC., 1984.
2. APHA-AWWA-WPCF Standard Methods for the Examination of Water and Wastewater, 17th ed., Port City Press, Baltimore, MD, 1989.
3. Hall, B, Schager, P., and Lindqvist, O. (1991) "Chemical Reactions of Mercury in Combustion Flue Gases." *Water, Air, and Soil Pollut.*, 56, 3.

For More Information:

Luis Garcia
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268
513-569-7932

APPLICATION OF AMBERSORB 563 ADSORBENT TECHNOLOGY FOR TREATMENT OF CHLORINATED ORGANICS IN GROUNDWATER

Russell W. Frye, Joseph F. Martino, and Russell E. Turner
Roy F. Weston, Inc.
1 Weston Way
West Chester, PA 19380
610-701-6173

Eric G. Isacoff and Deborah A. Plantz
Rohm and Haas Company
Research Laboratories
Spring House, PA 19477
215-641-7255

INTRODUCTION

Roy F. Weston, Inc. (WESTON®), in conjunction with Rohm and Haas Company (Rohm and Haas), conducted a field pilot study to demonstrate the technical feasibility and cost-effectiveness of Ambersorb® 563 (A-563) carbonaceous adsorbent for the remediation of groundwater contaminated with volatile organic compounds (VOCs). The project was conducted under the Emerging Technology Program of the EPA Superfund Innovative Technology Evaluation (SITE) program.

Ambersorb adsorbents are a family of patented, synthetic, tailorable carbonaceous adsorbents that were developed by Rohm and Haas in the 1970's for the treatment of contaminated water. In specific applications, Ambersorb adsorbent technology may offer a cost-effective alternative to air stripping or granular activated carbon (GAC), which are typically used in pump and treat systems for remediating groundwater contaminated with organic compounds.

Ambersorb adsorbents have been found to be effective in the removal of low levels of VOCs and other synthetic organic compounds from contaminated water (1). Previous applications using Ambersorb adsorbents have demonstrated several key performance benefits over GAC (2,3,4,5). Ambersorb 563 adsorbent can be regenerated onsite using steam, solvents, or other techniques, permitting the recovery of a concentrated organic stream which can be disposed of or reclaimed. Ambersorb 563 adsorbent has a significantly greater adsorption capacity than GAC for chlorinated hydrocarbons when the contaminants are present at low concentrations. Ambersorb 563 adsorbent systems can operate at higher flow rates than GAC systems, while maintaining effluent water quality below drinking water standards.

METHODOLOGY

The Ambersorb technology demonstration was conducted at Pease Air Force Base (AFB) in Newington, New Hampshire. The base has been included on the National Priorities List (NPL) and WESTON has been conducting an Installation Restoration Program (IRP) Stage 3 Remedial Investigation (RI) at Pease AFB over the past several years. Based on a review of groundwater data for various sites at Pease AFB, Site 32/36 was selected for the Ambersorb 536 adsorbent field trial. The groundwater in this area is contaminated with a number of chlorinated organics including vinyl chloride (VC), 1,1-dichloroethene (1,1-DCE), cis-1,2-dichloroethene (cis-1,2-DCE), trans-1,2-dichloroethene (trans-1,2-DCE), and trichloroethene (TCE).

The Ambersorb technology demonstration project under the SITE program used a 1-gallon-per-minute (gpm) continuous pilot system, consisting of two adsorbent columns, to evaluate the treatment of groundwater from Site 32/36 at Pease AFB. The field study was performed over a 12 week period during the spring/summer of 1994. The testing program included four service cycles and three steam regenerations. A summary of the conditions for the service cycles and steam regenerations is provided in Tables 1 and 2, respectively.

TABLE 1. SUMMARY OF CONDITIONS FOR SERVICE CYCLES

Parameter	Cycle 1		Cycle 2		Cycle 3		Cycle 4	
	Col. A	Col. B	Col. A	Col. B	Col. A	Col. B	Col. A	Col. B
	A-563 Virgin	F-400 Virgin	A-563 Regen	A-563 Virgin	A-563 Regen	A-563 Regen	A-563 Regen	A-563 Regen
Column Configuration	---	---	Lag	Lead	Lead	Lag	Lag	Lead
Column Diameter (inches)	4	6	4	4	4	4	4	4
Column Height (feet)	2	3	2	2	2	2	2	2
Flow Rate (gpm)	0.44/0.87*	0.29/0.58*	0.87	0.87	0.87	0.87	0.87	0.87
Hydraulic Loading (gpm/ft²)	5/10	1.5/3.0	10	10	10	10	10	10
Flow Rate Loading (gpm/ft²)	2.5/5	0.5/1.0	2.5†	5	5	2.5†	2.5†	5
Empty Bed Contact Time (EBCT) (minutes)								
Days to Saturation Breakthrough for Each Column‡	3.0/1.5	15.0/7.5	3.0†	1.5	1.5	3.0†	3.0†	1.5
Estimated Number of Bed Volumes (BV) Treated‡	12/6	12/6	12	6	6	12	12	6
	6,000	1,000	6,000	6,000	6,000	6,000	6,000	6,000

*Flowrate was increased after 7 days.
†Total system loading with columns operating in series.
‡Estimated value predicted from model using influent vinyl chloride concentration of 5 ug/L.

TABLE 2. SUMMARY OF CONDITIONS FOR STEAM REGENERATION

Parameter	Regeneration 1	Regeneration 2	Regeneration 3
Column Regenerated	Cycle 1, Column A	Cycle 2, Column B	Cycle 3, Column A
Temperature (°C)	155	145	140
Time (hours)	16	16.5	17.5
Total Bed Volumes	7.6	7.0	8.9

The first cycle consisted of a direct comparison of the performance of Ambersorb 563 adsorbent and Filtrasorb® 400 (F-400) GAC. The remaining cycles evaluated Ambersorb 563 adsorbent under varying process conditions. Concentrations of VOCs in the influent contaminated groundwater and the treated column effluent were monitored during each cycle to establish breakthrough curves. Process parameters including groundwater influent flowrate, temperature, and pressure were also monitored at periodic intervals throughout the field trial.

Following contaminant breakthrough, the service cycles were terminated. Steam regeneration of the lead Ambersorb adsorbent column was then performed onsite. The regeneration process yielded a condensate consisting of a distinct separable organic layer and an aqueous phase. Both the aqueous and organic phases were measured and analyzed to assess regeneration efficiency.

A test to demonstrate the use of a "superloading" adsorbent column to treat the aqueous condensate from a typical steam regeneration process was also conducted during the field trial. The superloading column takes advantage of Ambersorb adsorbent's higher adsorption capacity at higher concentrations. The aqueous phase from the third steam regeneration was passed through an Ambersorb adsorbent superloading column with a diameter of 2 inches and a bed height of 2 feet. Effluent samples from the superloading column were collected and analyzed for VOCs.

RESULTS

The average VOC levels measured in the influent groundwater during each of the service cycles is summarized in Table 3. Note that due to analytical limitations, the vinyl chloride and 1,1-DCE concentrations for certain cycles were estimated based on the amount of the contaminant subsequently recovered during regeneration.

TABLE 3. INFLUENT GROUNDWATER QUALITY

Compound	Maximum Contaminant Level* (ug/L)	Average Influent Concentration (ug/L)				
		Cycle 1		Cycle 2	Cycle 3	Cycle 4
		A-563	F-400	A-563	A-563	A-563
VC	2	3.4†	3.9†	4.8	5.7	11
1,1-DCE	7	0.31†	0.31†	5.8†	6.6†	<10
cis-1,2-DCE	70	312	329	351	373	357
trans-1,2-DCE	100	101	101	121	116	89
TCE	5	4,330	4,120	4,490	3,600	3,883

*National Revised Primary Drinking Water Regulations (40 CFR 141.61).
†Estimated concentration based on recovery during regeneration of A-563 column.

Vinyl chloride, cis-1,2-DCE, trans-1,2-DCE, and TCE were present in the influent groundwater at concentrations exceeding the maximum contaminant levels (MCL) established in the National Revised Primary Drinking Water Regulations. TCE was the contaminant measured at the highest average concentration, ranging between 3,750 ug/L and 4,330 ug/L.

The results of the Ambersorb 563 adsorbent demonstration study are summarized for each cycle in Table 4.

TABLE 4. DEMONSTRATION STUDY PERFORMANCE RESULTS

Compound	Bed Volumes to Drinking Water Standard				
	Cycle 1		Cycle 2*	Cycle 3*	Cycle 4*
	A-563	F-400	A-563	A-563	A-563
VC	7,900	1,740	8,500	6,500	5,000
1,1-DCE	>12,600	4,270	>11,800	>7,500	>15,690
cis-1,2-DCE	9,000	3,700	10,500	8,500	9,900
trans-1,2-DCE	>12,600	4,890	>11,800	>11,450	>15,600
TCE	7,700	4,820	9,300	5,300	7,500

*Results presented for the lead column.

The monitoring results for Cycle 1 column effluents showed that both the Ambersorb 563 adsorbent and GAC achieved water quality below the drinking water standards for each compound. However, when comparing the bed volumes treated to the drinking water standard breakthrough for each contaminant, Ambersorb 563 adsorbent, while operating at 5 times the flowrate loading as Filtrasorb 400, treated approximately two to five times the volume of water as GAC. The TCE breakthrough curves for Cycle 1 are shown in Figure 1.

Comparison of the performance results for the Ambersorb adsorbent for the four cycles indicated minimal loss in adsorption capacity during the course of the field trial. The reduction in bed volumes treated to the drinking water standard breakthrough observed in Cycles 3 and 4 resulted from the increase in vinyl chloride concentration in the influent groundwater. There was no significant reduction in capacity for any of the other contaminants.

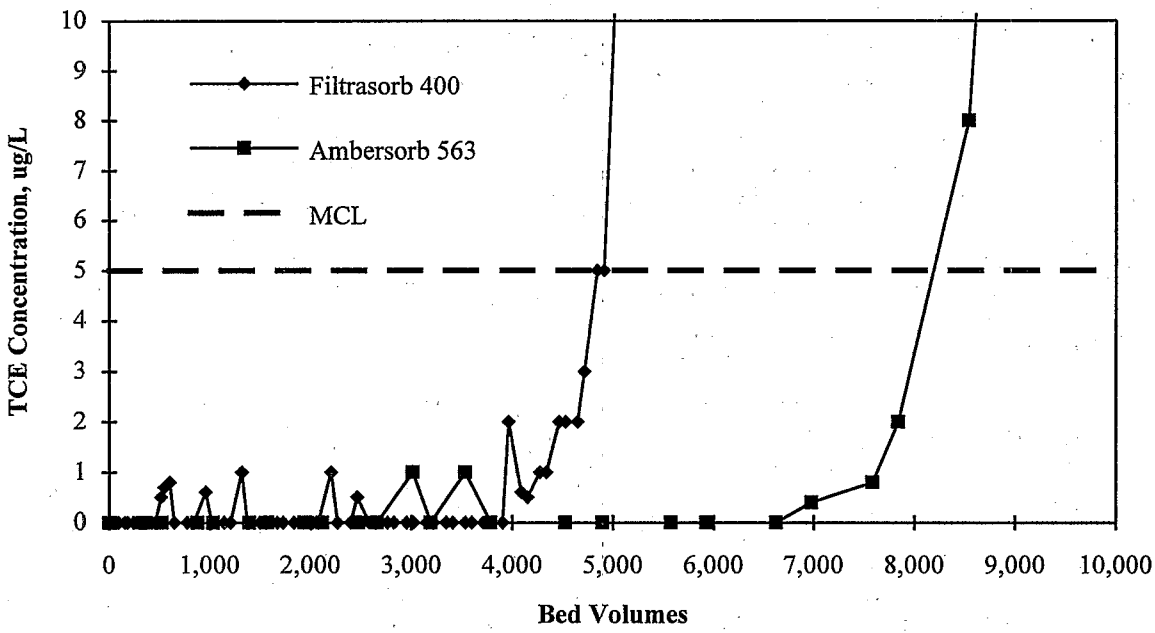


Figure 1 . Cycle 1 Ambersorb 563 and Filtrasorb 400 Breakthrough Curves for Trichloroethene.

The results of the steam regenerations are provided in Table 5.

TABLE 5. STEAM REGENERATION RESULTS

Parameter	Regeneration 1	Regeneration 2	Regeneration 3
Total Bed Volumes	7.6	7.0	8.9
VOC Mass Recovery in 3 Bed Volumes (%)	70	70	90
Total VOC Mass Recovery (%)	79	74	>95
VOC Mass Recovery Associated with Organic Phase (%)	86	90	81

The steam regeneration results indicated that a significant recovery of the VOC mass loaded onto the Ambersorb adsorbent during the service cycles, ranging from 74% to >95%, was achieved during the regeneration process. The results showed that the bulk of the VOC mass recovery occurred within the first 3 bed volumes of steam as condensate. Furthermore, the results indicated that approximately 80% to 90% of the VOC mass recovered was associated with the easily separable organic phase.

The differences observed in the VOC mass recovery for the three steam regenerations may be related to the dehydrohalogenation of chlorinated organics under elevated temperatures. The pH profiles for the steam condensate for each of the regenerations suggest the possibility of a dehydrohalogenation mechanism.

The results of the superloading test indicate that the condensate was effectively treated to levels below the drinking water standards. A total of 15 bed volumes of condensate, which averaged 700,000 ug/L VOCs (predominately TCE) was passed through the superloading column at an EBCT of 7.5 minutes (8.0 BV/hr). The effluent samples from the superloading column showed no detectable leakage of any VOCs for 11 bed volumes. TCE at 2 ug/L was the only compound detected in the final superloading column effluent sample collected after 15 bed volumes.

CONCLUSIONS

Ambersorb 563 adsorbent is an effective technology for the treatment of groundwater contaminated with chlorinated organics. The effluent groundwater from the Ambersorb 563 adsorbent system consistently met drinking water standards. The adsorption capacity of the Ambersorb system remained essentially unchanged following onsite regeneration of the adsorbent and multiple service cycles.

Direct comparison of the performance of Ambersorb 563 with Filtrasorb 400 using the bed volumes treated to the drinking water standard breakthrough indicated that Ambersorb 563 adsorbent was able to treat approximately two to five times the volume of water as GAC while operating at 5 times the flowrate loading.

Onsite steam regeneration was successfully demonstrated. The steam regenerations yielded a separate organic phase which contained approximately 80% to 90% of the total VOC mass loaded onto the adsorbent. The majority of VOC recovery was shown to occur within 3 bed volumes of steam as condensate.

The principle of superloading was demonstrated as an effective treatment method for the aqueous condensate layer resulting from the steam regeneration of the Ambersorb adsorbent. A condensate stream containing 700,000 ug/L VOCs was treated to below the drinking water standards using a superloading column.

REFERENCES

1. Neely, J.W. and Isacoff, E.G. Carbonaceous Adsorbents for the Treatment of Ground and Surface Waters. Marcel Dekker, Inc., New York, New York, 1982.

2. Vandiver, M. and Isacoff, E.G. THM Reductions with Ambersorb 563 Adsorbent. Paper presented at 41st Annual Conference, Society of Soft Drink Technologists, Albuquerque, New Mexico. April 19, 1994.

3. Parker, Jr., G.R. Comparison of Ambersorb 563 Carbonaceous Adsorbent and Granular Activated Carbon for the Removal of TCE from Water at Short Empty Bed Contact Times. Presented at American Institute of Chemical Engineers Annual Conference, Miami Beach, Florida. November 4, 1992.

4. Isacoff, E.G., Bortko, S.M., and Parker, Jr., G.R. The Removal of Regulated Compounds from Groundwater and Wastewater using Ambersorb 563 Carbonaceous Adsorbent. Paper presented at American Institute of Chemical Engineers Conference, Miami Beach, Florida. November 3, 1992.

5. Parker, Jr., G.R. and Bortko, S.M. Groundwater Remediation using Ambersorb Adsorbents. Paper presented at the Florida Environmental Chemistry Conference. October 30-November 1, 1991.

For More Information:

Ronald J. Turner
Project Officer
U.S. EPA
Risk Reduction Engineering Laboratory
Cincinnati, OH 45268
513-569-7775

Russell E. Turner
Project Manager
Roy F. Weston, Inc.
1 Weston Way
West Chester, PA 19380
610-701-3097

GEOSAFE IN SITU VITRIFICATION SITE DEMONSTRATION

James E. Hansen, Director
Brett E. Campbell, Site Manager
Craig L. Timmerman, Project Manager
Geosafe Corporation
2950 George Washington Way, Richland, WA 99352
(509) 375-0710

INTRODUCTION

This extended abstract presents the results of the EPA SITE Program Demonstration that was conducted on Geosafe Corporation's In Situ Vitrification (ISV) technology at the Parson Chemical/ETM Enterprises Superfund Site in Grand Ledge, Michigan. The significance of the demonstration results are also related to other Geosafe project experience and the current state of the ISV technology.

The ISV technology is a joule-heated electric melting technology that treats contaminated soil and other earthen materials (e.g., sediment, sludge, flyash, mill tailings) for the primary purposes of destroying, removing, or immobilizing hazardous, radioactive, and mixed contaminants. ISV may be applied to materials in their original location within the ground, or to materials placed in a specific location or container, below grade or above grade, for purposes of treatment. A melt is typically initiated at the surface of the material to be treated. Joule heating occurs as electric current flows through the molten material, thus causing the melt to increase in temperature and adjacent material to melt. Typical melt temperatures range from 1,600 to 1,800°C. Single Melts as large as 1,400 tons and exceeding 20-ft in depth have been achieved. Adjacent melts fuse together to form a single contiguous monolith.

Contaminants may be destroyed, immobilized, and/or removed during ISV. The high temperature typically destroys organics by pyrolysis. The predominant disposition of heavy metals is chemical or physical incorporation within the resulting vitreous monolith, which produces a permanent immobilization result. Some vaporizable contaminants may be removed by the process heat without undergoing destruction or immobilization. The specific disposition that may be expected for contaminants at a given site depends on many waste- and site-specific variables. Off-gas treatment is employed to treat and/or remove vaporized contaminants and to ensure gases evolved from the process are safe for release.

The ISV process and equipment system is illustrated in Figure 1. ISV is a truly mobile technology with the majority of process equipment being permanently mounted on trailers.

The Parsons Chemical site was previously owned and operated from 1945 through 1979 by the former Parsons Chemical Works, Inc. which was involved in the mixing, manufacturing, and packaging of agricultural chemicals including pesticides, herbicides, solvents, and mercury-based compounds. These activities resulted in the contamination of soil around the manufacturing facility and in ditch locations of a drainage system that flowed approximately 1/4 mile to a nearby creek. The typical depth of contamination around the site was 5-ft or less. A total of about 3,000 cu-yd of soil was found to be contaminated with a broad range of organics and metals associated with the Parsons Chemical Works' activities at the site. The four contaminants of primary regulatory concern, and their maximum concentrations measured in the site soil, included: chlordane (89,000 ppb), 4,4'-DDT (340,000 ppb), dieldrin (87,000 ppb), and mercury (34,000 ppb). Dioxins were also found on the site at very low levels.

The site soil is a silty clay with some sand present. A sandy layer exists approximately 8 to 10-ft below grade. Water flows through this layer, in a north easterly direction, on a variable basis related to recent rain and snowfall. The site soil is relatively homogeneous with nearly zero rock content. The

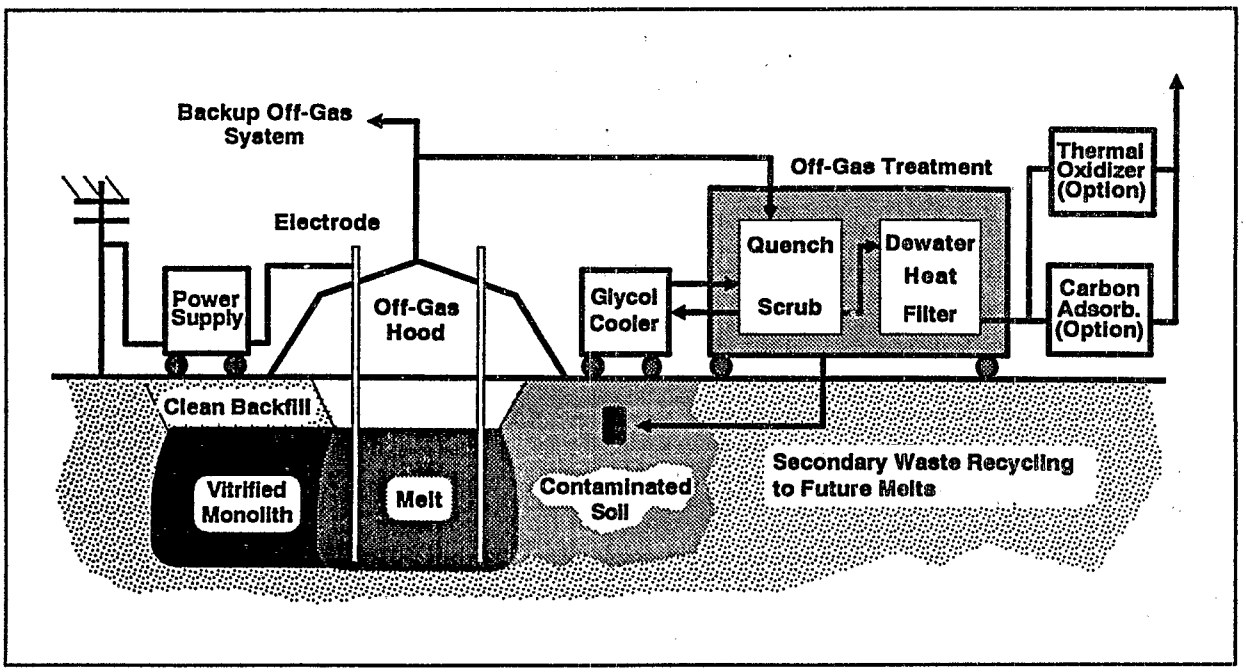


Figure 1. ISV Processing and Equipment Schematic

soil wet density is 1.8 ton/cu-yd; the dry density is 1.5 ton/cu-yd. The soil was found to be very low in load bearing capacity when wet, and very hard and strong when dry. These conditions made it difficult to work with regardless of the season.

METHODOLOGY

EPA and the Michigan State Department of Natural Resources (MDNR) established ARARs for the site including the following cleanup standards for the treated (vitrified) soil: chlordane (1,000 ppb), 4,4'-DDT (4,000 ppb), dieldrin (80 ppb), and mercury (12,000 ppb).

The contaminated soils from around the site were consolidated into a 16-ft deep trench for ISV treatment purposes. The treatment trench was laid out in a manner that would accommodate nine individual melts involving about 400 cu-yd of contaminated soil each. The treatment trench construction included a feature to intercept and divert groundwater that might flow into the site through the sandy layer at the 8 to 10-ft level. This was accomplished by placing a layer of cobble rock under the complete treatment area, deeper cobble-filled trenches along the outside (north-south) edges of the treatment area, and vertical walls of cobble around the complete treatment volume. In addition, two cobble-filled sumps were placed at the northernmost corners of the treatment area to serve as accumulation points for intermittent pumping of intercepted water to a nearby drainage ditch. Figure 2 illustrates the configuration of the treatment trench.

At the time of the project design, it was also believed that the cobble walls would be beneficial to the project as thermal barriers, which would limit melt width and thus minimize the extent of overmelting into clean adjacent soil. In order to construct the cobble walls, concrete walls were placed as vertical forms on the interior of the cobble (side toward the contaminated soil), and pressed wood sheeting was used as forming on the exterior (native soil) side. During the vitrification portion of the project, concern

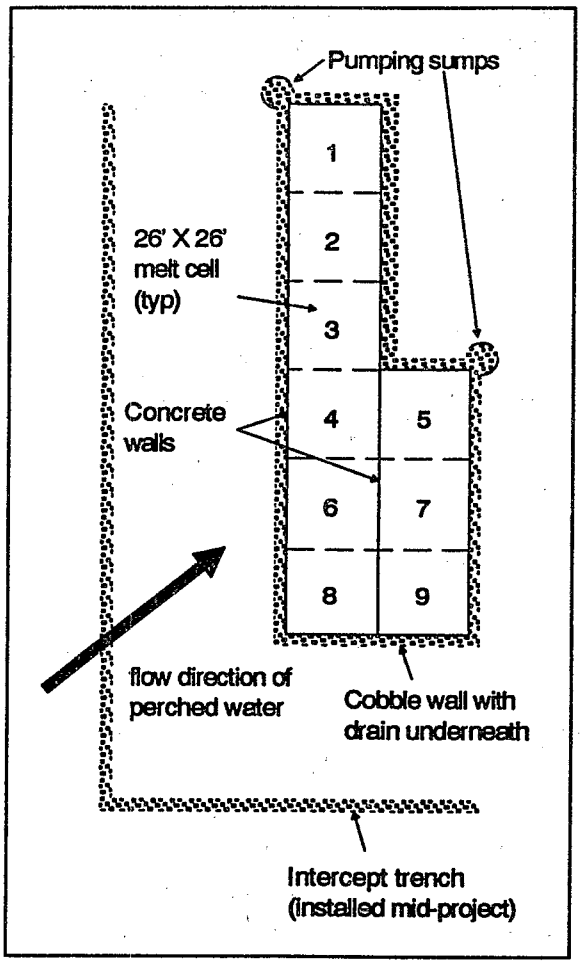


Figure 2. Treatment Trench Configuration

developed over having the intercept water and cobble materials located immediately adjacent and beneath the contaminated soil. Therefore, about midway through the project, another intercept trench was constructed away from the treatment trench for purposes of intercepting the groundwater before it could reach the vicinity of the treatment trench. This new intercept trench was successful in minimizing the amount of water reaching the original intercept and diversion system.

The SITE Demonstration Program identified one critical objective and seven secondary objectives for their evaluation of the demonstration. They determined that the demonstration would be performed on the sixth melt performed at the site. Their objectives were:

- To determine if the final soil cleanup levels were achieved (critical objective)
- To evaluate the leachability characteristics of the vitrified product using the TCLP
- To determine the approximate levels of residual contaminants in the vitrified soil
- To characterize the pesticide and mercury content of the off-gas scrubber water
- To evaluate emissions from the process
- To identify operational parameters of the technology
- To develop operating cost estimates and projections, and to assess equipment reliability
- To examine potential technical, institutional, operational, and safety impediments related to the use of the ISV technology.

Extensive sampling and analysis of the demonstration soil volume was performed to establish a pre-vitrification contamination level. Composite sample results for the contaminants of concern were: chlordane (2,000 ppb), 4,4'-DDT (72,000 ppb), dieldrin (12,000 ppb), and mercury (12,000 ppb). These values were reported as estimates since they were less than the reporting detection limit for the methods used, but greater than the method detection limits.

Geosafe utilized conventional ISV processing methods for performance of the individual melts. The "feeding electrode" concept was employed, wherein the depth of the electrodes were controlled by feeders. The depth of the melt could be determined at each electrode by lowering the electrodes to the bottom of the melt. Two notable changes from the initial operating mode were made midway through the project. First, because of the tendency for the soil conditions at the site to produce wider than usual melts, and because of the limited performance of the cobble walls to limit melt width, it was determined

to employ refractory concrete barrier panels in place of the cobble rock for the last five of the melts. Second, due to the presence of a nonhazardous but sometimes offensive odor present within the off-gas emissions, a thermal oxidizer was added as an off-gas polishing step midway through the project to eliminate the odor.

RESULTS

SITE Demonstration Program data indicated that cleanup objectives for the site were achieved. Table 1 presents pre-test, post-test, and regulatory limit values for the contaminants of concern. It should be noted that the pre-test value for chlordane was found to be below regulatory limits, although prior samples from the site were well above limits. The fact that the materials were excavated and staged for treatment could be expected to provide a mixing of soils and an "averaging down" of contamination levels. It should also be noted that the ISV process is a destruction and removal process for organics, and is primarily a removal process for mercury. Mercury is notable compared to other heavy metals in that its low solubility in silicate melts, and its high vapor pressure at ISV melt temperatures, result in nearly total removal by vaporization to the off-gases. This behavior is in contrast to other heavy metals of environmental concern, which predominantly are retained in and immobilized by the vitrified product.

Vitrified product TCLP data was obtained for the target contaminants as well as other priority pollutant metals (see Table 2). It should be noted that the indication of organics being present at below the detection limit for the analytical method used is an improbable result due to the fact that organics cannot exist at the temperatures experienced in the ISV melt. The TCLP results were all very good, and were in agreement with many prior tests of ISV vitrified product that show the benefit of vitrification for immobilization of heavy metals and destruction of organics.

Results of stack gas emissions analyses are presented in Table 3. The less than values for the target pesticides are based on detection limit values for the analytical methods used. No pesticides were detected in the off-gas. Because of the presence of other metals within the soil in addition to the target metal contaminant (mercury), the metals arsenic, chromium and lead were designated as critical analytes of the off-gas emissions. As indicated in Table 3, all metals emissions results were in compliance with established regulatory guidelines. Arsenic was below reporting detection limits in all samples.

The purpose of the wet scrubber in the off-gas treatment system is to remove particulate and condensible vapors that may escape the treatment zone and enter the off-gases. The concentration of such materials in the scrub solution increases over time. SITE Demonstration Program analyses of the scrubber water confirmed that it contained volatile organics, partially oxidized semivolatile organics, mercury, and other metals. Geosafe sent the scrubber solution offsite for treatment and disposal at the

TABLE 1. COMPARISON OF PRE-TEST AND POST-TEST SOIL CONTAMINANT CONCENTRATIONS WITH CLEANUP CRITERIA*

Contaminant	Pre-Test	Post-Test	Regulatory Limit
Chlordane	<80**	<80	1,000
4,4'-DDT	13,000	<16	4,000
Dieldrin	4,600	<16	80
Mercury	3,800	33	12,000

* All results by SITE Demonstration Program; all units are μg/kg

** < values indicate not detected at or above presented value (detection limit)

TABLE 2. VITRIFIED PRODUCT TCLP DATA FOR CONTAMINANTS OF INTEREST*

Contaminant	Post-Test Concentration (μg/kg)	TCLP Result (μg/L)	Regulatory Limit (μg/L)
Chlordane	<80**	<0.50	30
4,4'-DDT	<16	NA	NA
Dieldrin	<16	NA	NA
Arsenic	3,100	13	5,000
Barium	3,600	440	100,000
Cadmium	NA	<5.0	1,000
Chromium	13,000	<10	5,000
Lead	8,600	1,100	5,000
Mercury	33	0.18	200
Selenium	NA	<300	1,000
Silver	NA	<10	5,000

* All results by SITE Demonstration Program
** < values indicate not detected at or above presented value (detection limit)

TABLE 3. STACK EMISSIONS PERFORMANCE DATA COMPARED TO REGULATORY GUIDELINES*

Contaminant	Emissions Value (lb/hr)	Regulatory Limit (lb/hr)
Chlordane	$<1.0 \times 10^{-5}$**	2.5×10^{1}
4,4'-DDT	$<2.0 \times 10^{-6}$	1.0×10^{-2}
Dieldrin	$<2.0 \times 10^{-6}$	2.8×10^{-4}
Arsenic	$<1.9 \times 10^{-6}$	***
Chromium	2.1×10^{-5}	***
Lead	2.8×10^{-5}	***
Mercury	1.1×10^{-4}	5.9×10^{-4}

* All results by SITE Demonstration Program
** < values indicate not detected at or above presented value (detection limit)
*** Emissions levels were deemed acceptable by MDNR

end of the project. Alternatively, it is believed that several means may be employed to remove the contaminants from the water, such that the contaminants could be replaced in the soil for additional destruction/immobilization treatment by a subsequent ISV melt. Such alternatives were not attempted during the demonstration.

The SITE Demonstration Program also evaluated the reliability and operating efficiency of the ISV process and equipment. The demonstration melt was found to take 10 days to complete, melting approximately 600 tons of soil at an average specific power consumption of 0.72 MWh/ton. The ISV process equipment operated very well during the demonstration with only minimal downtime for addition of electrode segments and minor adjustments.

Lastly, the SITE Demonstration Program performed order of magnitude (+50%, -30%) estimates of cost for ISV processing based on the costs incurred during the demonstration melt. They estimated the cost for three cases involving different quantities of material treated and depth of treatment, as follows: Case 1: 1,700 tons at 5-ft depth - $740/ton; Case 2: 5,700 tons at 15-ft depth - $430/ton; and Case 3: 7,900 tons at 20-ft depth - $370/ton. It is noted that ISV costs should be computed on a per ton basis since the throughput capability is related to melting mass as opposed to volume. Processing rates vary directly with soil wet density. It is appropriate to use wet density in such determinations since the process consumes time and energy for removal of water as well as for melting soil.

CONCLUSIONS

The SITE Demonstration Program reported that the ISV technology performed well relative to all the critical demonstration objectives, and that the ISV technology should be applicable to other sites with similar contaminants and soil conditions.

The demonstration reporting noted that the contamination conditions at the Parsons Chemical site were not severe enough to enable measurements and calculation of destruction and removal efficiencies (DREs) for the pesticides treated at the site. This is a typical problem where contamination levels are too low relative to the capabilities of analytical methods to detect contaminants at low enough levels to determine DREs in the range of 4-9s (99.99%) or greater. Relative to this limitation of the demonstration, Geosafe notes that a large number of ISV tests have been performed that have demonstrated repeatedly the capabilities of the process to attain DRE's in the range of 99.99% to >99.9999% for volatile, semivolatile, and nonvolatile organics. One such demonstration was performed at large-scale immediately after the Parson Chemical Project. This demonstration was Geosafe's National TSCA Demonstration Project which was performed at a private site in Region 10. The site contained PCBs to a maximum level of 17,000 ppm. The project was performed under the auspices of EPA's TSCA organization, as a demonstration in support of Geosafe's application for a National TSCA Operating Permit for PCB treatment. The project clearly demonstrated the capability of the process to exceed 99.9999% DRE for PCBs.

Geosafe concurs with the SITE Demonstration Program's order of magnitude cost estimates for ISV based on the conditions experienced at the Parsons Chemical site. However, there are several factors that should be noted relative to considering the cost of ISV at other sites. It should first be recognized that specific conditions at the Parsons Chemical site made it a more costly endeavor than may be typical for other sites. The primary determinants of cost are four: 1) the price of electricity at the site, 2) the depth of processing, 3) the amount of water to be removed by the process, and 4) the amount of clean soil that is melted to ensure that the full target volume has been treated. The Parsons Chemical project was at the higher end of all these variables except processing depth.

Because of the large amount of electricity purchased, it is typically possible to obtain a negotiated project rate of approximately 1/2 the local residential rate. The price of electricity for ISV within the

U.S. typically falls in the range of $0.02/kwh (for large government applications) to $0.06/kwh. The price of power at the demonstration site totalled about $0.07/kwh. The 15-ft processing depth at the site is considered to be a good economical depth for ISV. Deeper processing depths are more economic than shallow depths because overall equipment utilization efficiency (time spent melting versus time spent moving equipment between melts) is greater for deeper depths. The amount of water that had to be removed at the demonstration site was considered to be extreme compared to typical sites. Whereas the process will operate on fully saturated soils, the energy and time-related costs associated with removal of water from the soil favors drier soil conditions. At the Parsons Chemical site, the saturated soil conditions, the ability of the high clay content soil to absorb water, and the probability that additional water entered the treatment zone from the sandy layer during the project, resulted in unusually high water removal requirements at this site. The soil moisture content and other properties also had the effect of producing melts with a higher width:depth ratio than was expected. This resulted in the necessity to overmelt, widthwise, into clean soil in order to allow additional time to reach the desired melt depth. Such overmelting has a significant cost impact. Geosafe believes that these factors contributed to the cost of this project being 10 to 20% higher than might be expected at more favorable sites. It should be noted that the Parsons Chemical site was Geosafe's first large-scale remediation project. A large number of improvements to the equipment and operating methods were made during and since the project with the effect of improving overall operating efficiencies. Geosafe's current cost estimate for ISV treatment of typical nonradioactive sites within the U.S. is in the range of $350-450/ton.

Lastly, Geosafe notes that the ISV technology has significant adaptability to varying site conditions. For example, modifications can be made to the off-gas treatment system to accommodate unusual contaminant conditions or specific State emissions standards as required. In addition, there is a broad range of application configurations that may be employed to most economically treat contaminated materials. The ISV technology may be a preferred technology for challenging sites due to its unique capabilities, including: 1) the ability to simultaneously treat mixtures of contaminant types, 2) high treatment efficiencies (contaminant destruction, removal, immobilization), 3) high volume reduction (25-50% for soils), and 4) onsite and in situ safety benefits.

REFERENCES

The reader is referred to the full suite of SITE Demonstration Program documents and the video for details regarding this demonstration. The reader is referred to Geosafe Corporation literature for details regarding other test, demonstration, and remediation projects that have been performed using the ISV technology.

FOR MORE INFORMATION:

Ms. Teri Richardson, Technical Project Manager
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
26 West Martin Luther King Drive
Cincinnati, OH 45268
(513) 569-7949

UNTERDRUCK-VERDAMPFER-BRUNNEN (UVB): AN IN SITU SYSTEM FOR REMEDIATION OF CONTAMINATED AQUIFERS

Michelle A. Simon
US EPA
Risk Reduction Engineering Laboratory
Cincinnati, OH 45268
(513) 569-7469 (phone) (513) 569-7676 (fax)

Roger R. Argus and Benjamin L. Hough
PRC Environmental Management, Inc.
4065 Hancock Street, Suite 200
San Diego, CA 92110
(619) 225-1883 (phone) (619) 225-9985 (fax)

INTRODUCTION

Traditionally, contaminated groundwater is pumped to a surface facility for treatment, often by air stripping. An innovative technology, the Unterdruck-Verdampfer-Brunnen (UVB), German for Vacuum Vaporizing Well, is an in situ groundwater remediation technology that combines air-lift pumping and air stripping to clean aquifers contaminated with volatile compounds. Additionally, the developer claims that in some cases the technology is capable of simultaneous recovery of soil gas from the vadose zone. An evaluation of this process is discussed in this abstract.

A UVB system consists of a single well with two hydraulically separated screened intervals installed within a single permeable zone. The air-lift pumping occurs in response to reduced pressure introduced at the wellhead by a blower. This blower creates a vacuum that draws water into the well through the lower screen and the water rises toward the top of the well. A submersible pump ensures a flow rate of approximately 20 gallons per minute (1.26×10^{-3} meter^3 per second). Air stripping occurs as ambient air, also flowing in response to the vacuum, is introduced through a sieve plate located within the upper screened section of the well.

Air bubbles form in the water column causing volatile compounds to transfer from the aqueous to the gas phase. The rising air transports volatile compounds to the top of the well casing, where they are removed by the vacuum blower. The blower effluent is passed through granular activated carbon before being released to the atmosphere.

The transfer of volatile compounds is further enhanced by a stripping reactor located immediately above the sieve plate. The stripping reactor consists of a fluted and channelized column that facilitates the transfer of volatile compounds to the gas phase by increasing the contact time between the two phases and by minimizing the coalescence of air bubbles.

Once the upward stream of water leaves the stripping reactor, the water falls back through the well casing and returns to the aquifer through the

upper well screen. This return flow to the aquifer, coupled with the inflow at the bottom of the well, circulates groundwater around the UVB well. The extent of the circulation pattern is known as the radius of influence, which determines the volume of water affected by the UVB.

The UVB technology is a process patented by IEG mbH in Reutlingen, Germany. IEG Technologies, Inc., located in Charlotte, NC, markets the technology in North America. IEG teamed with Roy F. Weston, Inc. to demonstrate the UVB technology at March Air Force Base (AFB), CA. March AFB allowed the US EPA Superfund Innovative Technology Evaluation (SITE) program to evaluate the technology. The SITE program retained PRC Environmental, Inc. to evaluate the performance of the UVB system at March.

METHODOLOGY

The objective of the demonstration was to determine the efficiency of UVB system, the reduction in concentration of trichloroethene (TCE) in the aquifer, and the radius of influence of the UVB system within the aquifer.

Two series of wells were placed downgradient of the UVB system, as depicted in Figure 1. The first series of wells were placed 40 feet from the system; the second 85 feet away. Each of the two series had three wells: a shallow well screened at a depth of 37 to 57 feet below ground surface (bgs), an intermediate well screened at a depth of 65 to 75 ft bgs, and a deep well screened from 90 to 105 ft bgs. The two shallow wells were screened at the same depth as the UVB system outlet; the intermediate wells were screened at the same depths as the UVB inlet. The deep wells were screened below the anticipated UVB circulation cell. The wells were sampled monthly and samples were analyzed for volatile organic compounds.

A dye trace study was performed on the system. No dyes were detected in the aquifer prior to start of this dye study. A two-dye approach was implemented. Sodium fluorescein, a bright green dye, was injected in the system outlet, in order to determine whether water discharged from the UVB system could be detected in any of the surrounding wells. A bright yellow-orange dye, rhodamine WT (red-purple xanthene) was injected into the intermediate well placed 40 feet downgradient of the UVB system, to determine whether this well was within the system's radius of influence.

RESULTS

Figure 2 is a graph of the change of the TCE concentration for the inlet versus outlet water. When the system operated properly, the inlet TCE concentrations averaged 33.75 micrograms per liter (µg/L) and the outlet concentrations averaged less than 1 µg/L (97% removal efficiency). Twice during the twelve month period, the system required adjustments.

Figure 3 is a graph of concentration of TCE versus time for the wells located 40 feet downgradient of the UVB system. Prior to UVB system startup, samples from the shallow well had TCE concentrations of 530 µg/L; the intermediate well - 750 µg/L; and the deep well - 100 µg/L. Initially, the TCE concentration in the water from all six wells remained constant or

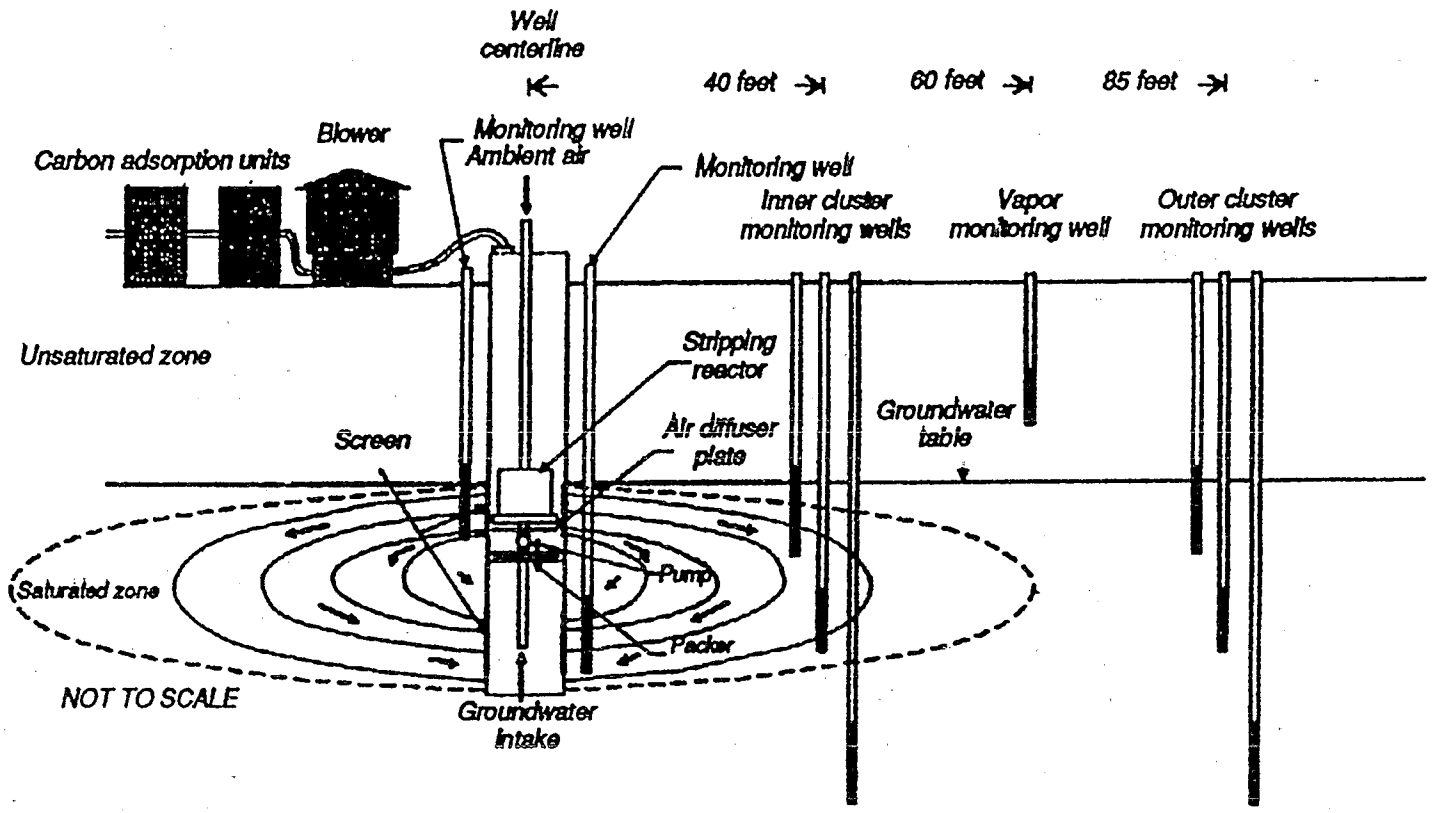


Figure 1. The Unterdruck-Verdampfer-Brunnen Technology as demonstrated.

increased. The TCE concentration in samples from the shallow well and the intermediate well increased to peak values of 620 and 2000 μg/L, respectively, after three months of system operation. Then, the concentration of TCE declined. TCE concentration in the deep well remained constant at 110 μg/L.

Figure 4 is a graph of the TCE concentration for the wells located 85 feet downgradient of the UVB system. The TCE concentrations in the samples collected from the outer well cluster initially increased after system startup, also. However, the concentrations peaked after seven months of UVB operation. The shallow well initially had a TCE concentration of 650 μg/L, which increased to 980 after seven months and then reduced to 290 after twelve months. Samples from the intermediate well measured 120, 640, 210 μg/L TCE, for the same respective time periods.

As for the dye study, the fluorescein dye that was injected into the outlet of the UVB was observed at the inner shallow well after 48 days. It was also observed in the deep inner cluster well after 59 days. It was never observed in the inner intermediate well which is located between the these two. The fluorescein dye was not observed in any other wells for the four month duration of the test, including those located 85 feet downgradient of the UVB.

The rhodamine dye that was injected into the inner intermediate well was observed <u>upgradient</u> at the UVB system after 85 days. The rhodamine dye was also observed in the inner deep well as soon as 17 days. Rhodamine dye was not detected in any other wells.

CONCLUSIONS

The UVB system can successfully remove TCE from inlet contaminated groundwater to a level less than 1 μg/L in the outlet under normal operating conditions. The dye study confirmed that the radius of influence for this application is at least 40 feet. A modeling study performed by the vendor predicted a radius of influence of approximately 80 feet. The TCE concentrations in samples from wells within the radius of influence initially increased but eventually declined to one-half their original levels after 12 months of treatment. March AFB continued to operate the UVB system for an additional 6 months and monitored its performance. These data show a continual decline in TCE concentration for the wells affected by the UVB.

FOR MORE INFORMATION

Contact Michelle A. Simon at the address above.

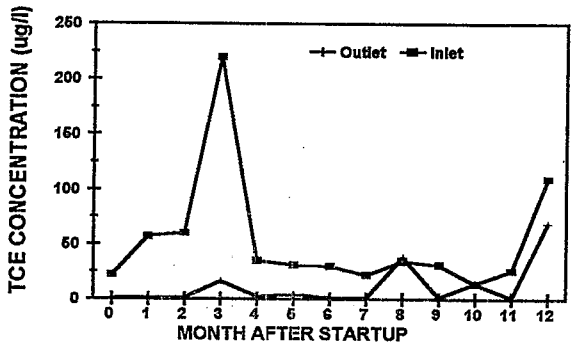


FIGURE 2
UVB SYSTEM INLET AND OUTLET

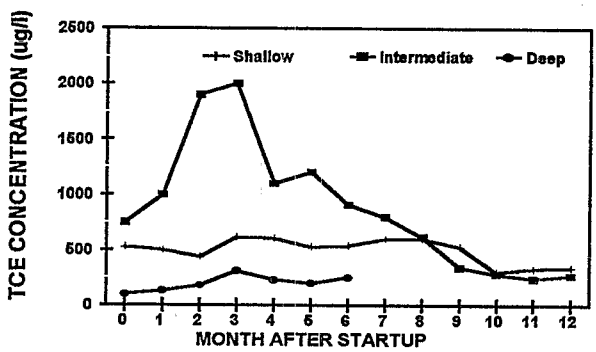


FIGURE 3
INNER CLUSTER OF WELLS

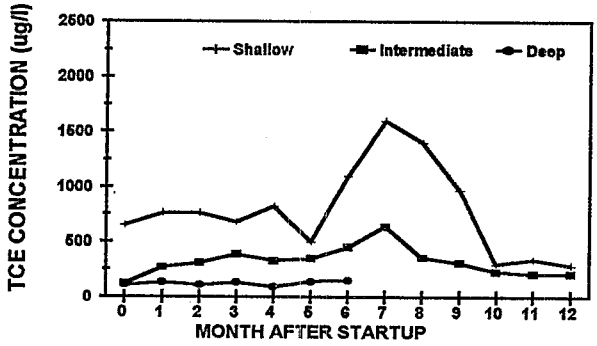


FIGURE 4
OUTER CLUSTER OF WELLS

SITE DEMONSTRATION OF TERRA-KLEEN RESPONSE GROUP'S MOBILE SOLVENT EXTRACTION PROCESS

Mark C. Meckes
U.S. Environmental Protection Agency
26 West Martin Luther King Drive
Cincinnati, Ohio 45268
(513) 569-7348

Scott W. Engle and Bill Kosco
PRC Environmental Management, Inc.
644 Linn Street, Suite 719
Cincinnati, Ohio 45203
(513) 241-0149

INTRODUCTION

In 1986 the Environmental Protection Agency (EPA) Office of Solid Waste and Emergency Response (OSWER) and the Office of Research and Development (ORD) established the SITE Program to Promote the development and use of innovative technologies to clean up uncontrolled hazardous waste sites across the country. The SITE Program is composed of four major elements: the Demonstration Program, the Emerging Technologies Program, the Measurement and Monitoring Technologies Program and the Technology Transfer Program. The Demonstration Program is designed to provide engineering and cost data for selected technologies, by evaluating their ability to treat wastes from Superfund sites.

The Terra-Kleen Response Group (TKRG) requested that EPA's SITE Program evaluate their mobile solvent extraction technology, and was selected for evaluation under the Demonstration Program. This technology is a batch process system which uses proprietary solvents to separate organic contaminants from soils, sediments, and/or sludges. Organic contaminants are concentrated during processing, thus reducing the volume of hazardous wastes for final disposal. Therefore, this technology is non-destructive.

TKRG's solvent extraction process is transportable and can be configured to treat both small or large quantities of solids. System components are often available from local suppliers throughout the United States. This reduces setup time and can reduce the amount of down time associated with equipment replacement.

Processing begins following excavation of contaminated solids and loading them into extraction vessels. The vessels are covered and clean solvent at ambient temperature and pressure is pumped into each one. Organic contaminants in the solids leach into the solvent without the aid of a mixing device. Contaminated solvent then flows into a clarifier where heavy solids are separated by gravity from the solvent. Clarified solvent is pumped through a microfilter which removes fines, and then through a proprietary regeneration unit which concentrates the organic contaminants. Clean solvent, discharged from the regeneration unit, is stored in a holding tank for reuse. This sequence of treatment steps is repeated until contaminant concentrations of the solids within the extraction vessels are reduced to a desired level. Some residual solvent still remains with the solids. Therefore, at this point in the process all solvent carrying lines are drained and vacuum extraction is used to reduce the concentration of solvent in the solids.

Treated solids are typically removed from the vessels by a front end loader and returned to the site. Concentrated contaminants are removed and disposed of off-site in accordance with applicable regulations. Regenerated solvent may be used for treatment of solids at other waste sites.

The SITE Demonstration of this technology was conducted during May 1994 in cooperation with the Naval Environmental Leadership Program (NELP) at Navel Air Station North Island (NASNI) which is located near San Diego, California. TKRG was contracted by NASNI to treat five tons of polychlorinated biphenyl (PCB) contaminated soil. This project was considered to be a pilot-scale demonstration of the capabilities of the TKRG's solvent extraction process. The primary objective of this demonstration was to determine if the process could achieve a soil clean up level of <2.0 mg/kg total PCB.

METHODOLOGY

A backhoe was used to excavate five tons of PCB contaminated soil from NASNI Site 4. The excavated soil was then homogenized by using the front end loader of the backhoe for mixing. Five extraction vessels were tared and each were filled with approximately one ton of the homogenized soil and weighed. A sampling grid was laid out across the top of each vessel and a core sampler was used to collect seven samples from each vessel. The seven samples were composited by vessel such that a composite sample represented the contents of an individual vessel. These samples were analyzed for PCBs, volatile organic compounds (VOCs), and semivolatile organic compounds (SVOCs) in accordance with Test Methods for Evaluation of Solid Wastes Physical/Chemical, 1992 (SW-846).

Following sample collection clean solvent was added to each extraction vessel and permitted to drain into a clarifier. Samples of the extraction solvent were periodically collected from the drain lines leading to the clarifier. The clarified solvent was pumped through a 5 micron bag filter and TKRG's proprietary solvent regeneration system. Samples of the regenerated solvent were collected periodically and analyzed for PCBs. Regenerated solvent was pumped into a storage tank and was held there until it was reutilized for subsequent extraction cycles.

When the solvent in all of the five extraction vessels had finished draining to the clarifier, the drain lines were closed and a second extraction cycle was initiated. The extraction cycles were continued until the measured concentration of PCBs in the drained solvent was <1.0 mg/L. At this point, the suction side of a centrifugal blower was connected to the drain lines of each extraction vessel and was operated continuously for three days. This was done to remove residual solvent from the solids. Following this treatment a mixture of nutrients and microorganisms were added to the extraction vessels to biologically degrade any remaining solvent. After two weeks of this biological treatment a sampling grid was reestablished for each extraction vessel and seven core samples of the solids were collected, composited, and analyzed as described above.

RESULTS

The characteristics of the soils obtained from each extraction vessel prior to treatment are shown in Table 1. Untreated soil was predominantly a dry sand with an average moisture content of 0.83 percent and 93.6 percent of the solids retained on a 0.075 mm screen. Polynuclear aromatic hydrocarbons (PAHs), hexachlorodibenzo furans (HxCDFs), and pentachlorodibenzo furans (PeCDFs) were identified, but only at very low concentrations. Bis(2-Ethylhexyl)phthalate was also identified at <0.7 mg/kg in the untreated soils. Other analyses showed the average Oil and Grease concentration at 759 mg/kg and the average total PCB concentration at 144 mg/kg.

TABLE 1
PHYSICAL AND CHEMICAL CHARACTERISTICS OF UNTREATED SOILS

Extraction Vessel	A	B	C	D	E	Avg.	S.D.
Particle Size (% >0.075 mm)	92.7	93.4	93.4	93.5	95.0	93.6	0.85
Moisture Content (%)	0.79	0.79	0.79	0.80	0.99	0.83	0.09
Total PAHs (mg/kg*)	2.10	2.23	3.38	1.55	1.94	2.24	0.69
Total HxCDF (ug/kg*)	0.658	0.629	0.647	0.848	0.704	0.697	0.089
Total PeCDF (ug/kg*)	<.409	0.144	<.343	0.162	0.218	<.255	-
Total PCB (mg/kg*)	130	140	134	146	170	144	15.7
Oil & Grease (mg/kg*)	753	726	713	737	868	759	62.5

* dry weight

A total of 11 extraction cycles were completed over 7 days for each of the 5 one ton batches of contaminated soil. Three days of vacuum extraction were then completed to reduce the concentration of residual solvent in the treated solids. Upon completion of vacuum extraction, a mixture of microorganisms and nutrients was added to each extraction vessel. After two weeks soil samples were collected from each vessel and analyzed for contaminants.

Low initial contaminant concentrations at or near method detection limits precludes the use of PAH, HxCDF, and PeCDF data for evaluation of the process. The results of PCB and Oil and Grease analyses and removal efficiencies for each are shown in Table 2.

Solvent concentrations in treated solids ranged from 4.7 to 3.6 percent prior to vacuum extraction. Following three days of vacuum treatment residual solvent in the solids was found to be between 2.7 and 1.8 percent. Fourteen days of biological treatment further reduced solvent concentrations to <0.5 percent.

TABLE 2
CONTAMINANT CONCENTRATIONS AND REMOVAL EFFICIENCIES OF TREATED SOILS

Extraction Vessel	A	B	C	D	E	Avg.	S.D.
Oil and Grease (mg/kg*)	327	300	252	167	318	273	65.8
Removal Efficiency (%)	56.6	58.7	64.6	77.3	63.4	64.0	8.1
Total PCB (mg/kg*)	1.79	1.63	1.79	1.88	1.96	1.81	0.12
Removal Efficiency (%)	98.6	98.8	98.7	98.7	98.8	98.7	0.1

* dry weight

CONCLUSIONS

TKRG's solvent extraction process was effective in removing PCBs and Oil and Grease from dry sandy soils. The extraction process was operated for 11 cycles to achieve a predetermined remediation goal of <2.0 mg/kg PCB in soil. Oil and Grease concentrations in the contaminated soils were also reduced to <330 mg/kg. All five batches treated met the remediation goal demonstrating that treatment of solids was consistent. Vacuum extraction combined with biological treatment was able to reduced the concentration of residual solvent in treated solids to <0.5 percent. Further reduction of residual solvent concentrations in solids may have been possible if treatment would have been allowed to continue.

FOR MORE INFORMATION:

Contact: Mark C. Meckes
U.S. EPA
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268

ELECTROKINETIC REMEDIATION: TECHNOLOGY STATUS

Yalcin B. Acar
Civil and Environmental Engineering Department
Louisiana State University
Baton Rouge, LA 70803
Phone: (504) 388-8638

Akram Alshawabkeh, Robert J. Gale, Robert E. Marks and Susheel Puppala
ELECTROKINETICS INC.
The Louisiana Business and Technology Center
Suite 105, South Stadium Drive
Baton Rouge, LA 70803
(504)388-3992

Randy Parker
Risk Reduction Engineering Laboratory, USEPA
26 West Martin Luther King Drive
Cincinnati, OH 45268
(513) 569-7271

and

Mark Bricka
US Army Engineer Waterways Experiment Station
Hal's Ferry Road
Vicksburg, MI 39180
(601) 634-3700

INTRODUCTION

The demand to develop innovative and cost-effective in-situ remediation technologies in waste management stimulated the effort to employ conduction phenomena in soils using an electric field to remove chemical species from soils (1-6). This technique variably named as *electrokinetic remediation, electro-reclamation, electrokinetic soil processing, electro-chemical decontamination , electrorestoration or electrochemical soil processing* uses low-level DC in the order of mA/cm^2 of cross sectional area between the electrodes or an electric potential difference in the order of a few volts per cm across electrodes placed in the ground in an open flow arrangement. The groundwater in the boreholes or an externally supplied fluid (processing fluid) is used as the conductive medium. Open flow arrangement at the electrodes allows ingress and egress of the processing fluid or the pore fluid into or out of the porous medium. The low-level DC results in physico-chemical and hydrological changes in the soil mass leading to species transport by coupled and uncoupled conduction phenomena in the porous media. Electrolysis reactions prevail at the electrodes. The species input into the system at the electrodes (either by the electrolysis reactions, or through the cycling processing fluid) and the species in the pore fluid will be transported across the porous media by conduction phenomena in soils under electric fields. This transport coupled with sorption, precipitation and dissolution reactions comprise the fundamental mechanisms affecting the electrokinetic remediation process. Extraction and removal are accomplished by electrodeposition, precipitation or ion exchange either at the electrodes or in an external extraction system placed in a unit cycling the processing fluid (1,2,4).

Electrokinetic remediation technology has recently taken significant strides. Electrokinetics Inc. of Baton Rouge has completed large-scale pilot studies using spiked and naturally contaminated soil deposits under the USEAPA SITE program. In collaboration with the US Army Waterways Experiment Station, Electrokinetics Inc. is currently carrying out a field study of extracting lead from soils at a Firing Range that belongs to the US Army. This demonstration study will be independently evaluated by the USEPA under the SITE program. The purpose of this paper is to present some of the recent developments in this technique and to outline the ongoing activities.

BACKGROUND

Three pilot-scale studies were conducted by Electrokinetic Inc. under the SITE program; two pilot-scale tests using kaolinite spiked with lead at initial concentrations of 850 mg/kg, 1,500 mg/kg and another using fine sand and kaolinite mixture spiked with lead at 5,322 mg/kg. The kaolinite used had lead adsorption capacity of about 1,100 mg/kg. Lead nitrate salt is used as the source of lead. Tap water is used both as the catholyte and the anolyte. Other details of testing are presented by Alshawabkeh and Acar (3) and EK (5). Figure 1 shows the lead concentration profile after 123 days of processing at a current density of 133 $\mu A/cm^2$. More than 90 % of the lead in the soil is transported across to the cathode compartment. Lead prematurely precipitates close to the cathode compartment at its hydroxide solubility value if the chemistry of the electrolyte at the electrodes is not altered or controlled (unenhanced electrokinetic remediation) . One objective of these pilot-scale tests was to formalize and validate the principles of multi-species transport under electric fields. An appreciation of the relation between the mechanics and chemistry is only possible when precipitation close to the cathode compartment is allowed. Therefore, pilot-scale tests did not employ any enhancement technique.

The development of the theoretical formalisms pertaining to multi-species transport under electric fields, preparation of the associated numerical model and design/analysis packages are supported by the USEPA under the Gulf Coast Hazardous Substance Research Center program at Lamar University. The total lead profile predictions of the model pertinent to the the specific initial and boundary conditions in

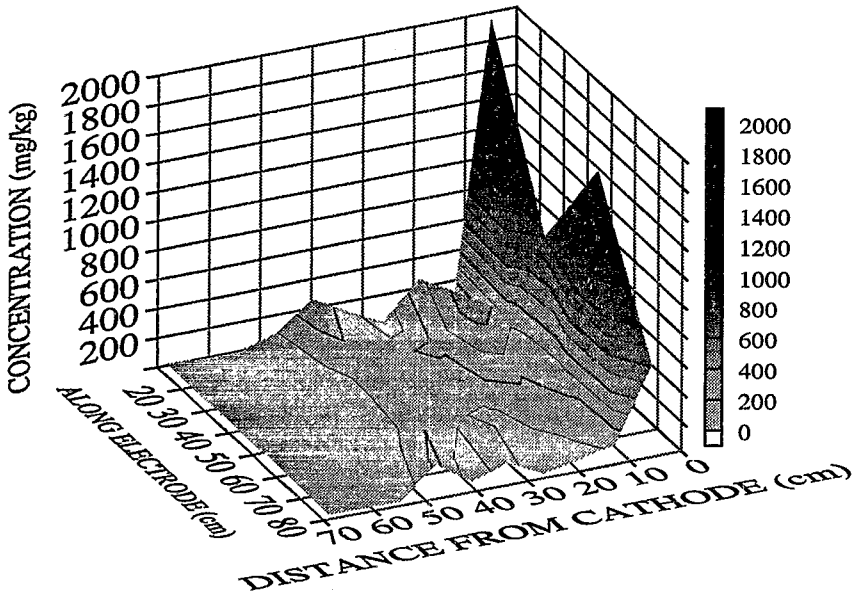


Figure 1. Lead concentration profile after 123 days of processing kaolinite/fine sand mixture spiked at 5,322 mg/kg (3).

the pilot-scale test presented in Fig. 1 are given in Figure 2. The acid generated by the electrolysis reactions at the anode and the lead released in to the pore fluid either by the dissolution or by the aqueous phase reactions travel towards the cathode compartment under the multi-species transport phenomena in soils under electric fields. Lead precipitates close to the cathode compartment at its hydroxide solubility value with the increase in the hydroxide concentration due to the prevailing cathodic reaction. The 50 day predictions shown in Fig. 2 are compared with the pilot-scale test results in Fig. 3. The agreement between the theoretical model and the pilot-scale test results demonstrate that the principles of the process are quite well rationalized and understood. The design analysis package which will include the generalized model is developed through joint collaborative effort between Electrokinetics Inc. and US Army Waterways Experiment Station.

The need to overcome the shortcoming of precipitation close to the cathode compartment prompted Electrokinetics Inc. and the US Army Waterways Experiment Station to collaborate and evaluate the feasibility of employing different techniques in enhancement of the process. The objective of the study was to promote transport of the positively charged species in to the catholyte where they could be removed either by electro deposition, by membrane separation or through ion exchange schemes. Acar and Alshawabkeh (1) discuss further the need for enhancement and propose different enhancement techniques which prevent the encountered precipitation. Figure 4 shows the extraction of different species in time from a 'real world' soil using the acetic acid cathode depolarization technique. The solubility of the species by the anodic acid and their migration under electrical fields are important considerations in electrokinetic remediation. The most soluble species will be the first ones to come out in solution and hence be transported towards the respective electrodes.

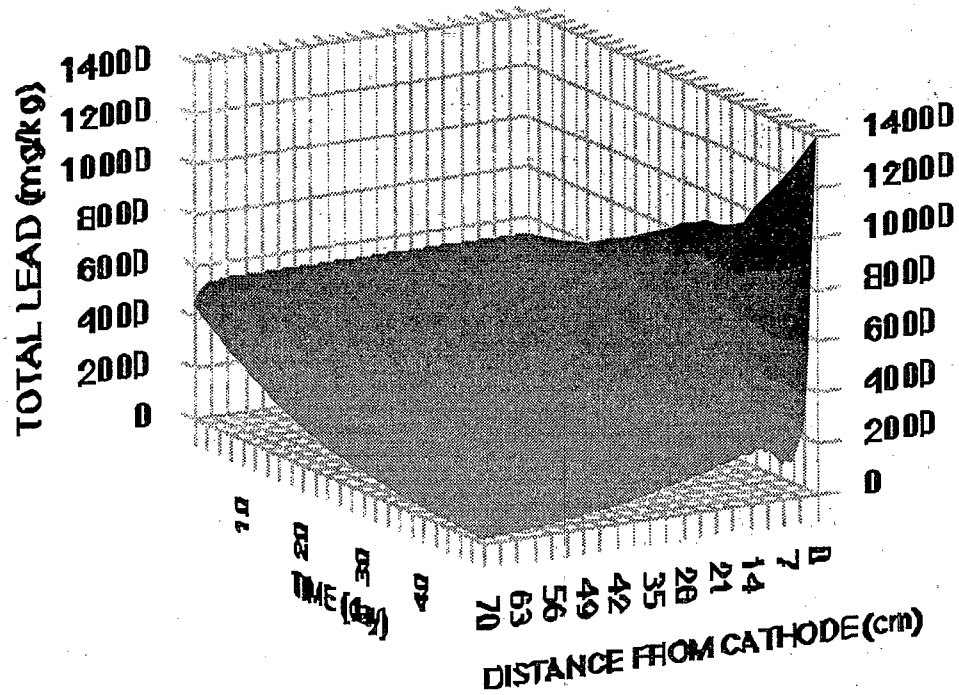


Figure 2. Prediction of total lead concentration across the electrodes using the Finite Element Model for Multi-Species Transport in Soils under Electrical Fields (FEM-MTSE) [Boundary and Initial Conditions pertinent to the Pilot-Scale Study are employed; 100 elements are used] (3,5].

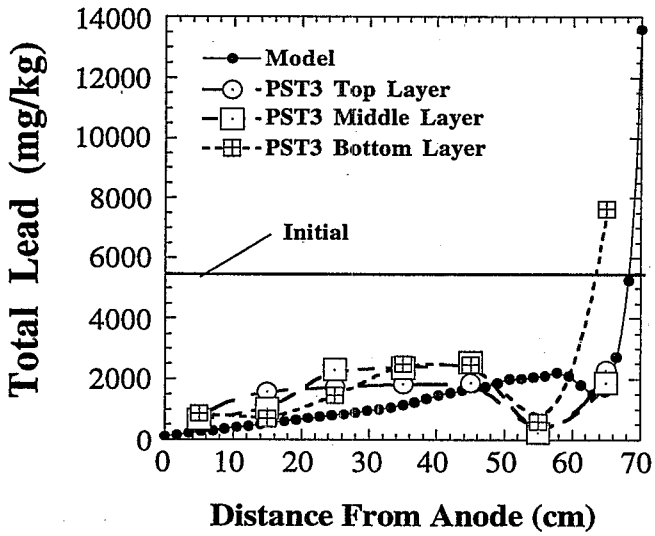


Figure 3. Comparison of lead profile predicted by the FEM-MSTEF with those measured in the pilot-scale study (3,5).

Although acetic acid depolarization technique is successfully used in remediating lead, chromium, zinc and other heavy metals from soils retrieved from sites across the nation and also from Europe, the technique generates significant amounts of liquid that needs to go through a secondary processing. Electrokinetics Inc. has developed an electrode system (CADEX™) that promotes electrodeposition of the species and minimizes the need for secondary processing.

In collaboration with the US Army Waterways Experiment Station, Electrokinetics Inc. is currently conducting a field-scale demonstration study at Fort Polk, Louisiana. The site is located in a creek. The surface deposits within the first two feet are contaminated with lead at concentrations of 3,500 mg/ kg (± 500 mg/kg). The lead in the deposits leached from the bullets left in the firing range over years of exposure to the environment. Preliminary chemical speciation and corrosion studies indicate that minute quantities of lead leach from the individual particulates and the contamination is mainly due to the quantity of the bullets left at the site. An area of about 2,000 ft^2 at this site is being processed. CADEX™ electrode system is used at this site. Onsite remediation is expected to continue for about six months to a year and the goal of the study will be to continue the process until levels of 100 mg/kg or less are reached. USEPA will have an independent evaluation of the demonstration study through the SITE program.

SUMMARY AND CONCLUSIONS

Electrokinetic extraction technique has gone through the phases of bench-scale testing and pilot-scale testing. Precipitation of species close to the cathode compartment has been a bottleneck for the process. Acetic acid depolarization technique and other depolarization schemes have been developed (4). Extraction of heavy metals by bench and pilot-scale tests from 'real world' soils retrieved from sites across the nation and from Europe demonstrate that the technique may be efficiently and cost-effectively used at selected sites. Currently, a field demonstration study is ongoing in the USA.

A theoretical model has been developed and its numerical implementation has been completed. The predictions of this model compared with the results of the pilot-scale studies demonstrate that the

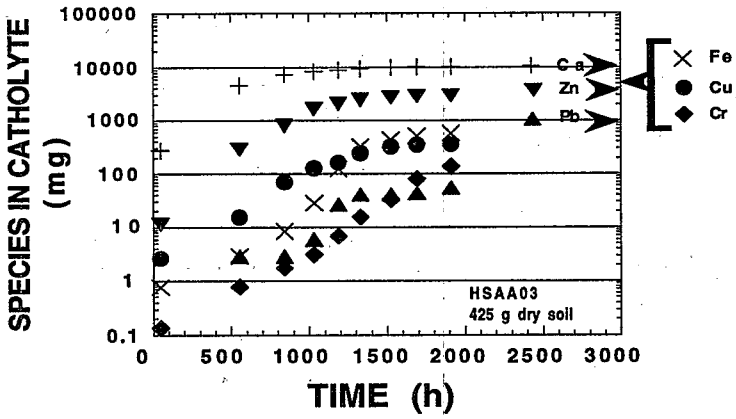


Figure 4. Breakthrough of Different Species in Enhanced Electrokinetic Remediation of a Specimen from a US Army site (EK 1994)

principles of the technique have been well rationalized. Currently, the model is being generalized and conditioning schemes are being incorporated. Design/analysis packages are being developed. Construction guidelines will be written upon completion of the field study. When cost-effectiveness and technical feasibility of other remediation optionsprohibit their use, electrokinetic remediation is expected to offer an alternative at sites contaminated with inorganic species. The technique also is in the process of being scrutinized and developed for injection, specifically to engineer insitu bioremediation of organic species through injection of process additives, nutrients and microorganisms.

REFERENCES

1. Acar, Y.B., Alshawabkeh, A. Principles of Electrokinetic Remediation . Environmental Science and Technology, vol. 27, n. 13, pp. 2638-December 1993.

2. Acar, Y. B., Gale R. J., Alshawabkeh, A., Marks, R. E., Puppala, S., Bricka, M., Parker, R. "Electrokinetic Remediation: Basics and Technology Status," Journal of Hazardous Materials, Elsevier Science B.V., Amsterdam, Netherlands, 40(3), February 1995, pp. 117-137.

3. Alshawabkeh, A., Acar, Y. B., "Electrokinetic Remediation: I. Pilot-Scale Tests; II. Theory" Journal of Geotechnical and Geoenvironmental Engineering, ASCE, (in review)

4. EK(1994). *An Investigation of Selected Enhancement Techniques in Electrokinetic Remediation,* Report submitted to US Army Waterways Experiment Station, Electrokinetics Inc., Baton Rouge, Louisiana, 1993, 160 p.

5. EK(1995). *Theoretical and Experimetal Modeling of Removing Contaminants from Soils by an Electrical Field,* Report submitted to USEPA by Electrokinetics Inc., Baton Rouge, Louisiana, 375 p. (in press).

6. Lageman, R.; Wieberen, P.; Seffinga, G. Electro-Reclamation:Theory and Practice. Chemistry and Industry, Society of Chemical Industry, London, pp. 585-590, 1989.

7. Shapiro, A. P.; Probstein, R.F. (1993) " *Removal of Contaminants from Saturated Clay by Electroosmosis,*" Environmental Science and Technology, 1993, 27 (2), pp. 283-291.

SITE Demonstration of Bioremediation of Cyanide at the Summitville Colorado Site

Leslie C. Thompson
Pintail Systems, Inc.
11801 E. 33rd Ave. Suite C
Aurora, CO 80010
(303) 367-8443

Randy Fischer
Dames & Moore
633 17th Street, Suite 2500
Denver, CO 80202
(303) 294-9100

Scott W. Beckman
Science Applications International Corp
411 Hackensack Ave, 3rd Floor
Hackensack, NJ 07601
(201) 489-5200

Introduction

The Summitville Mine in southern Colorado is located in the San Juan mountains at an average site altitude of 11,500 feet. Summitville was the site of mining operations that began in 1873 with the discovery and development of gold placer and lode deposits. The site was actively mined for gold, silver and copper between 1873 and 1947. From 1947 to 1986 the mine area was inactive until the Summitville Consolidated Mining Corporation, Inc. (SCMCI) a wholly-owned subsidiary of Galactic Resources, Ltd. started an open pit mine and heap leach operation at the site.

SCMCI ran a large tonnage open-pit and cyanide heap leach operation from 1986 to 1992. Gold ore (approximately 10 million tons) was mined, crushed and stacked on a lined, bowl-shaped leach pad. The mine experienced problems with water balance and unplanned solution discharges from the start of the mine life. Solution containment complications and ineffective water treatment contributed to environmental problems. Despite the production of 249,000 troy ounces of gold during the mine operation SCMCI was unable to meet remedial requirements and notified the state of Colorado of its intention to file a Chapter VII bankruptcy in December 1992. The EPA Region VIII Emergency Response Branch took over site operations on December 16, 1992 to prevent a catastrophic release of hazardous substances to the environment. The Summitville Mine site was added to the National Priority List in June 1994.

There are multiple sources of contamination at the site due to historic and SCMCI mining operations. Emergency response operations at the site have prevented releases of severely contaminated solution and studies are underway to define a permanent solution to detoxification or neutralization of the various mine waste units. This report addresses demonstration of an innovative bioremediation technology for treatment of cyanide and soluble leachable metals in the heap and heap solutions.

The heap leach pad consists of approximately 10 million tons of cyanide-leached ore and 90 to 150 million gallons of process solution. EPA Region VIII commissioned a Focused Feasibility Study (FFS) and Report of Investigation (RI) to evaluate remedial options for the Heap Leach Pad (HLP). The RI/FFS was completed by Morrison Knudsen Corporation and submitted to EPA Region VIII on August 19, 1994.

A Request for Proposal (RFP) was issued by Environmental Chemical Corporation (ECC) in October 1993 at the request of USEPA Region VIII, Department of the Interior and Bureau of Reclamation. The RFP requested interested companies to provide information on their ability to

implement innovative treatment technologies to improve treatment efficiency and reduce cost of treatment of the heap leach pad spent ore and leachate solutions. Dames & Moore and Pintail Systems, Inc. (PSI) jointly submitted a proposal suggesting application of biotreatment processes for treatment of the spent ore and process solutions in the HLP. The proposal was accepted for feasibility demonstration under the EPA Superfund Innovative Technology Demonstration Program (SITE) with additional funding from EPA Region VIII.

The primary objectives of the Dames & Moore/Pintail Systems proposal were to:

1. Demonstrate the feasibility of spent ore and process solution cyanide bio-detox.
2. Develop site-specific biotreatment processes for spent ore and process solution cyanide detox.
3. Provide treatment data for use in the RI/FS and Record of Decision (ROD) for the Spent Ore and Entrained Solutions operable units at the Summitville Mine.
4. Immobilize potentially leachable metals including zinc, copper, manganese, iron and arsenic within the heap to improve water quality.

Tests and demonstrations outlined in the proposal were conducted in PSI's Aurora, Colorado lab and pilot plant and at the mine site. Spent ore treatability testing included waste characterization, bacteria isolation and bioaugmentation, parallel column treatment tests, data evaluation and reporting.

Biotreatment processes for heap, tailings and process solution detox have been proven at other mine sites in a variety of environments. Biological processes are both site-specific and waste-specific and must be individually engineered and tested for each mine waste. Successfully adapting treatment bacteria to the spent ore environment is a key to developing successful bioremediation potential. Working with a biotreatment population that has been specifically adapted to the ore and augmented to improve cyanide metabolism insures that biotreatment will be effective.

Cyanide metabolism is known to occur in several species of bacteria. Bacteria that have the capacity for enzymatic hydrolysis of ionic cyanide or metallo-cyanide compounds use the carbon and/or nitrogen of the cyanide to meet their nutritional needs. The end-products of cyanide metabolism are natural and non-toxic.

LABORATORY WORKPLAN

Bacteria Source - Isolation and Development

Cyanide decomposition bacteria were isolated from Summitville spent ore samples and were augmented for remediation testwork with mine ores, tailings and waste rock. Preparation for the column tests included:

1. Isolating native bacteria from the spent ore;
2. Adapting the treatment bacteria to the Summitville Mine spent ore in a series of stress and waste infusion media;
3. Characterizing growth and enhancing the new "cyanooxidans" population.
4. Demonstrating bacteria growth and cyanide decomposition in an ore leach flask test.

Column Test Design

The following workplan was used for the column tests:

1. 75-85 kg of spent ore collected by SAIC and the SITE program was loaded into each of six 6"x10' PVC columns. The columns were fitted with a perforated screen and a tapped end-cap to allow treatment solutions to percolate through the ore and be collected for analysis. The columns were set up as follows:

   Column #1: sulfide zone ore, percolation leach biotreatment;
   Column #2: oxidized ore, 25-90 ft depth, percolation leach biotreatment;
   Column #3: oxidized ore, 90-130 ft depth (saturated zone), saturated with HLP solution, percolation biotreat;
   Column #4: oxidized ore, 0-90 ft depth, rinsed zone (1993 peroxide rinse program), percolation leach biotreatment;
   Column #5: oxidized ore, 0-25 ft depth, percolation leach biotreat;
   Column #6: Control Column, oxidized ore, 90-130 ft depth (saturated zone), saturated with HLP solution, percolation leach with peroxide-treated HLP solution.

2. The Detox population of bacteria was grown to working strength and transferred to a dilute nutrient solution for application in a percolation leach.

3. Thirty gallons of barren solution supplied by SAIC and ECC were used to saturate the ore in Columns 3 and 6 to simulate treatment in a saturated ore zone.

4. The treatment solutions were applied to each column at a nominal rate of 0.004 gpm/ft^2.

5. Bio-leach or detox barren solutions from the columns were collected and analyzed for total cyanide. Total cyanide, weak acid dissociable (WAD) cyanide, gold and select metals were analyzed in column leachate solutions during the course of the test.

6. Data was collected to allow calculation of contaminant reduction related to tons of treatment solution applied per ton of ore.

7. Leachate solutions were analyzed for copper to determine metal mobilization due to bacteria processing. Metal analyses were run on an Inductively Coupled Spectrophotometer and an Atomic Absorption Spectrophotometer.

8. Split samples of spent ore and column leachate solutions were collected by SAIC and were submitted to a contract laboratory for confirmation analysis.

Pilot Test Data

The data collected from the pilot column ore treatment program is presented in Figures 1 and 2. Treatment compliance for successful cyanide detoxification was 0.2 mg/L WAD cyanide measured in column leachate solutions. The control peroxide rinse column of saturated zone ore did not achieve compliance with a WAD cyanide standard. All other column treatments reached compliance levels. Total and WAD cyanide were plotted against the tons of solution applied per ton of ore. The amount of biotreatment solution required for complete cyanide detoxification is projected to be 25-30% of the amount of solution required by conventional chemical rinse detox treatments.

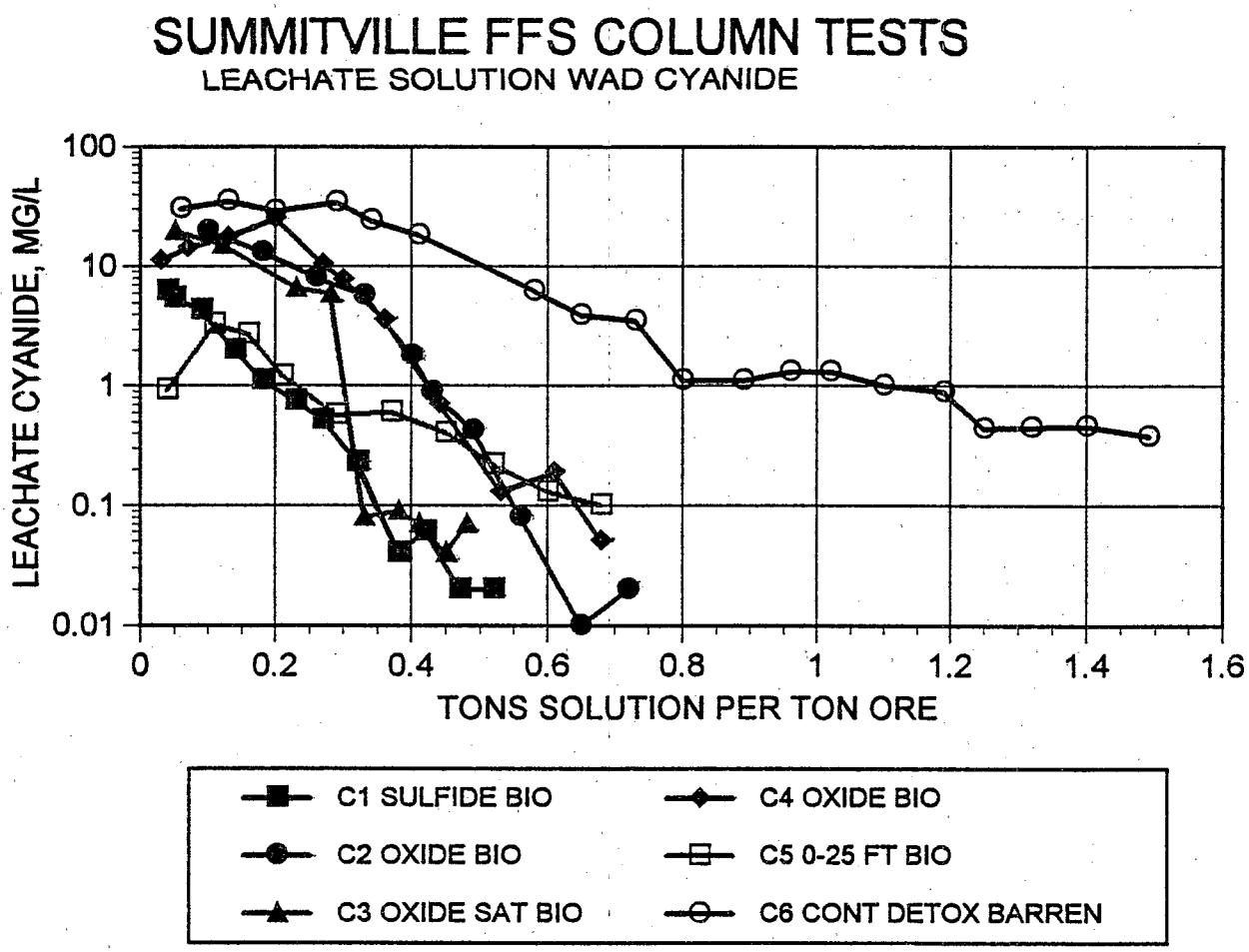


Figure 1. Column Leachate Solution WAD Cyanide

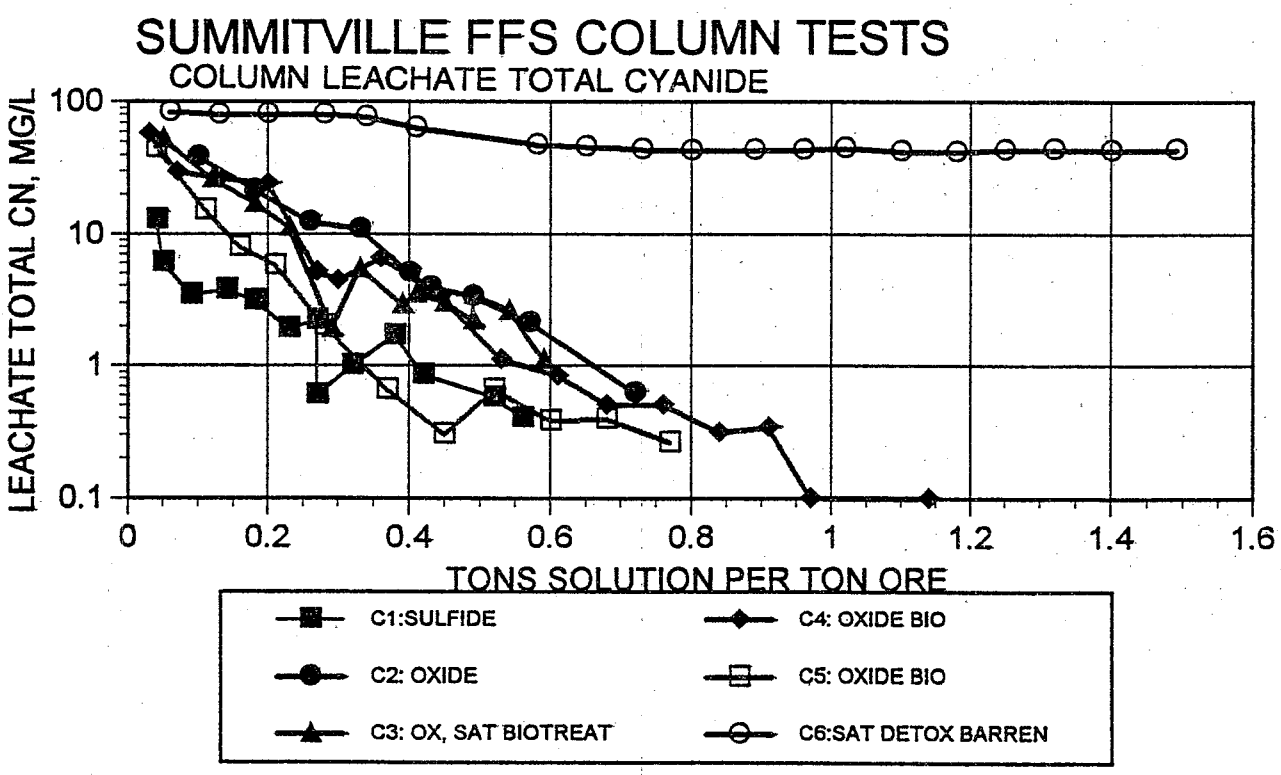


Figure 2. Column Leachate Total Cyanide

A secondary treatment goal in the Focused Feasibility Study was to reduce the amount of leachable or soluble metals in the spent ore and entrained heap leachate solution. Pintail Systems has observed a reduction of soluble metals such as copper in other pilot and field treatment applications. This test was designed to quantify reduction of metals in column leachate solution and to identify any remineralized products in the column tests. Copper in column leachate solutions is shown in Figure 3 for Column 3 and Column 6. Column 3 was the biotreatment test column run as a saturation zone sample. Column 6 was a control rinse using a barren solution detoxified with hydrogen peroxide in a saturation rinse.

Numerous species of bacteria, fungi and yeasts are capable of accumulating many times their weight in soluble metals. Both living and dead biomass are effective in removing soluble metals from waste streams containing gold, silver, chromium, cadmium, copper, lead, zinc, cobalt and others. Bacteria found in natural and extreme environments have developed a wide variety of metabolic functions to adapt to these environments. These natural microbial functions contribute to global mineral cycling that continuously forms, transforms and degrades minerals and metals in the environment. Biomineralization is described as a surface process associated with microorganism cell walls where the remineralization occurs. The biogeochemical activities initiated by microorganisms in ores, soils, surface and groundwater environments can dominate the formation and transformation of those mineral environments.

The metal remineralization process is catalyzed by biological processes alone and by biological processes initiating physical and chemical processes causing an alteration of the micro-environment. During the course of the column tests a series of observations were made on the changing surfaces in the test column. These observations are the basis of the following hypothesis for formation of bio-minerals.

1. Bacteria added to the ore columns attach to the ore surfaces forming a "bio-slime" layer,

2. Soluble metals bind to cell walls and extra-cellular products excreted by the microorganisms (exopolymers, pigments, waste organics, etc.),

3. Metal hydroxides, oxides and carbonates are formed in the primary "bio-slime" layer as amorphous mineral pre-cursors. Curing or maturation of the amorphous slimes suggests that a molecular rearrangement of the hydroxy-metals to more stable forms occurs,

4. Stabilization of the amorphous precipitates forms a remineralization nucleation crystal template for further mineralization to occur. The micro-environment alteration and bacteria metabolism continue to catalyze the remineralization by on-going formation of organometallic compounds, precipitates and transformation of metal oxidation states. The biomineralization appears to follow a sequential and "layered" development on many of the surfaces. Some of the possible minerals formed include calcite, gypsum, bornite, pyrite and covellite.

CONCLUSIONS

Cyanide detox in spent ore is a function of solution application efficiency and bacterial use of cyanide. The ore biotreatment in this test gave similar results and comparable detox time to prior PSI experiences. The treatment bacteria adapted well to the spent ore environment and effected a rapid detoxification of cyanide in spent ore and ore solutions. The Summitville ore is a suitable candidate for a field biotreatment.

The biological treatment column achieved a >99% removal of weak acid dissociable cyanide with

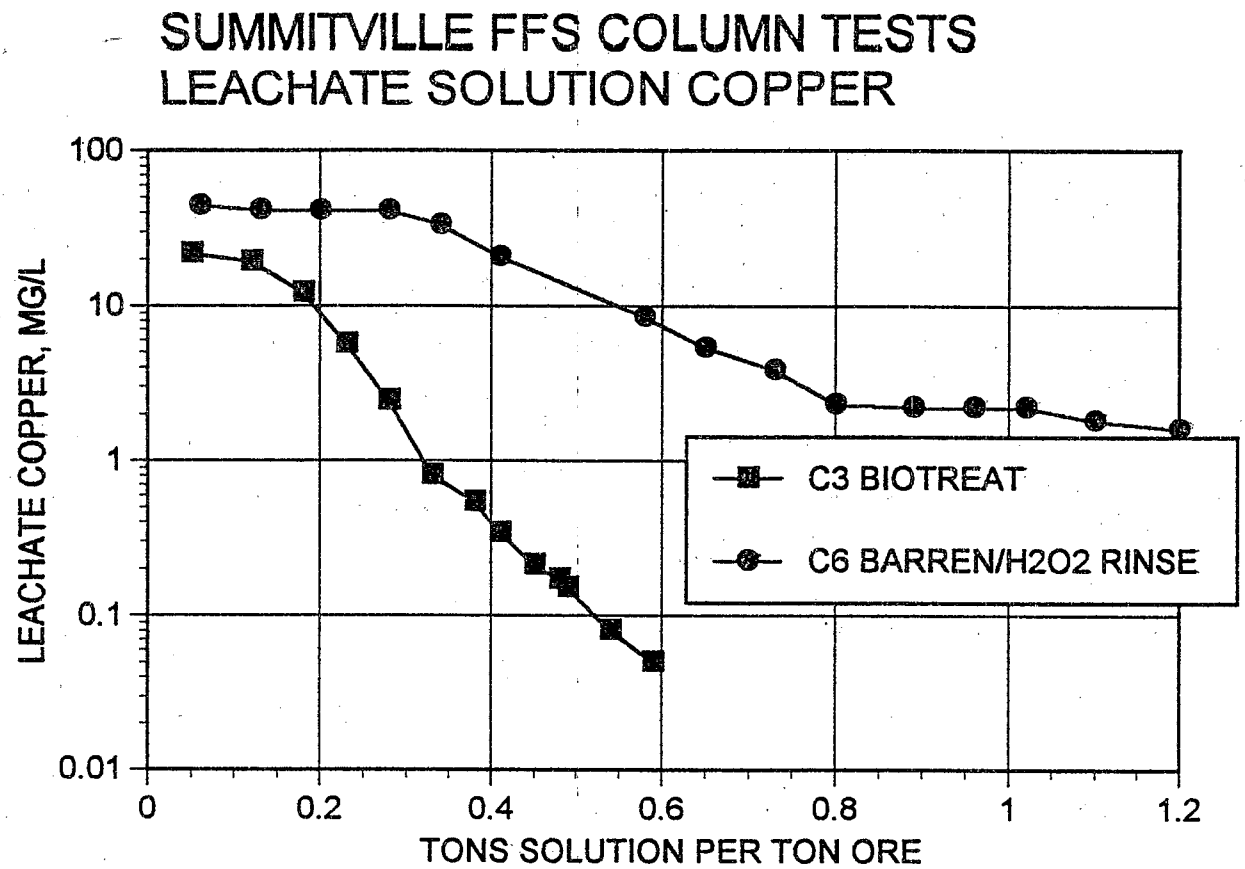


Figure 3. Column Leachate Solution Copper

application less than an average of 0.5 tons of solution per ton of ore. Total cyanide in column leachate solutions at the end of the test was <0.5 mg/L indicating that bacterial action in the treatment solution will metabolize strong metal-cyanide compounds. A field treatment of a leach pad cell or other division of spent ore could be planned for a treatment program using less than 0.5 tons of solution per ton of ore.

Biotreatment in this study achieved a greater reduction in total cyanide in a shorter application than chemical treatments can achieve. In Situ biotreatment is the most efficient heap cyanide detox as compared to peroxide rinse treatments. The data generated in this study indicate that the biotreatment processes have the potential to operate as an effective field treatment. Biological treatments are projected to be cost and time competitive with chemical rinse treatments.

The objectives of the pilot column tests were met in this biotreatment demonstration.

1. Existing strains of cyanide-oxidizing bacteria were adapted to grow in the ore environment and to use cyanide as a carbon and/or nitrogen source.

2. Flask and column tests of the adapted, augmented treatment population verified that bacteria would grow and metabolize soluble cyanide in the Summitville spent ore.

3. Cyanide was detoxified in biotreatment tests in spent ore and column leachate solutions with application of less than an average of 0.5 tons of solutions per ton of ore. Cyanide levels did not reach a 0.2 mg/L discharge criteria with the peroxide kill, saturated, barren rinse test column with application of more than 1.5 tons of treatment solution per ton of ore.

REDUCTIVE PHOTO-DECHLORINATION (RPD) PROCESS FOR SAFE CONVERSION OF HAZARDOUS CHLOROCARBON WASTE STREAMS

Moshe Lavid, Suresh K. Gulati, Moisey Teytelboym

ENERGIA, Inc.
Research and Consulting
P.O. Box 470, Princeton, NJ 08542
609-799-7970

INTRODUCTION

A novel technology designated "Reductive Photo-Dechlorination" (RPD) has been developed and successfully tested for environmentally safe treatment of waste streams containing hazardous chlorinated hydrocarbons. This RPD process employs ultraviolet (UV) light in a reducing atmosphere and at moderate temperatures to efficiently convert chlorocarbon contaminants into valuable hydrocarbons such as methane, ethane, ethylene, acetylene and hydrogen chloride. The UV light promotes carbon-chlorine bond cleavage and long-chain radical reactions with the hydrogenous bath gas leading to the thermodynamically and kinetically favored hydrocarbon products at a conversion of +99%.

The RPD process is schematically shown in Figure 1. The pilot-scale prototype consists of five main units: (1) Input/Mixer; (2) Photo-thermal Reactor; (3) Scrubber; (4) Separator/Storage; and (5) Recycling. Chlorinated waste streams can be introduced in one of three ways: liquid, vapor or adsorbates (to activated carbon). Chlorocarbon solvents are fed into a vaporizer, mixed with a reducing gas and passed into the Photo-thermal Reactor. Air laden with chlorocarbon vapors is first passed through a separator (condenser) which removes chlorinated materials as liquid. Chlorinated contaminants adsorbed onto activated carbon are removed as vapors by purging with a mildly heated reducing gas. Then, the vapors are passed into the Photo-thermal Reactor.

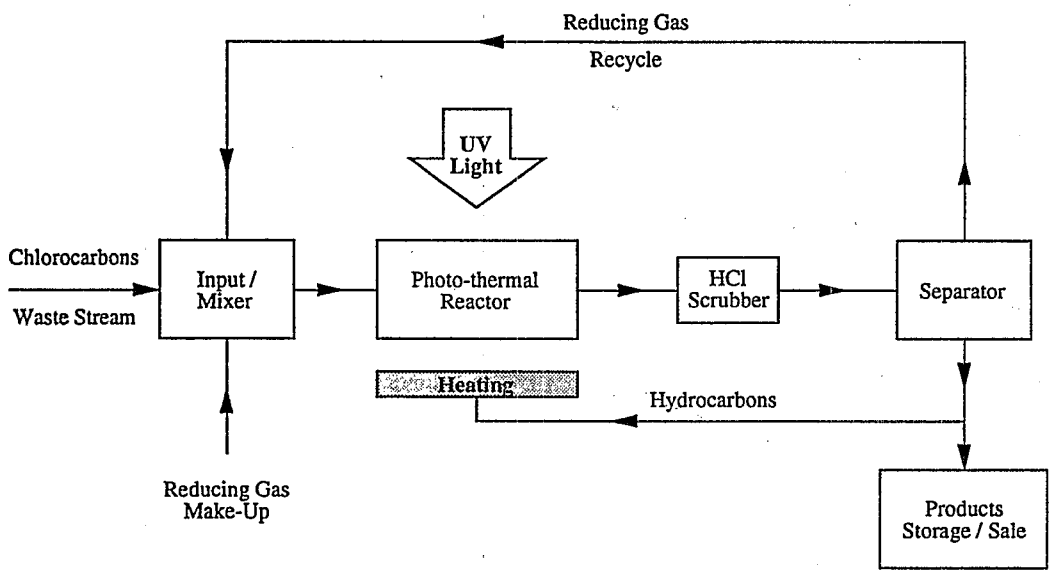


Figure 1. ENERGIA's Reductive Photo-Dechlorination (RPD) Process.

The Photo-thermal Reactor is the heart of the RPD technology. Here the mixture is irradiated and heated. The UV light breaks the C-Cl bond and the temperature sustains long-chain radical reactions. After a suitable residence time, conversion and dechlorination are fully completed. Hydrogen chloride is scrubbed from the mixture which proceeds to the separator. After separation, excess reducing gas is recycled back to the Input/Mixer. Valuable hydrocarbon products are collected and sold. There is also an option for recycling a portion of the hydrocarbon products as an auxiliary fuel to heat up the Photo-thermal Reactor.

METHODOLOGY

The RPD treatment was successfully tested with a representative chlorocarbon 1,1,1-trichloroethane (TCA). The tests were conducted in a Photothermal Annular Flow Reactor, schematically illustrated in Figure 2. The photothermal Annular Flow chamber is the volume bounded by two concentric tubes: an outer pyrex tube (l = 51 cm, ϕ = 4.5 cm) wrapped with a heating tape, and an inner suprasil quartz tube (l = 71 cm, ϕ = 2.5 cm) containing a low-pressure Hg lamp. The heated section of the reactor is insulated with a ceramic blanket. The reactor can be heated up to 750 °C.

The low-pressure Hg lamp is specially designed to ENERGIA's specifications. Inert gas (N_2 or Ar), transparent to UV irradiation, is continuously flown over the lamp, to displace air surrounding the lamp so that UV light is not attenuated by oxygen (present in air). This also reduces the thermal load due to external heating. To avoid lamp damage, the lamp electrodes are located in the cool end-zones of the reactor. And, if necessary, they can be cooled by auxiliary fans.

Mixtures of Chlorocarbon/H_2/Ar flow through the electrically heated reactor and are exposed to UV irradiation along the constant temperature thermal zone. Samples for GC and GC/MS analyses are drawn at the entrance and exit of the photothermal chamber.

Key Features of the annular flow reactor are: i. Operating Conditions: T = ambient - 650 °C, P = 1 atmosphere, ii. Long residence time, τ = 10 - 260 sec, iii. Large reactor volume = 451 cc, iv. Uniform exposure to UV irradiation, v. Optical path length = 1 cm, vi. Accessible wavelengths: 185, 254, 313 nm (Hg), 222 nm (Cd), 215 nm (Zn).

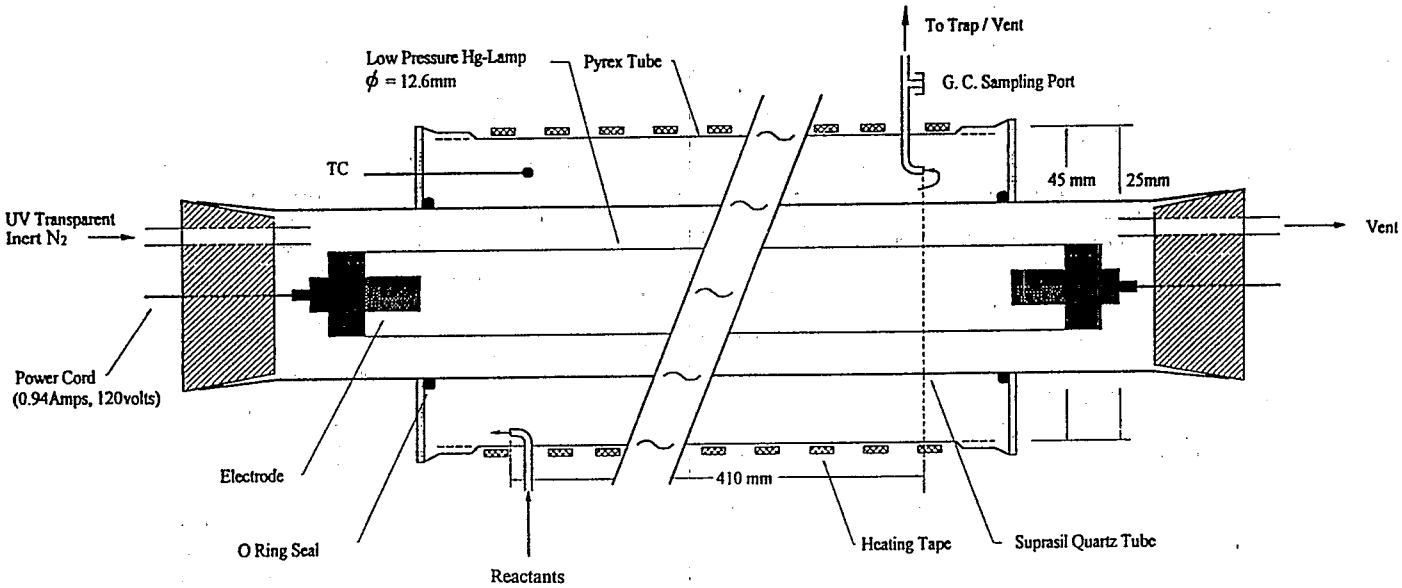


Figure 2. Schematic of the Annular Flow Reactor.

Experiments were performed without and with UV light, under otherwise identical conditions. Experiments with the UV light off are designated Reductive Thermal-only (RT), and experiments with the light on are designated Reductive Photo-Dechlorination (RPD).

The conditions selected for both sets of experiments (RT and RPD) are:

Flow Mixtures:	1.0% TCA/45.0% H_2/Balance Ar
Pressure:	1 atmosphere
Temperature:	430 °C, 520 °C, 590 °C
τ Range:	15 - 260 sec
Light Source:	Low-Pressure Hg Lamp

These conditions were chosen to optimize the process for achieving +99% (conversion and dechlorination).

RESULTS

Experimental results are presented in terms of Percent Conversion, Percent Dechlorination and Selectivity. Percent Conversion is the percent consumption (disappearance) of the parent molecule (i.e. TCA), without regard to the identification of the products. Percent Dechlorination is the percent conversion of TCA to chlorine free products. Selectivity is the normalized molar fraction of each product relative to <u>all</u> products.

Percent Conversion and Percent Dechlorination were measured as a function of residence time (τ) at three temperatures, 430, 520 and 590 °C.

At the lower temperature (430 °C), percent conversion was very low for RT (less than 30%) and significantly higher (80%) for RPD. At higher temperatures (520 °C and 590 °C), complete conversion (100%) was obtained for both RT and RPD processes. Consequently, the difference between the two processes was only in their respective selectivities. As will be pointed out below, RPD demonstrated almost complete dechlorination, whereas RT did not.

Percent dechlorination obtained during RT treatment at 430 °C and at 15 - 60 sec was quite low ~5% and at 260 sec it was still low, about 9.0%. However, during RPD treatment, it increased from 9 to 47% with the same increase in τ. At slightly higher temperature, i.e., at 520 °C, during RT treatment, it increased very slowly from 30 to 40%, with the increase in residence time from 15 to 260 sec. In contrast, during RPD treatment, it increased rapidly from 41 to 92% with modest increase in residence time (to 130 sec). At 590 °C (see Figure 3), percent dechlorination obtained during RPD treatment was remarkable. Even at the shortest studied τ (15 sec), reasonable amount of dechlorination (~65%) was obtained. It increased dramatically to +98% (at τ = 100 sec) and at τ > 100 sec, +99% dechlorination was obtained. There was also improvement during RT treatment. Percent dechlorination increased monotonically from 37 to 77%, with increasing in residence time up to 260 sec. But it fell short of complete dechlorination obtained by RPD.

These experimental results have demonstrated greater than 99% conversion and complete dechlorination at 590 °C and $\tau \geq 60$ sec. Figure 4 depicts products selectivity. It clearly shows the advantage of RPD (black bars) over Reductive Thermal-only (RT) (open bars) treatment under otherwise identical conditions. In both cases conversion is +99%. However, while the RT is limited to 51% dechlorination, the RPD exhibits +99%. It is apparent that the RPD process is capable of safe and efficient conversion of all chlorinated hydrocarbon contaminants to valuable hydrocarbon products (mainly ethane and methane).

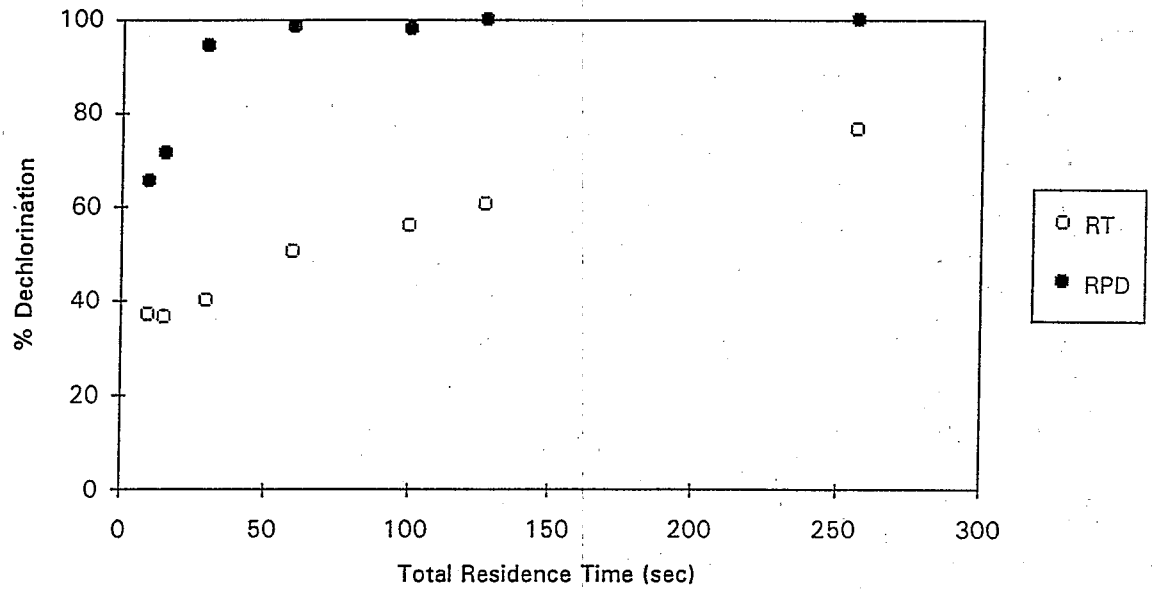


Figure 3. Percent Dechlorination as a Function of Residence Time (τ) during RT/RPD Treatment at 590 °C.

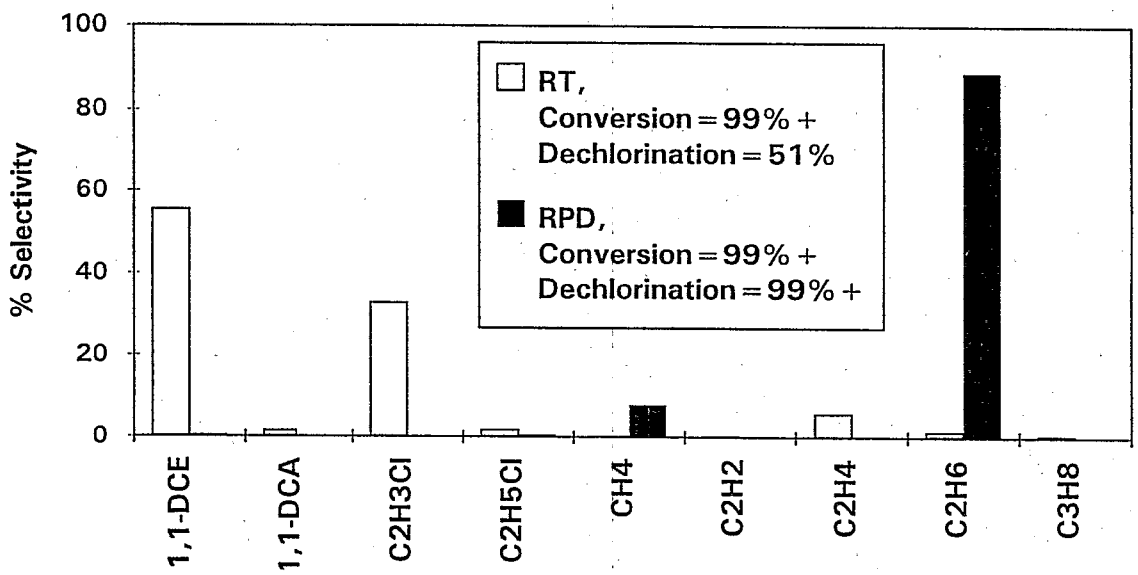


Figure 4. Product Selectivity during RT/RPD Treatment of TCA at 590 °C and 60 sec.

In order to compliment the experimental effort, a detailed kinetic modeling study was also performed. It provided insight into the reaction mechanism and identified the key elementary steps determining the reaction pathways for rapid conversion of chlorocarbons to environmentally acceptable products. Using this kinetic model, a comparison was made between experimental data and computer modeling results for RT and RPD treatments of TCA. A good agreement was evident.

WASTE APPLICABILITY

The RPD process can be effectively applied to liquid or gaseous waste streams containing saturated and unsaturated chlorocarbons. It was tested for TCA, TCE, DCE, DCA, vinyl chloride, ethyl chloride, DCM, and chloroform. It may also be applicable to PCE, carbon tetrachloride, and chlorinated aromatics to be tested.

The RPD process is specifically cost-effective for the following on-site remedial operations:

(1) In-situ treatment of chlorinated wastes discharged from Soil Vapor Extraction (SVE).

(2) Direct treatment of Off-Gas streams containing chlorocarbons.

(3) On-site regeneration of Activated Carbon saturated with chlorocarbons removed by adsorption from waste streams.

(4) Pretreatment of waste streams entering Catalytic Oxidation systems, reducing the chlorine content and thereby promoting oxidation and longevity.

(5) Small-scale, on-site remediations in R&D and testing laboratories, chemical hoods, clean rooms, etc.

CONCLUSIONS

Bench-top experimental results have successfully demonstrated the feasibility of the RPD process. They have established that the optimal operating conditions for achieving +99% dechlorination of TCA are ~ 590 °C and $\tau \geq 60$ sec. Preliminary cost analysis showed that the RPD is extremely competitive with other remedial processes. Its estimated cost is less than $1/lb. of treated chlorocarbons. The RPD process has successfully completed the bench-top developmental stage and is the basis on which a pilot-scale prototype unit is being constructed. A demonstration SITE program will follow after which the RPD technology will be available for commercialization.

For more information:

EPA Project Manager: Michelle Simon
U.S. EPA Risk Reduction Engineering Laboratory
26 West Martin Luther King Drive
Cincinnati, OH 45268
Tel: 513-569-7469
Fax: 513-569-7676

TREATMENT OF HAZARDOUS LANDFILL LEACHATE BY THE ROCHEM DTM MEMBRANE SEPARATION TECHNOLOGY

Douglas W. Grosse
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 West Martin Luther King Drive
Cincinnati, Ohio 45268
(513) 569-7844

Kyle Cook
Science Applications International Corporation
10260 Campus Point Drive
San Diego, CA 92126
(619) 546-6117

Introduction

The Disc Tube™ Module (DTM) technology was developed by Rochem Separations Systems, Inc. and designed to remove a variety of organic and inorganic contaminants from liquid hazardous waste streams. The DTM technology is a membrane based technology utilizing an innovative process configuration which allows for treatment of aqueous waste streams such as landfill leachate. Historically, membrane based technologies have been used as a secondary polishing step in treating effluents to meet pretreatment discharge standards. The DTM technology was designed to treat liquids containing higher dissolved solids, turbidity and contaminant levels than previously possible with conventional membrane processes.

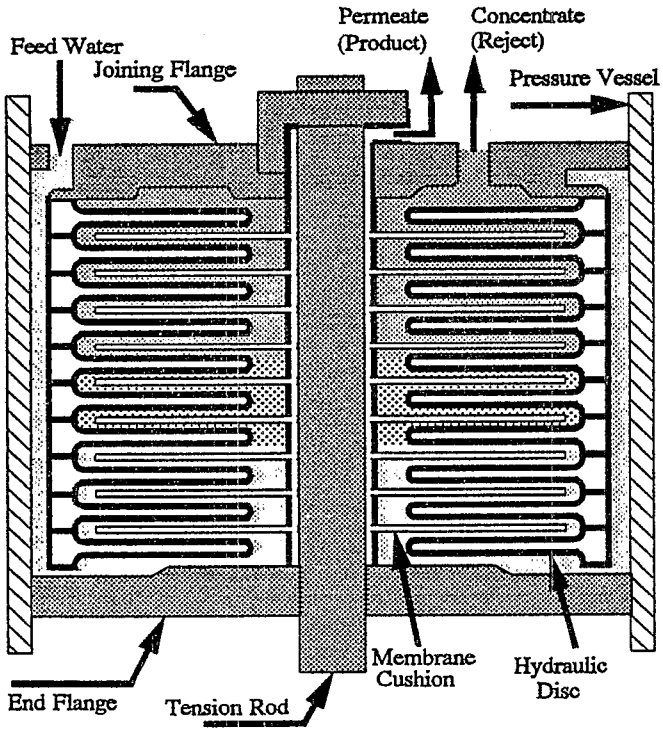
The DTM process was evaluated under the Superfund Innovative Technology Evaluation (SITE) program at the Central Landfill in Johnston, Rhode Island during the months of August and September 1994. Approximately 33,000 gallons of hazardous landfill leachate were treated by the DTM technology using reverse osmosis membranes. The leachate contained moderate to high levels of volatile organic contaminants, low levels of heavy metals, and high total dissolved solids. The Developer (Rochem) claimed that the technology was capable of (1) achieving a high percent rejection of the contaminants of concern; (2) recovering ≥75% permeate (treated water); and (3) allowing for a greater resistance to scaling and fouling of membranes than conventional membrane processes.

Technology

The DTM technology is a modular system which utilizes reverse osmosis (RO), ultrafiltration, or microfiltration membrane materials in a modular configuration which offers large feed flow channels for high feed flow velocity, generating a crossflow of feed water over stacked membranes. Purportedly, these system design features allow the DTM greater tolerance for dissolved solids and turbidity; hence, a greater resistance to scaling and fouling of the membranes. Suspended particulates are easily flushed away from the membranes and out of the module during operation.

Figure 1 shows a cutaway of a disc tube module. The modular disc tube is comprised of conventional RO membranes which are formed into octagonal cushions by ultrasonically welding two membranes together at the edges and separated by a layer of porous spacer material on the inside. These cushions are supported by a plastic disc which holds the membrane cushion in place and forms the flow channels for the feed. These membrane cushions are alternately stacked with hydraulic discs on a tension rod. The tension rod houses a conduit for permeate collection from each membrane cushion to facilitate discharge from the module into a product recovery tank. O-rings seal the permeate

water channels from the feed water channels. A stack of cushions and discs is housed in a pressure vessel; whereby, flanges seal the ends of the module and provide the feed water input, permeate and reject outlet connections. The number of discs per module, number of modules and the membrane materials can be custom designed to suit the application.



The RO membranes used for this demonstration test are more permeable to water than to organic and/or inorganic impurities. When pressure is applied to a solution (leachate), the aqueous phase (permeate) passes through a semipermeable membrane which, in turn, rejects the contaminants carried by the solution, causing them to be retained in a brine solution (concentrate). These impurities are selectively rejected by the RO membranes. The percentage of water that passes through the membrane is a function of operating pressure, membrane type and concentration of the contaminants.

Methodology

The DTM technology was evaluated for its ability to meet percent rejections established for the target contaminants (VOCs >90%, TOC >92%, TDS >99% and metals 99%) while operating at a treated water recovery rate of 75 percent or greater. In addition, the DTM system was evaluated for treating a hazardous leachate without experiencing an unacceptable level of membrane fouling or scaling, resulting in a loss of membrane flux (flow rate/membrane area).

The Central Landfill site comprises two areas: a 121 acre area and a 33 acre expansion area. The 121 acre area of the site is where disposal of hazardous and non-hazardous wastes took place in the past. Several wells on the site were being used to intercept leachate from a "hot spot" area (0.5 acre) of the site to prevent off-site migration of contaminated liquids. Leachate from one of these wells (MW91ML7) was characterized during a pump test previously conducted. This well was located downgradient from the hot spot area of the landfill; thereby, containing higher concentrations of contaminants than other wells on the site. Leachate produced from this well was deemed to be the

most suitable for the DTM field demonstration. Table 1 gives the target constituent profile of the leachate generated from well MW91ML7.

A three-stage DTM system was used for the field demonstration. Two stages were used in series to treat the landfill leachate to produce a final permeate. Both stages utilized standard thin film composite (TFC) RO membranes. The permeate from the first-stage DTM was used as a feed for the second-stage DTM for further removal of contaminants. A third-stage high pressure unit (HPU) was used to further squeeze the concentrate rejected by the first-stage to increase permeate recovery. The permeate from the HPU was directed to the second-stage DTM unit. Each unit was protected by media (sand) and cartridge (10 micron) filters to remove suspended particulates. Acid was also added at the first-stage and HPU for pH control. The system processed approximately 33,000 gallons of hazardous leachate at an average feed rate of 5 gpm. The system operated long enough to allow for several cycles of membrane cleaning (up to 8 hours a day, for 19 days).

Baseline testing was performed prior to and immediately following the Rochem Demonstration test to determine if there had been a loss of membrane flux due to fouling and scaling. Baseline testing procedures, as specified in the QAPP, were modified to account for varying conditions (pressure, flow rates, temperatures and brine concentrations) during the field test in accordance with the Standard Practice for Standardizing Reverse Osmosis Performance Data ASTM D 4516-85. This method allows for collected field data to be normalized against a chosen set of standard operating conditions (average). Using this method, the change in membrane flux was determined after the demonstration test was completed. A saline solution of known conductivity was used for baseline testing.

Table 1 - Target Contaminant Profile (MW91ML7)

Constituent	Average Concentration
VOC	(ug/1)
Chlorobenzene	35,000
Ethylbenzene	1,600
Toluene	2,800
Xylenes	2,300
1,2 - Dichlorobenzene	29,000
1,4 - Dichlorobenzene	1,600
Metals	**(mg/l)**
Calcium	140
Magnesium	200
Sodium	560
Barium	1.4
Iron	49
Manganese	22
Potassium	110
Strontium	0.82
Other Analytes	**(mg/l)**
Total Dissolved Solids	4,100
TOC	360
pH	6.8 Units

Results

During the field demonstration, both laboratory and field samples were collected for analyses. Field measurements included: pressure, temperature, flow, pH, turbidity, and conductivity of the process liquids. A portable organic vapor detector monitored for fugitive emissions during field operation. Laboratory samples were collected from: (1) the raw feed; (2) first-stage feed, reject and permeate; (3) second-stage reject and final permeate; and HPU feed, reject, and permeate. The target contaminants were analyzed along with TOC, TDS, total solids, MBAs and ammonia (see Table 1).

Based upon results obtained from preliminary data reduction, the Developers claim for percent rejection of the target contaminants appears to be met; especially, when considering established standard deviations (SD). Rejection of heavy metals and total dissolved solids was excellent by significantly surpassing the claim for >99% rejection. Similarly, percent rejection of TOC (>96.3) far exceeded the claim of >92%. For target VOCs the Developer's claim of >90% rejection was overall exceeded with 95% rejection of 1, 2-Dichlorobenzene (one of the primary contaminants of concern), and >95% for toluene, xylenes and ethylbenzene. Although, chlorobenzene only achieved 87% and 1, 4-Dichlorobenzene >87.6% rejection, 95% confidence intervals were calculated to be ±3.7% and ±4.1%, respectively.

The second of the three critical claims established for this demonstration pertained to the achievement and maintenance of a treated water recovery rate of 75% or greater. Recovery rates were calculated for each day of operation. There were a total of three (3) days of downtime attributed to system maintenance, resulting in 18 days of actual field data collection. The system water recovery rates ranged from, approximately, 65% to as high as 86%. Overall, the average recovery rate of 73.3% was achieved for the demonstration with a 95% confidence interval of ±2.6%.

The third critical objective of the demonstration test was to determine the extent, if any, of membrane scaling and fouling as measured by the difference in membrane flux before and after system field operation. It was considered an indication of membrane scaling and fouling if a loss of greater than 10% flux was obtained. Baseline procedures were employed for both the first-stage unit and the HPU, separately. One set of actual operating data (average operating conditions) was selected as the standard for each unit. At this time, not all of the data have been completely reviewed. In discussions with the Developer, preliminary results are in question (>10%$_\Delta$) due to the premise that the membranes were not adequately broken in. Manufacturers typically recommended 50-100 hours of continual running before the baseline can be determined for a given membrane on sea water systems. For leachate, Rochem has recently discovered that the same "break-in" period can be 200 hours and more before a baseline determination can be adequately made.

Conclusions

Preliminary results of the SITE demonstration of the DTM system shows that significant percent removal of target contaminants was achieved, exceeding the Developer's claim in most cases. The DTM technology can effectively treat hazardous landfill leachate to the extent that the treated water (permeate) can meet effluent discharge standards (the Rhode Island DEM discharge limits).

The DTM process was also capable of approximating (on the average) the claim of 75% or greater for water recovery efficiency. During peak days of operation as high as 86% was achieved.

Key findings of this SITE demonstration including analytical results will be discussed in detail with the submittal of the Technology Capsule, Innovative Technology Evaluation Report and a videotape.

SITE Demonstration of the SVVS Technology

Paul R. de Percin
Risk Reduction Engineering Laboratory
US Environmental Protection Agency
16 West Martin Luther King Dr.
Cincinnati, Ohio 45268

INTRODUCTION

The Subsurface Volatilization and Ventilation System is an integrated technology used for attacking all phases of volatile organic compound (VOC) contamination in soil and groundwater. The SVVS technology promotes in-situ remediation of soil and groundwater contaminated with organic compounds through the injection of air into the saturated and unsaturated zones, and extraction of vapors from the vadose zone. Through this process, volatile and semivolatile organic compounds are stripped from the soil and groundwater. The subsurface circulation of air also increases dissolved oxygen concentrations in the saturated zone, capillary fringe, and vadose zone, thereby promoting aerobic microbiological processes. The contaminated air extracted from the wells can be treated at the surface before being discharged to the environment.

The SVVS process was evaluated under the SITE program at the Electro-Voice, Inc. (EV) facility in Buchanan, Michigan. The soils were contaminated with aromatic hydrocarbons, and halogenated and non-halogenated volatile and semivolatile organic compounds (SVOCs) through discharge into a dry well. Baseline data indicated that approximately 1,000 kg of VOC and SVOC contamination was present in the dry well area soils, principally in a subsurface sludge layer. The developer claimed that their technology would reduce the sum of seven target VOCs by 30% over a one year period.

TECHNOLOGY

The SVVS process utilizes soil vapor extraction in conjunction with in-situ bioremediation to clean soil, sludge, and groundwater. A typical SVVS installation is comprised of a series of air injection and vacuum/extraction wells designed to circulate air below ground to 1) increase the flow of oxygen in the soil to enhance the rate of organics destruction by indigenous soil microbes and 2) volatilize and remove volatile organic contaminants from the soil. This system consisted of three individually plumbed rows of alternating vacuum extraction and air injection wells referred to as reactor lines. Each reactor line is plumbed to a single central vapor control unit (VCU) used to house air injection and vacuum pumps and gauging, as well as emissions control equipment.

The injection wells are installed below the groundwater table and are used to inject air into the groundwater. The Developer claims that the air strips volatile contaminants from the soil and water as it percolates through this saturated zone. Extraction wells installed in the vadose zone pull the percolated air through the soil under vacuum, further stripping contaminants. In addition, the increase in air circulation in the soil, specifically oxygen, increases the rate of biodegradation by soil microbes, according to the developer, and transforms contaminants into harmless end products such as carbon dioxide and water. To aid in the circulation process, sand chimneys can be installed. These are sand-packed borings which provide passive airflow between the subsurface layers, increasing both the soil vapor extraction and the biodegradation rates.

The SVVS process generates one major wastestream - vapors from the vacuum extraction wells. Depending upon regulatory requirements, the extracted air may be treated above ground or released directly to the atmosphere. In the early stages of SVVS implementation, the overall rate of mass transfer of contamination to the vapor phase may exceed biodegradation rates. It is during this period, which lasts anywhere from two weeks to a few months, that extracted vapors may need to be treated above ground before release to the atmosphere. However, the magnitude of treatment will decrease steadily over this

period until biodegradation rates surpass the net rate of transfer of contaminant mass into the circulating air. When this point is reached, the vapor extraction off-gas will consist predominantly of carbon dioxide, which is the major gaseous by-product resulting from the biodegradation process. To reduce these costs further and promote additional VOC destruction, the SVVS design employs the use of proprietary biofilters for treatment of the extracted vapors.

If required by permits, off-gas extracted from the vacuum extraction wells can be routed through a configuration of Biological Emissions Control™ (BEC™) units (a patent pending system which, according to the developer, through biodegradation, achieves up to 80% reductions in concentrations of VOCs in stack emissions at approximately 20% of traditional emission control costs). The off-gas is then expelled to the atmosphere through a vent pipe affixed to the extraction pump. Vacuum extraction emissions may also be favorably controlled within regulatory limits by adjusting the air injection and vacuum extraction rates. However, if the levels of VOCs in the off-gas are in excess of acceptable levels, the off-gas exiting the BEC™ units can then be routed through an activated carbon adsorption unit as a final polishing step prior to discharge.

METHODOLOGY

The SVVS process was evaluated for its ability to reduce volatile organic contaminants in the vadose zone soil of the "dry well" area at the Electro-Voice, Inc. site in Buchanan, Michigan. The primary objective of the demonstration was to evaluate the developer's claim of a 30% reduction in the sum of seven specific volatile organic compounds (i.e., benzene, toluene, ethylbenzene, xylene, tetrachloroethene, trichloroethene, and 1,1-dichloroethene) in vadose zone soils of the treatment plot over a 12 month period of operation. A one year time frame was chosen for testing purposes only, and the reduction claim does not reflect the limits of the technology. Under an actual remedial clean-up, the system may require a longer time than was possible during the present study.

Reductions in the volatile organics were proposed to occur through the combined effects of in-situ biodegradation and soil vapor extraction. These reductions were evaluated by comparing the sum of the concentrations of the select volatile organic contaminants in the matrix prior to system startup and after 12 months of system operation. Secondary objectives were established to determine the relative contributions of in-situ biodegradation and vapor extraction to the removal and degradation of volatile organics from the subsurface.

Soil samples were collected from borings within the physical boundaries of the SVVS system and sampled in a manner such that the entire vertical section of the vadose zone was represented. Five distinct subsurface zones were identified based on lithology and contaminant occurrence. These included the upper horizon (above the contaminant source), sludge layer (predominant source of contamination), and lower horizons A1, A2, and B (below the contaminant source).

Since the developer's claims were to reduce seven volatile organic contaminants by 30%, benzene, toluene, ethylbenzene, and xylenes (BTEX), tetrachloroethene (PCE), trichloroethene (TCE), and 1,1-dichloroethene (1,1-DCE) were considered the critical analytes for this demonstration. Analyses were also performed on select samples for the following non-critical parameters: total carbon (TC), total inorganic carbon (TIC), nutrients (nitrate, phosphate), total metals plus mercury, cyanide, pH, and particle size distribution (PSD). An additional objective of this demonstration was to develop data on operating costs for the SVVS technology.

The extracted vapor streams were analyzed by continuous emission monitoring (CEM) for O_2, CO_2, and total hydrocarbons (THC). Grab samples of the extracted vapor stream were collected for determining the concentration and distribution of individual volatile organic compounds.

Shut-down tests were periodically performed to assess the presence and magnitude of biological processes in the destruction of organic constituents in the subsurface. During a shut-down test, the

injected air stream is temporarily turned off resulting in the cessation of oxygen delivery to the subsurface. If there is a robust aerobic microbial population in the subsurface, the available oxygen will be quickly depleted. The shut-down test tracks the magnitude and rate of oxygen drop-off over a twenty-four hour period.

RESULTS

At the Electro-Voice site, the SVVS process achieved an overall 80.6% reduction of the sum of the seven critical VOCs over a one year period from vadose zone soils. This level of reduction greatly exceeded the developer's claim of a 30% reduction over a one year time frame. The average concentration of the sum of the seven analytes from the hot zone in the study area, prior to installation of the SVVS, was 341.5 mg/kg. The average concentration of the sum of the seven analytes after one year of operation was 66.20 mg/kg.

The data reveals that the most contaminated zone, the sludge layer, had an average reduction of 81.5%. The other less contaminated horizons exhibited reductions ranging from 97.8% to 99.8%. The reductions over the areal extent of the site, as determined from the individual boreholes, ranged from 71% to over 99%. This indicates the system operated relatively uniformly over the entire vadose zone of the treatment plot, and no significant untreated areas were encountered, regardless of VOC concentration or lithology.

The shut-down testing indicates that microbiological activity was stimulated at the site. Due to the inherently high organic content of the soil, it was not clear how much of this stimulation was due to contamination. The microbiological activity, as determined from the first shut-down test, was greatest in portions of the site where the VOCs were greatest, and least active in areas of the site where the contamination was small or absent. Seasonal variations as evidenced in the background wells, where presumably no contamination existed, introduced uncertainty in data interpretation. A comparison of three shut-down tests indicates that biological activity was greatest during the beginning of remediation and progressively decreased throughout the remainder of the demonstration, but at a rate that was less than the VOC mass removal rates attributed to vapor extraction alone. This would indicate that biological processes play an increasingly important but not a dominant role, relative to vapor extraction, as the remediation proceeds.

An analysis of the volatiles from the vapor extraction outlet reveals that the highest mass of volatiles was removed during the early phase of the project. Furthermore, the mass of volatiles in the off-gas stream gradually decreases to a low and constant level after approximately 230 days of operation.

The SVVS experienced no major operational problems over the twelve month study period. Once implemented, the system was easy to monitor and required minimal maintenance and/or operator attention.

The Biological Emissions Control™ (BEC™) unit, installed to biologically degrade VOCs from the off-gas stream, was removed from the system after a few months of operation and was not evaluated. Dispersive air modelling results showed that contaminant concentrations were below established air quality standards and discharge criteria for the site were met without any additional treatment.

The SVVS was installed at the site based on contaminant distribution information derived from remedial investigation data. During the baseline sampling event under the SITE Demonstration, it became evident that a portion of the system was installed within a clean area of the site. Operation of the system was easily adjusted while maintaining the existing hardware to concentrate remedial action in more contaminated areas. However, installation of the system in the non-contaminated area impacted costs since materials and labor were expended. The excess installation did not in any way impact the performance of the system. This situation stresses the importance of accurately defining the extent and magnitude of contamination prior to the implementation of in-situ technologies. In-situ technologies may require site characterization in greater detail than is commonly available from remedial investigations.

CONCLUSIONS

The results from the demonstration indicate the SVVS technology greatly exceeded their reduction claims by providing a site average 80.6% reduction of volatile organics in the vadose zone. Furthermore, aerial and vertical reductions across the site did not indicate the presence of any zones that were not treated by the system. The SVVS process proved to be reliable and required minimal operator oversight. The technology did not experience significant operational difficulties during the evaluation period.

The SVVS process is applicable to sites contaminated with gasoline, diesel fuels, and other hydrocarbons, including halogenated compounds. The system is very effective on benzene, toluene, ethylbenzene, and xylene (BTEX) contamination. The process can also be used to contain contaminant plumes through its unique vacuum and air injection techniques. The technology should be effective in treating soils contaminated with virtually any material that has some volatility or biodegradability. The technology can be applied to contaminated soil, sludge, free-phase hydrocarbon product, and groundwater. By changing the injected gases, anaerobic conditions can be developed, and a microbial population can be used to remove nitrate from groundwater. The aerobic SVVS can also be used to treat heavy metals in groundwater by raising the redox potential of the groundwater and precipitating the heavy metals.

The cost to remediate 21,300 yd^3 of vadose zone soils during a full-scale cleanup over a 3-year period at the Electro-Voice Superfund site in Buchanan, MI was estimated to be $192,237 or $9/$yd^3$, not including effluent treatment and disposal. The majority of this was incurred in the first year, primarily due to well drilling and associated site preparation. If effluent treatment and disposal, using vapor phase granular activated carbon, had been included, this would have added $164,500 to the first year of remediation and brought the total cleanup figure to $356,737 ($16.75/yd^3). This would have accounted for over 45% of the total cleanup costs.

USE OF SULFATE REDUCING BACTERIA IN ACID MINE DRAINAGE TREATMENT

Thomas J. Powers
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
26 West Martin Luther King Drive
Cincinnati, Ohio 45268
(513) 569-7550

INTRODUCTION

The environmental impacts caused by Acid Mine Drainage (AMD) were first recorded in 1556 by Georgius Agricola. In the United States 10,000 miles of streams and 29,000 surface acres of impoundments are estimated to be seriously affected by AMD. Abandoned surface mines are estimated to contribute about 15% of the drainage, while active mines (40%) and shaft and drift mines (45%) contribute the remainder.

AMD results when metal sulfide minerals, particularly pyrite (FeS_2), come in contact with oxygen and water. Acid generation occurs when metal sulfide minerals are oxidized according to the Initiator Reaction:

$$FeS_2(\text{pyrite}) + 3\tfrac{1}{2}O_2 + H_2O \dashrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

Figure 1 illustrates the pyrite oxidation cycle. This reaction is one of many that results in increased metal mobility and increased acidity (lowered pH) of the mine water. Figure 2 puts forth the oxidation of Iron Sulfides. The oxidation of ferrous sulfate is accelerated by bacterial action of Thiobacillus ferrooxidans, a naturally occurring bacterium that at pH 3.5 or less, can rapidly accelerate the conversion of dissolved Fe^{2+} (ferrous iron) to Fe^{3+} (ferric iron), and can act as an oxidant for the oxidation of pyrite. Ferric ions, as well as other metal ions, and the sulfuric acid have a deleterious influence on the biota of streams receiving AMD.

The Lilly/Orphan Boy Mine, located in the Elliston Mining District of Powell County, Montana, was selected as the Sulfate Reducing Bacteria (SRB) technology demonstration site. The mine is situated on a patented claim on Deerlodge National Forest Land about 11 miles south of Elliston, Montana. This abandoned mining operation consists of a 250-foot shaft, four horizontal workings, and some stoping. The shaft is flooded with AMD to the 74-foot level and is discharging about 3 gallons per minute (gpm) at a pH of 3.0 from the adit associated with this level. The total aluminum, arsenic cadmium, copper, manganese, iron, and zinc concentrations of the Lilly/Orphan Boy Mine Water are shown in Table 1. The pH range observed in the mine water is also presented.

METHODOLOGY

The main objective of conducting laboratory-scale tests was to determine the effectiveness of bacterial sulfate reduction in the reduction of metal concentrations at the ambient shaft water pH of 3.0 and temperature of 8°C. The temperature of the shaft water ranged from 6°C, at the portal, to 11°C, in the shaft, over a one-year period (5/93 to 7/94) during which time samples were collected from the site. This objective was facilitated by monitoring the laboratory-scale system over a period of 60 days through the collection and analysis of multiple samples, principally metals concentration in the influent and effluent waters. The sulfur cycle was observed throughout Phase 1 and Phase 2 of the pilot plant SRB experiment (Figure 3).

The experimental design of the laboratory-scale testing allowed for the comparison of two different bacterial preparation methods and three different substrate layering methods. The testing was performed at a typical shaft water temperature (8°C) and with influent water obtained from the shaft of Lilly Orphan Boy Mine one week prior to start up.

$$FeS_2(\text{pyrite}) + 3\tfrac{1}{2}O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

Initiator reaction

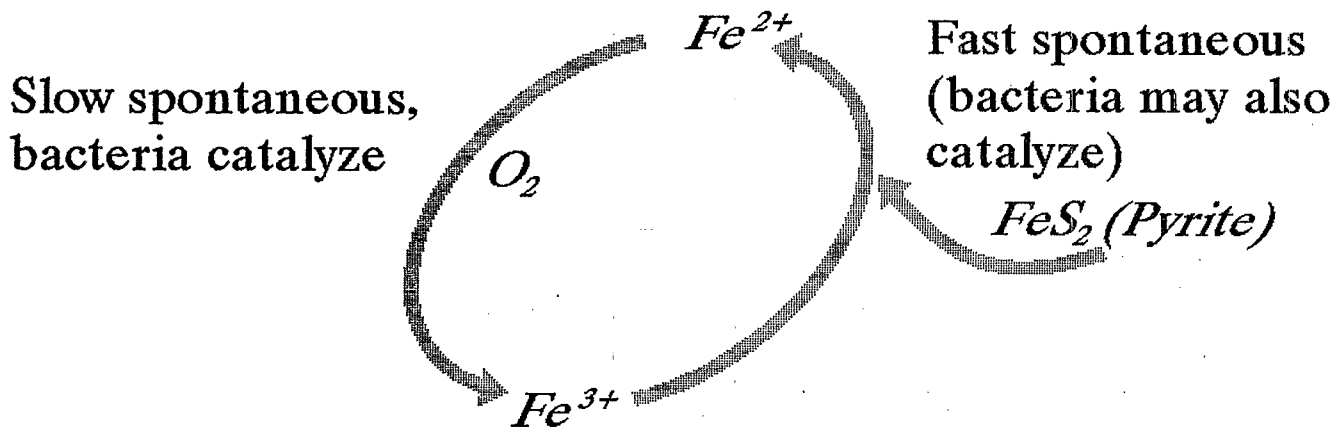


Figure 1. The Pyrite Oxidation Cycle

FERROUS SULFATE BY NON-BIOTIC OXIDATION :

$$2\,FeS_2 + 2\,H_2O + 7\,O_2 \rightarrow 2\,FeSO_4 + 2\,H_2SO_4$$

BACTERIAL OXIDATION OF FERROUS SULFATE BY **Thiobacillus ferrooxidans:**

$$4\,FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2\,Fe_2(SO_4)_3 + 2\,H_2O$$

FERRIC SULFATE IS REDUCED AND PYRITE OXIDIZED BY CHEMICAL REACTION :

$$Fe2(SO_4)_3 + FeS_2 \rightarrow 3\,FeSO_4 + 2\,S$$

$$2\,S + 6\,Fe_2(SO_4)_3 + 8\,H_2O \rightarrow 12\,FeSO_4 + 8\,H_2SO_4$$

ELEMENTAL SULFUR OXIDATION BY **Thiobacillus thiooxidans:**

$$2\,S + 3\,O_2 + 2\,H_2O \rightarrow 2\,H_2SO_4$$

Figure 2. The Oxidation of Iron Sulfides

Pilot scale testing was conducted in eight packed-bed reactors (4 foot, vertical, plexiglass columns) operated in up-flow configurations. This design was selected to closely model the actual conditions of the hydrogeologic flow of water entering the shaft via groundwater up-flowing to the adit level, and leaving the shaft through the mine adit. Eight tests were conducted in parallel. Four reactors had diameters of 14 inches while the remaining four reactors were 18 inches in diameter. The reactors were housed in a wooden, insulated, air-conditioned enclosure during the entire testing period to help maintain a temperature representative of the shaft water, nominally 8°C.

Mud from the Lilly/Orphan Boy Mine was used as a source of Sulfate Reducing Bacteria (SRB) for the pilot-scale testing. Approximately three cubic feet of mud was obtained from the portal area of the mine. In order to maintain the SRB in an anaerobic environment, the mud was placed in plastic bags within five gallon buckets until it was mixed with cow manure and decomposed woodchips to make the organic substrate that was packed into the reactors.

RESULTS

Seven of the eight pilot SRB reactors were very effective in reducing all metal concentrations from the Lilly/Orphan Boy Mine shaft water. The one reactor (using a fishnet containment system) allowed the untreated water to by-pass the substrate reactor. Water sampled in the shaft of the Lilly/Orphan Boy Mine was characterized and typical results are shown in Table 1. The Project Goals are also included in Table 1.

Table 2 shows no data for arsenic. This is because Sulfate Reducing Bacteria (SRB) were collected from mud outside the adit of the Lilly/Orphan Boy Mine. This mud contained high levels of arsenic that, when mixed with the manure, solubilized. Therefore, the data collected from the effluent were considered to be invalid measurements of the capabilities of the process in arsenic removal.

TABLE 1. LILLY/ORPHAN BOY SHAFT WATER CHEMISTRY (MG/L)

Fe	Mn	Cu	Zn	Al	Cd	As	Soluble Sulfide	SO_4^{-2}	pH
29.0	6.28	0.24	25.6	8.09	0.24	1.02	0.75	277	2.8-3.0
			GOALS: LILLY ORPHAN BOY PILOT MINE PROJECT						
1.0	2.0	0.1	4.0	1.0	0.1	0.03	---	---	6-8

LABORATORY-SCALE TESTING

The main objective of conducting laboratory-scale tests was to determine the effectiveness of bacterial sulfate reduction in the mitigation of metal concentrations at the ambient shaft water pH (Table 1) and temperature (Nominally 8°C). The temperature of the shaft water ranged on average from 6°C, at the portal, to 11°C, in the shaft, over a one-year period (5/93 to 7/94) during which samples were collected from the site. This objective was facilitated by monitoring the laboratory-scale system over a period of 60 days through the collection and analysis of multiple samples, principally metals concentration in the influent and effluent waters.

The experimental design of the laboratory-scale testing allowed for the comparison of two different bacterial preparation methods and three different substrate layering methods. The testing was performed at a typical shaft water temperature (8°C) and with influent water having a representative pH (3.0) of the ambient shaft water.

TABLE 2. SRB TECHNOLOGY RESULTS

Measurement	Effluent (mg/L)	Change
Iron (Fe)[1]	0.17	99% reduction
Manganese (Mn)[2]	1.84	71% reduction
Copper (Cu)[3]	0.0069U	97% reduction
Zinc (Zn)[3]	0.172	99% reduction
Aluminum (Al)[1]	0.03U	99% reduction
Cadmium (Cd)[3]	0.0047U	98% reduction
Soluble Sulfide	3.12	416% increase
Sulfate (SO_4^{-2})	257	8% reduction
pH	7.6	Approximately 4.6 pH unit increase

[1]Reduction probably due to hydroxide precipitation resulting from pH increase.

[2]Reduction probably due to either carbonate precipitation or absorption.

[3]Reduction due to sulfide precipitation.

U = non-detect (the number before the "U" is the instrument detection limit).

FIELD TESTING

The field testing of the 50 ton *in situ* bioreactor is in progress and will continue until at least December 1995. The final reporting is scheduled for April 1996. The field demonstration of sulfate-reducing-bacteria technology required the placement of an organic Substrate containing the SRB at positions in the two vertical shafts and horizontal tunnel (ADIT) of the mine where the natural flow of shaft water must pass through the substrate (Figure 4). The biological action of the SRB and subsequent chemical reactions 1) reduce the amount of sulfate in the water, 2) form soluble hydrogen sulfide, 3) form metal sulfides from a reaction of the metallic ions with the hydrogen sulfide, 4) precipitate the metal sulfides within the substrate and 5) increase the pH of the effluent discharge to 7.6+.

CONCLUSIONS

Sulfate reduction was accomplished by sulfate reducing anaerobic bacteria. Sulfate-reducing bacteria decompose simple organic compounds (substrate) using sulfate as a terminal electron acceptor, thus producing soluble hydrogen sulfide and bicarbonate as metabolic products. The hydrogen sulfide reacts with dissolved heavy metals in the water to form insoluble metal sulfides. The bicarbonate has the effect of increasing pH. These two processes have the potential to greatly reduce or eliminate the problems associated with some rural remote abandoned acid generating mine sites.

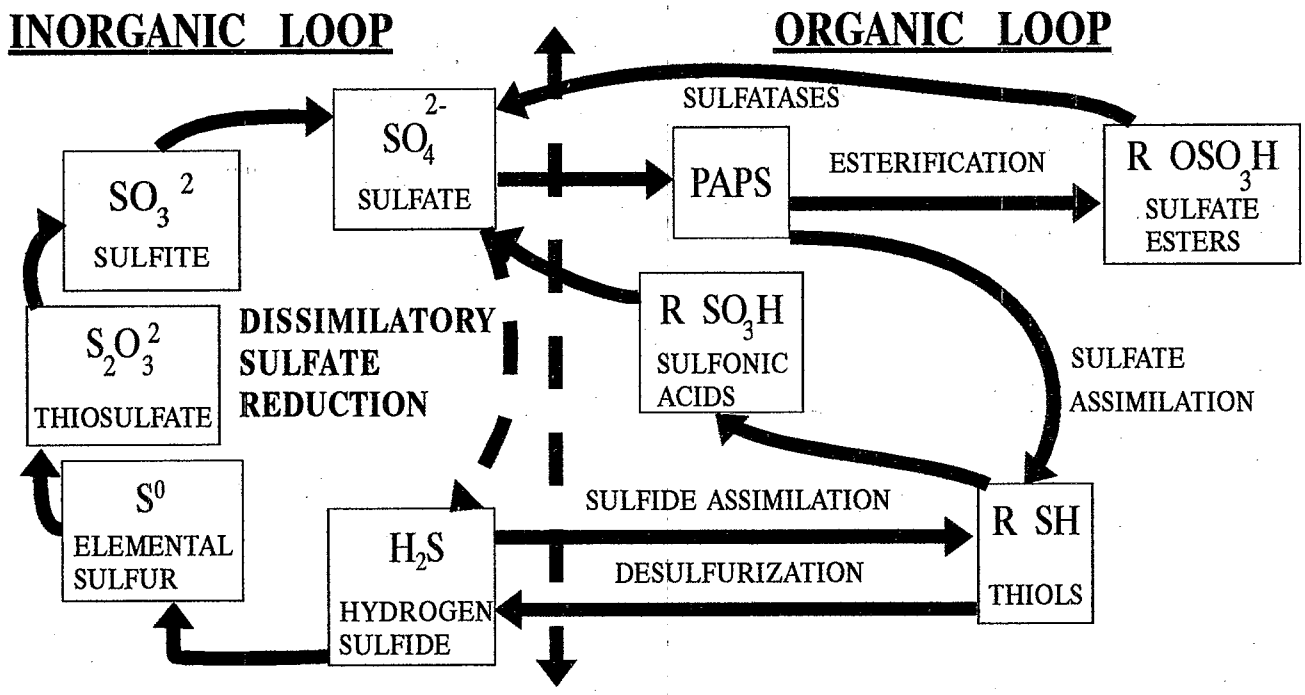


Figure 3. The Sulfur Cycle

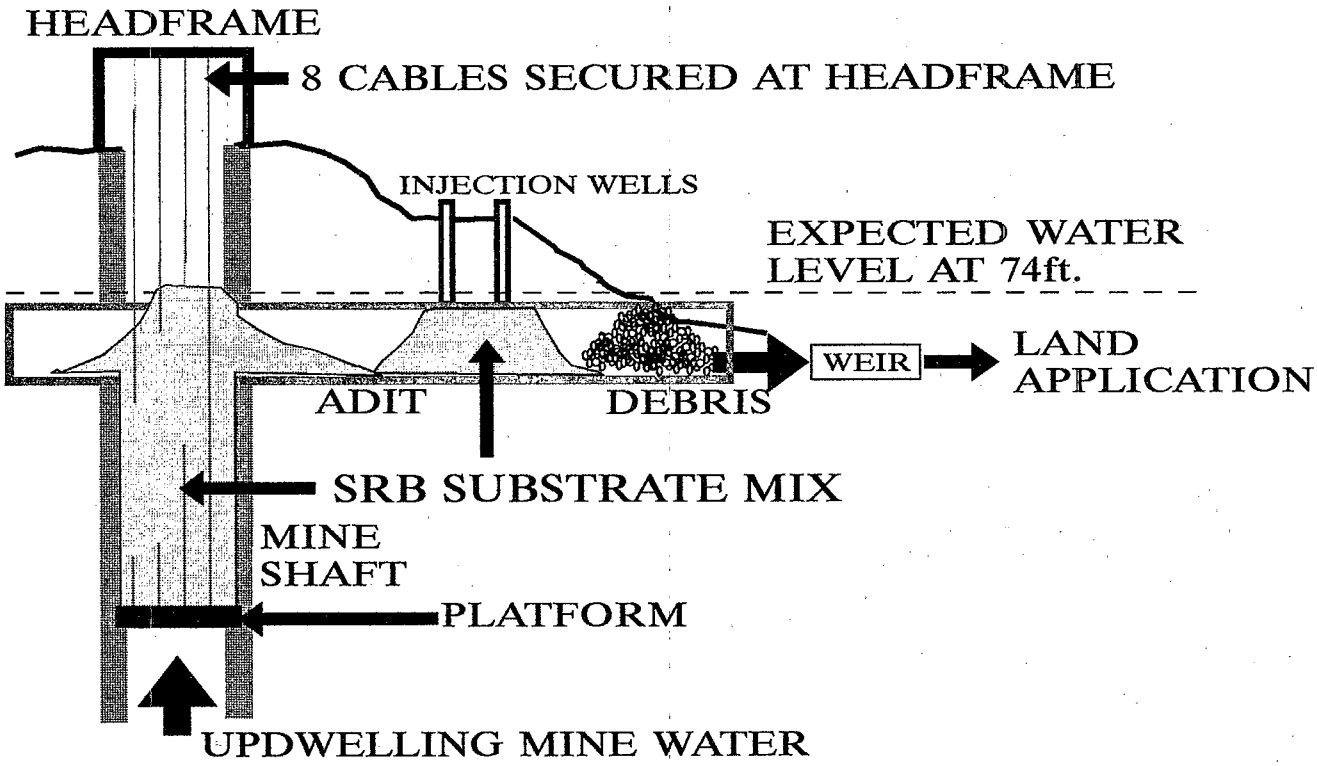


Figure 4. Lilly Orphan Boy Mine Profile

The Phase 1 (laboratory pilot plant) was successful in demonstrating the Sulfate-Reducing Bacteria (SRB) process. Metals were reduced by 90+% and the effluent discharge levels in milligrams per liter were within the project's goals in seven of the eight column reactors used in the laboratory experiment. The process worked at 8°C with a retention time of approximately 4-1/2 days.

The Phase 2 (Field demonstration of the SRB technology) required the placement of an organic substrate containing the Sulfate Reducing Bacteria (SRB) at positions in the vertical shafts and the horizontal adit of the Lilly Orphan Boy Mine where the natural flow of water was forced through the substrate. The effluent discharge criteria appears to have been met using the current data available.

REFERENCES

1. MSE, Inc. Laboratory Report for the Sulfate-Reducing Bacteria Laboratory Demonstration, Mine Waste Technology Pilot Program, Activity III, Project 3. MSE, Inc., Butte, Montana, October 1994.

2. Odom, J.M. and Singleton, R. The Sulfate-Reducing Bacteria: Contemporary Perspectives. ISBN 0-387-97865-8; ISBN 3-540-97865-8; QR92, S8585, Pages 211-249), 1992.

For more information, contact Thomas J. Powers, U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, 26 West Martin Luther King Drive, Cincinnati, Ohio 45268, (513) 569-7550.

BUFFING, BURNISHING, AND STRIPPING OF VINYL ASBESTOS FLOOR TILE

Bruce A. Hollett, Alva Edwards, and Patrick J. Clark
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
26 West Martin Luther King Drive
Cincinnati, Ohio 45268
(513) 569-7654

John R. Kominsky, Ronald W. Freyberg, and James M. Boiano
Environmental Quality Management, Inc.
1310 Kemper Meadow Drive
Cincinnati, Ohio 45240

INTRODUCTION

Studies were conducted to evaluate airborne asbestos concentrations during the three principal types of preventative maintenance (low-speed spray-buffing, ultra high-speed burnishing, and wet-stripping) used on asbestos-containing floor tiles. These were done under pre-existing and prepared levels of floor care maintenance. Airborne asbestos concentrations were measured before and during each floor care procedure to determine the magnitude of the increase in airborne asbestos levels during each procedure. Airborne total fiber concentrations were also measured for comparison with the Occupational Safety and Health Administration's (OSHA) Permissible Exposure Limit (PEL) of 0.1 f/cm^3. Low-speed spray-buffing and wet-stripping were evaluated on pre-existing floor conditions and three levels of prepared floor care conditions (poor, medium, and good). Ultra high-speed burnishing and wet-stripping were evaluated on two levels of prepared floor care conditions (poor and good). Floor care conditions were defined in consultation with the Chemical Specialty Manufacturers Association and other representatives of floor-care chemical manufacturers. Controlled studies were conducted in an unoccupied building at the decommissioned Chanute Air Force Base in Rantoul, Illinois, with the cooperation of the U.S. Air Force. The building offered approximately 8600 ft^2 of open floor space tiled with 9-inch by 9-inch resilient floor tile containing approximately 5% chrysotile asbestos.

METHODOLOGY

Configuration for Experiments

Approximately 6500 ft^2 of floor space was isolated as the experimental test area. A containment shell was constructed to provide five equally-dimensioned test rooms, each with approximately 1300 ft^2 of floor space and 7-foot ceiling height. The ceiling and walls were covered with polyethylene. Four high-efficiency particulate air (HEPA) filtration units were placed in the hallway outside of the five test rooms to ventilate the test rooms and reduce the airborne asbestos concentrations to background levels after each experiment.

Upon completion of the low-speed spray-buffing and wet-stripping experiments, the test area was reconfigured to accommodate the ultra high-speed burnishing and wet-stripping experiments. The test area was reconfigured to provide a single test room of approximately 6500 ft^2 of floor space and 7-foot ceiling height.

Experimental Design

Low-speed spray-buffing was first evaluated on the pre-existing floor-care condition. Low-speed spray-buffing of the pre-existing floor-care condition was evaluated five times, once in each of the five test rooms. Wet-stripping (including polish and sealant removal) was also evaluated on the pre-existing floor-care condition. Wet-stripping of the pre-existing floor-care condition was evaluated five times, once in each of the five test rooms.

Low-speed spray-buffing was evaluated on three levels of prepared floor-care conditions: (1) poor floor-care condition defined as a floor with one coat of sealant and one coat of polish; (2) medium floor-care condition defined as a floor with one coat of sealant and two coats of polish; and (3) good floor-care condition defined as a floor with two coats of sealant and three coats of polish. Each floor-care condition was evaluated five times, once in each of the five test rooms, to yield a total of 15 experiments. Wet-stripping after low-speed spray-buffing was evaluated on two levels of floor-care conditions (medium and good). This comparison addresses the effectiveness of two coats of sealant versus one coat of sealant to limit the extent of airborne asbestos concentrations during polish removal. Wet-stripping of each of the two floor care conditions was evaluated five times, once in each of the five test rooms, to yield a total of ten experiments.

Ultra high-speed burnishing was evaluated on two levels of prepared floor-care conditions: (1) poor floor-care condition (defined as a floor with two coats of sealant and one coat of polish) and (2) good floor-care condition (defined as a floor with two coats of sealant and four coats of polish). Each floor-care condition was evaluated four times to yield a total of eight experiments.

Wet-stripping after ultra high-speed burnishing was also evaluated on two levels of floor-care conditions (poor and good). Each of the two floor care conditions were evaluated four times to yield a total of eight experiments.

Analytical Methods

The mixed cellulose ester filters were prepared and analyzed in accordance with the non-mandatory transmission electron microscopy (TEM) method specified in the Asbestos Hazard and Emergency Response Act (AHERA) Final Rule (October 30, 1987; 52 CFR 4826) to achieve a sensitivity of 0.005 s/cc, plus the specific length and width of each structure were measured and recorded. The phase contrast microscopy (PCM) samples were prepared and analyzed according to the National Institute of Occupational Safety and Health (NIOSH) Method 7400, with an analytical sensitivity of about 0.01 f/cc. Specific quality assurance procedures outlined in the AHERA rule were used to ensure the precision of the collection and analysis of air samples, including filter lot blanks, open and closed field blanks, and repeated sample analyses.

Statistical Methods

The relative change in airborne asbestos concentration was measured by the ratio of the average concentration during the specific maintenance procedure to the average concentration before the maintenance procedure. These ratios were then compared by taking the natural logarithm and comparing the averages by standard analysis of variance (ANOVA) techniques.

RESULTS

Low-speed spray-buffing and wet-stripping was first evaluated on the pre-existing floor-care condition. Larger (and statistically significant) increases in the TEM airborne asbestos concentrations were observed during wet-stripping than during spray-buffing. None of the individual PCM concentrations exceeded the OSHA PEL of 0.1 f/cm^3. Consequently, 8-hour time-weighted average (TWA) concentrations based on these measured levels would not exceed the OSHA PEL. The highest individual PCM concentration (0.023 f/cm^3) was measured during wet-stripping.

For the prepared floor studies, the mean relative increase in TEM airborne asbestos concentrations during low-speed spray-buffing tended to decrease as the floor care condition improved (i.e., poor condition resulted in a larger relative increase than medium, and medium condition showed a larger relative increase than good); however, the differences between the three levels of floor care were not statistically significant ($p = 0.1149$).

Larger (and statistically significant) increases in TEM airborne asbestos concentrations were observed during wet-stripping of floors in medium condition than on floors in good condition. The relative increase in airborne asbestos concentrations (i.e., compared to baseline measurements) was approximately 14 times greater, on average, during wet-stripping

of floors in medium condition than during wet-stripping of floors in good condition. The stripping solution used on these floors was designed to remove only the polish from the floor, leaving the layer(s) of sealant on the floor. Therefore, although significant increases in airborne asbestos concentrations were observed during wet-stripping of floors in both medium and good condition, the extra layer of sealant on floors in good condition appears to significantly decrease the airborne asbestos levels that were generated by the activity. Overall, significantly larger increases ($p = 0.0001$) in airborne asbestos concentrations were observed during wet-stripping than during low-speed spray-buffing (this comparison was restricted to floors in medium and good condition since wet-stripping was not evaluated on floors in poor condition). The relative increase in airborne asbestos concentrations was approximately 18 times greater, on average, during wet-stripping than during low-speed spray-buffing.

PCM Concentrations

None of the individual PCM concentrations exceeded the OSHA PEL of 0.1 f/cm^3. Consequently, 8-hour TWA concentrations based on these measured levels would not exceed the OSHA PEL. The highest individual PCM concentration (0.032 f/cm^3) was measured during low-speed spray-buffing.

Ultra High-Speed Burnishing and Wet-Stripping Experiments

Similar increases in airborne TEM asbestos concentrations were seen during ultra high-speed burnishing and wet-stripping of floors in both poor and good condition. No floor condition or maintenance procedure resulted in significantly higher or lower increases in mean airborne asbestos concentration.

Overall, ultra high-speed burnishing and wet-stripping resulted in an 11-fold statistically significant increase, on average, in airborne asbestos concentration.

The ultra high-speed burnishing operation produced a fine, pale yellow, powdery dust from the wax and/or sealant. PCM concentrations measured during ultra high-speed burnishing were significantly higher than those measured during stripping. The elevated concentrations measured during ultra high-speed burnishing were due primarily to the white dust generated during the process. The fine dust particles (pulverized wax/sealant) that measured greater than 5 μm in length and had a length-to-width aspect ratio of 3:1 were counted as fibers (NIOSH Method 7400, A Counting Rules). The corresponding TEM concentrations show that the PCM concentrations do not reflect an accurate indication of the airborne asbestos concentrations.

The 8-hour TWA concentrations were calculated by assuming zero exposure beyond that which was measured during the experiment. None of the 8-hour TWA concentrations measured during wet-stripping (after ultra high-speed burnishing) exceeded the OSHA PEL of 0.1 f/cm^3 for total fibers.

CONCLUSIONS

This study shows that low-speed spray-buffing, ultra high-speed burnishing, and wet-stripping of asbestos-containing resilient floor tile can be sources of airborne asbestos in building air. Greater releases of airborne asbestos were observed during wet-stripping than during low-speed spray-buffing when performed on floors in both pre-existing condition and prepared conditions. The results of this study further suggest that multiple layers of sealant applied to the floor prior to the application of the floor finish can reduce the release of asbestos fibers during polish removal.

For more information, the EPA Work Assignment Manager, Alva Edwards, can be contacted at the U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, 26 West Martin Luther King Drive, Cincinnati, Ohio 45268, (513) 569-7693.

CONTAMINANTS AND REMEDIAL OPTIONS AT PESTICIDES SITES- A TECHNICAL RESOURCE DOCUMENT

Richard N. Koustas
USEPA Edison Facility
2890 Woodbridge Avenue
Edison, NJ 08837
Phone: 908-906-6898

INTRODUCTION:

Pesticide contamination includes a wide variety of compounds resulting from manufacturing, improper storage, handling, disposal, and/or agricultural processes. Remediation of pesticide-contaminated soils can be a complicated process, as most pesticides are mixtures of different compounds rather than pure pesticide. The remedial manager is faced with the task of selecting remedial options that will meet established cleanup levels. There are three principal options for dealing with pesticide contamination: containment/immobilization, destruction, and separation/concentration. This paper is condensed from the technical resource document (TRD) "Contaminants and Remedial Options at Pesticide Sites" and provides a brief summary on treatment technologies that are available or those being developed for pesticide contamination. Technologies that have not produced performance data are not included nor are water treatment technologies. This paper focuses on potential remediation techniques of soils.

CHARACTERISTICS OF PESTICIDES

Pesticides, as defined by the U.S. Federal Environmental Pesticide Control Act, are "...any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any insect, rodent, nematode, fungus, weed or any other form of terrestrial or aquatic plant, animal life, or virus, bacteria, or other microorganism which the Administrator declares a pest". Pesticides include insecticides, fungicides, herbicides, acaricides, nematocides, and rodenticides as well as any substance or mixture of substances intended for use a plant regulator, defoliant, or desiccant. Pesticides do not include such substances as fertilizers or veterinary medicines. Pesticide wastes are generally complex chemical mixtures and not pure pesticides. These mixtures can include solvents, carriers and other components that will have a direct effect on toxicity, mobility, transport, and treatment.

Several classification criteria are utilized when grouping pesticides. Conventional classification methods are based on the applicability of a substance or product to the type of pest control desired. In addition, the EPA has its own classifications under the Resource Conservation and Recovery Act (RCRA) and Superfund. For the purpose of treatment, pesticides may be classified based on three characteristics: water solubility, contains metals or contains halogen. Therefore, TRD categorizes pesticides into four waste groups based on data needs for available treatment technologies:

WG01 - Inorganic pesticides
WG02 - Halogenated water insoluble organics
WG03 - Halogenated sparingly water soluble organics and organo-linked compounds
WG04 - Non-halogenated organics and organo-linked compounds.

The TRD provides details of the four pesticide waste groups and gives examples of commonly found pesticides. These groups are subdivided further to show the chemical class or family each pesticide belongs to according to their molecular structure or key functional group. Applicable treatment technologies for each waste group are also provided. References to pesticides and pesticide wastes in this document use the above waste group categories.

Most pesticides are adsorbed easily on soils because of their molecular weight. In fact, adsorption of pesticides on the soil surface is a dominant factor that affects the extent of the site contamination. As a rule, when applied properly, pesticides migrate slowly. Concentrated pesticide from a spill or leak can move more quickly into the subsurface, especially if the pesticide is an aqueous phase or under the influence of percolating water. Mechanisms of pesticide fate and transport that affect the extent of site contamination include: adsorption, biodegradation, volatilization, downward and lateral migration, and photolysis.

Selecting a remedial strategy includes considering the individual contaminant's toxicity, persistence, migration pathways, and rate of transport from a site. The wide range of physical and chemical properties of pesticides also influences the selection of an appropriate remedial technology or combination of technologies (known as a treatment train). It is important to gain information specific to the pesticide(s) present in order to effectively identify the treatment technology(ies) that is most applicable and cost effective.

The following sections present an overview of treatment technologies that have been used to treat, destroy, or remove pesticides from soil contaminated with pesticides. The technologies discussed are at various stages of development and application and are separated into immobilization, destruction and separation/concentration technologies.

IMMOBILIZATION OPTIONS

Immobilization technologies minimize or prevent the migration of the contaminant by utilizing physical barriers to inhibit the flow of groundwater through contaminated soil. The use of chemical reactions and/or physical interactions may also be employed to retain or stabilize the contaminant to prevent its migration into the surrounding environment. Immobilization techniques limit the mobility of the pesticides and provide no detoxification or volume reduction. These technologies include containment, stabilization/solidification (S/S) and in-situ vitrification (even though in-situ vitrification is considered a thermal process, its primary goal is to immobilize the contaminant).

Containment of contaminant plumes via capping or vertical barriers is often a component of an overall remediation plan. These technologies are used with groundwater extraction and treatment. In S/S technologies, a chemical reagent is mixed with the contaminant to physically bind or chemically react to reduce its mobility or restrict contact with a mobile phase. Cement based processes are more suitable for inorganic pesticides (WG01) and are often effective in reducing the mobility or leachability of metals.

In-situ vitrification (ISV) is used to melt contaminated soils and convert them into a glass-like material of very high stability and chemical inertness. Typically, an electric current is used to generate temperatures of up to approximately 2,000°C in order to fuse the soil. Gases containing vaporized water and organic substances are collected at the surface for treatment. ISV is commercially available and can be used to destroy or capture organic pesticides in waste groups WG02, WG03, and WG04 as well as to immobilize inorganic pesticides (WG01) within the melt.

DESTRUCTION TECHNOLOGIES

Destruction technologies are used to reduce or eliminate toxicity and often decrease volume and/or mobility. Contaminated soils that are treated using destruction technologies regularly require materials handling steps such as excavation, dewatering, conveying, and screening prior to treatment. Additionally, large volumes of soil may require separation or concentration of the contaminants in order to reduce the total volume to be treated. Destruction technologies include thermal, chemical, and biological treatments.

Thermal destruction technologies include incineration and ultra-high temperature processes (e.g., plasma-arc). Incineration is commercially available that utilizes thermal energy (heat) in the presence of oxygen to combust the pesticides and other organic contaminants in soils. Incineration can be used to remediate soils contaminated with organic pesticides (WG02, WG03, and WG04). Incineration of inorganic pesticides from WG01 may result in volatilization of metals into off gases or concentration of metals in the ash.

Chemical destruction technologies that are potentially applicable for remediating pesticide-contaminated soils include chemical oxidation, dehalogenation, hydro processing/heteroatom removal, and hydrolysis/neutralization. These technologies use chemical reactions to reduce or eliminate the contamination in soil containing pesticides.

Chemical oxidation is the most well known of the chemical destruction technologies. Although its use in environmental remediaton has been very limited, it as been used successfully by the chemical processing industry. This treatment may be used to treat organic pesticides (WG02, WG03, and WG04). The possible formation of partially oxidized compounds due to incomplete oxidation should be considered. Variants of oxidation technology may employ air, oxygen or other oxidizing agents.

Dehalogenation removes the halogen atoms from halogenated organic compounds, resulting in significantly reduced toxicity. This technology is applicable to halogenated organic pesticides in waste groups WG02 and WG03. This technology has been demonstrated at the bench and pilot-scale levels as effective on pesticide-contaminated soils.

Hydrolysis/neutralization is a chemical treatment process that results in the destruction of the contaminant under acidic or alkaline conditions. The products of this reaction generally consist of smaller and less toxic molecules: however, an incomplete chemical reaction may produce toxic by-products. This technology can be used to detoxify waste groups WG03 and WG04 and has been demonstrated at the bench and pilot-scale levels.

Bioremediation is typically applicable for treatment of media contaminated with low concentrations of organic pesticides (WG01, WG02, WG03). Oxygen and nutrients are often supplied to the soil to allow microorganisms to metabolize the organic compounds present. The presence of inorganic pesticides (WG01) may inhibit the microbiological degradation process. This technology is available at full-scale.

SEPARATION/CONCENTRATION OPTIONS

Separation/concentration options utilize physical or chemical processes to concentrate contaminants by removing them from the media in which they are contained. These technologies do not reduce the toxicity of the contaminants or inhibit mobility. Rather, they reduce the volume of material requiring treatment by collecting the contaminents in a concentrated form or transferring them to another medium that is easier to handle or treat. These technologies include radio frequency (RF) heating, soil washing, thermal desorption, and solvent extraction.

Radio frequency heating utilizes electromagnetic energy to heat soil to temperatures as high as 300°C. Large volumes of contaminated soil can be heated, with resultant organic contaminant removal via steam stripping, boiling, and vaporization. This technique can be used to remediate soils contaminated with pesticides that typically volatilize between 80°C and 300°C, such as halogenated volatile alphatics in waste group WG03. Other pesticides that have been removed include WG02 pesticides such as aldrin, dieldrin, endrin, and isodrin. This technology is currently in the pilot and field-scale stage and has been demonstrated at the Rocky Mountain Arsenal.

Soil washing is used to remove contaminants from soils by dissolving or suspending them in a wash liquid. Fine particles such as clay and silt containing adsorbed insoluble contaminants also may be separated from the coarser soil fractions using soil washing. The wash liquid is then separated using conventional water treatment methods, while the cleaned coarse fraction that composes the bulk of the soil volume is backfilled or reclaimed. Soil washing can be used to treat soils contaminated with pesticides from all four waste groups (WG01, WG02, WG03, WG04). This technology is available for full-scale use and has been used to remove dieldrin in a bench-scale study at the FMC Fresno Superfund site.

Thermal desorption is used to remove volatile and semivolatile organic chemicals from contaminated soils by increasing the soil temperature. Depending on the vapor pressure of the contaminants in the soil, temperatures are raised to 200°-1000°F to desorb organic compounds. The compounds are then transferred to the vapor phase and are either destroyed, condensed and reclaimed, or treated with carbon. This technology is commercially available and can be used to remove pesticides in waste groups WG02, WG03, and WG04 from contaminated soil.

Solvent extraction uses organic solvents to remove organic compounds from contaminated soils and reduces the contaminant volume by transferring the contaminant from the soil and concentrating it in an extract phase. Solvent extraction treatment is applicable to soils contaminated with organic pesticides (waste groups WG02, WG03, WG04). Solvent extraction is commercially available.

REFERENCE:

USEPA Contaminants and Remedial Options for Pesticides-Contaminated Sites, EPA Number - Not yet available.

FOR MORE INFORMATION:

Richard N. Koustas, U.S. EPA, Risk Reduction Engineering Laboratory,
2890 Woodbridge Avenue, (MS 106), Edison, New Jersey 08837
Phone: (908) 906-6898, Fax, (908) 906-6990

CONTAMINANTS AND REMEDIAL OPTIONS AT SELECTED METALS CONTAMINATED SITES - A TECHNICAL RESOURCE DOCUMENT

Michael D. Royer
Technical Support Branch/RREL
U.S. EPA
Bldg.# 10 (MS-104)
2890 Woodbridge Avenue
Edison, NJ 08837-3679
Phone: 908-321-6633

Lawrence A. Smith
Battelle
505 King Avenue
Columbus, OH 43201-2693
Phone: 614-424-3169

INTRODUCTION

A technical resource document, Contaminants and Remedial Options at Selected Metals-Contaminated Sites, has been produced to assist site remediation managers to select treatment technologies for contaminated soils, sludges, sediments, and waste deposits at sites where inorganic arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), or lead (Pb) are the primary contaminants of concern. These five metals have been addressed because of their toxicity, industrial use, and frequency of occurrence at Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites and in Resource Conservation and Recovery Act (RCRA) hazardous wastes. This document should prove useful to all remediation managers, whether their efforts fall under federal, state, or private authority, and whether they are applying standards from RCRA, CERCLA, and/or state programs.

METHODOLOGY

A diligent effort was made (subject to the key limitations noted below), to identify, collect, analyze, and organize information, data, and pertinent references that a remediation manager would find useful for identifying and selecting remedial alternatives for soils, sediments, sludges, and waste deposits in which the principal contaminants are As, Cd, Cr, Hg, or Pb and selected inorganic compounds of these metals. The types of information collected to support preparation of this document include the following.

- Background information on As, Cd, Cr, Hg, Pb, and associated inorganic compounds regarding mineral origins, processing, uses, common matrices, chemical forms, behavior, transport, fate, and effects.

- Existing remediation performance data, listed below, in rough order of desirability: (a) full-scale remediation of As, Cd, Cr, Hg, and Pb contaminated sites; (b) technology demonstrations on As, Cd, Cr, Hg, or Pb contaminated sites under the EPA Superfund Innovative Technology Evaluation Program; (c) RCRA As, Cd, Cr, Hg, and Pb bearing hazardous wastes for which Best Demonstrated Available Technologies have been established; (d) waste applicability/capacity information for treatment technologies as described in technology guides and the EPA Vendors' Inventory of Superfund Innovative

Treatment Technologies (VISITT) database; (e) feedstock specification information for primary or secondary smelting or recycle/re-use markets; (f) Records of Decision (RODs) and corresponding summaries for As, Cd, Cr, Hg, and Pb contaminated sites; (g) Treatability test data on As, Cd, Cr, Hg, and Pb contaminated matrices where the results are well-documented and in an accessible form (e.g., Alternative Treatment Technology Information Center [ATTIC] and the Risk Reduction Engineering Laboratory treatability database) (h) Superfund National Priority List sites where As, Cd, Cr, Hg, or Pb contaminated media is a primary concern and remedial options are or will be under evaluation.

It is assumed that the remediation manager is familiar with appropriate policy issues (RCRA, CERCLA, and state), site characterization, sampling methods, analytical methods, risk assessment, determination of cleanup levels, and health and safety plans. It is also assumed that the manager or available support staff is familiar with widely available references from which physical and chemical data for the 5 metals of interest and their compounds can be obtained.

Containment and water treatment technologies are primarily addressed by reference, since they are well described and evaluated in recent, available documents, which are referenced in Section 4 of the technical resource document.

To avoid overlap with existing or forthcoming documents, information collection and coverage of four specific types of metals sites [lead battery recycling, wood preserving (As, Cr), pesticides (As, Hg), and mining] was intentionally limited to selected cases where innovative technologies have been chosen or applied.

In the interests of simplicity, brevity, and due to constraints imposed by limited project resources, the reference document does not attempt to systematically address remediation of organometallic compounds, organic-metal mixtures, and multi-metal mixtures. For example, while incineration is noted as a potential pretreatment for an organic-metal-soil mixture, the effects of As, Cd, Cr, Hg, or Pb on the technical and economic feasibility of incineration are not discussed. Another example is that several RCRA Best Demonstrated Available Technologies are cited for multi-metal wastes, but there is no discussion on how, in general, one should select a remedial technology for a multi-metal waste.

RESULTS

An approximately 200-page technical resource document has been produced. Section 4 (Remedial Options) and the appendices cited therein form the heart of the document. This section begins with a brief general discussion of the key applicable or relevant and appropriate regulations that influence cleanup goals. Soil and groundwater action levels and risk goals are tabulated for 24 metal-contaminated sites. TCLP limits for metals in selected metal-bearing RCRA characteristic hazardous wastes are also tabulated.

The bulk of Section 4 addresses the immobilization, and separation/ concentration technologies that are potentially applicable for remediating metal-contaminated solids, with the main emphasis on soils. Each technology is addressed in a similar manner.

- A technology description is provided, followed by a discussion of typical treatment trains, and a discussion of the applicability of the technology to various wastes. Specific reference is made to the 5 metals of interest, when applicable information is available.

- The status (e.g., bench, pilot, full-scale, applications to Superfund remediation) and performance of the technologies are also discussed and, where sufficient examples exist, tabulated.

- Cost factors and costs are also discussed with cost estimates often being drawn from applicable Superfund Innovative Technology Evaluation (SITE) program Applications Analysis Reports.

- Finally, data needs for assessing the applicability of each type of technology are tabulated.

The sub-section on immobilization addresses solidification/ stabilization (cement-based and polymer microencapsulation) and vitrification (in situ and ex situ) technologies. Containment technologies (capping and vertical and horizontal barriers) are noted, but only addressed by reference since: (1) the type of metal contaminant is not crucial to containment system selection, and (2) there is a recent, readily available EPA document (EPA 625/6-91/026) that already addresses the topic at the desired level.

Separation/concentration technologies are subdivided into two categories:

- Technologies applicable for excavated solids:

  -- physical separation technologies [i.e., screening, classification, gravity separation, magnetic separation, and flotation];

  -- soil washing technologies [i.e., extraction via water, solvents, or solutions containing surfactants, chelating agents, acids, or bases], and

  -- pyrometallurgical separation technologies [i.e., Waelz kiln, flame reactor, molten metal bath, secondary lead smelting via reverberatory and blast furnaces, submerged arc furnace, and mercury roasting and retorting], and

- Technologies applied in situ (i.e., soil flushing, and electrokinetics).

Water treatment options are very briefly discussed, and a summary table is provided. As with containment options, limited coverage is provided due to the availability of other recent, available EPA documents that address the topic in an adequate manner.

Section 4 on Remedial Options is complemented by a number of key appendices.

- Appendix B summarizes 68 technologies applicable to metals-contaminated media that are undergoing evaluation in the SITE program.

- Appendix C summarizes 67 innovative metals-contaminated technologies from 16 technology categories. This information was excerpted from EPA's Vendor Inventory of Superfund Innovative Treatment Technologies (VISITT) database version 2.0.

- Appendix D lists and briefly describes 44 selected metals-contaminated National Priority List Sites.

- Appendix E summarizes Best Demonstrated Available Technologies (BDAT) for 60 RCRA hazardous wastes that contain As, Cd, Cr, Hg, and Pb.

- Appendix F supplements the separation/concentration technology portions of Section 4 by providing a review of metal recycling options for metal-contaminated wastes from CERCLA Sites.

Section 2 briefly identifies typical mineral origins, industrial uses, and Superfund matrices of inorganic As, Cd, Cr, Hg, and Pb. Section 3 addresses possible chemical forms for the 5 metals under various conditions. Also described in Section 3 are typical environmental transport, partitioning, and transformation phenomena for the 5 metals in air, soil and sediment, and surface water and ground water. Section 3 also includes a brief overview of the human and environmental toxicity of the five metals and some of their compounds.

CONCLUSIONS

1. The technical resource document consolidates and organizes a substantial body of information pertinent to the remediation of As, Cd, Cr, Hg, and Pb contaminated soils, sediments, and sludges. During the development of remedial investigation and feasibility study (RI/FS) reports, users should be able to considerably reduce time and effort required to identify, describe, and make preliminary assessments of remedial technologies applicable to metals-contaminated sites.

2. The chemistry of these metals, particularly arsenic, mercury, and chromium, is quite complex. Significant differences in solubility, volatility, or toxicity are observed for various species of all five metals. These property differences may have a substantial impact (positive or negative) on the effectiveness, implementability, and cost of remedial alternatives. The technical resource document (Sections 2, 3, and portions of 4) clearly indicates the potential difficulties and thus alerts the RPM to the critical need for early and continuous consideration of the chemistry of these metals by a knowledgable person during site characterization, and remedy evaluation, selection, design, and implementation.

3. In addition to no action and excavation/offsite disposal, thirteen technologies were identified as be- ing potentially applicable to the remediation of metals-contaminated soils, sediments, and sludges.

   - Although by no means appropriate for all metal-matrix combinations, the mostly broadly applicable technologies for metals-contaminated soils are capping (not addressed in TRD), vertical barriers (not addressed in TRD), cement-based solidification/ stabilization, screening, gravity separation, and soil washing/acid extraction.

   - A second tier of technologies is applicable to a much narrower range of situations due to either effectiveness, implementability, or cost limitations. This second tier of technologies includes horizontal barriers, vitrification, polymer microencapsulation, flotation, pyrometallurgical separation, soil flushing, and electrokinetics.

   - The beneficial role of chemical treatment (e.g., oxidation, reduction, neutralization) is recognized, but not addressed as a separate technology, since it is always closely coupled with another technology (e.g., solidification/ stabilization, vitrification) when treating metal contaminated soils.

   - Biotreatment (e.g., extraction of metals from soils using bacteria) was considered for inclusion in the technical resource document, but rejected due to its early stage of development.

   - Only a very limited number of facilities recover the five metals in forms and concentrations likely to be arising from Superfund site remediation. Appendix F lists pertinent facilities, enabling the reader to easily identify and contact recyclers closest to the site to determine interest, acceptance criteria, and costs. Sixteen potential recyclers were identified for lead wastes and 7 for mercury wastes. For 18 other RCRA and specialized metal-bearing

wastes containing one or more of the 5 metals of interest, only 18 additional potential recyclers were identified.

4. Inorganic arsenic is difficult to treat successfully. It has multiple valences and can interconvert between species depending on pH and oxidation/reduction potential and species present. Care must be taken during treatment processes to ensure that volatile arsenic compounds are not formed. Arsenic forms anionic compounds in water, and thus does not form insoluble hydroxides during cement-based stabilization/ solidification. Solidification/stabilization may be applied in instances where arsenic is present in low concentrations. Polymer microencapsulation is an option for arsenic, but no instances of its application were identified. Best Demonstrated Available Technology (BDAT) for arsenic-bearing RCRA hazardous wastes is vitrification, but no Superfund applications of this technology have occurred to date. Potentially viable separation/concentration options include screening, gravity separation, and soil washing/acid/base extraction. These technologies have been selected for remediation of several wood preserving sites. Recycling of recovered arsenic is not very promising -- there is little demand and therefore little or no capacity for recycling arsenic.

5. Inorganic mercury also tends to be difficult to treat. It may be converted by microorganisms under some conditions to volatile organomercury compounds. It is amenable to stabilization/solidification, but only at very low concentrations (e.g., for RCRA hazardous wastes, S/S is a BDAT for Hg < 260 mg/Kg). Mercury does not form insoluble hydroxides, and is not amenable to cement-based S/S at higher concentrations. Polymer microencapsulation is a potential option for mercury immobilization. Physical separation techniques (e.g., screening or gravity separation) and soil washing should be applicable to removal of mercury from soils. These technologies are being evaluated by the Gas Research Institute and U.S. Department of Energy. Given its low solubility in glass and low boiling point, mercury is not a good candidate for vitrification. However, mercury's high vapor pressure, low boiling point, and ready decomposition of its oxides enables it to be separated from soils via thermal desorption and roasting. Only seven facilities appear to be potentially applicable to processing mercury recovered from Superfund remediation.

6. Chromium (III) forms insoluble hydroxides and is amenable to cement-based stabilization/solidification. Chromium (VI) does not form insoluble hydroxides, but it can be subjected to S/S after reduction to Chromium (III). Vitrification may be technically feasible, but cost is likely to pose a problem. Physical separation and soil washing are potentially applicable and have been selected for several wood preserving sites. Soil flushing has been applied at two chromium-contaminated sites. Electrokinetics shows some promise, particularly if success is demonstrated for in situ treatment of clayey soils.

7. Inorganic lead forms insoluble hydroxides, and cement-based solidification/stabilization has been applied full-scale to numerous lead-contaminated soils. Lead is amphoteric, so pH must be carefully controlled during S/S processing to ensure that lead solubility remains at a minimum. Although vitrification and polymer microencapsulation would appear to be technically feasible for lead-contaminated soils, solidification/stabilization would be expected to cost less to implement. Screening, gravity separation, and soil washing/acid extraction have been implemented at two lead-contaminated sites. Whether these separation/concentration technologies can economically attain treatment goals must be determined on a site specific basis. Recycling of lead has been accomplished as part of some lead site remeditions, but the value of the recovered lead typically does not offset processing costs. Soil flushing may be applicable in some circumstances. Electrokinetics may prove to be useful for clayey soils.

8. Inorganic cadmium occurs mostly in the +2 valence state and does not exhibit amphoteric behavior. It is amenable to stabilization/solidification, although pH must be maintained in the alkaline range to ensure that leaching does not occur. Although vitrification and polymer microencapsulation would appear to be technically feasible for cadmium-contaminated soils, solidification/ stabilization would be expected to cost less to implement. Screening, gravity separation, and soil washing/acid leaching are commercially available and would appear to be applicable, but examples of implementation where cadmium was a key contaminant were not found. Facilities that will take cadmium-concentrate from a Superfund remediation are scarce. Soil flushing and elecrokinetics may be applicable for special circumstances.

9. While this technical resource document consolidates information from the past in an attempt to accelerate and improve decisions in the future, it is recognized that site-specific factors ultimately drive the selection of the remedial alternative for any particular site. The remedial action objectives should be clearly established and cleanup levels designated. It is of particular importance to develop reasonable estimates of the volume, distribution, and physical and chemical composition of each significant contaminant/co-contaminant/medium combination at the site that will require remediation. It is similarly important to clearly define the parameters (e.g., total metal(s) concentration, leachable metals, filtered/ unfiltered aqueous metal concentrations), test methods (e.g., TCLP, EP Toxicity Test, other leaching test, total waste analysis), and numerical goals that will be employed to measure treatment effectiveness. A risk assessment should consider transport and fate of contaminants using the best methods available including Eh-pH, equilibrium and/or transport models where applicable.

REFERENCES

Battelle - Columbus Division. Contaminants and Remedial Options at Selected Metals-Contaminated Sites. EPA # Not Assigned Yet,
U.S. Environmental Protection Agency, Cincinnati, Ohio, 1995. 200 pp.

FOR MORE INFORMATION:

Michael D. Royer, Technical Support Branch/RREL,
U.S. EPA, Bldg. #10, (MS-104), 2890 Woodbridge Avenue,
Edison, NJ 08837-3679. Phone (908) 321-6633, FAX (908) 321-6640.
or
Lawrence A. Smith, Battelle, 505 King Avenue, Columbus, OH 43201-2693
Phone: 614-424-3169

OVERVIEW OF TECHNICAL RESOURCE DOCUMENT FOR SOLVENT CONTAMINANTS AND REMEDIAL OPTIONS AT SUPERFUND SITES

Uwe Frank, Daniel Sullivan, Kenneth Wilkowski
U.S. EPA
2890 Woodbridge Avenue
Edison, New Jersey 08837
(908) 321-6626
Fax (908) 906-6990

INTRODUCTION

Solvent contamination is a persistent problem found at numerous Superfund sites. Solvents at Superfund sites are usually halogenated or nonhalogenated organic liquids whose source can be traced to many manufacturing, industrial and commercial processes and uses. Almost half of all Superfund sites listed in the record of decision (ROD) summary database contain solvents as a contaminant.

The contamination usually emanates from the improper disposal of solvents used in a wide variety of industrial and commercial applications such as manufacturing of chemicals, preparation of products and use as cleaning agents. Also the inadequate storage, mishandling and improper applications of solvents have significantly contributed to the problem. Consequently, this has resulted in affecting every medium including soil, sediment, sludge, sub-surface strata, and secondary contamination into air and water, both surface and groundwater. This persistence throughout the environment and the mobility of solvents has created a potentially serious health hazard from toxic exposures to humans. To mitigate this threat, a remedial project manager (RPM) is faced with the challenge of selecting a remedial technology which will achieve established cleanup goals.

Consequently, EPA's Office of Research and Development (ORD) developed a technical resource document (TRD) to assist RPMs and other remedial personnel in making this decision. This TRD was published November 1994, and is available through EPA's Center for Environmental Research Information (EPA/600/R-94/203). The publication discusses solvents, their properties as environmental contaminants and most importantly, the selection of treatment technologies available to reach established cleanup levels in soil at solvent contaminated Superfund sites.

The TRD classifies the appropriate remedial technologies for solvent contaminated soil into 3 main categories; separation, destruction and immobilization. "Separation" includes a group of technologies that extract or separate the contaminant from the soil matrix and form a concentrate or medium that can be more effectively treated. Therefore, this group of technologies prepare or treat solvent contaminated soil matrices for further treatment by either destruction or recovery.

The "destruction" technologies aim to permanently remove the contamination problem and includes those processes that destroy the contaminant by the use of thermal, chemical or biological means. "Immobilization" is the category that includes those methods that stop the spread or minimize the migration of solvent contamination either through the construction of physical barriers, through chemical reactions, or by a combination of both. The remediation of most Superfund solvent sites usually requires a combination of treatment technologies and contaminant control methods. Even if only a single compound type or chemical class is present, generally no single technology is capable of remediating an entire site. As a result, a treatment train is developed which may include immobilization, separation and destruction technologies to achieve site specific objectives and prerequisite cleanup levels.

The technologies discussed in this TRD are in different development stages; proven, innovative, and emerging. For example, some such as incineration and capping, have been proven

on a commercial scale. Others, such as microbial degradation and soil flushing, are less proven, or innovative, and will require site-specific treatability tests to ensure they can meet the established cleanup levels. Emerging technologies, such as horizontal barriers, are expected to be appropriate but have yet to be shown effective in site remediation. To facilitate the remedy selection process and accelerate future cleanups some of these technologies are also being designated as presumptive remedies. This approach is one tool of acceleration within the Superfund Accelerated Cleanup Model (SACM) as is described in an EPA fact sheet (EPA 540/F/93/048).

IN-SITU SEPARATION TECHNOLOGIES

The TRD describes separation technologies as those which remove contaminants from soil to form a stream for either contaminant collection or destruction. They include in-situ technologies such as soil vapor extraction (SVE), steam extraction, radio frequency (RF) heating, and soil flushing; for ex-situ treatment they include thermal desorption (TD), soil washing and solvent extraction.

SVE is an in-situ process that applies a vacuum to sub-surface soil formations through a series of wells and removes volatile solvent contaminants. The technology is being widely applied and is well documented in this TRD and referenced SVE publications. SVE is applicable to vadose zones having permeabilities of 10^{-10} cm^2 or greater and contaminants with vapor pressures greater than 0.5 Torr. Innovative technologies such as hydraulic and pneumatic fracturing have been demonstrated through EPA's SITE program and found effective for extending SVE to less permeable formations.

SVE is usually combined with carbon adsorption or thermal destruction to treat the vapor and liquid waste streams. Other combinations include condensation, biological degradation, and ultraviolet oxidation. Contaminated groundwater can be treated and discharged. Highly contaminated soil tailings must be collected for treatment by another technology, such as incineration. Typical costs for SVE range from $10 - $150 per ton.

Steam extraction or steam injection physically separates volatile and semivolatile organics from soil, sediment, and sludge. The process uses a combination of thermal and mechanical energies generated by steam, hot air, infrared elements, and electrical systems to volatilize contaminants from soil into the vapor phase. Steam extraction is an emerging technology that appears promising, particularly if used in conjunction with SVE. Due to the heating of soil, steam extraction can remove more of the less volatile compounds than SVE. Limited field experience has demonstrated 90% removal of volatile and semivolatile compounds, with better recovery in higher permeability zones and lower recoveries of high aqueous-phase solubility compounds in lower permeability regions. The technology can be used in combination with carbon adsorption to treat both condensed water and vapor streams. Estimates place costs for a stationary system at $50-$300 per cubic yard.

Radio frequency heating is an innovative treatment technology for rapid and uniform in-situ heating of large volumes of soil. The process uses electromagnetic wave energy to heat the soil evenly to the point where volatile and semivolatile contaminants are vaporized in the soil matrix, and vented electrodes recover the formed gases. The concentrated extracted gas and particulate streams can be incinerated or subjected to other treatment methods such as carbon adsorption. The technology is applicable to material that typically volatilize in the temperature range of 80° to 300°C such as aliphatic and aromatic fractions of jet fuels and gasoline, chlorobenzene, trichloroethylene, dichloroethane, and tetrachloroethylene, and is predominantly for sandy soils. Costs vary between $50 - $90 per ton.

Soil flushing is another innovative technology that extracts contaminants from soil with water or other suitable aqueous solutions. Soil flushing introduces extraction fluids into soil using an in-situ injection or infiltration process. This method may apply to all types of soil contaminants, including halogenated aliphatics, aromatics, polar organic compounds and metals. It is used in series with other treatments that destroy contaminants or remove them from the recirculating extraction fluid and groundwater, such as carbon adsorption, metal precipitation and air stripping. Costs range from $50 - $120 per cubic yard.

EX-SITU SEPARATION TECHNOLOGIES

Thermal desorption is also a separation technology but is used for excavated soil. It uses indirect or direct heat exchange to volatilize contaminants and water from soil into a carrier gas stream for further treatment. The carrier gas stream may be either air or an inert gas. Depending on the process selected, this technology heats contaminated media to temperatures between 200° and 1,000° F. Off-gases may be burned in an afterburner, catalytically oxidized, condensed for disposal, or captured by carbon adsorption beds. Thermal desorption can successfully treat most of the contaminants found at solvent sites. It cannot effectively separate metals (arsenic, cadmium, lead, zinc, chromium) or PAHs with boiling points above 1,000° F. Mercury, a volatile metal, can be treated with some thermal desorption units. Bench, pilot, and full scale studies have demonstrated that thermal desorption achieves treatment efficiencies of 99 percent or greater for VOCs and semivolatile organic compounds (SVOCs). Some higher temperature units can treat PCBs, pesticides, and dioxins/furans. Costs range from $80 - $350 per ton.

Soil washing, also for excavated soil, is a water-based process for mechanically scrubbing excavated soil to remove contaminants by dissolving or suspending them in the wash solution, or by concentrating them into a smaller volume of soil through particle size separation techniques. Soil washing systems that incorporate both techniques yield the greatest success for soils contaminated with heavy-metal and organic contaminants. The soil-washing process uses various additives (surfactant, acids, chelating agents) to increase separation efficiencies. After successful testing, the washed soil can be returned to the site or reclaimed. The aqueous phase and the clay/silt/sludge fraction contain high concentrations of contaminants. These two streams become waste feed for other on-or off-site treatment by incineration, thermal desorption, or bioremediation. Soil washing is only now becoming more popular in the United States, but has been more widely used in Europe. Costs are from $50 - $205 per ton.

Solvent extraction is similar to soil washing but uses organic solvents to remove contaminants from soil instead of water solutions. Solvent extraction is more appropriate for organic contaminants than inorganics and metals; it reduces contaminant volume by concentrating them in the extract phase. The three broad categories of the solvent extraction process are conventional solvent extraction, critical solution temperature fluid, and supercritical fluid extraction. Solvent extraction is not generally used for extracting inorganics/metals, but would be specified for a solvent contaminated site if there were other, more difficult to remediate compounds, such as PCBs, which could not be treated by SVE or bioremediation. Costs are high, ranging from $100-$500 per ton.

DESTRUCTION TECHNOLOGIES

The destruction technologies described in this TRD are for remediation of contaminated soil, sludge, and sediment at solvent sites and can be divided into three categories: thermal, chemical, and biological. Destruction technologies either destroy or detoxify hazardous wastes by altering the chemical structure of the constituents or breaking down the chemical structure into its basic components. They include incineration, pyrolysis, biodegradation and chemical dehalogenation.

Incineration treats organic contaminants in solids, liquids, and gases by subjecting them to temperatures greater than 1,000° F in the presence of oxygen. This causes the volatilization and combustion of the organic contaminants and converts them to carbon dioxide, water, hydrogen chloride, nitrogen oxides, and sulfur oxides. Three common types of incineration systems can treat contaminated solids; the rotary kiln, the infrared incinerator, and the circulating fluidized bed (CFB) units. The rotary kiln and the infrared units contain a primary chamber that usually operates in the temperature range of 1,000° F - 1,800° F. The rotary kiln is a refractory-lined, slightly-inclined, rotating cylinder that serves as a combustion chamber. The infrared unit uses electric resistance heating elements or indirect-fired radiant U-tubes to heat material passing through the chamber on a conveyor belt. The CFB uses air to circulate and suspend waste in a combustion loop and operates from 1,500° F - 1,800° F. Pyrolysis differs from incineration in that it uses heat in the absence of oxygen to volatilize and decompose organics including PAHs, PCBs, and dioxins. Clean solids are discharged and the gases are condensed or incinerated. It operates between 1,000° F - 2,200° F. Pyrolysis is best for a mixture of organic wastes which have PCBs or dioxin as a component because it is energy intensive and expensive and may not be appropriate for solvents only. Costs for incineration and pyrolysis are similar ranging from $200-$1,500 per ton excluding added costs for waste stream treatment.

Chemical dehalogenation is a remedy applicable to contaminated soil, sludge and sediment at solvent sites. The dehalogenation process is effective potentially in detoxifying chlorinated organic contaminants such as dioxins, PCBs and chlorobenzenes. This converts the more toxic compounds into less toxic, sometimes more water-soluble products and leaves compounds that are more readily separated from the soil and treated. In the dehalogenation of chlorinated aromatic compounds, a nucleophilic substitution reaction replaces a chlorine atom with an ether or hydroxyl group. Dehalogenation of chlorinated aliphatic compounds occurs through an elimination reaction and the formation of a double or triple carbon-carbon bond.

Bioremediation uses microorganisms to biochemically degrade or transform organic contaminants. It attempts to foster and optimize the natural bioremediation and biotransformation processes which occur in soils. Complete degradation of organic contaminants to carbon dioxide, water, and inorganic products may be achievable in some cases. In terms of degree of contaminant removal and final residual levels, the extent of treatment achievable in bioremediation depends upon various factors including the types of contaminants present, and processes used, and site-specific environmental conditions. In general, bioremediation does not achieve contaminant destruction efficiencies comparable to incineration. Performance comparisons with other contaminant removal or destruction processes should be made on a case-by-case basis. Even when lower contaminant removal or destruction is achieved, as long as remedial action goals are met, bioremediation may be a favored alternative based upon factors such as cost, implementability, and public acceptability.

Three principal bioremediation processes generally apply to soils at solvent sites: solid-phase, slurry-phase, and in-situ bioremediation. The solid-phase method places contaminated soil in a thin layer in a lined treatment bed. It is relatively simple and inexpensive and may be effective for a wide range of contaminants, but is land intensive due to the thin soil layer required for aerobic microbial activity.

Slurry-phase bioremediation involves excavated soil or sludge that is mixed with water in a tank or lagoon to create a slurry, which is then mechanically agitated. The procedure adds appropriate nutrients and controls the level of oxygen, pH, and temperature. Potential advantages of slurry-phase treatment as compared to solid-phase bioremediation includes the possibility for more effective treatment due to the high degree of mixing, and the effective contact between contaminated soils and nutrients.

In-situ bioremediation promotes and accelerates natural processes in undisturbed soil. Under appropriate conditions, this technology can destroy organic contaminants in place without the high costs of excavation and materials handling. It can involve recirculation of extracted groundwater that is supplemented above ground with nutrients and oxygen. Vacuum or injection methods can supply oxygen to the subsurface soil. Bioventing combines in-situ bioremediation with SVE to destroy semivolatile and some nonvolatile compounds that cannot be treated by SVE alone. It is an emerging technology that takes advantage of aerobic biodegradation of organics by using forced air to carry an adequate supply of oxygen to subsurface soils. Recent studies also have attempted to bioremediate chlorinated solvents by cometabolism using low-molecular weight alkanes such as methane.

Costs for bioremediation range from $80-$150 per cubic yard for slurry and solid phase treatments, and $8-$15 per pound of contaminant for in-situ treatment.

IMMOBILIZATION TECHNOLOGIES

Technologies described in this group by the TRD include containment and solidification/stabilization (S/S) processes designed to minimize contaminant migration. Containment is a common component in the overall remediation of a solvent site and involves capping systems and vertical/horizontal barriers. It also requires that long-term monitoring be performed.

Capping can range from a native soil cover or plastic sheets to a RCRA subtitle C composite cover. Common vertical barriers include slurry walls in excavated trenches, group curtains formed by injecting grout into soil borings, cement-bentonite filled borings or holes formed by withdrawing beams driven into the ground, and sheet-pile walls formed of driven steel. Horizontal barriers underlie a sector of contaminated soil without removing any material. S/S technologies either physically reduce the mobility of a contaminant (solidification) or chemically alters or binds the contaminant (stabilization). Stabilization can be performed without solidification, while solidification usually includes stabilization. Solidification also includes the use of binders for waste bulking to facilitate the handling of liquid wastes.

Costs for the containment technologies are affected by many variables and are outlined in the TRD. Costs for some common S/S systems range from $75-$400 per ton for landfilling on site.

WATER TREATMENT TECHNOLOGIES

Although the focus of this TRD is soil remediation, groundwater treatment is also generally addressed. Groundwater treatment can be performed by both in-situ and ex-situ technologies. The effectiveness of an ex-situ technology is dependent upon removing contaminants along with the groundwater. This process usually is referred to as pump and treat. If it proves too difficult, other technologies such as steam extraction or surfactant flushing can be used to improve contaminant removal with the groundwater. Groundwater technologies are discussed in more detail in this TRD and referenced publications. The following summarizes the water treatment technologies applicable to solvent sites:

Separation/Concentration Technologies		Destruction Technologies
Adsorption	Membrane separation	Chemical oxidation
Filtration	Precipitation	Biological treatment
Ion exchange	Oil/water separation	
Air stripping	Air sparging	
Reverse osmosis		

SITE DEMONSTRATION OF THE DYNAPHORE/FORAGER SPONGE TECHNOLOGY TO REMOVE DISSOLVED METALS FROM CONTAMINATED GROUNDWATER

Carolyn R. Esposito
U.S. EPA Risk Reduction Engineering Laboratory
2890 Woodbridge Avenue
Edison, New Jersey 08837
(908) 906-6895

Gary Vaccaro
Science Applications International, Corp
411 Hackensack Avenue, Third Floor
Hackensack, New Jersey 07601
(201) 489-5200

INTRODUCTION

A Superfund Innovative Technology Evaluation (SITE) demonstration was conducted of the Dynaphore/Forager Sponge technology during the week of April 3, 1994 at the N.L. Industries Superfund Site in Pedricktown, New Jersey. The Forager Sponge is an open-celled cellulose sponge incorporating an amine-containing chelating polymer that selectively absorbs dissolved heavy metals in both cationic and anionic states. This technology is a volume reduction technology in which heavy metal contaminants from an aqueous medium are concentrated into a smaller volume for facilitated disposal.

The developer states that the technology can be used to remove heavy metals from a wide variety of aqueous media, such as groundwater, surface waters and process waters. The sponge matrix can be directly disposed, or regenerated with chemical solutions. For this demonstration the sponge was set up as a mobile pump-and-treat system which treated groundwater contaminated with heavy metals. The demonstration focused on the system's ability to remove lead, cadmium, chromium and copper from the contaminated groundwater over a continuous 72-hour test. The removal of heavy metals proceeded in the presence of significantly higher concentrations of innocuous cations such as calcium, magnesium, sodium, potassium and aluminum.

METHODOLOGY

The Forager Sponge is an open-celled cellulose sponge which contains a water-insoluble polyamide chelating polymer for the selective removal of heavy metals. The polymer is intimately bonded to the cellulose so as to minimize physical separation from the supporting matrix. The functional groups in the polymer (i.e., amine groups in the polymer backbone and pendent carboxyl groups) provide selective affinity for heavy metals in both cationic and anionic states, preferentially forming coordination complexes with transition-group heavy metals (groups IB through VIIIB of the Periodic Table). The order of affinity of the polymer for metals is influenced by solution parameters such as Ph, temperature, and total ionic content. The following affinity sequence is generally expected by Dynaphore:

$$Cd^{++} > Cu^{++} > Fe^{+++} > Au^{+++} > Mn^{+++} > Zn^{++} > Ni^{++} > Co^{++} > Pb^{++} > Au(CN)_2^- > SeO_4^{-2} > AsO_4^{-3} > Hg^{++} > CrO_4^{-2} > UO_4^{-2} > Ag^{+} > Al^{+++} > K^{+} > Ca^{++} > Mg^{++} >> Na^{+}$$

The high selectivity for heavy metals and the low selectivity for alkali and alkaline earth metals (Na^+, K^+, Mg^{++}, and Ca^{++}) is especially useful for the treatment of contaminated natural waters which may contain high concentrations of these innocuous chemical species. These monovalent and divalent cations do not interfere with or compete with absorption of heavy metals from contaminated waters.

The sponge is highly porous and thus promotes high rates of absorption of ions. Absorbed ions can be eluted from the sponge by techniques typically employed for regeneration of ion exchange resins. Following elution, the sponge is ready for the next absorption cycle. The useful life of the media depends on the operating environment and the elution techniques used. Where regeneration is not desirable or economical, the sponge can be compacted to an extremely small volume to facilitate disposal. The metal-saturated sponge can also be incinerated with careful attention given to the handling of resultant vapors.

The sponge can be used in columns, fishnet-type enclosures, or rotating drums. For this demonstration, the sponge was utilized in a series of four 1.7 cubic foot columns situated on a mobile, open trailer-mounted unit measuring approximately 50 square feet. Each column was 5 feet in height with an 8 inch inside diameter. The columns were connected for upward flow series and each column contained a removable fishnet bag filled with about 24,000 half inch sponge cubes. The trailer was equipped with a wastewater pump, water heater, and both a rotameter and positive displacement type flow totalizer.

This technology was evaluated over a continuous 72-hour operational period, resulting in a total treatment volume of approximately 4,300 gallons. Groundwater was pumped from an existing monitoring well into a 6500 gallon influent storage tank. Although concentrations of some of the critical metals exceeded cleanup goals for the site, the groundwater in the influent storage tank was then spiked with nitrate solutions of lead, copper, and cadmium to assure effective evaluation (quantification) of the developer's claim. The spiked solutions were added to the influent storage tank approximately 24 hours prior to the start of the demonstration and the tank was kept well mixed via recirculation throughout the demonstration.

The groundwater was pumped from the influent storage tank through the four-column system at a treatment flow rate of 1 gpm or 0.08 bed volumes per minute. The influent temperature was raised approximately 15°C to increase reaction rates in order to improve absorption of the critical metals. The treated effluent was initially discharged to a 250 gallon portable tank from which it was subsequently pumped to a 20,000 gallon effluent storage tank for transport off-site for treatment at a local POTW.

Grab samples for analysis of critical parameters were collected from the raw influent, final effluent and intermediate column effluent points. In addition, equal volume 24-hour composite samples were collected for total metals, chemical oxygen demand, total suspended solids, total dissolved solids, sulfate and gross alpha and beta radioactivity. Since the developer reported that replacement or regeneration of the columns should not be necessary, side tests on laboratory scale columns treating standard metal salt solutions were performed to aid in evaluating the absorption capacity and regenerative capabilities of the sponge.

In addition to the lead, cadmium and chromium which were the contaminants of concern at the NL site and therefore the critical parameters for this study, copper was also considered a critical parameter because of the high removal efficiency observed in predemonstration treatability tests.

The developer claimed that the technology would achieve at least a 90% reduction of lead and copper, an 80% reduction in cadmium and a 50% reduction of chromium (as trivalent chromium) in the groundwater.

RESULTS

Analytical results of the critical parameters for the raw influent and final effuent are presented in Table 1. These data show that the treatment claims for cadmium, copper, and lead were achieved. However the developer did not achieve treatment claims for chromium. The treatment claim was based on comparing the mean concentration of the raw influent to the mean concentration of the final effluent.

Table 1: Treatment Performance for Critical Metals

Parameter	90% Confidence Interval for Avg. Influent Conc. (ug/L)	90% Confidence Interval for Avg. Effluent Conc. (ug/L)	90% Confidence Interval for Percent Removal (%)	Developer's Treatment Claim (%)
Cadmium	537 +/- 11	56 +/- 13	90 +/- 2.7	80
Chromium	426 +/- 31	290 +/- 30	32 +/- 5.8	50
Copper	917 +/- 14	25 +/- 0	97 +/- 0.04	90
Lead	578 +/- 12	18 +/- 3	97 +/- 0.59	90

Effective removal of cadmium, copper and lead was achieved in the presence of a groundwater pH ranging from 3.1-3.8; a sulfate concentration of approximately 20,000 mg/L; a TDS concentration of approximately 23,000 mg/L and disproportionately higher concentrations of other cations such as magnesium (72 mg/L), potassium (82 mg/L), aluminum (149 mg/L), calcium, (224 mg/L) and sodium (6000 mg/L). The technology's low affinity for these cations was supported by the near zero removal rates of these ions.

Effective removal of chromium (based on the 50% claim) was achieved within the first 10 hours of operation until performance markedly decreased. The decrease in the removal efficiency could be the result of the sponge's higher affinity for the other critical metals. Based on the developer's regeneration tests on sponge cubes taken from the demonstration columns, regeneration is feasible for lead, copper and cadmium.

Following completion of the demonstration, the sponges were easily removed from the columns via an overhead pulley system installed on the trailer. They were then placed in plastic sleeve bags and hand compacted into 55-gallon drums. A waste compacting firm was able to compact 16 sleeves of sponges into one drum, using a standard industrial waste compactor.

The cost to treat heavy metal contaminated groundwater over a one year period with the Forager Sponge technology is estimated at $340/1000 gallons, assuming the sponges are not regenerated and are replaced upon saturation; or $238/1000 gallons, assuming the sponges are regenerated twice providing for three useful treatment cycles. This cost estimate assumes groundwater characteristics are similar to the demonstration groundwater and the cadmium, lead and copper are treated to demonstration performance claims utilizing a four-column, pump-and-treat unit similar to the demonstration unit. The system would operate 24 hours a day, 7 days a week at a flow rate of 1 gpm resulting in a total treatment volume of approximately 525,000 gallons.

CONCLUSIONS

The Dynaphore Inc. Forager Sponge represents a new approach for the selective removal of heavy metals from water. The developer contends that the cost can be greatly reduced by performing treatability tests on the particular water to be treated and thereby modifying the chelating polymer structure for that particular contaminated water. In addition, the sponge can be used for in-situ applications, e.g., placing a single container bag unit of sponge vertically at the neck region of convergent groundwater collecting zone downstream of the plume. The sponge can also be placed in a trench installation for groundwater remediation employing a multitude of containers of sponge horizontally placed in a sand bag type of arrangement. Containers of sponge can also be utilized tea-bag style or placed within a conduit through which water flows by gravity effect. Loose sponge is being evaluated in tumble operations in soil washing treatments and in stirred tanks for sludge remediation.

FOR MORE INFORMATION

Carolyn R. Esposito, EPA Office of Research and Development, Risk Reduction Engineering Laboratory, 2890 Woodbridge Avenue (MS-106), Edison, New Jersey 08837 (908) 906-6895

CASE STUDIES OF THE HIGH VOLTAGE ELECTRON BEAM TECHNOLOGY FOR WASTEWATER TREATMENT

William J. Cooper, Thomas D. Waite, Charles N. Kurucz, Michael G. Nickelsen, David C. Kajdi
High Voltage Environmental Applications, Inc.
9562 Doral Boulevard
Miami, Florida 33178

Friedemann Gensel
High Voltage Environmental Applications, Inc. - Deutschland GmbH
Magdeburger Str 66, 39167 Eichenbarleben

Mary K. Stinson
USEPA Technical Support Branch/RREL (MS-104)
2890 Woodbridge Avenue
Edison, New Jersey 08837-3679

INTRODUCTION

The development of innovative technologies for the remediation of contaminated sites is continually being considered as a treatment option for several reasons. From an economic standpoint, the treatment costs of conventional technologies continues to increase and from an environmental impact view, treatment technologies are sought that destroy contaminants without creating additional disposal problems.

The high energy electron beam process has been shown to be effective in destroying many organic compounds associated with contaminated sites[1-3]. The experiments to date have been conducted at both bench and full scale. Bench scale studies are performed using a 5000 Curie ^{60}Co-γ source whereas full scale studies have been completed at a pilot facility that has a daily capacity of 170,000 gallons (120 gallons per minute, gpm). The application of this technology to problems that face EPA could result in cost effective treatment of contaminated groundwater, soils, sediments and sludges, as well as demilitarization (chemical weapons), and as an industrial treatment unit process.

To provide "on-site" treatability/feasibility studies as well as small scale clean-ups we have now developed a mobile system. This system is capable of treating up to 50 gpm, employing a 500 kV, 40 mA accelerator. The system is self contained and can be used in remote locations if necessary.

We have received an US Environmental Protection Agency, SITE Emerging Technology project which has as its focus the application of this process to complex mixtures of contaminants in groundwater, wastewater, soils, sediments, and sludges. This paper will discuss the details of several case studies conducted at full scale using the mobile treatment process and review data obtained from on-going studies that have direct benefit to EPA and may assist groups within the environmental clean-up field to more effectively accomplish their mission.

METHODOLOGY

Aqueous Chemistry of High-Energy Electrons. The scientific foundation for the use of high energy electron beam in water treatment is based in the field of radiation chemistry[4]. The purpose of this section is to provide a brief overview of aqueous-based radiation chemistry which is intended to familiarize the reader with the chemistry and show its applicability to achieving the goals and objectives of this project.

Irradiation of pure water results in the formation of electronically excited states and/or free radicals along the path of the electron. 10^{-7} sec after the electron has passed through a solution the products that are present are shown in Equation 1:[4,5]

$$H_2O \text{ -\/\/\/-> } [2.7]\ OH\cdot + [2.6]\ e^-_{aq} + [0.6]\ H\cdot + [0.7]\ H_2O_2 + [2.6]\ H_3O^+ + [0.45]\ H_2 \qquad [1]$$

Unlike photochemical reactions where one photon of light initiates one (molecular) reaction, a high energy electron is capable of initiating several thousand reactions as it dissipates its energy. The efficiency of conversion of high energy electron radiation to a chemical process is defined as G (shown in brackets in Equation 1). G is the number of radicals, excited states or other products, formed or lost in a system absorbing 100 eV of energy. Of the products formed in Equation 1, the most reactive species are the oxidizing, hydroxyl radical (OH·), and the reducing, aqueous electron (e^-_{aq}) and hydrogen atom (H·). Thus, the chemistry of primary interest in the high energy electron irradiation process is that of these three species. The concentrations of these reactive species, at several radiation doses, are summarized in Table 1.

TABLE 1. ESTIMATED CONCENTRATION OF TRANSIENT REACTIVE SPECIES AT SEVERAL DOSES USING HIGH ENERGY ELECTRON IRRADIATION.

	e^-_{aq}	H·	OH·	H_2O_2
DOSE (Mrad)		mM		
1	2.7	0.6	2.8	0.7
2	5.4	1.3	5.6	1.4
4	10.8	2.6	11.2	2.8

High energy electron beam irradiation is the only process that is capable of forming both highly oxidizing and highly reducing reactive species in aqueous solutions at the same time and in relatively the same concentration. Furthermore, no other advanced oxidation process has the capability of generating as high an overall free radical yield per unit energy input as high energy electron beam treatment.

Aqueous Electron. The e^-_{aq} is a powerful reducing reagent with an E° (e^-_{aq} + H ---> ½H_2) of 2.77. The reactions of the e^-_{aq} are single electron transfer, the general form of which is:

$$e^-_{aq} + S^N \text{ -----> } S^{N-1} \qquad [2]$$

The e^-_{aq} reacts with numerous organic chemicals and of particular interest to the field of toxic and hazardous wastes are the reactions with halogenated compounds. A generalized reaction is shown below:

$$e^-_{aq} + RCl \text{ -----> } R\cdot + Cl^- \qquad [3]$$

Thus, reactions involving the e^-_{aq} may result in the dechlorination of organohalogen compounds. Further reaction of the organic radical formed could result in the complete destruction of the compound. The e^-_{aq} also reacts with other organic compounds and would contribute to the removal of these compounds from aqueous solutions.

Hydrogen Atom. The hydrogen atom accounts for approximately 10% of the total free radical concentration in irradiated water. The H· undergoes two general types of reactions with organic compounds, hydrogen addition and hydrogen abstraction.

An example of a typical addition reaction with an organic solute of interest in contaminate source water is that of benzene:

$$H\cdot + C_6H_6 \text{ -----> } C_6H_7\bullet \qquad [4]$$

The second general reaction involving the H· is hydrogen abstraction:

$$H\cdot + CH_3OH \text{ -----> } H_2 + \cdot CH_2OH \qquad [5]$$

Because of the relatively small second order reaction rate constant of H· with the common radical scavengers found in natural waters, it is possible that this transient radical may be important in removing some of the compounds of interest in drinking water treatment. This treatment process is the only one in which this particular radical is formed.

Hydroxyl Radical. The types of reactions that involve the OH· are addition, hydrogen abstraction, electron transfer, and radical-radical recombination.

Addition reactions occur readily with aromatic and unsaturated aliphatic compounds. The resulting compounds are hydroxylated radicals:

$$OH\cdot + CH_2{=}CH_2 \text{ -----> } HOCH_2\text{-}CH_2\bullet \qquad [6]$$

Hydrogen abstraction occurs with saturated and many unsaturated molecules, e.g., aldehydes and ketones:

$$OH\cdot + CH_3\text{-}CO\text{-}CH_3 \text{ -----> } \cdot CH_2COCH_3 + H_2O \qquad [7]$$

Case Studies. All case studies presented in this paper were conducted in Halle-Dieskau, Germany, utilizing a mobile electron beam treatment unit. The electron beam and ancillary equipment are mounted in a 48 foot tractor trailer. The trailer is completely self contained, self-shielded, and has the capability of treating waste flows of up to 50 gpm.

In all cases a 1 m^3 sample of the waste to be treated was transported by tank truck to the mobile unit and transferred into an internal 2 m^3 nalgene vessel. The waste stream was then recirculated through the electron beam treatment process, at a flow rate of 25 gpm, for a total of anywhere between 50 and 199 minutes (a total of 3 to 14 recirculation passes based on time), depending on the wastewater characteristics. The electron beam was maintained at full power for the entire study. Influent and effluent samples were collected by German scientists every one or two recirculation passes; again depending on the waste stream treated.

RESULTS

Table 1 summarizes the results obtained from one of the case studies. The results obtained in this study were typical of those observed for all studies conducted.

TABLE 1. SUMMARY OF ELECTRON BEAM REMOVAL OF VARIOUS ORGANIC COMPOUNDS FROM CASE STUDY #1.

Analyte		Zero Dose	0.7 Mrad	1.4 Mrad	2.8 Mrad	Overall % Removal
Σ Phenol	$\mu g\ L^{-1}$	2230	220	60	20	99.10
Benzene	$\mu g\ L^{-1}$	6200	150	10	3.5	99.95
Toluene	$\mu g\ L^{-1}$	498	9	<1	BMDL	100
Ethylbenzene	$\mu g\ L^{-1}$	118	2	BMDL	BMDL	100
m/p-Xylene	$\mu g\ L^{-1}$	201	4	<1	BMDL	100
o-Xylene	$\mu g\ L^{-1}$	108	2	BMDL	BMDL	100
Σ Aromatics	$\mu g\ L^{-1}$	7125	167	10	3.5	99.95
Naphthalene	$ng\ L^{-1}$	15207			<20	>99.87
Fluorene	$ng\ L^{-1}$	728			<20	>97.25
Phenanthrene	$ng\ L^{-1}$	48			<10	>79.17
Anthracene	$ng\ L^{-1}$	138			<10	>92.75
Pyrene	$ng\ L^{-1}$	56			BMDL	100
Benzo-(a)anthracene	$ng\ L^{-1}$	12			BMDL	100
Fluroanthene	$ng\ L^{-1}$	86			<10	>88.37
Σ PAH	$ng\ L^{-1}$	16277			BMDL	100

BMDL = below method detection limit.

CONCLUSIONS

Work to date has demonstrated that high energy electrons generated by electron beam accelerators can effectively and efficiently treat complex mixtures of hazardous compounds from aqueous solutions. Additionally, the electron beam equipment used for this study can easily be scaled up to handle increased waste stream flows, thereby making this innovative technology economically competitive with existing treatment processes.

REFERENCES

1. Cooper, W.J., M.G. Nickelsen, D.E. Meacham, T.D. Waite and C.N. Kurucz. (1992): High Energy Electron Beam Irradiation: An Advanced Oxidation Process for the Treatment of Aqueous Based Organic Hazardous Wastes. Wat. Poll. Res. J. Canada. 27:69-95.

2. Kurucz, Charles N; Waite, Thomas D.; Cooper, William J.; Nickelsen, Michael G. (1991): High Energy Electron Beam Irradiation of Water, Wastewater and Sludge. Chap.1 In: Advances in Nuclear Science and Technology. Vol.22. (Eds: Lewins, J; Becker, M) Plenum Press, New York, 1-43.

3. Nickelsen, Michael G; Cooper, William J; Kurucz, Charles N; Waite, Thomas D. (1992): Removal of Benzene and Selected Alkyl-Substituted Benzenes from Aqueous Solution Utilizing Continuous High-Energy Electron Irradiation. Environ. Sci. Technol. 26(1), 144-152.

4. Spinks, J.W.T. and R.J. Woods, An Introduction to Radiation Chemistry, John Wiley & Sons, Inc., New York, 1990, pp 574.

5. Buxton, G.V., C.L. Greenstock, W.P. Helman and A.B. Ross. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($^{\cdot}OH/^{\cdot}O^{-}$) in aqueous solution. J. Phys. Chem. Ref. Data, 17: 513-886, 1988.

FOR MORE INFORMATION:

Mary K. Stinson
USEPA Technical Support Branch/RREL (MS-104)
2890 Woodbridge Avenue
Edison, New Jersey 08837-3679
(908) 321-6683

SITE DEMONSTRATION OF THE ZENOGEM™ TECHNOLOGY TO TREAT HIGH STRENGTH WASTEWATERS

Daniel Sullivan
US EPA
2890 Woodbridge Ave
Edison, NJ 08837
(908) 321-6677

Michael Merdinger
Foster Wheeler Environmental Corporation
8 Peach Tree Hill Road
Livingston, NJ 07039
(201) 535-2379

William Kosco
PRC Environmental Management
644 Linn Street - Suite 719
Cincinnati, OH 45203
(513) 241-0149

F. Anthony Tonelli
Zenon Environmental Systems
845 Harrington Court
Burlington, Ontario
Canada L7N 3P3
(416) 639-6320

INTRODUCTION

High strength organic wastewaters are encountered at hazardous waste sites in the form of leachate and in some cases groundwater. The ZenoGem™ Process is designed to remove biodegradable materials, including most organic contaminants, from wastewater to produce a high quality effluent. This technology was accepted into EPA's Superfund Innovative Technology Evaluation (SITE) program in summer 1992; this paper summarizes the technology demonstration performed at a Superfund site in 1994.

DESCRIPTION OF THE TECHNOLOGY

The ZenoGem™ Process consists of an integrated bioreactor and ultrafiltration membrane system, or ultrafilter. After equalization, wastewater enters the bioreactor, where contaminants are biologically degraded. In this tank, a biomass develops which contains bacterial cultures that break down organic contaminants. Ideal conditions for biomass growth are maintained, including introduction of air to assure sufficient aerobic conditions and optimal process temperatures. The contents are constantly mixed by the introduction of air bubbles through a series of manifolds from the tank bottom. The tank is totally enclosed; air is recycled and a purge is emitted through a carbon adsorption unit before being discharged into the atmosphere. A mixture of sludge solids and un- filtered wastewater from the ultrafilter is recycled back to the bioreactor and remains in the treatment system for periods of several weeks. The bioreactor's size is significantly reduced because of this long sludge retention time. Conversely, the hydraulic residence time in the bioreactor is relatively short.

The ultrafilter receives feed flow from the bioreactor. It separates treated wastewater from biological solids and soluble materials with higher molecular weights. Ultrafiltration (UF) is a pressure-driven (typically at 60 to 70 pounds per square inch) cross flow filtration process in which the water to

be processed flows tangentially over the surface of a membrane filter capable of separating both insoluble materials (bacteria, colloids, suspended solids) and higher molecular weight soluble materials from the treated water. The membrane system consists of a series of tubes, in ten-foot modules and approximately three inches in diameter, into which the cylindrical membrane filters are inserted. Feed flow to the UF system is continuously pulled off the bioreactor and fed into the UF system: the treated filtrate (or permeate) flows through the membrane while the remaining feed is concentrated and returned to the bioreactor.

SITE DEMONSTRATION OF THE TECHNOLOGY

The SITE demonstration of the technology was conducted at the Nascolite Superfund site in New Jersey during the period from September through November 1994. The groundwater at this 17.5 acre site is contaminated with volatile organic compounds (VOCs) which result from past operations at the facility, which included manufacturing of polymethyl methacrylate plastic sheets, commonly known as acrylic or plexiglass.

The results of the remedial investigation/feasibility study for this site confirmed extensive contamination of the groundwater with VOCs. In March 1988, a record of decision (ROD) was signed requiring remedial actions of ground water extraction with on-site treatment and re-injection of the treated effluent. Methyl methacrylate (MMA) is the major contaminant, with groundwater levels approximating 12,000 mg/l. Other contaminants at the site include a number of VOCs, including toluene, ethylbenzene, carbon disulfide, styrene, 2,4-dimethylphenol, benzene, trichloroethylene, vinyl chloride.

For demonstrations, the ZenoGem™ process equipment has been mounted inside a trailer. Prior to the EPA SITE demonstration, it has performed major demonstrations on two types of residues: (a) a combination of firefighting training residues and contaminated groundwater containing burned and unburned fuel, and (b) wastewater containing aircraft fire fighting foam compounds, oil, greases, benzene, toluene, ethylbenzene, xylenes and suspended solids.

RESULTS

The results of the 89-day test run conclusively demonstrated the efficient removal of MMA and COD from the highly contaminated groundwater. Due to the timing of the end of the demonstration and the deadline for this extended abstract, the data presented is preliminary and has not yet been validated. The results of the analytical data are shown in Table 1. The concentration of MMA and COD in the groundwater feedstock, permeate, and product are shown in Table 1 as 10-day averages up to the shock loading on November 8. During start-up, process feed rate was approximately 300 gallons per day (gpd) and was gradually increased to 563 gpd by October 11, 1994. After the initial shock loading, the process feed rate started at 50 gpd and lined out at 150 gpd. The resulting reductions in MMA and COD are also shown. The MMA removal was essentially 100% for the entire operation. The COD removal for the permeate averaged 84% up to the shock loading and 95% after the shock loading. The product COD removal averaged 97% for the periods in which data are available.

The shock loading test demonstrated the flexibility of the process in handling a sudden increase of concentration of contaminants. The process was able to withstand the increased concentration and with the reduction of feedrate after the 4-hour shock was able to achieve the 95% reductions in MMA and COD very quickly. This indicated the dynamic nature of this integrated process.

TABLE 1. DEMONSTRATION TEST RESULTS

	Feedstock		Permeate				Product			
	MMA	COD	MMA		COD		MMA		COD	
Date	Conc. (mg/l)	Conc. (mg/l)	Conc. (mg/l)	% Red.	Conc. (mg/l)	% Red.	Conc. (mg/l)	% Red.	Conc. (mg/l)	% Red.
9/2-9/11*	1618	3467	2.968	99.80	467	84.28	N/A†	N/A	N/A	N/A
9-13-9/25	2307	5564	0.743	99.95	452	81.22	N/A	N/A	N/A	N/A
9/26-10/6	2209	5847	0.027	100.0	577	90.54	N/A	N/A	N/A	N/A
10/7-10/19	1720	4694	0.018	100.0	485	89.09	N/A	N/A	N/A	N/A
10/20-10/31	2142	4973	0.020	100.0	1007	78.21	0.020	100.0	54	99.01
11/1-11/7	2134	9317	0.020	100.0	3214	80.83	0.020	100.0	198	96.73
11/8	2020	5910	0.020	100.0	1170	80.20	0.020	100.0	100	98.31
11/8	7140	19600	0.020	100.0	1180	93.98	0.020	100.0	121	99.38
11/9-11/18	6984	17585	0.017	100.0	927	94.67	0.020	100.0	165	99.16
11/20-11/23	8342	19921	0.025	100.0	936	95.27	0.020	100.0	868	95.99

*Average values for days noted.
†Data not available

Overall, the process ran very smoothly. The system was computer controlled with an alarm system that activated a beeper retained by the operator. The run demonstrated that the process operation was so smooth and flexible that unattended operation is extremely viable for extended periods.

The groundwater used for the demonstration was very odoriferous and contained free product. The resulting product from the process was odorless, absent of suspended solids, and was accepted by the local sewage treatment plant for disposal at $22.50 per 6,000-gallon tanker. The sampling and analyses of all of the tankers showed a clear and odorless product.

CONCLUSIONS

The process was very effective in reducing highly concentrated organic contamination to POTW disposable levels. The process effectively demonstrated the complete removal of MMA and over 95% removal of COD.

The process demonstrated unattended operation, flexibility during sustained operations, and an ability to easily handled a four-fold increase in contaminant concentration during shock loading. The process could operate smoothly over a wide range of conditions and would recover quickly from upsets encountered in Superfund operations such as loss of electricity, quadrupling of feed concentration, free product in feedstock, and adverse weather conditions.

RECOVERY OF MONOMERS FROM RECYCLED PLASTICS

Laura L. Sharp (913) 651-4736, Robert O. Ness Jr. (701) 777-5209
University of North Dakota Energy & Environmental Research Center
15 North 23rd Street
Grand Forks, ND 58203
and
Jose M. Sosa (713) 884-0507
Fina Oil and Chemical Co.
PO Box 1200
Deer Park, TX 77536

INTRODUCTION

Plastics make up approximately 20% by volume of the material disposed of in landfills in the United States. The increased interest in recycling has focused attention on ways to expand our current recycling efforts. Such efforts to recycle more of our plastic waste must include versatile processes that can address the heterogeneous nature of postconsumer plastics streams in the most cost-effective manner. Types of commodity plastics typically found in a postconsumer stream include high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polystyrene (PS). In addition to plastics such as these, a number of organic and inorganic constituents will be present, including paper, paint, food, and various metals. These constituents are present as a result of introduction into the plastics during manufacturing (to give a plastic product selective properties) or as residual matter from use by the consumer. The Energy & Environmental Research Center (EERC) is one of several groups in the United States and Europe that, over the last several years, has worked toward developing a process to thermally break down postconsumer plastics to hydrocarbon liquids and gases. Such a process, sometimes referred to as thermal depolymerization, thermal recycling, or feedstock recycling, produces hydrocarbon liquids and gases that could be used for the manufacture of new plastics or other petroleum products. The specific slate of products depends on processing conditions. The EERC has completed studies on various aspects of thermal depolymerization using fluidized-bed technology, including a fundamental examination of the products as a function of temperature, bed material, and feed mix (1). This and subsequent studies have identified several relatively high-value products possible from the process, including ethylene ($C_2^=$), propylene ($C_3^=$), and butylenes. An U.S. Environmental Protection Agency (EPA)-sponsored program at the EERC, just beginning, proposes to better define optimal process conditions for making these olefins (propylene, ethylene, and butylenes). Past work at the EERC has also indicated that optimal processing conditions exist for these olefin yields. The proposed the EPA work is based on information, presented here, that was obtained in studies completed at the EERC under the sponsorship of the American Plastics Council (APC) and the U.S. Department of Energy (DOE).

METHODOLOGY

Two sets of screening tests were completed on the EERC's 1-4-lb/hr continuous fluid-bed reactor (CFBR) bench-scale test unit (Figure 1). The intention of these tests was to determine the effect of temperature and gas residence time on the olefin yield from a postconsumer plastics thermal decomposition process. Two different bed materials, sand and CaO, were used. From earlier work, it was apparent that product yields in general are dependent on feed material, decomposition temperature, gas residence time, and bed material. Twenty-five tests were run in the CFBR, the parameters and yield results of which are given in Table 1. The base blend material, used for the first set of tests, consisted of 60% HDPE, 20% PS, and 20% PP virgin resin (percentages are on a weight basis). The postconsumer

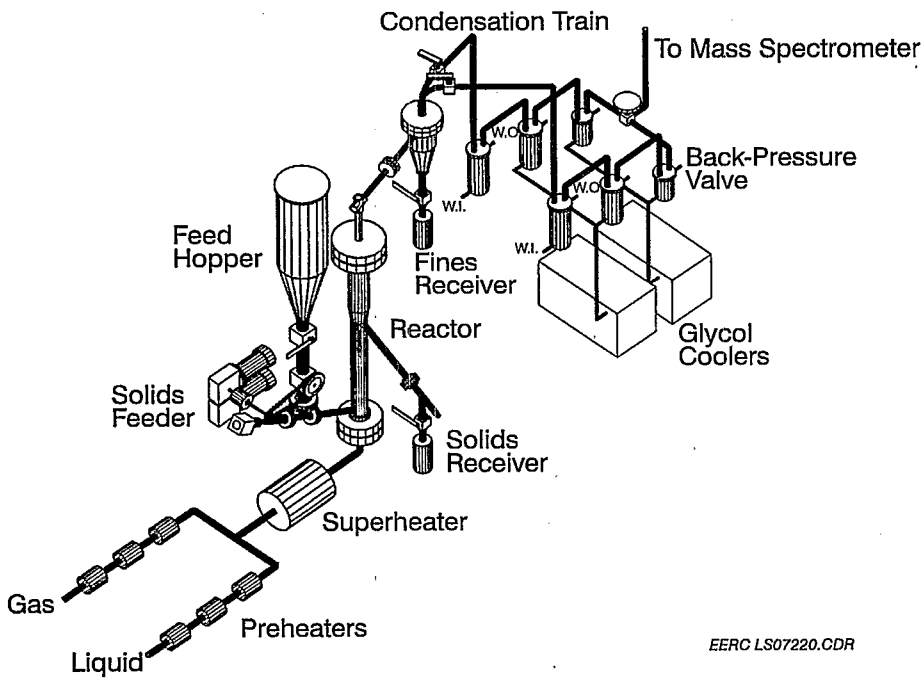


Figure 1. 1-4-lb/hr CFBR unit.

blend, used for the second set of tests, consisted of the following approximate composition 59.2% HDPE, 20.1% PET, 0.6% PVC, 10.7% PS, 10.7% PP, and 4.7% LDPE. The base blend was chosen for the first set of tests in order to separate the coking effects from PET (if any) from the coking that may result from severe temperatures. While coke formation was not quantified, it is desirable to know if it is a result of the particular composition of feed material or of the temperature chosen.

RESULTS

Figure 2 shows the $C_2^=$ + $C_3^=$ yields for the three test series performed with the base blend at residence times of 6, 16, and 30 seconds. Yields are calculated as weight of a particular product divided by the moisture-ash free feed material. The $C_2^=$ + $C_3^=$ yield will be referred to as "the olefin yield." Yield percent is defined as mass of a particular product divided by mass of moisture-, ash-free plastic fed. Even though other olefins (i.e., butylenes) are present in the gas stream, these two components are the most prevalent and will be used as an indication of conversion to olefins. Other components in the product gas stream include H_2, CH_4, CO, CO_2, C_2H_6, C_3H_8 and other hydrocarbon gases up to C_5's. The majority of the product gas stream is N_2 since it is used as the reactor fluidization gas. A small amount of uncondensed liquid are also present. The three test series using base blend were all completed in a sand bed. All three residence time series show an initial increase in olefin yield with temperature, a peak at about 700°C, then decreased olefin yield. This is consistent with earlier work with HDPE, which showed that at the higher temperatures (750°–850°C), liquids became more aromatic, liquid yield increased, and gas yield decreased (1). For the 6-second residence time tests, the $C_2^=$ maximum is at about 750°C, and for $C_3^=$ it is at about 700°C. CH_4 yield increases continually with temperature; H_2 increases until 825°C, where yield drops slightly. For the 16-second residence time test, $C_3^=$ yield peaks at about 650°C, and $C_2^=$ yield at about 700°C. CH_4 and H_2 yields increase with temperature over the entire temperature range. For the 30-second residence time series, $C_3^=$ yield is highest for the

TABLE 1. CFBR TEST RESULTS

Run Number	Temp. °C	Liquid Yield, wt%	Gas Yield, wt%	$C_2^=$ Yield, wt%	$C_3^=$ Yield, wt%	H_2 Yield, wt%	CH_4 Yield, wt%	Material Balance
6-second Residence Time, Base Blend, 10 psig, Sand Bed								
M422	600	72	28	2.1	2.6	0.0	0.7	107
M423	650	45	55	8.0	9.7	0.1	2.4	108
M424	700	30	70	17.9	15.8	0.3	6.0	98
M425	750	35	65	21.0	0.2	0.4	9.6	95
M426	800	32	68	17.4	0.9	1.2	14.0	95
M427	825	50	49	14.7	0.0	1.0	13.4	86
16-second Residence Time, Base Blend, 10 psig, Sand Bed								
M431	600	47	53	11.0	14.0	0.2	4.6	104
M430	650	32	68	15.3	17.2	0.3	6.9	103
M429	700	32	68	22.6	15.2	0.7	14.0	104
M428	750	35	65	21.0	5.6	0.9	16.7	103
30-second Residence Time, Base Blend, 30 psig, Sand Bed								
M432	600	48	50	11.9	15.2	0.2	7.8	101
M433	650	51	49	14.6	13.8	0.4	10.2	96
M434	700	30	70	24.6	7.4	1.1	27.2	105
M435	750	62	36	10.3	0.6	1.2	20.0	88
6-second Residence Time, Postconsumer Plastics Blend, 10 psig, Sand Bed								
M437	600	30	69	3.6	5.1	0.0	1.2	104
M438	650	13	82	9.3	9.9	0.3	3.9	108
M439	700	8	83	16.5	14.2	0.3	6.0	107
M440	750	13	82	18.2	6.9	0.5	8.7	110
M441	800	8	90	17.0	1.4	1.1	10.4	104
6-second Residence Time, Postconsumer Plastics Blend, 10 psig, CaO Bed								
M442	600	51	47	7.9	10.3	0.4	2.7	108
M443	650	30	60	16.8	19.3	0.7	6.0	96
M444	700	29	69	19.4	13.9	0.9	8.4	122
M445	750	28	69	32.1	0.0	1.5	17.7	117
15-second Residence Time, Postconsumer Plastics, 10 psig, CaO								
M447	700	28	59	21.7	6.9	1.3	18.4	106
M446	750	30	53	22.0	0.0	1.2	18.3	117

600°C test. $C_2^=$ and CH_4 yields peak at around 700°C, and H_2 yield increases over the entire temperature range. It should be noted that no tests were completed above 750°C for the 16- and 30-second residence time series because of prohibitive amounts of coking.

Figure 3 shows the $C_2^= + C_3^=$ yields for the three test series performed with postconsumer plastics at residence times of 6 and 15 seconds. Test series were completed using a sand bed at 6 seconds and a CaO bed at 6 and at 15 seconds. For the series in a sand bed, maximum olefin yield occurred at 700°C, similar to the series using the base blend. Ethylene yield peaked at 750°C, and $C_3^=$ yield at 750°C. The series in a CaO bed, however, had its maximum olefin yield at 650°C. Here, $C_2^=$ yield again peaked at 750°C, while $C_3^=$ reached a maximum at 650°C. CaO has been observed to act as a cracking agent, lowering the temperature required to produce a specified liquid yield, relative to sand (1). Only two tests were completed at the 15-second residence time because of a lack of time. These two points, though, are seen to follow the same general trend of lower olefin yield with increased temperature after the maximum.

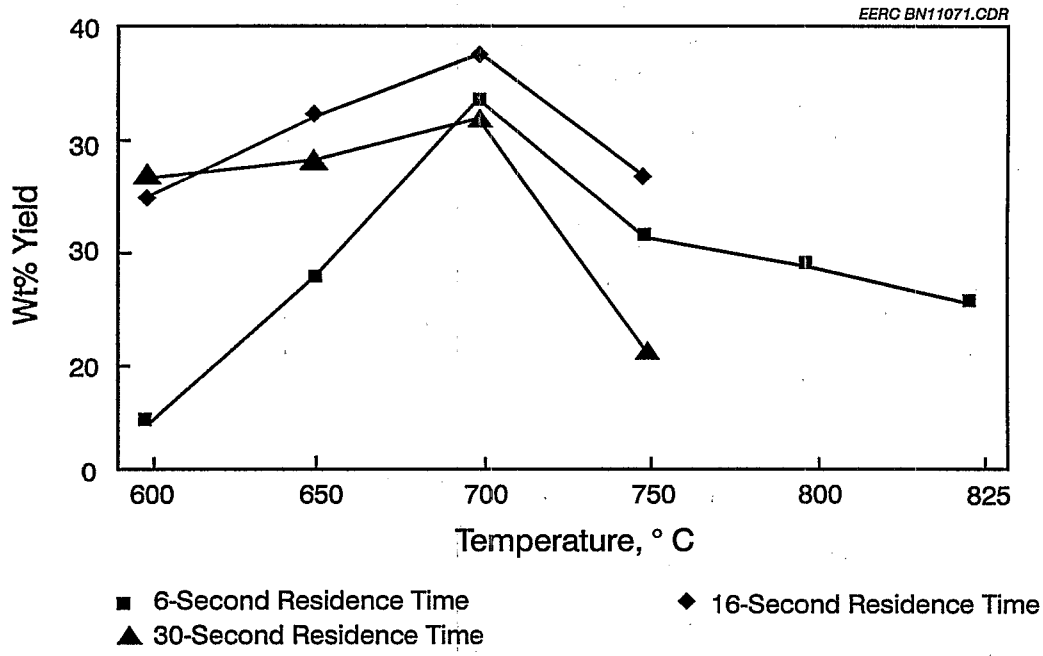


Figure 2. $C_2^{=} + C_3^{=}$ Yield from base blend in a sand bed.

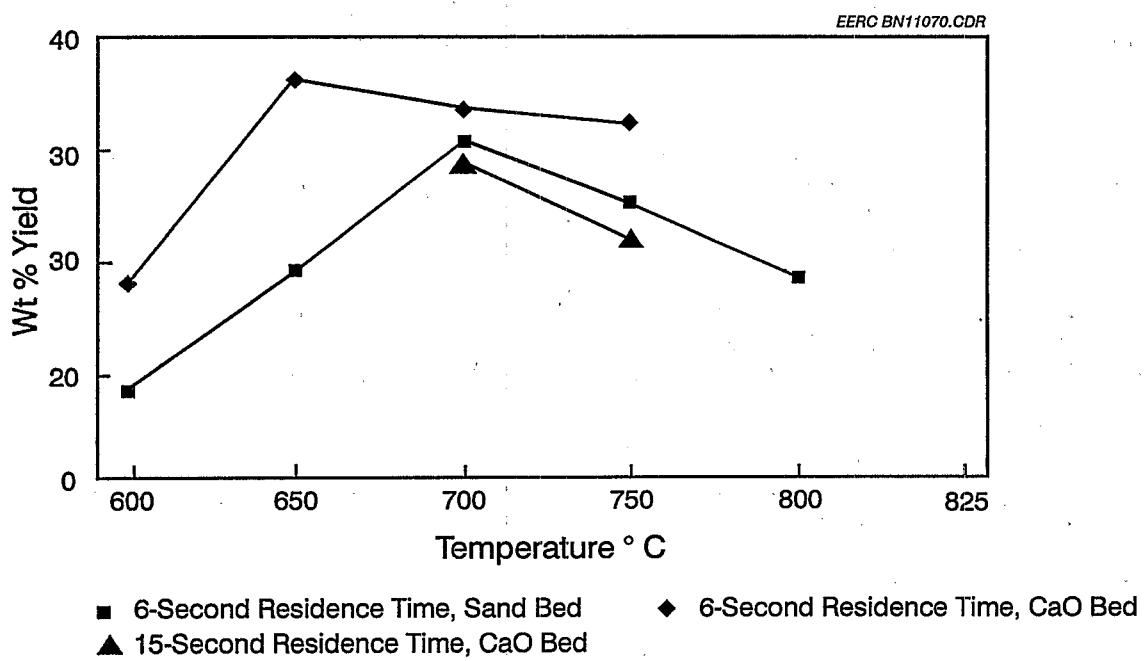


Figure 3. $C_2^{=} + C_3^{=}$ yield from postconsumer plactics.

Referring to Table 1, the base blend tests had maximum combined $C_3^=$ and $C_2^=$ yields at 700°C for all three residence times examined. The highest combined $C_3^=$ and $C_2^=$ yield occurred at a residence time of 16 seconds (38%), followed by the 6-second residence time (34%). For the postconsumer tests, the highest combined yield was at a temperature of 700°C for the 6-second sand bed test (31%), and at a temperature of 650°C for the 6-second CaO bed test (36%). The highest overall $C_3^=$ and $C_2^=$ yield, 38%, occurred at a 16-second residence time and a temperature of 700°C, using the base blend.

Conditions for producing olefins will also produce significant quantities of liquids. The character of the liquids from the tests presented here was determined using a gas chromatography flame ionization detector (GC-FID) to obtain simulated boiling point distributions and also by comparing this information with gas chromatography mass spectroscopy (GC-MS) data from known plastics decomposition products to identify specific components. These liquids are fairly aromatic and may be useful as a chemical feedstock.

CONCLUSIONS

The two most important conclusions from the olefin work performed to date at the EERC are 1) olefin yield from a thermal depolymerization process depends on decomposition temperature, gas residence time, feed material mix, and bed material and 2) a temperature can be identified for maximum olefin yields (at a fixed gas residence time and with a specific bed material). For an inert (sand) bed, the temperature for maximum olefin yield is about 700°C, and for a CaO (catalytic) the temperature is about 650°C. The existence of a maxima for olefin yield is of particular importance; if plastics are decomposed at a temperature higher than the optimal temperature for olefin yield, overall gas yield decreases, and the relative percentages of $C_2^=$, $C_3^=$, and $C_4^=$ in the gas stream decrease, while those of H_2 and CH_4 increase. CaO bed material acts as a catalyst, enabling processing at lower temperature with equivalent yields, relative to a sand bed. This effect was also observed in an earlier depolymerization studies at the EERC (1). In the upcoming work for EPA, temperature and residence time will be focused to a smaller range of conditions to more narrowly define the optimal process conditions. The effect of pressure is also being contemplated, as the olefins produced will be introduced into an (pressurized) olefin plant.

The effect of PET in thermal depolymerization processes has been examined in the APC/DOE-sponsored projects, as well as in a project for 3M. PET will be present in postconsumer streams in concentrations of 10% to 30% and has been seen to have a significant impact on fluid-bed operation and on liquid products. PET will continue to be considered in all of the research efforts concerning thermal depolymerization at the EERC.

A decision, based on an economic evaluation of the process will have to be made as to the fate of the liquids coproduced from a plastics-to-olefins process. These liquids will either be considered a coproduct or recycled to the process. Future efforts will include characterization of these liquids.

REFERENCES

1. Sharp, L.L.; Ness, R.O.; Aulich, T.A.; Randall, J.C. "Thermal Recycling of Plastics," EERC publication, March 1994.

FOR MORE INFORMATION

Don Brown, Office of Research and Development Risk Reduction Engineering Laboratory, USEPA (MLK-437), Cincinnati, OH 45268, (513) 569-7630.

TWO-PHASE OZONATION OF CHLORINATED ORGANICS

Dibakar Bhattacharyya, Amy Freshour, and Dan West

Department of Chemical Engineering
University of Kentucky
Lexington, KY 40506-0046
(606)-257-2794

INTRODUCTION

In the last few years the amount of research being conducted in the field of single-phase ozonation has grown extensively. However, traditional aqueous-phase ozonation systems are limited by a lack of selective oxidation potential, low ozone solubility in water, and slow intermediate decomposition rates. Furthermore, ozone may decompose before it can be utilized for pollutant destruction since ozone can be highly unstable in aqueous solutions. Naturally occurring compounds such as $NaHCO_3$ also affect ozone reactions by inhibiting the formation of OH· free radicals. To compensate for these factors, excess ozone is typically supplied to a reactor. Since ozone generation requires considerable electric power consumption (16 - 24 kWh/kg of O_3), attempts to enhance the ozone utilization rate and stability should lead to more efficient application of this process to hazardous waste treatment.

To improve the process, ozonation may be more efficiently carried out in a two-phase system consisting of an inert solvent (saturated with O_3) contacted with an aqueous phase containing pollutants. From practical considerations, the non-aqueous phase must meet the following criteria: 1) non-toxic, 2) very low vapor pressure, 3) high density (for ease of separation), 4) complete insolubility in water, 5) reusability, 6) selective pollutant extractability, 7) high oxidant solubility, and 8) extended O_3 stability. Previously published studies (1) have indicated that a number of fluorinated hydrocarbon compounds fit these criteria. For this project, FC40 (a product of 3M Co.) was chosen due to its low vapor pressure (3 mm Hg) and high specific gravity (1.9). The primary advantages of the FC40 solvent are that it is non-toxic, reusable, has an ozone solubility 10 times that of water, and that 85 % of the ozone remains in the solvent even after 2 hours. This novel two-phase process has been utilized to study the rapid destruction of pentachlorophenol (PCP), 1,3 dichlorobenzene (DCB), trichloroethylene (TCE), and organic mixtures.

METHODS

Ozonation studies were conducted using pentachlorophenol (PCP), trichloroethylene (TCE), and 1,3-dichlorobenzene (DCB) (Aldrich Chemical) as parent compounds. For all experiments, the non-aqueous solvent was FC40, obtained from 3M Co. The initial concentration ranges were varied for each compound: PCP at 10 - 100 mg/L for pH 3.5 - 11.7, TCE at 1442 mg/L for pH 4.4 - 10.0, and DCB at 26 mg/L and 78 mg/L for pH 2.1 - 11.2. The first stage of the study was to determine the partitioning coefficient for each compound studied. The next stage consisted of determining the effect of various variables on parent compound degradation (such as the ratio of O_3 to pollutant, reaction time, and initial pH).

Analysis of the parent compounds in the aqueous phase were conducted following the guidelines outlined EPA Methods 624 and 625 using a Hewlett-Packard 5890 Series II Gas Chromatograph with an attached 5971A Quadrupole Mass Selective Detector (GC/MS) equipped with NIST/EPA/MSDC 49K Mass Spectral Database. For analysis of the solvent phase, the parent compounds were extracted with methanol and analyzed by GCMS. Besides quantifying the parent compounds, selected intermediates and reaction products were also analyzed. Organics acids from PCP ozonation were monitored on HPLC

was 3 mg/L with ± 3% reproducibility. Chloride concentration in the aqueous phase was measured by an Orion combination electrode (Model 96-17B) with a reproducibility of ± 4%. In order to measure ozone concentration in the solvent phase, the modified indigo dye method was utilized (2). For quick analysis of ozone, the concentration could be determined by measuring the absorbance at $\lambda = 290$ nm with a Bausch and Lomb Spectronic 1001 spectrophotometer.

RESULTS

The major focus of this research was to quantitatively establish the feasibility of degrading chlorinated organics in a short reaction time. The major variables studied were O_3 dosage, feed pH, and reaction time. The experiments were characterized in terms of parent compound degradation, pH drop, free chloride formation, and selected intermediate identification. The only source of ozone is the solvent (FC40) phase. Feed ozone dosage is reported in terms of molar ratio of ozone to parent compound (M). Percent chloride formation is the amount of chloride measured in the aqueous phase after an ozonation run compared to the maximum amount of chloride that can be released by the parent compound. For 100% chloride formation, the compound has achieved complete dehalogenation.

A distribution coefficient, K_D, describes the extent that a compound partitions between the FC40 phase and the aqueous phase. The experimentally determined K_D at pH < pKa is 10.2 for PCP, 5 for DCB, 40 for TCE, and 0.003 for chlorendic acid. For ionizable compounds such as phenols, K_D is dependent on pH. The K_D for PCP at pH 10.3 is 0.03.

To demonstrate ozone stability in the fluorinated hydrocarbon, the solvent (in this case, FC40) was saturated with ozone and removed from the ozone source. No significant change in O_3 concentration was observed after the first five minutes, and after two hours in a closed container with no head space, the O_3 concentration remained steady at 85% ± 2% of the initial concentration. The effect of water phase on ozone decomposition was also established. At least 77% of the initial O_3 concentration remained even after 2 hours (92 mg/L O_3). It should be noted that the solvent used in this experiment had been used repeatedly in ozonation experiments (washed between experiments) for over a year, proving its reusability and capacity for long term ozone stability. Free radical scavengers (3), for example bicarbonate, are compounds which compete with other hazardous organics for the OH• during single phase ozonation. An experiment following the previous conditions was performed with the addition of 20 mM $NaHCO_3$ to the aqueous phase. The addition of sodium bicarbonate (20 mM) increased the ozone stability, with an ozone decomposition of only 10% after two hours.

To study the effect of initial pH on the degradation of PCP, experiments were conducted at pH 3-11 at an ozonation contact time of 5 minutes. Using a 10 mg/L solution of PCP, it was found that there was ~ 95% PCP degradation at initial pH 10.5 for **M** = 4.3, compared to ~ 92% PCP degradation at pH around 4. Since the partitioning coefficient is significantly lower at a higher pH, this result indicates that mass transfer is not a limiting factor in the degradation of PCP in the two-phase system, and that a higher pH is preferred for better PCP destruction. An enhanced reaction rate at a high pH is consistent with single aqueous phase ozonation results reported in the literature (4). PCP ozonation kinetics were studied at an initial pH of 3.5-4.5 and 10.3. The experiments indicate that a total of 79% degradation of PCP occurs within 30 seconds and nearly 92% total degradation occurs after 1 minute (pH=4, **M**=4.3). Faster destruction were found for PCP at a basic pH (**M**=6.66). 95% PCP degradation occurred in the first 30 seconds. Since the parent compound degradation was rapid, the order of the reaction at high pH was determined by varying the feed PCP concentration. The feed was varied from 10 - 100 mg/L while the initial pH, ozone dosage, and reaction time were held constant. First order kinetic rate constants were determined for the high and low pH reactions. These rate constants are respectively 200 min^{-1} and 6.7 min^{-1}. Calculations prove the reactions to be first order.

Within 1 minute, the majority of the bound chloride for PCP was converted to free chloride. All of the free chloride (Cl^-) remained in the aqueous phase, since Cl^- has no affinity for the FC40 phase. Approximately 70% of the bound chloride in the system was converted to free after 1 minute. The remaining 20 - 30 % of the chloride may have been bound within intermediate compounds instead of being converted to free chloride. 90% dechlorination of PCP occurs after 15 minutes in the two-phase batch reactor (M=6.66, pH 10.3). Bicarbonate is a hydroxyl radical scavenger and it has been shown that it can alter pollutant decomposition in a single-phase aqueous system (5). The addition of 20 mM $NaHCO_3$ decreased PCP degradation in the two-phase system by only 3% after 5 minutes reaction time (M=4.3, pH 10.3).

In an attempt to identify some intermediate organic acids formed during PCP ozonation, HPLC analysis was used on the ozonated products. One intermediate was shown to be oxalic acid. Studies by Stowell showed that oxalic acid is a product formed from single phase ozonation of 2-chlorophenol (6). From a calibration of oxalic acid on the HPLC, the maximum concentration of acid produced by ozonation of a 100 mg/L solution of PCP (M = 6.66, 60 minutes, pH 10.3) was determined to be 30 mg/L. Assuming that all the PCP is degraded to oxalic acid only (no CO_2), it would theoretically yield 101 mg/L acid. In order to simulate a continuous reaction system, one study was conducted by continuously bubbling O_3 into the reactor. The ozonation of 100 mg/L PCP (pH 11.7) yielded complete dehalogenation for a 5 minute ozonation (100% chloride formation) and 70 mg/L oxalic acid formation.

For comparison purposes, a single aqueous phase ozonation system was operated with 100 mg/L PCP initially at pH 10.3. Ozone was bubbled directly into the aqueous phase (400 ml) at a rate of 56.5 mg/min with no solvent present. PCP degradation and chloride formation were shown to occur at a slower rate than in the two-phase system. A value of 0.154 min^{-1} was determined as the first order rate constant (R^2 = 0.96) for PCP degradation. This value is 3 orders of magnitude lower than the rate constant in the two-phase system at the same pH (10.3).

PCP not only degrades faster in the two-phase system, but also the O_3 dosage requirement is lower. For 400 mL of solution of 100 mg/L PCP it would require at least 14 minutes reaction time (1200 mg O3) to achieve 90% PCP degradation, whereas over 95% PCP degradation can be acquired for the same volume in less than 5 minutes (48 mg O_3 if equal volumes solvent and water) with the two-phase system. These calculations lead to 25 times more ozone requirement in the traditional single-phase system. This value is significant because ozone generation requires substantial electrical power which increases operating costs.

The effect of molar ratio was found to be negligible for the degradation of both 1,3-dichlorobenzene (DCB) and trichloroethylene (TCE) so long as O_3 was in excess. To determine the effect of time on DCB degradation, individual runs were conducted with a feed solution of 77.3 mg/L and the reactions were quenched at 1, 5, and 10 minutes. Results showed that degradation occurred mainly in the first minute, and then appeared to cease after the first minute. Approximately 35 % of the DCB had been degraded and 30 % of the chloride was released, and these values remained relatively constant for the rest of the reaction, even after 120 minutes. To determine why the reaction slowed after the first minute, the experiments were repeated and the ozone concentration in the FC40 was quantified using the modified indigo dye method. The ozone concentration dropped significantly within the first five minutes. With a low ozone concentration, the ozone might not be in excess, and may have become a limiting reactant.

To study the effect of ozonation time on TCE, several semi-batch experiments were conducted in the 1 L reactor vessel. For the experiments, 500 mL of FC40 was saturated with ozone. Next the ozone was turned off and 300 mL of water buffered to pH 10.3 with 0.05 M KH_2PO_4added to the vessel. Finally 0.732 mg of TCE was pipetted into the vessel and the ozone was turned on again. A steady-state ozone concentration of 30 mg/L was measured in the solvent phase by the modified indigo dye method. If the solution were in equilibrium, these conditions would result in an aqueous TCE concentration of 36 mg/L

and a solvent phase concentration of 1442 mg/L. For a reaction time of 110 minutes, complete mineralization of TCE was achieved. The plot of the natural log of the percent chloride released versus time proved that the mineralization reaction was first order with an apparent rate constant of 0.036 min^{-1}. In order to rapidly dehalogenate TCE, other researchers have utilized UV light (7,8). As a comparison to literature, Sundstrom reported a first order rate constant of 0.0903 min^{-1} for the degradation of TCE in a H_2O_2/UV system (8). This indicates that TCE degradation by two-phase ozonation is 3.5 times faster than H_2O_2/UV.

Previously, studies had been conducted with only one parent compound present initially. Therefore, experiments were conducted with a mixture of compounds to study the effect that the presence of other organics might have on the degradation of each compound. The mixture examined contained 21.0 mg/L pentachlorophenol, 38.6 mg/L 1,3-dichlorobenzene, and 29.3 mg/L trichloroethylene. Pollutant degradation was determined by analyzing free chloride released, PCP concentration in the aqueous phase, and DCB concentration in the solvent phase. The chloride results from a batch reaction with pHi 10.3 (unbuffered) and equal volumes of solvent and water show that ~ 65% total dehalogenation occurs within 10 minutes. Within one minute, the pH dropped to 6.2, thus indicating significant organic degradation. The K_D values were taken into account when calculating compound concentrations. PCP degradation occurred similarly as it did in a system containing only PCP with ~ 95% degradation in 5 minutes, but DCB degraded faster than in a DCB only system with 70% degradation within 1 minute. This behavior might be explained by an increase in the production of OH• that are formed as a result of PCP degradation, however, increased PCP concentration did not increase DCB or TCE degradation.

A two-phase system with a continuous supply of O_3 was operated with the same mixture solution. It was found that the total chloride released is greater than it is for a batch reaction with as much as 78% dechlorination after 30 minutes. Although at 5 minutes there is a comparable amount of Cl^- released (approx. 65%) for both the batch and semibatch systems, at 10 minutes, where there is no increase in dechlorination for the batch system (probably due to O_3 requirements), there is an increase with the continuous ozone supply.

CONCLUSIONS

Overall, the two-phase ozonation system showed superior performance over single-phase systems in several areas: higher ozone solubility and stability, lower ozone generation requirements, faster pollutant destruction rates, and the potential for selective oxidation. Also, the solvent was reused repeatedly for over a year, proving its reusability. The solubility of ozone in FC40 is ten times higher than in water. Where O_3 decomposes completely within 40 minutes in water (pH 6), ozone in FC40 has decomposed only 10 % within the same amount of time. A comparison between single and two-phase ozonation systems with PCP showed that ~ 25 times more ozone must be used for a single phase system to achieve at minimum 90% PCP degradation.

In terms of pollutant degradation, the first order reaction rate constants for PCP and TCE were orders of magnitude larger in the two-phase system than in single phase systems. The presence of a free radical scavenger (sodium bicarbonate) in the aqueous phase did not inhibit the degradation of PCP. Actually, 20 mM $NaHCO_3$ decreased the rate of ozone decomposition by a factor of ~ 10. Complete dechlorination of PCP was still achieved after only 5 minutes when bicarbonate was present.

DCB and TCE were shown to degraded faster when reacted in a solution of PCP, DCB and TCE than in a single-pollutant system. It was also shown that using a continuous supply of ozone to the two-phase system increased the amount of free chloride released for the mixture solution.

REFERENCES

1. Stitch, F. A. and D. Bhattacharyya. Ozonolysis of Organic Compounds in a Two-Phase Flurocarbon-Water System. Env. Progr. 6: 224-229, 1987.

2. Bhattacharyya, D., T. F. vanDierdonck, S. D. West, and A. R. Freshour. Two-Phase Ozonation of Chlorinated Organics. J. Haz. Mat. In Press, 1994.

3. Singer, P. C. Assessing Ozonation Research Needs in Water Treatment. Journal AWWA. 82(10): 78-88, 1990.

4. Hoigne', J. and H. Bader. Rate Constants of Reactions of Ozone with Organic and Inorganic Compounds in Water-II, Dissociating Organic Compounds. Water Res. 17: 185-194, 1983.

5. Reckhow, D. A., B. Legube and P. C. Singer. The Ozonation of Hazardous Halide Precursors: Effect of Bicarbonate. Water Res. 20(8): 987-998, 1986.

6. Stowell, J. P., J. N. Jensen and A. S. Weber. Sequential Chemical/Biological Oxidation of 2-Chlorophenol. Env. Sci. Tech. 26(9-11): 2085-2087, 1992.

7. Glaze, W. H. The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and UV Radiation. Ozone Sci. & Eng. 9: 335-352, 1987.

8. Sundstrom, D.W., H.E. Klei, T.A. Nalette, D.J. Reidy, and B.A. Weir. Destruction of Halogenated Aliphatics by Ultraviolet Catalyzed Oxidation with Hydrogen Peroxide", Hazardous Waste & Hazardous Materials, 3: 101-110, 1986.

FOR MORE INFORMATION: Contact Richard P. Lauch, U.S. EPA, RREL, Cincinnati, OH 45268, Phone No. 513-569-7237

EVALUATION OF BASE-CATALYZED DECOMPOSITION (BCD) PROCESS FOR NEW YORK/NEW JERSEY HARBOR SEDIMENT DECONTAMINATION

Dennis L. Timberlake
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 W. Martin Luther King Drive
Cincinnati, OH 45268

INTRODUCTION

Dredging and disposal of sediments from the New York/New Jersey Harbor (Harbor) are conducted on a regular basis to ensure that shipping channels are maintained for safe navigation. Sediments that accumulate in these areas may contain a variety of contaminants at concentrations that pose a range of potential risks to ecological and human health. Heavy metals (Hg, Cd, Pb, Ni, Cu, Zn, and As), chlorinated pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and dioxins are the major contaminants of concern in the Harbor.

Most sediments dredged from the Harbor have been disposed at the New York Dredged Material Disposal Site which is located six miles off the New Jersey coast. Such material must pass recently revised tests for ocean disposal of dredged material, however. The updated testing manual contains more stringent chemical and biological testing guidelines for determining the suitability of dredged sediments for ocean disposal. As a result, the volume of contaminated dredged material prohibited from unrestricted ocean disposal may increase dramatically. Although alternatives to ocean disposal have been investigated on a preliminary basis, presently there are no long term non-ocean disposal alternatives in operation in the Harbor region.

The U.S. Army Corps of Engineers, in consultation with the U.S. Environmental Protection Agency, identified existing technologies for the treatment of contaminated dredged material. Screening level bench-scale tests were performed with the most promising technologies. The Base-Catalyzed Decomposition (BCD) process was one of the technologies tested at the bench-scale level which demonstrated high removal efficiencies for dioxin. The fact that the BCD process actually destroyed dioxins rather than merely removing them was a significant advantage.

Based on the promising screening level bench-scale tests, the decision was made to conduct a field demonstration of the BCD process. Prior to conducting the field demonstration, it was necessary to conduct detailed bench-scale tests, the results of which would be used to size equipment and determine operating conditions for the pilot unit. This paper details the results of these bench-scale tests.

METHODOLOGY

BCD is a two-stage chemical process which operates at moderate temperatures to remove organic contaminants and decompose chlorinated hydrocarbons from soils and sediments. In the first stage, sodium bicarbonate is added to the sediment, which is heated to about 340 C. As a result, (a) water is evaporated and separated from the sediment into one waste stream, and (b) organic contaminants are partially decomposed and removed in another waste stream. In the second stage, sodium hydroxide, a hydrogen-donor oil, and a catalyst are added to the organic waste stream at 340 C.

Sediment was collected from three Harbor sites: Newark Bay, Arthur Kill, and Newtown Creek. The plan was to use one of the sediments for initial tests to determine optimum conditions and then to

treat all three of the sediments at the optimum conditions. The Newtown Creek sediment was chosen as the sediment for the optimization tests because it had the highest concentration of the higher chlorinated dioxin, furan, and PCB congeners. The untreated sediment had a total dioxin concentration of 18 ppb (10 ppt 2,3,7,8-TCDD), a total furan concentration of 4 ppb, and a total PCB concentration of 1.5 ppm.

RESULTS

Three process variables were evaluated during the Stage 1 optimization tests: contact time, sodium bicarbonate dosage, and water content of the feed. The tests revealed that a contact time of one hour, a sodium bicarbonate dosage of 10%, and the use of a predried feed material resulted in the greatest destruction of dioxins. In addition to the treated sediment, the process also produced an aqueous condensate and an oil condensate.

While some destruction of chlorinated organics occurred in the Stage 1 reaction, the bulk of the chlorinated organics were transferred to the oil condensate. The oil condensate was to be treated by addition of the BCD reagents, but the aqueous condensate required only polishing. Oil extraction, flocculation, and carbon treatment were considered as treatment options. Testing revealed that a combination of flocculation and carbon treatment provided the highest removal efficiencies of chlorinated organics from the aqueous condensate.

Funds did not exist to treat all three sediments as planned, so only the Newtown Creek sediment was run at the optimum conditions. Four runs were performed to collect sufficient sidestream material to allow for characterization. The oil condensate underwent the Stage 2 BCD reaction with the addition of sodium hydroxide, catalyst, and a hydrogen donor. The aqueous condensate was treated with flocculants followed by carbon.

Preliminary results from the bench-scale testing indicate that the percent removals of dioxins, furans, and PCBs from the sediment were >99% with total dioxin and furan concentrations in the treated sediment at non-detect levels and total PCBs at 22 ppb. The aqueous condensate was relatively free of contaminants prior to flocculation and carbon treatment and these contaminants were at non-detect levels after polishing. The bulk of the contaminants ended up in the oil condensate where Stage 2 BCD treatment resulted in destruction efficiencies >99%.

There was no evidence of dioxin/furan destruction in the Stage 1 reactor, but there was evidence of partial dechlorination and congener shifting. Essentially all of the dioxins and furans ended up in the oil condensate where Stage 2 destruction efficiencies exceeded 99%. About 50% of the PCBs were completely dechlorinated in the Stage 1 reactor. The remaining 50% showed up in the oil condensate and were completely destroyed during the Stage 2 reaction.

Using the bench-scale data, a mass balance of the BCD process revealed that for every ton (2000 lbs) of wet sediment (67% water content) treated, 0.33 tons (660 lbs) of treated solids, 163 gallons of aqueous condensate, and 1.3 gallons of oil condensate would be generated. Contaminants from one ton of contaminated sediment would be concentrated into the 1.3 gallons of oil condensate where Stage 2 treatment would completely dechlorinate the remaining dioxins, furans, and PCBs.

CONCLUSIONS

The BCD process was successful in destroying chlorinated organic material present in Newtown Creek sediments collected from the New York/New Jersey Harbor. Destruction efficiencies for dioxins, furans, and PCBs were >99% and concentrations in the treated sediment were at or below detection limits.

Having completed the bench-scale testing portion of this study, effort is now being directed towards the pilot-scale field demonstration of the BCD process. The demonstration is being planned for the summer of 1995.

FOR MORE INFORMATION CONTACT:

Dennis L. Timberlake
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 W. Martin Luther King Drive
Cincinnati, OH 45268
(513)569-7547

ELECTROKINETIC SOIL REMEDIATION: IMPACT OF AQUEOUS PHASE PROPERTIES ON SOIL SURFACE CHARGE AND ELECTROOSMOTIC EFFICIENCY

Leland M. Vane and Gwen M. Zang
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
26 W. Martin Luther King Dr. (M/S 443)
Cincinnati OH 45268
Phone: (513) 569-7799

INTRODUCTION

The *in situ* remediation of a contaminated soil is an exercise in mass transfer limitations. The challenge is to mobilize the contaminant and transport it to a treatment/collection zone or to deliver nutrients, microorganisms, or destruction chemicals to degrade the contaminant where it resides. For soils with high hydraulic permeabilities, mobilization or treatment solutions can be hydraulically delivered to the contaminated zones. Mobilized contaminants and degradation products can be removed in the same manner. However, pressure driven hydraulic delivery/removal in low permeability soils, such as clays, is impractical.

One method of transporting solutions and compounds in low permeability soils is the application of an electric current to the soil in a process called Electrokinetic Soil Remediation (ESR). This form of remediation utilizes the response of charged molecules and particles to an applied voltage gradient to effect the movement of pollutants. Driving the remediation are the electrokinetic phenomena of electroosmosis, ion migration (electromigration), and electrophoresis. As depicted in Figure 1, most soil particles, including clays, carry a negative surface charge. When the soil is immersed in an electrolyte, the particles attract cations, creating a positively charged boundary layer (referred to as the *charged double layer*) next to the surface of the soil particles. Application of a voltage difference across a section of soil causes movement of the ions and associated water within the double layer toward the cathode (electron source). The remainder of the pore fluid moves in the same direction as the double-layer fluid due to viscous drag interactions. This net flow of pore fluid due to an applied voltage gradient is termed "electroosmosis" (EO). EO can be utilized to remediate contaminated soils *in situ* by flushing out the pore fluid and contaminants (or to deliver nonionic nutrients, surfactants, etc.).

The ions in the bulk pore fluid also respond to the applied voltage gradient with the anions being driven to the anode and cations driven to the cathode. This movement of aqueous ions and ion-complexes in response to the voltage gradient is referred to as ion migration or electromigration. Electromigration can be used to recover ionic contaminants from soil even in unsaturated soils (1). Larger charged molecules and particles also move due to an applied voltage gradient (electrophoresis). Substances which fall into this latter category include cationic or anionic surfactant molecules and micelles, clay particles, and polyelectrolytes. The degree to which each electrokinetic phenomenon occurs depends on the properties of the soil/pore fluid matrix including the degree of saturation, ionic strength of pore fluid, types of ions/charged particles present, pH of pore fluid, temperature, porosity of soil, soil composition (% clay, type of clay, etc.), and the surface charge of the soil particles. In this paper, the effect of pore fluid properties on the surface charge of clays and the resultant effect on electroosmosis in saturated clays will be examined.

When a charged particle is suspended in an electrolyte, ions with a charge opposite to that of the particle will concentrate in the charged double layer. The velocity of the particle (v_p) when placed in an electric field is dependent on the viscosity of the fluid (η), the applied voltage gradient (E), and the zeta potential (ζ), or surface charge, of the particle as described by Smoluchowski's classic equation (2):

$$v_p = \frac{\varepsilon \zeta E}{\eta} \tag{1}$$

Similarly, when a packed bed of clay particles is saturated with an electrolyte and exposed to a voltage gradient, the electroosmotic volumetric flow rate (q_{eo}) resulting from the movement of solvated ions concentrated outside the stationary layer is described by the Helmholtz-Smoluchowski equation (2):

$$q_{eo} = \frac{-\varepsilon\zeta i}{\eta\lambda_o} An = \frac{-\varepsilon\zeta E}{\eta} An \tag{2}$$

where i is the bulk current density in the sample and λ_o, A, and n are the bulk conductivity, total cross-sectional area, and porosity of the sample, respectively. The ζ of most charged particles is dependent on solution pH, ionic strength, types of ionic species, temperature, and type of mineral. According to equation (2), the electroosmotic flow rate observed in packed beds of charged particles should also be a function of these same parameters. Investigators of electrokinetic soil remediation processes have observed the development of often dramatic pH, conductivity, temperature, and species concentration gradients. The pH gradients arise from electrolysis reactions which occur at the powered electrodes (shown below for unreactive electrodes):

$$\begin{aligned} 2\ H_2O - 4e^- &\rightleftharpoons O_2\Uparrow + 4\ H^+ \quad \text{(Anode)} \\ 2\ H_2O + 2e^- &\rightleftharpoons H_2\Uparrow + 2\ OH^- \quad \text{(Cathode)} \end{aligned} \tag{3}$$

The anode region becomes acidic (pH as low as 2) while the cathode region is basic (pH as high as 12). Unfortunately, models for electrokinetic soil remediation processes have only recently included the ζ as a variable (3,4). Probstein et al. incorporated ζ as a fitting parameter, constant over the entire sample, while Eykholt introduced ζ as a function of pH. Recently, Jacobs et al. mentioned the inclusion of pH and ionic species/concentration effects on ζ in future versions of their model (5).

When electroosmosis is relied upon to transport contaminants (as with uncharged contaminants with or without nonionic surfactants), the time required to remediate a site is proportional to the electroosmotic flow rate - assuming that the contaminant in the pore fluid is in equilibrium with the sorbed contaminants. Therefore, based on equation (2), variations in ζ and E directly impact the remediation time. Even when electromigration is the desired transport process, the amount of electroosmosis must be factored into the remediation scheme. While E can be independently controlled at the electrodes, ζ is determined solely by the subsurface conditions which may be dramatically affected by the remediation process. For this reason, it is critical that the ζ of the soil be evaluated based on the expected conditions during the remediation as well as based on depth and position at the site.

METHODOLOGY

The zeta potentials of small particles in dilute suspensions have been routinely measured using instruments which range from relatively simplistic manually operated optical electrophoresis devices to more involved automated light scattering devices. These instruments allow for the rapid determination of zeta potential as a function of solution properties with a high degree of control over these properties. Therefore, a wide range of variables can be investigated in a reasonable amount of time. Conversely, bench-scale electroosmosis experiments in compressed clay samples suffer from little control over variables such as pH, conductivity, and types of ionic species both as a function of position in the sample and of time. As a result, it is difficult to distill ζ information from bench-scale data, although the larger scale data is required to more fully evaluate the process under field conditions.

The effect of pH, ionic strength, clay type, and ionic species on the zeta potential was evaluated using an automated microelectrophoresis instrument (ZetaSizer 4, Malvern Instruments). Dilute suspension (0.1 g/L) samples of kaolinite, bentonite, and a local silty clay soil were analyzed. Bench-scale electroosmosis experiments were performed with 3" diameter kaolinite clay samples of 1" or 4" length. The samples were placed between electrolyte reservoirs in which platinum electrodes were immersed. The pH and conductivity of the electrolyte was kept constant as was the electric current through the sample. A constant fluid level in the reservoirs was maintained by gravity overflow to a receiving container. The electroosmotic flow rate was determined from the weights of the inflow and outflow bottles for each

reservoir. The voltage gradient across the sample was measured using platinum mesh electrodes pressed into the ends of the sample cell.

RESULTS

The variation of zeta potential with pH for the kaolinite, bentonite, and soil samples in 0.01M KCl is shown in Figure 2. It is apparent that the zeta potentials of bentonite and the soil sample were relatively insensitive to pH. However, the zeta potential of kaolinite was found to be a strong function of pH, ranging from -50 mV under basic conditions to approximately 0 mV at pH = 2.0. Equation (2) predicts that the electroosmotic flow rate-voltage gradient ratio (q_{eo}/E) is proportional to the zeta potential. As a result, the flow/voltage ratio should be pH dependent for packed beds of kaolinite. In Figure 3, the flow/voltage ratio for a 4" long packed kaolinite bench-scale sample is plotted alongside the dilute suspension kaolinite zeta potential data (absolute value), both as functions of pH. As predicted, the flow/voltage ratio displays the same pH dependence as the zeta potential. For the same voltage gradient, the electroosmotic flow rate was about 3 times greater at pH=5.0 than at pH = 2.8. The zeta potential results suggest even more dramatic increases in flow at higher pHs.

The effect of various cations, anions, and ionic strength on the zeta potentials of bentonite and kaolinite was also investigated. Changes in ionic strength (KCl) did not greatly alter the zeta potential of either kaolinite or bentonite. More significant changes were observed when the concentrations of the +2 cations Pb^{2+}, Ca^{2+}, and Cu^{2+} were increased. For example, the magnitude of the zeta potential of bentonite was reduced by 1/3 when the Pb^{2+} concentration was increased to 100 ppm in 0.01M KCl. This same concentration of Pb^{2+}, Cu^{2+}, or Ca^{2+} (in 0.01M KCl @ pH=4) was sufficient to reverse the sign of the charge on kaolinite, indicating that the direction of electroosmotic flow would be reversed. Reduction of the background electrolyte concentration from 0.01 to 0.0005M KCl resulted in kaolinite charge reversal at 10 ppm Pb^{2+}.

CONCLUSIONS

Zeta potential results indicate that the electroosmotic efficiency (flow/voltage ratio) in bentonite should be relatively insensitive to pH and ionic strength variations. The zeta potential of kaolinite, however, was found to be quite sensitive to pH. The electroosmotic efficiency for kaolinite was found to be equally sensitive to pH. Zeta potential results further indicate that the electroosmotic efficiency as well as the direction of electroosmosis in kaolinite will be impacted dramatically by the presence of metal cations. These results suggest that zeta potential measurements could be used to study the impact on electrosmotic efficiency of initial site conditions as well as conditions expected during an electrokinetic remediation process.

REFERENCES

(1) Lindgren, E.R.; Mattson, E.D.; Kozak, M.W.; Electrokinetic Remediation of Contaminated Soils, NTIS Document DE91 018683, SAND--91-0726C.

(2) Hunter, R.J.; Zeta Potential in Colloid Science: Principles and Applications, Academic Press: London, 1981.

(3) Shapiro, A.P.; Probstein, R.F.; "Removal of Contaminants from Saturated Clay by Electroosmosis," Environ. Sci. Technol., 27, 283-291, 1993.

(4) Eykholt, G.R.; Driving and Complicating Features of the Electrokinetic Treatment of Contaminated Soils, Ph.D. Dissertation, The University of Texas at Austin, 1992.

(5) Jacobs, R.A.; Sengun, M.Z.; Hicks, R.E.; Probstein, R.F.; "Model and Experiments on Soil Remediation by Electric Fields," J. Environ. Sci. Health, A29, 1933-1955, 1994.

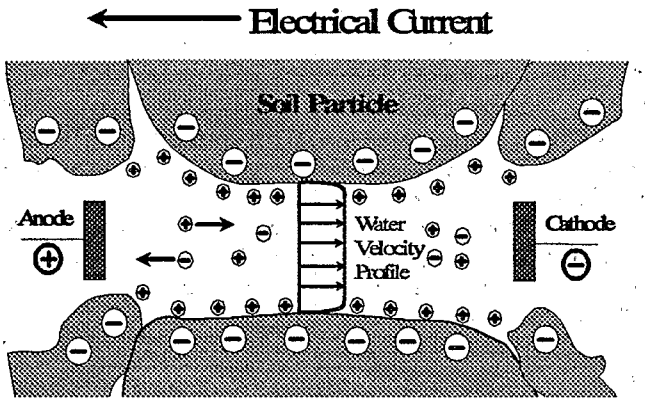


Figure 1. Illustration of Electrokinetic Processes in Soil Pore

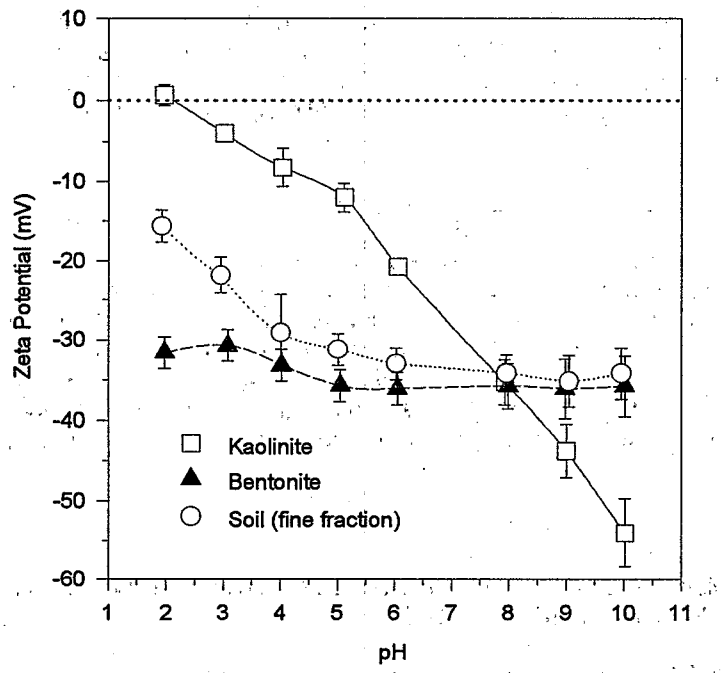


Figure 2. Variation of Zeta Potential with pH for Samples of Kaolinite, Bentonite, and a Silty Clay Soil. (25°C, 0.01M KCl, KCl-treated samples)

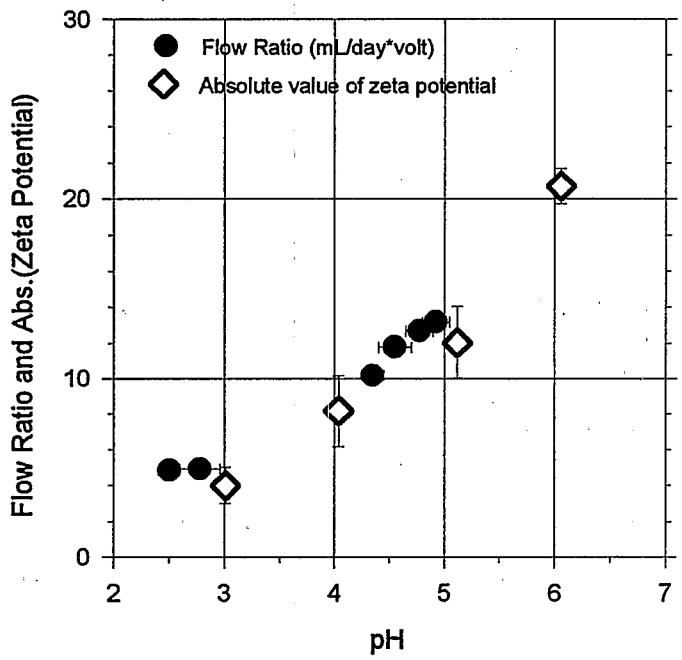


Figure 3. Variation of Flow-Voltage Ratio (mL/day*volt) and Absolute Value of Zeta Potential (mV) with pH for 3" dia. Kaolinite Packed Column (4" length) and 0.1 g/L Kaolinite Suspension, respectively.

FOR MORE INFORMATION

Leland M. Vane
U.S. EPA - Risk Reduction Engineering Laboratory
26 W. Martin Luther King Dr. (M/S 443)
Cincinnati OH 45268
Phone: (513) 569-7799 FAX: (513) 569-7677
e-mail: VANE.LELAND@EPAMAIL.EPA.GOV

BASE CATALYZED DECOMPOSITION - NEW HYDROGEN DONORS AND REACTION ACTIVATORS/CATALYSTS

Fred K. Kawahara and Peter M. Michalakos
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 W. Martin Luther King Drive
Cincinnati, OH 45268

INTRODUCTION

A significant challenge today is the need to develop a fast and complete detoxification process suitable for the destruction of polychloro biphenyl (PCBs) and all those chlorinated organic compounds lying as waste in soils, sediments, water, air and concentrates in waste dumps. This destruction is necessary because PCBs are toxic toward living species: trout have been killed by water containing 8 parts per billion (ppb) of PCBs while shrimp become lifeless when the water is contaminated with only 1 ppb of the toxic substance. Commercial mixtures of PCBs contain more than 50 compounds and are widely used in plasticizers, lubricants, hydraulic fluids, paints, inks, and coatings, as well as heat conductors in transformer fluids. These very stable compounds have persisted since the 1960s, have been recycled through the food chains, and have been found in humans where they cause nausea, dermatitis, bronchitis, and cancer. Since 1976 their manufacture has been banned by the U.S. Environmental Protection Agency owing to the cumulative storage of PCBs in the human body and their extremely high toxicity. Thus, methods for the removal and/or destruction of halogenated organic compounds such as PCBs are required.

The Risk Reduction Engineering Laboratory (RREL) at the EPA in Cincinnati, Ohio, confirmed in January 1989, that a chemical reaction conducted under basic conditions completely removed covalently bound chlorine from a variety of organic compounds. This reaction was referred to as Base Catalyzed Decomposition (BCD).[1,2] Laboratory tests since 1989 have been conducted to confirm the ability of the BCD process to dechlorinate 2,4-D and 2,4,5-T, completely converting the organically-bound chlorine to NaC1.

BCD chemistry has repeatedly demonstrated that it can destroy up to 100,000 ppm of PCBs in dielectric fluids and can also destroy these materials in the lower concentrations found with fluids in a soil matrix. The treatment is similar to the above with variation.[1,2] (An account of substitution processes at low and high temperatures, can be found in the monograph on innovative site remediation technology).[3]

The present Base Catalyzed Decomposition (BCD) process under prescribed conditions of two hours of heating and stirring at 340°C will hydrodechlorinate Aroclor 1242 to the extent of 97 to 99%.[1,2]

An investigation was undertaken of products and the yield of biphenyl from the dechlorination of PCBs resulting from the BCD reaction. One objective of the investigation was to determine the conditions under which complete hydrodechlorination of PCBs can occur at 340°C or lower at two hours or less. A second objective was to isolate and identify products in the "BCD" reaction mixture and thus cast light upon the hydrogen donor-transfer mechanism. Moreover, as the hydrogen radical has been observed to evolve from the donors in a copius manner, it was thought that the surplus, unused gas may be temporarily preserved in the reaction mixture by use of another reagent. (Amorphous carbon has been shown to be somewhat ineffective). An additional aim was to seek an effective, inexpensive catalyst that may accelerate the rate of reaction and shorten the reaction time required for complete hydrodechlorination of the PCBs.

EXPERIMENT

Reagents

Aroclor 1242 (Monsanto) contained 1 wt % monochlorobiphenyl, $C_{12}H_9Cl_1$; 13% dichlorobiphenyl, $C_{12}H_8C1_2$; 45% trichlorobiphenyl, $C_{12}H_7C_3$; 31% tetrachlorobiphenyl $C_{12}H_6C1_4$ and 10% pentachlorobiphenyl, $C_{12}H_5C1_5$. The following blends were used as solvents: n-paraffinic bright stock (PBS, Vulcan Oil Company, Cincinnati); naphthenic bright stock (NBS Vulcan Oil Company, Cincinnati), LW-110 (Sun Oil distillate) and 50W oil (Valvoline lubricant oil, Ashland Oil).

The following were tested as hydrogen donors: No. 5 Fuel Oil, (N5 Boswell Oil Company, Cincinnati); a derivative of No. 5 Fuel Oil; polyisobutene, (L14 Amoco Oil Company, Naperville, IL); polyalphaolefins, Rextac 2715 (R15) and Rextac 2780 (R80 Rexene Products, Odessa, TX); and trisopropyl benzene (Aldrich).

Materials tested as hydrogen acceptors or catalysts include proprietary catalyst; Parasol AN-3S--20% substituted naphthalene-- (Amoco Oil Company, Naperville, IL); Indopol L-14, polybutene polymer, (Amoco Oil); anthracene (An); 97+%, (Aldrich); phenanthrene (Ph), 99%, (Aldrich); and iron powder, Fe, 325 mesh size, (Aldrich).

Reactions

Reactions were conducted batchwise in a 250 ml three-neck flask fitted with two water-cooled reflux condensers, placed in series, a mechanical stirrer, and a thermocouple. The effect of a stainless steel reactor was briefly investigated as indicated in reaction K-182. The flask was heated by a heating mantle connected to a variable autotransformer and insulated with glass wool. Flow of evolved gas was indicated by a rotameter attached to the second serial top of the reflux condenser. The reaction mixture of 45g of solvent oil, 5g hydrogen donors/acceptors, 2.4g sodium hydroxide, 1-3g catalyst and 1g Aroclor 1242 (the nominal PCB content was 20,000 mg/kg) was heated to 280°-340°C for 2-4 h. Samples were obtained from the flask before and after reaction at 25-60°C and diluted 1:18 w:w with n-hexane (gas chromatographic grade, Fisher Scientific).

Analytical Methods

Reagents and reaction samples were analyzed by cool, on-column gas chromatography using a mass selective detector (GC-MSD). A Hewlett-Packard 5890 GC was equipped with Hewlett-Packard 5972 MSD and a J&W deactivated fused silica guard column (5 m X 0.25 mm ID) attached in series with a J&W DB-5MS fused silica capillary column (30 X 0.25 ms ID, with 0.25 um stationary phase coated with DB-5) The following isobaric (12 psig) program was used for the GC oven temperature: 40°C for 5 min, 25°C/min until 180°C, hold for 2.5 min, 5°C/min until 280°C, hold at 280°C for 10 min (or until the signal returns to baseline). Peak areas were summed for the extracted ion chromatogram (EIC) of each class of homologs and compared to calibration solutions of Aroclor 1242 in oil/hexane. Internal standards, spikes, and other quality control measures were used as related in EPA Method 8270B.[4]

RESULTS

Reagent Characterization

The multicomponent hydrocarbon reagents were characterized by GC-MS without a guard column. Various alkanes were detected in PBS including alkyl cyclohexanes, alkyl heptanes, and do-, hexa-, hepta-decanes. The major aromatic and alkane constituents observed in the total ion chromatogram of N5 included alkyl benzenes, alkyl naphthalenes, alkyl anthracene or phenanthrenes, and decanes. Manufacturer's information for the mixture of No. 6 and No. 2 is known to be 60%

alkanes 20% alkyl benzenes for the No. 5 fuel oil of Boswell Oil.

Reaction Solvents

Several high boiling solvents were studied: Paraffinic Bright Stock (PBC), Naphthenic Bright Stock (NBS), 50 W lubricating oil (50 W) (W110 oil (LW110). These were found, from the results of the BCD reaction, to possess varying degrees of hydrogen donation capability which is a function of the geometric constitution of the molecule.

For example, allylic hydrogen attached to naphthalene has a much lower bond strength than when attached to a nonaromatic moiety.

From our test results the hydrogen donor capability appears to be in the order of 50W>NSB>PBS>LW110. Differences in bond strengths, due to the effect of double bond and its location and due to the aromatic structural differences have significant influences in donor-acceptor qualities.

Acceptors-Donors

Test results, from the reaction in which naphthalene or dihydronaphthalene was employed separately, provided additional information that the aromatics are indeed acceptor-donor type of the hydrogen free radicals. However, they can be donor-acceptor-donor type if alkyl groups on the aromatic nucleus are substituted.

Polymers

Polymers act as donor type, releasing only hydrogen free radicals, when they are linear and prepared from a non-aromatic polymer or copolymer. An example is polypropylene.

Polymer may function as donor-acceptor type if an aromatic monomer is used. An example is a polymer made with styrene as a monomer in a copolymer.

Heavy Fuel Oil and Related Products

A limited number of heavy fuel oil or related products were studied as donor and/or acceptor of hydrogen free radicals. These are the following: No. 5 fuel oil (Boswell), No. 5 fuel oil (Ashland), refined oil N464, refined oil K158, refined oil K160.

From the research data No. 5 fuel oil and the N464 appear to possess better efficacy in the conversion of the polychlorobiophenyl to biphenyl as indicated by the percent of PBCs remaining in the test results column using N464 itself or with R15 (a polypropylene polymer).

A New Catalyst

To the modified "BCD" type reaction which utilizes a base, an oligomer (L14), petroleum solvent 3S and paraffinic bright stock, we introduced metallic iron particles of mesh size 325 as a possible aid for increasing the reaction rate or decreasing the reaction time. In this reaction 2.6g of L-14, 2.7g of 3S in 34g of PBS with 2.7g of powdered iron were added in a glass flask and heated to 340°C. After one hour, only 3% of PCBs remained. In a similar run when no iron was used 45% and 25% of PCBs remained after two and four hours.

CONCLUSION

We have met the objectives given in the introduction. A number of new hydrogen donors were used in the BCD reaction. One reaction mechanism pathway was discovered; its usage has led to hydrogen radical donor-acceptor transfer-donor reaction. In so doing we have been able to preserve some of the hydrogen radicals generated via use of the dicyclic aromatic which was converted to dihydronaphthalene which then as donor became naphthalene. A new catalyst which is inexpensive has been found effective in this hydrodechlorination of PCBs.

REFERENCES

1. Rogers, C. J., and Kornel, A. Hazpac (1991) 233.

2. Rogers, C. J, Kornel, A. and Sparks, H. L. U.S. Patent 5,064,526, Nov 12, 1991.

3. Weitzman, L. V., Gray, K., Kawahara, F. K., Peters, R. W. and Verbicky, J., "Chemical Technology," Anderson, W. C., ed (1994) American Academy of Environmental Engineers, Annapolis, MD. Kawahara, F. K. "Substitutions Reactions for the Detoxification of Hazardous Chemicals. Report RZ008 Dec. 1994, 35 pages.

4. "Test Methods for Evaluating Solid Wastes," Office of Solid Wastes, U.S. EPA Nov. 1992, SW 846, Third Edition. (Revision 2), Method 8270B.

FOR MORE INFORMATION

Carl A. Brunner
513/569-7655

SWIRL TECHNOLOGY: PROPER DESIGN, APPLICATION, AND EVALUATION

Richard Field and Thomas P. O'Connor
Storm and Combined Sewer Control Research Program
U. S. Environmental Protection Agency (MS-106)
2890 Woodbridge Avenue
Edison, NJ 08837-3679
(908) 321-6674

INTRODUCTION

Swirl and vortex technologies have been with us for over thirty years now, ever since Bernard Smisson incorporated a cylindrical vortex-type combined sewer overflow (CSO) regulator/settleable-solids concentrator into the Bristol, England sewerage system back in the early 1960's. In the early 1970's the U.S. Environmental Protection Agency (EPA) conducted a series of projects to develop and demonstrate swirl flow regulator/settleable-solids concentrator (*swirl*) technology. These projects resulted in the EPA swirl and helical-bend flow regulators/settleable-solids concentrators and the swirl degritter. New generations of this technology emerged after the EPA versions were developed including the Fluidsep™ and the Storm King™ vortex-hydrodynamic separators. However, despite different designs and applications, the main intent of the technologies are the same, i.e., to use the forces that arise from a change in flow direction to enhance settleable-solids separation from the storm flow. A variety of opinions have developed regarding the application of these technologies varying from overwhelming support to detractions that question their effectiveness. This abstract will show that proper design and placement in the sewerage system results in effective use of swirl technology.

Reliable swirl pollution control efficiency determination is principally dependent on proper sampling and suspended- and settleable-solids analysis techniques of the influent and effluent. Simultaneous flowrate measurement is also important. Without the complete capture of heavy and stratified suspended solids (SS) across the influent flow channel or water column, the apparent performance of the swirl will be less than the actual. Particle-settleability tests which are presented, must be conducted before and after installation, but especially before in order to decide if the inertial characteristics of SS in the storm flow warrants the use of a swirl.

General Description. Swirl SS separation performance depends upon its design flowrate, Q_d and the fraction of separable solids included in the total storm-flow influent SS. The swirl was developed through hydraulic modeling studies which used representative settleable particles (based on the Froude Number and Stokes Law) to simulate grit and organics with specific gravities (SG) = 2.65 (fine sand) and 1.2, respectively and effective diameters (d_e) from 0.2 to 5 mm. It is important to appreciate this aspect of the swirl's development and not expect significant removals of fine-grained and/or low-specific gravity particles. Floatables were simulated with a SG range between 0.9 and 0.96 and d_e's between 5 and 500 mm.

Figure 1 is an isometric of the swirl. Flow enters the swirl tangentially and follows the peripheral wall of the cylindrical shell (vortex chamber) creating a swirling-flow pattern. The swirling action causes separable solids to be concentrated at the bottom of the unit. The underflow (6 to 10% of the inflow at Q_d) containing the concentrated separable solids discharges through a foul-sewer outlet in the bottom, while the clarified supernatant exits the top through an annular overflow weir and weir-plate arrangement into a central downshaft for storage, treatment, or discharge. A baffle configuration captures floatables in the supernatant and directs them for containment under the weir plate and weir skirt. The floatables are carried out in the underflow as the storm flow subsides and the water level in the swirl falls. During low- and dry-flow conditions all flow discharges from the bottom foul-sewer outlet. Design information for the swirl is contained in the EPA publication "Design Manual: Swirl and Helical Bend Pollution Control Devices" (Sullivan *et al.* 1982). The design hydraulic loadings (HL) of the swirl typically ranges from 30 to 60 gpm/ft^2 and may vary as a function of the particle-settling-velocity distribution and associated SS removal objectives.

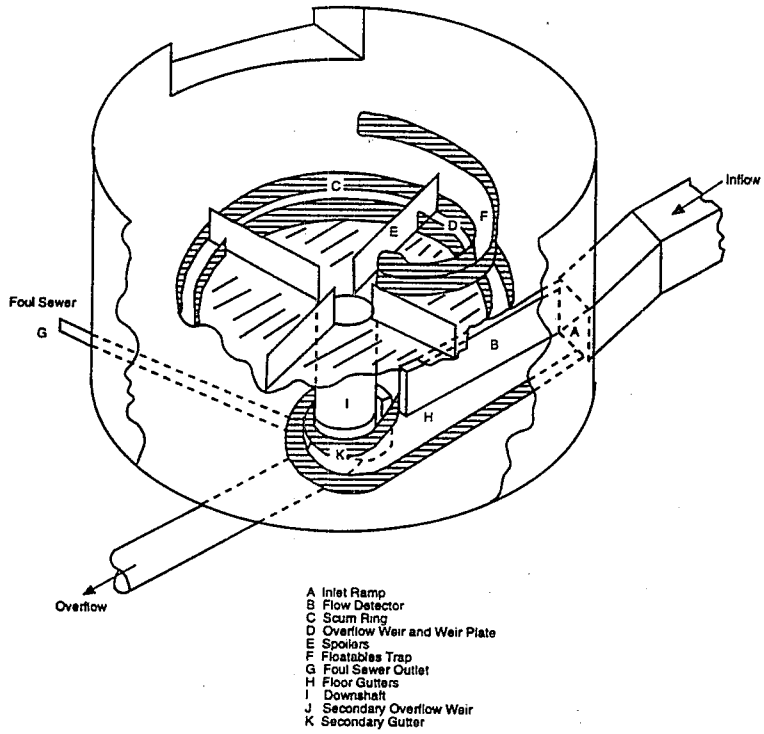


Figure 1. Isometric Drawing of Swirl (Sullivan et al. 1982)

Advantages of the swirl include the three simultaneous functions of flow regulation, settleable-solids concentration, and floatables capture, static operation (no moving parts to induce vortex-flow patterns), and high-rate operation (smaller size and lower cost than sedimentation). Comparatively, Storm King™ and Fluidsep™ designs are deeper and flow regulation is not a primary function. Disadvantages include potential underflow pumping requirements (especially for the Storm King™ and Fluidsep™ due to their relative depth) and a relatively dilute underflow which requires further treatment. Since the foul-orifice diameter is large enough to avoid blockages (> 1 ft diameter), pretreatment by coarse screening is unnecessary (unless the foul underflow is pumped).

Figure 2 is an elevation view of the swirl degritter. The swirl degritter (Shelley *et al.* 1981 and Sullivan *et al.* 1974a, 1977 and 1982) is a variation of swirl technology which does not have a continuous underflow to the wastewater treatment plant (WWTP). Instead a relatively dry mass of settleable solids (grit/detritus) collects in a 60° conical-bottom hopper for intermittent removal.

METHODOLOGY

To properly incorporate swirl and vortex technologies into a combined-sewerage or stormwater-drainage system, their limitations, control functions, applicability, and design idiosyncrasies must be clearly understood. Two major problems that continue to occur, which hinder the effectiveness and reputation of swirl and vortex technologies are: (1) inadequate or faulty sampling techniques for assessment of their applicability, design, and control performance evaluation; and, (2) their inappropriate application or placement in the sewerage system.

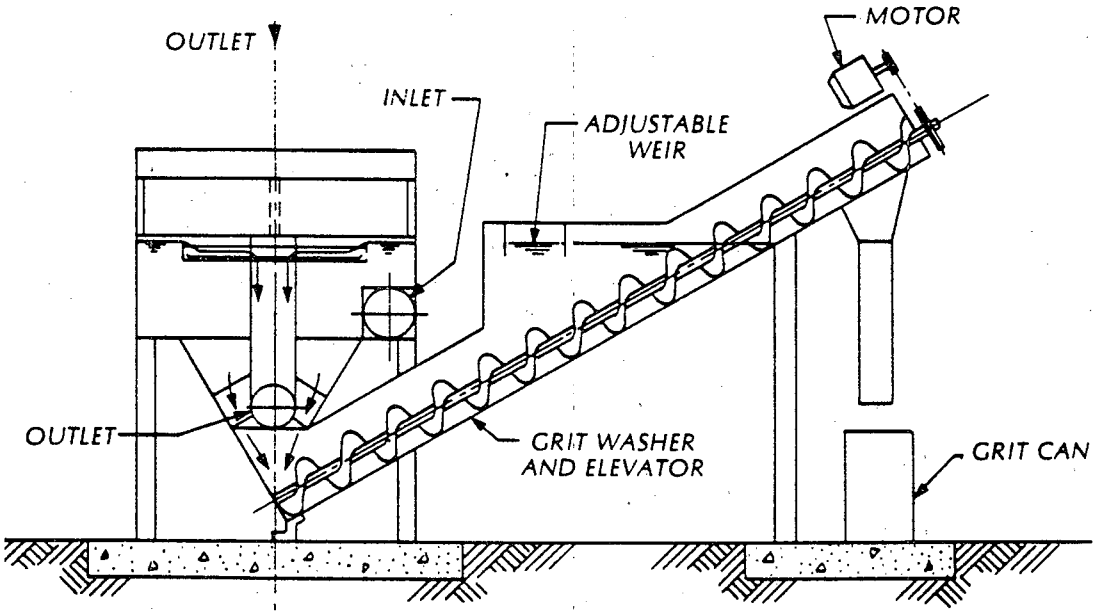


Figure 2. Elevation View of Swirl Degritter (Sullivan *et al.* 1982)

Proper sampling, flow measuring, and analyzing is a must for swirl application assessment, design, and treatability evaluation. The monitoring and analyses needed to properly assess potential application, design, and evaluate the removals of and by a swirl are expensive and complex; however, it may save additional construction costs. Money spent on monitoring and analyses that effectively assesses settleable solids concentration and expected swirl performance may result in lower long-term cost by eliminating unnecessary swirl facilities and/or additional controls.

Design. Prior to selecting the swirl for a combined-sewerage or separately-sewered-stormwater system, representative samples, collected by use of appropriate sampling techniques, should be analyzed for particle-settling-velocity distribution versus SS and associated pollutant content. This analysis will afford the proper assessment of the swirl's applicability. If the storm flow does not contain enough particulate matter with the associated settling velocities of grit-like particles (SG $\geq$ 2.65 and $d_e \geq$ 0.2 mm) and swirl separable-organic particles (SG $\geq$ 1.2 and $d_e \geq$ 1.0 mm), then application of the swirl will prove futile and alternative technologies should be used, e.g., standard, lower-cost flow regulators for situations where flow regulation is the basic objective.

If particle-settling velocities indicate that swirl technology is applicable then, hydrological and hydraulic studies must be conducted to determine the Q_d. This analysis of flow must be done on a long-term basis to achieve the best Q_d and settleable-solids removal prediction by directly measuring flowrates and mathematically modeling for calibration and verification. The use of the design storm concept for flowrate determination and the "polluted segment" for settleable-solids analysis will not give a proper design. To best determine whether the swirl is suited for a particular site, pilot-scale testing should also be conducted. While this increases preliminary design costs, it is only a fraction of the overall construction cost. A pilot test can be set up by diverting a pilot stream from the storm-flow mainstream. A pilot test is the only way of providing direct analyses of swirl treatability.

Under-designing the swirl will lead to poor treatability, while over-designing will lead to a costly and partially useless facility. Q_d selection should also consider the use and advantage of the secondary-overflow weir (emergency spillway) located on the periphery of the swirl. The secondary- overflow weir provides flow relief to maintain a level of settleable-solids separation by decreasing internal vortex flow. Design of secondary-weir elevation should limit the flowrate to the central downshaft to about twice Q_d and allow overflows a few (two to six) times a year while also alleviating upstream flooding.

If site constraints are encountered, the swirl affords some flexibility in its sizing. Depending on depth (e.g., difference in elevation between the trunk combined sewer and the interceptor) and area constraints of the site, the height to diameter configuration of the swirl can be adjusted, i.e., by using a greater diameter for a lesser height (Sullivan *et al.* 1974b and 1982). Design flexibility is also given for separable-solids removal as a function of swirl size, i.e., the greater the removal the larger the required size. Accessibility must also be included for the purposes of maintenance and monitoring. A careful assessment of additional cost requirements must be made before applying the swirl when underflow pumping is required.

Treatability Evaluation. To determine the swirl's settleable-solids treatment effectiveness, sampling techniques have to provide the representative fraction of relatively heavy SS in the influent and effluent channels. Some of the equipment and strategies recommended to achieve this goal are:

1) taking grab samples or 0.2 mm aperture screening (at intermittent, short intervals) of the treated overflow effluent. These samples should not contain significant amounts of grit-like or relatively large organic particles. Capture of theoretically-separable solids indicates poor treatability.
2) sampling for influent SS. To do this properly, samples must be taken across the flow's entire cross-section. This entails having a sampling system with intake velocities greater than the main stream velocity to draw up the heavier particles (particles to be separated out by the swirl) and multi-leveled ports to capture stratified heavy particles. This is essential for determining the SS separation performance of the swirl. Alternatively a "slice-sampler" capable of automatically taking a cross-sectional slice or segment of the whole influent pipe cross-section can be used.
3) performing SS analyses. Four recommended methods of SS analyses are: one for settleable solids (gravimetrically) (Standard Methods 1985) and three for settling-velocity distribution (classical, Brombach or German, and NIVA).

The first item (above) seems obvious but is never practiced. The second is complex and costly; however, without proper and comparative sampling techniques, reliable data and a base of results and performance cannot be established.

Samples taken of the influent and effluent have to be properly analyzed for SS and associated pollutants. A gravimetric (mg/l) settleable-solids analysis (Standard Methods 1985) should be conducted. Three methods for determining the particulate-settling-velocity distributions are the: classical, Norwegian Institute for Water Research (NIVA), and Brombach or German. The Brombach and NIVA methods specifically designed for the relatively high concentration of heavier particles in storm-generated flows, require less analyses, smaller testing volumes (column heights of 60 and 70 cm, respectively compared to 5 ft or greater for the classical method), and are amenable to field use. They also provide better representation of high-settling velocity SS at the test starting time, t_o since the samples are released into a settling column containing tap water from an elevated reservoir. It is almost impossible to attain a homogeneously mixed sample at t_o using a classical settling column.

Floatables Capture Analysis. Besides settleable solids, the swirl also removes floatable matter. A reliable analysis for the removal of floatables has not been done. These analyses are recommended for the assessment of swirl floatables capture ability: eyeball the floatable capture effectiveness; capture of the influent floatables with a coarse screen; and capture of the downstream clarified effluent with a coarse screen.

Placement and Application. Where the swirl is placed in the control system affects its pollutant removal effectiveness. Swirls have been improperly placed in certain projects. Swirls should not be placed downstream of storage/sedimentation basins or after a grit chamber since swirls were developed to remove the relatively heavy particulate matter that would be removed by upstream sedimentation. Effective placement or application of the swirl includes:

- upstream of a CSO storage/sedimentation facility. The swirl reduces the operation and maintenance necessary to remove grit and sludge from the storage facility as the heavier settleable solids are diverted directly to the WWTP.
- downstream of in-line or in-sewer CSO storage. An automated system will be able to maintain an optimum flowrate ($\leq$ twice Q_d) to the swirl which will increase its design effectiveness.
- as a CSO flow regulator/settleable-solids concentrator alone with the relatively clear effluent discharging directly to the receiving water. This applies only to cases where the receiving water can tolerate a partially treated CSO and still meet its water quality objectives.
- upstream of CSO tunnel storage to eliminate the grit removal burden.
- upstream of created wetlands to alleviate settleable and floatable solids problems.
- using the swirl degritter when coarse or preliminary treatment of CSO is the objective and flow regulation or splitting is not required.
- using the swirl degritter on the swirl foul-sewer underflow pipe to remove detritus, especially in cases requiring pumping (Pisano *et al.* 1984) and where the interceptor has a relatively flat slope to decrease wear and sedimentation, respectively.
- as separate stormwater discharge control.

RESULTS

The following case studies demonstrate some of the principles mentioned above. One of the most common occurrences is not making use of settling-velocity data before the swirl is selected for an application. This was inadvertently demonstrated at San Francisco, CA, where a small pilot-scale swirl was tested on dry-weather sanitary sewage. The swirl, as predicted, was not suitable since the settling velocities of the SS in the sanitary sewage were too low and not in the swirl's range of concentrating effectiveness.

In another case, the Northeast Boundary swirl facility in Washington D.C. (O'Brien and Gere 1992) (comprised of three 57-ft diameter swirls each having a Q_d = 133 MGD, with a nominal HL = 35 gpm/ft^2) averaged 38% SS-mass loading *Removal* for all the storm events; however, most of this removal, i.e., 26% was accomplished by direct foul-underflow diversion to the WWTP or *Reduction* and not by the swirl concentrating effect. *Efficiency* (= *Removal* - *Reduction*) was less than expected, averaging 12%. The primary cause of low *Efficiency* was the relatively low SS-settling velocities of particles in the influent CSO (based on settling-velocity-distribution analyses).

The previously mentioned "slice-sampler" was specially constructed during a 1980-81 demonstration in Lancaster, PA (Pisano *et al.* 1984). Prior to using the slice-sampler, the Lancaster swirl had shown "...negligible to negative solids treatment efficiency..." and further that "...samples taken manually for settleability analyses typically contained SS concentrations much lower than concentrations of samples..." taken by the slice-sampler. As compared to a Manning model 6000 sequential sampler, the slice-sampler collected samples 1.5 to 7 times more concentrated with SS. The non-flow weighted average SS *Removal* and *Efficiency* were 55% and 37%, respectively.

A demonstration in Syracuse, NY (Drehwing *et al.* 1979) using a 12 ft diameter swirl having a Q_d = 6.8 MGD with a nominal HL = 40 gpm/ft^2 was evaluated by samplers with an adequate intake sampling technique. SS Mass loading *Removal* and *Efficiency* averaged 52 and 18%, respectively.

CONCLUSIONS

Certain procedures must be followed to maximize swirl application including:

- predetermination of the particulate-settling-velocity distribution of representative samples and/or a pilot study to assess treatment suitability;
- proper placement of the swirl as part of the storage/treatment system (e.g., not downstream of a storage/sedimentation basin, grit chamber, or flow regulator);
- proper selection of Q_d based on a long-term hydrological/hydraulic study;
- use of the secondary- (emergency-) overflow weir on the swirl chamber's outside cylindrical wall to enhance separable-solids concentration at high influent flowrates;
- capture of heavy and sometimes stratified particles for treatability and suitability assessment; and
- applying the right technology, e.g., using the swirl degritter when treatment alone is the objective.

The swirl is a high-rate, relatively small and low-cost device which serves three simultaneous functions: flow regulator, settleable-solids concentrator, and floatables-material collector. The performance of swirl devices is dependant on the settling characteristics of the SS and fraction of dissolved solids in the storm flow. When correctly combined with other controls of the combined-sewerage or separately-sewered-stormwater system, swirl devices will serve a beneficial purpose.

REFERENCES

Drehwing, F.J. *et al.*, Disinfection/Treatment of Combined Sewer Overflows, USEPA, Edison NJ. EPA-600/2-79-134, 1979.

Field, R. and H. Masters, Swirl Device for Regulating and Treating Combined Sewer Overflows, USEPA, Edison, NJ. Report EPA-625/2-77-012, 1977.

O'Brien and Gere Engineers, Inc., CSO Abatement Program: Segment I - Performance Evaluation, Water and Sewer Utility Administration, Washington, DC, April 1992.

Pisano, W.C. *et al.* , Swirl and Helical Bend Regulator/Concentrator for Storm and Combined Sewer Overflow Control, Environmental Design & Planning, Inc., Hanover, MA. EPA-600/2-84/151, 1984.

Shelly, G.J. *et al.*, Field Evaluation of a Swirl Degritter at Tamworth, New South Wales, Australia, G.J. Shelly Consulting Engrs., Tamworth, N.S.W., Australia. EPA-600/2-81-063, 1981.

Sullivan, R. H. *et al.*, The Swirl Concentrator as a Combined Sewer Overflow Regulator Facility, American Public Works Association (APWA), Chicago, IL. EPA-R2-72-008, 1972.

Sullivan, R.H. *et al.*., The Swirl Concentrator as a Grit Separator Device, APWA, Chicago, IL. EPA-670/2-74-026, 1974a.

Sullivan, R.H. *et al.*, Relationship between Diameter and Height for Design of a Swirl Concentrator as a Combined Sewer Over-flow Regulator, APWA, Chicago, IL. EPA-670/2-74-039, 1974b.

Sullivan, R.H. *et al.*, Field Prototype Demonstration of the Swirl Degritter, APWA, Chicago, IL. Report EPA-600/2-77-185, 1977.

Sullivan, R.H. *et al.*, Design Manual - Swirl and Helical Bend Pollution Control Devices, APWA, Chicago, IL. EPA-600/8-82/013, 1982.

A MULTI-CHAMBERED STORMWATER TREATMENT TRAIN FOR THE TREATMENT OF STORMWATER

Robert Pitt, Brian Robertson,
Department of Civil and Environmental Engineering,
University of Alabama at Birmingham,
Birmingham, Alabama 35294

Richard Field
U.S. Environmental Protection Agency
Storm and Combined Sewer Pollution Control Program
2890 Woodbridge Avenue
Edison, New Jersey 08837

INTRODUCTION

Runoff from paved parking and storage areas, and especially gas station areas, has been observed to be heavily contaminated with concentrations of many pollutants being 3 to 600 times greater than typical receiving water criteria. These paved areas are usually found to contribute most of the toxicant pollutant loadings to the stormwater outfalls in residential and commercial areas. PAHs, the most commonly detected toxic organic compounds found in urban runoff, are mostly from fossil fuel combustion. These compounds are very hard to control by eliminating their use, and, unfortunately, their control by typical stormwater management practices is not well understood. The major benefit of this research project will be to better understand how these toxicants can be controlled at critical source areas, especially automobile service facilities, with the use of a special treatment device or Multi-Chambered Treatment Train (MCTT).

METHODOLOGY

Earlier bench scale treatability studies of this U. S. Environmental Protection Agency (EPA) sponsored research found that the most beneficial treatment for the removal of stormwater toxicants (as measured using the Microtox™ test) included column settling for at least 24 hours (generally 40% to 90% reductions), screening through at least 40 micron (μm) screens (20% to 70% reductions), and aeration and/or photo-degradation for at least 24 hours (up to 80% reductions) (1). Based on these tests and a computer model based upon hydrologic conditions in Birmingham, Alabama, a pilot-scale MCTT has been constructed and is currently being tested on the University of Alabama at Birmingham campus. Two full-scale MCTT units are also scheduled to be constructed in Wisconsin as part of their EPA 319 grant.

The MCTT includes a special catchbasin followed by a two chambered tank that is intended to reduce a broad range of toxicants (volatile, particulate, and dissolved). The runoff enters the catchbasin chamber by passing over a flash aerator (small column packing balls with counter-current air flow) to remove highly volatile components. This catchbasin also serves as a grit chamber to remove the largest (fastest settling) particles. The second chamber serves as an enhanced settling chamber to remove smaller particles and has inclined tube or plate settlers to enhance sedimentation. This chamber also contains fine bubble diffusers and sorbent pads to further enhance the removal of floatable hydrocarbons and additional volatile compounds. The water then enters the final chamber at a slow rate to maximize pollutant reductions. The final chamber contains a mixed media (sand and peat) slow filter, with a filter fabric layer. The MCTT would typically be sized to totally contain all of the runoff from a 12.7 millimeter (mm) (0.5 inch) rain from a typical 0.2 hector (ha) (0.5 acre) gas station. If the area is larger, then multiple, or larger, units will be needed. Figure 1 is a diagram of this device.

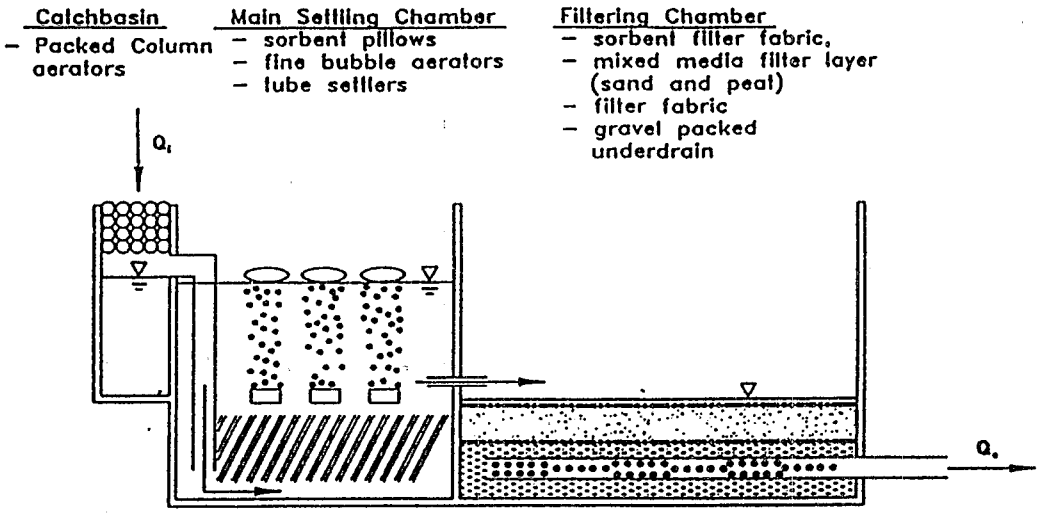


Figure 1. Multi-Chambered Treatment Train (MCTT) schematic.

Catchbasins have been found to be effective in removing pollutants associated with coarser runoff solids (2,3). High reductions in total and suspended solids (SS) (up to 44% reduction, depending on the inflowing water rate) were indicated by a number of prior studies. While relatively few pollutants are associated with these coarser solids, their removal will decrease maintenance of the other chambers of the MCTT. The size of the MCTT catchbasin sump is controlled by three factors: the runoff flow rate, the suspended solids (SS) concentration in the runoff, and the desired frequency at which the catchbasin will be cleaned so as not to sacrifice efficiency. Figure 2 is a plot of the accumulation of SS versus accumulative rain for approximately sizing the catchbasin.

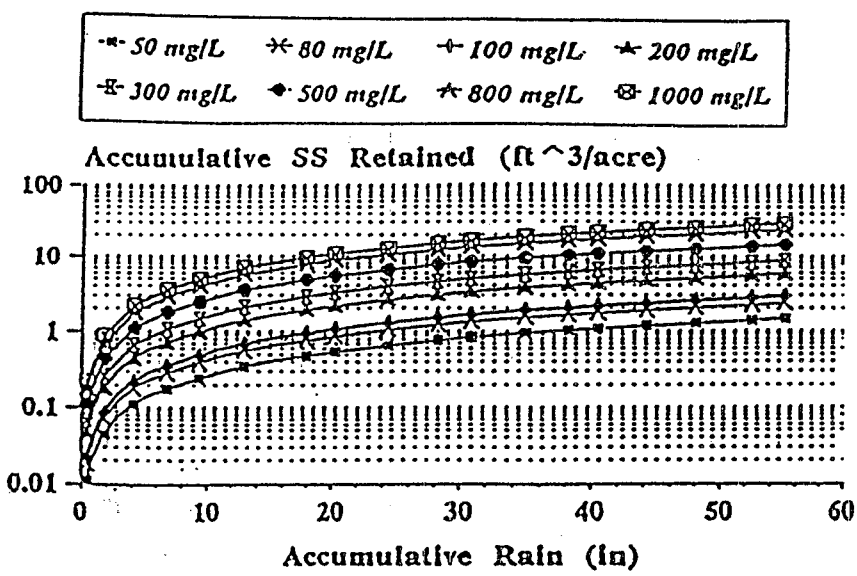


Figure 2. Accumulation of suspended solids in catchbasin sump.

The main settling chamber mimics completely mixed settling column bench-scale tests and uses a treatment ratio of depth to time for removal estimates. In addition to housing plate or tube settlers, the main settling chamber contains floating sorbent "pillows" to trap floating grease and oil and contains a fine bubble diffuser. The settling time in the main settling chamber usually ranges from 20 to 70 hours.

For the pilot-scale MCTT set up to capture runoff from a parking and vehicle service area on the campus of the University of Alabama at Birmingham, the catchbasin/grit chamber is a 25 centimeter (cm) vertical PVC pipe containing about 6 liters (L) of 3 cm diameter packing column spheres. The main settling chamber is about 1.3 square meters (m^2) in area and 1 meter (m) deep which with a 48 to 72 hour settling time should result in a median toxicity reduction of about 90 to 95%. The filter chamber is about 1.5 m^2 in area and contains 0.5 m of sand and peat directly on 0.15 m of sand over a fine plastic screen and coarse gravel that covers the underdrain. A Gunderboom™ filter fabric also covers the top of the filter media to distribute the water over the filter surface by reducing the water infiltration rate through the filter and to provide additional pollutant capture.

During a storm event, runoff from the parking lot is pumped into the catchbasin/grit chamber automatically. During filling, an air pump supplies air to aeration stones located in the main settling chamber. When the settling chamber is full, all pumps and samplers cease. After a quiescent settling period of up to 72 hours water is pumped through the filter media and discharged.

In evaluating the pilot scale MCTT located in Birmingham, samples are collected before and after each chamber of the device. To better estimate fate and treatability of toxicants, samples are partitioned into filterable ("dissolved") and non-filterable ("particulate") components before being analyzed for a wide range of toxicants using detection limits from about 1 to 10 micrograms per liter (μg/L) and conventional pollutants. Constituents being analyzed include heavy metals (copper, cadmium, lead, and zinc) and organics (phenols, PAHs, phthalate esters, herbicides, and pesticides). Particle size distributions, using a Coulter Multi-Sizer IIe™, are also being made, in addition to conventional analyses for COD, major ions, nutrients, suspended and dissolved solids, turbidity, color, pH, and conductivity. Samples are also screened using the Microtox™ toxicity test to measure relative reductions in toxicity.

RESULTS

For runoff of 13 storm events treated by the MCTT over a period of four months, 10 were found to be above a threshold value of 12% as measured using the Microtox™ test . The reduction in toxicity ranged from 70 to 100%, with a median reduction of 90% which was the value predicted by initial design. The toxicity of the filtered samples were also substantially reduced (50 to 100%, median of 88%). As expected, almost all of the total sample toxicity reduction occurred in the sand and peat filter and in the main settling chamber. This can be seen in Figure 3 which is a plot of relative toxicity through the MCTT for runoff treated from each storm event. The results from the specific metal and organic analyses are not yet available, but these toxicity data indicate excellent toxicant removals, as expected based on earlier bench-scale tests.

Overall COD reductions varied substantially ranging from 0 to 100% (median of 53%) with influent concentrations ranging from 0 to 197 mg/L (median of 56 mg/L). Most of these reductions occurred in the filtering chamber. Dissolved COD reductions also showed substantial variations with concentration increases occurring in the filtering unit for some events and most of the dissolved COD reductions occurring in the main settling chamber.

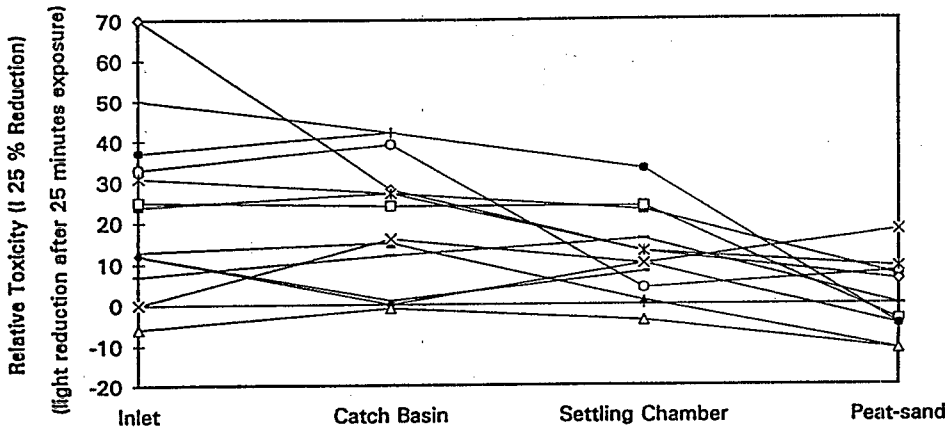


Figure 3. Relative toxicity through MCTT.

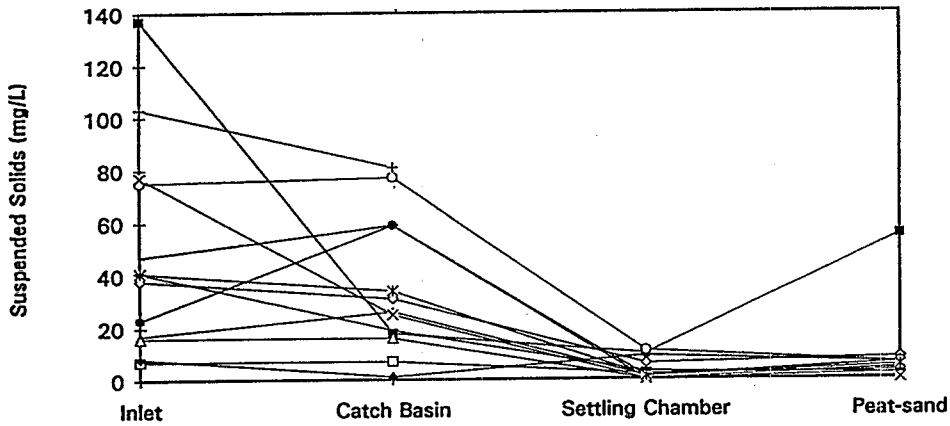


Figure 4. Suspended solids concentration through MCTT.

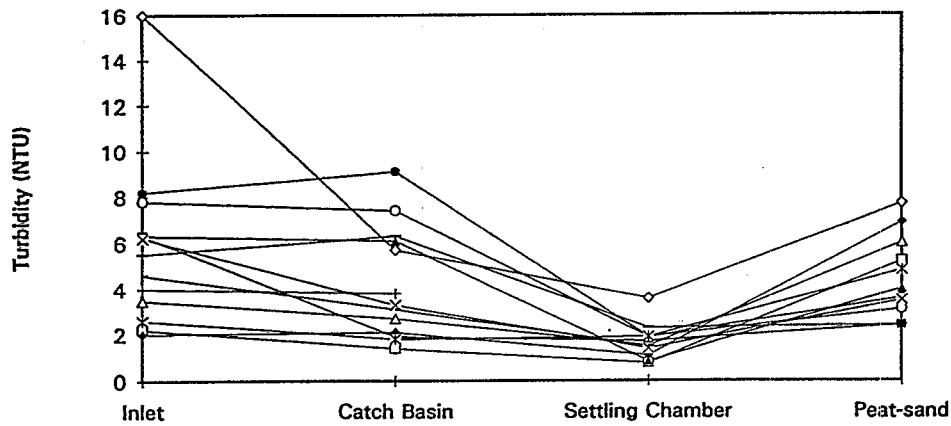


Figure 5. Turbidity changes through MCTT.

Suspended solids reductions ranged from 25 to 100% overall for samples with concentrations ranging from 7 to 137 mg/L. This includes increases that occurred in the sand and peat filter due to limited media washout during filtration. The first filtration run resulted in the largest washout, as would be expected. The suspended solids reductions before the filter was much greater, being

about 70 to 100%. Figure 4 shows suspended solids concentrations through the MCTT for each storm. Turbidity, shown in Figure 5, and color also experienced substantial increases during the filtration process (turbidity going from 2 to 16 NTU in the influent to the complete treatment unit to effluent values of 2.4 to 7.7 NTU, still relatively low, and color going from 20 to 58 HACH units in the influent to 30 to 100 HACH units in the effluent). The peat also apparently caused a reduction in pH, from 6.29 to 7.27 in the filter influent to 5.93 to 6.78 in the effluent.

CONCLUSIONS

This research examined the design of a multi-chambered tank to collect and treat stormwater runoff from critical urban source areas, including gas stations, oil change facilities, transmission repair shops, and other auto repair facilities. The collected runoff will first be treated in a catchbasin chamber where larger particles will be removed by settling. The water would then flow into a main settling chamber containing oil and grease sorbent material where it will undergo a much longer treatment period (20 to 70 hours) to remove finer particles and to remove oil residues. In practice, the MCTT would be utilized as a subterranean unit for space limited sites.

These preliminary results show that the treatment unit is providing substantial reductions in stormwater toxicants (both in particulate and filtered phases), organics, and suspended solids. Slight increases in turbidity and color and about a unit in pH reduction also occurred during the filtration step. The filter unit appears to be responsible for most of the toxicity reductions. However, the main settling chamber also resulted in substantial reductions in the dissolved toxicity fraction, total and dissolved COD, suspended solids, turbidity, and color. The catchbasin/ grit chamber also showed suspended solids reductions. The use of the MCTT is seen to be capable of reducing a broad range of stormwater pollutants that have been shown to cause substantial receiving water problems (4).

REFERENCES

1. Pitt, R., Field, R., Lalor, M., and Brown, M. Urban Stormwater Toxic Pollutants: Assessment, Sources, and Treatability. Water Environment Research. February 1995.

2. Lager, J. and W. Smith. Catchbasin Technology Overview and Assessment. U.S. Environmental Protection Agency. 1976.

3. Pitt, R. and P. Bissonnette. Characterizing and Controlling Urban Runoff through Street and Sewerage Cleaning. U.S. Environmental Protection Agency. Storm and Combined Sewer Program, Risk Reduction Engineering Laboratory. EPA/600/S2-85/038. PB 85-186500. Cincinnati, Ohio, June 1985.

4. Pitt, R. "Biological Effects of Urban runoff Discharges." In: Urban runoff and Receiving Water Systems: An Interdisciplinary Analysis of Impact, Monitoring, and Management. Engineering Foundation and ASCE. Lewis Publishers, Chelsea, Michigan. to be published in 1995.

For More Information: Richard Field
U.S. Environmental Protection Agency
Storm and Combined Sewer Pollution Control Program
2890 Woodbridge Avenue
Edison, New Jersey 08837
Phone: (908) 321-6674

GROUNDWATER CONTAMINATION FROM STORMWATER INFILTRATION

Robert Pitt, Shirley Clark and Keith Parmer
Department of Civil and Environmental Engineering, The University of Alabama at Birmingham
University Station, Birmingham, AL 35294-4461
(205) 934-8430

Richard Field and Thomas P. O'Connor
Storm and Sewer Pollution Control Program, U.S. Environmental Protection Agency
2890 Woodbridge Avenue, Edison, NJ 08837
(908) 321-6674

INTRODUCTION

The research summarized here was conducted during the first year of a 3-yr cooperative agreement (CR819573) to identify and control stormwater toxicants, especially those adversely affecting groundwater. The purpose of this research effort was to review the groundwater contamination literature as it relates to stormwater.

Prior to urbanization groundwater is recharged by rainfall-runoff and snowmelt infiltrating through pervious surfaces including grasslands and woods. This infiltrating water is relatively uncontaminated. Urbanization, however, reduces the permeable soil surface area through which recharge by infiltration occurs. This results in much less groundwater recharge and greatly increased surface runoff. In addition the waters available for recharge carry increased quantities of pollutants. With urbanization, waters having elevated contaminant concentrations also recharge groundwater including effluent from domestic septic tanks, wastewater from percolation basins and industrial waste injection wells, infiltrating stormwater, and infiltrating water from agricultural irrigation. The areas of main concern that are covered by this paper are: the source of the pollutants, stormwater constituents having a high potential to contaminate groundwater, and the treatment necessary for stormwater.

METHODOLOGY

An extensive literature review of stormwater pollutants that have the potential to contaminate groundwater was collected by searching prominent databases. This paper, a condensation of a larger, more detailed report (Pitt *et al.* 1994), addresses the potential groundwater problems associated with stormwater toxicants and describes how conventional stormwater control practices can reduce these problems. Potential problem pollutants were identified, based on their mobility through the unsaturated soil zone above groundwater, their abundance in stormwater, and their treatability before discharge. This information was used with earlier EPA research results of toxicants in urban runoff sheet flows (Pitt and Field 1990) to identify the possible sources of these potential problem pollutants. Recommendations were also made for stormwater infiltration guidelines in different areas and monitoring that should be conducted to evaluate a specific stormwater for its potential to contaminate groundwater.

RESULTS

Sources of Pollutants. Tables 1 and 2 summarize toxicant concentrations and likely sources or locations having some of the highest concentrations found during an earlier phase of this EPA-funded research (Pitt and Field 1990). The detection frequencies for the heavy metals are close to 100% for all source areas, and the detection frequencies for the organics ranged from about 10% to 25%. Vehicle service areas had the greatest frequencies and/or quantities of observed organics.

TABLE 1. CONCENTRATIONS OF HEAVY METALS IN OBSERVED AREAS

Toxicant	Highest Median	(μg/l)	Highest Observed	(μg/l)
Cadmium	Vehicle service area runoff	8	Street runoff	220
Chromium	Landscaped area runoff	100	Roof runoff	510
Copper	Urban receiving water	160	Street runoff	1250
Lead	CSO	75	Storage area runoff	330
Nickel	Parking area runoff	40	Landscaped area runoff	130
Zinc	Roof runoff	100	Roof runoff	1580

TABLE 2. MAXIMUM CONCENTRATIONS OF TOXIC ORGANICS FROM OBSERVED SOURCES

Toxicant	Concentration (μg/L)	Detection Frequency(%)	Significant Sources
Benzo(a)anthracene	60	12	Gasoline, wood preservative
Benzo(b)fluoranthene	226	17	Gasoline, motor oils
Benzo(k)fluoranthene	221	17	Gasoline, bitumen, oils
Benzo(a)pyrene	300	17	Asphalt, gasoline, oils
Fluoranthene	128	23	Oils, gasoline, wood preservative
Naphthalene	296	13	Coal tar, gasoline, insecticides
Phenanthrene	69	10	Oils, gasoline, coal tar
Pyrene	102	19	Oils, gasoline, bitumen, coal tar, wood preservatives
Chlordane	2	13	Insecticide
Butyl benzyl phthalate	128	12	Plasticizer
Bis(2-chloroethyl)ether	204	14	Fumigant, solvents, insecticides, paints, lacquers, varnishes
Bis(2-chloroisopropyl)ether	217	14	Pesticide manufacturing
1,3-Dichlorobenzene	120	23	Pesticide manufacturing

Potential Contaminates to Groundwater. NUTRIENTS. Nitrates are one of the most frequently encountered contaminants in groundwater (AWWA 1990). Phosphorus contamination has not been as widespread or as severe as that of nitrogen compounds. Nitrate is highly soluble (>1 kg/L) and will stay in solution in the percolation water.

PESTICIDES. Urban pesticide contamination of groundwater can result from municipal and homeowner use for pest control and the subsequent collection of the pesticide in stormwater runoff. The greatest pesticide mobility occurs in areas with coarse-grained or sandy soils without a hardpan layer, and with soils that have low clay and organic matter content and high permeability (Domagalski and Dubrovsky 1992). Pesticides decompose in soil and water, but the total decomposition time can range from days to years. In general, pesticides with low water solubilities, high octanol-water partitioning coefficients, and high carbon partitioning coefficients are less mobile. The slower moving pesticides that may better sorb to soils have been recommended for use in areas of groundwater contamination concern.

OTHER ORGANICS. The most commonly occurring organic compounds found in urban groundwaters include phthalate esters and phenolic compounds. Polycyclic aromatic hydrocarbons (PAHs) have also been found in groundwaters near industrial sites. Groundwater contamination from organics occurs more readily in areas with sandy soils and where the water table is near the land surface (Troutman *et al.* 1984).

METALS. Studies of recharge basins receiving large metal loads found that most of the heavy metals are removed either in the basin by sedimentation or in the vadose zone. The order of attenuation in the vadose zone from infiltrating stormwater is: zinc (most mobile) > lead > cadmium > manganese > copper > iron > chromium > nickel > aluminum (least mobile) (Harper 1988).

SALTS. Sodium and chloride used for deicing collects in the snowmelt and travels down through the vadose zone to the groundwater with little attenuation. Salts that are still in the percolation water after it travels through the vadose zone will contaminate the groundwater (Sabol *et al.* 1987; and Bouwer 1987). Studies of depth of pollutant penetration in soil have shown that sulfate and potassium concentrations decrease with depth, whereas sodium, calcium, bicarbonate, and chloride concentrations increase with depth (Close 1987; Ku and Simmons 1986).

MICROORGANISMS. Viruses have been detected in groundwater where stormwater recharge basins were located short distances above the aquifer (Vaughn *et al.* 1978). The factors that affect the survival of enteric bacteria and viruses in the soil include pH, antagonism from soil microflora, moisture content, temperature, sunlight, and organic matter (Jansons et al. 1989; and Tim and Mostaghim 1991). The major bacterial removal mechanisms in soil are straining at the soil surface and at intergrain contacts, sedimentation, sorption by soil particles, and inactivation.

Treatment of Stormwater. Table 3 summarizes the filterable (dissolved solids) fraction of toxicants found in storm runoff sheetflows from many urban areas found during an earlier phase of this EPA-funded research (Pitt and Field 1990). Pollutants that are mostly in filterable forms have a greater potential of affecting groundwater and are more difficult to control with the use of conventional stormwater control practices which mostly rely on sedimentation and filtration principles. Fortunately, most of the storm-flow toxic organics and metals are associated with the nonfilterable (suspended solids) fraction. Possible exceptions include zinc, fluoranthene, pyrene, and 1,3-dichlorobenzene. Pollutants in dry-weather storm drainage flows, however, tend to be much more associated with filtered sample fractions and would not be as readily controlled with the use of sedimentation (Pitt *et al.* 1994).

TABLE 3. FILTERABLE FRACTIONS OF STORMWATER TOXICANTS FROM SOURCE AREAS

Metals	Filterable (%) Fraction	Organics	Filterable (%) Fraction
Cadmium	20 to 50	Benzo(a)anthracene	None found in filtered fraction
Chromium	<10	Fluoranthene	65
Copper	<20	Naphthalene	25
Iron	Small amount	Phenanthrene	None found in filtered fraction
Lead	<20	Pyrene	95
Nickel	Small amount	Chlordane	None found in filtered fraction
Zinc	>50	Butyl benzyl phthalate	Irregular
		Bis(2-chloroethyl)ether	Irregular
		Bis(2-chloroisopropyl)ether	None found in filtered fraction
		1,3-Dichlorobenzene	75

Sedimentation is the most significant removal mechanism for particulate-related (nonfilterable) pollutants. Volatilization and photolysis are other important pollutant removal mechanisms in wet-detention ponds. Biodegradation, biotransformation, and bioaccumulation (into plants and animals) may also occur in larger and open ponds. Infiltration devices can safely deliver large fractions of the surface flows to groundwater, if carefully designed and located (EPA 1983). Grass-filter strips may be quite effective in removing particulate pollutants from overland flows. The filtering effects of grasses, along

with increased infiltration/recharge, reduce the particulate sediment load from urban landscaped areas. Grass swales are another type of infiltration device.

CONCLUSIONS AND RECOMMENDATIONS

With a reasonable degree of site-specific design considerations to compensate for soil characteristics, infiltration may be very effective in controlling both urban runoff quality and quantity problems (EPA 1983). This strategy encourages infiltration of urban runoff to replace the natural infiltration capacity lost through urbanization and to use the natural filtering and sorption capacity of soils to remove pollutants; however, the potential for some types of urban runoff to contaminate groundwater through infiltration requires some restrictions. Infiltration of urban runoff having potentially high concentrations of pollutants that may pollute groundwater requires adequate pretreatment or the diversion of these waters away from infiltration devices. The following general guidelines for the infiltration of stormwater and other storm drainage effluent are recommended in the absence of comprehensive site-specific evaluations:

- Divert away from infiltration devices - dry-weather storm drainage effluent (probable high concentrations of soluble heavy metals, pesticides, and pathogenic microorganisms); combined sewage overflows (poor water quality with high pathogenic microorganism concentrations and clogging potential); snowmelt runoff (potential for having high concentrations of soluble salts); runoff from manufacturing industrial areas (potential for having high concentrations of soluble toxicants); and construction site runoff (high suspended solids (sediment) concentrations, which would quickly clog infiltration devices).
- Runoff from other critical source areas (e.g., vehicle service facilities and large parking areas) should receive adequate pretreatment to eliminate the groundwater contamination potential before infiltration.
- Runoff from residential areas (the largest component of urban runoff in most cities) is generally the least polluted urban runoff flow and should be considered for infiltration.

Most past stormwater quality monitoring efforts have not adequately evaluated stormwater's potential for contaminating groundwater. These are the urban runoff contaminates with the potential to adversely affect groundwater (with the most prominent and/or analyses recommendations in parentheses):

nutrients (nitrates); salts (chloride); VOCs (if expected in the runoff [e.g., runoff from manufacturing industrial or vehicle service areas] could screen for VOCs with purgeable organic carbon analyses); pathogens (especially enteroviruses, if possible, along with other pathogens [e.g., *Pseudomonas aeruginosa*, *Shigella*, and pathogenic protozoa]); bromide and total organic carbon (to estimate disinfection by-product generation potential, if disinfection by either chlorination or ozone is being considered); pesticides, in both filterable and total sample components (lindane and chlordane); other organics, as filterable and total sample components (1,3 dichlorobenzene, pyrene, fluoranthene, benzo(a)anthracene, bis(2-ethylhexyl)phthalate, pentachlorophenol, and phenanthrene); and heavy metals, as filterable and total sample components (chromium, lead, nickel, and zinc).

The following urban runoff components can adversely affect infiltration and injection operations: sodium, calcium, and magnesium (calculate sodium adsorption ratio to predict clogging of clay soils); and suspended solids (determine the need for sedimentation pretreatment to prevent clogging).

REFERENCES

AWWA (American Water Works Association). Fertilizer Contaminates Nebraska Groundwater. AWWA Mainstream. 34 (4): 6, 1990.

Bouwer, Herman. Effect of Irrigated Agriculture on Groundwater. Jour. of Irrigation and Drainage Eng. ASCE. 113 (1): 516-535, 1987.

Close, M.E. Effects of Irrigation on Water Quality of a Shallow Unconfined Aquifer. Water Resources Bulletin. 23 (5): 793-802, 1987.

Domagalski, J. L. and Dubrovsky, N. M. Pesticide Residues in Groundwater of the San Joaquin Valley, California. Journal of Hydrology. 130 (1-4): 299-338, 1992.

EPA. Results of the Nationwide Urban Runoff Program. NTIS No. PB 84-185552, U.S. Environmental Protection Agency, Water Planning Division, Washington, D.C., December 1983.

Harper, Harvey H. Effects of Stormwater Management Systems on Groundwater Quality. Final Report for DER Project WM190. Florida Department of Environmental Regulation, 1988.

Jansons, J., Edmonds, L. W., Speight, B. and Bucens, M. R. Survival of Viruses in Groundwater. Water Research. 23 (3): 301-306, 1989.

Ku, H. F. H. and Simmons, D. L. Effect of Urban Stormwater Runoff on Groundwater beneath Recharge Basins on Long Island, New York. U.S. Geological Survey (USGS) Water Resources Investigations Report 85-4088. USGS, Denver, Colorado, 1986.

Pitt, R., and Field, R. Hazardous and Toxic Wastes Associated with Urban Stormwater Runoff. In: Proceedings of the 16th annual RREL Hazardous Waste Research Symposium: Remedial Action, Treatment and Disposal of Hazardous Waste. U.S EPA, Cincinnati, OH, EPA/600/9-90-37, 1990.

Pitt, R., Clark, S. and Parmer, K. Potential Groundwater Contamination From Intentional and Non-Intentional Stormwater Infiltration. EPA/600/SR-94/129. U.S. EPA, Cincinnati, Ohio, 1994.

Sabol, G. V., Bouwer, H. and Wierenga, P. J. Irrigation Effects in Arizona and New Mexico. Journal of Irrigation and Drainage Engineering, ASCE. 113 (1): 30-57, 1987.

Tim, U. S. and Mostaghim, S. Model for Predicting Virus Movement through Soil. Groundwater. 29 (2): 251-259, 1991.

Troutman, D.E., Godsy, E. M., Goerlitz, D. F. and Ehrlich, G. G. Phenolic Contamination in the Sand-and-Gravel Aquifer from a Surface Impoundment of Wood Treatment Wastewaters, Pensacola, Florida. USGS Water-Resources Investigations Report 84-4230. USGS, Denver, Colorado, 1984.

Vaughn, J.M., Landry, E.F., Baranosky, L.J., Beckwith, C. A., Dahl, M. C. and Delihas, N.C. Survey of Human Virus Occurrence in Wastewater Recharged Groundwater on Long Island. Applied and Environmental Microbiology. 36 (1): 47-51, 1978.

FOR MORE INFORMATION: Richard Field, EPA Project Officer
Chief, Storm and Combined Sewer Pollution Control Program
U.S. Environmental Protection Agency (MS-106)
Edison, NJ 08837-3679
(908) 321 - 6674

COLLOIDAL CONTAMINANTS IN URBAN RUNOFF

M.R. Wiesner, G. Characklis, and D. Brejchová
Department of Environmental Science and Engineering
Rice University
P.O. Box 1892
Houston, Texas 77251
phone: 713-285-5129

INTRODUCTION

Rivers typically account for the largest single sediment input to lacustrine and estuarine systems. Pesticides, metals, chlorinated hydrocarbons and other contaminants sorbed to particles carried by rivers may be transported to the sediments of lakes and estuaries. Urban runoff is often an important non-point source of particles to surface waters. For example, under average conditions, over 40% of the suspended solids entering Galveston Bay are estimated to originate from high density urban and residential non-point sources and, in some cases, the fractions of specific contaminants entering Galveston Bay associated with these particles (such as oil and grease) approach 100%[1].

Information on the size distribution of particles in urban runoff has been surprisingly limited despite its importance in providing a strategy for pollution control. While many studies have been done on urban runoff, in only a few instances has the role of specific particle fractions as transport vectors for pollutants in urban runoff been considered.

In this paper, we summarize field data on particle size distributions and contaminant concentrations in urban runoff and streams obtained over a 2-year period. Much of the previous research done in this area has concentrated on particles, larger than10 μm in diameter. While larger particles may represent a significant fraction of suspended materials, we show that the majority of the particles and particle surface area in runoff from one urban center resides within the smaller size fractions.

Inextricably linked to the problem of pollutant transport is the question of whether or not there is significant aggregation of particles in the runoff stream. The degree of aggregation that occurs in the runoff stream will directly affect the fate and transport of the particles, and thus the pollutants sorbed to them. For example, if sub-micron particles aggregate significantly in the runoff stream, particle settling rates will be accelerated in lakes and estuaries, as will the transport of particles and associated contaminants to the sediments.

METHODOLOGY

An urban waterway (Brays Bayou) and several of its tributaries were sampled over a two year period. Brays Bayou drains areas of Fort Bend and Harris counties in Texas within the Houston metropolitan area. The watershed selected as a study area for this research begins at the start of Brays Bayou in west Houston and continues down through southwest Houston until the Bayou reaches South Main St. This portion of the watershed equates to a drainage area of approximately 92 sq. mi. The majority of the watershed is under stress from a wide variety of urban uses consisting mostly of residential and commercial properties. Research was concentrated primarily on four sampling sites. The sites are, from west to east; 1) Keegan's Bayou at Roark Rd., 2) Brays Bayou at Gessner, 3) Poor Farm Ditch, and 4) Brays Bayou at Main Street.

Samples were obtained by dropping a 12-quart, detergent cleaned, polyethylene bucket into the center of the runoff stream from overpasses spanning the Bayou. The bucket containing the sample was retrieved by means of a rope attached to the handle. Approximately one liter of sample was retained in two 500 ml polyethylene bottles. Each bottle had been washed with Alconox® cleaner, rinsed three times with distilled water and then given three final rinses with Milli-Q®, deionized water. Samples were transported back to the lab for analysis. Surface water samples were obtained under both storm and ambient conditions. Upon returning to the lab, all samples were analyzed for turbidity, pH, particle size distribution, total suspended solids (TSS), total organic carbon (TOC), and a suite of metals. Particle size analyses were performed using an electronic particle counter (Coulter Electronics Ltd., Luton, England). The Coulter Multisizer operates on the electronic sensing zone (ESZ) principle. The effective measurement range for such devices usually varies from 2-60% of the orifice diameter. A 19μm orifice tube was used for these experiments with an effective measurement range of approximately 0.5 to 15 μm. Samples were also filtered through various size membranes in order to analyze the composition of the

filtrates in each size fraction. The filtration system consisted of four 250 ml vacuum filter holders (Nalgene, Prod. 315-0047) mounted on 1000 ml Erlenmeyer flasks. Each flask was connected to a vacuum pump (Gast, No. 1HAB25BM100X) by means of Tygon® (R-3603) tubing. The cutoffs for membranes used in the fractionation procedure were reported by the manufacturer to be 0.45 μm, 0.1 μm and 10^5 daltons. All of these membranes are cellulose nitrate filters (Sartorious AG, Goettingen, Germany, 47 mm circular).

Membrane-fractionated samples were analyzed for suspended solids, TOC, and metals. All determinations of suspended solids were made according to procedure 2540D in Standard Methods[2]. In the best cases, solids measurements yielded data on the mass of particles in the size ranges >20 μm, 0.45 to 20 μm, 0.1 to 0.45 μm and 10^5 daltons to 0.1 μm. Unfortunately, it was often difficult to obtain data for the smallest size range, as the 10^5 dalton filter would frequently foul to the extent that filtration was not possible.

In preparation for metals analysis, each filtrate was concentrated through a Nitric Acid-Hydrochloric Acid Digestion, method 3030F in Standard Methods[2]. Digestion resulted in concentrating the samples 5-10 times. Samples were stored in detergent washed, acid rinsed glass vials and refrigerated at 4°C until analysis. Metal concentrations (Fe, Sr, Ba, Pb, Zn, Ca, Cu and Mn) were measured by Inductively Coupled Plasma (ICP) -Atomic Emission Spectrometry (Perkin-Elmer).

Samples were also obtained for the purpose of evaluating particle aggregation under controlled conditions. In aggregation experiments, "background" or storm water was transported back to the laboratory, and the largest particles were allowed to settle from suspension. The supernatant was then transferred to a 2-liter beaker and mixed at a prescribed speed. Mixing conditions as a function of paddle rotational speed were known for this system. An rpm was selected toprovide the mean velocity gradient, G, of approximately 70 per second estimated to occur in the bayou under stormwater flow conditions. Particle size distributions were measured at regular time intervals to evaluate the kinetics of particle aggregation in the system and to quantify the collision efficiency factor, α.

Aggregation was further investigated by following a plug of water in Brays Bayou from the west side of Houston through the Houston Ship Channel. During this phase of the project, three more sampling sites were added to the four used for stormwater sampling ; Brays Bayou at Old Spanish Trail, Brays Bayou at the Houston Ship Channel, and the Houston Ship Channel at the San Jacinto Monument. The Houston Ship Channel represented the last leg of stormwater travel from Houston to the Galveston Bay. It is an unconcreted, man-made channel approximately a half mile wide by the time it reaches the San Jacinto Monument. Particles from Brays Bayou have been significantly obscured by dilution and subsequent industrial additions by the time they reach this point. There is also a significant increase in salinity at this sampling location due to its proximity to the Bay. These samples were analyzed for pH, turbidity, particle size distribution, fractional organic carbon and fractional metals in the same manner as those measured during the stormwater phase of this work.

RESULTS

Particle size data show that more than 90% of the particle number exists between 0.45μm and 2μm. Photon Correlation Spectroscopy measurements also show a peak in the distribution varying from 0.4μm to 0.7μm. Particle size distributions in runoff were taken under both storm and ambient conditions. Although the profiles under both sets of conditions were similar, the concentration of particles in the storm samples was much higher, both in particle number and calculated particle surface area (Figure 1). These higher concentrations, coupled with much higher flow rates in the runoff stream during a storm event, produce high particle loadings during storm events.

TOC analysis indicated that the particulate phase was composed of 1 to 10% organic carbon. Functional groups on particulate organic carbon may complex metals and enhance the transport of metals with particles. Under storm conditions TOC concentrations increased as the bayou water progressed downstream. TOC tended to be bimodally distributed between the largest and smallest (dissolved) size fractions (Figure 2). Thus, metals readily complexed by TOC would also be expected to exhibit a bimodal distribution with respect to size fraction.

Metals analysis of the samples yielded detectable levels of Fe, Ba, Cu, Mn, Pb and Zn. The metals concentrations in the runoff, expressed per mass of suspended solids, were comparable with concentrations reported in previous studies evaluating the metals content of Galveston Bay sediments. With regards to all metals analyzed, except Zn, there was good correlation between the profiles of the runoff samples and the Bay sediments. While elevated concentrations of zinc have been reported in the

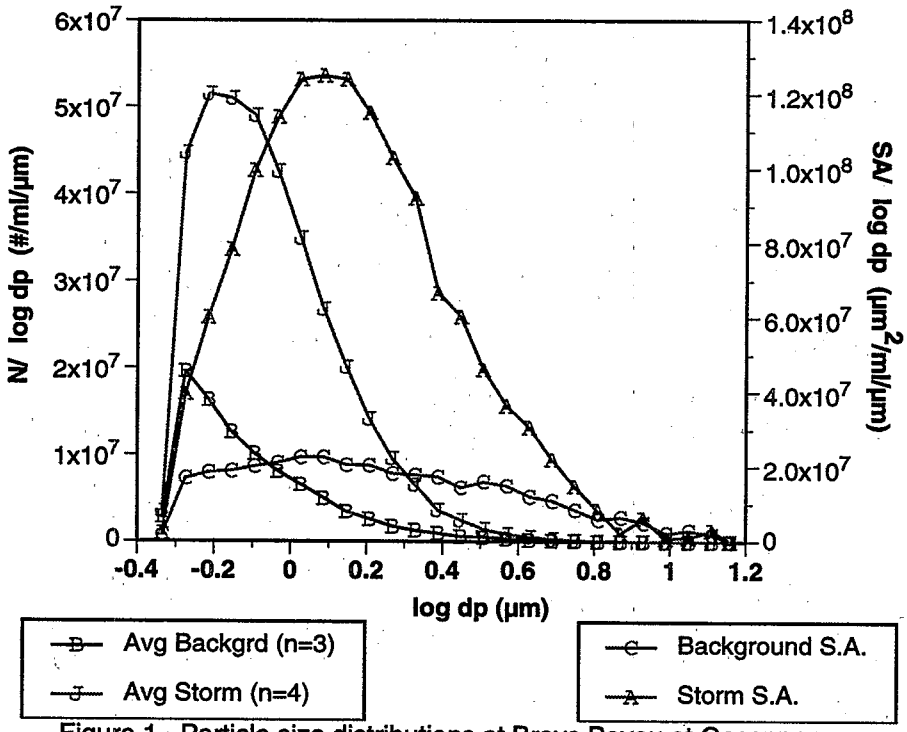


Figure 1. Particle size distributions at Brays Bayou at Gessner averaged over 3 sampling dates for background conditions and 4 separate storm events.

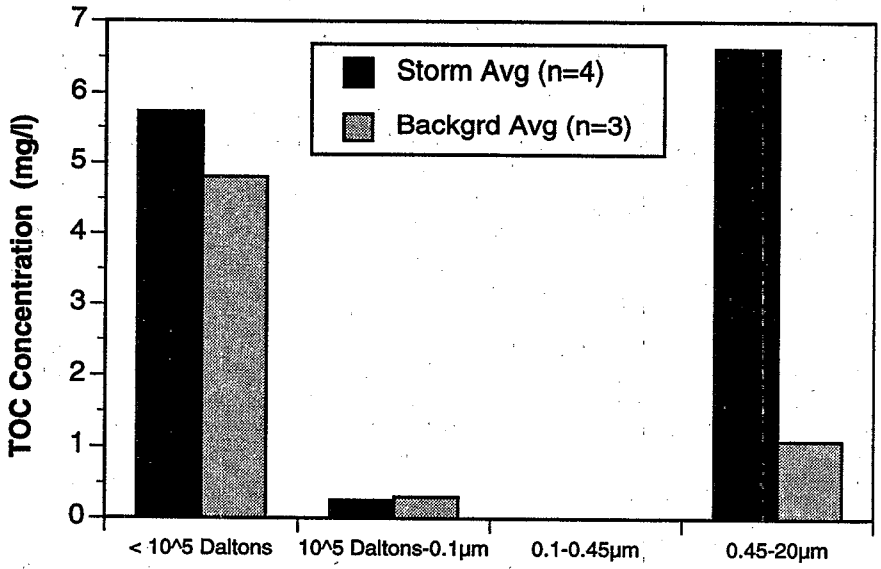


Figure 2. Size fractionation of TOC in Brays Bayou at Main Street averaged over 3 background samples and 4 storm events.

runoff from other urban centers, it remains to be determined why enriched concentrations of zinc apparently are not observed in the sediment record for Galveston Bay. Zinc, like barium and strontium displayed a bimodal distribution with respect to size fraction (Figure 3). However, unlike zinc, barium and strontium decreased in concentration during storm events relative to the background concentrations observed.

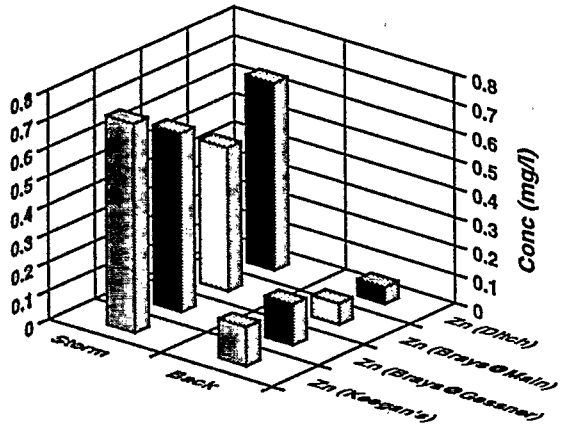


Figure 3. Variations in average zinc concentrations during storm and background conditions at the four sampling sites.

Intensive sampling of individual storm events produced a similar picture of the materials loadings to this urban waterway. Different fractions of materials were "eluted" to the bayou at different times during storm events. For example, larger particles tended to peak in concentration earlier during a storm than did smaller particles. This is reflected in the data summarizing settleable (within 15 minutes) and unsettleable suspended solids as compared with particle number concentrations (Figure 4). Similarly, metals tended to peak in concentrations at different times. Iron concentrations peaked at approximately the same time as the unsettleable solids (4 to 8 hours) and remained above background concentrations for at least 24 hours after the onset of the storm. In contrast, zinc concentrations peaked at 4 hours and then decreased to, or below, background concentration. Although zinc and TOC concentrations correlated significantly ($r^2 = 0.8$) TOC concentrations were observed to remain above background levels for at least 24 hours after the onset of the storm events monitored.

Laboratory simulations of mixing and particle aggregation in Brays Bayou indicated that significant aggregation is likely to occur in runoff water within 1-3 hrs. The number concentration of particles measured by the particle analyzer with a 19 μm orifice increased consistently to a maximum in the first few hours of mixing. Particle number then displayed a drop back down to approximately the original concentration, eventually settling into a slow, steady decline. After 24 hours of continuous mixing in the lab, large aggregates of particles were readily visible. The original increase in particle number is attributed to the aggregation of particles which are initially below the 0.45μm threshold of the particle analyzer. As these particles reach the threshold there is a rise in the number of measurable particles. However, a monotonically decreasing number concentration was observed in aggregation experiments when particle concentrations were measured using a 50 μm orifice. Because this orifice provides a window on a slightly larger fraction of particles, the effect of aggregation into the smaller size classes observed with the 19 μm orifice is masked. A least-squares fit to a semi-log plot of particle concentration yields values of the collision efficiency factor on the order of 10^{-2} (Figure 5).

Although it is evident from laboratory mixing studies that significant aggregation of particles entering the bayou is probable, aggregation was not evidenced in samples obtained following a a single plug of water down the bayou; particle size distributions remained largely unchanged with distance. Aggregation of particles present in the upper reaches of the bayou may be masked by the introduction of particles from the numerous small tributaries that feed into Brays Bayou as it makes its way through the city.

CONCLUSIONS

The number and surface area concentrations of particles in the urban runoff studied were dominated by particles 2 to 5 μm in diameter. Zinc and barium were observed to be distributed bimodally with respect to the size fractions where they predominate, while lead and iron tended to associate almost exclusively with the largest size fraction. Most metals are associated with size fractions either larger than 0.45 μm or less than 10^5 daltons. This bimodal distribution of metals is similar to that observed for total organic carbon. Materials in different size classes were observed to reach a maximum in concentration at

different times during a storm, larger particles reaching their maximum concentration before smaller particles.

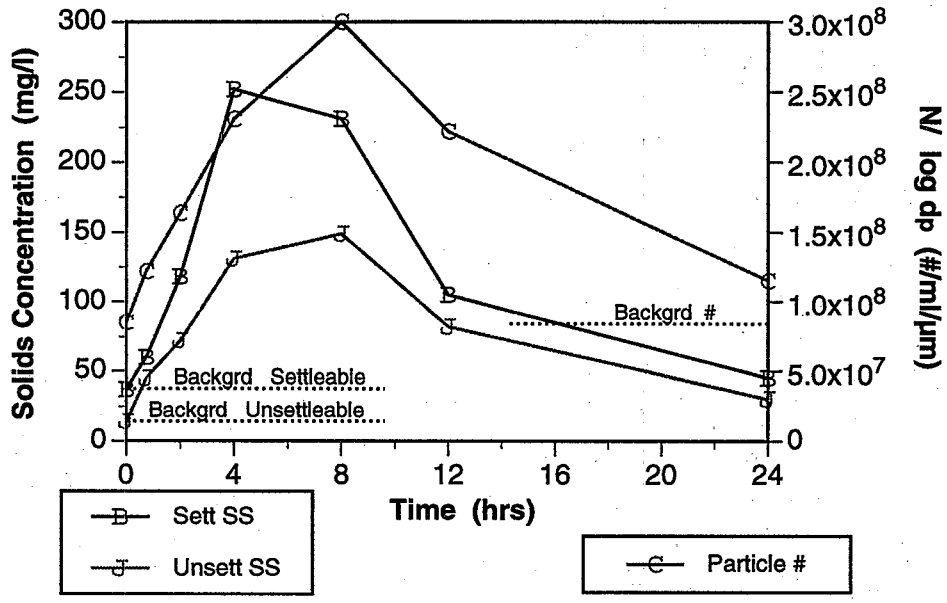


Figure 4. Comparison of suspended solids and particle number concentrations in Brays Bayou at Main Street on 27 August 1993.

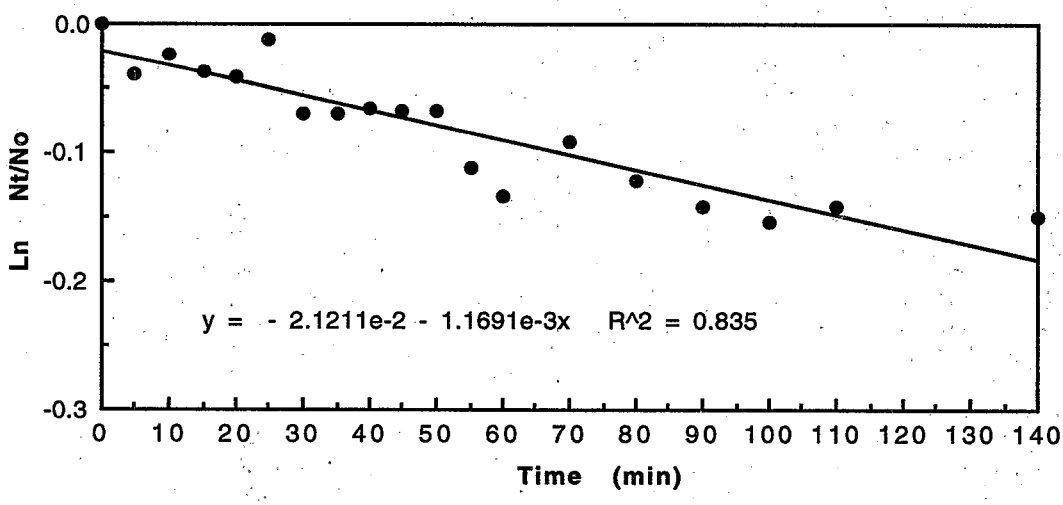


Figure 5. Log particle number concentration (normalized to initial concentration) in Brays Bayou at Main Street during storm event on 12 May 1994.

LITERATURE CITED

1. Newell, C. J., Rifai, H. S. and Bedient, P. B. *Characterization of Non-Point Sources and Loadings to Galveston Bay.* Galveston Bay National Estuary Program, (1991).
2. Clesceri, L. S., Greenberg, A. E. and Trussell, R. R. Standard Methods for the Examination of Water and Wastewater. (1989).

MODELLING AIR EMISSIONS FROM CONTAMINATED DREDGED MATERIALS

L J Thibodeaux[1], K T Valsaraj[1], D D Reible[1] and J M Brannon[2]
[1]Department of chemical engineering,
Louisiana State University, Baton Rouge, LA 70803
[2]U S Army Waterways Experiment Station,
Vicksburg, MS

INTRODUCTION:

A confined disposal facility (CDF) is a diked area for gravity separation and dredged material solids. When contaminated dredged material is placed in a CDF, the potential exists for volatile organic chemicals (VOCs) associated with the sediment to be released to the air. Sediments from the New Bedford Harbor (NBH) Superfund Site, MA, contain significant amounts of polychlorinated biphenyls (PCBs), some of which may be released to the air during evaporative drying in a CDF.

Models for evaluation of volatile emissions to air during dredged material disposal have been developed (Thibodeaux, 1989). These theoretical models may be applied to calculate potential PCB emissions from CDFs proposed for containment of NBH sediment. Four locales associated with a CDF operation were identified as separate volatile sources. These locales were: (1) the sediment (dredged material) relocation locale, (2) the exposed sediment locale, (3) the ponded sediment locale and, (4) the vegetation-covered sediment locale. The exposed sediment locale was ranked the highest. Field or laboratory emission data suitable for comparison to model predictions were not available for any of the locales. Brannon (1989) reported some preliminary data for locale 2 for the emission of Aroclor-1242 from a drying sediment exposed to air under laboratory conditions. This paper compares the experimental values against theoretical predictions.

METHODOLOGY:

A series of four experiments were performed with an emission isolation flux chamber. This apparatus was placed atop the sediment to collect the PCB vapors as air was passed over the sediment in the chamber for 1 hour. The vapors were trapped in fluorisil tubes and analyzed by gas chromatography. Two adsorption tubes, and an air rate of 900 cm^3/min were used. In general the experiments can be placed into two classes, wet and dry. The first three experiments were performed with sediment saturated with water; these are called *wet sediment experiments*. The last experiment showed significant cracking and drying of the surface sediment. The soil porosity decreased from 0.774 on day 1 to 0.103 on day 10, while the solid fraction increased from 0.33 to 0.88 during this period. The laboratory was maintained at 20±0.3 °C and low relative humidity throughout the experiment. The experiment number 4 shall be termed the *dry sediment experiment*.

The following is a brief presentation of the model that applies for the exposed sediment locale. Contaminated sediment that is wet and exposed directly to air results in the highest VOC emission rates. VOCs sorbed on the particles at the soil surface have a relatively short pathway to the air. The top layers eventually become depleted of the chemical. Continuing losses will come from within the soil pores. The following equation applies for this transient volatilization rate

$$N_A = \frac{W_A K^* - C_a}{\left[\dfrac{\pi\ t}{D_{Aa}\left(1 + \dfrac{\rho_b}{\epsilon_a K^*}\right)}\right]^{1/2} + \dfrac{1}{k_A}} \qquad (1)$$

where N_A is the emission flux from the soil ($\mu g.m^{-2}.h^{-1}$), K^* is the air/soil partition constant ($g.m^{-3}$), W_A is the chemical concentration on soil ($\mu g.g^{-1}$), t is time (h), D_{Aa} is the diffusion constant of the chemical in the air-filled pores ($m^2.h^{-1}$), ρ_b is the soil bulk density ($g.m^{-3}$), ϵ_a is the air-filled porosity ($m^3.m^{-3}$), k_a is the air-side mass transfer coefficient ($m.h^{-1}$), and C_a is the chemical concentration in the background air ($\mu g.m^{-3}$). The above equation is for an

unsaturated (with respect to water) or dry sediment. As the sediment looses its water content by evaporation and drainage, the air-soil equilibrium partition constant changes. Three water content regimes exist and require as many partition constants. These are wet, damp and dry. Each can be expressed by the simple equilibrium expression, $C_a^* = K^* W_A$. The partition constant for the wet case is the ratio of Henry's constant to the soil-water partition constant, $K^* = \frac{H_c}{K_d}$, whereas for the dry case at soil loadings it is $K^* = \frac{p_A^* M_A}{B_1 RT\ W_A^*}$, where K_d is the soil-water equilibrium constant ($m^3.g^{-1}$), p_A^* is the chemical vapor pressure (atm), B_1 is the BET adsorption constant (dimensionless), M_A is the chemical molecular weight ($\mu g.mol^{-1}$), R is the gas constant (= 82 x 10^{-6} $atm.m^3.mol^{-1}.K^{-1}$), T is the temperature (K) and, W_A^* is the chemical loading on the sediment for a monolayer coverage ($\mu g.g^{-1}$).

RESULTS:

In the section in which the experimental data was reviewed it was noted that the experiments fall into two classes. These were the initial period with the wet sediment and the long-term run with the dry sediment. Equation (1) applies for both cases with the appropriate wet and dry equilibrium expressions given earlier.

During the initial phase of the experiment evaporation time is short (i.e, t ~ 0) and the sediment surface is wet. If the incoming air is also PCB free Equation (1) simplifies to

$$N_A = k_A\ W_A K^* \qquad (2)$$

where K^* is given by the equation for the wet case. At 25°C it is 0.132 $g.m^{-3}$. The air side mass transfer coefficient can be estimated using four different methods (Thibodeaux and Scott 1985). The estimates for Aroclor 1242 at 25°C range from 30 to 96 $cm.h^{-1}$. Based on the range of coefficients the predicted emission rates for A-1242 with a sediment loading of 887 $\mu g.g^{-1}$ ranges from 36 to 113 $\mu g.m^{-2}.h^{-1}$. The experimental values ranged from 12 to 62 $\mu g.m^{-2}.h^{-1}$. These values are shown in Figure 1. The fact that the predicted and experimental ranges substantially overlap each other suggests that the wet soil portion of the model is correct.

By the third day of the experiment the sediment was essentially dry. In this case, time is large and Equation (10 applies as written. The air-sediment partition constant should reflect the dry state of the sediment.

A procedure based on the theory of gas mixtures adsorbing competitively on a solid surface that extends the classical Brauner-Emmett-Teller (BET) model to account for water vapor was used to estimate K^* for Aroclor 1242 on dry sediment (Valsaraj and Thibodeaux, 1988). A key factor in the procedure is the surface area of the soil. In the case this was determined from the fractional organic matter and clay of the sediment. Together with the sediment surface area S ($m^2.g^{-1}$) so determined the monolayer coverage of Aroclor 1242 on the sediment W_A^* was computed. Other relevant parameters used were: B_1 = 20, 18.4% of S active for adsorption and Aroclor 1242 density was 1.5 $g.cm^{-3}$. All other Aroclor 1242 properties were from Thibodeaux (1989). Two estimates of K^* for the dry case were obtained; one for the estuarine composite sediment 0.056 $kg.l^{-1}$ and the other for the sediment from the hot spot 0.016 $kg.l^{-1}$.

The necessary information is available in Equation (1) to arrive at predicted values of the flux. The working form of Equation (1) is

$$N_A = \frac{887\ K^*}{[\ 0.097(tK^*)^{1/2} + 3.29\ ]} \qquad (3)$$

with t in days, K^* in $g.m^{-3}$ and N_A in $\mu g.m^{-2}.h^{-1}$. The value of k_A was 0.304 $m.h^{-1}$, D_{Aa} was 0.035 $\epsilon_a^{4/3}$ in $cm^2.s^{-1}$, the soil bulk density was 0.69 $g.cm^{-3}$ and porosity ϵ_a was 0.774.

The predicted values for Aroclor 1242 flux assuming dry soil conditions appear in Figure 1. The experimental values are also given alongside. Comparison of predicted and measured flux values should be done for t ≥ 3 days, since the sediment was wet or damp before this time. The average measured fluxes for days 3 through 10 is 0.885 ± 0.432 $\mu g.m^{-2}.h^{-1}$, whereas the predicted

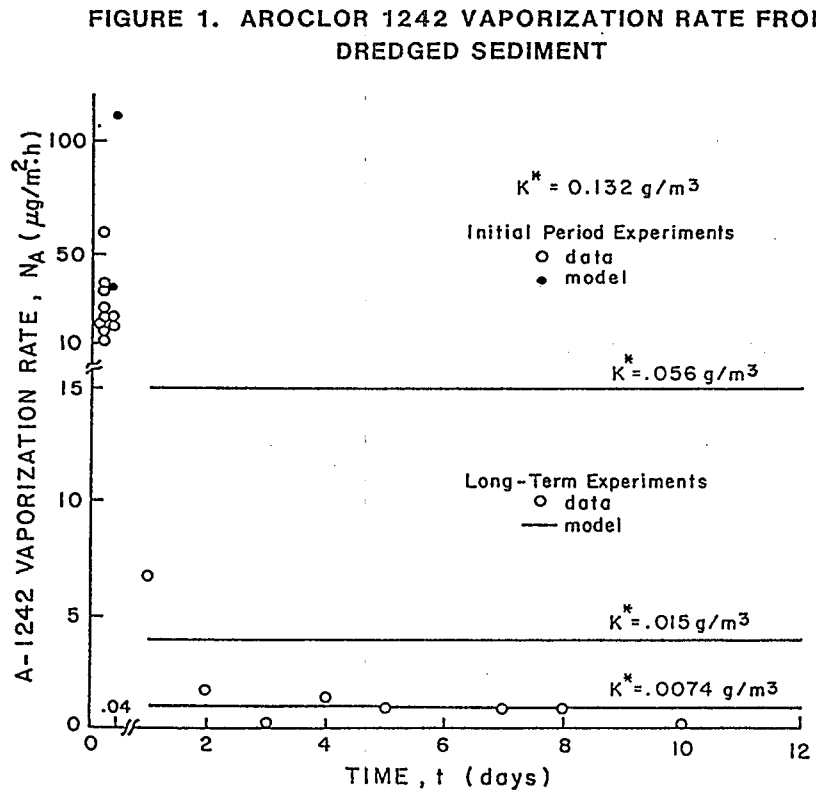


Figure 1. Aroclor 1242 vaporization rate from dredged sediment.

fluxes were 15 and 4 $\mu g.m^{-2}.h^{-1}$ for the two calculated values of K^*. At best the predicted values are 4.7 times larger than the measured values. The model predicts a very weak time dependance on the rate. At day 10 the soil-side mass tranfer resistance accounts for only 1.1% of the transport resistance for the organic. The measured values also seem to display a time dependance. This behavior may be due to several factors including cracking and other soil porosity changes with time. However, it appears that K^* is the primary factor that controls the flux in this set of measurements. A value of 0.0074 $g.m^{-3}$ in the model equation yields predicted fluxes in line with the experimental values. The model predicted and measured values appear in Figure 1. An overall mass balance indicates that 2.32 g of Aroclor 1242 were present initially in the isolation flux chamber. Using 1.7 $\mu g.m^{-2}.h^{-1}$ as the average evaporation rate yields 59 μg lost from the sediment in 10 days. This is 0.0026%, so the bulk of the original Aroclor 1242 remained in the soil and did not evaporate.

CONCLUSIONS:

The theoretical model does a satisfactory job in predicting the Aroclor 1242 emission rate from exposed sediment. The measured values for wet sediment averaged 26 ± 13 $\mu g.m^{-2}.h^{-1}$. The model yielded values of 36 to 113 $\mu g.m^{-2}.h^{-1}$ depending on the k_A values used. The measured values for the dry sediment averaged 0.855 ± 0.432 $\mu g.m^{-2}.h^{-1}$. The most sensitive parameter in the model was K^*, the air-sediment partition constant. In general, the theoretical model overpredicts the measured values by a factor of 1.4 to 18.

Additional experimental measurements are needed to reduce this range of uncertainty and explore the effects of cracking. These experiments should involve re-wetting the soil in order to observe any increase in flux. Field measurements at a CDF site should be performed with the

isolation flux chamber or a similar method. Laboratory experiments should be performed and the air-sediment partition constant K^* measured for damp and dry conditions. This critical parameter has a very weak data base (Valsaraj and Thibodeaux, 1988).

REFERENCES:

Thibodeaux L J (1988): *Theoretical Models for Evaluation of Volatile Emissions to Air During Dredged Material Disposal with Applications to New Bedford Harbor, Massachussetts*, Miscellaneous Paper EL-89-3, US Army Engineer Waterways Experiment; Vicksburg, MS.

Brannon, J M (1989): *Laboratory Assessment of Volatilization from New Bedford Harbor Sediment*, Memorandum for Record, WESES-A, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Thibodeaux L J and H D Scott (1986), Chapter 4 in *Environmental Exposure from Chemicals, Volume 1*, W B Neely and G E Blau (editors), CRC Press, Boca Raton, FL.

Valsaraj K T and L J Thibodeaux (1988), *J. Haz. Materials*, **19**: 1979 - 1989.

ACKNOWLEDGEMENT:

This work was supported by a grant from the US Environmental Protection Agency (Grant No: R 819165-01) to the Hazardous Substance Research Center (South and Southwest). Dr. Dale Manty is the Project Officer.

BIOREMEDIATION OF CONTAMINATED SEDIMENTS

J B. Hughes, V. Jee, and C. H. Ward
Department of Environmental Science and Engineering
P.O. Box 1892
Rice University
Houston, TX 77251

INTRODUCTION

Contaminants in bottom sediments have historically been considered to have minimal environmental impact because they are buried, sorbed or electrostatically bound to clay particles, or incorporated into humus. Physical and chemical conditions such as alkalinity, pH, and redox of the sediments also play a part in sequestering contaminants. (2,3) As long as the sediments are undisturbed, the contaminants are considered stabilized and not an immediate environmental problem. Resuspension of bottom sediments makes contaminants more available for dispersal into the marine environment. Events that can cause resuspension include storm surges, construction activity, and dredging.

A conceptual model of the effect of a resuspension event on contaminated sediments is shown in Figure 1. During resuspension, sediment particles move from an anaerobic to aerobic environment, changing their redox characteristics, and allowing the indigenous aerobic bacteria to grow and utilize certain classes of contaminants as energy sources. The contaminants are also more available for use because the mixing energy imparted to the particles during resuspension enhances mass transfer, allowing contaminants to enter the aqueous phase more rapidly.

The contaminants targeted in this research are polynuclear aromatic hydrocarbons (PAHs), a class of contaminant commonly found in bottom sediments near highly industrialized areas. A major source of PAH contamination is the combustion of fossil fuels. (8,5) Other sources are industrial wastewater effluents, petroleum spills and oilfield produced brine disposal into waterways. PAHs consist of multiple benzene rings fused in linear, angular, and cluster arrangements. PAHs are non-ionic and hydrophobic and as such, are lipid soluble and can be bioaccumulated in the food chain. Exposure to polycyclic compounds has also been associated with higher risks for cancer.

Previous research has shown that PAHs can be biodegraded. Size and structure, i.e., number and configuration of condensed rings, can affect compound disappearance. (4,7) PAHs of up to three condensed rings have been shown to serve as growth substrates. Compounds with more than three rings may be subject to cometabolic degradation.(1) Probably the most important parameter affecting biodegradation is the redox character of the sediment or sediment/water system. Studies of sediment slurries under various redox conditions have shown that rates of compound disappearance and mineralization increase with increasing redox potential. (3,6)

The focus of this research was to examine the relationship between resuspension and biodegradation of PAHs in lab scale slurry reactors. The rate and extent of contaminant release from the sediments into an uncontaminated water column was determined. Oxygen demand of initially anaerobic sediments were investigated. Then rate and extent of phenanthrene biodegradation was examined. Final partitioning of the phenanthrene, after the degradation test, was determined based on mass balance calculations made on the radiolabeled carbon in the tracer. Several factors which may influence the design or operation of bioreactors used for remediation of contaminated sediments were also evaluated.

METHODOLOGY

Sediments used in these experiments were collected from Dickinson Bayou, Galveston County, Texas. The natural environment is esutarine with total dissolved solids (TDS) of the water measuring

5,000 parts per million (ppm). An artificial seawater (ASW) medium based on Difco marine broth without the organics and diluted to the proper TDS was used in all tests. The sediments were artificially contaminated with phenanthrene (a 3-ring PAH). Special care was taken to keep the sediments anaerobic, with all handling done in a nitrogen atmosphere glove box.

Concentration in the various system compartments - liquid, solid, and vapor was monitored using a Hewlett Packard HP 5890 gas chromatograph with photo-ionization detector (GC-PID). Sediments were extracted using a modification of EPA Method 3550 (Sonication) with dichloromethane (DCM) as the solvent. Liquids were extracted by shaking with DCM. The sorbent of the ORBO hydrocarbon vapor traps were also extracted by shaking in DCM. ^{14}C labeled phenanthrene was added to trace mineralization in the biodegradation tests. Radiation levels were measured using a Beckman Model LS 3801 Scintillation counter.

The slurry reactor used in the experiments is shown in Figure 2. CO_2 traps were used in the biodegradation tests. The traps were removed for the abiotic contaminant release experiments. Sediments and artificial seawater (ASW) medium were loaded into the reactors inside the glove box. Three solids loadings were tested - 5, 10, and 15% dry weight sediment. ASW used was purged for 30 minutes with N_2 gas before being brought into the anaerobic environment of the glove box.

The first experimental series determined the rate and extent of phenanthrene release from the sediments to uncontaminated liquid under various conditions of mixing and aeration. These were short term tests (48 hours) with an emphasis on early time measurements. Each solids loading was tested under three mixing conditions - (1) unmixed, (2) continuous mixing, and (3) initial mixing only, both with and without aeration.

Mineralization to CO_2 was tracked in the biodegradation tests using ^{14}C tracer and dual CO_2 traps containing 1N KOH. All reactors in this test series were continuously aerated. At the end of the 7 day biodegradation tests, the reactors were poisoned with mercuric chloride and samples of each system compartment (solid, liquid, and vapor trap) was extracted. A mass balance approach was utilized to determine final partitioning of carbon from degraded phenanthrene. Non-solvent extractable carbon was measured in the sediment fraction using a modified chemical oxygen demand (COD) test. Output gases from the oxidation were passed through dual CO_2 traps and the residual radiation measured by scintillation counting.

Additional tests were performed to evaluate the effect of various parameters on rate and extent of phenanthrene mineralization. Factors examined included intermittent aeration, nutrient amendment, and bioaugmentation. The objectives of these tests were to reduce volatilization losses and shorten degradation time.

RESULTS

Contaminant release into the aqueous phase of sediment/water slurries was rapid in mixed reactors. Solids loading has no effect on rate of contaminant release and little effect on extent with mixing. All reactors reached 80 to 90% of theoretical aqueous concentration within 30 minutes. Mixing, itself, had the greatest effect on rate and extent. Rate of contaminant release was 2 to 4 times slower for unmixed systems. Maximum extent of release was also less than half that seen in mixed reactors. This is shown by Figure 3 which shows contaminant release in reactors loaded with 10% solids.

Aeration effects appear to be masked by mixing effects. No differences in release rates were seen between mixed reactors which were aerated and those that were not. In unmixed reactors, aerated systems showed faster rates of contaminant release than unaerated systems, indicating that the aeration process itself provides some degree of mixing.

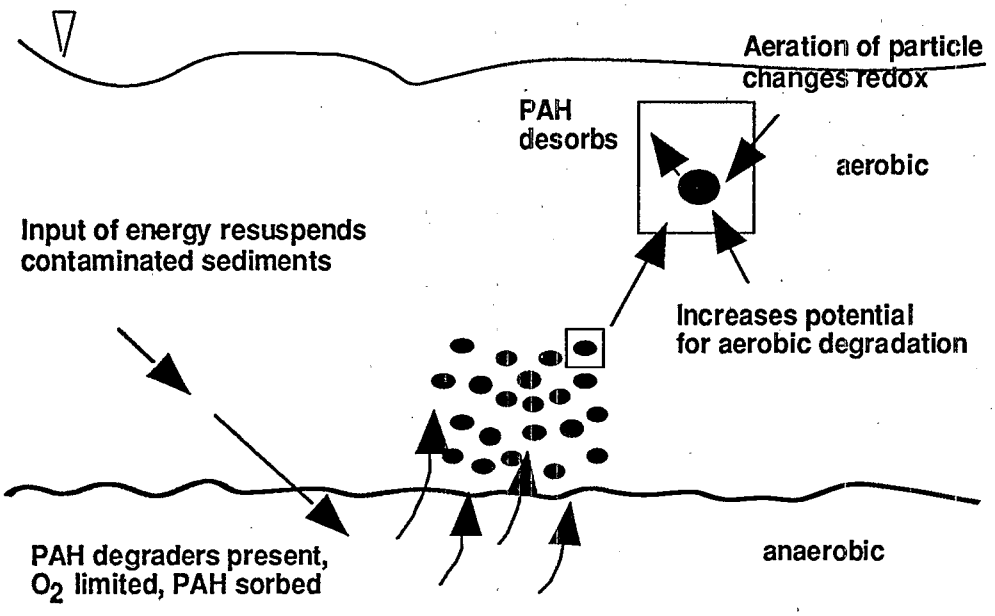


Figure 1. Conceptural model of the resuspension of process and the effect it has on the ability of indigenous bacteria to biodegrade polynuclear aromatic hydrocarbons (PAHs).

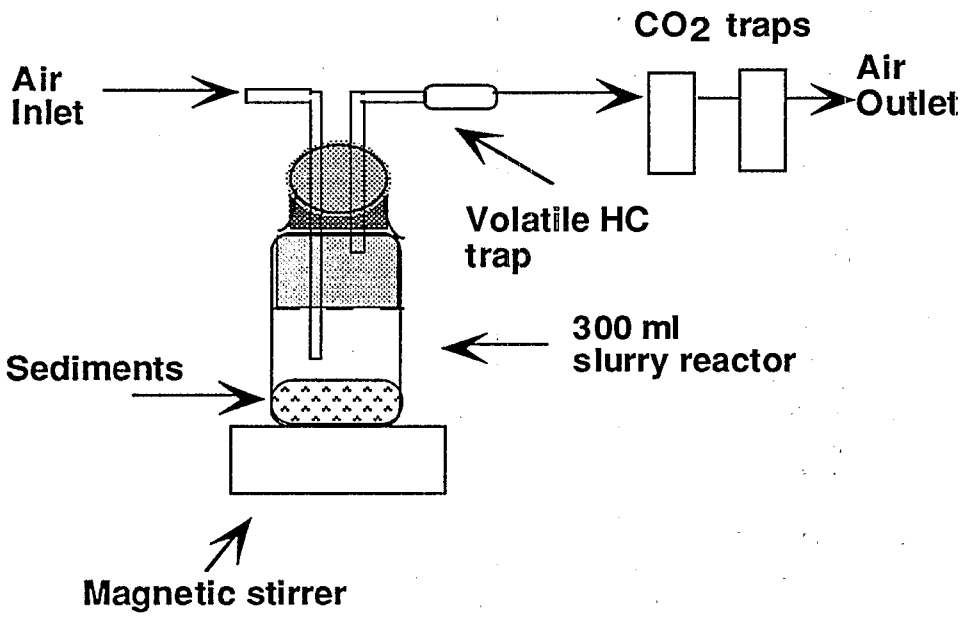


Figure 2. Slurry reactor used in experiments. CO_2 traps are included only in biodegradation tests where radiolabeled CO_2 is a byproduct of phenanthrene mineralization.

Several observations can be made about the biodegradation experiments. Volatilization over the 7 day test period was considerable. A two (2) day lag period was seen before significant mineralization occurred in all reactors. Maximum extent of mineralization appeared to be reached within five (5) days in mixed systems. The effect of mixing on mineralization is clearly evident. Figure 4 shows mineralization in reactors loaded with 10% solids. Significantly higher mineralization was seen in reactors which were mixed.

Mass balance calculations were performed based on tracking of the radiolabeled carbon. Table 1 shows the mass balance for mixed reactors at the end of the biodegradation test. Analysis of the mass balance partitioning in relationship to expected partitioning based on stoichiometry indicates that the phenanthrene was being used as a growth substrate by the indigenous bacteria.

The amount of phenanthrene lost to volatilization is much higher than might be expected from low vapor pressure (6.8×10^{-4} torr.). Therefore the effect of intermittent aeration on mineralization and stripping was tested. The test results show that not only does mineralization still occur without continuous aeration, but also that the final extent of mineralization is higher for the intermittently aerated reactor.

Reactors were amended with various amounts of fertilizer to determine if the low nutrient (nitrogen and phosphorus) content of the ASW could be causing the lag period seen before mineralization. Nutrient amendment had no effect on rate and extent of mineralization. Augmenting the slurry reactor with an aged slurry (2 - 3 days), however, did eliminate the lag time.

CONCLUSIONS

It can be concluded from this series of experiments that resuspension of anaerobic sediments can affect the degradation of phenanthrene sorbed to them. Sediments with contamination levels of 50 ppm phenanthrene were remediated in lab scale slurry reactors to the point that only trace phenanthrene was found after 5 days. Mixing and aeration, natural byproducts of the resuspension process, were the only treatment used. Due to the time required to see complete degradation, it is unlikely that the mixing and aeration provided solely by dredging can be considered a remedial treatment.

The lab scale slurry reactors used in this project show that this type of reactor holds promise as a potential remediation methodology. A slurry reactor can be defined as an enclosed system where sediments and water are maintained in a homogeneous slurry over a fixed period of time. It is envisioned that the reactors will be a batch treatment process. As such its size will be limited.

Ex-situ reactors for sediment remediation could be built on barges or on shore. Both the bottom sediments and a liquid phase would have to be moved to the reactor to form the slurry. If hydraulic dredges are used, the sediments are removed in slurry form and could be pumped directly to the reactors. In-situ reactors would isolate small areas of the contaminated bottom and utilize the overlying water to make the slurry. Potential methods of isolation include caissons, sheet piling, or other types of physical barriers.

Design factors that should be considered include mixing intensity, aeration, and the use of sequential treatment cells. The lab scale reactors used had minimal to insufficient mixing capacity. Any field or full scale test should be designed to provide adequate mixing for the desired slurry. Mixing not only enhances mass transfer of the contaminant from the sediment to the aqueous phase, but also helps to maintain oxygenation of the slurry when open to the atmosphere. Optimum design will utilize intermittent aeration or some form of chemical oxidation, for example addition of peroxide. The purpose will be to minimize contaminant loss due to volatilization or stripping.

Since it was shown that augmenting the reactor with aged slurry eliminated the lag period, an

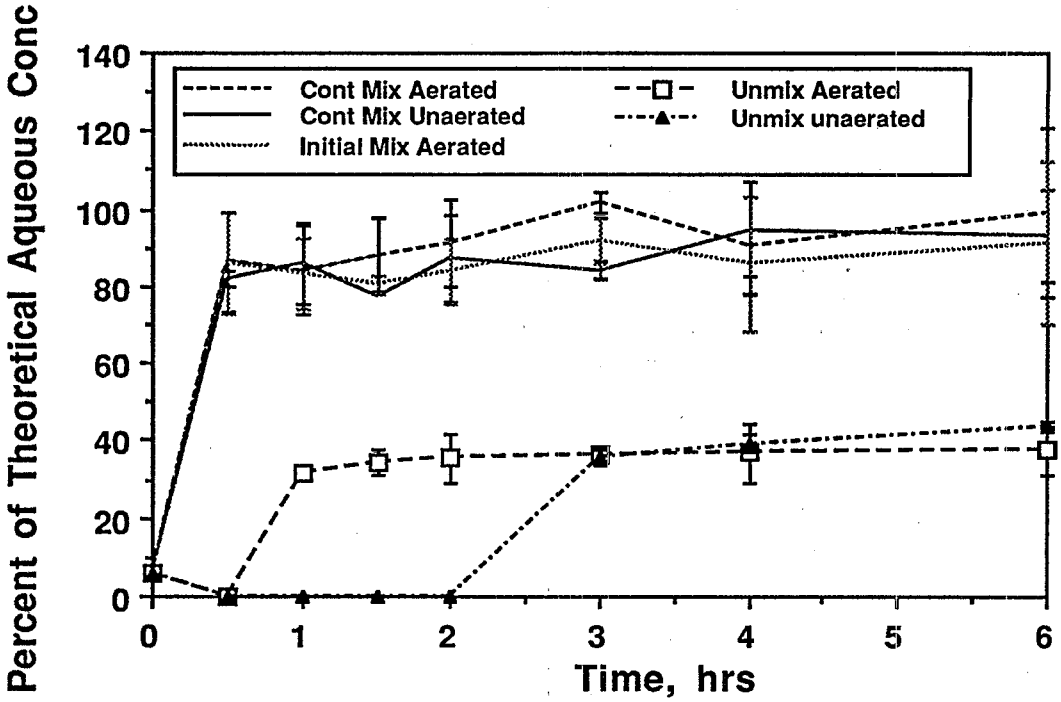


Figure 3. The effect of mixing and aeration on contaminant release in slurry reactors loaded with 10% solids. Error bars represent one standard deviation.

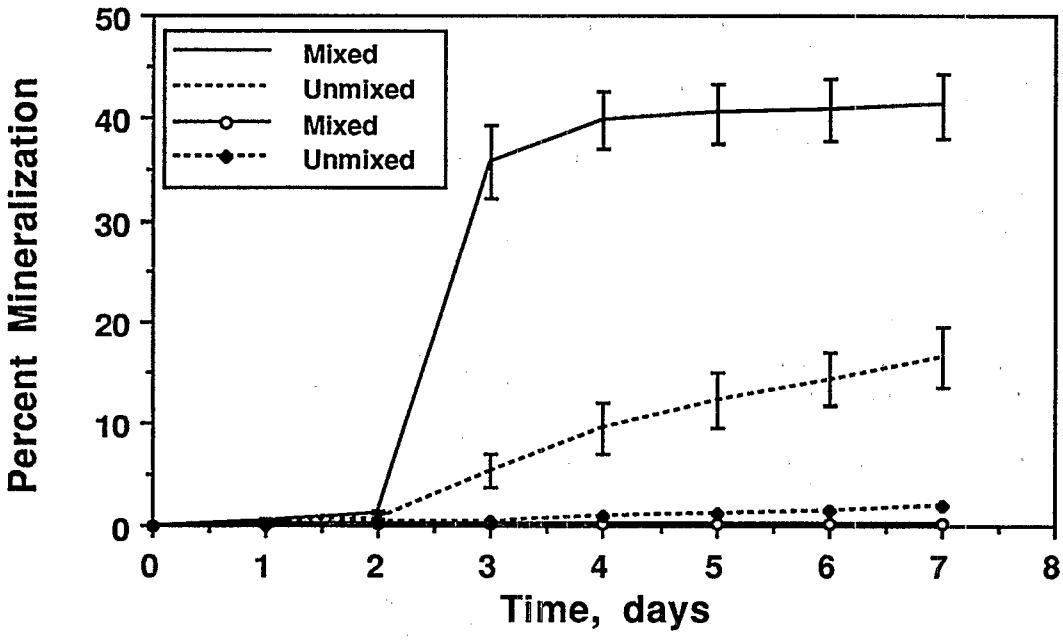


Figure 4. Phenanthrene mineralization in slurry reactors loaded with 10% solids. Error bars represent one standard deviation. Curves with symbols are for the abiotic controls.

overall treatment scheme utilizing some form of sequential treatment seems prudent. Treatment times were reduced by 40% when the reactors were seeded, going from 5 to 3 days to reach maximum extent of mineralization. Ex-situ treatment would require two reactors. Slurry from the initial reactor would be used to seed the second reactor which then would be used to seed the first reactor, etc. In-situ treatment cells could be built so that each successive cell would be seeded by the previously built cell. Removable barriers for only two cells would be required. Cell construction could be timed so that the materials from the first cell would be moved to build the third cell, etc.

From the research conducted, it appears that engineering intervention would be most effective in treating small areas of highly contaminated sediments before dredging. This assumes that in-situ reactors would be more cost effective than ex-situ reactors. Since batch biological treatment requires, at minimum, 3 days, an in-situ approach also eliminates problems associated with sediment storage that would arise if the sediment were treated after dredging.

REFERENCES

1. Cerniglia, C. E. and Heitkamp, M. A. 1989. Microbial Degradation of Polycyclic Aromatic Hydrocarbon (PAH) in the Aquatic Environment. Metabolism of Polycylic Aromatic Hydrocarbons in the Aquatic Environment. Boca Raton, FL, CRC Press.

2. Cullinane, M. J., Averett, D. E., Shafer, R. A., Male, J. W., Truitt, C. L., Bradbury, M.R., Requegnat, W. E. 1990. Contaminated Dredged Material, Control, Treatment and Disposal Practice. Park Ridge, New Jersey, Noyes Data Corporation.

3. Hambrick, G. A., DeLaune, R.D., et al. 1980. "Effect of Estuarine Sediment pH and Oxidation-Reduction Potential on Microbial Hydrocarbon Degradation." Applied and Environmental Microbiology 40(2): 365-369.

4. Heitkamp, M. A. and Cerniglia, C. E. 1987. "Effects of Chemical Structure and Exposure on the Microbial Degradation of Polycyclic Aromatic Hydrocarbons in Freshwater and Estuarine Ecosystems." Environmental Toxicology and Chemistry 6: 535-546.

5. Hites, R. A., LaFlamme, R. E., et al. 1980. Polycyclic Aromatic Hydrocarbons in Marine/Aquatic Sediments: Their Ubiquity. Petroleum in the Marine Environment. Washington, D. C., American Chemical Society. 289-311.

6. Leduc, R., Samson, R. et al. 1992. "Biotic and Abiotic Disappearance of Four PAH Compounds from Flooded Soil Under Various Redox Conditions." Wat. Sci. Tech 26(1-2): 51-60.

7. Lee, R. F., Gardner, W. S. et al. 1978. "Fate of Polycyclic Aromatic Hydrocarbons in Controlled Ecosystem Enclosures." Environmental Science & Technology 12(7): 832-838.

8. Wakeham, S. G., and Farrington, J. W. 1980. Hydrocarbons in Contemporary Aquatic Sediments. Contaminants and Sediments. Ann Arbor, Michigan, Ann Arbor Science. 3-32.

Table 1 Mass balance and partitioning of radiolabeled carbon for mixed reactors after 7 day biodegradation tests.

	5% Solids		10% Solids		15% Solids	
	% Initial	% STDV	% Initial	% STDV	% Initial	% STDV
Mineralized	26.8	20.9	41.1	7.5	30.5	12.8
NS Extract	26.9	36.4	33.7	19.9	59.4	7.4
Volatilized	44.1	25.2	15.2	59.9	8.5	17.6
Sediment	2.3	95.7	0.8	175.0	5.2	61.5
Liquid	8.3	24.1	6.5	61.5	2.6	73.1
Total	108.4	6.1	97.4	3.5	106.1	4.6

POLLUTANT FLUXES TO AQUATIC SYSTEMS VIA BED-SEDIMENT PROCESSES

V Popov, L Maranto, K T Valsaraj[1], D D Reible, L J Thibodeaux, M A Todaro and J Fleeger

Departments of Chemical Engineering and of Zoology
Louisiana State University
Baton Rouge, LA 70803
Phone: 504 388 1426

INTRODUCTION

Hydrophobic organic contaminants (HOCs) sorb strongly to sediments and partition weakly into the porewater and overlying water. This leads to the detection of HOCs in sediments long after their original introduction to the environment. Water bodies with active sediment processes have larger fluxes of HOCs to overlying water. In the absence of sediment resuspension by erosive processes, the normal life cycle activities of benthic organisms will predominate in the transport of particles from within the sediment bed to the sediment-water interface. As a result the HOCs associated with the particles are released to the water column. This process is called *bioturbation* and is the focus of this paper. There are a number of species that act as bioturbators. The most prevalent ones, especially in contaminated sediments across many sites in the U.S. are the Tubificidae species that burrow within the sediment and defecate at the surface.

Capping with clean sediment is a possible remediation measure for isolating the aquatic system from contaminated sediments (Thoma *et al*, 1993). The placement of the cap will effectively increase the pathlength for contaminant transport by diffusion and advection and, will also decrease pollutant release by direct bioturbation of contaminated particles. This paper describes our experiments on contrasting the flux of HOCs from bioturbated capped and uncapped sediments in small laboratory microcosms with those of control microcosms (capped and uncapped) without bioturbators.

METHODOLOGY

The experiments were conducted in laboratory microcosms which have been described in detail elsewhere (Reible *et al*, 1994). They were designed to simulate the flow of water over a sediment surface. Each microcosm was 15 cm x 5 cm x 4.5 cm in dimension and was constructed out of 0.64 cm thick plexiglass. Two flat overflow slots were located on both ends of the microcosms to make water flow more uniformly over the sediment surface. Fifteen such microcosms were used. The total sediment thickness in each was 3.5 cm that included the clean sediment used as cap in some of the microcosms. Seven of them were control microcosms that contained no organisms. Of the seven, three were uncapped and four were capped with clean sediment to a thickness of 0. 5 cm. The remaining eight microcosms contained 200 organisms each. Of the eight, four were uncapped and four were capped with cleam sediment to a thickness of 0.5 cm. The sediment used was obtained from a local area (Bayou Manchac, Baton Rouge, LA). It had an organic carbon content of 2.8% and a porosity of 0.67. The sediment was processed and inoculated with a mixture of three polyaromatic hydrocarbons (pyrene, phenanthrene and dibenzofuran). In this paper we report our results only for pyrene. The pyrene concentration in the sediment was 31.9±1.1 mg/kg. The sediment inoculation procedure was described in an earlier publication (Reible *et al*, 1994). The bioturbators used were *Limnodrillus hoffmeisteri*, head-down feeders often found in many freshwater estuarine environments (Stimpson *et al*, 1985).

In the experiments reported here, the average flow rate of water over the sediment was 500 ml/h. This high flow rate ensured that water-side mass transfer resistance was negligible in the transport of pyrene from sediment to water. The effluent water was collected periodically to estimate the contaminant concentration on an HPLC by an EPA standard method (Reible *et al*, 1994). The flux of contaminant was determined from $N = C\,\Delta V/\Delta t$, where ΔV is the volume collected in time Δt. The experiments were run for sixty days and then the sediment was cored into 4 mm thin sections and analyzed for pyrene.

---

[1]Author for correspondence

RESULTS

The measured fluxes of pyrene from the experimental microcosms are shown in Figure 1. The open symbols represent the chemical flux from the bioturbated systems while the solid symbols represent the flux from the non-bioturbated control microcosms. All fluxes represent the average of four replicate microcosms (except the controls which represent three microcosms); the error bars indicate the standard deviation in the measured fluxes. The standard deviation among the replicate microcosms was typically about 20%, indicating the variability associated with the worm biological activity, liquid extraction and concentration procedures for HPLC analysis. In figure 1 are shown the pyrene flux from both the capped and uncapped Bayou Manchac sediments populated with 200 worms. For comparison the pyrene flux from the control channels are also presented. Pyrene flux in uncapped control channels decreased gradually from ~ 250 ng/cm^2/d at the start of the experiment to about 10 ng/cm^2/d after 25 days. The flux remained stable at the lower value for approximately 30 days. In the capped control channels the pyrene flux observed in the outlet water was zero indicating the effectiveness of the cap in retarding the movement of a hydrophobic compound from the underlying sediment. The data is in agreement with the observed trend in earlier experiments on capping (Thoma *et al*, 1993). The organisms were added after six days of the experiment, the influence of which is obvious in the flux of pyrene. Whereas the pyrene flux in the control channels was about 60 to 70 ng/cm^2/d at the time of worm incorporation into the sediment, the bioturbated microcosms showed a flux of 140 ng/cm^2/d. Even towards the end of the experiment the flux in the bioturbated microcosms remained about 60 ng/cm^2/d. In the capped microcosms populated by the worms, the flux was quite stable during the course of the experiment and varied between 30 to 40 ng/cm^2/d. Towards the end of the experiment, the fluxes from both the capped and uncapped sediments with worms were almost identical.

Figure 2 represents the sediment concentration profile for pyrene in uncapped control without worms, capped control without worms, uncapped sediment with worms and capped sediment with worms. The profiles in the uncapped controls without worms showed the expected exponential profile over the first 4 mm of the contaminated layer where the sediment concentration decreased from an initial loading of 32 mg/kg to 7 to 12 mg/kg. In the uncapped microcosms with worms the depletion of pyrene was larger at the surface. In the capped control without worms, the expected effect of decreased movement of pyrene at the surface was apparent; in fact, there was only minimal amout of pyrene that migrated into the clean cap. In the microcosm with cap and worms, there was a clear indication of the worm transporting pyrene through the cap. It was observed that the worm fecal pellets collected at the surface contained about 5 mg/kg of pyrene, while the underlying 3 mm of the cap contained no pyrene. The depletion layer in this case was ~ 10 mm.

The above results clearly indicate that bioturbation significantly increased the contaminant flux from the sediment over control capped and uncapped microcosms. The total contaminant flux from the sediment can be regarded as the sum of the diffusive flux from the porewater and the bioturbation flux. The latter is a combination of the sediment particle transport and water pumping during feeding activities by worms. Initially the diffusion from the sediment surface will be large; however, with time the effective depletion of the surface sediment will lead to a decrease in the rate of molecular diffusion. As the diffusive flux decreases with time relative significance of bioturbation will increase. The bioturbation flux from the sediment can be determined by subtracting the flux in the controls without worms from those of the microcosms with worms. For pyrene the average bioturbation related fluxes estimated thus were: 55±14 ng/cm^2/d in the uncapped microcosms, and 33±6 ng/cm^2/d in the capped microcosms. Therefore the decrease in pyrene flux as a result of the cap was only 40% in the presence of the worms. The flux due to bioturbation as obtained above was observed to remain relatively constant for pyrene during the course of the experiment.

An effective bioturbation mass transfer coefficient can be defined as the ratio of the flux due to bioturbation to the contaminant concentration in the sediment:

$$K_b = \frac{(N_{obs} - N_{cont})}{(\rho_b \cdot W_{sed})} \qquad (1)$$

The numerator represents the bioturbation flux, viz., the difference in flux between the microcosms with the species (N_{obs}) and the microcosms without the species (N_{cont}). ρ_b is the

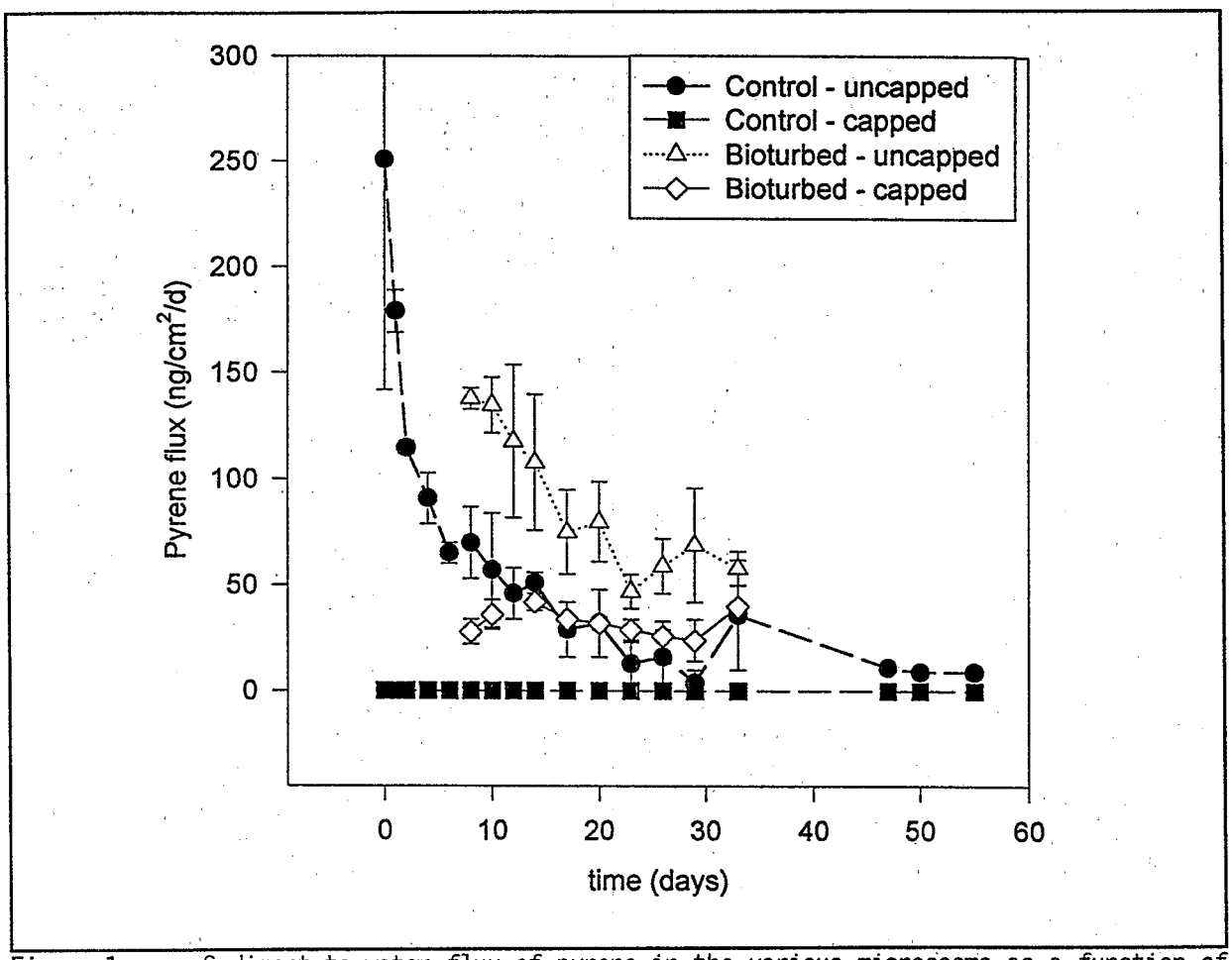


Figure 1. Sediment-to-water flux of pyrene in the various microcosms as a function of time.

sediment bulk density and W_{sed} is the sediment concentration of pyrene. The effective bioturbation mass transfer coefficient for pyrene was 0.7 cm/y. This is comparable to measured values in the field for other compounds which range from 0.1 to 10 cm/y (Reible *et al*, 1994). Assuming that the effective bioturbation depth is limited to ~ 3 cm, an effective bioturbation diffusion constant can be estimated from $D_{bio} = K_b \bullet (3\ cm)$, which for pyrene would be 2.1 cm^2/y.

CONCLUSIONS

The major focus of these experiments was to evaluate the effects of a conveyor-belt worm *Limnodrilus hoffmeisteri* on capping as a control technology for contaminated sediment remediation. The overall approach was to inoculate the sediment with contaminants and then monitor its effluent concentration in small microcosms inhabited by the species. The pyrene flux in uncapped control microcosms decreased gradually from 250 $ng/cm^2/d$ at the start of the experiment to about 10 $ng/cm^2/d$ after 30 days. The flux then remained constant for the next 30 days. The addition of the worms after six days of the experiment markedly increased the flux of pyrene. The flux due to bioturbation from an uncapped sediment was 55±14 $ng/cm^2/d$ and from a capped sediment was 33±6 $ng/cm^2/d$. Towards the end of the experiment the flux from both capped and uncapped sediments were similar. The effective bioturbation mass transfer coefficient for pyrene was 0.7 cm/y. Capping effectively reduced the contaminant release to the water column only in the absence of the worms. In the presence of the worms, a 5 mm layer of cap was found to be less effective in retarding the movement of pyrene from the underlying contaminated sediment to the overlying water.

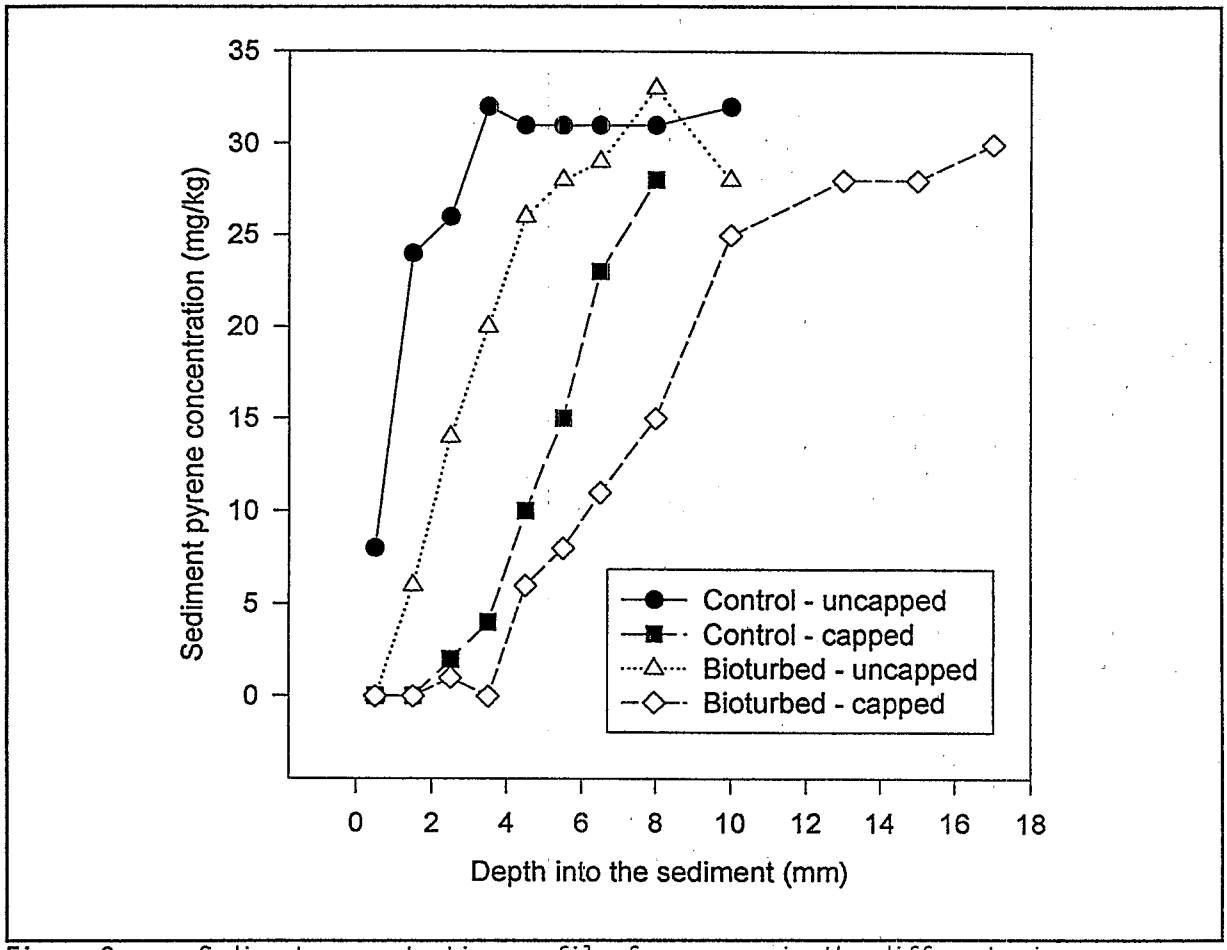


Figure 2. Sediment concentration profile for pyrene in the different microcosms as a function of depth into the sediment.

REFERENCES

Reible D D, V Popov, K T Valsaraj, L J Thibodeaux, M Dikshit, F Lin, M A Todaro and J F Fleeger (1994), Contaminant fluxes from sediment due to tubificid oligochaete bioturbation, *Water Research* (under review).

Stimpson K S, D J Klemm and J K Hiltunen (1985), Freshwater tubificidae: Annelida Oligochaeta. *In A Guide to the Freshwater Annelida (Polychaeta, Naidid and Tubificid Oligochaeta and Hirudenia) of North America*, Klemm D J (ed), Kendall/Hunt, Dubuque, IA, p.44.

Thoma, G J, D D Reible, K T Valsaraj and L J Thibodeaux (1993), Efficiency of capping contaminated sediments in situ 2. Mathematics of diffusion-adsorption in the capping layer, *Environ. Sci. Technol.*, *27*, 2412-2419.

ACKNOWLEDGEMENT

This work was funded by a grant (R 819165-01) from the US EPA to the LSU Hazardous Substance Research Center (South and Southwest).

ACCELERATING RESEARCH AND DEVELOPMENT OF INNOVATIVE TECHNOLOGIES

Norma M. Lewis and Randy A. Parker
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
Office of Research and Development
26 West Martin Luther King Drive
Cincinnati, OH 45268
(513) 569-7665

The U.S. Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation (SITE) Program encourages the development of innovative technologies for faster, more effective, and less costly treatment of hazardous waste. The SITE Program demonstrates full scale technologies through the Demonstration Program, and provides financial and technical assistance to developers of bench- and pilot-scale technologies through the Emerging Technology Program. Other SITE programs support assessment of innovative technologies for site characterization (Monitoring and Measurement Technologies Program), and for dissemination of information on innovative technologies (Technology Transfer Program).

The primary focus of this panel discussion is the SITE Emerging Technology Program. This Program brings government and the private sector together to foster and accelerate research and development of innovative technologies for commercialization. The Emerging Technology Program seeks to accelerate the development of innovative an alternative technologies by:

- Entering into Cooperative Agreements with innovative technology developers for technical and financial assistance;
- Providing access to national and international scientific and engineering information resources;
- Promotion of technologies to a level of confidence where they can be demonstrated in the field; and
- Encouraging technologies with potential to move into the commercial marketplace.

The panel discussion will bring together representatives of government agencies, private sector and university developers of innovative technologies, and representatives of environmental policy makers in an open forum to discuss the opportunities and impediments associated with the development of innovative technologies. Panelists and audience members will discuss the various aspects of innovative technology development from both the government and private sector perspectives.

SUPERCRITICAL EXTRACTION OF POLYCHLORINATED BIPHENYLS FROM SOILS AND SEDIMENTS: REMEDIATION AND POSSIBLE RISKS

Lawrence L. Tavlarides*, Pairu Chen, Wu Zhou, Wayne S. Amato
Department of Chemical Engineering and Materials Science, Syracuse University
320 Hinds Hall, Syracuse University
Syracuse, NY 13244-1190
Tel: (315) 443-1883
Fax: (315) 443-2559

INTRODUCTION

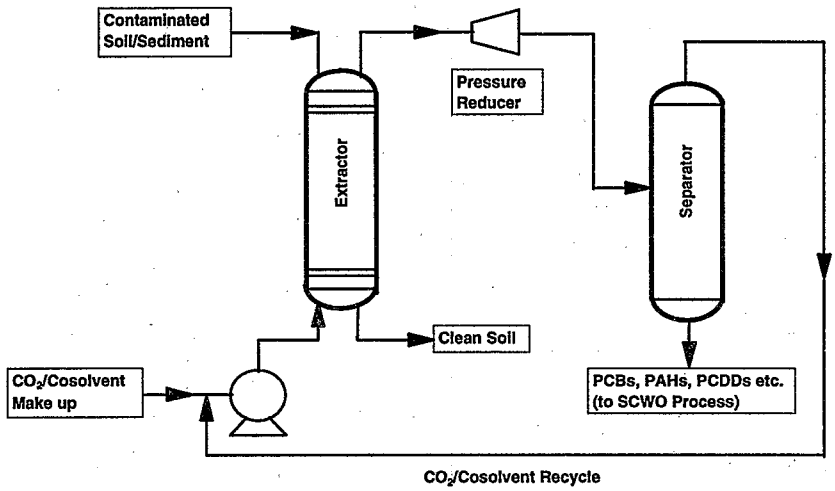
It is estimated that there exists about 350 million pounds of polychlorinated biphenyls (PCBs) in landfill and other storage, and another 24 million pounds in sediments, soil, vegetation and animals (1). The potential environmental threat of the large amount of PCBs has called for the development of effective PCB cleanup techniques. Although some PCB remediation technologies such as incineration and in-situ vitrification have been commercial available, many efforts are still being conducted in order to develop more economic and social acceptable methods (1-3). Among these efforts, the application of supercritical fluid extraction (SFE) in the removal of toxic organics from environmental samples is receiving much attention due to the unique properties of supercritical fluids (SCFs) such as low viscosity, high diffusivity, and easily tunable solvent power (2-5). A process concept advanced at Syracuse University will be presented here.

The process to treat PCB contaminated soils with supercritical technique may involve some risks. These risks could include additional contamination of underground waters due to fracture and permeation through underground structure when contaminated soils are excavated; removal of organic matter from soil and rendering it inert; hazardous operation of large scale high pressure mobile apparatus; and hazards in surface transportation of PCB soil extracts to a central site for supercritical water oxidation (SCWO) destruction. These issues will be discussed.

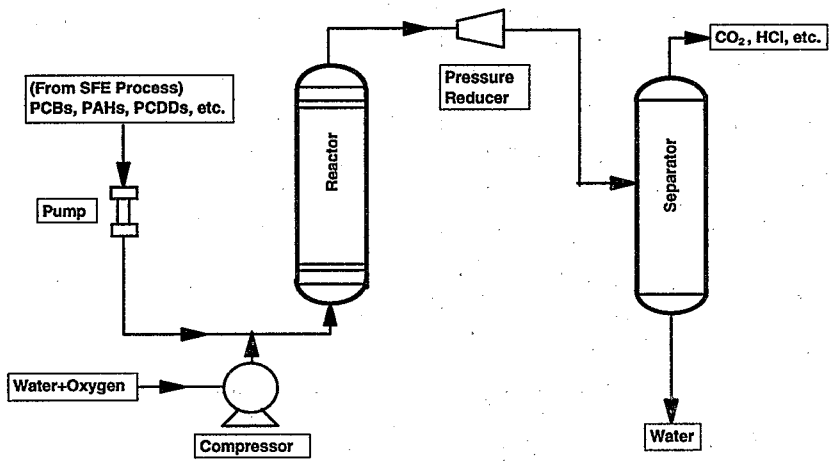
METHODOLOGY

We are developing a new generation of soil remediation technology at Syracuse University to clean soils and sediments contaminated with chlorinated hydrocarbons such as PCBs as well as polycyclic aromatic hydrocarbons (PAHs). The two-stage concept advanced is shown in Figure 1. First (Figure 1a), the toxic PCBs or PAHs are extracted from the sediments or soils using SFE with high-pressure carbon dioxide fluids. The clean soils/sediments are returned to the site, the concentrated toxic organics are separated from the supercritical fluids for further processing, and the supercritical fluids are recycled. In the second process step (Figure 1b), SCWO, the concentrated toxic organics are destroyed by wet oxidation to form harmless carbon dioxide, water and hydrochloric acid.

A laboratory scale extraction unit is employed to obtain desorption data for PCB removal from laboratory-spiked and native contaminated soils with supercritical carbon dioxide and cosolvents. Various conditions of extraction for a variety of soils/sediments have been studied. A flowsheet of the unit is shown in Figure 2. The fixed-bed unit can be operated at pressures and temperatures as high as 680 atm and 100 °C.



(a) Supercritical Fluid Extraction(SFE)



(b) Supercritical Water Oxidation(SCWO)

Figure 1. Supercritical Methods for Soil Clean-up

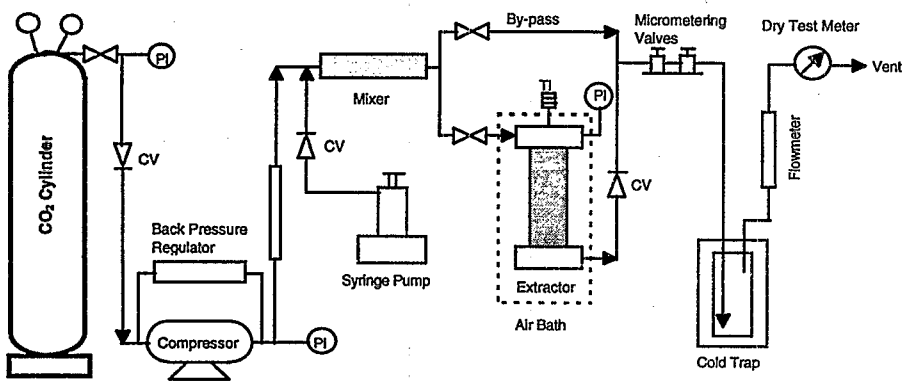


Figure 2. Schematic of Laboratory SFE System

RESULTS

Experiments have been executed with the laboratory scale unit in a wide range of experimental conditions such as temperature, pressure, cosolvent type and concentrations, soil type and initial PCB concentration. A summary of results are shown in Table 1 which shows the contact times necessary to achieve sub 10 ppm removal of PCB congeners (Aroclor 1248) from various soil types at specific initial concentration.

TABLE 1. SUMMARY OF EXPERIMENTS WITH SUB 10 PPM REMOVAL OF AROCLOR 1248

Soil	Initial Conc. (ppm)	Pressure (atm)	Temp. (°C)	Cosolvent (mol%)	Moisture (wt.%)	Contact Time (min.)	Residual Conc. (ppm)
		P1	T1	5	10	60	2.6
Till	1150	P2	T2	5	10	45	3.2
		P2	T3	5	10	30	3.0
		P2	T1	0	10	120	3.4
Sediment (Native, St. Lawrence River)	370	P1	T2	5	0	60	18.9
		P1	T2	5	10	60	15.1
		P1	T2	5	0	45	6.5
Sediment (Native, Hudson River)	71	P1	T2	5	20	45	5.7
		P1	T3	5	0	60	4.3
		P1	T3	5	20	60	3.2
		P2	T2	5	10	60	4.4
Surficial (4" - 12")	4200	P2	T3	5	10	30	6.7
		P2	T2	5	0	30	8.0
Sand	950	P1	T2	5	10	15	1.2

These results show that sub 10 ppm residual concentrations can be achieved at fixed-bed contact times of 15 to 60 minutes.

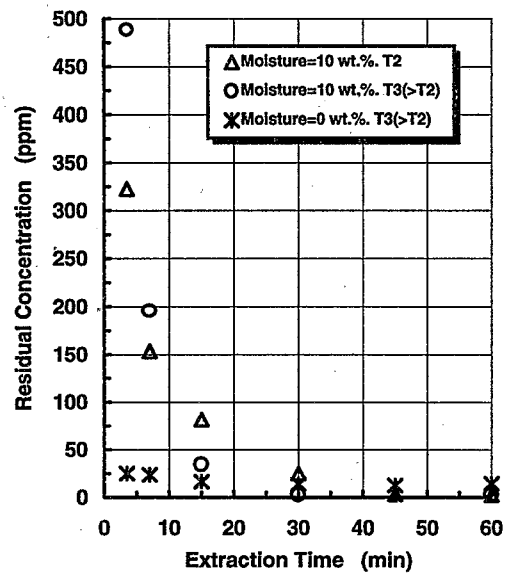


Figure 3. Temperature and Moisture Effects on SFE of Arolor 1248 from Lab-spiked Till
Conditions: P2, MOD1=5 mol%,
Initial Concentration=1150 ppm.

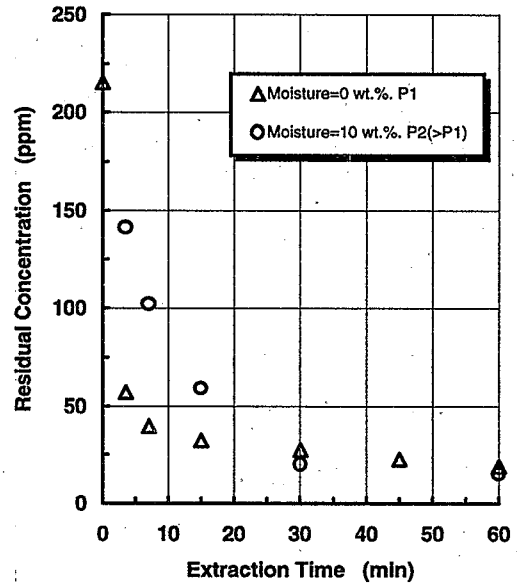


Figure 4. Moisture Effects on SFE of PCBs from Contaminated Sediment of St. Lawrence River
Conditions: T2, MOD1=5 mol%,
Initial Concentration=370 ppm.

Figures 3 and 4 are the experimental results whereby the residual Aroclor 1248 concentration is plotted versus time of extraction during which the supercritical carbon dioxide with cosolvent is passed through the bed of contaminated soil. In Figure 3, the results for till are illustrated. Higher temperature of T3 is preferred to remove Aroclor 1248 from wet till to sub 5 ppm. At T2, it takes 45 minutes, but 30 minutes at T3. It is also seen that a rapid drop occurs without moisture present, to about 25 ppm after 3.5 minutes of contact, however, an equilibrium value is reached and the final concentration is 12 ppm.

In Figure 4, it is seen that the residual concentration drops to 19 ppm between 30 to 45 minutes for extraction of Aroclor 1248 from contaminated, St. Lawrence River sediment of initial concentration of 370 ppm for either dry or 10 wt.% moisture content sediment. These results occur although the dry samples were extracted at a lower pressure. The residual concentrations remain at the same level even after 60 minutes of extraction which indicates the achievement of equilibrium value. Desorption rate models are being applied to correlate these data.

Economic estimates have been made comparing treatment costs for supercritical extraction of PCBs from soil with other competing technologies. This comparison is based on an up-date of work by Carpenter (15) and has built into it the soil handing costs and shown in Table 2.

The comparison shows the favorable economics for SFE/SCWO of PCBs from soils.

CONCLUSIONS

The results of laboratory scale SFE clearly indicate that supercritical carbon dioxide/cosolvent fluids can remove PCBs in various contaminated soil matrices to sub 10 ppm level under proper conditions of contact.

An economic analysis based on laboratory scale unit results shows that the SFE/SCWO of PCBs from soils to be a favorable process.

Despite the advantages of the supercritical technology for remediation of contaminated soils, risks may still occur during the processing procedures. The risks involved would be disturbing underground structure and causing dispersion of contaminants beyond the hazardous waste site; removal of organic matter from soil and producing an inert soil which may be unsuitable for reuse; hazards in transporting PCB laden extracted hydrocarbons to a central site for SCWO destruction; and hazardous operation of large scale high pressure mobile apparatus. These risks do not appear insurmountable, however.

SCWO studies are in progress to determine conditions for acceptable PCB destruction efficiencies, kinetics of the reaction, and economic estimates of this process step.

A bench scale unit has been fabricated and installed for experiments to confirm the laboratory conditions and to establish suitable extractor geometry and contacting schemes for a viable process.

TABLE 2* COMPARISON OF TREATMENT PROCESSES

Process (order of rank)	Cost Range ($/m³ processed)
O.H.M. Methanol Extraction	$513 to $658
Advanced Electric Reactor (thermal treatment)	$1063 to $1206
Acurex Solvent Wash (hexane/trichlorotrifluoro-ethane extraction	$251 to $728
Bio-Clean	$245 to $474
Vitrification	$326 to $702
LARC (isopropanol extraction and radiation treatment)	$286 to $430
Modar Supercritical Water	$320 to $938
Soilex Solvent Extraction (kerosene extraction)	$1096 to $1169
SFE/SCWO (estimate in this work)#	$220 to $270

* First eight process costs taken from Carpenter (15); 1985 dollars updated to 1994 dollars using 1.35 M&S factor.
# Assumptions for this estimate are given in the text.

REFERENCES

1. Amend, L. J. and Lederman, P. B. Critical Evaluation of PCB Remediation Technologies. Environmental Progress 11(3):173-177,1992.
2. Chen, P.; Zhou, W.; Zhang, J. and Tavlarides, L. L.Desorption of Polychlorinated Biphenyls from Soils with Supercritical Fluids. Environmental Science and Technology in preparation.
3. Zhou, W.; Chen, P. and Tavlarides, L. L. Supercritical Fluid Extraction of Polychlorinated Biphenyls from Sediments. Environmental Science and Technology in preparation.
4. Richter, M.; Chen, P.; Zhou, W. and Tavlarides, L. L. Modeling of Desorption of Polychlorinated Biphenyls from Soils under Supercritical Conditions. Ind. Eng. Chem. Res. in preparation.
5. McHugh, M. and Krukonis, V. In: M.A. Stoneham (ed.),Supercritical Fluid Extraction, Butterworth Publishers, 1986, p. 10.
6. Chester, T. L.; Pinkton, J.D. and Raynie, D.E. Supercritical Fluid Chromatography and Extraction. Anal. Chem. 64:153R-170R, 1992.
7. Hawthorne, S.B.; Miller, D.J.; Burford, M.D.; Langenfeld, J.J.; Eckert-Tilotta, S. and Louie, P.K. Factors Controlling Quantitative Supercritical Fluid Extraction of Environmental Samples. J. Chrom. 642:301-317, 1993.
8. Burford, M.D.; Hawthorne, S.B. and Miller, D.J. Extraction Rates of Spiked versus Native PAHs from Heterogeneous Environmental Samples Using Supercritical Fluid Extraction and Sonication in Methylene Chloride. Anal. Chem. 65:1497-1505, 1993.

9. Hawthorne, S.B.; Krieger, M.S. and Miller, D.J. Supercritical Carbon Dioxide Extraction of Polychlorinated Biphenyls, Polycyclic Aromatic Hydrocarbons, Heteroatom-Containing Polycyclic Aromatic Hydrocarbons, and n-Alkanes from Polyurethane Foam Sorbents. Anal. Chem. 61:736-740, 1989.
10. Langenfeld, J.J.; Hawthorne, S.B.; Miller, D.J. and Pawliszyn, J. Effects of Temperature and Pressure on Supercritical Fluid Extraction Efficiencies of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls. Anal. Chem. 65:338-344, 1993.
11. Hawthorne, S.B.; Langenfeld, J.J.; Miller, D.J. and Burford, M.D. Comparison of Supercritical $CHClF_2$, N_2O, and CO_2 for the Extraction of Polychlorinated Biphenyls and Polycyclic Aromatic Hydrocarbons. Anal. Chem. 64:1614-1622, 1992.
12. Fahmy, T.M.; Paulaitis, M.E.; Johnson, D.M. and McNally, M.E.P. Modifier Effects in the Supercritical Fluid Extraction of Solutes fro Clay, Soil, and Plant Materials. Anal. Chem. 65:1462-1469, 1993.
13. Bøwadt, S. and Johansson, B. Analysis of PCBs in Sulfur-Containing Sediments by Off-line Supercritical Fluid Extraction and HRGC-ECD. Anal. Chem. 66:667-673, 1994.
14. Alexandrou, N. and Pawliszyn, J. Supercritical Fluid Extraction for the Rapid Determination of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Municipal Incinerator Fly Ash. Anal. Chem. 61:2770-2776, 1989.
15. Carpenter, B.H. PCB Sediment Decontamination-Technical Economic Assessment of Alternative Treatments. EPA 600/2-86/112. U.S. Environmental Protection Agency, 1986.

BY-PRODUCTS FROM SUPERCRITICAL WATER OXIDATION: PATHWAYS, KINETICS, AND MECHANISMS

Phillip E. Savage* and Sudhama Gopalan
University of Michigan, Chemical Engineering Department
Ann Arbor, MI 48109-2136 phone (313) 764-3386

INTRODUCTION

Supercritical water oxidation (SCWO) is an emerging technology for the ultimate destruction of organic wastes. Organic compounds and oxygen can be intimately mixed in a single homogeneous aqueous phase at supercritical conditions ($T_C = 374°C$, $P_C = 218$ atm). Thus, the rapid oxidation reactions are unhindered by inter-phase transport limitations that could occur at subcritical conditions where multiple phases exist. Savage et al. (1) describe current research into SCWO reactions in their review of reactions at supercritical conditions.

The rational design, optimization, control, and analysis of SCWO processes requires a knowledge of SCWO kinetics and potential byproducts formed from the oxidation of real pollutants. Our research group has focused on the oxidation of phenolic compounds (2-10), and this presentation will provide an overview of our most recent work.

METHODOLOGY

All oxidation experiments were performed in a reactor that nominally operated isothermally, isobarically, and in plug flow. Aqueous solutions of O_2 and the phenol were prepared separately and used as the reactor feed streams. The feed streams were pressurized and pumped through the reactor using two liquid chromatography pumps. The phenol and oxygen streams were preheated in separate coils of Hastelloy C-276 tubing. These preheater lines meet in a mixing union, where the temperature was measured by a thermocouple and the mixed feed streams enter the 4 m. long by 0.125 in. O.D. Hastelloy reactor. The preheater lines, mixing tee, and reactor coil are housed in an isothermal fluidized aluminum-oxide bath equipped with a temperature controller.

The reactor effluent was cooled in two consecutive tube-in-tube heat exchangers and decompressed in a back pressure regulator. The exiting stream was separated into gas and liquid phases (at ambient conditions) in a liquid trap. The gas flow rate was measured with a bubble meter at the outlet of the system, and the gas stream was then sent to an on-line gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). The liquid flow rate was measured, and samples of the liquid phase were retained for analysis.

A reverse-phase high-performance liquid chromatograph (HPLC) was used to determine the concentration of phenolics in the liquid effluent samples. Analyses were performed isocratically with a mobile phase of water/acetonitrile in a 5:2 v/v ratio flowing at 1 ml/min. The UV absorbance at a wavelength of 210 nm was monitored, and detector response factors were determined experimentally.

Before additional products in the liquid phase were analyzed, the samples were concentrated because many products were present in low concentrations. 20 mL of the reactor effluent was extracted with three successive 10 mL aliquots of dichloromethane. The 30 mL volume of this organic phase was subsequently reduced to 1 mL using a Kuderna-Danish concentrator in a water bath at 50°C. 10 mL of a dichloromethane solution containing a standard was added to each sample prior to concentration.

Reaction products in these concentrated samples were identified by GC-MS. The reaction products were quantified by GC with a flame ionization detector (FID). When a suspected reaction product was available commercially, we positively identified that product by matching both the mass spectrum and retention time with those of the authentic sample. The FID response factor was then determined experimentally for these compounds. Other suspected products, for which the authentic compound was not available commercially, were tentatively identified by inspecting the mass spectra and

matching them to spectra stored in the GC-MS computer database. The response factors for these products were assumed to be equal to those determined experimentally for chemically similar compounds. The GCs were equipped with12 m x 0.2 mm O.D. HP-1 capillary columns. Helium served as the carrier gas, and 1mL of the sample was injected in the splitless mode.

RESULTS

Thornton et al. (5), Li et al. (3), Martino et al. (10), and Gopalan and Savage (8) identified several multi-ring products (e.g. dibenzofuran, 2 and 4-phenoxyphenol, dibenzo-*p*-dioxin and 2,2'-biphenol) from the oxidation of phenols in supercritical water at temperatures up to 480°C. The formation of dimers is important because some of these are potentially more toxic than the reactant. By determining the concentrations, molar yields, and selectivities of many of these products, we have been able to develop reaction networks that describe the formation of these multi-ring species.

The data of Thornton and Savage (7) for phenol SCWO, and Li et al. (2,3) for SCWO of 2-chlorophenol show some general trends for product selectivities. The dimer selectivity tends to decrease with increasing phenol conversion while the selectivity to gases (CO, CO_2) tends to increase with increasing phenol conversion. We developed a reaction network that was consistent with these qualitative trends in the experimental product selectivities. This network considered phenol, dimers, carbon oxides, and "others" as the distinct chemical species. In this network, phenol is consumed by parallel paths that form dimers and "other" products. The dimers decompose to the ring-opening and other products. Finally, the "other" products are oxidized to CO and CO_2.

The mathematical modeling of each network involved differential equations for each of the product categories. To determine the rate parameters for each of the four reactions in the model, we employed SimuSolv (11). The parameter estimation process incorporated an integration routine in addition to the optimization. A linear multistep predictor-corrector integration routine, LSODE, was employed in concert with the generalized reduced-gradient method. The entities for which experimental data were obtained; viz. phenol, dimers, and gases, were the response variables. The criterion for parameter estimation was the maximization of the log likelihood function for each of the response variables. The reaction orders (a_i,b_i) for the organic compound and oxygen for each pathway were determined from data at a single temperature, 460°C.

The reaction orders obtained from the regression of data at 460°C were then fixed in the subsequent parameter estimation. Also, the water order for each step was fixed at 0.42, the value obtained for phenol disappearance kinetics. Data at four temperatures; 420, 440, 460 and 480°C were then used to determine the Arrhenius parameters for the four individual reactions. Table 1 displays the results of the parameter estimation process for the network model. The units are kcal, moles, liters, and seconds.

Table 1. PARAMETERS IN REACTION NETWORK MODEL

	Reaction 1	Reaction 2	Reaction 3	Reaction 4
a	0.89 ± 0.26	0.86 ± 1.19	0.86 ± 0.30	0.50 ± 0.15
b	0.49 ± 0.23	0.48 ± 1.15	0.60 ± 0.32	1.49 ± 0.31
E_a (kcal/mol)	10.0 ± 4.7	25.5 ± 15.0	28.8 ± 4.1	44.8 ± 9.0
A ($M^{0.58-a-b}\ s^{-1}$)	$10^{1.8 \pm 1.5}$	$10^{5.6 \pm 5.5}$	$10^{8.5 \pm 2.6}$	$10^{13.5 \pm 2.8}$
k @ 460°C,250 atm	0.026± 0.009	.0034 ± 0.0001	0.398 ± 0.023	0.293 ± 0.054

(M = moles of carbon per liter)

We used the model with the parameters in Table 1 to predict the results of phenol SCWO reported by Thornton and Savage (6,7), and Li et al. (2). Figure 1 shows a comparison of the effect of residence time on the phenol conversion and the dimer and gas selectivities at 380°C and 278 atm. The curves, which give the model predictions, capture the trends in the experimental data well.

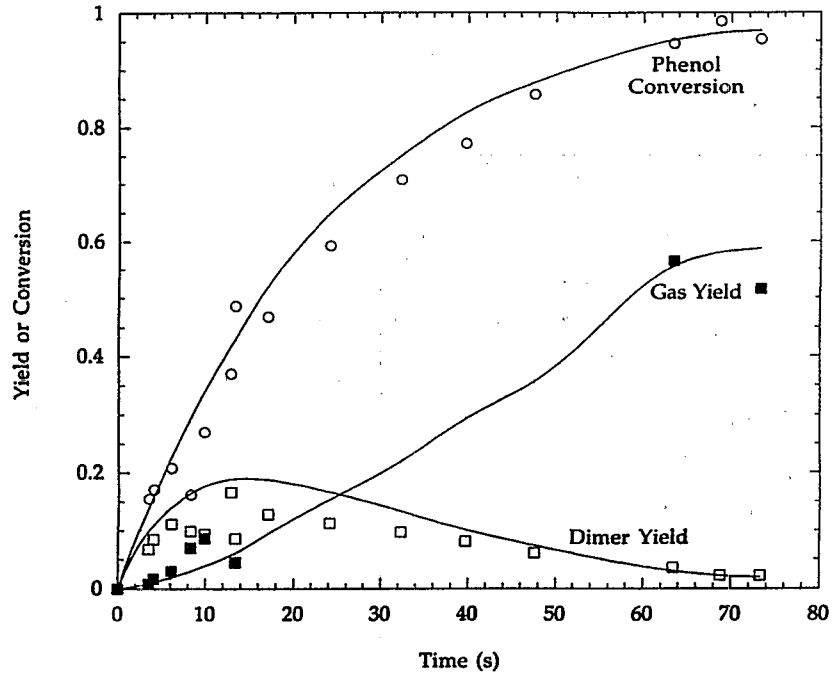


Figure 1. Product Yield vs. Residence Time for Phenol SCWO at 380°C and 278 atm

The estimated activation energies in Table 1 enable us to compare the rate constants for phenol consumption along the competing parallel paths as a function of temperature. The initial dimer selectivities calculated from the model (calculated as k_1/k_1+k_2) range from 89% at 420°C to 78% at 480°C. These rate constants when extrapolated to 600°C predict an initial selectivity to dimers of ~45%, which shows that even at higher temperatures dimerization and ring-opening reactions are likely to be equally important. Examining lower temperatures we note that at 380°C, nearly 95% of the initial selectivity of phenol is towards dimers as shown in Figure 1. These results show that dimerization is the main primary pathway for phenol. In fact, at 380°C, the path from phenol to ring-opening and other products is negligible, and the reaction network could be reduced to a set of consecutive reactions.

The model also shows that although the formation of dimers cannot be prevented, the selectivity to dimers decreases with increasing phenol conversion (Figure 1). At complete conversion of phenol the selectivity towards dimers is essentially zero. Also, the destruction of dimers is aided by higher temperatures as is evident from the activation energy for the destruction of dimers (29 kcal/mol) exceeding that for dimer formation (10 kcal/mol). This difference in activation energies translates to an increase in the ratio of the rate constant for destruction of dimers to that for the formation of dimers (k_3/k_1) by a factor of 7 when the temperature increases from 380°C to 480°C.

The parameters in Table 1 also show that higher temperatures have the desirable effect of favoring the formation of gases. This is evident from the activation energy for the formation of gases (45 kcal/mol) exceeding the activation energies for the steps leading to the formation of the ring-opening and other intermediates (25 and 29 kcal/mol).

The reaction orders for phenol in Table 1 for the two primary paths are nearly equal, so varying the phenol concentration will have little effect on the product selectivities. The reaction orders for oxygen are also nearly equal for all the steps except for step 4 which has an oxygen order of 1.5. This high oxygen order indicates that high oxygen concentrations will result in higher rates of formation of gases.

In addition to modeling the reactions using empirical reaction networks, we have developed detailed chemical kinetics models based on the reaction mechanisms. This work (9) focuses on adapting gas-phase combustion kinetics to SCWO conditions as the basis for a quantitative model.

CONCLUSIONS

The products of phenol oxidation in SCW can be categorized as dimers, gases, and ring-opening and other products. The variation of the selectivity of phenol to these products with residence time, temperature and species concentrations can be quantitatively described using a reaction network and the parameters in Table 1. The network includes parallel pathways for phenol to dimers and to ring-opening and other products, secondary decomposition of dimers to ring-opening and other intermediates, and oxidation of these intermediates to carbon oxides.

Dimerization of phenol is the main primary pathway for phenol consumption between 380 and 480°C. A successful strategy for treatment of phenolic wastes by SCWO must ensure the destruction of these dimers and the formation of CO_2 in high selectivities. Our quantitative reaction model showed that long residence times and high reaction temperatures favor the destruction of dimers and the formation of CO and CO_2. Moreover, the influence of intermediate reaction products (dimers and other products) on the rate of formation of the carbon oxides shows that phenol disappearance kinetics alone constitutes insufficient information for process design. Identifying and quantifying reaction intermediates and developing accurate quantitative reaction models is of vital importance for any rational SCWO process design.

REFERENCES

1. Savage, P. E., Gopalan, S., Mizan, T. I., Brock, E. E., Martino, C. J. Reactions at Supercritical Conditions: Fundamentals and Applications. AIChE J. accepted, 1995.
2. Li, R., Thornton, T. D., and Savage, P. E. Kinetics of CO_2 Formation from the Oxidation of Phenols in Supercritical Water. Environ. Sci. Technol., 26, 2388, 1992.
3. Li, R., Savage, P. E., and Szmukler, D. 2-Chlorophenol Oxidation in Supercritical Water: Global Kinetics and Reaction Products. AIChE J., 39, 178, 1993.
4. Thornton, T. D., and Savage, P. E. Phenol Oxidation in Supercritical Water. J. Supercritical Fluids, 3, 240, 1990.
5. Thornton, T. D., LaDue, D. E., and Savage, P. E. Phenol Oxidation in Supercritical Water: Formation of Dibenzofuran, Dibenzo-p-dioxin, and Related Compounds. Environ. Sci. Technol., 25, 1507, 1991.
6. Thornton, T. D., and Savage, P. E. Kinetics of Phenol Oxidation in Supercritical Water. AIChE J., 38, 321, 1992.
7. Thornton, T. D., and Savage, P. E. Phenol Oxidation Pathways In Supercritical Water. Ind. Eng. Chem. Res., 31, 2451, 1992.
8. Gopalan, S., and Savage, P. E. Reaction Network for Phenol Oxidation in Supercritical Water: A Comprehensive Quantitative Model. AIChE J, accepted, 1995.
9. Gopalan, S., and Savage, P. E. Reaction Mechanism for Phenol Oxidation in Supercritical Water J. Phys. Chem. 98, 12646, 1994.
10. Martino, C. J., Savage, P. E., and Kasiborski, J. Kinetics and Products from o-Cresol Oxidation in Supercritical Water. Ind. Eng. Chem. Res. submitted, 1995.
11. Steiner, E. C., Rey, T. D., and McCroskey, P. S. SimuSolv Modeling and Simulation Software Reference Guide. The Dow Chemical Company, 1990.

FOR MORE INFORMATION

Prof. Phillip E. Savage, University of Michigan, Chemical Engineering Department, Ann Arbor, MI 48109-2136, Phone (313) 764-3386, e-mail: psavage@engin.umich.edu

OXIDATION AND HYDROLYSIS OF ACETIC ACID AND METHYLENE CHLORIDE IN SUPERCRITICAL WATER AS A MEANS OF REMEDIATION

Philip A. Marrone, Russell P. Lachance, Joanna L. DiNaro,
Brian D. Phenix, Jerry C. Meyer, Jefferson W. Tester,
William A. Peters
Chemical Engineering Department and Energy Laboratory
Massachusetts Institute of Technology
Room E40-455
77 Massachusetts Avenue
Cambridge, MA 02139
(617) 253-3401

K.C. Swallow
Merrimack College
North Andover, MA 01845

INTRODUCTION

Supercritical water oxidation (SCWO) is a promising technology proposed for the destruction of hazardous organic wastes. Unlike its well known behavior under ambient conditions, water above its critical point (374°C, 221 bar) has properties similar to that of a nonpolar solvent, primarily due to the effect of a decrease in hydrogen bonding and density that occurs near and above the critical point. The result is that nonpolar organics and oxygen exhibit complete solubility in supercritical water, while polar species such as inorganic salts are insoluble and precipitate out. In the single homogeneous phase formed, oxidation of organics with oxygen in supercritical water is rapid and complete to CO_2 and H_2O. Organic heteroatoms such as halogens, sulfur, or phosphorus are converted to inorganic acids (HCl, H_2SO_4, H_3PO_4) which precipitate as salts when neutralized with added base, while nitrogen is converted to N_2 and N_2O. No NO_x compounds are formed due to the relatively low temperatures that exist in the SCWO process (400 - 650°C) relative to that of air incineration processes (typically 900 - 1300°C). Oxidation in supercritical water is thus an appealing means of destroying toxic organic compounds while simultaneously separating out undesired inorganics by precipitation. Applications to decontaminating soils and dilute aqueous wastes are of special interest. Earlier work has demonstrated high destruction efficiencies for various organics in SCWO (1).

METHODOLOGY

Our methodology includes laboratory-scale experiments and interpretive mathematical modeling to deduce global kinetic parameters and a fundamental mechanistic understanding of the destruction pathways of model organic compounds. These model organics are compounds that are either typical and representative wastes and soil contaminants themselves, refractory intermediate compounds formed in the oxidation of a more complex compound, or surrogates for compounds too dangerous to use in the lab (such as chemical weapon agents) but that are chemically similar in some respect to the more toxic compound they represent. Waste destruction efficiencies, yields, and identities of resulting products are measured over ranges of key operating variables (e.g. temperature, pressure, reaction time, organic/oxidant feed ratio, possible presence of solids) pertinent to normal and upset conditions. This paper describes the experimental results of oxidation and hydrolysis (no added oxygen) in supercritical water of two model compounds that have been investigated in our lab - acetic acid and methylene chloride.

RESULTS AND CONCLUSIONS

Acetic acid (CH_3COOH) and methylene chloride (CH_2Cl_2) oxidation and hydrolysis in supercritical water were examined in an isothermal plug flow tubular reactor. Acetic acid experiments were conducted over the range of 425-600°C, 160-263 bar, and 4.4-10 sec reactor residence times, with stoichiometric, substoichiometric, and superstoichiometric oxygen to organic feed ratios. Acetic acid oxidation was globally observed to be 0.72 ± 0.15 order in acetic acid and 0.27 ± 0.15 order in oxygen (differing from the usual trend of first-order in organic and zero-order in oxygen), with an activation energy of 168 ± 21 kJ/mol and pre-exponential factor of $10^{9.9 \pm 1.7}$. Complete conversion was achieved above 550°C and 8 sec reactor residence time at 246 bar. Major products formed included CO, CO_2, H_2, and CH_4. For hydrolysis, where some conversion was observed but not as much as under similar oxidation conditions, an assumed first order global rate expression had an activation energy of 94 ± 17 kJ/mol and pre-exponential factor of $10^{4.4 \pm 1.1}$. Pressure (water density) variations were observed to have a small effect on acetic acid oxidation.

Methylene chloride experiments were carried out at 450-600°C, 246 bar, and 4-9 seconds reactor residence time, with O_2/CH_2Cl_2 feed ratios ranging from substoichiometric to superstoichiometric. Major products of both hydrolysis and oxidation of CH_2Cl_2 were carbon monoxide (CO), carbon dioxide (CO_2), formaldehyde (HCHO), methanol, (CH_3OH), hydrogen (H_2), and hydrochloric acid (HCl). Small amounts of methane (CH_4) were detected above 575°C, and trace amounts (< 1% of total gas volume) of chloromethane (CH_3Cl), 1,1-dichloroethylene ($C_2H_2Cl_2$), cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, chloroform ($CHCl_3$), and trichloroethylene (C_2HCl_3) were found in the vapor phase effluent.

Unlike that seen with earlier model compounds such as acetic acid, conversion of methylene chloride under hydrolysis conditions was very similar to that under oxidation conditions. In fact, the rate of destruction of CH_2Cl_2 was globally determined to be zero order in O_2 concentration. The presence of O_2 did affect the product distribution, however, with more CO and CO_2 and less HCHO, CH_3OH, and H_2 produced under oxidation conditions than under hydrolysis conditions. Complete conversion of CH_2Cl_2 was achieved above 563°C at a reactor residence time of 6 seconds under oxidation conditions. Significant corrosion was observed in the coil used to preheat the organic feed. This corrosion occurred in a hot but subcritical region within one to two feet of the coil entrance, indicating considerable CH_2Cl_2 breakdown before reaching the reactor and oxygen feed. All of this experimental evidence suggests a global oxidation mechanism of initial CH_2Cl_2 reaction with water to form HCl, HCHO and/or CH_3OH, and then reaction of these intermediates with O_2 to form CO and CO_2.

REFERENCE

1. Tester, J.W., H.R. Holgate, F.J. Armellini, P.A. Webley, W.R. Killilea, G.T. Hong, and H.E. Barner, Oxidation of Hazardous Organic Wastes in Supercritical Water: A Review of Process Development and Fundamental Research, ACS Symposium Series 518: Emerging Technologies in Hazardous Waste Management III, D.W. Tedder and F.G. Pohland, Eds. Washington D.C. (1993).

SOIL LEAD REMEDIATION: IS REMOVAL THE ONLY OPTION?

James A. Ryan and Pengchu Zhang
US EPA Risk Reduction Engineering Laboratory
Cincinnati, OH 45268
(513) 569-7653

INTRODUCTION

Lead, a naturally occurring metal, has always been present in soils, surface waters and ground waters. Lead content of agricultural soils ranges from > 1 mg/kg to 135 mg/kg with a median value of 11 mg/kg (1). Inner-city neighborhoods in most of our major cities have mean or median soil Pb concentrations in excess of 1000 mg/kg (2-6) with values as high as 50,000 mg/kg being reported (7). Most of these elevated lead concentrations observed in the urban soils are assumed to come from various anthropogenic sources: industrial emissions, vehicular emissions and exterior lead paint (8). Additionally, lead has been added to soil as the insecticide lead arsenate, impurity in fertilizers as well as from mining and smelting activities (9). Further, lead is a contaminant of concern in about one third of the National Priority List (NPL) sites and over 400 Superfund sites have excessive soil Pb concentrations (10). Thus, its use by society; paints, chemical additives, tools and weapons, as well as other consumer and industrial products, coupled with inadequate disposal or recycling by society have caused environmental systems (soils) to become repositories for the metal. It is also apparent that not only are soils the repository for environmentally released Pb, but it is retained in the zone of addition (9).

According to the Center for Disease Control (CDC) lead poisoning is the most common and most devastating environmental disease affecting young children. Over the past decade the blood Pb level associated with impairment has decreased from 25 μg/dL to 10 μg/dL, as we have learned that levels above 10-15 μg/dL can significantly reduce IQ and learning ability in children (11). Because of the reduction of Pb in automotive emissions, and reduction of Pb in food due to changes in canning technology, both food and automotive emission Pb levels have decreased nearly 10 fold in the past 15 years (12). During the same time frame median blood Pb levels in suburban children have fallen from about 20-25 μg/dL in 1970 to 3-4 μg/dL in 1990. With the normal variance (and varied amounts from Pb in plumbing systems) some suburban children exceed 15 μg/dL. But over 50% of children in the center city exceed 15 μg/dL limit (13). Thus, lead risk to young children is now recognized as the most sensitive limit for Pb in the environment (11). CDC estimates that Pb poisoning in children costs billions of dollars in medical and special education expenses and decreased future earnings. Lead paint, Pb in drinking water and Pb in soil are the major sources of exposure. Children exposed to high levels of soil and dust Pb have been found to have high blood Pb in numerous cases (7). Lead in soils contaminated by smelter emissions, automotive emissions, or paint residue have been found to cause increased blood Pb in children when soil Pb exceeds 500-1000 mg/kg (14-17). In other cases, social factors and/or soil chemical factors alter exposure and/or bioavailability of the soil Pb and little or no increases in blood Pb are observed even with soils containing 5000 mg Pb/kg (18). Further, Pb in mining soils appears to have lower bioavailability than Pb in urban dusts (19-21). Cotter-Howells and Thornton (18) reported low blood Pb levels in children living in an area with soils (about 5000 mg/kg) derived from PbS mining wastes. Studies have found the relationship (slope of blood Pb/soil Pb) for children in smelter and urban areas to range from 1.1 to 7.6 μg/dL/1000 mg/kg, while for children in mining areas the relationship ranges from 0 to 4.8 μg/dL/1000 mg/kg (22). Suggesting that Pb in soils contaminated from mining activities is less bioavailable than Pb in soil derived from urban and smelting sources. Three possible explanations have been offered for the observations: the size of the Pb containing particle, the species of Pb in soil, and the geochemical matrix incorporating the Pb species. These results are interpreted as indicating that because of specific adsorption, soil Pb bioavailability increases with increasing soil Pb concentration and that the form of soil Pb alters its bioavailability.

Programs to reduce exposure from Pb paint and Pb in drinking water are moving forward. No program exists on contaminated soil Pb because, according to CDC and EPA, there is insufficient

information available on which to base such a program. They state that far less is known about the hazards of soil Pb-- and how to address those hazards-- than about paint or water. Thus, information is needed to better characterize the problem, determine pathways of exposure, and determine effective remediation methods.

Remediation treatments for soils attempt to capitalize on the differences in physical and chemical properties between a contaminant and soil constituents. For example, remediation efforts for metal contaminated sites use properties such as solubility, density, particle size distribution, surface chemistry, boiling point or magnetic susceptibility to allow separation and recovery. Metals found as relatively soluble species or weakly sorbed to soil clays might be solubilized by the application of mild organic acids. If the metals are present as separate mineral particulates, then their typically higher density might permit the physical separation of these species from the less dense aluminosilicate and organic constituents of soils. Otherwise, these forms could be bound in a solid cement or vitreous glass matrix. If the metal species are volatile, then a soil heating method might allow recovery. Separation methods relying on the magnetic susceptibility of ferromagnetic or strongly paramagnetic metal species have also been attempted. More detailed discussions of remediation technologies can be found in the literature (23-28).

Many biological, chemical and physical process have been proposed for soil remediation. Some of the processes can be either applied to excavated soil or used in situ. However, reduction in exposure to soil Pb has typically been accomplished by soil removal for off site disposal, covering, or diluting by mixing with uncontaminated soil. Cost, logistical concerns, and regulatory requirements associated with excavation, ex situ treatment and disposal can make in situ treatment an attractive option. Our current understanding of Pb exposure and factors which effect its bioavailability as well as its environmental chemistry may allow development of less costly and environmentally less disruptive methods of remediation.

METHODOLOGY

In response to the need for cost effective technology to immobilize Pb, we have collaborated with Ohio State University to examine the feasibility of Pb immobilization by phosphate rocks. This approach is based on the hypothesis that Pb phosphates are the most insoluble Pb minerals, these materials are resistant to acid weathering, and these materials are less bioavailable than other Pb forms. The experimental approaches utilized in this research have been laboratory scale solution studies, resin studies, dialysis studies, soil studies, and feeding studies.

RESULTS

We have shown that Pb is rapidly and effectively precipitated from solution by orthophosphate (aqueous P, hydroxyapatite, or phosphate rock) to form a series of Pb phosphates (29-31). We have used hydroxyapatite and phosphate rock as the primary P source and have shown that they are effective in attenuating Pb in aqueous solution, exchangeable form and contaminated soil material, to below the U.S. EPA action level of 15 μg/L dissolved Pb. Phosphate rocks from Florida, North Carolina and Idaho are also shown to be effective in removing Pb from aqueous solution (29). The final product of Pb immobilization is primarily hydroxypyromorphite ($Pb_{10}(PO_4)_6(OH)_2$), which is stable even at pH as low as 3. Results of chemical and x-ray diffraction (XRD) analysis, scanning electronic microscopy (SEM), and scanning transmission electronic microscopy (STEM) strongly support the mechanism of dissolution of hydroxyapatite and precipitation of hydroxypyromorphite. Aqueous P concentration is a key factor in determining the effectiveness of Pb immobilization and the formation of hydroxypyromorphite. Thus pH is important since it determines solubility of hydroxyapatite or phosphate rock. Hydroxyapatite or phosphate rock not only supplies P to immobilize Pb, but also provides Ca to replace Pb from exchange sites. This is especially important in contaminated soils and solid wastes where the bulk of the Pb is in labile rather than soluble form.

We have also shown that hydroxyapatite can effectively immobilize aqueous Pb in the presence

of common soil solution anions: NO_3^-, Cl^-, F^-, SO_4^{2-}, and CO_3^{2-} (30). Lead concentrations were reduced from initial levels of 5 - 100 mg/L to below the EPA dissolved Pb action level of 15 μg/L except at very high CO_3^{2-} concentrations, whose levels are unlikely to be found in contaminated soils and wastes. Hydroxyapatite was transformed to hydroxypyromorphite after reaction with $Pb(NO_3)_2$ in the presence of NO_3^-, SO_4^{2-}, and CO_3^{2-}; to chloropyromorphite ($Pb_{10}(PO_4)_6Cl_2$) after reaction with $PbCl_2$; and to fluoropyromorphite ($Pb_{10}(PO_4)_6F_2$) after reaction with PbF_2, respectively. Hydroxyapatite dissolution followed by precipitation of hydroxypyromorphite, chloropyromorphite, or fluoropyromorphite was the main process during the reaction, but Pb adsorption by hydroxyapatite and cation substitution of Pb for Ca on hydroxyapatite may also have occurred.

We have also investigated the effects of metals such as Zn, Cd, Ni, Cu, Fe^{2+}, and Al on Pb immobilization by hydroxyapatite as well as the effectiveness of hydroxyapatite in attenuating these metals (31). We have shown that not only do these metals have no significant effect on Pb immobilization by hydroxyapatite at low concentrations (<20 mg/L), but also these metals themselves are removed by hydroxyapatite. The amount of metals removed depends on the concentrations of Pb and metals, as well as the types of metals. At higher concentrations (>20 mg/L), Cu is most effective in inhibiting Pb immobilization by hydroxyapatite, followed by Fe^{2+}, Cd, Zn, Al, and Ni. Hydroxypyromorphite was the only mineral detected by XRD besides hydroxyapatite after Pb reaction with hydroxyapatite in the presence of these metals. The amounts of hydroxypyromorphite formed decreased with an increase in metal concentrations, according to XRD. The order of inhibition of hydroxypyromorphite formation is positively correlated with the solubility of the other metal phosphates and supports a mechanism of competitive precipitation.

Hydroxyapatite also removed Pb^{2+} from Pb-EDTA solution in the presence of excess EDTA. Indicating that basic Ca-phosphates can sequester Pb even in the presence of strongly complexing organic ligands. In longer term experiment, hydroxyapatite was effective in immobilizing Pb^{2+} for up to 16 weeks, confirming the stability of the reaction product. In another experiment, a mixture of hydroxyapatite and hydroxypyromorphite were reacted with anion exchange resin. Lead concentrations in the suspension of hydroxyapatite and hydroxypyromorphite were low (< 168 nmol/L) in spite of the fact that the anion exchange resin extracted PO_4^{3-} from solution, which again demonstrated the stability of hydroxypyromorphite over hydroxyapatite. Additionally, the mixture of hydroxyapatite and hydroxypyromorphite was also reacted with aqueous Ca^{2+} to study the possibility of Ca^{2+} substitution for Pb^{2+} on hydroxypyromorphite. Higher Ca^{2+} concentrations resulted in slightly higher Pb^{2+} concentrations (< 158 nmol/L), possibly as a result of hydroxyapatite precipitation and hydroxypyromorphite dissolution. We have illustrated that exchangeable Pb can be precipitated by reacting hydroxyapatite with a cation exchange resin saturated with Pb. No hydroxypyromorphite was detected in the hydroxyapatite residue, indicating the reaction did not occur in bulk solution. The resin was coated with hydroxypyromorphite indicating that hydroxyapatite not only immobilized Pb, but supplied cations (Ca) to displace Pb from the resin which, was immediately precipitated as hydroxypyromorphite. In further evaluations of the reaction we mixed hydroxyapatite with several Pb contaminated soils and allowed them to react for several days. Sequential extraction of the samples illustrated that the hydroxyapatite addition reduced the labile fractions of soil Pb (soluble and exchangeable) and increased the residual fraction of soil Pb.

In animal feeding experiments we have illustrated that Pb bioavailability followed the order: Pb-acetate >> contaminated soil> pyromorphite = control and that the addition of apatite or rock phosphate to the contaminated soil reduced the bioavailability of the contaminated soil Pb. Thus, illustrating that the formation of phyromorphite in soils not only reduce the solubility of the soil Pb, but reduce its bioavailability. In fact even without allowing time for reaction, the addition of the phosphate (apatite or rock) to the contaminated soil was effective at reducing soil Pb bioavailability.

CONCLUSIONS

Our results strongly demonstrate that both hydroxyapatite and phosphate rocks were effective in reducing Pb solubility and bioavailability through dissolution of hydroxyapatite or phosphate rocks and

precipitation of pyromorphite. The effective and rapid Pb^{2+} immobilization from solution and contaminated soils by hydroxyapatite or phosphate rock, the limited effects from other minerals, anions, and cations, the apparent environmental stability of the reaction products, along with the ready availability and low-cost of hydroxyapatite or phosphate rock suggest that this approach might have great merit for cost-effective in situ immobilization of Pb contaminated water, soils, and wastes.

REFERENCES

1. Holmgren, G.G.S., M.W. Meyer, R.L. Chaney, and R.B. Daniels. 1993. Cadmium, lead, zinc, copper, and nickel in agricultural soils of the United States of America. Jour. Environ. Quality. 22:335-348

2. Angle, C.R., M.S. McIntire, and A.V. Colucci. 1974. Lead in air, dustfall, soil, housedust, milk, and water: correlation of blood lead in urban and suburban school children. Trace Substan. Environ. Health, 8:23-29.

3. Johnson, D.E., J.B. Tillery, and R.J. Prevost 1975. Levels of platinum, palladium, and lead in populations of Southern California. Environ. Health Presspect. 12:27-33.

4. Bornschein, R. 1986. Lead in soil in relation to blood lead levels in children. Trace Substan. Environ. Health. 20:322-332.

5. Mielke, H.W., J.L. Adams, P.L. Reagan, and P.W. Mielke. 1989. Soil-dust lead and childhood lead exposure as a function of city size and community traffic flow: the case for lead abatement in Minnesota. Environ. Geochem. Health.

6. Madhaven, S., K. Rosenman, and T. Shehata. 1989. Lead in soil: recommended maximum permissible levels. Environ. Research. 49:136-142.

7. Chaney, R.L., H.W. Mielke and S.B. Sterrett. 1989. Speciation, mobility and bioavailability of soil lead. [Proc. Intern. Conf. Lead in Soils: Issues and Guidelines. B.E. Davies and B.G. Wixson (eds.)]. Environ. Geochem. Health 11(Supplement):105-129.

8. EDF, 1990. Environmental Defense Fund. "Legacy of Lead: America's Continuing Epidemic of Childhood Poisoning". (Washington DC: EDF, March, 1990)

9. Davies, B.E. 1990. Lead. In Heavy Metals in Soils. B.J. Alloway (Ed) Blackie and Son Ltd., Glasgow.

10. Komianos, W.L. 1992. "Managing the risk of lead exposure". Environmental Protection (July/August 1992).

11. U.S. Department of Health and Human Services. 1991. Preventing Lead Poisoning in Young Children. A statement by the centers for disease control October, 1991.

12. Bolger, P.M., C.D. Carrington, S.G. Caper and M.A. Adams. 1991. Reductions in dietary lead exposure in the United States. Chem. Spec. Bioavail. 3:31-36.

13. Agency for Toxic Substances and Disease Registry (ATSDR). 1988. The Nature and Extent of Lead Poisoning in Children in the United States: A Report to Congress. DHHS Doc. No. 99-2966. US Dept. Health Human Service, Public Health Service. Atlanta, GA.

14. US CDC (Center for Disease Control). 1985. Preventing lead poisoning in young children: A statement by the Centers for Disease Control. Jan. Atlanta, GA., No.99-2230.

15. US-EPA (Environmental Protection Agency) 1989. OSWER Directive #9355.4-02 "Interim Guidance on Establishing Soil Lead Cleanup Levels at Superfund Sites. Sept. 1, 1989.

16. US-EPA. (Environmental Protection Agency)1986. Air Quality Criteria for Lead., EPA-600/8-83/02cF.

17. Duggan, M.J. and M.J. Inskip. 1985 Childhood exposure to lead in surface dust and soil: A community health problem. Public Health Rev. 13:1-54.

18. Cotter-Howells, J. and I. Thornton. 1991. Sources and pathways of environmental lead to children in a Derbyshire mining village. Environ. Geochem. Health 13:127-135.

19. Freeman, G.B., J.D. Johnson, J.M.Killinger, S.C.Liao, P.I.Feder, A.O.Davis, M.V.Rudy, R.L.Chaney, S.C.Lovre, and P.D.Bergstrom. 1992. Relative bioavailability of lead from mining waste soil in rats. Fundamental and Applied Toxicology 19:388-398.

20. Davis, A., M.V. Rudy, and P.D.Bergstrom. 1992. Mineralogic controls on arsenic and lead bioavailability in soils from the Butte mining district, Montana,U.S.A. Environ. Sci. Techol 26:461-468

21. Rudy, M.V., A.Davis, J.H Kempton, J.W. Drexler, and P.D. Bergstrom. 1992. Lead bioavailability: Dissolution kinetics under simulated gastric conditions. Environ. Sci. Techol. 26:1242-1248.

22. Steele, M.J., B.D. Beck, B.L. Murphy, and H.S. Strauss. 1990. Assessing the contribution from lead in mining wastes to blood lead. Reg. Tox. Pharm., 11:158-190.

23. US-EPA. (Environmental Protection Agency)1994. Engineering Forum Issue. Considerations in deciding to treat contaminated soils in situ. EPA/540/S-94/500

24. US-EPA. (Environmental Protection Agency)1994. A literature review summary of metal extraction processes used to remove lead from soils. EPA/600/SR-94/006

25. Wommel, S. etal, 1993, " Cleaning of contaminated soils - a treatment concept," in Contaminated Soil '93, edited by F. Arendt, Kluwer, The Netherlands, pp. 1287-1294.

26. Pearl, M. and P. Wood, 1993, "Separation Processes for the Treatment of Contaminated Soil," in Contaminated Soil '93, edited by F. Arendt, Kluwer, The Netherlands, pp. 1295-1304.

27. Swartzbaugh, J. etal, 1992, "Remediating Sites Contaminated with Heavy Metals, Parts I, II and III," Hazardous Materials Control, Nov/Dec 1992.

28. Sims, R., 1990, "Soil Remediation Techniques at Uncontrolled Hazardous Waste Sites, A Critical Review," Journal of the Air and Waste Management Association, Vol. 40, No. 5, May 1990, pp. 704-732.

29. Ma, Q.Y., S.J. Traina, T.J.Logan, and J.A.Ryan. 1993. In situ lead immobilization by apatite. Environ. Sci. Technol. 27:1803-1810.

30. Ma, Q.Y., T.J.Logan, S.J. Traina, and J.A.Ryan. 1994. Effects of NO^{3-}, Cl^-, F^-, SO_4^{2-}, and CO_3^{2-} on Pb^{2+} immobilization by hydroxyapatite. Environ. Sci. Technol. 28:408-418.

31. Ma, Q.Y., S.J. Traina, T.J.Logan, and J.A.Ryan. 1994. Effect of aqueous Al. Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by hydroxyapatite. Submitted to Environ. Sci. Technol.28:1219-1228

REVIEW OF MATHEMATICAL MODELING FOR EVALUATION OF SVE APPLICATIONS

David L. Jordan[1]
James W. Mercer
GeoTrans, Inc.
46050 Manekin Plaza, Suite 100
Sterling, Virginia 20166
703-444-7000

INTRODUCTION

Soil vapor extraction (SVE), a demonstrated technology, enhances the removal of volatile chemicals from the subsurface through application of a vacuum at an extraction well to induce air flow through the subsurface toward the well. As of 1991, SVE comprised 13% of selected remedies at Superfund sites, and approximately 7% of leaking underground storage tanks. The flow of air enhances volatilization of compounds from the residual NAPL phase in soil pores and from the dissolved phase in soil pore water. The technology is particularly applicable to relatively volatile organic compounds (Henry's law constant > 10^{-3} atm-m^3/mole) residing in the vadose zone. The technology may also be applicable for removal of volatile light non-aqueous phase liquids (LNAPLs) floating on the water table or entrained in the capillary fringe, if the chemicals of concern have high vapor pressures (e.g., benzene). During SVE, contaminant removal is expected to be enhanced by decreasing soil moisture. As percent moisture decreases, air permeability increases. Increased soil organic carbon content will increase sorption to the soil matrix, decreasing SVE efficiency. Heterogeneous flow conditions also affect the efficiency of contaminant removal, with higher flow zones (preferential flow zones) cleaning up faster than low flow zones (less permeable zones).

Air sparging, another SVE-related technology, generally involves use of injection wells to inject gas (typically air) into the saturated zone below areas of contamination. Ideally, dissolved, separate-phase and sorbed contaminants will partition into the injected air, effectively creating an in-situ air-stripping system. This can take place within a single-well system or the stripped contaminants can be transported in the gas phase to the vadose zone and collected by SVE wells. The advantage of such a system is that the treatment of groundwater and soil takes place in-situ, reducing the need for disposal of treated material. Although air sparging is a physical/chemical treatment process, the addition of air has the potential to promote biodegradation.

The SVE process involves installation of vacuum extraction wells or trenches at strategic locations and depths. Air extraction can also be combined with air injection. The spacing of wells or trenches depends on soil properties such as permeability and porosity. Where the objective is to remove both air and water, dual vacuum extraction wells may be used. The injection wells for air sparging can be vertical or inclined, ranging to horizontal. Effective design and prediction of system performance can be difficult, depending on site conditions.

Tools are now available, in the form of numerical models, that allow one to both screen for the potential feasibility of SVE, and design and estimate performance of the system. While modeling should not be considered an end in itself, it provides a means by which to quantify some of the important SVE operating processes. Modeling can provide estimated answers for numerous questions concerning the feasibility and usage of SVE. Screening models can be used in conjunction with site characterization data and best professional judgment to determine the potential feasibility of SVE at a contaminated site. Flow and transport models can then be used to enhance the system design

---

[1]Now at Daniel B. Stephens & Associates

process and estimate performance. The work performed as part of this effort included a review of models that can be applied to SVE applications. This review includes a summary of critical information required in a SVE application. It also includes a model selection process, model usage guidelines, and case studies.

METHODOLOGY

At an "Integrated In Situ Treatment System Design Workshop" that took place on August 10 and 11, 1993 in Edison, New Jersey, a need was identified to provide environmental managers with guidance on how models may be used to (1) determine the viability of using SVE, (2) if viable, help design the SVE system, and (3) estimate system performance. The methodology used to provide this guidance was a literature review and analysis of the various codes that may be applied to SVE. The literature review, and basic information on SVE system design, are provided. This includes introductory material, model selection tips, and example applications. In addition, information is provided on flow and transport theory.

Applicable codes were divided into the categories of screening, air flow, and compositional flow and transport. For each of these categories, currently available models were compiled and reviewed. Several example applications utilizing a number of the codes are presented, along with three case studies.

RESULTS

The results of this review is a guidance document that highlights the following topics and guide the user through the processes of selecting and applying models to SVE sites. Technical information is provided in order to: (1) Determine the types of problems that can be addressed by modeling; (2) Highlight the methods that are commonly used to solve such problems; (3) Assist potential users in determining the presence or absence of a need for modeling at their site and, if a need is shown to exist, selecting a model for their site; (4) Identify and illustrate the major processes governing air flow and contaminant transport in the subsurface; (5) Present a discussion of model data needs; (6) Review available commercial and public domain codes; and (7) Present a suite of example model applications and case studies.

CONCLUSIONS

Modeling can provide estimated answers for numerous questions concerning the feasibility and usage of SVE. Screening models can be used in conjunction with site characterization data and best professional judgment to determine if SVE at a contaminated site is feasible. Flow and transport models can be used to enhance the system design process and estimate performance. In some cases, no complex model is necessary, and decisions can be made based on simple analytical solutions and/or best professional judgment. Geographical information systems (GIS) can provide valuable assistance in organizing and presenting site data graphically in order to enhance the remedial alternative selection process.

Table 1 presents a summary of the screening, air flow, and compositional flow and transport codes that were evaluated. For screening, these models include the HyperVentilate and VENTING codes, as well as other analytical solutions. Air flow models available at this time include AIRFLOW, CSUGAS, and AIR3D. For compositional flow and transport, the VENT2D/VENT3D model is available and capable of simulating contaminant transport and removal via SVE.

The selection and application of any model will ultimately lie with the model user. This document attempts to guide the potential model user through a decision-making process that is

intended to help decide how and when to select a model, to make users aware of the processes governing flow and transport in the vadose zone, and highlight the limitations of model results.

FOR MORE INFORMATION

Chi-Yuan Fan
Superfund Technology Demonstration Division
Risk Reduction Engineering Laboratory
Edison, New Jersey 08837
908-906-6924

TABLE 1. SUMMARY OF THE SCREENING, AIR FLOW, AND COMPOSITIONAL FLOW AND TRANSPORT CODES THAT WERE EVALUATED.

Model	Type	Capabilities	Advantages	Limitations	Hardware/Software Requirements	Availability
Hyper-Ventilate, v2.0 (IBM PC) v1.01 (Apple Macintosh)	Screening	Calculates air permeability, well flow rates, mass removal rate, mass removal from several idealized diffusion-limited scenarios Calculates contaminant concentrations over time for multiple constituents	Provides rapid estimates for determination of the potential feasibility of SVE Provides rapid estimates of contaminant concentrations in extracted gas, allows comparison of removal rates of different constituents	Analytical air flow solution Should not be used to design SVE systems	IBM PC or Compatible: 80386/80387 coprocessor or 80486, 4 MB RAM, DOS 3.1 or higher, Microsoft Windows 3.x and runtime version of Object PLUS Apple Macintosh (Plus, SE, SE/30, II, IIX, or portable): 1 MB RAM, Apple HyperCard Software (v2.0 or greater)	Available from EPA as EPA/600/R-93/028 (EPA ORD Publications, 513-569-7562) Price: FREE while supplies last[1] Object PLUS available from Object PLUS Corp., 125 Cambridge Park Dr. Cambridge, MA 02140 Price: $100 (runtime version)[2]

[1]From NTIS: Report with disk (PB93-502664/AS) $140.00
Report only (PB93-134880/AS) $27.00

[2]From NTIS: IBM PC Disk (S/N 055-000-00427-7) $22.00
MacIntosh Disk (S/N 055-000-00403-0) $17.00

TABLE 1. SUMMARY OF THE SCREENING, AIR FLOW, AND COMPOSITIONAL FLOW AND TRANSPORT CODES THAT WERE EVALUATED (continued).

Model	Type	Capabilities	Advantages	Limitations	Hardware/Software Requirements	Availability
VENTING, v3.01	Screening	Calculates contaminant concentrations over time for multiple constituents	Provides rapid estimates of contaminant concentrations in extracted gas, allows comparison of removal rates of different constituents	User supplies flow rate to extraction well Simplistic one-dimensional representation of mass transport Should not be used to design SVE systems	IBM PC/AT or Compatible, DOS, 512 KB RAM, math coprocessor	Environmental Systems & Technologies, Inc. 2608 Sheffield Drive, Blacksburg, VA 24060-8270 703-552-0685 Price: $400.00
AIRFLOW[EM] v2.07	Air flow	Calculates pressure distribution in a radial domain, calculates air flow pathlines and velocities	Easy-to-use 'CAD-type' graphical user interface which simplifies model input and setup Rapid setup aids in hypothesis testing for simple problems Many sample problems included with the code	Only allows for one extraction well No mass transport	IBM PC or compatible, 80386/80486, 4 MB RAM, DOS 2.0 or higher, mouse and math coprocessor for 80386-based machines recommended	Waterloo Hydrogeologic Software 19 McCauley Drive (RR#2) Bolton, Ontario, Canada L7E SR8 905-880-2886 Price: $650.00

TABLE 1. SUMMARY OF THE SCREENING, AIR FLOW, AND COMPOSITIONAL FLOW AND TRANSPORT CODES THAT WERE EVALUATED (continued).

Model	Type	Capabilities	Advantages	Limitations	Hardware/Software Requirements	Availability
CSUGAS	Air flow	Calculates vacuum distribution in the subsurface, in inches of water	Allows full, three-dimensional analysis of heterogeneous, multi-well air flow problems Text-based input/output is flexible and up to the user	Lack of easy-to-use input/output interface may intimidate beginners No steady-state solution option No mass transport	IBM PC AT/XT or compatible, 640 KB RAM, DOS 2.0 or higher	Dr. James W. Warner Department of Civil Engineering Colorado State University Fort Collins, CO 80523 303-491-5048 Price: $125
AIR3D	Air flow	Calculates pressure distribution in the subsurface	Easy-to-use 'CAD-type' graphical user interface which simplifies model setup and input Allows three-dimensional analysis of complex problems	Users need an awareness of the operation and limitations of the MODFLOW code No mass transport	IBM PC or compatible, DOS 3.3 or higher, 4 MB RAM, VGA card and color monitor, mouse is highly recommended	American Petroleum Inst. 1220 L Street Northwest Washington, DC 20005 Price: $500.00 The original version of AIR3D (without the GUI) is available free of charge from: USGS Book and Open File Reports BLDG 810, Box 25425 Denver, CO 80225 Price: FREE

TABLE 1. SUMMARY OF THE SCREENING, AIR FLOW, AND COMPOSITIONAL FLOW AND TRANSPORT CODES THAT WERE EVALUATED (continued).

Model	Type	Capabilities	Advantages	Limitations	Hardware/Software Requirements	Availability
VENT2D/ VENT3D	Air flow and multicom-ponent contam-inant transport	Calculates pressure distribution in the sub-surface, multi-component contaminant constituent concentrations over time in the subsurface	Only readily available compositional flow and transport code Source code is available Text-based input/output is flexible and up to the user	Grid size limited to 25 x 25 cells (can be increased with a different version available from the author)	IBM PC or compatible, 80X86 with math coprocessor, DOS 3.0 or higher, 525 KB RAM	David A. Benson 524 Claremont Street Reno, NV 98502 702-322-2104 Price: $495.00

REPRESENTATIVE SAMPLING AND ANALYSIS OF HETEROGENEOUS SOILS

Ann Leitzinger
U. S. Environmental Protection Agency
26 W. Martin Luther King Drive
Cincinnati, OH 45268
(513) 569-7635

Joseph Evans
Science Applications International Corporation
545 Shoup Avenue
Idaho Falls, ID 83402
(208) 528-2168

Sam Hayes
Science Applications International Corporation
Suite 403
635 W. Seventh Street
Cincinnati, OH 45203
(513) 723-2600

Ken Partymiller
PRC Environmental Management, Inc.
5326 Paris Pike
Georgetown, KY 40324
(502) 867-1397

Gregory Swanson
S-Cubed
3398 Carmel Mountain Road
San Diego, CA 92121
(619) 587-7221

INTRODUCTION

Sampling and analysis presents specific problems with heterogeneous soils. These problems have been carefully evaluated in several projects for the Risk Reduction Engineering Laboratory (RREL), specifically Superfund Innovative Technology Evaluation (SITE) demonstrations. Of particular concern is the inability of standard analytical methods to account for heterogeneous samples. While a typical analytical method may normally accommodate only 2 grams (g) of sample (and therefore requires that "oversized material" be removed from a sample before analysis, potentially biasing analytical results), a representative sample aliquot from a heterogeneous site may require a sample size that is orders of magnitude greater than this. The inability to analyze representative samples may be the result of various factors, including the presence of oversized material (such as rocks or other debris); highly concentrated contaminants (such as lead chunks or tar balls), which may preclude taking large laboratory samples that would overwhelm instrument capabilities; or volatile contaminants which cannot be mixed to

create a more homogeneous aliquot because of the volatility of the contaminant being investigated. This paper contains several case studies that present the problems associated with sampling and analyzing heterogeneous soils; approaches to specific problems encountered in each of the projects discussed; and the relative success of these approaches.

Approaches previously recommended for selected RREL projects include the following: (1) screening pre-treated soil and then treating and analyzing the screened fraction; (2) grinding large amounts of material, followed by homogenization and analysis of a representative aliquot; (3) screening, sieving, and then analyzing separate portions of a sample; (4) removing oversized material from a sample, analyzing the sample portion that remains, and correcting for the percentage of oversized material in the sample; and (5) analyzing larger sample sizes. While one approach may be valid for a particular site or type of contamination, the case studies presented below emphasize how particular approaches were tailored to the perceived problems. For example, heterogeneous soils may include large rocks, (which are usually relatively free of contamination) or tar balls, which are highly concentrated forms of organic contamination. Excluding either of these materials may bias sample results. Typical laboratory glassware or the unavailability of concentrated laboratory spikes can also present problems particularly when analyzing larger sample sizes. Grinding and sieving samples may lead to loss of contaminants through volatilization or may release contamination from the inside of the oversized material, thereby producing biased results. In addition, there may be physical limitations to sampling based on the sample type. For example, oily samples or samples containing metallic lead may not mix, sieve, or grind well.

Data comparability is also an important consideration when sampling. Therefore, it may be more important to use a consistent approach from one event to the next, rather than to use a more accurate technique at a subsequent event. Another consideration, when sampling, is project cost limitations which may prevent the analysis of numerous samples necessary to fully characterize the contamination at a specific site. The examples presented below illustrate approaches used by RREL investigators to alleviate specific sampling and analysis problems associated with heterogeneous soils.

METHODOLOGY

A variety of sources were used during the preparation of this paper. A literature search was performed and previously published documents were reviewed. In addition, individuals considered knowledgeable in the area of sampling were contacted to provide further information. Quality Assurance Project Plans for RREL projects were also surveyed from the last five years to identify projects for the accompanying case studies.

The case studies below are structured as follows. First, a brief project description is presented with a discussion of site characteristics, the technology, the nature of the problem, the options considered, and the option chosen. The results of the chosen option are then presented, with the last section of each case study presenting the lessons learned for that particular site.

CASE STUDY 1 - RADIO FREQUENCY (RF) HEATING

The RF Heating technology uses electromagnetic energy in the RF band to heat contaminated soil. The soil is heated by providing power to an array of antennae located in drilled bore holes within the soil. Petroleum hydrocarbon, volatile, and semivolatile contaminants present are volatilized, collected, and treated. Soil moisture is also volatilized to provide a steam sweep inside the treatment zone. The organic vapors and moisture are recovered by applying a vacuum to vapor extraction wells near the antennae.

Particle size distribution (PSD) results indicated that the top 4.9 meters (m) of soil consisted of 25 to 48 percent gravel by weight, and that between 5.5 m and 9.1 m below the ground surface, the soil consisted primarily of gravel (64%-86%).

Due to the large amount of gravel, considerations were given to the manner in which a representative sample might be analyzed. The options considered included: (1) grinding and homogenizing; (2) screening and analyzing the different portions; and (3) removing the rocks and analyzing the portion that remained, with subsequent correction of the results based on PSD results for each sample. The third option was chosen. The analytical results were evaluated both with correction and without. This comparison indicated that the chosen method did not change the site evaluation.

CASE STUDY 2 - BIOGENESIS SOIL WASHING TECHNOLOGY

The BioGenesis soil washing technology uses a proprietary solution to transfer organic contaminants from a soil matrix to a liquid phase. The technology uses a specially designed wash unit that can treat contaminated soil at rates of up to 10 metric tons per hour. After washing, soil is stored in containers, and the liquid waste stream is either treated or recycled. The combination of the surfactant that remains on the soil and the water left over from washing enhances microbial activity, which biodegrades any residual contamination.

The critical parameter measured in soil samples was petroleum hydrocarbons. To determine the removal efficiency of petroleum hydrocarbons, multiple waste streams were sampled and analyzed, including feed soils and treated soils. The presence of large rocks and tar balls prompted questions about the homogeneity of the soils and the representativeness of the sampling process. As a result, the sampling staff began subjectively excluding both rocks and tar balls from pre- and post-treatment samples. In addition, the means for excluding tar balls differed between pre- and post-treatment samples, which introduced further sampling bias.

To address the above concerns, the first samples were recollected by sampling large amounts of soil (346 kilograms). This entire amount of soil was screened through a 12.7 millimeter (mm) diameter screen; separated by hand into soil, tar ball, and rock fractions; and weighed to determine the percent composition of each. An aliquot from each fraction was analyzed. For rocks, 100 g to 200 g aliquots were obtained before rinsing the rocks with solvent. A 1 g aliquot of the tar ball material was also obtained and dissolved in

freon. The solvent extract from both matrices was analyzed separately for petroleum hydrocarbons. The analytical data was then mathematically recombined to yield sample results. Results showed that the presence of rocks and tar balls were offsetting factors and did not affect the petroleum hydrocarbon data during the demonstration.

CASE STUDY 3 - TORONTO HARBOUR SOIL RECYCLING DEMONSTRATION

The Toronto Harbour demonstration is a three-phase operation consisting of a soil washer (used to separate the soil into different sized sample streams), a chelating process (for removal of metals), and a bioslurry process (to treat organics remaining in the fine material). SVOCs, metals, and oil and grease were the critical parameters for this project.

Two concerns, discovered in the field, were associated with representative sampling. First, the feed material consisted of a significant amount of rock and contained high concentrations of organics. Secondly, the oversize sample stream from the soil washer consisted of rocks ranging from about 6 mm to 25 mm in diameter.

To address these concerns, the feed material sample size was increased to 100 g to improve representativeness. Samples were then split by the laboratory into soil and rock fractions using a 9.5 mm sieve, and analyzed separately. This allowed the soil fraction to be homogenized and analyzed by SW-846 Method 3540 (soxhlet extraction) using 2 g aliquots. The rock fraction obtained from the 100 g aliquot was also analyzed by Method 3540 to ensure soil clinging to the outside of the rocks would be fully included.

For the oversize sample stream, the original plan was to grind and homogenize the samples. This was rejected as the grinding of these samples would expose surfaces of the rock that would not otherwise be exposed for extraction thus creating a non-representative sample. It was decided that a 200 g aliquot would be obtained for the laboratory and the entire sample would be extracted and analyzed for organics. Any organic contaminants on the surface of the rocks could then easily be extracted by using a solvent wash. This allowed large quantities to be extracted without the usual limitations associated with laboratory glassware. For both the oversized fraction and the feed material, several sample aliquots had similar analytical results indicating samples were representative.

CASE STUDY 4 - BESCORP SOIL WASHING PROCESS

The Bescorp process uses a combination of soil washing, size segregation, and density separation to remove heavy metals from soils. This demonstration was carried out at a previous lead-acid battery reclamation site. Native soil consisted of approximately 50% gravel (>6.4 mm), 40% sand (6.4 mm to 0.1 mm), and 10% fines (<0.1 mm). Lead tended to be most concentrated in the fine fraction, but the coarser fractions also contained significant fractions of lead as battery posts, lead plates, and lead materials attached to battery casings.

This project represented a serious sampling and analytical challenge in that it required sampling a heterogeneous soil for lead that was present both as lead chunks and as fines. The primary challenge was measuring total lead in the coarse fractions. The standard laboratory digestion procedure digests only a 1 g aliquot, which is unsuitable for samples containing pieces of rock and lead that can weigh several grams each.

For this project, a 1 kilogram (kg) sample was first dried and then screened into four weighed fractions: 64 mm to 6.4 mm, 6.4 mm to 2 mm, 2 mm to 0.1 mm, and < 0.1 mm. Each fraction was examined visually for pieces of lead, which were removed and weighed. The two larger fractions were then placed in a polyethylene bottle and digested with 6% HNO_3 overnight on a rotating apparatus, while 2 g aliquots of the two smaller fractions were placed in beakers and digested with SW-846 Method 3550 and analyzed. The masses measured were then combined to arrive at an average concentration for the entire sample.

The approach described above was satisfactory for the sand and fine fractions, but marginal for the larger fractions due to the intermittent occurrence of lead chunks. A larger initial sample size (e.g., 50 to 100 kg) could have alleviated this problem.

CASE STUDY 5 - THE COGNIS INC. (COGNIS) TERRAMET™ LEAD EXTRACTION PROCESS

The COGNIS Inc. TerraMet™ lead extraction process uses chemical leaching to remove metals bound to sands and fines (including silts and clays). Sands and fines are separated before leaching, and particulate lead is collected for recycling by density separation. Lead present in the liquid phase is precipitated for recovery, and the leaching solution is recycled.

Samples were collected from the feed soil and several sand and fine streams before and after leaching. Obtaining representative samples of some of the coarse-grained soil streams became an issue due to the presence of lead shards in the samples. Grinding soil samples prior to analysis was determined to be the most appropriate method of obtaining representative samples. Originally, soils were to be ground finely enough to pass through a 0.11 mm sieve. However, based on time and cost evaluations, it was decided that this approach would not be applicable in this situation. Samples from the Cognis demonstration are presently being analyzed to determine the most appropriate methods of sample preparation and analyses.

CASE STUDY 6 - BIOVENTING FOR ENHANCED BIODEGRADATION

The Bioventing process is an in-situ biological process that increases aerobic degradation of organic materials in soil. Specifically, several wells are drilled into the contaminated soil plot and air is pumped into the wells for a period of several years to increase aerobic activity and thereby stimulate biodegradation. In-situ soil samples are taken at pre- and post-demonstration periods to determine removal efficiency for the process.

While at the site, it was observed that soil cores contained what appeared to be a significant number of rocks and creosol balls, which were

later referred to as cinder chunks. The rocks and cinder chunks were separated from the soil and saved. The soil samples that remained were then homogenized in the field and sent to the laboratory for analysis as per standard procedures. The total volume of the rocks and cinder chunks was determined for the entire site. A ratio was then calculated for the volume of rocks and cinders in comparison to the total soil volume at the site. This was based upon estimations of soil core volumes and the number of soil cores collected. A representative sample of the rocks and cinder chunks was then analyzed by the laboratory. It was determined that no significant bias existed by excluding these materials in the analyses. Thus, the analysis of a rock/cinder sample was necessary, but the number of analyses was minimized, with the results obtained from the soil analyses verified as being representative of the entire site.

CONCLUSIONS

RREL investigators perform a variety of research projects and frequently encounter unusual sampling situations. The following conclusions have been drawn from heterogeneous soil sampling efforts associated with RREL projects:

- No single approach for sampling and analyzing heterogeneous soils will be applicable for all sites or technologies.
- Multiple approaches for sampling and analyzing heterogeneous soils may need to be used at different sampling locations for a specific technology.
- New approaches for sampling and analyzing heterogeneous material must continue to be developed.
- The risk of collecting unusable data is reduced by developing an adequate sampling approach *before* an actual sampling episode. Before selecting an approach, investigators should review the site characteristics, the technology, the nature of the problem, and the approaches available. Once an approach is selected, investigators should review its success and document the outcome.

In light of the above conclusions, RREL will continue to handle the sampling of heterogeneous soils on a case-by-case basis, while drawing on the knowledge base it has developed. RREL anticipates maintaining a database of heterogeneous sampling approaches, and their results, so that RREL investigators can improve their future planning decisions.

FOR MORE INFORMATION CONTACT: Ann Leitzinger
Technical Project Manager
U.S. Environmental Protection Agency
26 W. Martin Luther King Drive
Cincinnati, OH 45268
(513) 569-7635

BIOREMEDIATION OF TRINITROTOLULENE BY A RUMINAL MICROORGANISM

Taejin Lee, Graduate Research Assistant
Department of Civil Engineering

Dr. Kenneth J. Williamson, Professor
Department of Civil Engineering
(503)737-6836

Dr. A. Morrie Craig, Professor
College of Veterinary Medicine
(503)737-4282
Oregon State University
Corvallis , Oregon 97331-2303

INTRODUCTION

2,4,6-trinitrotoluene (TNT) has been widely used for the production of explosives because of its low boiling point, high stability, low impact sensitivity, and safe manufacture. TNT is known to produce adverse health effects from occupational exposure including increased incidences of aplastic anemia, liver damage, dermatitis, ocular disorders, and gastrointestinal distress. In addition, TNT is of ecological concern based on its toxicity to certain aquatic organisms. More than 1,100 military facilities, each potentially contaminated with munitions waste, are expected to require treatment of more than one million cubic yards of contaminated soils. The cost associated with remediation of these sites has been estimated to be in excess of $1.5 billion.

Recently, researchers have studied ruminal microorganisms in relation to their ability to degrade xenobiotic compounds. Many of these organisms are strict anaerobes with optimal redox potentials as low as -420 mV . Ruminal organisms have been shown capable of destroying some pesticides, such as parathion, p-nitrophenol, and biphenyl-type compounds; thiono isomers, (8, 33); and nitrogen-containing heterocyclic plant toxins such as the pyrrolizidine alkaloids (5). Many of these compounds have structures similar to TNT.

A TNT-degrading ruminal microorganism has been isolated from goat rumen fluid with successive enrichments on triaminotoluene (TAT) and TNT. The isolate, designated *G.8*, utilizes nitrate and lactate as the primary energy source. *G.8* was able to tolerate and metabolite levels of TNT up to the saturation point of 125 mg/l.

Objectives

Based upon the results of previous studies, the present research was directed at understanding the process of TNT degradation by the denitrifying ruminal microorganism *G.8* (5). The objectives of this study were: 1) to identify specific metabolites and define TNT destruction pathways and 2) to understand TNT and the metabolites transformation mechanisms on the different primary electron acceptors.

METHODOLOGY

Growth Medium

The media used to incubate the isolate in serum bottles consisted of (mg/l) $CH_3CHOHCOONa$ (500), $MnSO_4.H_2O$ (8.5) $FeSO_4.7H_2O$ (10), KNO_3 (2000), $ZnSO_4.7H_2O$ (5), $CaCl_2.2H_20$ (24), $Na_2HPO_4.H_2O$ (2550), H_3BO_3 (1.5), $NaMo_4.2H_2O$ (1.5), $NaH_2PO_4.H_2O$ (975), $CoCl_2.6H_2O$ (0.6),

Na_2EDTA (21.5), yeast extract (100), $CuCl_2.2H_2O$ (0.05), $MgSO_4.7H_2O$ (30), and $NiCl_2.6H_2O$ (1). The nutrients were mixed and well-stirred. pH was adjusted to 7.0 with 0.1 N NaOH, then boiled for 3 minutes under argon gas flow and dispensed into serum bottles, which were then stoppered and autoclaved for 25 minutes. To prevent the precipitation of salts from the medium, 0.3 ml of 800 ppm $CaCl_2 \cdot 2H_2O$ was injected following autoclaving. An 0.2 % inoculum was used for all experiments. Serum bottles were cultivated anaerobically at 37°C for given periods of time using a mechanical shaker. Ethanol was used to prevent contamination at the contact points for the inoculant and samples, and sample aliquots were indexed and frozen at -14°C.

Analytical Methods

TNT, 4-amino,2,6-dinitrotoluene (4A26DNT), 2,6-dinitrotoluene (26DNT), 2-amino,6-nitrotoluene (2A6NT), and 2-nitrotoluene (2NT) were measured by high performance liquid chromatography (HPLC),. Gas chromatography/mass spectrometry (GC/MS) analysis was performed using a Hewlett-Packard Model 5988A connected to a Model 5890 gas chromatography (GC) with a XTI-5 fused-silica capillary column. A Dionex 4000i ion chromatography (IC) with a HPIC-CS3 anion column was used to measure anions such as nitrate and nitrite. Culture turbidity in the serum tubes was measured using a spectrophotometer at 660 ηm absorbance (Bausch and Lomb, Spectronic 20D) for cell-growth analysis.

Microorganism

A TNT degrader was isolated from rumen fluid with successive enrichment of TNT and TAT.. The isolated microorganisms from a fistulated goat was named *G.8*. The gram negative *G.8* was identified based fatty acid analysis as a *Escherichia Coli* with similarity index (SI) of 91.4 percents.

RESULTS

G.8 growth was monitored by optical density using different energy sources including nitrates, nitrites, or TNT to investigate the relation of TNT to *G.8* metabolism. *G.8* growth occurred in the presence of only nitrate, but not on nitrite, or TNT, indicating that nitrate serves as a viable terminal electron acceptor. Fermentation was not observed with the presence of lactate only in the medium. *G.8* growth was detected in the absence of lactate (TNT and nitrate present), suggesting that TNT could have been potentially used as the carbon source and electron donor. *G.8* growth was observed in the medium without lactate (only nitrate present) as much as in the medium containing TNT and lactate, probably from the use of the yeast extract as the electron donor and carbon source.

Additional experiments were conducted to investigate the influence of TNT on the utilization of primary energy source with *G.8* growth. Nitrate was converted to nitrite completely within 10 hours, followed by further reduction of the nitrite. Nitrate was converted to nitrite and then less transformation of the nitrite in the medium was observed when TNT is present.

In the preliminary experiments, *G.8* growth was not observed with nitrite or TNT as the primary electron acceptor, indicating *G.8* does not initially utilize the nitrite or TNT. When TNT was absent from the medium, further transformation of the nitrite from nitrate was observed and less transformation of the nitrite with presence of TNT in the medium. Thiese results demonstrate that nitrite or TNT conversions takes place in the presence of nitrate. It suppose that the nitrite and TNT appear to compete as cometabolic electron acceptors, with the TNT being preferrentially used.

G.8 Experiments to Determine Metabolic Pathways

Based on evidence of co-metabolic TNT transformation, we decided to attempt to identify the TNT biotransformation pathways and limiting factors. TNT and each of its transformation

products were incubated individually with a *G.8* medium containing lactate as the electron donor and nitrate or nitrite as the primary electron acceptor. A medium containing lactate and TNT metabolites was also prepared.

TNT Transformation

G.8 was incubated for three days in serum bottles containing 20 mg/l of TNT. From Bottle A (containing lactate and nitrate as primary energy sources), the metabolites were identified as 4A26DNT. The complete TNT transformation in Bottle A and the non-transformations of TNT in Bottles B (containing lactate and nitrite as primary energy sources) and C (containing only lactate) showed that TNT is co-metabolically degraded in the presence of nitrate, and not degraded in the presence of nitrite.

4A26DNT Transformation

G.8 was incubated for eight days in serum bottles containing 20 mg/l of 4A26DNT. In Bottle B, 4A26DNT was reoxidized to TNT and deaminated to 26DNT. In Bottle A, only negligible amounts of TNT and 26DNT were detected. No 4A26DNT transformation occurred in Bottle C. Nitrites in the medium appeared to stimulate the *G.8* reduction and oxidation systems.

26DNT Transformation

In the same manner described for the 4A26DNT incubations, 26DNT was incubated for 20 days with *G.8* in Bottles A, B, and C. The transformation of 26DNT to 2A6NT was not detected or was negligible in Bottles A and B. The reduction of the 26DNT ortho-position nitro group was detected in bottle C, suggesting that *G.8* utilized 26DNT as a primary electron acceptor.

2A6NT Transformation

During 18 days of incubation, 2A6NT in Bottle B was transformed to 2NT and 26DNT. Oxidation and reduction of 2A6NT trends were identical to those for the 4A26DNT incubation. The absence of a primary electron acceptor in Bottle C did not stimulate 2A6NT transformation, and the oxidation of 2A6NT was faster than the reduction processes.

2NT and 2AT Transformations

During 18 days of incubation, 2NT metabolites were not detected from either HPLC or GC/MS analysis, but it was noteworthy that 2-aminotoluene (2AT) completely disappeared from Bottles A and B, suggesting that 2AT transformed more rapidly than 2NT. It is reasonable to suppose that the 2AT transformation products converted rapidly to other metabolites, but that the transformation of 2NT to 2AT was too slow. The 2AT transformation products were identified as o-cresol, toluene, and small amounts of 2NT. These trends for amino group transformation were identical to those for 4A26DNT and 2A6NT.

TNT transformation pathways were established with series connections of each transformation products presented above. Proposed pathways for the TNT degradation are shown in Figure 1. The TNT biotransformation steps shown are the reduction process, wherein the nitro group is reduced to an amino group, followed by deaminization and oxidation when the amino group was present. As observed previously, para-nitro group reduction was the most susceptible transformation .

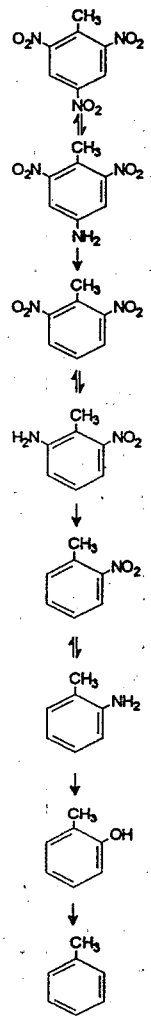


Figure 1. Proposed pathways for TNT biotransformation with *G.8* incubation. The pathways are established with series connection of the identified transformation products by GC/MS and HPLC.

CONCLUSIONS

The *G.8* isolate was capable of reducing the TNT nitro group to an amino group and was also involved in deaminization as a co-metabolite, resulting in nitrogen free compounds such as toluene or o-cresol.

The reduction (deaminization) and oxidation (hydroxylation) reactions took place simultaneously when the amino group was present. From previous studies, it had been reported that oxidation and reduction processes occurred jointly subject to anaerobic conditions. Vogel et al. (4) demonstrated that *Cytochrome* P450 could mediate both the oxidation and reduction reactions for degradation of halogenated aliphatic compounds. For *Pseudomonas* sp. strain PN-1, it was also found that oxidation steps proceeded under conditions of denitrification (1). CO_2 and chloroform formations from carbon tetrachloride in the culture of *Escherichia Coli* K-12 was found by Criddle et al. (1). These mechanisms are coincident with the present mechanisms of *G.8*.

Degradation of compounds is dependent upon the characteristics of the parent compounds, the microbial consortium, and environment factors (3). In the experiments described, the patterns of TNT metabolite transformation were dependent on the type of electron acceptors. The presence of nitrates in the medium stimulated the reduction of para-positioned nitro groups, and nitrites stimulated the deaminization and hydroxylation processes. The absence of such primary energy sources as nitrates or nitrites stimulated the reduction of the ortho-positioned nitro groups.

It is assumed that the incomplete TNT transformations are related to inadequate combinations of the terminal electron acceptors. Nitrate consumption in the medium was complete while TNT was transformed to 4A26DNT and 26DNT. For certain periods of time, nitrite accumulated in the medium does not support *G.8* metabolism and subject to termination of 26DNT reduction process, as was indicated at 26DNT transformations with presence of nitrite in the medium.

From these findings, it is concluded that an appropriately designed sequencing reactor system, or other alternatives to control such energy source as nitrates, or nitrites in the TNT degradation system, could result in obtaining the full transformation of TNT to o-cresol or toluene.

REFERENCES

1. Berry, D. F., A. J. Francis, and J. M Bollag. 1987. Microbial Metabolism of Homocyclic and Heterocyclic Aromatic Compounds under Anaerobic Conditions. Microbiol. Rev., 51:43-59.

2. Criddle, C. S., J. T. Dewitt, and P. L. McCarty. 1990. Reductive Dechlorination of Carbon Tetrachloride by *Escherichia coli* K-12. Appl. Environ. Microbiol., 56:3247-3254

3. Nicholson, D. K., S. L. Woods, J. D. Istok, and D. C. Peek. 1992. Reductive Dechlorination of Chlorophenols by a Pentachlorophenol-Acclimated Metanogenic Consortium. Appl. Environ. Microbiol. 58: 2280-2286.

4. Vogel, T. M., S. C. Criddle, and P. L. McCarty. 1987. Transformation of Halogenated Aliphatic Compounds. Environ. Sci. Techonol. 21:722-736

5. Wachenheim, D. E., L.L. Blythe, and A. M. Craig. 1992. Characterization of Rumen Bacterial Pyrrolizidine Alkaloid Biotransformation in Ruminants of Various Species. Vet. Hum. Toxicol. 34:513-517.

FULL-SCALE *IN SITU* BIOREMEDIATION OF TRICHLOROETHYLENE IN GROUNDWATER: PRELIMINARY MODELING STUDIES

Mark N. Goltz, Brett T. Kawakami, and Perry L. McCarty
Western Region Hazardous Substance Research Center
Department of Civil Engineering
Stanford University
Stanford, CA 94305-4020
Phone: 415-723-8574
Fax: 415-725-3164

INTRODUCTION

A full-scale study of in-situ bioremediation is being planned for implementation at Edwards Air Force Base. The bioremediation system that is being proposed has been developed over 8 years of research and testing in the laboratory and at a pilot field site located at Moffett Naval Air Station in Mountain View, California. Studies conducted at the Moffett field site have demonstrated that trichloroethylene (TCE), the contaminant found at Edwards, can be effectively biodegraded cometabolically through the introduction into the subsurface of a primary substrate (such as phenol or toluene) and an oxygen source (such as hydrogen peroxide) to support the growth and energy requirements of a native population of microorganisms (1,2,3).

One of the main questions that needs to be answered, prior to full-scale demonstration of this technology on the Edwards TCE plume, is how best to mix a primary substrate, an oxygen source, and TCE, and subsequently get the mixture to the microorganisms. At Moffett Field, mixing of these three components was accomplished above ground, with the mixture then introduced into the subsurface through an injection well. In the full-scale demonstration, the TCE will, of course, already be in the groundwater. A major objective of the demonstration will be to investigate how a primary substrate and an oxygen source can be efficiently mixed and transported to indigenous microorganisms, in order to promote cometabolic degradation of TCE. For the demonstration, it is anticipated that a subsurface recirculation system, similar to that described by Herrling (4) and McCarty and Semprini (5) will be used. The proposed remediation system is shown in Figure 1. The system consists of a pair of recirculation wells, each screened at two depths. In operation, a submersible pump installed between the two screens of each well would draw TCE contaminated water into the well at one of the screened intervals. The primary substrate (toluene) and oxygen source (hydrogen peroxide) will then be introduced into the well through feed lines, and the water, which contains TCE, toluene, and oxygen, will be discharged into the aquifer from the second screened interval. An in-situ treatment zone will be created in the aquifer, around the discharge screen. The second treatment well will extract water from the injection zone of the first well, and inject water at the level where the first well is extracting water. Thus. water will circulate through the aquifer, from one treatment well to the other. The injection/extraction levels of each well can be periodically reversed.

METHODOLOGY

To help plan and design the demonstration, a computer model which incorporates all the significant flow and transport processes was used. A two-dimensional flow code was used, to simulate pumping through the two treatment wells. The streamtubes which were output by the flow code were used as input for the transport code. The one-dimensional transport code (6,7) was applied along each streamtube. The transport code includes the microbial processes of bacterial growth, toluene and oxygen utilization, and the cometabolic transformation of TCE coupled with the transport processes of advection, dispersion, and rate-limited sorption onto aquifer solids. Model simulations could be run for different parameter values, with TCE concentrations output as a function of space and time. In addition, TCE concentrations may be numerically integrated over space, to obtain plots of TCE mass versus time.

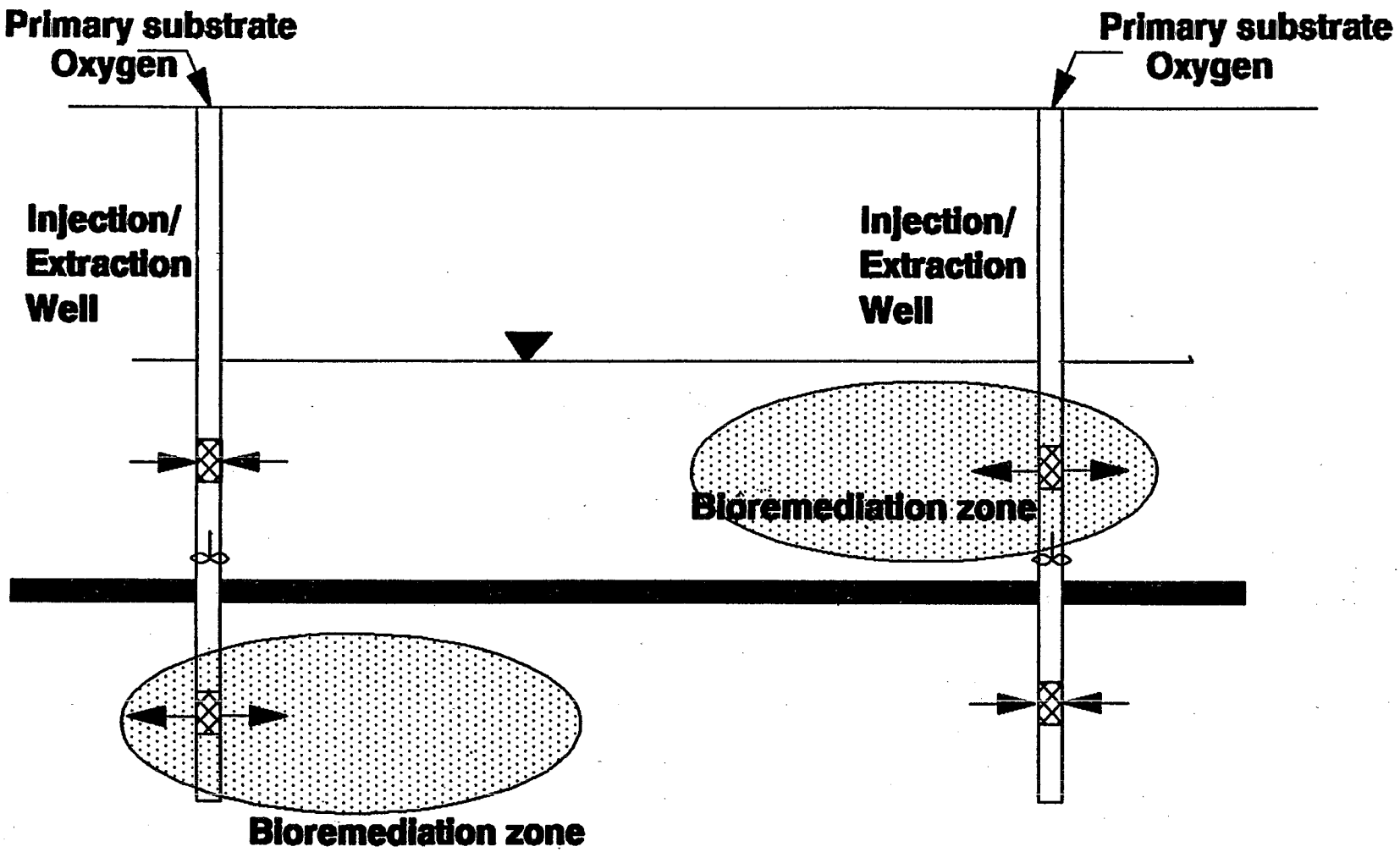


Figure 1. Bioremediation concept.

RESULTS

Based on preliminary data obtained from the Edwards demonstration site and the Moffett Field experimental site, and using "best-guess" design values for the treatment system, a base line simulation was run. Base line parameter values are listed in Table 1.

TABLE 1. PARAMETER VALUES USED FOR BASELINE SIMULATION OF BIOREMEDIATION MODEL

Parameter	Value
Distance between treatment wells	10.0 meters
Flow rate through each treatment well	15.0 gallons per minute
Treatment well screen length	4.0 meters
Concentration of oxygen source (hydrogen peroxide) added	100 milligrams per liter (mg/L)
Time-averaged concentration of primary substrate (toluene) added	9 mg/L
Toluene pulse length	20 minutes every 8 hours
Initial TCE concentration in aquifer	0.2 mg/L
Sorption distribution coefficient	0.2 milliliter per gram
Sorption/desorption rate coefficient	0.010 per day
TCE retardation factor	2.0
Cometabolism rate constant	0.015 per day
TCE half-saturation coefficient	0.5 mg/L

The simulation shows how TCE mass declines in both the dissolved and sorbed phases over the four months planned for the demonstration (figure 2). Notice that initially, the mass of TCE in the dissolved and sorbed phases is equal. This is due to the fact that the retardation factor used for the simulation is 2.0, and TCE concentrations in the dissolved and aqueous phases are initially assumed to be at equilibrium. Over approximately the first 50 days of the simulation, dissolved mass drops relatively rapidly, due to biodegradation of TCE in the aqueous phase. After about 70 days, the mass of TCE in the aqueous phase becomes relatively constant, while the mass in the sorbed phase shows a slow but steady decline. What has happened is that after about 70 days, slow desorption has begun to control the rate of mass removal. A pseudo-steady state has been attained where the rate of biodegradation of dissolved TCE equals the rate at which TCE desorbs from the aquifer solids into the aqueous phase. Thus, based on the assumed parameter values, we see that the decline in total mass after the initial 70 days of bioremediation is controlled by the rate of TCE desorption from aquifer solids. A critical value in the simulations is thus the sorption/desorption rate coefficient, a value which was estimated. Because of its importance, this value needs to be determined experimentally in the laboratory for the Edwards site. The simulation also demonstrates that using preliminary design values, a significant drop in TCE mass may be expected to be seen in the demonstration area over the course of the four month demonstration. Figure 3 shows aqueous and sorbed TCE concentrations between the two treatment wells along one of the streamtubes after 120 days of bioremediation. Note how the aqueous concentration drops rapidly near the injection well, and then slowly rises. The rapid drop results since most of the microbial mass is predicted by the model to reside close to the injection well. This prediction is consistent with the results from the Moffett Field studies. The slow rise in TCE concentrations is due to the relatively clean water moving through the aquifer towards the extraction well. The clean water causes sorbed TCE to desorb, thus leading to the concentration rise in the aqueous phase. Also note that the TCE concentrations after 120 days are well below the initial values of 0.2 mg/L in the dissolved phase and 0.04 mg/kg in the sorbed phase.

CONCLUSIONS

Based on reasonable parameter values and results of prior work at an experimental field site, preliminary modeling studies have been used to show that the planned operation of an in-situ aerobic cometabolic bioremediation system can be expected to result in observable decreases in TCE mass and concentration at the proposed technology demonstration site.

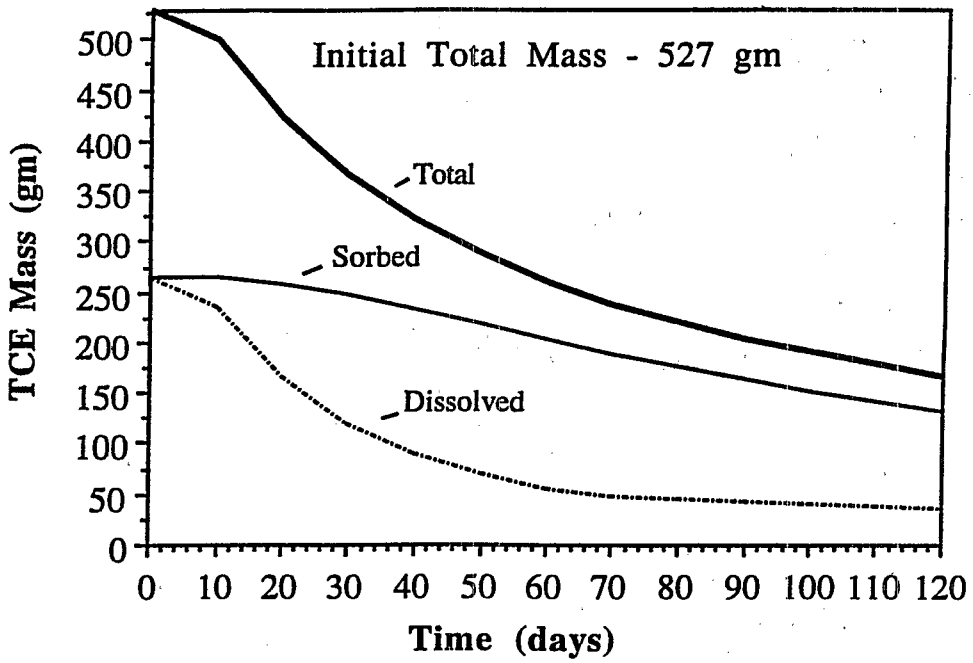


Figure 2. TCE mass vs. time

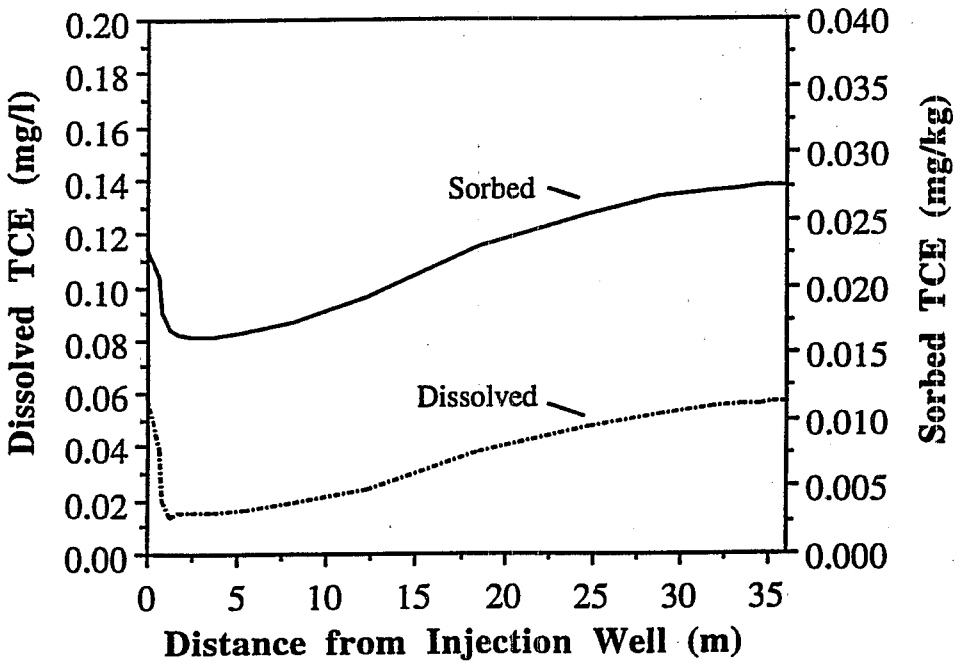


Figure 3. Dissolved and sorbed TCE concentration vs. distance between wells

REFERENCES

1. Hopkins, G. D., Semprini, L., and McCarty, P. L. Microcosm and In Situ Field Studies of Enhanced Biotransformation of Trichloroethylene by Phenol-Utilizing Microorganisms. Applied and Environmental Microbiology. 59(7): 2277-2285, 1993.

2. Hopkins, G. D., Munakata, J., Semprini, L., and McCarty, P. L. Trichloroethylene Concentration Effects on Pilot Field-Scale In-Situ Groundwater Bioremediation by Phenol-Oxidizing Microorganisms. Environmental Science and Technology. 27(12): 2542-2547, 1993.

3. Hopkins, G. D. and McCarty, P. L. Field Evaluation of In Situ Aerobic Cometabolism of Trichloroethylene and Three Dichloroethylene Isomers Using Phenol and Toluene as the Primary Substrates. Submitted Environmental Science and Technology. 1994.

4. Herrling, B. Hydraulic circulation system for in situ bioreclamation and/or in situ remediation of strippable contamination. In: R.E. Hinchee and R.F. Olfenbuttel (eds.), On-Site Bioreclamation, Butterworth-Heinemann, Boston, Massachusetts, 1991. pp. 173-175.

5. McCarty, P.L. and Semprini, L. Ground-water Treatment for Chlorinated Solvents. In: R.D. Norris et al. (eds.), Handbook of Bioremediation, Lewis Publishers, Boca Raton, Florida, 1993. pp. 87-116.

6. Lang, M. M. Design and Optimization of In Situ Bioremediation Relying on Cometabolic Degradation. Ph.D. Dissertation, Stanford University, Stanford, CA, 1995. 185 pp.

7. Semprini, L. and McCarty, P. L. Comparison Between Model Simulations and Field Results for In Situ Biorestoration of Chlorinated Aliphatics: Part 2. Cometabolic Transformations. Ground Water. 30(1): 37-44, 1992.

FOR MORE INFORMATION

Mark N. Goltz
Western Region Hazardous Substance Research Center
Department of Civil Engineering
Stanford University
Stanford, CA 94305-4020
Phone: 415-723-8574
Fax: 415-725-3164
Email: goltz@cive.stanford.edu

A MICROBIOLOGAL SURROGATE FOR EVALUATING TREATMENT EFFICIENCY

Eugene W. Rice, Kim W. Fox, Richard J. Miltner,
Darren A. Lytle and Clifford H. Johnson

Drinking Water Research Division
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

INTRODUCTION

In this study we report on the use of a microbial surrogate system which can be used to evaluate the efficiency of various unit processes used in drinking water treatment for the removal of microbial contaminants. The proposed procedure uses Gram-positive, mesophilic, aerobic spore-forming bacteria as the surrogate organisms. These bacteria do not pose a public health threat and are naturally occurring in most surface water supplies. The aerobic spore-formers are easy to culture and are present throughout the treatment train. This group of organisms consists primarily of species of the genus *Bacillus*. These organisms form endospores which are ellipsoidal to spherical in shape and measure on average approximately 0.5 X 1.0 X 1.5 micrometers, and are environmentally resistant. Like pathogenic *Giardia* cysts and *Cryptosporidium* oocysts endospores of aerobic bacilli may be found far into the treatment train.

MATERIALS & METHODS

Both naturally occurring aerobic spore-forming bacteria and pure cultures of *Bacillus subtilis* spores were used in this study. *B. subtilis* spores were purchased from a commercial laboratory (Raven Biological Laboratories, Omaha, Nebraska 68106). The protocol for the enumeration of the aerobic spores was a modification of a procedure used for the detection of *Bacillus* spores in raw milk (1). The following equipment is used in the protocol:

- Sterile Erlenmeyer flasks with screw-caps or sterile bottles with closures.
- Thermostatically controlled water bath with shaker for constant agitation
- Thermometer
- Sterile pipettes
- 60 x 15 mm Petri dishes with loose lids
- 47 mm, 0.45 μm porosity membranes
- Membrane filtration apparatus
- Incubator, 35°C

The medium used for growing the bacteria consisted of nutrient agar plus the dye trypan blue. The dye was added to aid in the visualization of the colonies.

The formulation for the medium is:

- Nutrient Agar
  - Peptone 5 g
  - Beef extract 3 g
  - Agar 15 g
- Trypan blue dye 0.015 g
- Distilled water 1,000 ml
  - Heat to boiling dissolve completely.
  - Sterilize in the autoclave for 15 minutes at 15 psi (121°C)
  - pH 6.8 ± 0.2 at 25°C

The spore-forming bacteria were enumerated using the membrane filter method. The following steps outline the experimental procedure:

- Place sample in sterile flask and cover with cap
- Prepare pilot flask with same volume as sample and thermometer
- Place sample flask(s) and pilot flask in water bath at 82°C and agitate throughout heat treatment
- Lower temperature of bath to 80°C when flask(s) reaches 79°C
- When contents of flask(s) reach 80°C, keep samples in bath for an additional 12 min.
- Immediately cool sample flask(s) in ice bath
- Membrane filter (0.45 μ m pore size) appropriate volumes and place membrane on medium
- Incubate plates 20-22 hr at 35°C
- Count colonies

Heating the sample to 80°C inactivates vegetative bacterial cells but does not inactivate spores. During aerobic incubation at 35°C the spores germinate and are counted as bacterial colonies.

Total coliform bacteria were enumerated by the membrane filter procedure using m-Endo LES agar, and heterotrophic plate count (HPC) analyses were conducted by the spread plate procedure using R2A agar with incubation of plates at 28°C for 5-7 days. Cultures of *B. subtilis* spores were used in the bench-scale coagulation studies (jar tests). Standard procedures were used to conduct the jar test experiments (3). An electronic particle counter, HIAC/ROYCO, model 9064 (Pacific Scientific Co., Montclair, Calif.) was used for particle sizing and counting analysis.

RESULTS & DISCUSSION

Levels of indigenous aerobic spores found in the Ohio River over a ten month period are listed in Table 1. These results are typical of the numbers of aerobic spore-formers which would normally be encountered in a surface water supply.

Table 1.

Levels of Indigenous Spores

in

Ohio River Water

1994

Month	CFU/100 ml
January	7,500
February	31,000
March	11,000
April	27,000
May	5,800
June	3,700
July	3,900
August	310,000
September	2,600
October	1,800

Table 2 lists the mean log removals of several microbial parameters and total particles (>1 μm) and particles in the size range of 3.1-7 μm in a pilot conventional drinking water treatment plant sampled daily over seven days. This table lists the log removals achieved through the settling and filtration processes. The spores were the only microbial parameter which could be found throughout the treatment train and their removals closely paralleled both total particle counts and counts in the 3.1-7 μm size range. Table 2 also indicates that the spores, like *Giardia* and *Cryptosporidium*, are much more resistant than coliforms or HPC to chlorination.

Log removals of spores and particles in a full-scale water treatment plant which utilizes Ohio River water are listed in Table 3. These data collected over three seasons again show the parallel between particle counts and levels of indigenous spores.

CONCLUSIONS

Indigenous aerobic bacillus spores can serve as surrogates for particle removal and potentially for *Giardia* and *Cryptosporidium* removals. Generally, optimal removals were achieved with spores when optimal removal efficiencies were achieved for turbidity and particle removals. The aerobic spore forming bacteria are ubiquitous in nature and thus can be used to evaluate treatment without adding potential surrogates to the source water. Since these bacteria and their spores are primarily soil organisms their numbers increase with increasing amounts of run-off. Unlike the general heterotrophic plate count parameter, these organisms would not propagate in the treatment plant (e.g. as the result of increased AOC after ozonation) and are more resistant to disinfection. Also, unlike inanimate particles, which are counted by electronic particle counters, the spores would not be created or broken up while passing through various unit processes. While these organisms have no public health significance and are not indicators of fecal contamination, they may serve as useful indicators of treatment plant efficiency.

REFERENCES

1. American Public Health Assoc. 1985. Standard Methods for the Examination Dairy Products. 15th ed. Am. Pub. Health Assoc. Washington, D.C.

2. American Public Health Assoc. 1992. Standard Methods for the Examination of Water and Wastewater. 18th ed. Am. Pub. Health Assoc. Washington, D.C.

Table 2.

Removals During Pilot Study

Parameter	Log_{10} Removal Settled	Filtered Chlorinated
Total coliforms	0.47	>1.79*
HPC	0.38	>4.58*
Spores	0.85	2.11
3.1-7 μm particles	1.11	2.10
Total particles	0.91	1.70

* Below detection limit:
Total coliforms 1 cfu/100 ml
HPC 1 cfu/ml

Table 3.

Seasonal Removal - Ohio WTP

	Log_{10} Removal from Raw Water		
	Spores Particles	3-6 μm Particles	Total
Winter			
settled	1.35	1.62	1.37
finished	2.86	3.52	3.26
Spring			
settled	1.51	1.08	1.47
finished	2.80	2.22	2.50
Summer			
settled	2.11	0.61	0.73
finished	2.08	2.09	1.97

EVALUATION OF MEMBRANE PERFORMANCE AND FOULING BY PYROLYSIS-GC/MS

Thomas F. Speth
USEPA
26 W Martin Luther King Dr.
Cincinnati, OH 45268
(513) 569-7208

William R. Fromme
and R. Scott Summers
University of Cincinnati
Cincinnati, OH 45221

INTRODUCTION

The loss of membrane efficiency due to fouling is one of the main impediments to the development of membrane processes for use in drinking water treatment. Membrane fouling is dependent on the water quality and the membrane properties and construction. In general, fouling is defined as the accumulation of material on the surface, or in the pores, of a membrane that decreases the water flux through the membrane. The consequences of fouling can be severe, fouling can reduce the water flux through a membrane up to 90 percent (1). There are five broad fouling categories: sparingly soluble inorganics, colloidal or particulate matter, dissolved organics, chemical reactants, and microorganisms.

Dissolved organics and colloidal matter are considered to be the most serious of the foulants due to the difficulty in removing them with pretreatment processes. Membranes can be fouled either by cake-layer formation or adsorption. Cake-layer formation refers to a layer of material on top of the surface of the membrane. Cake-layer fouling can be removed hydrodynamically. Adsorption refers to materials attached within the pores of the membrane. This type of fouling is generally considered irreversible although chemical cleaning can be effective in some cases. The nature of the organic molecules that foul nanofiltration membranes is not known. Knowledge of the characteristics of the natural organic matter responsible for membrane fouling may lead to optimal membrane and pretreatment selection. Improved nanofiltration performance will lead to an increased use of nanofiltration as a drinking water treatment method.

Pyrolysis-gas chromatography/mass spectroscopy (Py-GC/MS) has the ability to elucidate natural organic matter characteristics. Pyrolysis is used to thermally cleave organic molecules into volatile fragments that are then separated by gas chromatography and identified by mass spectroscopy. The Py-GC/MS method used herein was developed by Bruchet et al. (2) at the Lyonnaise des Eaux in Paris, France. Bruchet's method categorizes natural organic matter in terms of polysaccharides, proteins, polyhydroxyaromatics, and aminosugars. The fractions are calculated relative to a known standard mixture of dextran, bovine serum albumin, cellulose acetate, and Fluka humic acids. A simple empirical algorithm was developed for computing relative peak areas among the various classes of biopolymers (2).

The objective of this research is to relate the productivity of membrane systems that treat different waters to natural organic characteristics as determined by Py-GC/MS. Membrane studies will be completed with a cellulose acetate membrane that has a nominal molecular-weight cutoff of 500 Daltons (Amicon YC05), and a thin-film polyamide membrane (Fluid Systems) that has a nominal molecular-weight cutoff of 200 Daltons. Waters from the Ohio River (southern Ohio), East Fork Lake (southern Ohio), and Manatee County (Florida) were used. The three waters have very different

characteristics. The Manatee County water (MCW) has a very high dissolved organic carbon (DOC) concentration (near 20 mg/L). It also has very low alkalinity (12 mg/L as $CaCO_3$) and hardness (29 mg/L as $CaCO_3$). Py-GC/MS results indicate that the Manatee County water is very aromatic in nature. The Ohio River water (ORW) is low in DOC (approximately 2.5 mg/L). It is moderately hard (110 mg/L as $CaCO_3$), and has a moderate alkalinity (56 mg/L as $CaCO_3$). Preliminary Py-GC/MS results suggest that it has aromatic and proteinaceous character. The East Fork Lake water (EFLW) has a moderate DOC (approximately 5 mg/L), and has the highest hardness (126 mg/L as $CaCO_3$) and alkalinity (100 mg/L as $CaCO_3$) of the three waters. The EFLW Py-GC/MS results indicate a polysaccharide nature.

METHODOLOGY

The membrane experiments were conducted in a 450 ml dead-end pressure vessel that was stirred. The membrane experiments were run until the flux decreased to approximately 50 percent of the initial flux, or until a steady flux was obtained. At the end of each experiment, the concentrate was collected and rotoevaporated to a concentration that allowed for adequate organics to be spiked into 50µl pyrolysis tubes. Likewise, the feed and the permeate streams were rotoevaporated to a similar concentration. The membrane was then turned over and approximately 100 ml of organic-free water was used to backflush the membrane. Finally, the membrane was turned back over and a short run with organic-free water was completed to check the flux recovered after backflushing. The backflush sample was also rotoevaporated to the same concentration as the other samples. The Manatee water experiments had a layer of material on top of the membrane that did not come off with backflushing. This material was physically scraped off and analyzed.

The DOC, total dissolved solids (TDS), and ultraviolet @254nm (UV) of the feed, concentrate, and numerous permeate samples were assessed. These results allowed for a mass balance to be completed over the membrane experiment. Also, small aliquots of the rotoevaporated samples were taken and diluted into 100 ml of organic-free water. DOC, TDS, and UV of the diluted samples were assessed. This was completed to determine the volume of the samples to be spiked into the pyrolysis tubes to obtain the same total DOC in all of the tubes (130 µg). It also allowed for determination of the amount of organics that adhered to inorganic precipitation during rotoevaporation. Rotoevaporation losses of organics may be important with regard to the pyrolysis results if the organics removed were not similar in make-up to the organics that remained in solution.

Each Py-GC/MS sample was run in triplicate. The pyrolysis tubes were weighed before and after pyrolysis to confirm that similar sample sizes were being used, and to show that similar amounts of the samples were being pyrolyzed. The three waters being used were each concentrated on two separate occasions to confirm that each water's characteristics were not changing over time.

After the fouling of the membranes, a small (0.3mg) sample of each of the fouled membranes was pyrolyzed. The membrane sample was measured on a balance sensitive to 0.01mg. As with the previously discussed samples, each Py-GC/MS sample was run in triplicate. Clean membranes were also pyrolyzed in triplicate to determine the background pyrograms.

The analytical procedure for Py-GC/MS entailed ramping the pyrolysis sample from 35°C to 750°C at 20°C/ms in a heated-filament pyrolysis probe. The final temperature was held constant for 20 seconds. Splitless injection to the GC was used. The GC was ramped from 35°C to 260°C at a rate of 2°C/min. A 60-meter Supelco WAX-10 column was used.

RESULTS

Table 1 contains the flux decline results for the matrix of experiments performed in this study. The Manatee County water showed the greatest flux reduction for the Amicon membrane experiments.

The East Fork Lake water showed the greatest flux reduction for the Fluid System membrane experiments. The reason for this behavior is made clear by electron microscope analysis. Electron microscopy of the fouled Amicon membranes showed no inorganic deposits. This indicates that the fouling agents were organic in nature. Electron microscopy of the Fluid System membranes for the EFLW and ORW experiments, however, showed large deposits of calcium (most probably calcium carbonate). The Manatee County water showed no inorganic fouling with the Fluid System membrane.

TABLE 1. FLUX DECLINE RESULTS FOR MATRIX OF EXPERIMENTS

Membrane/Water	Liters of Water Passed	Percentage Flux Decline
Amicon/Manatee County Water	7.8	35
Amicon/Ohio River Water	21.5	30
Amicon/East Fork Lake Water	18.6	15
Fluid System/Manatee County Water	6.8	55
Fluid System/Ohio River Water	6.8	60
Fluid System/East Fork Lake Water	3.9	68

As mentioned above, the Amicon membranes were fouled by organics. Therefore, it is not surprising that the Manatee County water, which had the highest DOC concentration, showed the greatest amount of fouling. The organic nature of the foulant was also confirmed by the UV, DOC, and TDS balances of the membrane run. The Amicon membrane had a large enough molecular-weight cutoff to pass inorganic ions while rejecting most of the organic molecules.

The Fluid System membrane rejected both organics and a great deal of the inorganic ions. This was shown by UV, DOC, and TDS mass balances over the membrane experiments. This was expected because of the Fluid System membrane's designation as a "softening" membrane. The East Fork Lake water had the greatest concentration of hardness and alkalinity, and hence the greatest amount of inorganic fouling. The Fluid-System/MCW experiment showed a lack of inorganic fouling as mentioned above. This was due to the water's extremely low hardness and alkalinity. This was visually confirmed by noticing that the final concentrate solutions of the Fluid-System/EFLW and the Fluid-System/ORW experiments were salty in appearance, whereas the Fluid-System/MCW concentrate was clear.

Py-GC/MS of the Manatee County water showed that the water is primarily polyhydroxyaromatic in nature. Polyhydroxyaromatics accounted for over half of the organics. Proteins, polysaccharides, and aminosugars accounted for a much lower percentage of the total. The pyrolysis results for the feed water, concentrate, permeate, and membrane scrapings showed that the concentrate had a marked decrease in polysaccharides as compared to the feed water. The pyrolysis results of the other fractions were roughly similar to the feed-water results.

Figure 1 contains the mass balance for the Amicon/MCW experiment. The mass balance shows that the biopolymer groups were primarily found in the concentrate stream as expected due to the high organic rejection. The permeate, backflush, and membrane scrapings contained small amounts of all the biopolymers. The mass balance closed very well for the protein, polyhydroxyaromatic, and aminosugar groups. However, a large amount of the polysaccharides fed to the system was not accounted for. When the membrane was pyrolyzed, the unaccounted for polysaccharides were found. Figure 1 also shows the amount of polysaccharides found in the membrane. This additional amount of polysaccharides closes the mass balance reasonably well. Therefore, these results suggest that polysaccharide material was irreversibly adsorbed (operationally defined) to the membrane, and was responsible for the membrane fouling.

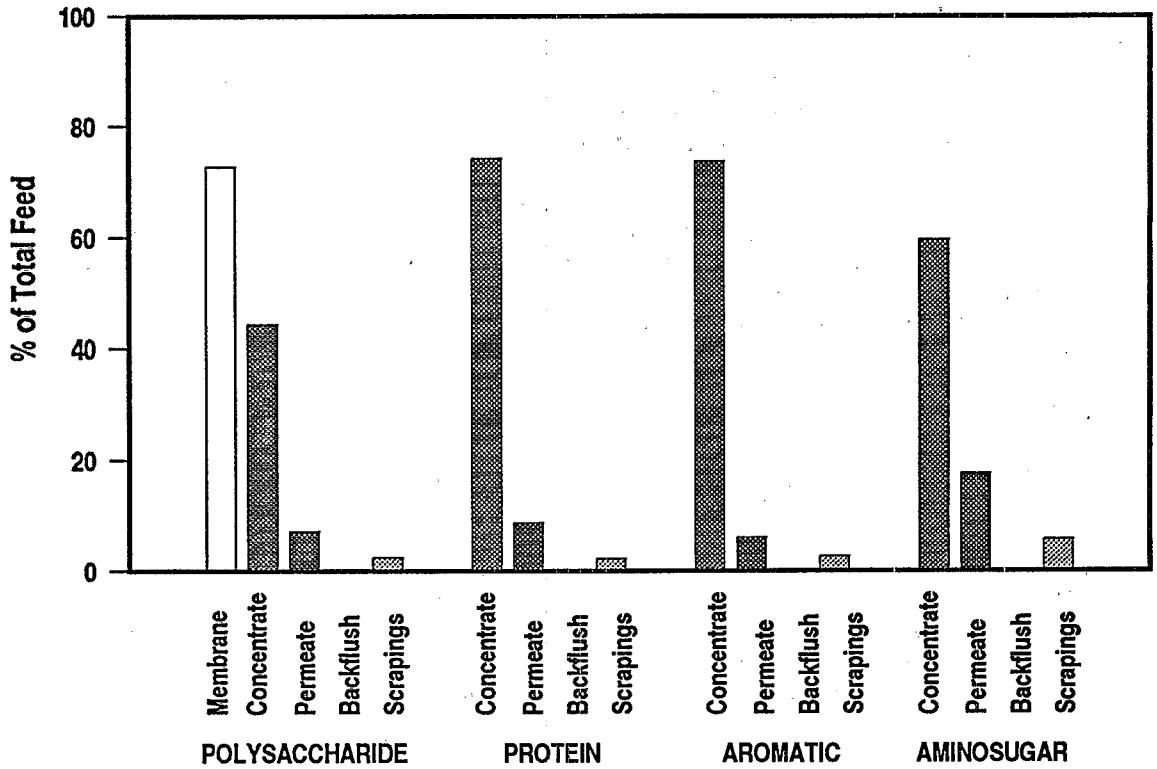


Figure 1. Pyrolysis-GC/MS mass-balance results for Amicon-YC05 membrane run with Manatee County water.

The Amicon/MCW results agree with the work of Mallevialle et al. (3) who showed that polysaccharides were one of the fouling agents for ultrafiltration membranes. Mallevialle et al. (3) indicated that inorganics also were present in the fouling mechanism. In this work, however, the electron microscopy results do not show an inorganic presence.

The Fluid-System/MCW results show that all of the Bruchet et al. (2) groups were rejected, and thereby remained in the concentrate. However, the mass balance indicates that significant portions of all four groups remained unaccounted for. Co-elution problems with membrane pyrolysis fragments obscured the membrane pyrolysis results for polysaccharides and polyhydroxyaromatics. Therefore, it is unknown as to whether they were irreversibly adsorbed to the membrane.

The EFLW results are unique. For the Amicon experiment, all four Bruchet et al. (2) groups were rejected by the membrane and thereby remained in the concentrate solutions. The mass balances suggest that no significant amounts of organics were adsorbed to the membrane. Direct pyrolysis of the membrane showed a similar result. The very low flux drop over the course of the Amicon/EFLW experiment also suggests that the membrane was not significantly fouled. The membrane run was stopped because TDS, UV, and DOC broke through the membrane at elevated levels. The lack of fouling was surprising because of the high polysaccharide concentration in the East Fork Lake water.

The Fluid System/EFLW pyrolysis results suggest that proteinaceous material was adsorbed onto the membrane. The percentage of flux reduction that was caused by the proteinaceous material in relation to that caused by the above mentioned inorganic foulant is unknown. The combined mixture of inorganic and organic foulants corresponds to the results of Mallevialle et al. (3).

The ORW results are also unique. The concentrates for both the Amicon-YC05 experiment and the Fluid System experiment show high concentrations of polysaccharides. The pyrolysis mass balances, however, give inaccurate results. The inaccurate results suggest that the high ratio of salts to organics affected the pyrolysis results. The ORW concentrate solutions had the greatest amount of organics removed by salt precipitation during rotoevaporation.

The varied fouling results for the different waters and different membranes suggest that it may be possible to choose a pretreatment process that delays flux reduction. For inorganic contaminants, acid addition or antiscalent agents can be used, as they are currently. For organic foulants, Py-GC/MS can identify the major foulant and a pretreatment process could be selected to remove the foulant. Also, if membrane properties can be related to fouling agents, the choice of the optimal membrane can be made from analysis of the water.

CONCLUSIONS

The cellulose-acetate-based Amicon-YC05 membrane was fouled to the greatest extent by the Manatee County water which had high organic levels. The polysaccharide fraction of the Manatee County water was determined to be responsible based on a mass balance over the membrane experiment and by direct evaluation of the fouled membranes. The East Fork Lake water did not foul the Amicon-YC05 membrane severely. The pyrolysis-GC/MS results for the East Fork Lake experiment confirmed that organics were not adsorbing onto the membrane. The Ohio River water results were inconclusive, probably due to the presence of salts. Electron microscopy results showed that there was no inorganic fouling of the Amicon membranes by any of the waters.

The polyamide-based Fluid-System membrane was fouled to the greatest extent by the East Fork Lake water which had the highest hardness and alkalinity. Calcium carbonate precipitation was deemed to be the causative fouling agent by electron microscopy for both the East Fork Lake water and Ohio River water. The East Fork Lake water pyrolysis results suggest that proteins also adsorbed to the membrane with the inorganic foulants. The Ohio River water pyrolysis results were inconclusive probably due to the presence of salts. The Manatee County membrane experiment showed no inorganic fouling, The pyrolysis-GC/MS results for the Manatee County water experiment suggest that all four biopolymer classes may be involved in the observed fouling.

REFERENCES

1. van den Berg, G.B. and Smolders, C.A. Flux Decline in Membrane Processes, Filtration and Separation, 2, 115-121, 1988.

2. Bruchet, A., Rousseau, C., and Mallevialle, J. Pyrolysis-GC-MS for Investigating High-Molecular Weight THM Precursors and Other Refractory Organics, Jour. Amer. Water Works Assoc., 82(9): 66-74, 1990.

3. Mallevialle, J., Anselme, C., and Marsigny, O. Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants, Suffet, IH and P MacCarthy (eds), ACS Press, 1987, pp. 749-767.

FOR MORE INFORMATION

Thomas F. Speth
US Environmental Protection Agency
26W Martin Luther King Drive
Cincinnati, OH 45268
(513) 569-7208

BIOFILTRATION FOR CONTROL OF VOLATILE ORGANIC COMPOUNDS (VOCS)

Dolloff F. Bishop
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 West Martin Luther King Drive
Cincinnati, Ohio 45268

Rakesh Govind
Department of Chemical Engineering
University of Cincinnati
Cincinnati, Ohio 45221

INTRODUCTION

Air biofiltration is a promising technology for control of air emissions of biodegradable volatile organic compounds (VOCs). In conjunction with vacuum extraction of soils or air stripping of ground water, it can be used to mineralize VOCs removed from contaminated soil or groundwater. The literature (1) describes three major biological systems for treating contaminated air bioscrubbers, biotrickling filters and biofilters. Bioscrubbers, which are not evaluated here, use counter current gas-liquid spray columns with microorganisms freely suspended in the aqueous phase. Biofilters and biotrickling filters use microbial populations in biofilms immobilized on support media to degrade or transform contaminants in air. Filter media can be classified as: bioactive fine or irregular particulates, such as soil, peat, compost or mixtures of these materials; pelletized, which are randomly packed in a bed; and structured, such as monoliths with defined or variable passage size and geometry. The media can be made of sorbing and nonadsorbing materials. Nonbioactive pelletized and structured media require recycled solutions of nutrients and buffer for efficient microbial activity and are thus called biotrickling filters. Filters with bioactive fine or irregular particulates as media, referred to as biofilters, usually do not recycle solutions of nutrients and buffers to prevent media compaction and gas channeling. All filters humidify the contaminated air before biotreatment.

Soil biofilters are relatively large because soil pores are smaller and compounds have low permeability in soil. They also have limited bed depths, required for maintaining humidity in soil and minimizing pressure drop. Peat/compost biofilters, used commercially, are suitable for treating large volumes of air containing biodegradable VOCs at low concentrations (<200 ppmv). However, both soil and peat/compost biofilters are susceptible to channeling and maldistribution of air and require periodic media replacement.

Extensive work has been conducted to improve biofiltration by EPA's Risk Reduction Engineering Laboratory and the University of Cincinnati in biofilters using pelletized and structured media and improved operational approaches. Representative VOCs in these studies included compounds with a range of aqueous solubilities and octanol-water partition coefficients. The compounds include iso-pentane, toluene, methylene chloride, trichloroethylene (TCE), ethyl benzene, chlorobenzene and perchloroethylene (PCE) and alpha (α-) pinene. Comparative studies were conducted with peat/compost biofilters using isopentane and α-pinene. Control studies were also conducted to investigate adsorption/desorption of contaminants on various media using mercuric chloride solution to insure the absence of bioactivity.

MATERIALS AND METHODS

The typical experimental set-up of a biofilter bed (Figure 1) packed with support media was operated at steady-state conditions to characterize process performance. Contaminated air, synthesized by injecting VOC stock solutions into a controlled air stream, was passed through the biofilter bed. The inlet air was humidified

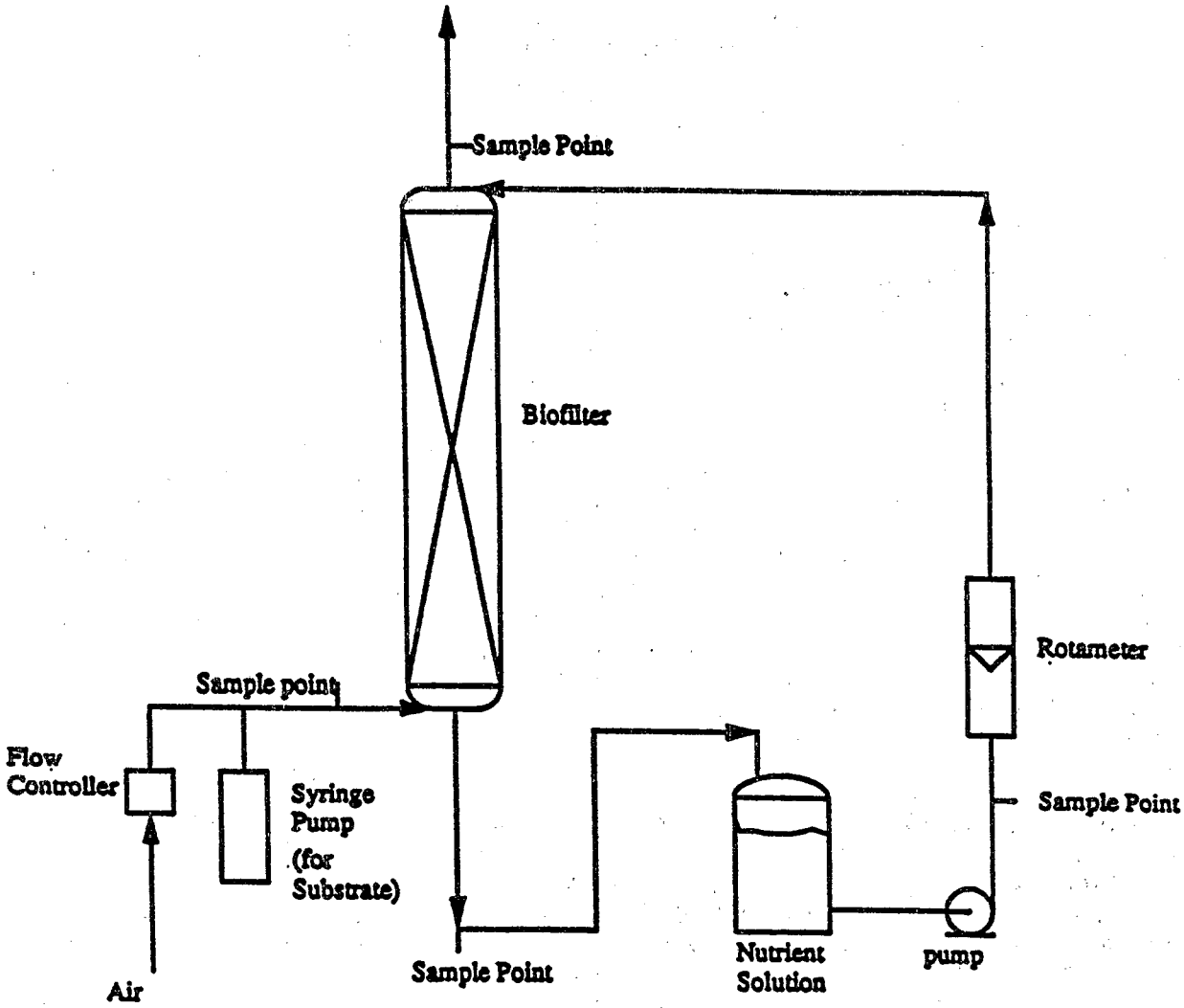


Figure 1. Typical experimental set-up of biofilter system.

before contamination. In the case of pelletized and structured media, solutions of nutrients and buffers were introduced at the top of the bed and allowed to trickle countercurrent to the air flow through the media. The solutions were collected at the bottom of the bed and recycled with appropriate additions for nitrogen consumption and pH control. The water in the solutions insured effective wetting of the media.

Initially the pelletized and structured geometry (straight-passages) media filters were seeded with acclimated biomass from an activated sludge process. Attachment or encapsulation of the seed on the various media was successful. Garden variety peat humus (2204.6 gms) was thoroughly mixed with foam fluff (144.8 gms) providing a peat mixture with high void fraction. Similarly, compost (1358.5 gms) and foam fluff (145.5 gms) were mixed thoroughly for the compost column studies. Foam fluff was made by shredding polystyrene foam into pieces with an average size of 2 mm. Control studies conducted with foam fluff showed that no VOC adsorption occurred on the foam material. Contaminated air for all studies was prepared by injecting appropriate VOC stock solutions into the humidified air flow controlled by a mass flow controller.

Gas samples to characterize biofilter performance were collected from the inlet and outlet ports of the biofilter using gas tight syringes. Samples were collected in 250 mL glass sampling tubes by diverting the gas flow through the tubes for 1 hour. The 250 microliter samples were injected into a gas chromatograph (Tracor 585 GC, with 703 PID 10.0 ev lamp, 1000 Hall ECD, Tekmar LSC 2000 purge and trap concentrator). Liquid samples (5 mL) were collected in syringes with luer locks for purge and trap analysis.

In evaluating mineralization of the chlorinated VOCs, 100 mL samples of the effluent nutrient solution were taken and mixed with 2 mL of 5 M sodium nitrate to adjust the ionic strength, and analyzed for chloride ion with an Orion solid state combination electrode (9617 BN) in an Accumet 1003 pH/mV/ISE meter. The pH of the effluent nutrient solutions was measured by the Accumet 1003 pH/mV/ISE meter. Carbon dioxide concentrations in the inlet and outlet gas streams were determined in a Fisher 1200 gas partitioner.

RESULTS

The studies evaluated peat and compost biofilters, pelletized (activated carbon, ceramic and encapsulated biomass) biofilters and structured geometry (ceramic and carbon coated ceramic straight-passages) biofilters. Biofilter performances, expressed in terms of removal efficiencies of the compounds were calculated from the amount of compound removed per unit time in the biofilter, expressed as a percentage of the amount of that compound entering the biofilter per unit time.

Peat and compost biofilters:

Studies of peat and compost biofilters treating slightly soluble iso-pentane at high (360-960 ppmv) concentrations in humidified air were completed using the indigenous microorganisms and nutrients of each media to establish bioactivity. Initial abiotic control tests on peat and compost revealed poor adsorption of iso-pentane. The effluent air content of iso-pentane became equal to the influent concentration (350 ppmv) in about 30 minutes.

Pseudo-equilibrium removal efficiencies were established for iso-pentane by operating at selected air retention times (2 minutes to 13 minutes) until the increasing removal efficiencies reached steady removal values. Equilibrium removal values, achieved in one to three weeks of operation at each retention time, increased with decreasing influent iso-pentane concentration and increasing gas residence time. The compost biofilter exhibited substantially higher removal efficiencies at the 360 ppmv iso-pentane concentration than the peat biofilter. At higher influent concentrations, the two materials exhibited roughly similar performances.

Water content in peat and compost effected removal efficiencies. Performance studies, with varying water content in the media, revealed critical water contents of 0.48 gm of water/gm of peat and 0.58 gm of water/gm of compost, below which biofilter performance deteriorated substantially. The loss in removal

efficiencies below the critical water content were caused by irreversible shrinkage of the media permitting gas by-passing. Subsequent addition of water did not expand the media nor eliminate the cracks and voids. Removal of iso-pentane exhibited optimal removal efficiencies at 0.56 gm of water/gm of peat and 0.67 gm of water/gm of compost. As the water content increased above the optimal value, removal efficiencies gradually decreased for both media. These decreasing efficiencies probably resulted from partial filling of bed void fraction with free water and increased mass transfer difficulties for the slightly soluble iso-pentane. The losses of efficiency, above and below the optimal water content, illustrated the need for maintaining appropriate media water content through effective humidification of influent air entering peat and compost biofilters.

Studies of temperature effects on removal efficiency in fully humidified air revealed, for both media, increasing efficiencies with increasing temperatures and maximum removal at 35°C. Below 25°C, the removal efficiencies decreased nearly linearly with temperature. Thus for influent air temperatures below 25°C, substantial improvement in biofilter performance could be achieved by heating the air to increase bed temperature.

A study using α-pinene was also conducted in a compost biofilter to assess the effects of pH on media with limited buffering capacity. Monounsaturated α-pinene, a major contaminant in press vent and dryer gas, is a slowly degradable complex bridged ring compound (2) and biodegrades through a variety of pathways, producing organic acids and neutral compounds that accumulate as intermediate products. The study revealed that a compost biofilter with an air retention time of 3.5 minutes supported nearly complete removals and mineralization of the α-pinene at an inlet concentration of 25 ppmv. At inlet concentrations of 50 ppmv and above, however, the removal efficiencies and mineralization sharply decreased. Tests on mixtures of the compost and water revealed that organic acids were accumulating in the compost bed, limiting degradation and indicating a need for additional buffer capacity in the compost for inlet α-pinene concentrations above 25 ppmv.

Biofilters with pelletized media

Two biofilters, one packed with 3 mm activated carbon pellets (void fraction 0.35), the other with 6 mm porous ceramic (celite) pellets (void fraction 0.40) were studied to characterize performance of biofilters randomly packed with pellets and using nutrient recycle. The research also revealed performance differences and similarities between adsorptive and non-adsorptive media. The activated carbon biofilter, operated at 2 minutes of gas retention time and a nutrient solution loading of 1000 L/m^{2}day, initially revealed high adsorptive removals of the inlet contaminants; toluene (520 ppmv), methylene chloride (180 ppmv), and TCE (25 ppmv) followed by a rapid decrease in contaminant removal as the wetted carbon became saturated with contaminants. In this first biofilter study, the initial buffered nutrient solution had insufficient ammonia which limited biomass growth and substantially prolonged start-up time by delaying biomass growth. Indeed, the carbon media fortuitously became saturated with adsorbed VOC contaminants, especially with toluene. Subsequent increase of ammonia in the nutrient solution accelerated biofilm development. Removal efficiencies increased to nearly 100% for all three contaminants. The buffered nutrient also maintained the liquid phase pH above 6.2. The activated carbon biofilter continued to effectively remove (>99%) of the contaminants for an additional 3 months before excessive pressure losses and flooding occurred.

The start-up of the ceramic celite biofilter with appropriate nutrients at a nutrient solution loading of 250L/m^{2}day and a 2 minute air retention time revealed gradual increases in contaminant removals as the seeded biomass grew on the celite pellets. After about 40 days, sufficient biofilm growth occurred to substantially degrade (>95%) four of the five inlet contaminants; toluene (450 ppmv), methylene chloride (150 ppmv), ethyl benzene (25 ppmv) and chlorobenzene (40 ppmv). In contrast to the performance of the activated carbon biofilter, the fifth inlet contaminant, TCE (25 ppmv) was only partially removed by the bioactivity in the celite biofilter.

Folsom et al. (3) showed that TCE is usually degraded only as a secondary substrate in the presence of a primary metabolite, such as toluene or phenol. Examination of contaminant concentration profiles in the celite

biofilter revealed that toluene was rapidly removed in the bottom third of the biofilter. As a result toluene was not available as a primary metabolite in the upper two-thirds of the filter. Thus the slowly degrading TCE was degraded only in the bottom third of the column.

In the activated carbon biofilter, toluene should also rapidly degrade, probably in the bottom third of the biofilter. Apparently the adsorbed toluene from the prolonged start-up of the activated carbon biofilter acted as a toluene reservoir desorbing toluene to the attached biofilm on the carbon over the full height of the biofilter bed. The desorbing toluene produced complete degradation of the TCE at the 2 minute retention time in activated carbon bed but was unavailable over full height of the biofilm in the nonadsorbing celite biofilter, thus limiting TCE degradation.

The celite biofilter with larger void space in the 6mm bed continued to substantially remove all of the contaminants except TCE for about 210 days of operation after full acclimation. The biofilter then exhibited increasing pressure losses and flooding similar to that which occurred in the activated carbon biofilter. The biofilm plugging the biofilter, however, adhered less strongly to the celite pellets than to the carbon pellets and was easier to remove. Studies on the degree of mineralization of the contaminants due to biodegradation were also conducted on both pelletized media. Abiotic control columns, identical to the biofilter beds but without biomass seeding, revealed breakthrough of the contaminants typical for adsorptive and non-adsorptive beds. The amounts of contaminant absorbed in the small volume of nutrient solution were negligible compared to that in the inlet air. There were no increases in carbon dioxide concentration in the air stream.

In the carbon and celite biofilters, carbon dioxide increases in the air stream during treatment of contaminated air ultimately revealed nearly complete mineralization of the removed contaminants. Initially, a portion of the contaminants removed by the biofilters were converted to biomass. With increasing biofilm buildup and negligible releases of biomass, carbon dioxide increases in the effluent air approached increases expected from full mineralization of the removed contaminants. This indicated that the biomass decay rates began to approach the biomass growth rates in both biofilters. Chloride ion increases in the effluent nutrient solution also revealed complete conversion of organic chlorine in the contaminants to chloride ion. These results along with the absence of partially degraded VOC products in the effluent air, verified by gas chromatography measurements, confirmed efficient mineralization of the removed VOCs.

A comparative study of α-pinene biodegradation was also conducted in a celite biofilter with trickling nutrient and buffer solution. In contrast to the compost biofilter, the results revealed that nearly complete removal and mineralization occurred at biofilter air retention times of 4 minutes for inlet concentrations of α-pinene of 25, 50, and 75 ppmv. Reduction of the air retention time to 1.5 minutes at an inlet α-pinene concentration of 75 ppmv did not significantly reduce celite biofilter performance.

PCE, a VOC recalcitrant to aerobic biodegradation, and TCE are easily dechlorinated under anaerobic conditions. The partially dechlorinated products are also easily degraded under aerobic conditions. Thus a nonbiodegradable hydrogel pellet (3 by 6mm cylinder), encapsulating biomass from an activated sludge process, was developed to retard oxygen transport, producing an anaerobic core and an aerobic outer zone for synchronous anaerobic/aerobic treatment of contaminated air. The pellet included an outer stainless steel mesh for structural stability. Biofilter tests of the pellets with trickling nutrient and buffer solution revealed complete mineralization of inlet TCE (21 ppmv) and PCE (20 ppmv) at air retention times of 1.5 minutes and 4 minute, respectively. The hydrogel pellets exhibited long term stability.

Structured Geometry (Straight-Passages) Biofilters

Biofilter studies on straight-passage media with trickling nutrient and buffer solutions at typical loadings of 150 $L/m^2/day$ included a celite plate biofilter and extruded cordierite and carbon coated cordierite biofilters. The celite plate biofilter constructed of thick-walled plates with low surface area per unit volume (10 m^2/m^3), required relatively high air retention times (15 minutes) for nearly complete biodegradation of four of the five

inlet contaminants; toluene (450 ppmv), methylene chloride (150 ppmv), ethylbenzene (25 ppmv), and chlorobenzene (40 ppmv). As in the biofilter with celite pellets, the fifth contaminant, TCE (25 ppmv), was only partially removed (35%) because of lack of a cometabolite in the upper region of the biofilter. Increasing the inlet toluene concentration in air to 850 ppmv and subsequently increasing the air flow rate in an attempt to increase the availability of cometabolite produced little impact on TCE removal. Addition of phenol to the nutrient solution, as an alternative TCE cometabolite available over the entire bed height, however, increased the TCE removal, ultimately to nearly 100% removal.

Biomass release from straight-passages celite media was observed in the effluent nutrient solution. The amount of released biomass depended upon the nutrient flow rate and biomass loading. In addition, during 240 days of operation, the straight-passage media in the bench-scale filter never exhibited pressure drop buildup. These results suggested possible self-cleaning or easier cleaning for straight-passages media compared to the extensive cleaning required for pelletized media.

Biofilter studies on isopentane using extruded (straight-passages) cordierite and carbon and activated carbon coated (0.1 mm films) cordierite media, with high surface area per unit volume ($80m^2/m^3$) and high void fraction (80%), were evaluated at isopentane concentrations varying from 360 to 960 ppmv in the inlet air to compare their removal efficiencies with those of peat and compost biofilters. The removal efficiencies of slightly soluble isopentane in the cordierite biofilter, as a function of contaminant concentration and air retention time, were similar to those observed in peat and compost biofilters. The removal efficiencies in the cordierite biofilter were limited by poor adhesion of the biofilm on the vertical walls. The removal efficiencies in the carbon coated and activated carbon coated cordierite biofilter, however, were substantially better than observed in peat, compost or uncoated cordierite media. The average biodegradation rates of isopentane in activated carbon coated cordierite biofilters were also significantly greater than those in the other biofilters, substantially reducing biofilter size.

Media surface effects on start-up and dynamic response to sudden contaminant concentration changes were examined for straight-passages cordierite media without coatings and with coatings of resin, carbon (0.1 mm) and activated carbon (0.1 mm) as a function of time. Biofilter start-up with carbon coated cordierite was faster than uncoated and resin coated cordierite media. Start-up for activated carbon coated media was fastest. High adsorption capacity and strong adhesion of the activated carbon coating accelerated the start-up process. Similarly, dynamic responses to sudden contaminant concentration changes were also fastest on the cordierite media coated with activated carbon.

Biodegradation Kinetics

Kinetic experiments on aerobic degradation were conducted for various VOC on a range of media types. Monod kinetics satisfactorily described the biodegradation of the tested VOCs and led to development of design models for each type of biofilter media. The kinetic results on isopentane revealed that activated carbon coated or activated carbon media provided best overall performance for slightly soluble VOCs. For soluble and moderately soluble VOCs, non adsorbing pelletized and structured media with good biofilm adhesion provided removals and kinetics equivalent to those obtained in biofilters with activated carbon or carbon coated media.

CONCLUSIONS

Biofilters using porous pellet or structured (straight-passages) media and recycled nutrient and buffer solutions have potential advantages over conventional soil or peat/compost biofilters for removal of biodegradable VOCs from contaminated air. These include:

- improved distribution of air flow and moisture control in the media with lower operating pressure losses and improved process performance;

- improved neutralization of acid degradation products (pH control);
- increased capacity for efficiently treating higher VOC loading (up to 800 ppmv); and
- capability for removal of excess biomass from the biofilter, thus preventing clogging and eventual media replacement.

Biofilters with porous pellet media, however, require development of effective cleaning methods for field-scale applications. Biofilters with structured media (straight-passages) offer easier cleaning options, including release of biomass (self-cleaning) into the recycling nutrient and buffer solution. Biofiltration with activated-carbon-coated or activated carbon pelletized or structured media is an effective technology for control of slightly soluble VOCs. Novel media supporting anaerobic/aerobic treatment extend the range of application of biofiltration to VOCs recalcitrant to aerobic biodegradation.

REFERENCES

1. Ottengraf, S.P.P. and R. Diks, "Biological Purification of Waste Gases," Chim Oggi 8 (5), 41 (1990).

2. Gibbon, G.H., Millis, N.F., and Pirt, S.J. "Degradation of α-pinene by Bacteria," Procs IV IFS: Forment. Technol. Today, 609-612, (1972).

3. Folsom, B.R., Chapman, P.J., and Pritchard, P.H. "Phenol and Trichloroethylene Degradation by Pseudomonas Cepacia G4: Kinetics and Interactions Between Substrates." Appl. Environ. Microbiol., 56; 1279, (1990).

FOR MORE INFORMATION:

Dolloff F. Bishop
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 West Martin Luther King Drive
Cincinnati, OH 45268
Phone: 513/569-7629

POTENTIAL *CRYPTOSPORIDIUM* SURROGATES AND EVALUATION OF COMPRESSIBLE OOCYSTS

Sylvana Y. Li, James A. Goodrich, James H. Owens, and Robert M. Clark
Drinking Water Research Division, US EPA
26 W. Martin Luther King Dr., Cincinnati, OH 45268

Gene E. Willeke
Institute of Environmental Sciences
Miami University, Oxford, OH 45056,

Frank W. Schaefer III
EMSL, US EPA
26 W. Martin Luther King Dr., Cincinnati, OH 452683

INTRODUCTION

Cryptosporidium has been recognized as an important waterborne agent of gastroenteritis and a biological contaminant in drinking water. The widespread presence of *Cryptosporidium* in surface source water and either untreated or insufficiently treated drinking water has led to *Cryptosporidium* outbreaks in the United States and worldwide.

Cryptosporidium is highly resistant to commonly used drinking water disinfectants. Typical dosages of chlorine or monochloramine currently used in water plants appear to have no significant inactivation effect on *Cryptosporidium*.[1] High-dose ozonation may constitute an effective treatment technology to inactivate *Cryptosporidium* in drinking water.[2] Among the conventional control practices, filtration[3] and high temperature distillation[4] appear to be the potentially viable technologies for protection against *Cryptosporidium* in drinking water.

As employed in many water plants, filtration is likely to be the most practical treatment technology utilized for *Cryptosporidium* removal in the near future. Consequently, accurate and reliable methods for evaluation of *Cryptosporidium* removal rates for filtration-based systems are necessary to assist States in determining drinking water quality and complying with the up-coming national standard for *Cryptosporidium* in drinking water. Furthermore, searching for reliable and non-hazardous surrogates for evaluation of treatment plant efficiency has been intensified because of the potential health risk associated with *Cryptosporidium*. Additionally, during the filtration procedure *Cryptosporidium* may squeeze and fold through pores size of the filtration systems that are smaller than the diameter of the organism; a fraction of these *Cryptosporidium* oocysts may still remain a certain degree of viability. These uncertainties are critical for the evaluation and optimization of filtration-based physical treatment systems.

The in-house research studies described below consist of two parts. One is a potential surrogate study using bag filtration systems at the US EPA Test & Evaluation Facility in Cincinnati, Ohio. The second is *Cryptosporidium* compressibility and viability investigation.

METHODOLOGY

Part 1. Potential Surrogate Studies

The potential surrogates for the non-preserved *Cryptosporidium* tested include 4.5 μm polystyrene beads, 1-25 μm particle counts, 4-6 μm particle counts, turbidity, and preserved *Cryptosporidium*. A given volume of influent solution spiked with either polystyrene beads or *Cryptosporidium* was injected into the raw water ahead of the inlet pump of the bag filter system. An influent sample was collected from the spiked solution before each test. An effluent sampling consisted of collecting approximately 5% of the total effluent volume using a manifold and a 1.0 μm polycarbonate membrane filter. The effluent sample was concentrated to

approximately 8 ml using centrifugation (1200 rg) to a given small volume. A flow meter was used to determine the total effluent volume of each test. The duration of each test was also recorded. Both collected influent and effluent samples were scanned and examined under a UV microscope to determine the number of beads or *Cryptosporidium* oocysts using a hemacytometer. The preserved *Cryptosporidium* oocysts were from neonate male holstein calves and stored in dichromate. Indirect fluorescent antibody was used to label the effluent *Cryptosporidium* oocysts. Particle count analyses were conducted using a Met One® particle counter equipped with a light scattering liquid 211 sensor. The turbidity measurements were performed with a Hach® 2100P portable turbidimeter.

Three bag filter systems were used in the studies. Bag filter #1 was supplied by Strainrite Inc. Lewiston, Maine, and Bag filter #2 was manufactured by Filtration Systems, a division of Mechanical Mfg. Co. at Sunrise, Florida. Bag Filter #3 was obtained from the 3M Company. The studies were performed using 50 psi inlet pressure as recommended by the manufacturers, at varying pressure drops across the bag filter and influent flow rates of 12.5, 25 and 40 gpm.

Part 2. Compressibility and Viability Tests

A unique compressibility test device was developed which made it possible to examine *Cryptosporidium* passage through a membrane of designated pore size using a manifold under various inlet pressures. The non preserved *Cryptosporidium* oocysts that we used for this study came from neonate male holstein calves. A given number of *Cryptosporidium* oocysts were suspended in 0.01% Tween 20 (v/v) contained in a 5 L pressure reservoir. The influent *Cryptosporidium* oocysts passed through the system equipped with a 25 mm polycarbonate membrane filter. The collected effluent was centrifuged to approximately 200 μl and then was scanned and counted under the microscope. The membrane filter used in this study was made of polycarbonate with a pore size of 3 μm, which is smaller than the *Cryptosporidium* average size 4-6 μm. Polystyrene beads were used to demonstrate membrane integrity; no beads were detected. This advantageous filter characteristic allows precise determination of removal rates for both the beads and *Cryptosporidium* at various inlet pressures.

Three blank tests without a filter were performed under 50 psi inlet pressures in order to evaluate *Cryptosporidium* loss in the system. Four tests were conducted under 50 psi inlet pressure and one test under 25 psi with the 3 μm filter. Non-preserved *Cryptosporidium* was used in the blank tests. In order to compare the system loss difference between non-preserved and preserved *Cryptosporidium*, one blank test using preserved *Cryptosporidium* was performed under 50 psi inlet pressure.

For the compression test using the 50 psi inlet pressure conditions, a viability test was performed on the non-preserved *Cryptosporidium* recovered from the effluent. *Cryptosporidium* concentrated from the effluent was fed to neonatal mice at two dosages, 340 and 3400 *Cryptosporidium* oocysts per animal. A control sample consisted of 18 mice fed with 63 unfiltered non-preserved *Cryptosporidium* oocysts per animal.

RESULTS

The initial bag filter testing results indicated that the removal rates for 4.5 μm polystyrene beads, turbidity, and particle counts in the 1-25 μm and 4-6 μm size ranges, vary significantly among the three bag filters. The log reduction ranges from 0.14 to 3.42 for the 4.5 μm beads, from 0.04 to 1.89 for turbidity, from 0.09 to 2.84 for 1-25 μm particle counts, and 0.06 to 2.99 for 4-6 μm particle counts. Initial bag filter testing for preserved *Cryptosporidium* reveals a log reduction of 1.8.

Inspection of the bag filter testing results reveals varying relationships between the 4.5 μm beads, 4-6 μm particle counts, 1-25 μm particle counts, turbidity and non-preserved *Cryptosporidium*. The correlations between log reductions for beads and turbidity or particle counts for three bag filters at varying pressure drops and inflow rates, are consistent with the linear model:

$$\text{Log (beads)} = \alpha \text{ Log (turbidity or particle count)} + \beta$$

where α is the slope constant of the linear correlation, and β is the regression constant. The 4.5 μm beads and turbidity have a linear correlation with α and β of 0.52±0.15 and 0.04±0.24, respectively. The squared coefficient of determination (R^2) is 0.79. The beads and 4-6 μm particle count have a 1:1 correlation in removal rates as shown by the linear regression results: α and β are 0.97±0.35 and -0.29±0.54 respectively, and a squared coefficient of determination (R^2) is 0.79. On the other hand, 1-25 μm and particle counts display the correlation departured from 1:1 relationship and closer to the correlation exhibited between beads and turbidity. The linear correlation between 4.5 μm beads and 1-25 μm particle counts has the slope constant (α) of 0.73 and coefficient of determination (R^2) of 0.55.

Detailed size analyses show that the size distribution of non-preserved *Cryptosporidium*, 4.5 μm beads, and particle counts, primarily determines their similarities and dissimilarities in the removal rates for bag filters. The similar removal rates between 4.5 μm beads and non-preserved *Cryptosporidium* are consistent with their similar size distributions. *Cryptosporidium* has the size ranging 3.50-6.50 μm with an abundance peak at 4.01-4.50 μm, whereas the 4.5 μm beads range in size from 3.50-7.00 μm with the peak at 4.51-5.00 μm. Furthermore, the 4-6 μm particle counts have a similar size distribution with 4.5 μm beads. In contrast, the 1-25 μm particle counts have two abundance peaks at 5.01-6.00 μm and <2.00 μm. This size distribution is significantly different from those of the *Cryptosporidium* and 4.5 μm beads. The difference appears to be the explanation for the distinct removal rates of 1-25 μm particle counts from those of 4.5 μm beads and non-preserved *Cryptosporidium*.

The determined correlations in removal rates among *Cryptosporidium* and its potential surrogates do not appear to be the artifacts of influences from operational parameters including pressure drop, flow rate, or spiked influent level of surrogates. Testing results for the beads at varying pressure drops and flow rates for bag filter #1 show that the variation in log reduction is approximately 0.5, within the range of experimental variations determined with duplicate testing. Similarly, the number of influent beads does not appear to have a statistically significant influence on the removal rates.

Compression study results lead to two important observations regarding non-preserved *Cryptosporidium* removal efficiency of the filtration process and the reliability of surrogates. First, about 0.7% of the non-preserved *Cryptosporidium* at 3.50-5.00 μm size passed through the 3 μm polycarbonate filter at 50 psi inlet pressure. In contrast, the polystyrene beads of the same size range were completely removed. Different removal rates of the non-preserved *Cryptosporidium* and the beads are believed to reflect the ability of *Cryptosporidium* to squeeze and fold through the pressurized membrane filter. Furthermore, compressibility tests at 25 psi inlet pressures show an increased removal rate of *Cryptosporidium*. Only about 0.0021% non-preserved *Cryptosporidium* passed through the filter. It is possible that the *Cryptosporidium* squeezing and folding effect on the removal rate of the filter may diminish at lower inlet pressures.

Secondly, 4 blank tests on non-preserved *Cryptosporidium* at 50 psi inlet pressure lead to the observation that 53.61±5.30% of *Cryptosporidium* in oocysts in the influent was lost in the system. However, the result from one blank test on preserved *Cryptosporidium* at the same experimental conditions show the system loss less than 1%. Such a large difference in system loss between preserved and non-preserved *Cryptosporidium* indicate that the non-preserved *Cryptosporidium* not only can squeeze and fold through membrane filter, but also adhere to physical surfaces at applied inlet pressure. Both characteristics of the *Cryptosporidium* have substantial influence on apparent removal rates.

Initial viability test results show that the non-preserved *Cryptosporidium* collected from effluent of compression study are still viable. Five of seven mice were infected with a dose of 340 *Cryptosporidium* oocysts per animal. Ten of ten mice were infected with a dose of 3400 *Cryptosporidium* oocysts per animal. Control samples of 63 *Cryptosporidium* oocysts per dose infected 13 out of 18 animals.

CONCLUSIONS

The *Cryptosporidium* surrogate investigation, compressibility study and viability test, lead to the following conclusions:

Accuracy and reliability of the *Cryptosporidium* surrogates are determined by similarities of size

distribution between *Cryptosporidium* and its surrogates. The 4.5 μm polystyrene beads have a similar size distribution as the *Cryptosporidium* with a peak distribution in the 4-5 μm range. Consequently, the 4.5 μm beads and *Cryptosporidium* show the closest removal rates. This similarity will be further characterized in future studies. Studies on surrogate interchangeability show that the 4-6 μm particle counts and 4.5 μm beads have a 1:1 correlation in removal rate. On the other hand, 1-25 μm particle counts and turbidity are not directly interchangeable surrogates with 4.5 μm beads. As the latter most closely resemble the *Cryptosporidium*, both 1-25 μm particle counts and turbidity are less reliable surrogates for *Cryptosporidium* removal evaluation.

Compression test results demonstrate that unlike the 4.5 μm beads, a small fraction of 3.50-5.00 μm *Cryptosporidium* oocysts squeeze and fold through smaller pore sizes of a membrane filter. This unique characteristic of *Cryptosporidium* leads to apparently lower removal rates than that of the 4.5 μm beads. However, the influence of *Cryptosporidium* size change at the membrane filter appears diminished at low inlet pressures. A large fraction of *Cryptosporidium* oocysts that passed through membrane filter remain viable. Therefore, a high removal rate might be required for filtration-based treatment technology to ensure safety of the treated drinking water.

It is noted that both surrogate and compressibility studies are presently on-going. Results from future studies will be supplemental to the conclusions presented here.

REFERENCES

1. Pontius, F. W. Protecting the Public Against *Cryptosporidium*. J. AWWA. p. 18-22 and cont'd on p. 122-123. August, 1993

2. Finch, G. R., Black, E. K., Gyurek, L., and Belosevic, M. Ozone Inactivation of *Cryptosporidium* Parvum in Demand-free Phosphate Buffer Determined by in Vitro Excystation and Animal Infectivity. Applied and Environmental Microbiology. v. 59, p. 4203-4210. 1993

3. Chapman, P. A. and Rush, B. A. Efficiency of Sand Filtration for Removing *Cryptosporidium* Oocysts from Water J. Med. Microbiol. v. 32, p. 243-245. 1990

4. Fayer, R. Effect of High Temperature on Infectivity of *Cryptosporidium* Parvum Oocysts in Water. Applied and Environmental Microbiology. v.60, p. 2732-2735. 1994

For more information:

Sylvana Y. Li, Systems & Field Evaluation Branch
Drinking Water Research Division, 26 W Martin Luther King Dr.
Cincinnati, OH 45268, (513)-569-7074, (513)-569-7185(Fax)

REMOTE MONITORING AND CONTROL OF SMALL DRINKING WATER PACKAGE PLANT SYSTEMS

John M. Teuschler, James A. Goodrich, Benjamin W. Lykins, Jr.
and Robert M. Clark
Drinking Water Research Division
US EPA
26 W. Martin Luther King Dr.
Cincinnati, OH 45268

INTRODUCTION

Remote telemetry, metaphorically referred to as the "electronic circuit rider", offers an attractive alternative to an "on the road" operator. Substantial cost savings in addition to the improvement of drinking water quality can be achieved through the use of the remote telemetry. Using remote telemetry, an operator has the ability to call a remote data logger unit and review the operating parameters in "real time" of a plant within minutes using the central site personal computer. Likewise, several sites may be reviewed in this manner. An operator normally requires hours to physically visit the remote drinking water plant sites. Therefore, remote telemetry can significantly reduce operator time required to visit remote plants.

With remote telemetry, the operator has the ability to display the current operating parameters of a remote drinking water (DW) plant on the central site computer. The operator then, can prioritize the plant site visits accordingly. Also, immediate attention can be given to a drinking water plant with critical problems. Preventive maintenance can be scheduled for plants with operating parameters showing the need for maintenance. The overall effect from remote telemetry is an improvement in operator efficiency and hence a net improvement in water quality.

In addition to displaying parameters when the operator calls a remote site, the remote data logger unit has the ability to call the operator via a phone line to alert the operator of an immediate problem. Commercial remote sensing units have the ability to auto dial a pre-programmed phone number to alert an operator of site problems. This is typically referred to as "exception reporting." The operator defines the conditions which cause the remote unit to dial the pre-programmed phone numbers. The exception limits can be set for turbidity, pressure, flow, etc.. The operator of a specific plant defines the limits for the plant. Through exception reporting, water quality is improved by quickly alerting the operator of potentially harmful site conditions. Again, the net effect of remote telemetry is the improvement in operator efficiency thereby improving the overall, drinking water quality at the consumers tap.

METHODOLOGY

This project demonstrated remote telemetry using commercially available hardware and telemetry software. Specifically, a CUNO ultrafiltration drinking water package plant was remotely monitored and controlled. Monitoring consisted of permeate flow, pH, finished turbidity, hi and low trans-membrane pressure, chlorine residual, raw pressure, permeate pressure, reject flow, raw flow, and raw turbidity. Control of the plant via electrically actuated proportional valves included: raw water flow, hi trans-membrane flow, lo trans-membrane flow, and reject flow. The telemetry software allowed the "on line" data display, data analysis, trend reporting, and history reporting. Proportional control of the valves was accomplished via the remote telemetry software.

Remote telemetry hardware requirements include an Acromag Inc. remote data logger, a central site generic personal computer, a modem for communications, and selected monitoring instrumentation. The central site control and acquisition software is commercially available from Total Systems Resources (TSR). The process control and data acquisition software from TSR contain the hardware drivers necessary to communicate with the specific remote data logger used in this project.

Data Logger:

A commercially available remote data logger was purchased from Acromag Inc.. The data logger is a microprocessor unit with programmable memory, random access memory, a serial port, analog input/output and digital input/output. The remote logger is customized to a specific site. Information concerning the analog to digital conversions and the digital to analog control can be downloaded to the data logger's Electrically Erasable Programmable Read Only Memory (EEPROM) from the central site personal computer. Power failures will not cause the unit to loose specific site control information.

The data logger does not use electromechanical digital storage devices like disks or tapes for data or program storage. Read only memory (ROM) is used for CPU control and is hard coded at the factory. The ROM software controls the operation of the CPU. It is similar to a mini disk operating system (DOS). Commands are received in predefined format via the serial link, and appropriate actions are taken. Approximately seventy commands are available in the Acromag ROM system. The commands range widely in capability. The commands are as simple as "IS" which is identify station. And the commands are as complex as "LL" or log list all the data remotely stored.

The versatility of the microprocessor unit is a result of its field programmability. User field program control is stored in EEPROM. The field program control defines data collection rates, data channels to be collected, data channels to be used as analog outputs, communicates with the central site computer, and in general, controls the customization of the data acquisition and control of the remote data logger.

The microprocessor random access memory (RAM) stores data from the sensors. Approximately 9000 data points can be stored with the data logger used in this project. The data points are collected at user programmed data rates. The remote data logging is activated by the operator. The RAM is the internal buffer for the collected data. At operator selected intervals, remote data is downloaded from the data logger to the central site computer for display and time series plotting. After dumping the data to the central site, the RAM is free to start storing a new series of data points.

The microprocessor unit contains a serial communication link. It is through this link that the microprocessor receives control information and sends the collected information to the central site computer. The communication port is user programmable via the standard serial port capability. Programmability includes baud rate, parity checking, etc.. The microprocessor unit's serial link may be hardwired to a modem, radio transmission link, or other serial ASCII communication systems.

Data loggers typically have the ability to communicate with a variety of data acquisition modules. These include analog to digital (A/D) modules, digital to analog (D/A) modules, or digital input/output modules. As discussed earlier, the data logger is able to be customized to a particular site. System setup personnel customize the data logger to the site requirements. The customization is transparent to an operator. Data from the sensors will be numerically displayed as flow, pressure, turbidity, etc. on the computer display. All raw data transformations will be computed internally in the central site software. The transformations will be programmed by the setup personnel.

Most monitoring instrumentation can be specified with a 4 to 20 ma current loop interface. The 4 to 20 ma interface was chosen as the standard for this project. All instrumentation for the project was ordered with the 4 to 20 ma current loop interface. This included the "data in" as well as the "data out." The remote monitored parameters included chlorine, turbidity, pH, pressure, temperature, and flow.

Control of the package plant is accomplished using 115 volt AC electrically actuated control valves. For proportional control, the actuator movement is initiated with the standard 4 to 20 ma current loop. Note that 4 ma. is the full closed control signal. And 20 ma. is the full open signal. Feedback potentiometers on the actuator control valves indicate the current position of the control valve. The feedback potentiometers will allow the current position of the valve to be displayed, upon system bootup. Control of DW site valves is accomplished via the remote control system. The operator may initiate a change in

the process control, and instantly evaluate the effect of the process control change through the real time display of the monitored parameters.

Data acquisition and control software:

The central site software package, can communicate via modem, radio, or direct link with the remote data logger. The central site software provides a high level (mouse driven), sophisticated interface to the remote data logger. The software package used in this demonstration has extensive graphical capability which can provide complete monitoring and control information at a glance. The software is user friendly and can be easily applied to a variety of small drinking water package plant systems, nationwide.

The central site software communicates with the remote data logger by channels (one to sixteen). In this project, for standardization purposes, all Acromag units were programmed in a standard configuration. Channels 1 to 12 were defined as analog to digital modules. Channels 13 to 16 were defined as digital to analog modules. Channels 1 to 12 monitored remote parameters. Channels 13 to 16 controlled remote servo valves for process control.

All sites will require some customization of the software channels. Software channel 1 may be turbidity at site 1. Whereas at site 2 turbidity may be on channel 4. The system software setup personnel require some computer expertise. The computer expertise required is equal to a Harvard Graphics user or a Freelance Graphics user. For sites lacking "in house" computer expertise, the central site software vendor will gladly customize the software for a nominal fee.

In this demonstration, the software was partially customized by Drinking Water Research Division personnel. Customization by DWRD personnel included: adding the remote servo valves for variable flow rate control, adding a number of additional sensors not in the original system setup file. Modifying the graphics display to accommodate the additional sensors and control valves. Modification of the system was relatively painless. Sufficient technical support was obtained from both the software and hardware vendors.

CONCLUSIONS

As more small DW system operations utilize personal computers for billing, personnel tracking, etc., remote telemetry adds an additional cost benefit to the acquisition of a personal computer. The computer availability at the central office, in addition to attractive pricing of remote data loggers and data logger software makes remote "telemetry and control" an affordable option to a small systems operation. Cost of the remote data logger is under $5,000. Central site software is approximately $3,000 without customization. Sensors at the remote DW site usually have an option for an external computer interface (4 to 20 ma output). The external 4 to 20 ma interface is typically under $200. The fax can also function as a 9600 baud modem for data acquisition and control.

Computer expertise is probably the main impediment to remote telemetry. However, with each new generation, computers and computer control are becoming more commonplace. Remote telemetry and control is quickly coming into the reach of small system operations both from the standpoint of cost and personnel capabilities.

For more information:

John M. Teuschler
Systems & Field Evaluation Branch
Drinking Water Research Division
26 W. Martin Luther King Drive
Cincinnati, OH 45268

CONTROL OF COPPER CORROSION OF HOUSEHOLD PLUMBING MATERIALS

Michael R. Schock
and
Darren A. Lytle
Drinking Water Research Division
Risk Reduction Engineering Laboratory
U. S. Environmental Protection Agency
26 West Martin Luther King Drive
Cincinnati, Ohio 45268
(513)569-7412

INTRODUCTION

The promulgation of the "Lead and Copper Rule" by the USEPA in 1991 has forced hundreds of water utilities nationwide to become concerned with controlling the uniform corrosion of copper plumbing materials. The exact extent of the problem is hard to quantify, but in the first round of monitoring by the large water systems (about 682), approximately 6 % exceeded the 1.3 mg/L action level according to an AWWA study. The highest copper levels for these utilities appeared to be in the southeastern and western regions of the United States, in utilities covering a considerable range of water qualities. The cuprosolvency problem apparently increases with decreasing utility size. When medium-sized water systems are included, large numbers of action level exceedences for copper occurred in the central and north-central midwest, implicating areas having hard and high alkalinity ground waters of approximately neutral pH. These water qualities are not those conventionally considered "corrosive".

Unfortunately, the regulatory monitoring data are of limited use for extracting details of copper chemistry behavior and understanding potential copper passivation strategies. Nonetheless, several interesting gross-scale trends have been discerned for large water systems. One example is that there is a poor correlation between 90th-percentile lead and copper levels. Another trend is that copper exceedences tended to be highest at very low alkalinities (<25 mg $CaCO_3$/L) and increasingly greater over 75 mg $CaCO_3$/L. Finally, no action level exceedences were reported for systems having a pH above approximately 8.

The data thus far suggest that cuprosolvency (copper solubility) will be a major concern across the United States, especially for smaller water suppliers that are less likely to employ corrosion control and use ground water sources. Further, the poor correlation between reported 90th-percentile lead and copper levels suggests that different control strategies for copper than those considered appropriate for lead may need to be developed or employed by affected utilities. Understanding how copper will respond to lead control measures and the results of other regulatory treatment requirements is therefore of considerable interest. Indeed, a response that effectively controls lead corrosion might exacerbate copper corrosion. Moreover, a utility must distribute aesthetically-pleasing water. A good example of the conflicts between control of corrosion of iron mains and reducing copper corrosion rates has been given for a study in Vancouver, BC.

In attempting to address some of the data gaps for cuprosolvency control by utilities, a variety of experimental systems have been constructed and operated in USEPA laboratories. During these experiments, some perplexing data was generated that appeared to either contradict some "conventional wisdom" on copper corrosion, or showed unexpected sensitivities to important water chemistry variables and experimental system operational protocols. These observations provided the motivation to begin

exploring the "cuprosolvency" (copper solubility) issue in detail. The initial results of this ongoing research are reported in the new U. S. Environmental Protection Agency publication[1].

An accurate equilibrium model for cuprosolvency provides utilities and consultants with a useful and practical tool for reliably selecting and applying corrosion control programs that will work over the long term. A sound theoretical and practical understanding of the important factors affecting cuprosolvency greatly obviates the need for complicated, costly, and sometimes misleading bench-top and pilot-plant experimental studies. Small and medium-sized water systems frequently lack the technical sophistication as well as the mechanical and financial resources needed to conduct elaborate "demonstration" studies. For water systems able to conduct experimental treatment evaluations, an accurate model for cuprosolvency reduces the need for including fundamental tests (*e.g.* pH and carbonate concentration effects) in their evaluations. Utilities may then concentrate on determining the need for additional experimental evaluations of inhibitor treatments or investigation of other unusual chemistry characteristics of particular water systems.

A better understanding of roles of pH and DIC (dissolved inorganic carbon) in cuprosolvency greatly improves the accuracy of regulatory "desk-top" corrosion optimization evaluations, thereby providing a better assessment of long-term treatment impacts than those ascertained over a short time-frame (*i.e.* weeks, months). Finally, an accurate solubility model for copper allows many utilities to achieve the requirements of the Lead and Copper Rule without the need to conduct the treatment studies.

A newly-emerging indirect constraint on copper corrosion control in drinking water is by wastewater effluent guidelines and limits that are becoming increasingly stringent. Ironically, ambient corrosion of domestic, commercial and institutional plumbing systems is now becoming a "contaminant" of wastewater that is becoming difficult to control to an adequate degree through normal waste treatment processes. The development of an accurate model for copper solubility allows the evaluation of treatment alternatives for optimizing the control of cuprosolvency beyond drinking water regulatory requirements, to achieve adequate levels at the end of wastewater treatment.

OXIDATION REACTIONS OF COPPER

Because of the positive cell potentials for copper metal oxidation, copper pipe in water containing oxidizing agents will continue to corrode until either all of the oxygen is depleted, or until precipitated oxide films arrest the rate of corrosion. There is some evidence that the overall transformation from Cu^{+} to Cu^{2+} is essentially the rate-limiting factor, with Cu^{+} existing in reversible equilibrium with the Cu metal at the pipe surface.

In drinking waters, the oxidizing agents (electron acceptors) that will cause the corrosion of metallic copper are predominantly dissolved oxygen and aqueous chlorine species. These reactions may be composed of several intermediate steps, any of which can be rate-controlling. Many studies have documented (to some degree) the impact of dissolved oxygen or aqueous chlorine species on copper oxidation and dissolution rates. Free chlorine species (i.e. HOCl , OCl^{-}, Cl_2) have not been conclusively shown to affect the equilibrium solubility of copper, other than by influencing the valence state of the copper by its presence or absence.

---

[1] Schock, Michael R., Lytle, Darren A., and Clement, Jonathan A. Effect of pH, DIC, Orthophosphate and Sulfate on Drinking Water Cuprosolvency. EPA Office of Research and Development, Cincinnati, Ohio, 1995. In press.

Oxidants may have several other potential impacts on the observed copper levels in the water and the nature of the passivating solids on the pipe. The effect of chlorine on the oxidation rate of the copper metal might be alteration of the crystalline characteristics and porosity of the oxide corrosion product film produced at the pipe surface. For example, by reducing the formation of a protective $Cu_2O(s)$ underlayer through maintaining a high E_H level, or by indirectly influencing scale structure and conductivity through chloride formation as the chlorine is reduced. However, many of the apparent effects of chlorine on copper solubility may merely result from accelerated corrosion kinetics (rates), rather than changes in equilibrium conditions.

Copper plumbing can be exposed to a wide environment of E_H-pH conditions. This environment evolves as oxidation and reduction reactions occur through corrosion and deposition processes for different lengths of stagnation times, and in different diameters of pipes. Therefore, all three normal copper valence states (metal, +1, +2) could reasonably occur under drinking water conditions either geographically or with time. The relative stabilities of Cu(I) and Cu(II) species in aqueous solution depend very strongly on the nature of anions or other ligands present in the water.

Solubility Chemistry of Copper (I) and Copper(II)

Because the immune region for copper corrosion extends well above the minimum E_H for water stability, water does not corrode copper in the absence of oxygen or other added oxidants. With the addition of electron acceptors to the solution (e.g. HOCl , O_2), either or both of the oxide solids Cu_2O (cuprite) or Cu(OH) may form. The equilibrium solubility of cuprous copper, $S_{T,Cu(I)}$, may be described as the sum of the concentrations of all dissolved cuprous species:

$$S_{T,Cu(I)} = [Cu^+] + [CuCl^\circ] + [CuCl_2^-] + [CuCl_3^{2-}] + [Cu_2Cl_4^{2-}] + [CuNH_3^+] + [Cu(NH)_3^+]$$

in which [ ] (brackets) indicate concentration in mol/L. The total solubility may then be computed by standard techniques. Under relatively anoxic drinking water conditions, such as many well waters, pH and chloride concentrations are the dominant controls on copper solubility. Metastable solid formation and the rate of the oxidation reaction are important in governing copper levels at the tap. Ammonia forms strong complexes, but little research has been done to determine its significance in drinking water.

Under oxic conditions, copper(II) aqueous speciation is dominated by hydroxide, carbonate, and hydroxycarbonate complexes. Weak complexes are formed with sulfate, orthophosphate and chloride. Strong complexes are formed with ammonia, but the high concentrations of carbonate, bicarbonate and hydroxide usually swamp out any expected impact on the speciation. Generally, copper(II) solubility is given by the equation:

$$S_{T,(OH,CO_3)} = [Cu^{2+}] + [CuOH^+] + [Cu(OH)_2^\circ] + [Cu(OH)_3^-] + [Cu(OH)_4^{2-}] + 2[Cu_2(OH)_2^{2+}] + 3[Cu_3(OH)_4^{2+}] +$$
$$[CuHCO_3^+] + [CuCO_3^\circ] + [Cu(CO_3)_2^{2-}] + [CuCO_3OH^-] + [CuCO_3(OH)_2^{2-}]$$

In new plumbing systems, copper(II) solubility is generally controlled by a poorly-crystalline form of cupric hydroxide, $Cu(OH)_2$. This scale ages, and after some time becomes either CuO (cuprite) or $Cu_2CO_3(OH)_2$ (malachite), depending on pH and the dissolved inorganic carbon concentration. Below about pH 7.5, orthophosphate reduces copper(II) solubility. The effect is particularly strong in the pH range of 6.5 to 7, and is fairly consistent with the hypothesis of the formation of a solid of approximately the composition of $Cu_3(PO_4)_2 \bullet 2H_2O$. Orthophosphate also appears to interfere with the normal formation of cupric oxide, cupric hydroxide, and malachite, at low DIC concentrations.

Little research has been done on the effect of sulfate on copper solubility in potable water. Results of this ongoing research project so far suggest that sulfate plays a major role in the increase of soluble copper(II) through the formation of a metastable basic cupric hydroxide solid, such as $Cu_4(OH)_6SO_4 \bullet 2H_2O$. This effect appears to be particularly strong above pH 8.

PRACTICAL CONSEQUENCES OF REDOX POTENTIAL ON CUPROSOLVENCY

In water supplies maintaining oxidizing disinfectant residuals, copper oxidation and dissolution into the water will take place until both that residual and dissolved oxygen are depleted. However, copper levels will stop climbing after saturation equilibrium is reached with a passivating solid (e.g. $Cu(OH)_2$). The profile of copper concentration versus time in oxidizing systems will depend upon the water chemistry and the relative stabilities of copper(I) and copper(II) aqueous species. The copper concentration in the water may continue to rise for many hours, perhaps substantially beyond the "overnight standing" period normally used for sampling, depending on the operative kinetics in a given system. Complexation of either copper(I), copper(II), or both, will be important in these systems.

In undisinfected water systems having low levels of dissolved oxygen, such as many closed ground water systems, complicated copper versus time profiles may result, as the initial small quantity of oxygen is consumed. This behavior is consistent with the observation of short-term copper concentration maxima, followed by decrease in concentration, reported in several studies. Copper(I) aqueous speciation and solid reactivity are extremely important in these systems. Different parts of a distribution system, particularly ones fed by a combination of different water sources (such as multiple wells or a mix of wells and conventionally-treated surface water), may exhibit different stagnation profiles.

For the anoxic systems, the use of aeration for VOC, radon or iron removal may cause increased copper levels, because copper(II) solids are virtually always more soluble than copper(I) solids. Unanticipated violations of copper corrosion action levels may result from the installation of any new oxidation processes for water treatment. In contrast, for oxic systems, proper aeration may strip DIC from the water and increasing pH, both favorable effects in reducing copper(II) solubility.

Significant variability in copper levels from site to site in the same water system will likely be found in water after the normal number of hours of stagnation found in most sampling programs. This results from the interaction of aqueous complexation and oxidation chemistry of copper, plus effects of the existence or development of passivating films in the pipe. Examination of copper concentrations in experimental coupon cells and pipe loop systems after various standing times frequently show almost linear increases in concentration extending far beyond the 6-16 hour standing time requirement of regulatory sampling.

SIGNIFICANCE OF pH AND DIC IN CUPROSOLVENCY CONTROL

The relationship between DIC and copper(II) solubility is very complex. DIC can play several significant roles, depending upon its concentration, other water chemistry factors, age of plumbing, water flow amount and pattern of use.

This research has shown conclusively that trends in copper concentrations resulting from uniform corrosion are predictable for a range of appropriate water qualities. Given that field conditions frequently do not reflect equilibrium conditions, some discrepancy between the model predictions and the results of normal tap water monitoring programs is completely understandable. Nonetheless, using a comprehensive equilibrium solubility chemical model, water quality objectives for copper corrosion control

by pH and DIC adjustment can be predicted without the necessity of complicated experimental and field studies.

In new plumbing or at high pH, where cupric solubility is controlled by either cupric hydroxide or cupric oxide, DIC complexes dominate copper speciation above pH 7.5, resulting in increased cuprosolvency. The solubility enhancement effect is strongest in the DIC range of 0 to 20 mg C/L, but the predicted soluble copper at equilibrium is still below about 1 mg/L.

DIC serves to control the buffer intensity in most water systems. Therefore, sufficient DIC is necessary to provide a stable pH throughout the distribution system for corrosion control of copper (and lead). In treatment practice, the increase in DIC to ensure pH control through buffering will probably need to be offset by increasing pH to maintain lowered cuprosolvency.

Possibly offsetting the solubility enhancement of copper(II) by carbonate complexes is the possibility that moderate DIC levels would logically accelerate the formation of passivating $Cu_2CO_3(OH)_2$ (malachite) films in the pH/DIC region where it would be thermodynamically stable. Thus, enhancement of conditions that would hasten the formation of $Cu_2CO_3(OH)_2(s)$ (malachite), CuO(s) (tenorite), or both, relative to cupric hydroxide, would result in a net lower copper(II) solubility, even with the existence of some additional carbonate complexation.

In the region of pH from approximately 8.5 to 10, this solubility model developed occasionally predicts slightly lower copper(II) solubility than has actually been observed in some well-controlled pipe loop and precipitation studies. The discrepancies are most likely the result of formation constant errors, inadequacies of understanding copper(II) aqueous complexation with hydroxide and carbonate, or the presence of metastable copper solids associated with anions other than carbonate or hydroxide.

SIGNIFICANCE OF pH AND ORTHOPHOSPHATE IN CUPROSOLVENCY CONTROL

Because cupric hydroxide solubility has been shown to be a better estimate of cuprosolvency tendencies in many water systems than previously presented models based on $Cu_2CO_3(OH)_2$ (malachite) equilibrium, orthophosphate in sufficient dosage is now predicted by the models to have an ability to further reduce copper levels in the pH range of approximately 6.5 to 7. The necessary dosage is hard to quantify, but the calculations suggest that 3-5 mg PO_4/L orthophosphate may be necessary to achieve substantial improvements in cuprosolvency over the DIC/pH system at approximately pH 8, but perhaps only 1-3 mg PO_4/L at approximately pH 7. More investigation is still needed to ascertain objectively and consistently if any synergistic cuprosolvency reduction effect exists from the use of blended phosphates rather than orthophosphate, as has been suggested by one research project.

IMPLICATIONS FOR CONTROLLING HIGHEST COPPER EXPOSURES

The distinct aging process noted for recrystallization and development of cupric hydroxide, cupric oxide, and cupric orthophosphate films raise an important caution for determining the highest exposures to copper in drinking water. While the Lead and Copper Rule was specifically intended to bias the sampling site selection towards locations with high relative risks for lead exposure, these sites do not generally correspond to commensurately high risks for copper exposure, which include: newest construction and remodeling, areas with unstable pH, and dead ends.

Changes in solubility of copper as pipes age, and films build up, has been indicated in several studies and by practical experience. This investigation has shown how such a phenomenon may have a

firm chemical basis that has heretofore been unappreciated. In practice, when attempting to predict the impact of different water treatment scenarios on cuprosolvency, a fruitful strategy may be to apply different solubility models depending on the general age of the plumbing systems involved. For example, for older neighborhoods where $Cu_2CO_3(OH)_2$ (malachite) and CuO (tenorite) have had sufficient time to form an integral part of the passivating film, a better prediction of pH, DIC and orthophosphate dosing impacts would be obtained using their solubility constants to predict copper levels and success of different hypothetical control strategies. Conversely, for areas predominantly of new construction, a "cupric hydroxide model" would be more applicable.

SIGNIFICANCE OF THE "CUPRIC HYDROXIDE MODEL" FOR DEMONSTRATION STUDIES

Utilities may encounter some complications in projecting pipe loop or coupon leaching cuprosolvency data obtained in demonstration studies to behavior across the whole distribution systems. In the absence of significant concentrations of orthophosphate, this research indicates that for the short timeframes of most experimental studies conducted to satisfy Lead and Copper Rule requirements (6 months to 2 years in most cases), cupric hydroxide will usually be the most important solid phase, rather than CuO(s) (tenorite) or $Cu_2CO_3(OH)_2(s)$ (malachite). Both pH and DIC effects will be magnified in the experimental systems, relative to significantly aged piping in the distribution system.

Because of the slow oxidation rate relative to diffusion rates, it is unlikely that copper concentrations are at "equilibrium" when samples are taken from experimental pipe rig systems operated to allow "overnight" standing times, unless the systems have been operated long enough that the passivating films are well-developed, perhaps for years.

When orthophosphate dosing is tested, overestimates of its effectiveness could be obtained for distribution system areas having old copper plumbing with well-developed passivating films. The experimental systems may also be very sensitive to minor dissolved oxygen, chlorine residual, sampling, and stagnation time fluctuations, because of the highly non-equilibrium nature of copper behavior in the 6-16 hour time period.

OTHER IMPORTANT APPLICATIONS OF EQUILIBRIUM CUPROSOLVENCY MODELS

In addition to the applications to drinking water corrosion control, the solubility model has considerable application to several other important environmental research areas, namely:

- aqueous speciation of copper in relation to aquatic toxicity
- estimation of the impact of domestic and institutional plumbing corrosion on wastewater loading
- estimation of the feasibility of various wastewater effluent guidelines for copper
- estimation of copper removal from wastewater by hydroxide or carbonate precipitation

HYDRAULIC FRACTURES AS SUBSURFACE ELECTRODES: EARLY WORK ON THE LASAGNA PROCESS

Larry Murdoch, Jiann-Long Chen, Phil Cluxton, Mark Kemper, Jim Anno and Dave Smith
Center for GeoEnvironmental Science and Technology
Department of Civil and Environmental Engineering
University of Cincinnati
1275 Section Rd.
Cincinnati, Ohio, 45237

INTRODUCTION

Fine-grained sediments present the greatest obstacle to in situ remediation at many contaminated sites. Where fine-grained sediments are continuous, discharges from wells are slow and contaminants are recovered at negligible rates. In contrast, at sites underlain by interbedded sand and silt or clay, volumetric discharges from wells can be significant as water is readily recovered from the more transmissive sands. The rate of recovery of contaminants can be rapid as the sands are flushed during initial operations, but the clay interbeds act as persistent sources of contaminants so that concentrations can be maintained at small but serious values for many years.

Hydraulic fractures filled with coarse-grained sand provide high permeability layers that increase fluid flow primarily by reducing the large losses of hydraulic head in the vicinity of a well (1,2). These features have been shown to increase the discharge from wells by an order of magnitude or more (2). Nevertheless, current applications of hydraulic fractures are designed to improve the recovery and removal of contaminants from the subsurface by advective processes. Effects related to adsorption, preferential flow and other processes can result in mass transfer limitations that require a large number of pore volumes of fluid to be moved through porous material before it is remediated using hydraulic flow alone.

Electrokinetics is an effective method of inducing the movement of water, ions, and colloids through fine-grained sediments. In this process, typically a direct current is applied to the sediment, inducing osmotic movement of water away from a positively charged anode and toward a negatively charged cathode (3). Ions and colloids migrate toward the electrode with a charge opposite from the one that they carry (3,4). In addition, electrolysis of water results in a decrease in pH at the anode and an increase at the cathode (4). The acidic conditions at the anode and the basic conditions at the cathode will propagate into the region between the electrodes, potentially forming a sharp discontinuity in pH (4,5).

Based on the results of laboratory tests and limited field applications (7), electrokinetics has been shown to be a promising method of recovering ionic and water-soluble contaminants. However, the process is not without problems. Acidic conditions and electrolytic decay can corrode some anode materials. Sharp discontinuities in pH induced within the soil mass by electrokinetics could result in a deposition front where minerals are precipitated in soil pores, markedly reducing permeability and inhibiting recovery. It may be possible to mitigate problems related to pH by circulating a buffering solution across the electrodes (7).

Another drawback to conventional electrokinetic remediation is that it requires contaminants to migrate from their initial location to an electrode and then up to the groundsurface. In some cases, the migration path could be long or there could be stagnant zones between wells where the rate of migration is particularly slow, both of which result in incomplete remediation of the contaminated zone. Moreover, sharply convergent electrical fields can result in heating and potential losses in the vicinities of electrodes, just as convergent flow paths result in head losses in the vicinities of wells. Electroplating, or pH-related deposition can cause contaminants to be removed from solution prior to arrival at the ground surface.

Recent investigations have shown that it may be possible to address some of the shortcomings of electrokinetics by degrading contaminants in situ. Our colleagues have developed a solid compound (8), which slowly releases oxygen, that can be injected into

hydraulic fractures along with slowly dissolving nutrients to stimulate in situ aerobic biodegradation of organic compounds in soils. In addition, it is feasible to fill hydraulic fractures with metal catalysts, such as iron particles, which Gillum and Burris (9) have proposed as a method of degrading a wide range of organic compounds. By degrading compounds in situ it should be possible to shorten the migration paths of contaminants. Periodically reversing the polarity of the field is intended to repeatedly pass contaminants through a degradation zone while limiting the development of high or low pH conditions in the vicinities of electrodes and reducing fouling of electrodes by precipitation. This approach to in situ remediation is the essence of the so-called "Lasagna" process (Fig. 1; ref 10).

Hydraulic fracturing appears to be a method of improving the performance of electrodes and of creating zones where contaminants are degraded in situ. An investigation into this application was initiated in the summer of 1994, with pilot-scale testing scheduled for 1995 and full-scale testing at a contaminated site anticipated for 1996.

METHODS

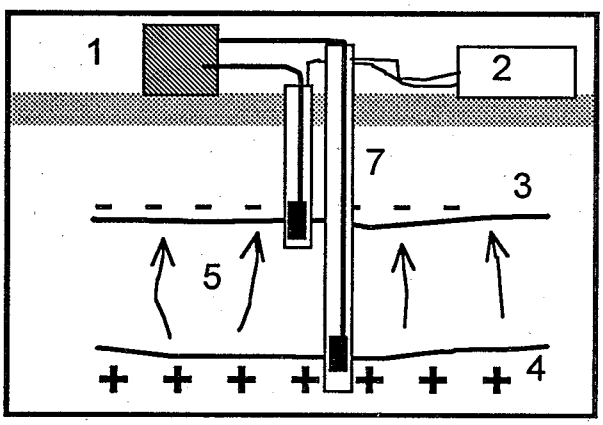


Figure 1. Configuration of fractures, electrical delivery, and fluid delivery system. 1. DC Power supply; 2. Water delivery apparatus; 3. Graphite-filled hydraulic fracture as cathode; 4 anode.; 5. water flow by electroosmosis; 6. graphite contactor on the end of power cable; 7. Well casing.

Recent work on the project has consisted of identification or development of methods to monitor in situ electrokinetics and degradation, as well as preliminary evaluation of hydraulic fractures as electrically and hydraulically conductive electrodes.

Monitoring

The monitoring efforts have assembled techniques to measure the following parameters

- temperature
- moisture content
- fluid pressure/suction
- electrical conductivity
- electrical potential
- pore fluid pH
- pore gas composition

The configuration shown in Figure 1 will result in strong vertical gradients, so monitoring systems have been designed to obtain data along relatively close vertical spacing in order to resolve those gradients. Moreover, we have sought to measure several parameters at each location in order to reduce the number of subsurface devices that must be installed. This effort has produced two types of devices, the T-type and S-type, that will be used to measure the subsurface parameters.

The T-type of monitoring device consists of a 2.5-inch (nominal) PVC pipe that fits snugly into a reamed borehole. The wall of the pipe is penetrated by stainless steel rivets, which are flush on the outside and protrude slightly on the inside. A probe is lowered into the pipe to contact each rivet and measure the electrical potential of that point relative to the cathode, thereby providing a profile of electrical potential. When it is not being used to measure potential, the pipe is thermally insulated and a thermocouple, which contacts the inner wall, is used to measure the temperature with respect to depth. The pipe also provides access for a neutron probe, which has been calibrated for losses due to neutron absorption by the PVC. Neutron probe data will be used to estimate the moisture content of soils in the vicinity of the pipe.

Some of the 2.5-inch PVC pipes are wrapped with a series of stainless steel bands riveted to their exterior. The bands are 1 cm wide and spaced every 5 to 10 cm along the axis of

the pipe. A probe that can contact four bands simultaneously is lowered into the pipe and the upper and lower bands are energized with approximately 10V of low frequency AC. The potential difference between the middle two bands is proportional to the electrical conductivity of soil in the vicinity. This modification of the T-type device will be used to monitor changes in electrical conductivity during electrokinetics, which result from electrochemical processes and have been reported in laboratory experiments (11).

The S-type monitoring system is used to measure fluid potentials and composition. It consists of a suite of sensors that are pushed horizontally into the side of a vertical borehole. A prototype device has been fabricated that pushes a tube into the sidewall of a bore to obtain a soil sample and create a hole suitable for either a ceramic-cup tensiometer, or a porous soil-gas sampler. Those devices are installed at various depths along the vertical bore to obtain pore water pressure or suction, and pore gas pressure or composition as functions of depth.

Electrical potential

We created two roughly circular, horizontal hydraulic fractures filled with electrically conductive graphite to evaluate their effect on the electric field in the subsurface. The hydraulic fractures were approximately 3 m in radius, 6 mm thick and contained graphite whose electrical conductivity was approximately 190 S/m when saturated with water. They were separated by 0.9 m vertically, sandwiching roughly 25 m^3 of soil between them. The fractures were enveloped in silty clay soil whose electrical conductivity was 0.05 to 0.1 S/m, or 2000 to 4000 times less than that of the fracture.

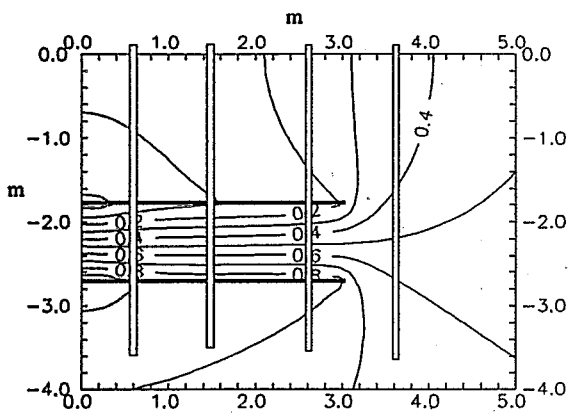


Figure 2. Axisymmetric view of electrical potential distribution in the vicinity of two charged disks representing hydraulic fractures. Potential is with respect to the upper fracture and is normalized to the potential difference between the fractures. Vertical bands are T-type casings used to measure potential.

A potential difference of 40 V DC was maintained between the two fractures with a current of 30 amps. The potential difference could be adjusted by changing the current, with a ratio of current:potential difference of 0.75 amps/volt observed for a wide range of power conditions. The design of the constant current power supply used during the initial tests limited the potential difference to 40 V for continuous operation--greater potential differences could be applied for testing over short durations. T-type monitoring tubes were placed at radial distances of 0.6, 1.5, 2.6 and 3.5 m from the power electrodes (Fig. 2), and rivets were spaced every 7.5 to 15 cm along the length of the tubes.

Preliminary theoretical analyses of the electric field were conducted using both analytical solutions to the potential in the vicinity of a charged circular disk and numerical solutions to the potential in the vicinity of a highly conductive disk. The analytical solution indicates that under ideal conditions of a homogeneous, isotropic medium, the electrical field around two, horizontal, conductive, circular disks beneath an insulated free surface is as shown in Figure 2.

RESULTS

The theoretical analyses indicate that there should be strongly positive vertical gradients between the fractures. Indeed, the strong vertical potential gradients are intended to drive the electrokinetic process. The gradients are more subtle in other regions, with weakly negative

vertical gradients over the fractures and weakly positive gradients at radial distances beyond the edge of the fractures (Fig. 2).

Electrical potential was measured along the T-type casings at distances of 0.6, 1.5, 2.6, and 3.5 m, the data were normalized to the applied potential difference and compared to the results of the theoretical analysis (Fig. 3). The field data show that strong vertical electrical potential gradients are produced between the hydraulic fractures, at least within the region bounded by the radial extent of the fractures (about 3 m). The subtle predictions of the character of the electrical field are represented in the field data, with gentle negative gradients overlying the fractures and gentle positive gradients beyond the edge of the fractures. The potential in the vicinity of the lower fracture is less than predicted by the analysis, perhaps because that fracture is thinner than assumed in the analysis.

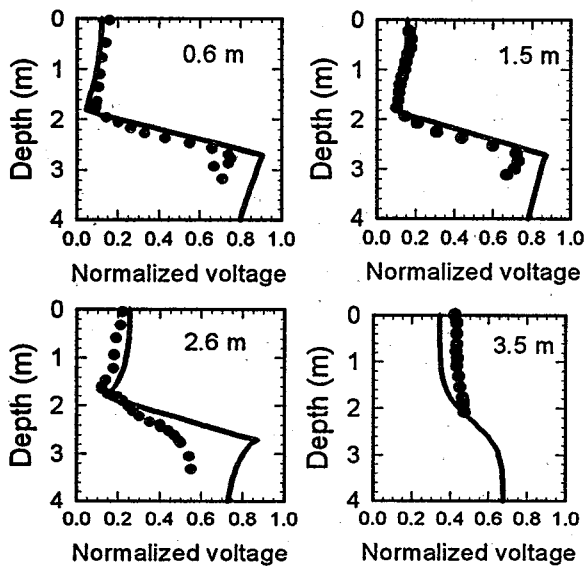


Figure 3. Electrical potential as a function of depth at various distances from the power electrode. Line is from theoretical analysis, points are field data.

The field data and ratio of applied current to potential difference given above indicates that the vertical electrical potential gradient available for electrokinetics is

$$dV/dz = C\,Q/h \qquad (1)$$

where Q is the applied current, h is the fracture spacing, and C is a constant that depends on the design of the fractures. The available results indicate that C = 0.6 to 0.9 V/amp for the design used here. Accordingly, for an applied current of 30 amps, the potential gradient is 0.2 to 0.3 V/cm. Gradients 0.2 to 0.4 V/cm are reported during field tests by Langeman and others (1989), and slightly greater gradients are described from laboratory experiments; e.g. Bruell and others (12) used gradients of 0.4 V/cm, whereas Acar and others (11) report gradients of 0.5 V/cm or more. Potential gradients of 0.4 V/cm appear to be achievable over most of the 25 m^3 of soil between the fractures by increasing the current provided by the power supply to approximately 50 amps.

CONCLUSIONS

The field observations indicate that graphite-filled hydraulic fractures behave as broad, sheet-like electrodes capable of providing useful electrical potential gradients distributed over a reasonably large volume of soil. These results indicate hydraulic fractures can be used to create the electrical field required to conduct the Lasagna process outlined by Ho and Brodsky (10). Preliminary measurements of fluid flows suggest that the observed potential gradients will induce electroosmotic migration of water through the region between the fractures. A pilot test designed to provide detailed data on electroosmotic flow is underway, and those data should be available in the near future.

REFERENCES

1. Murdoch, L.C.. A field test of hydraulic fracturing in glacial till. Proc. 15*th Annual USEPA Research Symposium*, Cincinnati, Ohio, 1990.

2. Murdoch, L.C., G. Losonsky, P. Cluxton, B. Patterson, I. Klich, B. Braswell. The feasibility of hydraulic fracturing of soil to improve remedial actions. Final Report USEPA 600/2-91-012. NTIS Report PB91-181818. 298, 1991.

3. Shapiro, A. P. and Probstein, R. F. Removal of contaminants from saturated clay by electroosmosis. *Environ. Sci. Tech.* 27:283-287, 1993.

4. Acar, Y.B., R.J. Gale, G.A. Putnam, J. Hamed, and R.L. Wong. Electrochemical processing of soils: theory of pH gradient development by diffusion, migration, and linear convection. *J. Eviron. Sci. Health,* A25(6), 687-714, 1990.

5. Probstein, R. F. and Hicks, R. E. Removal of contaminants from soils by electric fields. *Science* 260:498-503, 1993.

7. Lageman, R., Pool, W. and Seffinga, G. Electro-reclamation theory and practice. *Chem. Ind. London.* 18:575-579, 1989.

8. Vesper, S. J., L.C. Murdoch, S. Hayes, and W.J. Davis-Hoover. Solid oxygen source for bioremediation in subsurface soils. *Journal of Hazardous Materials* 36:265-274, 1994.

9. Gillham, R.W. and D.R. Burris. In-situ treatment walls -- Chemical dehalogenation, denitrification, and bioaugmentation. Proceedings of *Subsurface Restoration Conference*, Dallas, Texas, June 21-24, 66-68, 1992.

10. Ho, S.V. and P.H. Brodsky. Integrated In Situ Technology for Soil Remediation--The Lasagna Process. Presented at Amer. Chem. Soc. Annual Meeting, Atlanta, GA, Sept. 19-21, p 504-506, 1994.

11. Acar, Y. B., Li, H. Gale, R. J. Phenol removal from kaolinite by electrokinetics. *J. Geotech. Eng.* 118:1837-1841, 1992.

12. Bruell, C. J., Segall B. A., and Walsh, M. T.. Electroosmotic removal of gasoline hydrocarbons and TCE from clay. *J. Environ. Eng.* 118:68-74, 1992.

For more information: Mike Roulier, EPA Project Officer
US EPA Center Hill Lab
5995 Center Hill Rd.
Cincinnati, OH 45223
513-569-7796

HYDRAULIC FRACTURES AS ANAEROBIC AND AEROBIC BIOLOGICAL TREATMENT ZONES

Wendy Jo Davis-Hoover, Ph. D., Michael Roulier, Ph.D., L. Taras Bryndzia, Ph. D.
Risk Reduction Engineering Laboratory (RREL), 5595 Center Hill Ave., Cincinnati, Ohio 45224
513-569-7206, 513-569-7796, 513-569-7857; fax 513-569-7879
Jonathan Herrmann,P.E., Leland Vane, Ph.D.
RREL, 26 W. M.L. King Jr. Dr., Cincinnati, Ohio 45268
513-569-7839, 513-569-7799; fax 513-569-7787
Lawrence C. Murdoch, Ph. D., Stephen J. Vesper, Ph.D.
University of Cincinnati, Cincinnati, Ohio
513-556-2568, 513-556-2538

Hydraulic fractures were initially developed to be used in bedrock to enhance oil recovery. We have modified the procedure for use in the environmental field in shallower subsurface soils to increase the permeability of the soils to liquids, gases, and solids. This has allowed us to significantly enhance in situ methods of soil cleaning (pump and treat, steam injection, solvent extraction) (1) and aerobic bioremediation (2) .

We are now concentrating on enhancing movement of contaminants between hydraulic fractures and into hydraulic fractures using electrokinetics and destruction of contaminants within the hydraulic fractures. Bioremediation, very specific to the unusual conditions that electrokinetics presents to the subsurface soil is being developed. This work is being done as a result of the RTDF and in conjunction with researchers at Monsanto, Dupont, General Electric, and DOE.

Hydraulic fracturing allows for the insertion of a pancake-shaped lens of sand. The sand lens increases the soil permeability of the area allowing a 10 fold increase in the area of influence of the well allowing for a 10 fold increase in vapor extraction, and a 10 fold increase in liquid addition (such as solubilized nutrients and hydrogen peroxide), which leads to a 100 fold increase in aerobic bioremediation (1). The process also allows for other solid addition to contaminated subsurface soils such as solid slow-releasing oxygen which increases aerobic bioremediation (2, 3, and 4).

The Lasagna technology uses 2 outer hydraulic fractures as two dimensional electrodes in the electrokinetic process moving contaminants into 3 inner hydraulic fractures designed to be zones of biodegradation (5). Several experiments that the members of the research consortium have performed have indicated that the process of electrokinetics modifies the pH of the soil to a spectrum of 2 to 10 and increases the temperature significantly. Thus as a result of this we decided to naturally select for thermophilic organisms that will degrade contaminants at these high and low pHs .

We have been successful in obtaining thermophilic organisms that will degrade contaminants at high and low pHs (6). These are being tested in lasagna microcosms (6). The next step is to test them in the field.

REFERENCES

1. U. S. Environmental Protection Agency. Hydraulic Fracturing Technology: Applications Analysis and Technology Evaluation Report. EPA/540/R-93/505, U. S. Environmental Protection Agency, Cincinnati, Ohio, 1993. 60 + pp.

2. Vesper, S. J., L. C. Murdoch, S. Hayes, and W. J. Davis-Hoover. Solid Oxygen Source for

Bioremediation in Subsurface Soils. Journal of Hazardous Materials. 36:265-274, 1994.

3. Vesper, S., L. Murdoch, W. Davis-Hoover. Oxygen Pellets Spike Bioremediation. Soils. May 1994. p 14-17, 1994.

4. Davis-Hoover, W. J. , L. C. Murdoch, S. J. Vesper, H. R. Pahren, O. L. Sprockel, C. L. Chang, A. Hussain, W. A. Ritschel. Hydraulic Fracturing to Improve Nutrient and Oxygen Delivery for In situ Bioreclamation.In: R. E. Hinchee and R. F. Olfenbuttel (eds.) In Situ Bioreclamation. Butterworth-Heinemann, Boston.1991. p. 623.

5. Murdoch. L. C., J.-L. Chen, P. Cluxton, and M. Kemper. 1995. Hydraulic Fractures as Subsurface Electrodes: Early work on the Lasagna Process. In: RREL Symposium Proceedings. paper before this.

6. Vesper, S. J., et al. 1995. Advances in TCE-degrading Thermophilic, Mesophilic and Alkaline-Resistant Organisms . In: RREL Symposium Proceedings. paper after this.

FOR MORE INFORMATION: Wendy Jo Davis-Hoover, Ph. D.
RREL, 5595 Center Hill Ave., Cincinnati, Ohio 45224
513-569-7206, fax 513-569-7206

ADVANCES IN TCE-DEGRADING THERMOPHILIC, MESOPHILIC, AND ALKALINE-RESISTANT ORGANISMS

Stephen J. Vesper
University of Cincinnati
1275 Section Road
Cincinnati, Ohio 45237-2615
513-5562538

Wendy J. Davis-Hoover
The U.S. Environmental Protection Agency
5595 Center Hill Road
Cincinnati, Ohio 45424
513-569-7206

Michael H. Roulier
The U.S. Environmental Protection Agency
5595 Center Hill Road
Cincinnati, Ohio 45424
513-569-7796

Lawrence C. Murdoch
University of Cincinnati
1275 Section Road
Cincinnati, Ohio 45237-2615
513-556-2568

Leland M. Vane
The U. S. Environmental Protection Agency
26 W. Martin Luther King Dr.
Cincinnati, Ohio 45268
513-569-7799

Jonathan G. Herrmann
The U. S. Environmental Protection Agency
26 W. Martin Luther King Dr.
Cincinnati, Ohio 45268
513-569-7839

INTRODUCTION

Trichloroethylene (TCE) is a chlorinated organic solvent that has been widely used in metal processing, electronics, dry cleaning, paint and many other industries. The methylotrophic bacteria have been shown to co-metabolize TCE. These organisms have been utilized as degraders of TCE in aquifers (Semprini et al. 1987) which suggests that the use of methylotrophs is a practical solution for TCE contamination.

Electroosmosis is a relatively old technique used to dewater soils (Casagrande, 1949). Electroosmosis uses a direct-current electric field to induce a motion of a liquid and dissolved ions that transports the contaminants in the electric field. This technique is limited to fairly soluble contaminants like benzene, toluene, xylene, phenol, and chlorinated solvents (Bruell et al. 1992; Acar et al. 1992; Shapiro and Probstein, 1993). This technique creates highly acidic and basic zones in the soil. The process can also raise the temperature of the soil substantially. We are selecting methylotrophs to survive and degrade TCE in this environment.

METHODOLOGY

Soil samples were taken at 10 major locations in Yellowstone Park and shipped back to the laboratory the next day. When the samples arrived in the laboratory, they were placed in water baths at 50, 60, 70, or 80°C, whichever temperature was closest to the temperature from which they came. Five grams of sample were placed in 20 ml of "L" medium (ATCC, 1984) in serum stoppered bottles. These were then purged with 0.6% methane in air. The bottles were then placed in water baths at the appropriate temperature. After 10 days, the bottles were sub-sampled by placing 1 ml of the aqueous phase on L agar plates containing 2% agar. These plates were placed in desiccators which were sealed then purged with the methane:air mixture for 30 minutes. The desiccators were then placed in incubators at the appropriate temperature. As different colonies appeared they were picked and placed in L medium or L medium diluted 1:10 with water and returned to serum stopped bottles. These were grown-up in the methane in air mixture and restreaked for purity. These isolates were then ready for screening for TCE degradation

Each isolate was grown in duplicate 60 ml serum stoppered bottles for at least one month in 20 ml of L medium, L medium diluted 1:10 with deionized water, or AMS medium (Whittenbury et al. 1970) or AMS medium diluted 1:10 with deionized water. The medium was adjusted to pH 2, 4, 8 or 10 with concentrated NaOH or HCl. The bottles were periodically purged with a mixture of 2.5% methane in air to provide a carbon source.

After the growth period of at least one month, each isolate was tested for TCE degradation. The methane was first removed by placing them in the laminar flow hood for 1 hour. At that point, the serum bottle was resealed. Two microliters of a TCE stock solution were added to each bottle so that the final concentration of TCE added was approximately 10 ppm. On the same day that the serum bottles received the TCE, the starting concentrations of TCE were determined. TCE concentration was measured using a GC-FID. Headspace samples (0.5ml) were removed from the serum bottles and injected into the GC. On the fifth day, the bottles were resampled for TCE concentration. The concentration of TCE obtained from the second analysis was then subtracted from the initial value of TCE to indicate the level of TCE degradation or disappearance.

A model electroosmosis microcosm (EM) was developed to test the bioremediation process. This design now allows for maintenance free operation for at least a month. This design also allows for the manipulation of various components of the EM to test concepts for field applications. The EM chamber is 20 cm long and 10 cm wide and is made of polyethylene phthalate (PET). (The chamber is a two liter soft drink bottle). The bottom of each EM is filled with 400 grams of sand. This acts as a reservoir for water. On top of the sand, a mixture of 100 grams of granular graphite and 50 grams of granular activated carbon is layered. This makes up the anode. Next a soil slurry is made. It contains 1500 grams of soil obtained from subsurface soil environment. The soil is mixed for one hour in a Hobart mixer with 600 ml of tap water. The whole soil slurry can be added to make a complete soil column. If a remediation zone

is to be added, half of this mixer is then gently poured onto the anode electrode. The remediation zone is created by adding 150 grams of granular activated carbon on top of the first layer of soil plus 50 ml of tap water. Then the rest of the soil is added gently on top of the remediation layer. Another electrode, identical to the first, is then poured on top of this soil. This is the cathode. On top of the cathode is added 400 grams of sand and then the rest of the chamber is filled with tap water. A Mariotte Bottle is used to control the water level. A gas relief valve is added to the anode to remove oxygen gas generated process. Tests were made using the EM. Some tests were run at constant 100 volts for 6 hrs. All other tests were run at a constant 25 volts. (The soil temperature does not exceed the ambient temperature at this voltage.) At the end of the test, the pH of the soil is taken with pH paper every 2 cm along the soil column length.

RESULTS

The screening program to date has identified 20 (Table 1) isolates that appear to have degraded more than 20 % of the TCE in 5 days; two isolates showed more than 30% degradation in 5 days. Thirteen of the isolates came from 50°C (total of 59) and seven came from 60°C (total of 27). Most isolates came from more basic pH's. Ten came from pH 8 and 3 from pH 10 but six came from pH 4 conditions. We have no pH 2 isolates that reached 20 % degradation within 5 days but we have one pH 2 isolate that was close to 20 %.

In general the low pH isolates (pH 2 and 4) degraded more TCE when grown in the AMS medium at full strength (data not given) . Similarly, the high pH isolates (pH 8 and 10) degraded more TCE in full strength L medium. However, there were exceptions in each case.

Some EMs were run for 6 hrs at 100 volts to simulate a long field experiment. The temperature rose as high as 82°C in these chambers. At 25 volts, the chambers stay in equilibrium with the ambient temperature. When the EM is run at 25 V, the current and monitoring voltage both started high but dropped quickly. The purge water started flowing immediately but slowed after about 400 hours. It took nearly 600 hours to move 2 pore volumes (pore volume is 969 ml).

If an activated carbon layer was added in the middle of the soil column, the current started out higher than in the soil alone configuration but the current rapidly dropped to about 35 mA. Voltage also started very high, declined then rose again. About 3 pore volumes were moved in 300 hours. The results of the pH analysis of the soil at the end of the experiments indicated that the pH near the anode was 4 or higher but near the cathode the pH was as high as 12 (data not given).

CONCLUSIONS

It must be noted that we have not proven that any of these isolates are methylotrophs nor that the TCE was biodegraded. These questions will await further analysis. It does appear that the isolates we have obtained have the capacity to survive the extreme pH and high temperatures expected in the electroosmosis process. So far these organisms grow very slowly and we have much to learn about the optimal growth conditions. The design of the EM has allowed us to create conditions expected in the field

TABLE 1. SUMMARY OF ISOLATES TESTED FROM YELLOWSTONE NATIONAL PARK, WYOMING

LOCATION	# ISOLATES	# DEGRADATION > 20%	% TOTAL
A. Mammoth Hot Springs (MHS)	16	2	13
B. Norris Geyser Basin (NGB)	8	1	13
C. Madison Junction (MAD)	6	1	17
D. Paint Pot (PP)	7	1	14
E. V Road Site (VRS)	0	0	0
F. Near Obsidian Cliff (OBS)	2	1	50
G. Mud Volcano Site (MVS)	4	0	0
H. Above Sulfur Caldron (ASC)	4	0	0
I. Calcite Spring Site (CSS)	19	7	37
J. Artist Paint Pots Site (APPS)	20	7	35
Total	86	20	24

and this should be a useful laboratory model to test electroosmosis. Next, the isolates will be tested in the EMs for biodegradation of TCE.

REFERENCES

1. Semprini, L., Roberts, V. P., Hopkins, G. D., and Mackay, D. M. 1987. A Field Evaluation of In-Situ Biodegradation for Aquifer Restoration. U. S. EPA. EPA/600/2-87/096. Washington, D. C.

2. Casagrande, L. 1949. Electroosmosis in Soils. Geotechnique 1(3): 159-166.

3. Bruell, C. J., Segall, B. A., and Walsh, M. T. 1992. Electro-Osmotic Removal of Gasoline Hydrocarbons and TCE from Clay. J. Environ. Eng. 118 (4): 68-74.

4. Acar, Y. B., Li, H., and Gale, R. G. 1992. Phenol Removal from Kaolinite by Electrokinetics. Geotech. Eng. 118:(2):1837-1841.

5. Shapiro, A. P. and Probstein, R. F. 1993. Removal of Contaminants from Saturated Clay by Electroosmosis. Environ. Sci. Tech. 27 (3):283-287.

6. ATCC. 1984. Media Handbook. American Type Culture Collection, Rockville, MD.

7. Whittenbury, R., Phillips, K. C. and Wilkinson, J. F. 1970. Enrichment, Isolation and Some Properties of Methane-utilizing Bacteria. J. Gen. Microbiol. 61: 205-218.

INTEGRATED PNEUMATIC FRACTURING AND BIOREMEDIATION FOR THE IN-SITU TREATMENT OF CONTAMINATED SOIL

Sankar N. Venkatraman and David S. Kosson
Rutgers, The State University of New Jersey
Department of Chemical and Biochemical Engineering
P.O. Box 909
Piscataway, NJ 08855-0909
Tel.: (908) 445-4346

Thomas M. Boland and John R. Schuring
New Jersey Institute of Technology
Department of Civil and Environmental Engineering
Newark, NJ 07102
Tel.: (201) 596-5849

Uwe Franks
U.S. EPA - ORD
Releases Control Branch (MS-106)
2890 Woodbridge Avenue
Edison, NJ 08837-3679
Tel.: (908) 321-6626

INTRODUCTION

In-situ bioremediation is often limited by the rate of transport of nutrients and electron acceptors (e.g., oxygen, nitrate) to the microorganisms, particularly in soil formations with moderate to low permeability. An investigation was conducted to integrate the process of pneumatic fracturing with bioremediation to overcome these rate limitations. Pneumatic fracturing is an innovative technology which utilizes high pressure air to create artificial fractures in the contaminated geologic formations, resulting in enhanced air flow and transport rates in the subsurface. Following the fracturing, the pneumatic fracturing system can be used to inject electron acceptors and other biological supplements directly into the formations to stimulate biodegradation.

Pneumatic fracturing is an innovative technology which enhances the in situ removal and treatment of contaminants from low permeability soil and rock formations. The process may be generally described as injecting air (or another gas) into a contaminated geologic formation at a sufficient pressure and flow rate so that artificial fractures are created. Once established, the fractures increase the permeability of the formation, thereby making contaminant removal and/or treatment more efficient. Pneumatic fracturing is designed to be integrated with other in situ treatment technologies such as vapor extraction, bioremediation, thermal injection, and pump and treat. The technology can be applied to a range of hydrogeologic conditions including vadose zones, perched water zones, and saturated zones.

Research which led to the development of pneumatic fracturing began in 1988 with bench scale studies and analytical modeling at the Hazardous Substance Management Research Center (HSMRC) located at New Jersey Institute of Technology (NJIT). The first industrial site demonstration of pneumatic fracturing was performed in 1990 at a site in Richmond, Virginia . In 1992, the technology was evaluated under the U.S. EPA Superfund Innovative Technology Evaluation (SITE) Demonstration Program at a contaminated industrial site in New Jersey for enhancement of a soil vapor extraction system [USEPA, 1993}. Pneumatic fracturing is now available commercially through Accutech Remedial Systems for

applications involving soil vapor extraction and pump and treat enhancement, and is being applied to production clean-ups. Pneumatic fracturing is a patented process, and the assignee is HSMRC.

The sequence of steps required to apply the integrated pneumatic fracturing/bioremediation process are as follows. During the first step, the formation is pneumatically fractured by inserting a proprietary device known as an "HQ Injector" into a drilled well. The HQ injector applies pressurized air along a discrete two foot interval, and is subsequently repositioned at various elevations to create a fracture network. The injector is then moved to additional bore holes and the process repeated until the entire contaminated formation is fractured.

After the formation has been initially fractured with air, the second step is to introduce nutrients into the fracture network to provide substrates for enhance biological activity. This is accomplished by inserting liquid nutrients into the main injection air stream which are then dispersed throughout the already established fracture network. By maintaining a high air to liquid ratio, the liquid supplements actually become atomized during injection, which increases their ability to penetrate the formation. Additional nutrient injections are made periodically to replenish the substrates, and to provide beneficial aeration. Optionally, other biological supplements such as innoculum and/or granular media could be injected into the fracture network.

In the final step of the process, the site is operated as in situ bioremediation cell to degrade the contamination. A continuous air flow is maintained throughout the fracture network via a vacuum pump connected to a central extraction well. Outlying wells vented to the atmosphere serve as a passive source of oxygen. In the present application, air flow was purposely maintained at a low level, to minimize off-gas treatment and to maximize biological effects.

It is important to note that within the fracture network, pneumatically induced fractures will be separated by zones of unfractured soil. The distance between adjacent fractures will vary according to the geologic structure, but is generally believed to be on the order of 1 foot. As a result, a "stacked" system of microbial degradation will develop according to the availability of electron acceptors. Aerobic processes will dominate at the fracture interfaces where the oxygen supply is the highest, and to a limited distance into the soil away from the fracture. Depletion of oxygen during aerobic biodegradation and the presence of exogenous nitrate allows the formation to develop a denitrifying zone a short distance away from the fracture surface. Continued depletion of nitrate in the denitrifying zone further decreases the ambient oxidation-reduction potential and results in the formation of methanogenic populations at greater distances from the fracture. During methanogenic processes, methane is generated and diffuses to the fracture where it is removed by the sweep air extracted from the formation. The final result is contaminant degradation by a stacked series of aerobic, denitrifying, and methanogenic microbial zones which are staggered throughout the fracture network.

A project to investigate the coupling of these two technologies was sponsored by the US EPA under the Superfund Innovative Technology Evaluation (SITE) Emerging Technologies Program and an industrial sponsor. A field pilot demonstration of the integrated technologies was carried out at a gasoline refinery site over the interval of 20 months from October 1992 to May 1994.

METHODOLOGY

The site selected for the process demonstration was a gasoline bending area of a refinery located in Pennsylvania. The site stratigraphy was a surficial layer of fill comprised of clayey silts mixed with varying amounts of sand and gravel, ranging from 1 to 4 feet in thickness. The fill was underlain by a stratum of orange-tan clayey silt which extended to a depth of 9 to 10 feet below the ground surface. The consistency of the clayey silt ranged form medium stiff to stiff, indicating a high degree of over-consolidation. The upper few feet of this stratum were stained dark brown to black, apparently from infiltration of petroleum residues. The clay silt stratum graded into a gray silty sand at a depth of approximately 9 to 10 feet below the surface and extended to depths greater than 20 feet. The groundwater table was at a depth ranging from 13 to 15 feet below ground surface.

Spilt spoon boring samples were extracted and chemically analyzed to determine the extent of BTX contamination at the site. Contaminant distributions were heterogeneous, but with a general trend of total BTX concentrations of approximately 1500 mg/kg at a depth of 1 to 3 feet and decreasing with depth to less than 1 mg/kg at a depth of 9 to 11 feet. These results indicated that the pneumatic fracturing and subsequent bioremediation should focus on the soil contaminants to a depth of 7 feet. This approach also maintained an unfractured buffer of clayey silt between the shallow BTX contamination and the water bearing silty sand stratum.

The site was pneumatically fractured, and periodic injections were performed over a period of 12 months. Subsurface injections included introduction of nitrate and ammonium salt in the form of calcium ammonium nitrate to facilitate the development of aerobic, denitrifying and methanogenic biodegradation zones with respect to increasing distance from the fracture interface. Off-gases from the monitoring wells and vapor extraction well were analyzed for benzene, toluene and xylenes (BTX), oxygen, methane and carbon dioxide to evaluate process effectiveness. At the conclusion of the process demonstration, additional soil borings were carried out and samples analyzed to measure the change in the extent of site contamination as a result of the process. Carbon mass balances considering contaminant reduction, carbon dioxide evolution, methane evolution, and contaminant recovery through vapor extraction, were used to evaluate process performance.

RESULTS

Initial site characterization indicated low subsurface permeability and the presence of BTX at concentrations of up to 1500 ppm in the soil phase. Results show that fracturing increased subsurface permeability by up to 40 times within an effective radius of approximately 20 feet.

Thermodynamically, for BTX biodegradation, presence of oxygen (aerobic conditions) are more favorable for the microbial populations to effectively degrade the contaminants. In the absence of oxygen, the microbes seek an alternate electron acceptor in the form of iron, nitrate or sulfur to carry out the bioconversion. In this study nitrate served as an alternate electron acceptor and hence denitrification process, which biodegrades the organic contaminants into carbon dioxide and water, was initiated. Thermodynamically least favorable metabolic pathway for BTX biodegradation is methanogenesis and this occurs under strictly anaerobic conditions resulting in methane generation. Thus in the absence of oxygen and nitrate as electron acceptors methane generation is enhanced. This classic thermodynamic hierarchy in biodegradation pathways was observed in our field study as well. Following each nitrate injection, the methane concentration in the well decreased, while the carbon dioxide concentration increased indicating a shift towards aerobic and denitrification processes and away from methanogenesis upon the availability of an alternate electron acceptor.

After one year of sampling and monitoring, soil samples obtained from the site at the end of the demonstration show a 79% reduction in soil-phase BTX concentrations. Results from the analysis of soil samples obtained from three distinct depths of the soil bed in the pre-demonstration stage was compared with that in the post-demonstration stage. From these results the total mass of BTX removed, based on BTX concentrations was computed to be 22 kg. Based on periodic soil-gas sampling, the mass of BTX removed through vapor extraction was computed to be 3.1 kg or 11%. Vapor extraction was the predominant abiotic mode of BTX removal. The other abiotic pathways - BTX losses through fracture and amendment injections, perched water removal and passive volatilization accounted for a total of 0.8 kg (4%) based on mean BTX concentrations.

To independently ascertain the biodegradation process a mass balance was made on the nitrate introduced into the system. Based on the mass balance calculations 790 moles were depleted indicating an active denitrifying microbial population in the soil bed. Although the nitrate depletion and several positive factors such as carbon dioxide evolution following amendment injection and subsequent methane generation in the absence of available nitrate or oxygen did point towards an active biodegradation process, several constraining factors made it impractical to independently determine the

mass of BTX biodegraded. Hence all possible BTX losses were accounted for, and the mass of BTX removed by biodegradation was computed by difference. Based on these calculations over 82% of the BTX reduction can be assigned to bioremediation demonstrating the synergistic effect of the two processes.

CONCLUSIONS

Pneumatic fracturing, an innovative technology for enhancing subsurface flow rates, was employed to overcome rate limitations in the transport of nutrients and electron acceptors to the microorganisms in consolidated soil, for efficient in-situ biodegradation of organic contaminants. A field-scale pilot demonstration was carried at a petroleum refinery over a period of 20 months from October 1992 to May 1994. This integrated technology has clearly been shown to be a efficient process for removal of aromatic hydrocarbons such as benzene, toluene and xylenes, especially in over-consolidated soils. Following a successful implementation of this technology at the preliminary stage, this technology is ready to be scaled up to a full-scale demonstration.

REFERENCES

US EPA, RREL, Office of Research and Development. "Accutech Pneumatic Fracturing Extraction and Hot Gas Injection, Phase I", US EPA SITE Program, Application Analysis Report, 1993.

ACKNOWLEDGMENT

This project demonstration was performed as a part of the Emerging Technologies Program of the US EPA Superfund Innovative Technology Evaluation (SITE) under cooperative agreement No. CR818207-01-0. Our thanks are due to EPA project officer Uwe Franks for his help in the field demonstration of this project. The funding for this project was also received from the North East Hazardous Substance Management Research Center (HSMRC). The assistance of students from Dr. Lily Young's group at Rutgers University AgBiotech Center in the microbial work is greatly acknowledged.

FOR MORE INFORMATION:

Mr. Uwe Franks, Project Officer
U.S. EPA - ORD
Releases Control Branch (MS-106)
2890 Woodbridge Avenue
Edison, NJ 08837-3679
Tel.: (908) 321-6626

FUNDAMENTAL CRITERIA FOR THE BETTER DESIGN OF SECONDARY COMBUSTION CHAMBERS

Guido F. Sacchi, Tai-Gyu Lee, John P. Longwell, Adel F. Sarofim
Massachusetts Institute of Technology - Department of Chemical Engineering - Room 66-053
77 Massachusetts Avenue, Cambridge, MA 02139 - tel. (617) 253-6533

INTRODUCTION

The major concern regarding organic emissions from hazardous waste incineration systems is the formation of products of incomplete combustion (PICs). The toxic and, possibly, mutagenic character of these compounds represents one of the major problems to public acceptance of incineration as a safe waste disposal technology. Ongoing studies at MIT, sponsored by the US EPA Northeast Hazardous Substance Research Center (NHSRC), have shed light on the mechanisms of formation and emission of PICs, showing that the formation of PICs is highly dependent upon the local ratio of fuel and oxidant, and their amount and composition are sensitive to both turbulent mixing and chemical kinetic constraints.

A recent critical review on incineration science and technology, presented as a plenary lecture at the XXV International Symposium on Combustion by J.O.L. Wendt of University of Arizona, has clearly encouraged the scientific community to focus on turbulent mixing, rather than kinetics alone, in order to reach the goal of controlling and minimizing PIC emission from incinerators [1]. Also, it has shown that PIC emissions are closely related to transient phenomena (as rogue droplets formation caused by poor atomization, formation of puffs in kilns, fluctuations in feed rate and composition, etc.) which lead to failure modes tied to incomplete mixing. The current approach followed at MIT during the NHSRC-sponsored project thus seems to be very promising in giving a correct interpretation of the complex mechanisms involved in PIC formation, and in providing useful application of combustion science to incineration technology.

METHODOLOGY

The experimental facility has been designed to simulate the conditions in actual incinerator systems. It consists of a Toroidal Jet-Stirred Combustor (TJSC), which simulates the primary chamber of an incinerator, followed by a Plug Flow Reactor (PFR), as shown in Fig. 1. The hot combustion products from the TJSC are directed into the PFR, which represents the secondary combustion chamber, through a flow straightener. Mean flow velocities in the PFR range from 20 to 30 m/s for reacting flow.

An injector positioned at the PFR entrance allows injection of a selected species (oxidant, hydrocarbon, or chlorocarbon) directly into the PFR. The PFR injection system, and its turbulence intensity and chemical system, allow one to investigate the combined effects of turbulent mixing and chemical kinetic inhibition on PIC emissions. The experimental system is operated at high enough velocities to yield a Reynolds number corresponding to turbulent flow.

The PFR is equipped with optical access for application of a laser Rayleigh scattering diagnostic, leading to the definition of temperature probability density functions (PDFs) at a given location along the PFR axis. A water-cooled probe is used for sampling of the combustion gases whose concentrations are determined by gas chromatography/mass spectrometry.

Modeling of the experiment has been carried out using the Linear Eddy Model approach [2]. A semi-quantitative model coupling detailed chemical kinetics in homogeneous conditions with the interpretation of the effects of mixing constraints has also been developed. Furthermore,

use of CHEMKIN/SENKIN codes to investigate the temperature/time equivalence ratio history of the chemical system allows the selection of the most interesting conditions to be tested in the experimental facility.

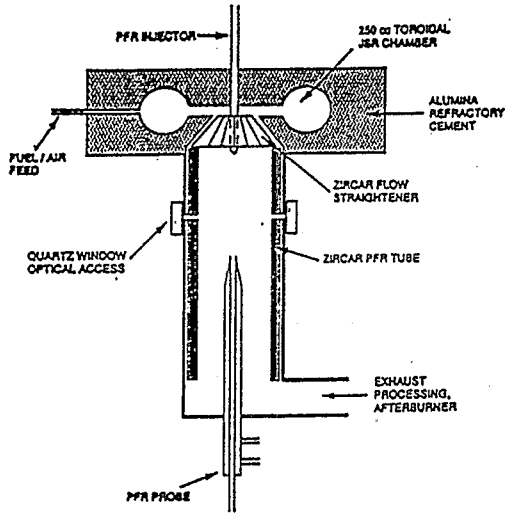


Figure 1. Schematic of the TJSC/PFR experimental system

RESULTS

The evolution of PDFs obtained by applying the Rayleigh scattering diagnostic technique shows evidence of mixing constraints in the PFR (Fig. 2).

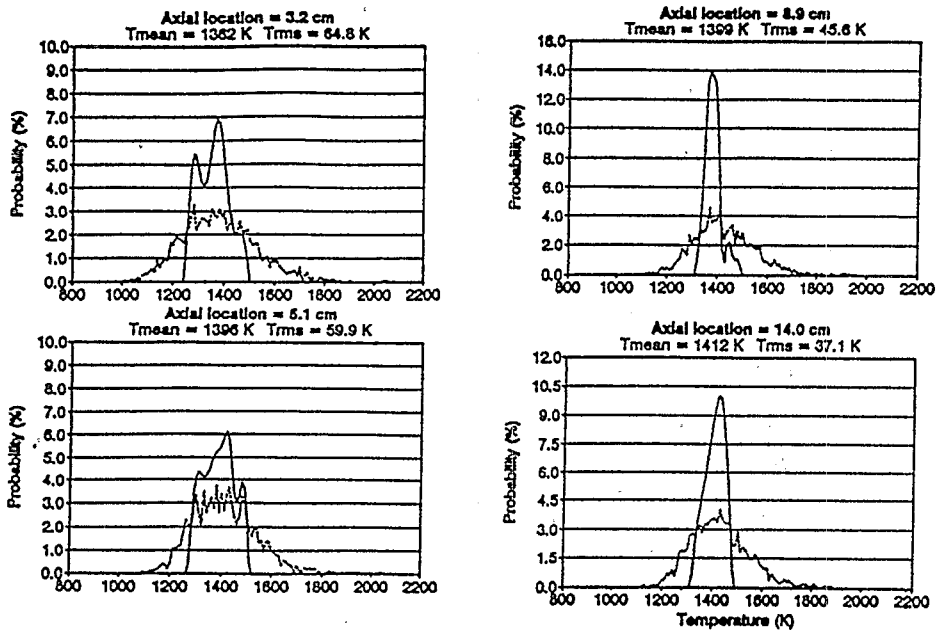


Figure 2. Temperature PDFs evolution for CH3Cl injection in the PFR (ϕ = 1.25)

The evolution of the turbulent system can be characterized by the decay of the fluctuating component of the injected material concentration distribution (in non-reacting conditions) with the distance from the injection point:

$$\sigma^2(x) = \sigma^2(0)\exp[-(1/\chi_d)x] + C$$

where σ^2 is the variance in the distribution, x is the distance from the point of injection, χ_d is the characteristic distance describing the approach of the concentration distribution to uniformity, and C is a constant which is determined experimentally. The mixing distance can be related to the mixing time τ_d, and to turbulence quantities such as the turbulent dissipation rate, ε, and the integral scale, L. Calculations made in order to obtain χ_d as a function of ε and L for the experimental conditions tested (injection of CH_3Cl in a N_2 baseline flow) gave a value of $\chi_d = 0.6$ cm, which is in good agreement with the value of $\chi_d = 0.7$ shown by the experimental trend.

Stable species concentration measurements were made along the length of the PFR, i.e., for different residence times. For example, as shown in Fig. 3, benzenes and chlorinated benzenes have been observed when methyl chloride was injected for an overall fuel-lean condition. Since aromatic compounds are only formed under pyrolysis conditions (high local value of the equivalence ratio ϕ) this indicates mixing controlled PIC formation (no aromatic compounds are produced when CH_3Cl is injected into the well-mixed environment of the TJSC) [3].

Research activities at MIT under the NHSRC program have thus proven evidence of mixing constraints in incinerator environments, whose interaction with the chemistry of the system is twofold. First, mixing constraints have the effect of decreasing the extent of reaction by delaying molecular mixing, compared to the case of a premixed environment. Second, they cause a distribution of the values of the local equivalence ratio (ϕ), compared to the theoretical ϕ value. Some of the high values of ϕ will result in pyrolytic pockets that can lead to the detection of species that would not otherwise be formed, and to a difference in concentrations of species which have a strong non-linear dependence on ϕ, compared to the conditions occurring in a completely mixed flow field.

The scale-up of the experimental and modeling activities has been achieved through collaboration between MIT, New Jersey Institute of Technology (NJIT) and EPA-Combustion Research Branch (CRB) by application of the experimental and modeling studies to the EPA-CRB's pilot scale facility, with emphasis on the secondary combustion chamber of the 73 kW rotary-kiln incinerator (Fig. 4).

Experimental results obtained from tests in which a dopant (CCl_4 and CH_2Cl_2) was injected in the secondary combustion chamber have confirmed the laboratory-scale results about PIC production and equivalence ratio history [4], encouraging the research groups to carry out an ongoing complementary test program.

An approach for the definition of a failure mode diagnostic system for application to practical incineration systems has also been developed. Experimental and modeling results have highlighted the possibility of a relationship between the PIC speciation measured in the exhaust and the kinetic and/or mixing failure mode that has led to the emissions. The strategy for the implementation of the diagnostic system is based on the presence of species, and on the value of selected ratios, which are sensitive to variations in operating parameters. For example, species having a strong non-linear dependence on the equivalence ratio, such as aromatics and soot which are produced above a critical ϕ, can provide insights on the mixing history. Figures 5 and 6 show the expected trend of selected ratios between species versus equivalence ratio as obtained by computer simulation of a perfectly mixed combustion environment.

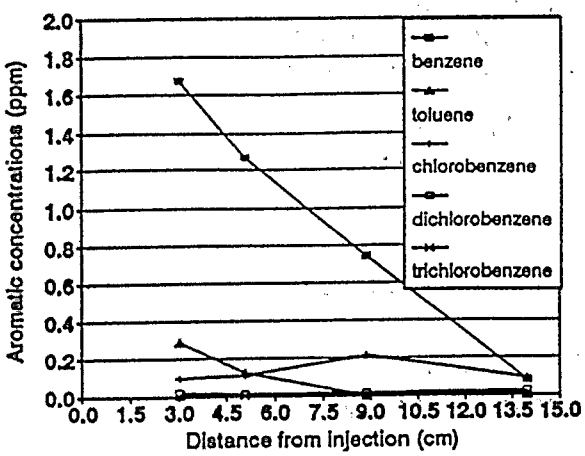


Figure 3. Concentration of aromatic species in the PFR (ϕ= 0.75)

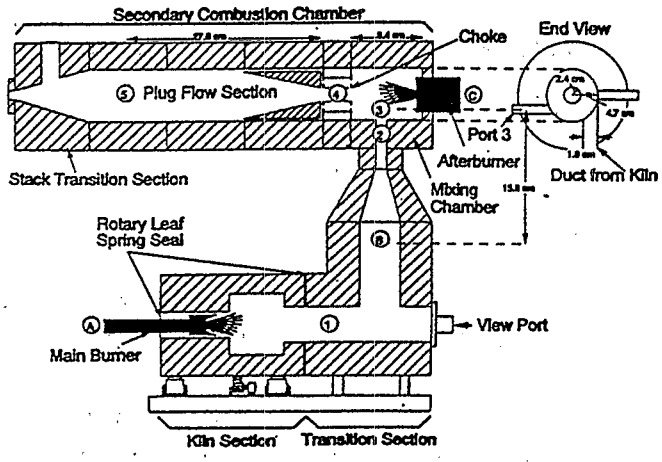


Figure 4. Schematic of the EPA-CRB pilot scale incinerator facility

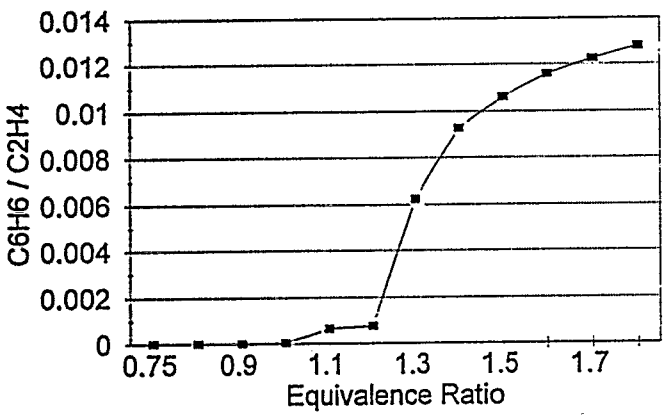


Figure 5. Evolution of C6H6/C2H4 ratio vs. ϕ

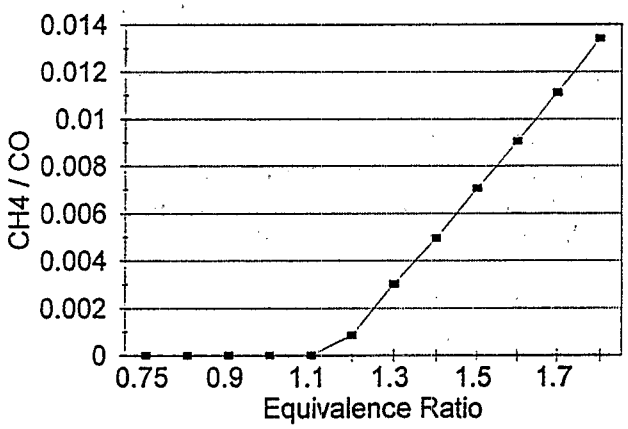


Figure 6. Evolution of CH4/CO ratio vs. ϕ

CONCLUSIONS

Experimental results have indicated effects of both incomplete mixing and chemical constraints on the formation of PICs. Evidence of mixing controlled PIC formation is given by the presence of species like aromatics, chlorinated aromatics, and high molecular weight species, in the exhaust gases. These species should not be formed under perfectly mixed conditions. The distribution of the value of the equivalence ratio is the most critical indicator in the interpretation of the effects of mixing constraints. Hence, evolution of species showing a strong non-linear dependence on the equivalence ratio provides insights on the mixing history in the incinerator.

The correct interpretation of exhaust composition data can lead to the development of a failure mode diagnostic for practical incinerator systems based on the detection of species which have a strong non-linear dependence on ϕ (as well as on other selected parameters). A

feed-back control system based on the presence of selected species in the gases leaving the secondary combustion chamber can be used to adjust the practical devices (air injectors, fuel and air flow controls, etc.), and quickly restore the optimal operating conditions.

Application of the results to the EPA-CRB's incineration facility plays a major role in transferring the research findings into practical industrial application.

REFERENCES

1. Wendt, J.O.L. Combustion Science for Incineration Technology, Paper presented at XXV International Symposium on Combustion, Irvine, CA., 1994.
2. Brouwer J., Sacchi, G., Longwell, J.P., Sarofim, A.F. and Kerstein, A.R. A Turbulent Reacting Flow Model that Incorporates Detailed Chemical Kinetics, Combust. Sci. Tech., in press.
3. Brouwer J., Sacchi, G., Longwell, J.P. and Sarofim , A.F. Mixing and Chemical Kinetic Constraints on PIC Production during Chlorocarbon Combustion, Combustion and Flame 99, pp.231-239, 1994
4. Bass C., Barat, R.B., Sacchi, G., Lee, T., Longwell, J.P. and Lemieux, P.M. Fundamental Experimental and Modeling Studies of Chlorocarbon Incineration in Afterburners, paper presented at XXV International Symposium on Combustion, Irvine, CA, 1994

EPA MANAGER

Dale Manty, Ph.D., Director
Hazardous Substance Research Centers Program
Office of Exploratory Research (RD-675)
U.S. Environmental Protection Agency
401 M St., S.W.
Washington, DC 20460
(202) 260-7445

KINETICS OF METAL LEACHING FROM HEAVY METAL CONTAMINATED SOILS

John E. Van Benschoten, Associate Professor
Department of Civil Engineering
State University of New York at Buffalo
Buffalo, NY 14260
(716) 645-2114 ext. 2330

Chandragupta Ganguly, Research Engineer
Mark R. Matsumoto, Professor
College of Engineering
University of California, Riverside
(909) 787-5318

INTRODUCTION

The evaluation of the rate and extent of heavy metal leaching from contaminated real waste site soils is an important aspect in the design of soil washing processes. Although the technology of soil washing is well established in Europe, until recently it had been demonstrated only on a pilot scale in the United States. In January 1992, the first full scale soil washing system in the United States started operation at the King of Prussia Technical Corporation Superfund site at Winslow Township, New Jersey (1). Of the 498 Records of Decision published through 1991, only 18 specified soil washing as the primary remediation technology. Currently, models that may yield design information are not available and the soil washing technology is at an empirical level of development. This goal of this project was to develop a deterministic model to describe the kinetics of metal leaching from contaminated soils. Specific objectives of the project were to: 1) experimentally measure leaching kinetics under acidic conditions from real waste site soils, 2) determine through numerical simulation the fate and interactions of the various contaminant phases during the washing process, and 3) identify the rate controlling steps and gain insight into design and operational aspects of the washing process. The focus of the study was on Pb contaminated soils.

METHODOLOGY

BET analyses were conducted on the soil samples by a contract lab to obtain soil surface area, pore volume and pore diameter data. Sieve analyses (ASTM Method D422-63) were performed to obtain particle size distribution data from which the geometric mean was calculated and used for model simulations. A standard acid digestion procedure (EPA Method 3050) was conducted on soil samples to determine total Pb content.

A sequential extraction method developed by the DuPont Corporate Remediation Group (2) was used to determine the distribution of Pb in various geochemical phases. This technique was developed specifically for Pb contaminated soils. Soil samples were air dried and only material passing through a #10 sieve (2 mm mesh size) was used for analysis by sequential extraction. Pb was partitioned into the following ten fractions: 1) water soluble; 2) exchangeable; 3) Ag-displaceable; 4) carbonates; 5) Mn oxides; 6) organic; 7) amorphous Fe-oxide; 8) crystalline Fe-oxide; 9) sulfides; 10) residual. For modeling purposes, it was assumed that fractions 1, 2 and 4 form the easily leachable phase, and fractions 3 and 5 through 8 constitute an adsorbed phase. Phases 9 and 10 form the residual phase and were assumed to be immobile, even under strongly acidic washing conditions.

Bench scale soil washing experiments were performed to obtain kinetic data during acid washing of soils in a batch reactor system under vigorous mixing. pH was carefully controlled throughout the

experiments by means of pH controllers and an acid delivery system to maintain the set point pH. Typically, experiments were run at a liquid to solid (L/S) ratio of 20 (1.6 L of solution with 80 g of soil) with HCl as the extractant, although experiments at different L/S ratios were carried out. The L/S ratio changed slightly during the course of the experiments due to sampling and evaporation losses. During each experiment, samples were collected periodically up to 5 hours; a final sample was collected after 24 hours of washing. Samples were collected using a plastic syringe which was fitted with a filter holder containing a 0.22 μm membrane filter. The filtered sample was analyzed for metal content by flame atomic absorption spectroscopy. It was assumed that the filtered metal concentration was equal to the total dissolved metal species in solution. During the experiments, the solution conductivity also was measured periodically and used to calculate the ionic strength of the bulk solution.

Quality Assurance/Quality Control (QA/QC) procedures were followed throughout the study. For analysis of Pb by flame atomic absorption spectroscopy, calibration standards were checked every ten samples, matrix interference spikes were tested every twenty samples, and duplicate analyses were performed every ten samples. QA/QC for soil washing kinetic experiments involved analyzing blank samples collected at the beginning of each experiment to test for Pb contamination of glassware, mixing impellers, or sampling syringes, performing duplicate samples for 10% of the samples taken within an experiment, and duplicating 10% of the soil washing experiments performed.

MODEL DEVELOPMENT

Leaching of contaminant metal was assumed to take place from porous, homogeneous spherical soil particles of uniform radius, which were immersed in an extractant solution (Figure 1). As noted above, it was assumed for modeling purposes that metals in contaminated soils exist in three phases only: metal precipitates (primarily carbonates and other easily leachable forms, e.g., water soluble + ion exchangeable + carbonate fractions), adsorbed metal (e.g., metal adsorbed to soil surfaces + organic coatings + Fe/Mn oxides) and an immobile residual phase. Complexing anions (e.g. Cl^-) and H^+ ions in the extractant diffuse into the pores of a particle as a result of both pore and film diffusion. H^+ reacts with precipitated (M(s), e.g., $PbCO_3(s)$) and adsorbed (≡M, e.g., $\equiv Pb^+$) contaminant metal, and the resulting metal ions (M, e.g. Pb^{+2}) are released into the pore solution. Metal ions may also undergo complexation reactions due to the presence of complexing anion(s). Concentration gradients within the particles result in the diffusion of free and complexed metal ions out of the pores and into the bulk solution. Similar reactions occur at the particle surface, with only film diffusion controlling the movement of species in and out of the bulk solution. Because the leaching process is assumed to take place in a well mixed system, diffusion within the bulk solution is ignored.

Sorption is assumed to be a reversible process and is treated as a pseudo-first-order reversible reaction with respect to the metal phase,

$$[\equiv M] + [H^+] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [M] + [\equiv H] \qquad (1)$$

where, ratio $k_1/k_{-1} = K_{ads}$, the equilibrium constant for adsorbed metal.

For soil washing using acidic solutions, dissolution of metal carbonates is assumed to follow an irreversible reaction:

$$M(s) + H^+ \xrightarrow{k_2} M + products \quad (2)$$

While the model accounts for metal complexation, adsorption of metal complexes to the soil surface is ignored. The formation of metal complexes with Cl^-, for example, during soil washing with HCl is assumed to be rapid and is described by the equilibrium reaction,

$$M + Cl^- \underset{k_{-3}}{\overset{k_3}{\leftrightarrow}} MCl \quad (3)$$

where $k_3/k_{-3} = K_{Cl}$, the equilibrium constant for the reaction.

Double layer effects are ignored because at higher ionic strength (> than about 0.1 M) the coulombic contribution to adsorption is constant in the acidic pH range (3).

The activity of adsorbed metal is assumed to be unity. Activity coefficients are calculated based on the Bronsted-Guggenheim equation and may vary with leaching time as ionic strength typically increases as ions are leached from the soil. Also, within the soil particle a radial gradient in ionic strength is assumed to exist that is the same as the simulated Pb gradient.

The model was formulated by linking the pore diffusion equation of each ion (4) with its corresponding chemical reaction. The transfer of metal from the particle surface to the bulk solution across the liquid film is assumed to follow Fick's first law of diffusion.

The resulting system of partial differential equations was transformed to a set of ordinary differential equations (ODEs) in time by using a finite difference (central difference) approach for the spatial derivatives. The resulting set of ODEs with the appropriate initial and boundary conditions was solved using an ODE solver. Details of the modeling approach are described elsewhere (5,6).

Model parameter estimates were based on laboratory measurements (soil particle size characteristics, Pb content and distribution, ionic strength), calculation (diffusion coefficients, activity coefficients), and data fitting. Equilibrium data were used to fit the equilibrium constant K_{ads} (equation 1) and a total site density, S_T. Kinetic data then were used to determine the rate constants k_1 (equation 1) and k_2 (equation 2) and a particle tortuosity factor. Parameters were fit by minimizing the sum of squares between measured and fitted data.

RESULTS

Fitted and measured data under pseudo-equilibrium conditions (24 hrs leaching) for four soils are shown in Figure 2. The data for each soil were fitted using two parameters, the metal adsorption equilibrium constant, K_{ads} and the total site density, S_T ($S_T = [\equiv H] + [\equiv Pb]$). The parameters, K_{ads} and S_T, estimated by the equilibrium modeling approach are soil specific. The values of the site density, S_T, across different soils falls within the range of site densities reported in the literature. The equilibrium constants, K_{ads}, across the soils are similar (Table 1). Differences across soils may be attributed to differences in surface characteristics, soil heterogeneity and site density. Considering the complexity of real waste site soils, the fit of the data is good, possibly because at low pH and the contaminant levels for these soils, the system is dominated by H^+ and Pb^{2+}.

Model calibration results to kinetic data for two of the waste site soils studied are shown in Figure 3.

For each of the soils, one set of model parameters describes the range of pH conditions shown. From Table 2 it is observed that the kinetic parameters, k_1 and k_2, for the four soils are in relatively close agreement. The slight variation between the values of the kinetic coefficient from one soil to another may be due to inherent differences in these soils or the manner in which lead geochemical phases were combined for modeling purposes. The dissolution coefficient, k_2, for the soils studied are close to those reported by Tuin and Tels (7). However, lack of available literature values hinder additional comparisons. From the calibration results it is also observed that the soil particles have a tortuosity greater than unity (Table 2), which is consistent with values reported in the literature. The similarity in model parameter estimates across different soils may be due to the similarity in Pb distribution across different soils. Although the parameters estimates are soil specific, they apply to leaching data at pH 1 to 3 and a range of ionic strength from 0.01 to 0.6M.

A sensitivity analysis was undertaken to gain insight to the relative importance of parameters affecting metal leaching. The analysis showed that model simulations were most sensitive to metal geochemical phase distribution (i.e., precipitated vs adsorbed) and metal location (i.e., surface vs pores). These results, in addition to sensitivity to pH (see Figure 3) indicate the importance of chemical factors in influencing leaching from real waste site soils.

While preliminary modeling efforts were successful in simulating metal leaching under acidic conditions, the effects of a strong ligand (i.e., EDTA) were not modeled successfully.

CONCLUSIONS

A numerical model, developed to simulate the removal of lead from soils, was applied to experimental data from four waste site soils based on parameters which were estimated through a combination of independent experiments, literature correlations and mathematical optimization. The lead contaminant pool was divided into easily leachable, adsorbed and residual phases based on sequential extraction data. The parameters obtained from the model calibration are consistent to those observed in the literature for adsorption of Pb to mineral surfaces. The similarity in the parameters estimated by the model may be due to similar geochemical phase distribution of lead across the soils. The results obtained show that the model is capable of matching experimental data over a range of solution pH (pH 1 to 3) and ionic strength (0.01 to 0.6M).

Although the model matched the experiment leaching data well, improvement in its performance can be further achieved by better characterization of metal geochemical phases distribution. Quantifying the radial distribution of metal across the particle would also improve the model performance. The effect of strong ligands on metal leaching was not adequately described and needs to be incorporated in the model.

REFERENCES

1. Anderson, W.C. Innovative Site Remediation Technology: Soil Washing/Soil Flushing. American Academy of Environmental Engineers, Annapolis, MD, 1993.

2. Igwe, G. J., Koehler, L. R. T, and Walling, P. D. Bonding/Binding Properties of a Lead Contaminated Soil. In: Proceedings of an International Symposium sponsored by the Extraction and Processing Division of TMS. San Francisco, California. 1994.

3. Dzombak, D.A. and Morel, F.M.M. Surface Complexation Modeling, Hydrous Ferric Oxide. John Wiley & Sons, New York, 1990.

4. Crank, J. The Mathematics of Diffusion, 2nd ed. Oxford Clarendon Press, 1975.

5. Ganguly, C., VanBenschoten, J. E., Matsumoto, M. R., and Rabideau, A. J. Metal Contaminant Leaching from Waste Site Soils: 1. Model Development. Environ. Sci. Technol., (submitted for publication) 1994.

6. Ganguly, C., VanBenschoten, J. E., Matsumoto, M. R., and Rabideau, A. J. Metal Contaminant Leaching from Waste Site Soils: 2. Model Calibration and Application to Lead Contaminated Soils. Environ. Sci. Technol., (submitted for publication) 1994.

7. Tuin, B. J. W. and Tels, M. Extraction Kinetics of Six Heavy Metals from Contaminated Clay Soils. J. Environmental Technolog, 11: 541, 1990.

TABLE 1. EQUILIBRIUM MODEL CALIBRATION RESULTS

Parameters	Soil 1	Soil 2	Soil 3	Soil 4
S_T (sites/nm^2)	1.95	1.95	7.65	0.53
K_{ads}	3.38×10^{-3}	1.42×10^{-3}	1.30×10^{-3}	2.08×10^{-4}
r^2	0.99	0.99	0.99	0.99
Std. Error (mg Pb/L)	11	1.5	8.3	1.0

TABLE 2. KINETIC MODEL CALIBRATION RESULTS

Parameters	Soil 1	Soil 2	Soil 3	Soil 4
k_1 (L/mol-min)	0.644	0.019	0.39	0.134
k_1 (L/mol-min)	10.4	11.6	9.03	9.97
Toruosity	13.6	21.8	1.5	1.74
r^2	0.99	0.95	0.96	0.97
Std. Error (mg Pb/L)	2.28	4.45	3.97	0.57

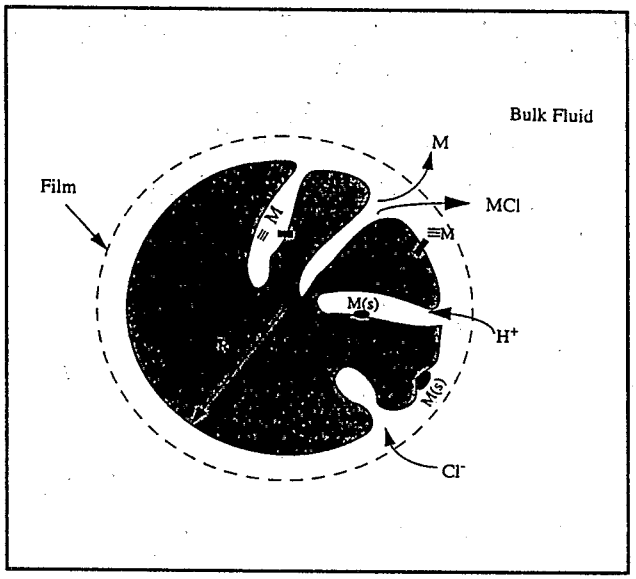


Figure 1. Conceptualization of metal leaching.

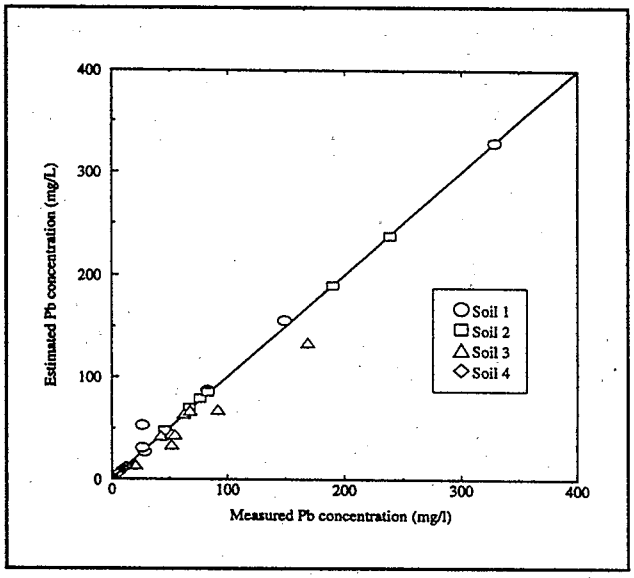


Figure 2. Equilibrium model calibration results.

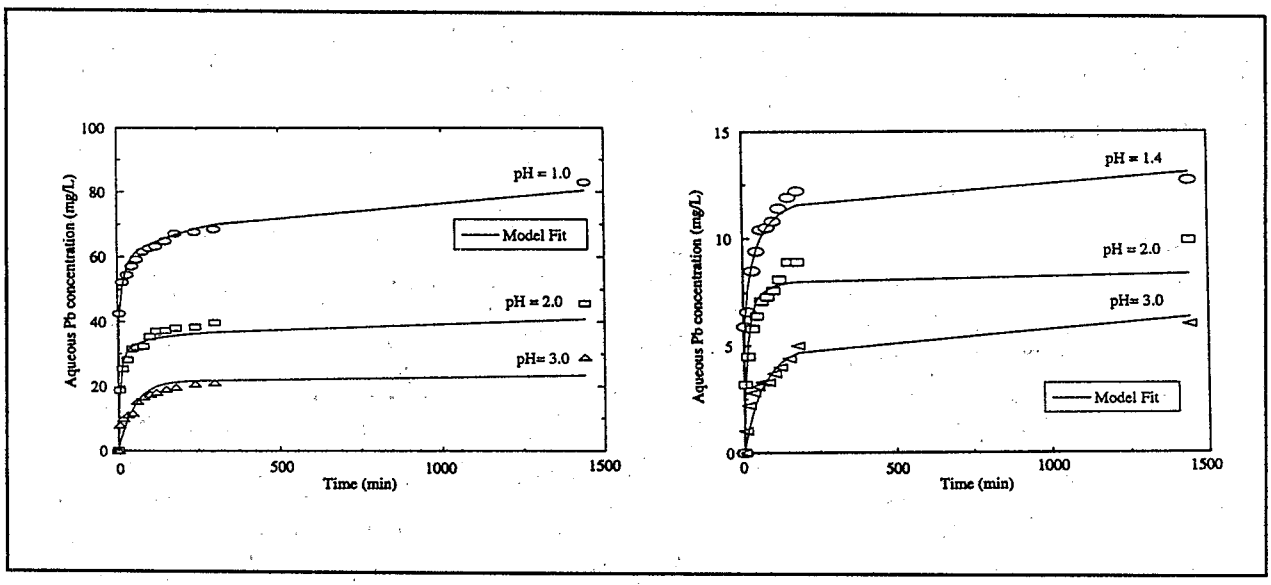


Figure 3. Kinetic modeling results for two waste site soils.

INTRINSIC BIOREMEDIATION OF CHLORINATED SOLVENTS AT THE ST. JOSEPH, MI AQUIFER - LAKE MICHIGAN INTERFACE

Peter Adriaens, Jack Lendvay, Nikolaos Katopodes, and Sean Dean
The University of Michigan, Department of Civil and Environmental Engineering
181 EWRE Building, 1351 Beal St. Ann Arbor MI 48109-2125
(313) 763-1464

and

John Wilson, and Don Kampbell
U.S. EPA Robert S. Kerr Environmental Laboratory
Ada, OK

1. INTRODUCTION

The anaerobic aquifer at the St. Joseph, MI National Priority List (NPL) site has been contaminated with trichloroethylene (TCE) of up to 160 mg/L, which in the last decade has been shown to have dechlorinated to cis- and trans-dichloroethylene (DCE), 1,1-dichloroethylene, vinyl chloride (VC), ethylene, and ethane. Previously, it was established that the occurrence of these products was due to intrinsic bioremediation, based on both laboratory investigations (1,2) and temporal monitoring of the groundwater , which showed significant levels of ethene and methane (3-5).

The flux of all alkyl halides into Lake Michigan is of major public concern due to the suspected carcinogenicity of VC. Moreover, as the plume moves towards and emanates into the aerobic surface water, the dominant redox conditions can be expected to change due to wave action and vertical seepage which promote the interchange of oxygen-rich lake water with the anaerobic groundwater. This phenomenon is likely to have an impact on the microbial community structure, and thus the biodegradative processes. The current presentation provides the results of field investigations at the interface with Lake Michigan, and presents some preliminary results on the fate of chlorinated solvents at a simulated interface between earobic and anaerobic conditions using using both experimental and modeling approaches.

2. METHODOLOGY

Off shore sampling was conducted using a truck-mounted Geoprobe chained on a 80' x 30' barge, which could be anchored using steel spuds (The Probing Times, 1994). The barge was put in place with the help of a tugboat, and an on-shore surveying team. Barge locations were based on a previously determined offshore survey plan, generated based on ground penetrating radar (GPR) and sonar measurements (B. Sauck, Eastern Michigan University). The four sampling points were approximately 100 m off shore at a depth of approx. 15', which corresponds to the expected hydraulic connection between the aquifer and Lake Michigan. A specially designed drill pipe was centered with a two-inch PVC sleeve, which was anchored with a steel plate in the lake sediment surface. A 0.5' vertically slotted screen well point was advanced to depths of up to 21 feet into sand and silt layers in 15-20' of water off shore, at depth intervals of 2-3'. Water samples were collected and analyzed for conductivity, pH, inorganic redox couples, methane, ethane, ethene, and chlorinated volatile hydrocarbons. Sediment samples were collected in the more reduced regions, were saturated with anaerobic groundwater, and shipped to the University of Michigan laboratories, where they were transferred to an anaerobic chamber.

On shore sampling was conducted using a Geoprobe with a 1' screen, which was driven into the beach sands using an 80lb electric hammer to depths of up to 32'. Groundwater samples were collected at 3' depth increments, and sediment samples were collected from the most reduced zones at 17-20'. The locations of the barge and the beachhead sampling points are shown on Figure 1, relative to the five previously developed transects on shore (modified from Wilson et al., 1994).

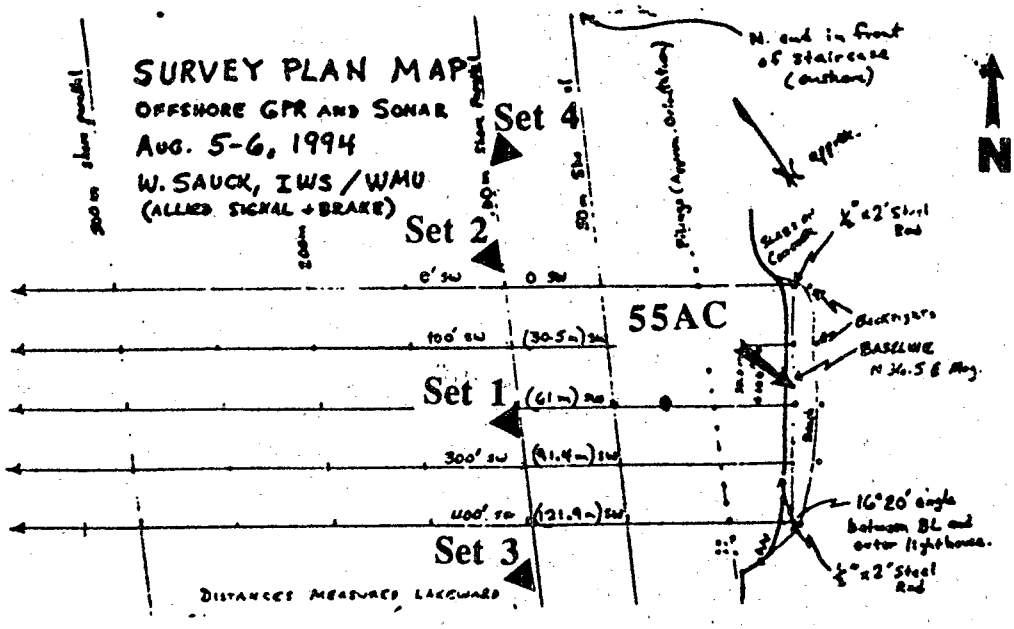


Figure 1. Location of beachhead and offshore sampling points at St. Joseph, MI.

Field simulation experiments are conducted in two separate column configurations, to allow for both spatial and temporal differentiation. The sequential column configuration (Figure 2, A) consist of two water-jacketed columns (20 °C) packed with approx. 250 g of saturated aquifer material, in which the first column is maintained methanogenic, and the second methanotrophic. This setup emulats the movement of groundwater from the anaerobic zone to the aerobic zone, as water moves toward Lake Michigan. The second configuration (Figure 2, B) consists of one column in which the redox conditions are temporally switched (every 12 hours) between anaerobic (terminal electron acceptors, HCO_3^- and SO_4^{2-}) and aerobic methanotrophic media. This emulates the zone of the aquifer that is impacted on a temporal basis between aerobic and anaerobic conditions as the wave action of the lake changes. A syringe pump

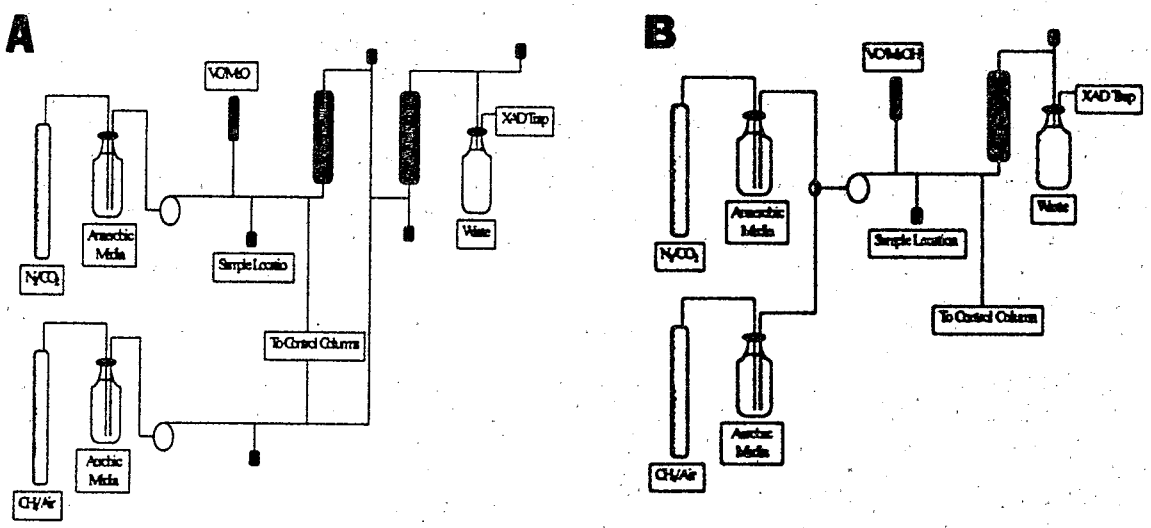


Figure 2. Configuration of the sequential (A) and temporally switched column (B).

located in the media supply line contains vinyl chloride in water (500 mg/L), which will provide solvent pulses no higher than 10 mg/L in the medium. Identical inactive column configurations are monitored along with the active columns.

Laboratory microcosms are established in 125-mL serum bottles, which are inoculated with 50 grams of wet sediment and filled with media (no headspace) specific to the redox conditions of interest. Based on field and laboratory evidence, methanogenic, sulfate-reducing, Fe^{2+}-reducing, and aerobic methanotrophic microcosms have been developed. Some vials, selected at random, are then injected with 10 ppm of vinyl chloride to measure transformation rates.

A numerical model is being developed which will simulate the hydrodynamic, physico-chemical and biological processes that take place at the aquifer-lake interface. Although the hydrodynamic processes are three-dimensional, most of the phenomena of interest can be modeled by a two-dimensional model on the vertical plane. The phenomena of interest include the migration of TCE, DCE, and VC into the lake and transfer of dissived oxygen into the aquifer from water infiltrating through the surf region. Due to the significant time-scale difference between the nearshore circulation, wave run-up and breaking in the lake compared to the flow in the aquifer (estimated at 7.5 m/day), two separate models are being constructed for the corresponding hydrodynamic phenomena. The resulting flow fields are then integrated in a single mass transport and contaminant fate model. All three components of the model are two-dimensional in space, covering a vertical plane extending from a location on land where uniform flow and mass flux are observed in the aquifer, to a distance inside the lake where most nearshore current activity has diminished.

The nearshore/free surface flow simulation is based on a numerical solution of the Navier-Stokes equations by means of the finite element method. The model can predict the vertical structure of the flow from the seepage face between the aquifer and the lake to the free surface. Wave action is incorporated and special attention is focused on wave run up and breaking. The beach is assumed to be a porous bed so that water from the surf-and-break region is allowed to infiltrate and reach the aquifer.

3. RESULTS AND CONCLUSIONS

Vertical profiles of contaminant and inorganic solute concentrations, as well as measured redox potential values are shown in Figure 3, as a function of depth for sample location AC on the beach.

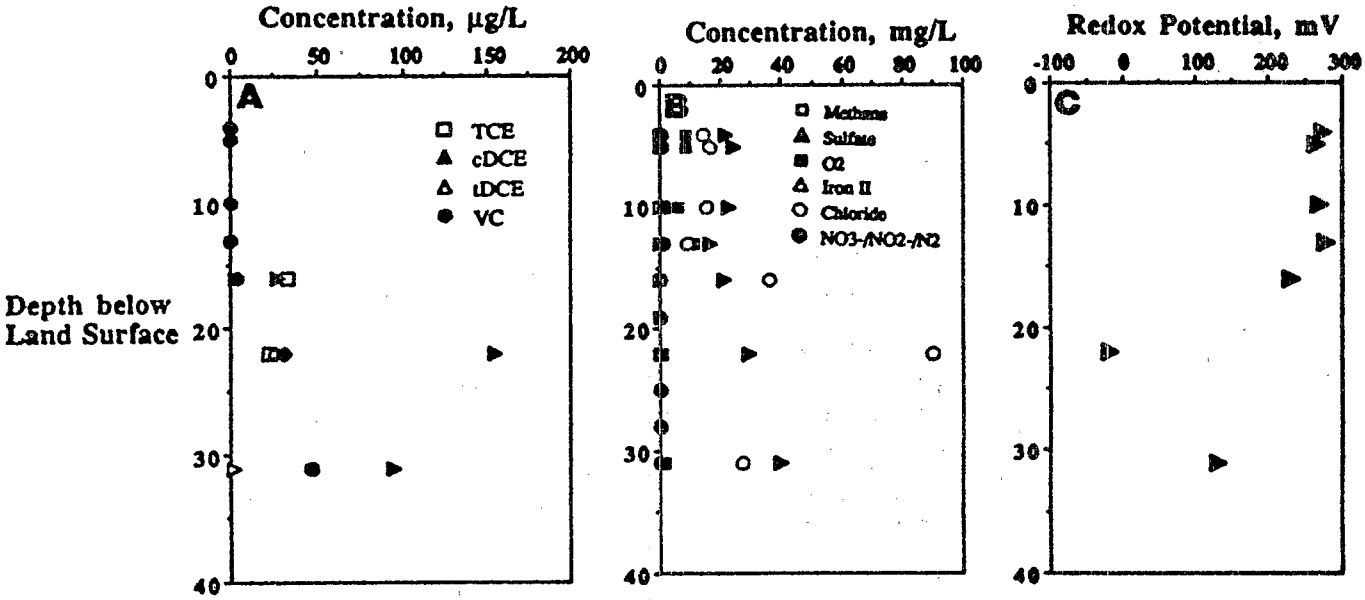


Figure 3. Vertical Profiles of Contaminants (A), Electron Acceptors (B), and Redox Potentials (C) at Beachhead Sampling Location AC.

It can be observed that DCE concentrations peak at a depth between 20-30 feet, while VC concentrations increase up to 32 feet. This region corresponds with the highest inorganic chloride concentrations (up to 90 mg/L), and the lowest redox potential values. However, the measured field potentials are too high for effective methanogenesis to occur, and coincide with high sulfate levels. Sulfide levels were not measured in the water samples, thus no conclusive evidence for sulfidogenic activity was evident, less its importance in dechlorination reactions. Though soluble iron (Fe^{2+}) was only sporadically detected and its concentration was low (< 0.05 - 0.2 mg/L), indirect evidence of active iron reducing activity was based on the observation of magnetite crystals in the water and sediment samples. This informatrion is contrary to the data from well upstream in the aquifer, where reductive dechlorination resulting in ethene and ethane was strongly correlated to methanogenic activity (3).

The profiles for electron acceptors, chloride and redox potential in Lake Michigan sediments are exemplified for Barge Set 4 (for location please see figure 1), as a function of depth below lake surface (Figure 4). Note that the lake bed is at approximately 15' depth. A very strong correlation can be noted between the chloride peak (18-25' below surface) and the reduced environmental conditions (> -100 mV), signifying high microbial activity. Again, methane concentrations were extremely low, but the chloride peak and redox potential minimum appear to coincide with a decrease in sulfate concentrations. Sulfide concentrations measured were very low (< 0.1 mg/L). This observation does not preclude the absence of sulfate reducing activity, as the sulfide produced may have precipitated as iron sulfide (FeS) (note the low remaining Fe (II) concentrations (0.1 - 0.2 mg/L). Contaminants were not observed, as their concentrations were probably below the detection limit.

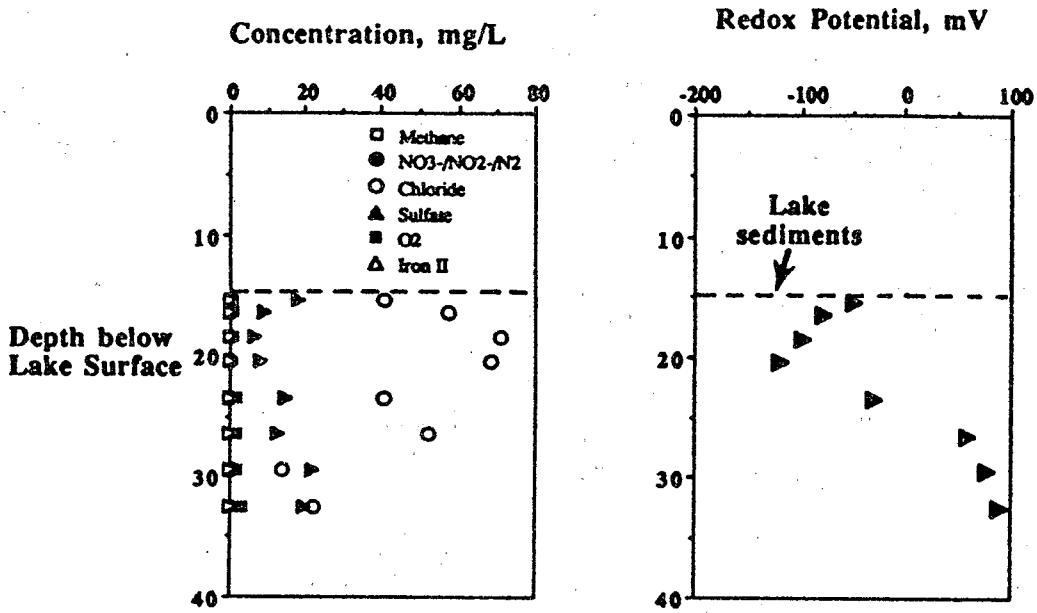


Figure 4. Vertical Profiles of Electron Acceptors (A) and Redox Potentials (B) at Barge Set 4.

The field data suggested that under anaerobic conditions, methanogens, sulfate-reducers and Fe-reducers may play a role at the interface, as well as methanotrophic and aerobic heterotrophs. Thus far, we have stimulated methanogenic and Fe-reducing activity in aquifer material obtained from the beach borings. Microcosms incubated under methanogenic conditions, and spiked with 10 mg/L of VC showed a slight decrease of the VC concentrations after three months of incubation, relative to the inactive controls. Similarly, we have established methanotrophic and methanogenic activity in the sequential soil columns. Microbial characterization of methanotrophic column effluent has resulted in the detection on a single dominant heterotrophic microorganism, as well as two distinct methanotrophic populations. Dechlorination studies have recently been initiated.

A three dimensional regional groundwater flow model based on MODFLOW is being developed. This regional model will be used for parameter estimation as well as to validate the groundwater flow model that

has been developed for this site previously. A computational grid reflecting the actual conditions at the St. Joseph site is currently being implemented for the groundwater model. Following validation of the groundwater model, the nearshore/free-surface flow simulation will be adapted from a code that has already been completed.

4. REFERENCES

1. McCarty, P.L., L. Semprini, M.E. Dolan, T.C. Harmon, C. Tiedeman, and S.M. Gorelick. In Situ Methanotrophic Bioremediation for Contaminated Groundwater at St. Joseph, Michigan. In R.E, Hinchee and R.F. Olfenbuttel (eds.), On Site Bioremediation. Butterworth-Heinemann, Boston, Massachusetts, 1991. p. 16.

2. Haston, Z.C., P.K. Sharma, J.N.P. Black, and P.L. McCarty. Enhanced Reductive Dechlorination of Chlorinated Ethenes. In Symposium on Bioremediation of Hazardous Wastes (Abstracts), EPA/600/R-94/075, San Francisco CA, 1994, p. 11-15.

3. Wilson, J.T., J.W. Weaver, and D. H. Kampbell. Intrinsic Bioremediation of TCE in Groundwater at an NPL Site in St. Joseph, Michigan. In Symposium on Intrinsic Bioremediation of Ground Water, EPA/540/R-94/515. Denver, CO, 1994, p. 154-163.

4. McCarty, P.L., and J.T. Wilson. Natural Anaerobic Treatment of a TCE Plume at the St. Joseph, Michigan NPL Site. In U.S. EPA Bioremediation of Hazardous Wastes (abstracts. EPA/600/R-92/126. p. 47-50.

5. Kitanidis, P.K., L. Semprini, D.H. Kampbell, and J.T. Wilson. Natural Anaerobic Bioremediation of TCE at at the St. Joseph, Michigan, Superfund Site. Symposium of Bioremediation of Hazardous Wastes. EPA/600/R-93/054, p. 57-60.

MONITORING AND CONTROL OF *PSEUDOMONAS* SP. STRAIN KC FOR *IN-SITU* BIOAUGMENTATION OF CARBON TETRACHLORIDE CONTAMINATED SITES

Craig S. Criddle, Center for Microbial Ecology and Department of Civil and Environmental Engineering, Engineering Research Complex A126, Michigan State University, East Lansing, MI, 48824, (517) 355-8241

Michael J. Dybas, Center for Microbial Ecology, Engineering Research Complex A119, Michigan State University, East Lansing, MI, 48824, (517) 353-9059

Gregory M. Tatara, Center for Microbial Ecology and the Department of Microbiology, Engineering Research Complex A135, Michigan State University, East Lansing, MI, 48824, (517) 353-9059

David C. Wiggert, Department of Civil and Environmental Engineering, Engineering Research Complex A120, Michigan State University, East Lansing, MI, 48824, (517) 355-5155

Michael Witt, Department of Civil and Environmental Engineering, Engineering Research Complex A121, Michigan State University, East Lansing, MI 48824, (517) 353-9059

James M. Tiedje, Center for Microbial Ecology and Departments of Crop and Soil Science and Microbiology, Plant and Soil Science 540, Michigan State University, East Lansing, MI, 48824, (517) 353-9021

Serguei Bezborodnikov, Center for Microbial Ecology, Plant and Soil Science 540, Michigan State University, East Lansing, MI, 48824, (517) 353-9021

David Lubman, Department of Chemistry, 4545 Chemistry Building, The University of Michigan, Ann Arbor, MI, 48109, (313) 764-1669

Scott Fogler, Department of Chemical Engineering, The University of Michigan, Ann Arbor, MI, 48109, (313) 763-0459

INTRODUCTION

Pseudomonas sp. strain KC converts carbon tetrachloride (CT) to carbon dioxide, formate, and non-volatile product(s) without the production of chloroform under denitrifying conditions [1,2]. Most other organisms that transform CT under such conditions do so slowly and/or produce chloroform, making strain KC an attractive candidate for bioaugmentation applications. For strain KC, the mechanism of CT transformation involves secretion of a low molecular weight factor under iron-limiting conditions [3]. The secreted factor fortuitously transforms CT and is activated for transformation by live whole cells [3,4].

To determine whether the capabilities of strain KC can be applied for in-situ remediation of CT contamination, the Michigan Department of Natural Resources is supporting a field experiment in a CT-contaminated aquifer at Schoolcraft, MI. The present report describes laboratory work funded by the Great Lakes and Mid-Atlantic Hazardous Substance Research Center in support of the field project. These laboratory efforts have focused on: (1) isolation and identification of the secreted factor, (2) development and testing of a laboratory-scale model aquifer and numerical simulator to describe establishment and maintenance of a CT-transforming zone, (3) development and testing of a gene probe for detection and monitoring of strain KC, (4) identification of characteristic biochemical markers for strain KC, and (5) identification of key transport and retention mechanisms for strain KC.

METHODOLOGY

Organisms and culture conditions. *Pseudomonas* sp. strain KC (DSM deposit no. 7136, ATTC deposit no. 55595), derived originally from aquifer solids from Seal Beach, CA, (1) is routinely maintained in our laboratories on nutrient agar plates. *P. fluorescens* (ATTC deposit no. 13525) was obtained from the culture collection of the Department of Microbiology at Michigan State University. Medium D was prepared as described elsewhere [1].

Fractionation of CT transformation activity. To localize the CT transformation activity of strain KC, actively transforming cultures were fractionated by centrifugation and ultrafiltration. Cells from 300 ml of actively transforming culture were harvested by centrifugation, and the supernatant filtered through a 0.2 µm filter. In general, cell-free supernatant and its filtered fractions (10,000 and 500 MW filtrate) did not mediate appreciable CT transformation alone. Rapid transformation was usually obtained only when these fractions were combined with viable whole cells. Filtrate and retentate from the 10,000 and 500 MW filters were combined with washed cells of strain KC before being assayed for CT transformation or they were tested in the *P. fluorescens* bioassay.

Bioassay for the secreted factor using *Pseudomonas fluorescens*. Tatara et al. (4) discovered that rapid CT degradation occurs when the secreted factor generated by strain KC is combined with diverse cell types, such as cells of *Pseudomonas fluorescens*. This finding enabled the development of a bioassay for the secreted factor. *P. fluorescens* cells were harvested by centrifugation and resuspended to one tenth the original culture volume in medium D at a cell density of approximately 2×10^9 cfu/ml. Five hundred microliters of the resulting 10 X concentrated cell suspension was added to 4.5 ml samples generated during the fractionation procedure. The samples were rendered anoxic, sealed under N_2 headspace in 28 ml Balch tubes, and spiked with CT. Levels of CT were followed by headspace gas chromatography as previously described [5].

Purification of secreted factor. Filtrate passed through an Amicon 500 MW filter was lyophilized to dryness. The lyophilized filtrate was suspended in approximately 5% of the original filtrate volume (254 mg lyophilized filtrate/ ml) in ultra pure deionized water. The sample was then transferred to a 28 ml test tube and 9 ml of HPLC grade acetone were added Samples were stored at 4°C for 2 hours to allow precipitation. A visible precipitate formed during the first minute after acetone addition. The supernatant was decanted and filtered through a 0.45 µM PTFE filter to remove any particulate matter. The acetone water phase was evaporated to dryness under nitrogen at room temperature. Approximately 80% of the bioassay activity was recovered in the dried acetone fraction. The yield was approximately 7 µg partially purified material per mg dry 500 MW filtrate precipitated. The secreted factor recovered in the acetone extract was further purified by reverse phase HPLC using a methanol-water mobile phase and a C18 column. Samples collected in the HPLC effluent were evaluated for the presence of secreted factor using the *P. fluorescens* bioassay.

Model aquifer column. A PVC column (183 cm length x 5.2 cm i.d.) was fabricated and served as a model aquifer system. The column was equipped with 30 injection/extraction ports along its length at 76-mm intervals, with seven additional holes located between ports 5 and 6 for an injection zone. The column was wet packed with Ottawa sand using groundwater obtained from the Schoolcraft site (containing 60 mg/L nitrate). The column was operated at a bulk flow rate of 90 mL/min (a linear velocity of 150 mm/d), with an inflow CT concentration of 80 µg/L.

To evaluate the feeding pattern planned for the field experiment, pulse injections of nutrients and organisms were simulated using slugs of tritiated water (^3H_2O) followed by inoculation with *Pseudomonas* strain KC (at approximately ~2×10^8 cells/mL), acetate (60 mg/L), phosphate (10 µg/L), and bromide (20 mg/L). Acetate was added in weekly pulses thereafter. Strain KC was monitored using an MPN (Most Probable Number) method, in which growth in medium D and CT transformation were used to indicate presence of strain KC. The presence of strain KC was also confirmed by gene probe. CT was analyzed by headspace sampling and gas chromatography as described elsewhere [5]. Acetate, bromide, nitrate, and nitrite were analyzed by ion chromatography. To simulate column results, we

developed a one-dimensional code for coupled transport of five constituents (acetate, nitrate, CT, attached and suspended organisms) in the 2 m long laboratory columns. We have tested the code for numerical stability and accuracy.

Development of a gene probe for strain KC. Twenty random clones of approximately 1 kb from the *Pseudomonas* KC chromosome were screened against 200 isolates from Schoolcraft groundwater to determine their specificity for KC. Five fragments showing no non-specific hybridization were selected for further evaluation. Fragment #40 was selected as superior for specificity and reliable PCR-amplification. Two sets of primers of 20-22 mer (P1F, P2F and P2R-P1R) have been selected and tested against aquifer isolates, aquifer groundwater and Genbank and found to be specific for strain KC. The primers have been used with PCR amplification to test the movement of strain KC after injection into the test column of aquifer material, described in the previous section. One milliliter water samples were taken from sampling ports along the model aquifer column for DNA extraction using SDS/proteinase K followed by CTAB extraction and propanol precipitation of the DNA. PCR amplification with this template DNA was performed after adding 50 pmol of the two primers and Ampli Tag polymerase. Any PCR products were separated by electrophoresis in 1% agarose gels and stained with ethidium bromide. If any target (KC) DNA is present, a band of 1.35 kb should be observed.

RESULTS

Separation of the secreted factor. As illustrated in the chromatogram of Figure 1, the acetone extraction and HPLC separation procedure was successful, and the secreted factor (as indicated by a strong positive bioassay response) was recovered in a single, separated peak at a retention time of 14 minutes.

We are currently purifying sufficient secreted factor for identification preparative HPLC. The identification step will be conducted by mass spectrometry, using other analytical techniques as needed. Identification will be conducted in collaboration with Dr. David Lubman (UM, Chemistry) and Dr. Douglas Gage (MSU, Biochemistry).

Model aquifer column. As shown in Figure 2, a biologically active region of CT removal was sustained by weekly feeding pulses. By day 29, effluent CT concentration had fallen to approximately 1 µg/L, a CT removal efficiency of 98%. Experimental results from the physical model were compared with numerical simulations to confirm the numerical model's applicability or suggest the need for refinement. The numerical model was capable of simulating the activity of strain KC.

MPN data were consistent with information obtained from the gene probe. Samples taken from all 23 ports before KC injection showed no DNA bands. After injection at port 5, strain KC DNA was detected in ports 4-12 only. Sampling over each of the next 4 weeks showed strain KC movement to ports 14, 15, 18 and 22. This progressive spread of KC with the water flow path over time is consistent with the movement of strain KC as indicated by MPN results.

Factors affecting cell attachment and detachment. In order to assess the initial attachment of KC cells on subsurface solids during the injection stage, we measured the zeta potential of KC cells over the pH range expected in the field experiment (7.5-9). The results indicate a high net negative charge (-49 mV at pH 7.5 increasing to -61 mV at pH 9). Assuming that subsurface minerals will present a negative charge, this suggests that electrostatic repulsive forces will be important in predicting cell retention and placement in the Schoolcraft aquifer. However, over the anticipated operating pH range of 7-10, changes in cell surface charge are small. Therefore, pH fluctuations in the Schoolcraft aquifer will not significantly affect cell retention to subsurface materials.

CONCLUSIONS

1. A bioassay for the secreted factor was successfully developed and tested. The assay consisting of combining the sample to be assayed with *P. fluorescens* cells and with CT and monitoring the rate of CT disappearance.

2. Purification of the low molecular weight factor secreted by strain KC was accomplished by: filtration of supernatant through 0.2 µm, 10,000 MW, and 500 MW filters; acetone extraction; and HPLC separation.

3. A zone of CT transformation was sustained in the model aquifer by weekly pulsing of acetate. The bulk of the CT transformation occurs over a narrow region, close to the inoculation site.

4. The gene probe appears to sensitive, specific, and efficient for tracking strain KC in aquifer samples, and thus is ready for use in the field.

5. Strain KC was readily transported through the aquifer materials, glass beads, and sands tested to date. This is apparently due to repulsive forces between the cells and the solids. Strain KC cells have a high net negative charge.

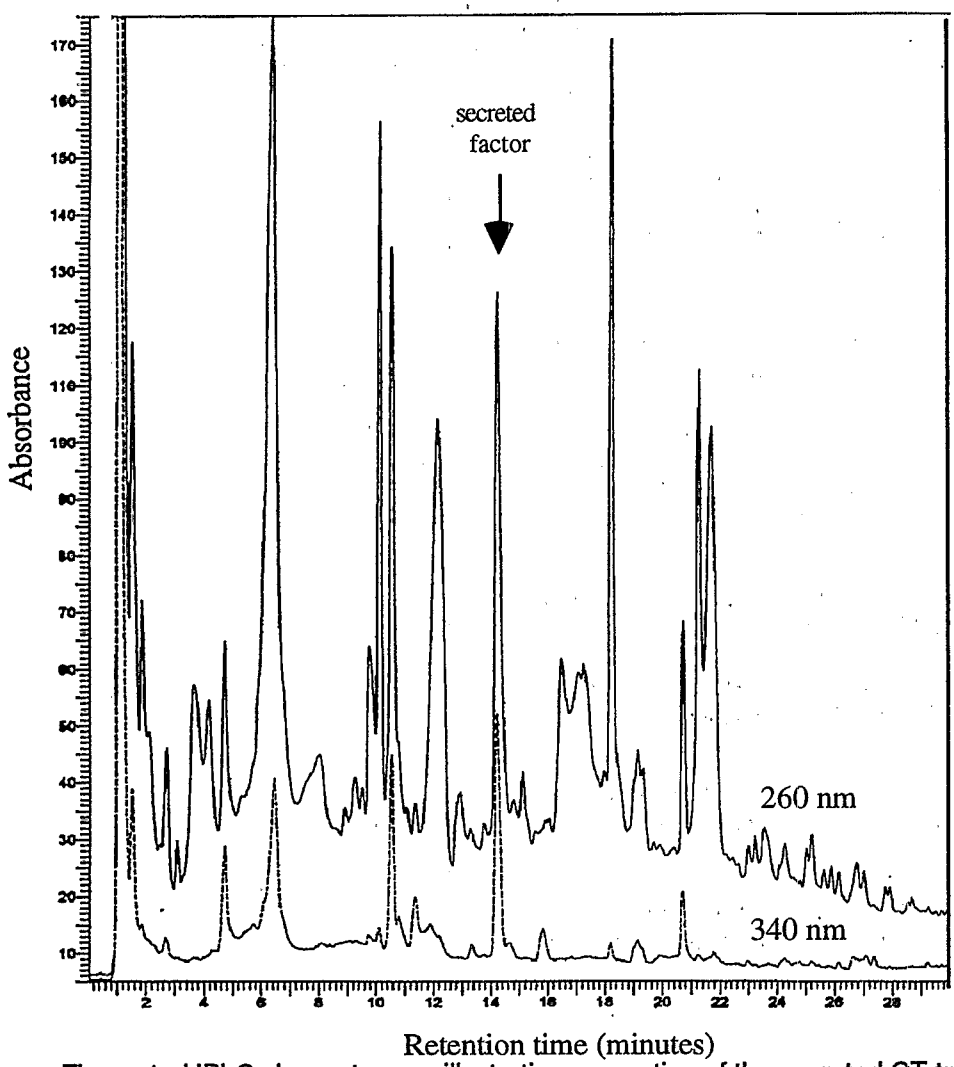


Figure 1. HPLC chromatogram illustrating separation of the secreted CT-transforming factor produced by *Pseudomonas* sp. strain KC.

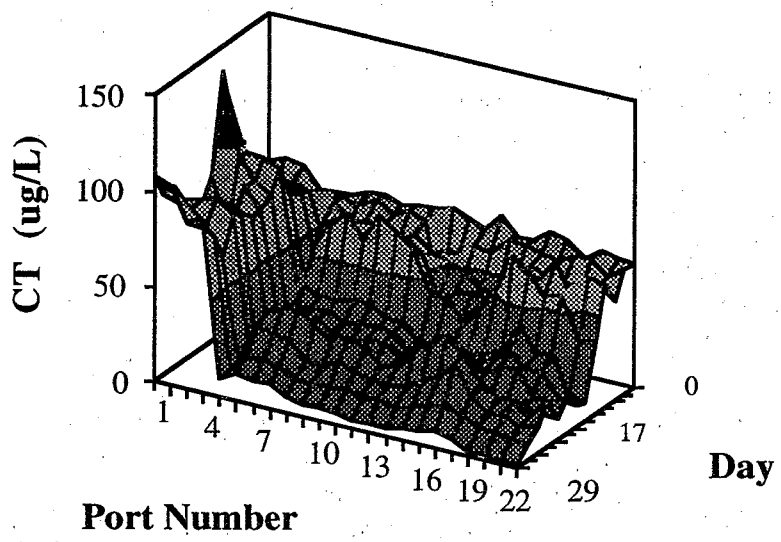


Figure 2. Carbon tetrachloride concentration profile for the model aquifer following inoculation. Acetate is provided once a week as a single pulse.

REFERENCES

1. Criddle, C.S., J.T. DeWitt, D. Grbrić-Galić, and P.L. McCarty. 1990. Transformation of carbon tetrachloride by *Pseudomonas* sp. strain KC under denitrifying conditions. *Appl. Environ. Microbiol.* 56:3240-3246.

2. Lewis, T. A., and R. L. Crawford. 1993. Physiological factors affecting carbon tetrachloride dehalogenation by the denitrifying bacterium *Pseudomonas* sp. strain KC. *Appl. Environ. Microbiol.* 59:1635-1641.

3. Dybas, M. , G. Tatara, and C. S. Criddle, 1995. Localization and characterization of the carbon tetrachloride transformation activity of *Pseudomonas* sp. strain KC. Accepted for publication in *Applied and Environmental Microbiology*

4. Tatara, G., M. Dybas, K. Jewison, and C. S. Criddle, 1995. Carbon tetrachloride transformation by a factor secreted by Pseudomonas sp. strain KC and activated by diverse cell types. Submitted for publication.

5. Tatara, G.M., M.J. Dybas, and C.S. Criddle. 1993. Effects of medium and trace metals on kinetics of carbon tetrachloride transformation by *Pseudomonas* sp. strain KC. *Appl. Environ. Microbiol.* 59:2126-2131.

FOR MORE INFORMATION: contact Dale Manty, Program Director, Hazardous Substance Research Centers Program, Office of Exploratory Research 8703.

REMEDIATING MUNITIONS CONTAMINATED SOILS

Patrick J. Shea and S.D. Comfort
Department of Agronomy
University of Nebraska
Lincoln, NE 68583-0915
402-472-1502

INTRODUCTION

The former Nebraska Ordnance Plant (NOP) at Mead, NE was a military loading, assembling, and packing facility that produced bombs, boosters and shells during World War II and the Korean War (1942-1945, 1950-1956). Ordnances were loaded with 2,4,6-trinitrotoluene (TNT), amatol (TNT and NH_4NO_3), tritonal (TNT and Al) and Composition B (hexahydro-1,3,5-trinitro-1,3,5-triazine [RDX], and TNT). Process waste waters were discharged into wash pits and drainage ditches. Soils within and surrounding these areas are contaminated with TNT, RDX and related compounds. A continuous core to 300 cm depth obtained from an NOP drainage ditch revealed high concentrations of TNT in the soil profile and substantial amounts of monoamino reduction products, 4-amino-2,6-dinitrotoluene (4ADNT) and 2-amino-4,6-dinitrotoluene (2ADNT). Surface soil contained TNT in excess of 5000 mg kg^{-1} and is believed to contain solid phase TNT. This is supported by measuring soil solution concentrations at various soil to solution ratios (1:2 to 1:9) and obtaining similar TNT concentrations (43 and 80 mg L^{-1}).

Remediating munitions-contaminated soil at the NOP and elsewhere is of vital interest since many of the contaminants are carcinogenic, mutagenic or otherwise toxic to humans and the environment. Incineration, the most demonstrated remediation technology for munitions-containing soils, is costly and often unacceptable to the public. Chemical and biological remediation offer potentially cost-effective and more environmentally acceptable alternatives. Our research objectives are to: (a) characterize the processes affecting the transport and fate of munitions in highly contaminated soil; (b) identify effective chemical and biological treatments to degrade and detoxify residues; and (c) integrate these approaches for effective and practical remediation of soil contaminated with TNT, RDX, and other munitions residues.

METHODOLOGY

Transport and Sorption. Transport experiments were conducted with repacked, unsaturated soil columns comprised of either uncontaminated soil or a contaminated soil layer over uncontaminated soil. A constant pore water velocity was established in the columns and used to pass multiple pore volumes of a solution pulse containing 6.3 or 70 mg TNT L^{-1} in 3 m*M* $CaCl_2$ spiked with ^3H_2O. After conditioning, multiple pore volumes of TNT were pulsed onto the top of the columns by a syringe pump and displaced through the soil with 3 m*M* $CaCl_2$. After the TNT pulse was eluted from the columns, the experiment was terminated and collection tubes were weighed to determine the volume collected as a function of time and pore volumes. Effluent was analyzed for TNT, 2ADNT, and 4ADNT by HPLC. Relative concentrations (C/C_o) were calculated from the ^3H_2O and TNT concentrations (C) in the effluent fractions and the initial concentrations (C_o) of the TNT pulse.

TNT sorption to soil was determined by batch equilibration using 5 g of Sharpsburg silty clay loam soil and 15 mL TNT solution (1:3 soil:solution ratio) at initial concentrations ranging from 3.53 to 61.81 mg L^{-1} in 3 m*M* $CaCl_2$. Solutions were shaken for 24 h in 35-mL teflon centrifuge tubes and centrifuged (3450 *x g*) at room temperature for 30 min. Supernatant was filtered and analyzed by HPLC. The difference between soil-free blanks and equilibrium solutions was assumed to be the result of adsorption. Adsorption was described by a linear isotherm and by the Freundlich equation ($Q = KC^{1/n}$, where Q = amount adsorbed per gram adsorbent, C is the equilibrium TNT concentration, K is the distribution coefficient and 1/n is a constant).

Long-term TNT sorption and bound residue formation were determined by batch equilibration, following a similar procedure, but using a TNT solution spiked with ^{14}C-ring labeled TNT. Soil solutions were agitated at room temperature for 0, 7, 14, 28, 84, and 168 d. At the end of each equilibration period, supernatant was analyzed for TNT and degradates by HPLC and ^{14}C-activity by scintillation counting. The soil was extracted with acetonitrile to determine available TNT. Humic and fulvic acid fractions were extracted from the soil with 0.5 *N* NaOH and separated by precipitation with 1 *N* H_2SO_4. ^{14}C-activity in the fractions was determined by scintillation counting. The remaining soil was extracted with hexane-propanol and supernatant was analyzed. The residual soil was oxidized to $^{14}CO_2$; liberated ^{14}C was termed bound residue. Alkali and acid hydrolyzable residue were determined by sonication with 10% KOH in ethanol and 1 *M* HCl-ethanol.

Microbial Transformation. A species isolated from munitions-contaminated NOP soil, *Pseudomonas savastanoi*, was grown on Pseudomonas minimal media (PMM), transferred to sterile centrifuge tubes and centrifuged to separate cell mass from media. Cellular pellets were washed with saline solution and resuspended in PMM containing 70 mg (^{14}C-labeled) TNT L^{-1}. The suspensions were placed in reaction flasks, kept in the dark and agitated in an enclosed water bath at 30°C. The headspace of each flask was continuously flushed with CO_2-free air and sequentially swept through a volatile trap and CO_2 trap. Traps were changed every 24 h and total ^{14}C activity determined by scintillation counting. At the end of the experiment, total ^{14}C activity was determined, cellular pellets were fractionated, and supernatant was analyzed by HPLC with radioisotope detection. Nitrate and nitrite concentrations were determined.

Abiotic Oxidation and Reduction. Fenton oxidation of TNT was performed in aqueous solutions of TNT, aqueous washings of contaminated soil, and soil-slurry mixtures. Reactions were either performed in the dark or in conjunction with incandescent or UV light. The Fenton reagent consisted of 1% H_2O_2 and 80 mg Fe^{2+} L^{-1}. TNT solutions were prepared from technical grade TNT in distilled deionized water and fortified with ^{14}C-TNT. Initial TNT concentration was 70 mg L^{-1} and reaction solutions were adjusted to pH 3 with 0.5 *N* H_2SO_4. The reaction was initiated by adding one mL of 4000 mg Fe^{2+} L^{-1} and 1.75 ml 30% H_2O_2 to 47.25 mL TNT solution. The flasks were agitated in the dark, periodically subsampled for analysis by HPLC and scintillation counting. Aqueous extracts of soil were prepared by mixing 20 g soil with 60 mL water (1:3) and shaking for 2 d. The solution was centrifuged, supernatant removed, adjusted to pH 3 and fortified with ^{14}C-TNT. Contaminated soil was collected from the upper 5 cm of the soil profile in a drainage ditch adjacent to a munitions production building at the NOP site. Light-mediated experiments utilized an incandescent lamp (emission spectrum of 400-1000 nm, relative intensity less than 4% of full sun spectral radiation), or UV light chamber (254 nm, 12.8 mwatts cm^{-1}). Fenton oxidation was similarly used to treat water and soil solution containing RDX.

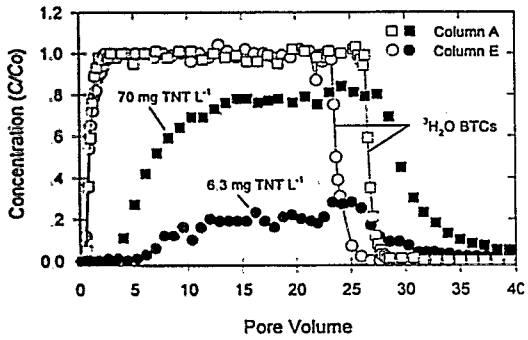
The feasibility of increasing TNT mineralization by chemically reducing the nitro-moieties was investigated. Reduced TNT was prepared by acidifying an 80 mg L^{-1} TNT solution and passing through a column of Zn metal. TNT and the products of acid-metal treatment were added to 50 g of munitions contaminated soil and incubated at 30°C. Head spaces were continuously swept with CO_2 free air and bubbled into CO_2 traps. Zn metal also was used to induce RDX transformation in acidified water and soil solution.

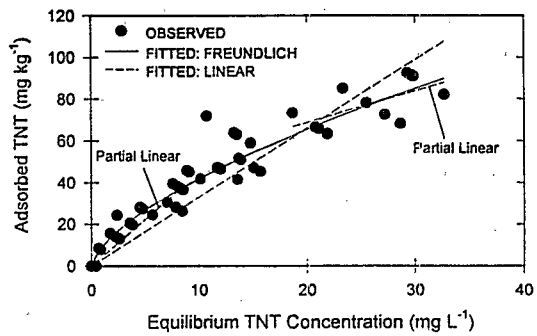
Soil Washing and Plant Growth. The effects of TNT concentrations on germination and seed vigor were determined. Solutions of 0, 7.5, 15, 30, 45, and 60 mg TNT L^{-1} were prepared, mixed with agar, and poured into plastic petri dishes. Tall fescue (*Festuca arundinacea* Schreb, cv. Rebel Jr.) seeds were surface sterilized in 5% hyperchlorite solution and rinsed with sterilized deionized distilled water. Seeds were sown onto the TNT-agar media at 10 seeds per plate and placed in a germinator. Daily germination counts were made; every third day root and shoot length were measured. Seed respiration also was measured.

We determine whether soil washing could be combined with an abiotic treatment and phytoremediation for an effective treatment train of TNT contaminated soil. One part contaminated soil was mixed with five parts water and shaken for 24 h. The solution was then removed, TNT concentration was determined, and the washed soil was extracted with acetonitrile. The process was repeated after two, three, four and five soil washes. Tall fescue was seeded in the contaminated soil after each washing and percent germination determined.

RESULTS

Transport and Sorption. TNT breakthrough curves (BTCs) never reached initial solute pulse concentrations (Fig. 1). Apex concentrations were between 0.6 and 0.8 for an initial pulse of 70 mg L^{-1} and 0.2 to 0.3 for a solute pulse of 6.3 mg L^{-1}. TNT mobility was affected by TNT pulse concentration with an earlier breakthrough observed at the higher concentration. The mobility difference was predicted from the nonlinear adsorption isotherm determined for TNT sorption (Fig. 2). In all experiments a significant fraction of added TNT was recovered as 2ADNT and 4ADNT. A higher percentage of amino degradates was eluted from soil columns receiving the 6.3 mg TNT L^{-1} pulse. Mass balance estimates indicated 81% of the added TNT was recovered (as TNT and amino degradates) from columns receiving the 70 mg TNT L^{-1} pulse compared to 35% from columns receiving the 6.3 mg TNT L^{-1} pulse. Most of the unaccountable TNT was hypothesized to be unextractable. This was supported by a 168-d sorption experiment, in which 80% of ^{14}C added (as ^{14}C-TNT) was adsorbed and approximately 40% was unextractable. These data indicate TNT sorption and degradation are concentration-dependent and the assumptions of linear adsorption and adsorption-desorption singularity commonly used in transport modeling may not be valid for predicting TNT transport in highly contaminated soils.





Figures 1 and 2.

Microbial Transformation. Loss of TNT and $^{14}CO_2$ evolution indicated that *Pseudomonas savastanoi* has the capacity to degrade and partially mineralize TNT (Fig.3). Liberation of NO_2 and NO_3 into solution suggests the ability of the organism to denitrate TNT. While a high rate of $^{14}CO_2$ evolution was not sustained, reinoculation of the TNT solution produced another burst of CO_2. Addition of killed cells did not produce a CO_2 burst, as would be expected if co-metabolism was occurring. The decline in CO_2 production may be due to toxicity at high TNT concentration in the media.

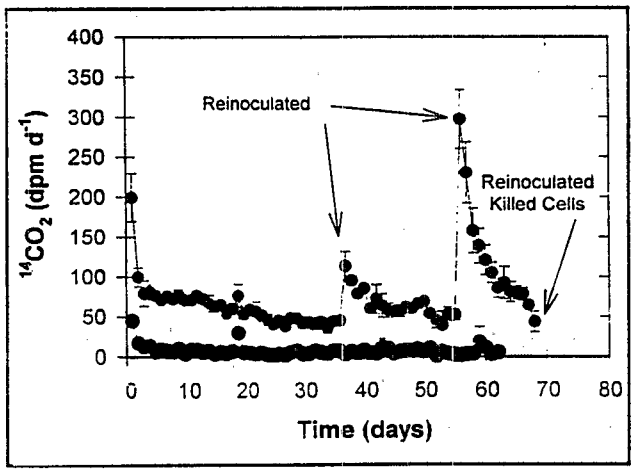


Figure 3.

Abiotic Oxidation and Reduction. When 70 mg TNT L^{-1} was treated with Fenton reagent (1% H_2O_2, 80 mg Fe^{2+} L^{-1}) and agitated in the dark, complete (100%) destruction of TNT was achieved within 24 h (Fig. 4). This coincided with partial ^{14}C-TNT mineralization (40-60%). Subsequent photolysis of the remaining ^{14}C in solution resulted in near complete mineralization (95-100%). Fenton oxidation of aqueous extracts of contaminated soil required higher H_2O_2 and Fe^{2+} concentrations to maintain TNT transformation and mineralization efficiencies similar to those observed in pure aqueous solutions. TNT destruction occurs by free radical attack with removal of $-NO_2$ moieties and production of a number of hydroxylated intermediates. Oxalic acid was identified as the main end product of TNT oxidation when the Fenton reaction occurred in the dark. In the Fenton reaction system, Fe^{3+} would complex with oxalate ligands to form Fe(III)-oxalato complexes which decompose rapidly on exposure to visible light (400-700 nm). Trinitrobenzene, picric acid, 2,4-dinitrophenol, 4-nitrophenol, and 2-nitrophenol were identified as some of the reaction intermediates in Fenton oxidation of TNT. Fenton oxidation similarly removed RDX from soil solution, producing formic acid as the oxidation product.

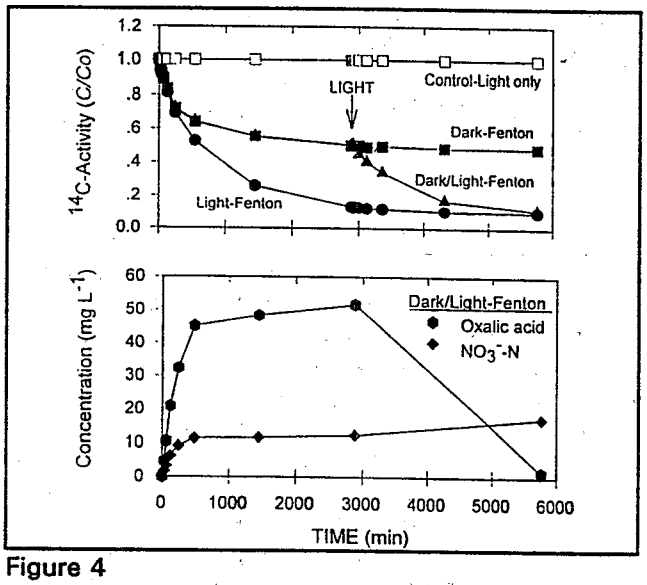


Figure 4

Reduced TNT was over ten times more prone to mineralization than untreated TNT (Fig. 5), and a much larger proportion of treated TNT ended up as bound, unextractable residue. Addition of Zn metal to a soil-water slurry containing RDX at pH 5 resulted in complete destruction of the RDX. While our experiments have primarily utilized Zn, it appears that Fe may be used as the catalytic agent for the reductions.

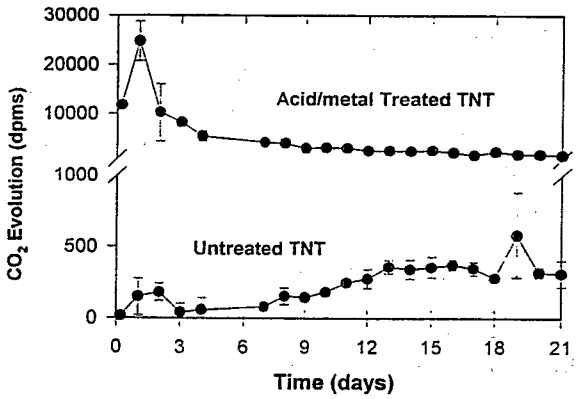


Figure 5.

Soil Washing and Plant Growth. A contaminated soil with approximately 500 mg acetonitrile-extractable TNT kg^{-1} required four to five washes before it was within the range of the preliminary remediation goal of 17.2 mg kg^{-1} (Fig. 6). However, near complete TNT mineralization was achieved by treating the wash water by Fenton oxidation. Since considerable volumes of water would be needed to reach the remediation goal, an alternative would be to wash the soil once, thus lowering the concentration, return the soil to the site and use plants to remediate the remaining contamination. No significant effect of TNT on Tall Fescue seed respiration, germination, or seedling

growth was observed at a concentration of 10 mg L^{-1} or lower. We also found that 4ADNT was less toxic to the grass than TNT. The soil washing data indicate that this level of contamination could be achieved after one or two washings. Tall fescue germination and seedling growth were not significantly affected after planting in contaminated NOP soil after one washing.

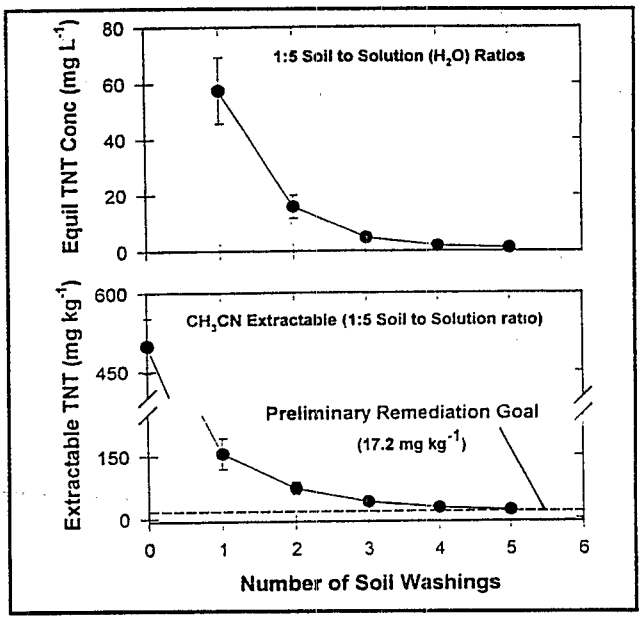


Figure 6.

CONCLUSIONS

Our experiments indicate that soil has a high potential to dissipate TNT once particulate TNT is removed. When a solution containing 70 mg radiolabeled TNT L^{-1} was added to uncontaminated soil, roughly 80% of the radiolabel was adsorbed within 24 h, and half of this fraction was unextractable by organic solvents, acid and alkali. Within 7 d after application, the amount of TNT extractable from soil was below the preliminary remediation goal of 17.2 mg kg^{-1}. TNT amino degradation products are readily produced and may form bound residues in soil via condensation reactions. This represents a permanent detoxification of TNT residues, which in our studies were not extractable with organic solvent, acid or alkali.

We have demonstrated that microorganisms present in the NOP soil can tolerate TNT and have the potential to utilize them as sources of carbon or nitrogen. Respiration experiments showed the flux of CO_2 emission resembled that of a growth curve and suggested a lag period may be required to build up sufficient degradate pools for carbon flux through microbial metabolism.

Where particulate or solid phase TNT is present, chemical pretreatment may be used to rapidly transform the TNT into more biodegradable and environmentally benign products. Fenton oxidation (treatment with H_2O_2 and Fe^{2+}) of TNT solution resulted in loss of TNT within 8 h and 40-50% mineralization within 24 h. RDX loss was more rapid than TNT. Oxalic acid and other oxidation products were readily photodegraded. Acid/metal treatment of TNT solution efficiently reduced TNT, probably to triaminotoluene (TAT), which is readily hydrolyzed in water to trihydroxytoluene. Addition of the products produced from the acid/metal treatment of TNT to soil resulted in rapid CO_2 evolution, indicating more biodegradable products were formed. Fenton oxidation and acid-metal reduction products were more strongly sorbed to soil than TNT, the majority of which were unextractable.

Tall fescue, already growing in some areas at the NOP site, along with other grass and broadleaf species, may be used to contain the residues by maintaining high evapotranspiration and remediate through the biologically active rhizosphere. Our studies provide guidance for the design and implementation of remediation protocols. Knowledge obtained from this work can be used to construct an efficient treatment-train for highly contaminated soil, or optimally manage marginally contaminated soil *in situ*.

RISK REDUCTION THROUGH WASTE MINIMIZING PROCESS SYNTHESIS

J. B. Varga[2], F. Friedler[1,2,3], and L. T. Fan[1]
[1]Department of Chemical Engineering, Kansas State University
Manhattan, KS 66506, Phone: (913)-532-5584
[2]Department of Computer Science, University of Veszprém, Veszprém, H-8200, Hungary
[3]Department of Systems Engineering, Research Institute of Chemical Engineering
Hungarian Academy of Sciences, Veszprém, Pf. 125, H-8201, Hungary

INTRODUCTION

Various approaches are available for minimizing the generation of waste in a process system. They include source reduction, recycling, waste separation, waste concentration, and waste exchange at the highest level of U.S. EPA's waste reduction hierarchy (1). All of these approaches, however, depend primarily on the structure of the process. For instance, various processes may need different waste treatment systems even if they generate the same product. Similarly, the risk depends on the structure of the process. Thus, the design of facilities for waste minimization and risk reduction can not be isolated from that of the process for product generation as often done conventionally. All the steps of process design and waste minimization and risk reduction should be integrated into one consistent method. The integration, however, renders the already complex tasks involved in process synthesis exceedingly cumbersome. A highly efficient and mathematically rigorous technique is indeed required to overcome this difficulty. The present work aims at establishing such a technique.

METHODOLOGY

Conventional graphs are suitable for analyzing a process structure (2). Nevertheless, Friedler *et al.* (3) have demonstrated that such graphs are incapable of uniquely representing process structures in synthesis. Thus, a special directed bipartite graph, a process graph or P-graph in short, has been conceived to circumvent this difficulty.

Operating units are usually represented on a process flowsheet by figures of various configurations; however, such configurations are inconsequential for mathematical analysis. In a P-graph, an operating unit is represented by a horizontal bar, and a material, by a circle. If a material is an input to an operating unit, the vertex representing this material is connected by an arc to the vertex representing the operating unit. Similarly, if a material is an output from an operating unit, the vertex representing this operating unit is connected by an arc to the vertex representing the material. The conventional and P-graph representations of a reactor and a distillation column are given in Figure 1. Obviously, a P-graph is bipartite since its vertices are partitioned into two sets, and no two vertices are adjacent in the graph.

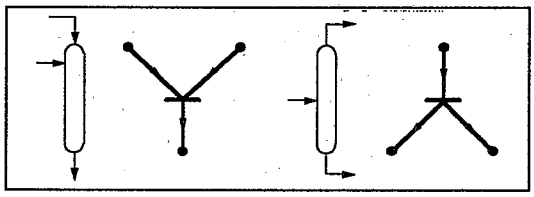


Figure 1. Conventional and P-graph representations of a reactor and a distillation column.

In our P-graph based method of process synthesis (4), all materials in the process being synthesized are divided into five disjoint classes; these classes are raw materials, required products, potential products, disposable materials, and intermediates. A *raw material* is available as feed to the process

Correspondence concerning this paper should be addressed to L. T. Fan.

being synthesized; a *required product* is to be produced from the process; a *potential product* can be produced, if profitable to do so; a *disposable material* can be safely discharged to the environment or marketed as a by-product; and an intermediate need be fed to some operating units of the process, if produced.

Similar to the potential product, the production of the disposal material is not mandated. The disposable material can only be produced by those operating units, each of which is essential for generating a product or treating an undesirable output from the process. Although it is not always necessary to do so, a raw material, a required product, a potential product, or a disposable material can be fed to some operating units. Production of an *intermediate* is similar to that of a disposable material; nevertheless, unlike the disposed material, the intermediate must be fed to some operating units for treatment or consumption. The intermediate would be a waste which may induce detrimental effects if it is discharged to the environment. Obviously, it need be treated or consumed within the process. Specific symbols are assigned to the different classes of materials in their graphical representations; see Figure 2. For illustration, a process yielding product H, potential product G, and disposable material D, from raw materials A, B, and C by operating units 1, 2, and 3 is given in Figure 3.

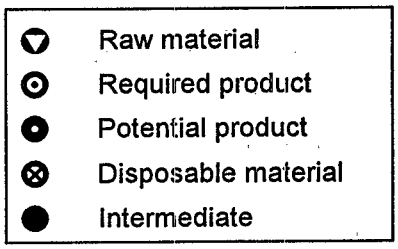


Figure 2. Graphical representation of the five classes of materials on a P-graph.

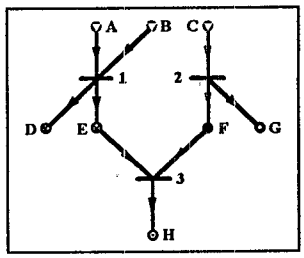


Figure 3. P-graph of the process manufacturing required product H and also yielding potential product G and disposable material D from raw materials A, B, and C.

In the conventional synthesis of a process, the design for the product generation and that for the waste minimization or treatment are performed separately, as mentioned earlier. This frequently yields a locally optimum process. Let us now integrate these two design steps into a single method for process synthesis.

Our method is rigorously founded on an axiom system, describing the self-evident fundamental properties of combinatorially feasible process structures, and combinatorics (4, 5, 6).

A set of six axioms, axioms (SW1 through SW6), of process synthesis for integrated in-plant waste treatment is given in Friedler *et al.* (7). For example, axiom (SW6) states the following: If a material is not consumed by any operating unit, it must be a product or disposable material.

Example 1. Suppose that operating units given in Figure 4 are available for producing required product P1 and potential product P2 from raw materials R1, R2, R3, and R4. Moreover, the only other materials allowed to be produced are disposable materials.

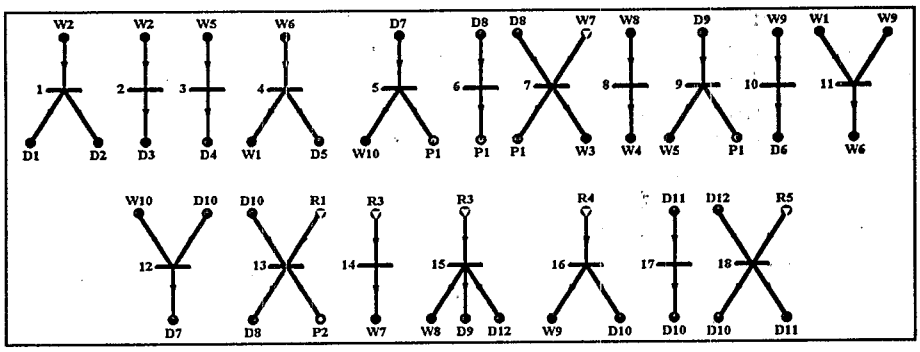


Figure 4. Operating units of Example 1.

Note that some of the operating units given in Figure 4 are excluded from all the combinatorially feasible structures. In other words, it is unnecessary to include them in the problem definition; examples are operating units 3, 7, and 8. This, however, can not be known a priori.

In this truly integrated approach which is based on our accelerated branch-and-bound algorithm (8), the product generation and waste treatment are considered simultaneously in synthesizing the process; therefore, in theory, the optimal structure can be generated. The enumeration tree is given in Figure 5 for the worst case. The cost-optimal structure corresponds to node #14, and it consists of operating units 2, 8, 9, 10, 15, 20, 25 and 26, as shown in Figure 6. It should be noted that risk is yet to be considered in this version of our method for process synthesis.

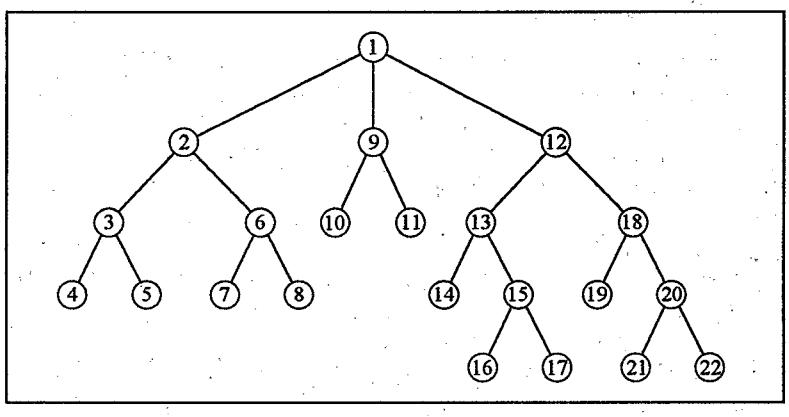


Figure 5. Enumeration tree of the accelerated branch-and-bound search for the optimal structure of the process with integrated in-plant waste treatment: the worst case.

RESULTS

Integration of Process Synthesis Incorporating In-plant Waste Treatment and Risk Reduction

The same product or products can be manufactured by various structurally different processes, each of which may generate disposable materials besides the product or products. Frequently, materials participating in these structurally different processes pose varying degrees of risk. Moreover, even if a material produced by any process can be safely disposed in an environmentally benign manner, the risk associated with it is not always negligible.

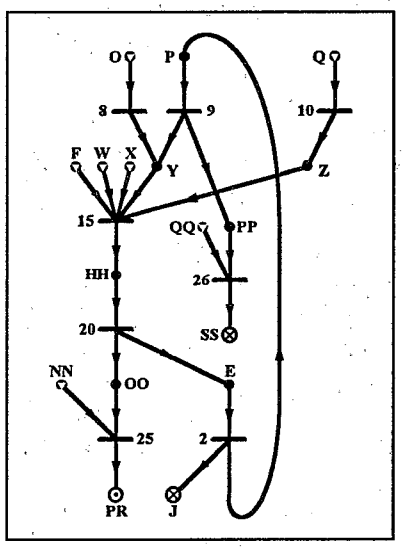


Figure 6. Structure of the optimally synthesized process integrating in-plant waste treatment but without consideration of risk.

Every material participating in a process to be synthesized possesses risks varying in magnitude, such as the potential for pollution, the hazard of explosion and the toxicity to human-life. This can readily be envisioned even for the simplest group of materials, e.g., hydrogen, ammonia and benzene. These materials widely serve as raw materials, frequently appear as intermediates or often are manufactured as final products in a variety of chemical processes. Obviously, various risks associated with different materials can generally be reduced with additional expenditure for designing and constructing the process. The extent of reduction, however, depends heavily on the complex interplay among the factors to be taken into account in synthesizing the process, which may be economic, environmental, toxicological or health-related. Moreover, the dichotomy between any pair of such factors tends to be extremely fuzzy. Nevertheless, for convenience, the present approach views that a process can be optimally synthesized by simultaneously taking into account only three factors, i.e., (i) cost; (ii) waste generation; and (iii) risk posed by the participating materials. Specifically, the first factor, cost, is defined as the objective function to be minimized subject to the additional constraints on both the second and third factors.

Two types of risk indices are introduced: (a) internal risk index associated with a material consumed within the process, e.g., a raw material or intermediate; (b) external risk index associated with a material discharged to the environment, e.g., a disposable material. Both risk indices are defined on the basis of unit amount of material.

The overall risk of a process is determined as the sum of the risks of all materials participating in the process. The risk of each material is obtained as the sum of its internal and external risks, each of which in turn, is obtained by multiplying the amount of the material and the corresponding risk index. A material may have both internal and external risks if it is partially consumed in a process as a recycled material and is also discharged to the environment as a disposable material.

The branch-and-bound algorithm of process synthesis incorporating integrated in-plant waste treatment has been extended to include the consideration of risk. This algorithm generates the cost optimal solution of synthesis problem, satisfying the constraints on both waste generation and risk.

Example 1 revisited for risk consideration. The enumeration tree of branch-and-bound algorithm remains the same for the worst case; see Figure 5. The optimal solution with the integrated in-plant waste treatment, resulting from the subproblem corresponding to node #14, does not satisfy the constraint on risk; instead, subproblem corresponding to node #17 gives rise to the optimal solution of the problem. Although the cost of this solution is higher than that obtained from the subproblem corresponding to node #14, it has the minimal cost among the solutions satisfying the constraint on risk; the resultant structure is given in Figure 7.

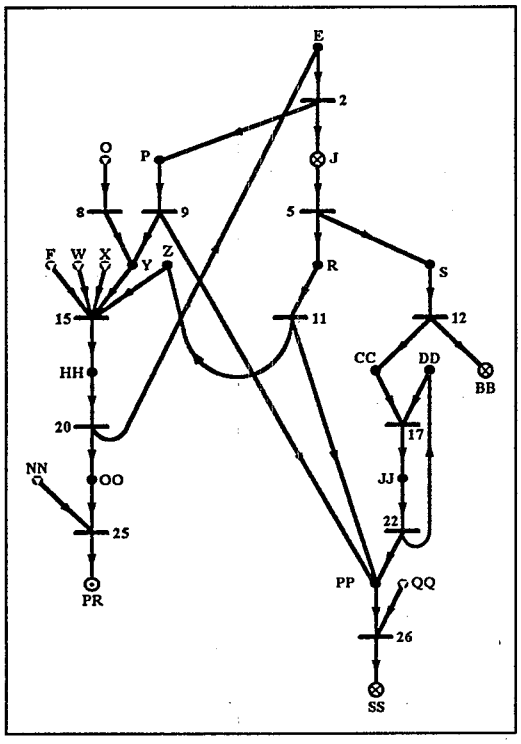


Figure 7. Structure of the optimally synthesized process integrating in-plant waste treatment and risk consideration.

CONCLUSIONS

By defining a risk index, our method for synthesizing an optimal process with integrated in-plant waste treatment capability has been extended to the synthesis of a cost-optimal process structure satisfying the constraints on both waste generation and risk. It has been demonstrated with an industrial process synthesis problem that the process' optimal structure synthesized by taking into account risk can be substantially different from that by disregarding it.

ACKNOWLEDGMENTS

Although the research described in this article has been funded in part by the United States Environmental Protection Agency under assistance agreement R-819653 to the Great Plains-Rocky Mountain Hazardous Substance Research Center for U.S. EPA Regions 7 and 8 with headquarters at Kansas State University, it has not been subjected to the Agency's peer and administrative review and, therefore, may not necessarily reflect the views of the Agency. No official endorsement should be inferred. This research was also partially supported by the Kansas State University Center for Hazardous Substance Research. This research was partially supported by the Hungarian Ministry of Education Grant No. 167/94.

REFERENCES

1. Rittmeyer, R. W. Prepare an Effective Pollution-Prevention Program. *Chemical Engineering Progress* **87**, 56-62, 1991.

2. Mah, R. S. H., Chemical Process Structures and Information Flows. Butterworths, Stoneham, MA, 1990.

3. Friedler, F., Tarjan, K., Huang, Y. W., and Fan, L. T. Combinatorial Algorithms for Process Synthesis. ESCAPE-1 Conference, Elsinore, Denmark, May 24-28, 1992; *Computers chem. Engng* **16**, S313-20, 1992a.

4. Friedler, F., Tarjan, K., Huang, Y. W., and Fan, L. T. Graph-Theoretic Approach to Process Synthesis: Axioms and Theorems. *Chem. Eng. Sci.* **47**, 1973-1988, 1992b.

5. Friedler, F., Tarjan, K., Huang, Y. W., and Fan, L. T. Graph-Theoretic Approach to Process Synthesis: Application to Waste Minimization. *In*: Proceedings of the 5th Conference on Hazardous Waste Research. Kansas State University, Manhattan, KS, U.S.A., May 21-22 1990. **2**, 877-892.

6. Friedler, F., Tarjan, K., Huang, Y. W., and Fan, L. T. Graph-Theoretic Approach to Process Synthesis: Polynomial Algorithm for Maximal Structure Generation. *Computers chem. Engng* **17**, 929-942, 1993b.

7. Friedler, F., Varga, J. B., and Fan, L. T. Algorithmic Approach to the Integration of Total Flowsheet Synthesis and Waste Minimization. Submitted for publication in the AIChE Symposium Series on Pollution Prevention Through Process and Product Modifications, 1995.

8. Friedler, F. and Fan, L. T. Reduction of Subproblem Size for the Accelerated Branch and Bound Method of Process Synthesis. AIChE National Meeting, Houston, TX, U.S.A., March 28-April 1, 1993a.

PREPARED BED REACTOR FOR FULL SCALE REMEDIATION OF SOIL CONTAMINATED WITH WOOD PRESERVING WASTES: FIELD BIOREMEDIATION EVALUATION

Ronald C. Sims, Judith L. Sims, Darwin L. Sorensen, and Joan E. McLean
Division of Environmental Engineering and Utah Water Research Laboratory
Utah State University, Logan, UT 84322-4110
Telephone No. (801) 797-2926
and Scott G. Huling
U.S. Environmental Protection Agency, Ada, OK 74820
Telephone No. (405) 436-8610

INTRODUCTION

The Champion International Superfund Site, a former wood perserving site in Libby, Montana, was nominated by the Robert S. Kerr Environmental Research Laboratory (RSKERL), Ada, OK, as a candidate site for bioremediation performance evaluation under the Bioremediation Field Initiative (BFI) sponsored by the U.S. Environmental Protection Agency (U.S. EPA). The Initiative was designed to address the need for additional field experience concerning the implementation of bioremediation techniques, including the collection and dissemination of performance data from field experiences.Target chemicals for bioremediation at the Libby Site included the polycyclic aromatic hydrocarbons (PAH) naphthalene, phenanthrene, and pyrene

The field performance evaluation was designed and conducted by Utah State University (USU) with support from the U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, to provide information on the effectiveness of bioremediation in addition to the information generated by Champion International personnel as part of regulatory monitoring requirements. Champion International, agreed to cooperate with the RSKERL and USU in conducting the proposed bioremediation performance evaluation studies for biological treatment processes in operation at the Libby Site.

The Libby Site uses three distinct biological processes in the site remediation scenario: (1) surface soil biological treatment in a prepared bed system,consisting of two lined land treatment units, liners, and leachate collection; (2) extraction of ground water, followed by aqueous phase treatment in an above-grade, fixed-film bioreactor; and (3) *in situ* bioremediation of the Upper Aquifer . Results of the evaluation of bioremediation in the prepared bed system are presented in this paper.

Contaminated soils were located in three primary source areas at the Libby Site: a former tank farm, an unlined butt dip area, and an unlined waste pit. In 1989, contaminated soils from these three areas (approximately 75,000 cubic yards of materials) were excavated down to the water table. Before the tank farm and butt dip areas were filled with clean soil, samples were collected and analyzed to verify that contamination had been removed.

Since the major contaminants of concern were expected to be associated with finer-grained materials, the soils excavated from the tank farm and butt dip areas and any previously excavated contaminated materials from the waste pit area were physically screened to remove rocks larger than one inch in diameter (referred as de-rocking). The screened soils from all three areas (approximately 45,000 cubic yards) were placed in the excavated waste pit area. The separated rocks were placed upgradient to the waste pit area to construct sub-grade infiltration galleries. This rock percolation bed is used for biological treatment of the contaminated rocks using effluents from the above grade, fixed-film bioreactor.

After a lift of contaminated soil is treated to target remediation levels in the prepared bed system, another lift of contaminated soil is added and treated until target remediation levels are obtained. Target

chemicals for bioremediation at the Libby Site include three polycyclic aromatic hydrocarbon (PAH) compounds, naphthalene, phenanthrene, and pyrene, total carcinogenic PAH compounds (TCPAH), and pentachlorophenol (PCP). Target remediation levels for soil treated in the two LTU cells at the site are: naphthalene, 8.0 mg/kg; phenanthrene, 8.0 mg/kg; pyrene, 7.3 mg/kg, total carcinogenic PAH compounds, 88 mg/kg; and PCP, 37 mg/kg as specified in the Record of Decision (ROD).

Objectives of the evaluation of bioremediation in the prepared bed system were to: (1) describe and summarize previous and current remediation activities; (2) develop an approach to the evaluation of the prepared bed; (3) conduct a comprehensive field evaluation to assess performance of the unit in terms of treatment effectiveness, treatment rate, and detoxification of contaminated soil; and (4) perform a laboratory evaluation using field samples to determine indigenous soil microbial potential to accomplish bioremediation of target chemicals in the soil matrix under site conditions of temperature and soil moisture.

METHODOLOGY

Three-dimensional sampling of the two full-scale LTU cells was conducted over a two-year period. Analyses of over 300 soil samples were conducted, from which greater than 4,000 individual chemical concentrations were determined for 16 U.S. EPA priority pollutant PAH compounds using gas chromatography/mass spectrometry (GC/MS) and for PCP using gas chromatography/electron capture detector (GC/ECD). The field performance evaluation was based upon results obtained with regard to: (1) soil chemical concentrations compared with target remediation levels for target chemicals; (2) evaluation of downward migration of target chemicals as a result of the application of additional lifts; (3) detoxification of contaminated soil using bioassays; and (4) a laboratory evaluation for confirmation of indigenous soil microbial metabolic potential to biodegrade the target chemicals.

A chemical mass balance approach (1) was used to focus the evaluation of bioremediation at the Libby Site. Field-scale sampling and analysis were used in conjunction with a laboratory evaluation to provide complementary information for assessing the extent and rate of bioremediation and therefore, the effectiveness of bioremediation at the site. Specifically, a field-scale mass balance evaluation approach was used to develop information that could be used to eliminate the possibility of escape of target chemicals in air, water, and soil phases as a cause of disappearance of PAH compounds and PCP from the LTU cells. This was accomplished by evaluating the tendency of target chemicals to be associated with each phase and by identifying the containment of each phase within an LTU. The laboratory-scale mass balance approach was used to provide direct information concerning the biological degradation (mineralization) of target chemicals in the site soil, and the influence of site environmental and management factors on the extent and rate of bioremediation.

The field-scale methodology used for data collection and evaluation of soil remediation consisted of four activities (1): (1) site characterization, (2) assessment of the problem, (3) evaluation of the treatment (train) selected, and (4) monitoring treatment performance.

The first step involved characterizing the chemical/soil/site interactions to address the question "Where is the contamination and in what form(s) does it exist?" The target contaminants, PAH compounds and PCP, originally contaminated the soil as part of an oily matrix currently present in a residual saturation phase. The target chemicals are strongly associated with the soil (sorbed residual saturation of total petroleum hydrocarbons and soil solid phase), with the exception of naphthalene. Naphthalene was present in low concentrations in contaminated soil applied to the LTU cells, generally below the target remediation level (8.0 mg/kg), and therefore did not present a problem with regard to volatilization. The remaining target PAH compounds and PCP are only slightly soluble in water, are non-volatile, and are strongly associated with the soil/oil matrix (log K_{ow} and log K_d values greater than 4.0). Therefore, the focus of this investigation was on the soil solid/oil sorbed phase.

The second step addressed the question "Where is the contamination going under the influence of natural processes?" The target PAH compounds and PCP will remain associated with the residual oily saturation in the soil and with the soil solid phases within each LTU cell. Each lift of contaminated soil was applied on the top of each LTU cell, thus providing potential for downward migration of PAH compounds in an oily/water phase (leachate) within the LTU cells. This downward migration was identified as a potential escape process from the top lift that could be misinterpreted as bioremediation. Therefore, to determine if downward migration of target chemicals was occurring, the soil was sampled through depth at each sampling event in order to determine if the concentration of PAH compounds within previously treated and buried soil increased with time.

The third step was the evaluation of the treatment train used for remediation of the contaminated soil at the Libby Site. This treatment train consists of containment of contaminated soil in the lined LTU cells, with provisions for leachate collection, and followed by long-term bioremediation of sorbed contaminants. Berms provide effective containment of the soil phase, and the leachate collection system provides effective containment of the water phase within the LTU cells. Therefore, changes in concentrations of target chemicals within the LTU could be attributed to changes occurring within the LTU cells and the possibility of escape of target chemicals from the system through phase transport, including air, water, and soil phases, could be eliminated.

Finally, a monitoring strategy for determining the extent and rate of degradation was developed for the soil solid phase that consisted of taking discrete samples through depth and through time. With regard to interpretation of results in the context of bioremediation, this monitoring strategy was supported with a laboratory mass balance evaluation using site soil spiked with radiolabeled PCP and phenanthrene. Results of three-dimensional field sampling for determination of the decrease in target chemical concentration within each LTU cell and laboratory determination of biological mineralization were used to evaluate the effectiveness of bioremediation.

The objective of the methodology for the location of sample site collection points was to develop a random systematic sampling technique to minimize statistical bias and increase coverage of the contaminated area. To gain confidence that target remediation levels have been reached, the amount of data is increased by collecting and analyzing discrete samples rather than composited samples so that the variance of the concentration of contaminant(s) across the treatment site is accurately estimated (i.e., the information available is maximized). Since the goal of treatment is to protect public health and the environment, extremes in concentrations and not their central tendency (i.e., mean concentration) are of concern. Compositing of samples, in effect, averages the concentration in the composited samples, which only tends to indicate the central tendency of the concentrations. No estimate of the variance of the mean and thus the precision with which the mean is estimated can be obtained from a composite of samples. In addition, compositing does not provide information about the likelihood of the existence of relatively high concentrations (i.e., above the target remediation levels) within the soil being treated. Concentrations of compounds in soils, both natural and contaminant-related, are typically highly variable over small distances, both horizontally and vertically).

The boundaries of the LTU beds at the Libby Site are well-defined, which allowed the design of a systematic sampling protocol that maximized coverage of the soil materials, provided sufficient samples to indicate the variance of the contaminants of concern, and increased the probability that more highly contaminated soils were sampled. The systematic approach used a sample selection grid to assure that sample locations were not close to one another, which resulted in the distribution of samples over essentially all of the treatment bed. Samples taken at locations that are close together tend to result in redundant information.

RESULTS

The field performance evaluation of a prepared bed bioremediation system at the Libby, Montana Superfund Site indicated that biodegradation of wood preservative chemicals in a prepared bed system was effective and resulted in the treated soil meeting target remediation levels for target contaminants, as specified in the Record of Decision (ROD). Downward migration of target chemicals as a result of the application of additional lifts was not observed. The contaminated soil was detoxified to background levels as a result of the treatment, based upon results of toxicity and mutagenicity assays.

Design of the performance evaluation was based on analysis of discrete soil samples collected using a random systematic sampling technique to minimize statistical bias and increase coverage of the contaminated area. This design allowed identification of areas within the LTU cells where individual soil samples exceeded the target remediation level, even though the mean value for a sampling event was less than the target remediation level. In addition, statistical analysis of the results provided information concerning variation in chemical concentrations both horizontally and vertically and with time.

Based on the results of the field evaluation, a possible management tool may be to place a new lift on top of a lift after some significant treatment has been accomplished, but before the lower lift reaches target remediation levels for individual chemicals. This conclusion is based on limited field results that demonstrated that concentrations of pyrene and PCP appeared to continue to decrease with time after subsequent lifts had been placed on the first lift in the LTU cells. Follow-up field-scale measurements at the Libby Site are continuing to evaluate this management tool for accelerating prepared bed bioremediation.

Results of the field performance of the land treatment units at the Champion International Superfund Site in Libby, Montana, indicated that bioremediation using indigenous microorganisms was the process that accomplished soil treatment. Soil treatment included degradation of target PAH compounds and PCP in contaminated soil to target remediation levels and detoxification of contaminated soil.

CONCLUSION

Information obtained through field evaluation, and supporting laboratory evaluations not reported here, based upon a chemical mass balance approach provided the necessary confidence that results observed through analysis of field samples were due to bioremediation and not due to interphase transfer or escape pathways for the target chemicals including PAHs and PCP.

REFERENCES

Sims, R.C. Soil Remediation Techniques at Uncontrolled hazardous Waste Sites: A Critical Review. Journal of the Air & Waste Management Association 40(5): 703-732, 1990.

FORE MORE INFORMATION: Contact

Mr. Scott Huling, U.S. EPA Project Officer, Robert S. Kerr Environmental Research Laboratory, U.S. EPA, Ada, OK 74820. Telephone Number (405) 436-8610.

THE EPANET WATER QUALITY MODEL

Lewis A. Rossman
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 W. Martin Luther King Drive
Cincinnati, OH 45268

EPANET is a software package developed by US EPA's Drinking Water Research Division for modeling hydraulic and water quality behavior within water distribution systems. Starting with a geometric description of the pipe network, a set of initial conditions, estimates of water usage, and a set of rules for how the system is operated, EPANET predicts all flows, pressures, and water quality levels throughout the network during an extended period of operation. In addition to substance concentration, water age and source tracing can also be simulated.

EPANET offers a number of advanced features including:

- modular, highly portable C language code with no pre-set limits on network size
- a simple data input format based on a problem oriented language
- a full-featured hydraulic simulator
- improved water quality algorithms
- analysis of water quality reactions both within the bulk flow and at the pipe wall
- an optional graphical user interface running under Microsoft® Windows™.The Windows user interface allows one to edit EPANET input files, run a simulation, and view the results all within a single program. Simulation output can be visualized through:
- color-coded maps of the distribution system with full zooming, panning and labeling capabilities and a slider control to move forward or backward through time,
- spreadsheet-like tables that can be searched for entries meeting a specified criterion,
- time series graphs of both predicted and observed values for any variable at any location in the network.

EPANET is currently being used to analyze a number of water quality issues in different distribution systems across the country. These include: chlorine decay dynamics, raw water source blending, altered tank operation, and integration with real-time monitoring and control systems.

For More Information: Lewis A. Rossman
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 W. Martin Luther King Drive
Cincinnati, OH 45268
Telephone: 513/569-7603

REMOVAL OF ALKANES FROM DRINKING WATER USING MEMBRANE TECHNOLOGIES

Carol Ann Fronk
Research Chemical Engineer
Drinking Water Research Division
26 W. Martin Luther King Dr.
Cincinnati, Ohio 45268
513/569-7592

Increasingly, the public is concerned about the quality of its drinking water. The chlorinated alkanes are saturated, aliphatic, synthetic organic compounds(SOC's). When hydrocarbon feedstocks are chlorinated, a wide variety of chlorocarbons and chlorohydrocarbons are produced that are used as industrial solvents, degreasers and intermediaries. Because compounds such as Carbon Tetrachloride and 1,2-Dichloroethane are widely used, they often find their way into drinking water, particularly groundwaters. Surface waters are somewhat less affected because of the high volatility of many chlorinated alkanes.

The Drinking Water Research Division is responsible for evaluating various membrane technologies that may be feasible for meeting Maximum Contaminant Levels. Several membrane processes are under investigation to determine their effectiveness in removing SOC's from drinking water. One study addressed the removal of a variety of alkanes from spiked groundwater by six reverse osmosis membranes: a cellulose acetate, a polyamide (hollow fiber), and four different types of thin-film composite membranes. The following alkanes were tested:

METHANES	ETHANES	PROPANES
Methylene Chloride	1,1-Dichloroethane	1,2-Dichloropropane
Chloroform	1,2-Dichloroethane	
Bromoform	1,1,1-Trichloroethane	
Carbon Tetrachloride		
Bromodichloromethane		
Dibromochloromethane		

Progressive chlorination of methanes, ethanes and propanes produces compounds that exhibit differing physicochemical properties. The differences in compound properties have an effect on the removal of these compounds by reverse osmosis membranes. For example only 25% of the methylene chloride (Dichloromethane) was removed by one thin-film composite versus 90% removal of the carbon tetrachloride. In addition, the various membranes are made of different polymeric materials and showed a wide range of removals. Generally, the thin-film composite membranes out performed the other membranes and the more highly chlorinated the compound the better the removal.

Pervaporation is yet another membrane process that may prove effective in removal of alkanes and future studies will address its usefulness as a drinking water

AN EVALUATION OF DRINKING WATER SAMPLES TREATED WITH ALTERNATIVE DISINFECTANTS

Kathleen Schenck Patterson, Benjamin W. Lykins, Jr.,
Lucille M. Garner and Bradford L. Smith

U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
Drinking Water Research Division
(513/569-7947, -7460, -7417, -7238)

Due to concern over potential human health risks associated with the use of chlorine (Cl_2) for disinfection of drinking water, many utilities are considering alternative disinfectants. An evaluation is thus needed of the potential risks associated with the use of alternative disinfectants relative to those posed by Cl_2.

At a pilot-scale drinking water plant in Jefferson Parish, LA., two studies were conducted in which clarified and sand filtered Mississippi River water was treated with either ozone (O_3), monochloramine (NH_2Cl), Cl_2 or was not disinfected. Ozonated water was also post-disinfected with either NH_2Cl or Cl_2, to provide a disinfectant residual. For each treatment stream total organic carbon (TOC), total organic halide (TOX) and microbiological contaminants were determined. XAD resin concentrates were also prepared for mutagenicity testing in the Ames Salmonella assay.

Water samples disinfected with O_3 alone had low levels of mutagenic activity, the same as the non-disinfected water. The level of mutagenicity observed following chlorination was approximately twice that observed following treatment with NH_2Cl. Disinfection with O_3 prior to treatment with either Cl_2 or NH_2Cl resulted in a significantly lower level of mutagenicity than when either disinfectant was used alone. The concentrations of TOX present in the water samples showed a pattern similar to that of the mutagenicity data. The levels of TOC, by contrast, were similar for all the treatment streams. No significant baterial contamination was observed in water samples treated with either Cl_2 or NH_2Cl alone or in combination with O_3, as determined by heterotrophic plate counts. However, O_3 alone did not insure an acceptable level of disinfection at the end of the treatment stream. These studies indicate that the use of ozone in conjunction with either Cl_2 or NH_2Cl may be beneficial in drinking water treatment. (This abstract does not reflect EPA policy.)

For more information contact Kathleen. S. Patterson, U.S. EPA, RREL, DWRD, 26 W. M.L. King Drive, Cincinnati, OH 45268. (513/569-7947)

A MEASUREMENT METHOD FOR POLLUTION PREVENTION PROGRESS

David G. Stephan, Robert M. Knodel, and James S. Bridges

A software program (P2P) has been developed for measuring progress P2 resulting from product redesign, product reformulation, or product replacement. The program compares the pollution generated by the original product with that from the modified or replacement product. It can take into account the various lifecycle stages of the product if desired. The pollution prevented (or sometimes increased) as a consequence of the redesign can be delineated with respect to the media affected (air, water, and soil/groundwater). and with respect to three categories of pollution impact (human health impacts, use impairment impacts, and disposal capacity impacts). Information is also provided as to the "classes" of pollution prevented such as toxic organics, heavy metals, global warmers, nutrients, aquatic life toxicants, or hazardous wastes. Reports can also be generated that show on which EPA regulatory lists the "prevented" or the "increased" pollutants appear.

In the initial version of P2P (released in January 1995), pollution prevented is indicated simply in terms of mass. In a subsequent version now being developed, the relative "potency" of various pollutants within a class will be considered. Also, the method will be extended for application to P2 projects of all types, not just product changes.

POLLUTION PREVENTION POSSIBILITIES FOR SMALL AND MEDIUM-SIZED INDUSTRIES: THE WASTE REDUCTION INNOVATIVE TECHNOLOGIES EVALUATION (WRITE) PROJECT SUMMARY

Ivars J. Licis
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 West Martin Luther King Drive
Cincinnati, OH 45268
(513) 569-7718

The Waste Reduction Innovative Technologies Evaluation Program (WRITE) was a pilot program with six (6) states and one (I) local government to identify priority needs at the respective governmental level, find promising waste minimization technologies and perform an evaluation to determine performance, pollution prevention impact and costs in a before and after scenario. The research concentrated on environmental problems and Pollution Prevention (P2) opportunities for small to medium-sized businesses, technology at pilot- or full-scale, and use of voluntary business/EPA partnerships for the evaluation of innovative ways of reducing pollution at the source.

A total of 41 technologies were tested and evaluated. For the applications investigated, a large portion demonstrated that the technology could provide equal or better performance in service or product produced, while reducing amounts and toxicities of the primary pollutants traditionally generated, and realize cost savings, at times with payback periods of less than two years.

Pollution Prevention Research and Outreach

Ruth Corn
Pollution Prevention Research Branch
Waste Minimization, Destruction and Disposal Research Division
Risk Reduction Engineering Laboratory
(513) 569-7215

KEY ISSUE: How should consumer and industrial products and services be designed, manufactured, and used for a minimal effect on the environment?

Since 1988, the Pollution Prevention Research Branch (PPRB) at USEPA's Risk Reduction Engineering Laboratory in Cincinnati, Ohio, has supported projects and provided technical assistance to encourage the development and adoption of technologies, products, and pollution prevention (P2) techniques to reduce environmental pollution. To date, approximately $10 million dollars have been expended to support this program. The program focuses on five major areas which include:

Cleaner Production Technologies: To develop, demonstrate and evaluate innovative processes for reducing pollution through source reduction.

Cleaner Products: To support the design and development of products whose manufacture, use, recycle and disposal represent reduced impacts on the environment.

Tools to Support Pollution Prevention: To develop life cycle assessment and measurement methodologies to guide pollution prevention strategies.

Pollution Prevention Assessments: To identify P2 opportunities in a variety of industries and to transfer that technical information to assist others in implementing pollution prevention.

Cooperative P2 Projects with Other Federal Agencies: To promote pollution prevention in other Federal Agencies through cooperative research, training, and demonstration projects.

This poster displays personnel and newer manuals produced by the Branch. Handouts will be available describing the ongoing projects and Branch publications. Members of the Branch will be available periodically for discussion.

For further information, please contact Ruth Corn, Phone (513) 569-7215, FAX (513) 569-7111.

COMPUTER SUPPORTED INFORMATION SYSTEM FOR MEASURING POLLUTION PREVENTION PROGRESS

Rada Olbina, Cindy Flowers, Jordan M. Spooner
U.S. Environmental Protection Agency
Office of Research and Development
Risk Reduction Engineering Laboratory
26 W. Martin Luther King Avenue
Cincinnati, OH 45268
Phone: (513) 569-7526

The objective of this research is to build an information system (IS) for pollution prevention (P2) which comprises a simulation model of an industrial production and waste generation system (IPWGS). An IPWGS model is used to predict waste generation, carry out cost-analysis of already existing waste management practices, and after applying appropriate P2 strategies and technologies, measure P2 progress. An IS for P2 could provide industry, research organizations, and governmental institutions with a powerful tool for implementation of P2 strategies and introduction of efficient waste reduction/minimization practices by: (1) predicting waste generation in industrial production, (2) introducing process optimization while minimizing waste generation in production processes, (3) suggesting the application of P2 strategies and technologies, and (4) measuring P2 progress.

The essential part of the IS is a model of an IPWGS. Current research is applying systems analysis approach to quantify parameters in an IPWGS. However, system inputs (raw and other materials) as well as system outputs (products, by-products, process losses, waste, emissions, discharges, nonproducts, releases) are not always precisely defined nor yet standardized. Moreover, environmental costs are usually not placed into separate accounts and real costs of the waste generation and its management are hardly ever considered. Therefore, the main parameters of an IPWGS model are defined and the boundaries of such a system are determined. A model is tested in a selected industrial production process, cost-analysis of waste management is carried out, and after applying P2, source reduction, waste minimization and/or resource recovery measures, P2 progress will be measured. Computer simulation is applied to study the system capability and behavior under a variety of conditions. The model for measuring of waste generation/P2 in an industrial production is a basic part of a IS.

Commercially available database management systems (DBMS) for IS building and dynamic simulation software applicable on IBM PC are analyzed. ACCESS and ITHINK are selected for this purpose.

QA OF FORTUNE

Kim A. McClellan
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268
(513) 569-7214

At the U.S. EPA Risk Reduction Engineering Laboratory (RREL), commitment to quality is embedded in a continuous process of total quality management that is an ever-present part of RREL's culture. Just what is this culture and how does the RREL Quality Assurance (QA) Office go about promoting this culture? Our expert staff of dedicated professionals provide daily assistance, Quality Assurance reviews, audits, sage wisdom, and the newest addition, the **QA of Fortune**.

This modern rendition of the "Wheel of Fortune" is similar to the popular TV game show. Rather than puzzle categories such as familiar phrases, places, or people, the QA of Fortune is educational and includes exciting quality assurance information.

To play this game, each player spins the wheel. If the spinner stops on a number, the player selects a letter they believe may be in the puzzle. A QA staff member goes to the board and moves the slide to the right to find the location(s) of that letter in the puzzle. Then the corresponding numbered door(s) is flipped down to reveal the letter in the puzzle. If a player spins "Lose A Turn" or "Bankrupt" they loose their accrued points. If the player's solution to the puzzle is correct in every detail, the player wins and the round is over.

Most people are eager to recall popular phrases from their past including: quality circles and total quality management. Both experts and non-experts in the field are invited to participate during this poster session. No knowledge of statistics is required. There is a reward, of course, for your participation and the number of points accrued.

For more information: Kim A. McClellan, U.S. EPA, 26 W. Martin Luther King Drive, Cincinnati, OH 45268, (513) 569-7214

TREATABILITY DATA BASE, VERSION 5.0

Glenn M. Shaul and Jerry D. Waterman
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
26 West Martin Luther King Drive
Cincinnati, Ohio 45268
(513) 569-7408

The purpose of the Risk Reduction Engineering Laboratory Treatability Data Base is to provide a thorough review of the effectiveness of proven treatment technologies in the removal/destruction of chemicals in various types of media including, but not limited to, municipal and industrial wastewater, drinking water, groundwater, soil, debris, sludge, and sediment.

The database contains 1,217 chemical compounds and over 15,800 sets of treatability data. The chemicals contained in the database are often those regulated under the Clean Water Act, Safe Drinking Water Act, Resource Conservation and Recovery Act, Toxic Substances Control Act, Superfund Amendments and Reauthorization Act, and other environmental laws enacted by Congress. For each chemical, the database includes: physical/chemical properties, aqueous and solid treatability data, Freundlich isotherm data, other environmental database information sources, and data references including a reference abstract. The physical/chemical properties included are those most routinely used, such as molecular weight, boiling point, melting point, etc. The treatability data summarize the treatment technologies used to treat the specific chemical; the type of waste/wastewater treated; the size of the study/plant; and the treatment efficiency achieved. Data sorting capabilities allow for comparison of treatability data. In addition, each data set is referenced to sources of information, operational information on process(es) sampled and quality-coded based upon analytical methods and reported quality assurance.

For more information, contact Glenn M. Shaul, Risk Reduction Engineering Laboratory, U.S. EPA, 26 West Martin Luther King Drive, Cincinnati, Ohio 45268, (513) 569-7408.

MINE WASTE TECHNOLOGY PROGRAM

Roger C. Wilmoth and Thomas J. Powers
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
26 West Martin Luther King Drive
Cincinnati, Ohio 45268
(513) 569-7509

The Mine Waste Technology Program (MWTP) was initiated to address mining waste generated by active and inactive mining production facilities. In June 1991, an Interagency Agreement was signed between the U.S. Environmental Protection Agency and the Department of Energy which outlined the following activities.

- To identify and prioritize treatment technologies as candidates for demonstration projects.
- To propose and conduct large pilot-/field-scale demonstration projects of several innovative technologies that show promise for cost effectively remediating local, regional, and national mine waste problems.
- To develop and implement a plan to conduct bench-/pilot-scale research of several innovative technologies that show promise for most cost effectively remediating local, regional, and national mine waste problems.
- To conduct a series of symposia/workshops to convey the continuing and final results of the pilot program to user communities and to publicize information concerning mine waste treatment technologies developed under the pilot program to facilitate early commercialization of those technologies.
- To develop and implement a plan to establish training/educational programs directed toward current and future personnel interested in mine waste treatment technologies.

The operation of the MWTP includes the following activities.

- Identifying mine waste problems that are most severely affecting human health and the environment at local, regional, and national levels.
- Evaluating engineering and economic factors for selected technologies.
- Prioritizing the most promising mine waste treatment technologies based on their engineering and economic value.
- Planning and documenting the demonstration, testing and evaluation of the most promising mine waste treatment technologies.
- Accelerating the commercialization of selected mine waste treatment technologies that are developed, tested, and evaluated.
- Planning the transfer of knowledge gained from the above through systematic training of user communities.

For more information, contact Roger C. Wilmoth, U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, 26 West Martin Luther King Drive, Cincinnati, Ohio 45268, (513) 569-7509.

COMPARISON OF REACTOR DESIGNS FOR BIOLOGICAL EX-SITU SOIL TREATMENT

Carl Potter
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
Cincinnati, OH 45268
(513) 569-7231

Roy Haught
IT Corporation
11499 Chester Road
Cincinnati, OH 45246
(513) 569-7067

The goal of this project is to evaluate the potential of biological *ex-situ* soil treatment systems to remediate soils contaminated with hazardous chemicals. A laminar-type flow pilot-scale reactor with volume of 3 cu. yd has been constructed at EPA's Test & Evaluation (T&E) Facility in Cincinnati. Laminar-type flow from one side of the reactor to the other may provide even aeration to all areas of the reactor while avoiding the use of pipes inside the reactor. This design greatly facilitates loading and unloading the reactor and is readily scalable to larger systems.

Passing smoke through the reactor for visual observation of flow indicated uniform flow in the empty reactor. Further testing involves filling the reactor with vermiculite, flushing with Argon, and then passing air through the reactor at about 1 volume change per day to evaluate air flow through this uniform solid matrix. Oxygen probes, located at 27 positions within the reactor, provide information on air progression through the system. Analysis of gas flow through an empty reactor and through a uniform matrix (vermiculite) allows separation of reactor flaws from soil inhomogeneities as causes of any nonuniform aeration of the reactor space. Soil contaminated with polynuclear aromatic hydrocarbons (PAHs) from The Reilly Tar Pit Superfund Site in St. Louis Park, MN has been shipped under the samll quantity treatability exemption to the T&E Facility for research on soil aeration and effectiveness of this *ex situ* reactor design for biological treatment of contaminated soils.

FOR MORE INFORMATION

Carl L. Potter, U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, Telephone (513) 569-7231, FAX (513) 569-7105.

INTEGRATED PNEUMATIC FRACTURING/BIOREMEDIATION FOR THE IN-SITU TREATMENT OF CONTAMINATED SOIL

Uwe Frank
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
2890 Woodbridge Avenue
Edison, New Jersey 08837
(908) 321-6626

John R. Schuring
Hazardous Substance Management Research Center
New Jersey Institute of Technology
Newark, New Jersey 07102
(201) 596-5849

The objective of this project is to demonstrate that for low permeability soils, treatment by pneumatic fracturing to increase permeability will enhance bioremediation. For in-situ bioremediation to be successful in a timely manner, the microbial population must be stimulated by injecting nutrients and an oxygen source to the microbes. Normally, formations with low permeability make it extremely difficult to supply microbes with the necessary subsistence making bioremediation technically and economically infeasible. This project involves pneumatic fracturing of contaminated soils followed by biodegradation using indigenous or cultivated microbes. The soils under investigation are contaminated with benzene, toluene and the xylenes (BTX) in concentrations ranging from 120-1500 mg/kg soil. The end point target of the remediation is a 95% reduction in the BTX concentration in the top five feet of the soil bed.

The pneumatic fracturing process involves the injection of high pressure air at controlled flow rates and pressures in the zone of contaminated soil. In fine-grained, low permeability soils such as clay, this process creates conductive channels in the formation. The vapor movement in the formation becomes convection and diffusion-controlled instead of just diffusion-controlled. This increases the permeability and the exposed surface area of the soil, facilitating the treatment and removal of contaminants.

Pneumatic fracturing is also used to enhance stacked aerobic, denitrifying and methanogenic microbial processes in staggered spatial distribution for maximum effectiveness. Aerobic processes will dominate at the fracture interfaces, and to a limited distance, into the soil away from the fracture. Depletion of oxygen during aerobic biodegradation will allow the formation of a denitrifying zone a short distance away from the fracture. Depletion of nitrate by denitrifying biodegradation processes allows the formation of methanogenic populations at greater distances from the fractures. During methanogenic processes, methane will be generated and diffuse out with the fracture sweep air. Results of pilot-scale testing will be presented.

For more information, contact Uwe Frank, U.S. EPA, RREL, 2890 Woodbridge Ave., Edison, New Jersey 08837. Phone (908) 321-6626, FAX (908) 906-6990.

RESULTS OF A SITE DEMONSTRATION OF THE COGNIS TERRAMET® LEAD EXTRACTION PROCESS TO REMOVE HEAVY METALS FROM SOIL

Pinaki Banerjee
PRC Environmental Management, Inc.
1921 Rohlwing Road
Rolling Meadows, IL 60008
Phone: 708-255-4166

Michael D. Royer
Technical Support Branch/RREL
U.S. EPA
Bldg. #10 (MS-104)
2890 Woodbridge Avenue
Edison, NJ 08837-3679
Phone: 908-321-6633

The COGNIS, Inc. Terramet® process is a chemical process that extracts and recovers lead and other metals from contaminated soil, dust, sludge, or sediment. The process begins by removing and washing oversize material and then separating the remaining soil into sands and fines fractions. The sands fraction is further treated by density separation methods to isolate particulate metals as a concentrate. The sands and fines fractions are then separately leached in the Terramet® portion of the process by a proprietary leachant to bring fine metallic particles and ionic metals into solution. Leached metals are recovered through proprietary reductive electrochemical cells, producing a metal concentrate and regenerating the leachant for recycling. Clean soil exiting the system can be returned to the site. The recovered metals are recyclable. No wastewater streams are generated during process operations.

The COGNIS, Inc. Terramet® process was selected to remediate approximately 10,000 tons of heavy-metal (predominantly lead) contaminated soil at the Twin Cities Army Ammunition Plant (TCAAP), New Brighton, Minnesota. EPA's Superfund Innovative Technology Evaluation (SITE) program is currently evaluating the COGNIS, Inc. Terramet® process. The evaluation included a 4-day sampling effort (August 2-5, 1994) during the TCAAP remediation. The SITE sampling effort focussed primarily on determining the effectiveness of the leaching processes for removing lead from both the sands and the fines fractions of the soil. Other results that will be reported as part of the evaluation include overall effectiveness of lead removal, efficiency of lead recovery cells, and costs.

For More Information: Contact Michael Royer, See Address Above

RREL SITE REMEDIATION TECHNICAL SUPPORT PROGRAM

Benjamin L. Blaney
Technical Support Branch
Superfund Technology Demonstration Division
Risk Reduction Engineering Laboratory
U. S. Environmental Protection Agency
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268
(513) 569-7406

The Risk Reduction Engineering Laboratory provides a variety of technical support to EPA Remedial Project Managers and other site remediation managers. This poster will highlight some of these support activities in the areas of site-specific assistance and technology transfer, including:

- treatability study assistance
- site-type specific remediation guidance documents
- technology specific documents
- computerized databases

Forms for ordering technology transfer documents will be available.

FOR MORE INFORMATION

Benjamin L. Blaney

LOCATION OF LEAKS IN PIPELINES USING ACOUSTICAL PRINCIPLES

Anthony N. Tafuri and Robert W. Hillger

United States Environmental Protection Agency
Risk Reduction Engineering Laboratory
2890 Woodbridge Ave. Edison, N.J. 08837
Tel. (908) 321-6604 or (908) 321-6639

Thousands of miles of pipeline are used in this country to transfer petroleum and chemical products from both underground and aboveground storage tanks (USTs & ASTs). Pressurized pipelines commonly found at retail service stations are typically 2 inches in diameter and operate at 20 to 30 psi; larger lines (4 to 12 inches in diameter) used at bulk storage tank facilities generally operate at much higher pressures. In either case, these pipelines are usually constructed of steel and small leaks resulting from corrosion can result in catastrophic releases unless they are detected, located, and repaired. Passive-acoustic measurements, combined with advanced signal-processing techniques, provide a nondestructive method of leak location that is accurate and relatively simple, and can be applied to a wide variety of pipeline systems.

Experiments were conducted at the Edison, NJ UST Test Apparatus in which three acoustic sensors separated by a maximum distance of 125 feet were used to monitor signals produced by 3.0, 1.5, and 1.0 gal\h leaks in the wall of a 2 inch diameter pressurized petroleum pipeline. The line pressures and hole diameters used in the experiments ranged from 10 to 20 psi and 0.01 to .03 inches, respectively. Application of a leak location algorithm based upon the technique of coherence function analysis resulted in a mean difference between predicted and actual leak locations of approximately 4 inches.

Spectra computed from leak-on and leak-off time series indicate that the majority of acoustic energy received in the far field of the leak is concentrated in a frequency band from 1 to 4 kHz. The strength of the signal within this band was found to be proportional to the leak flow rate and line pressure. Energy propagation from leak to sensor was observed via three types of wave motion: longitudinal waves in the product, and longitudinal and transverse waves in the steel.

The similarity between the measured wave speed and the nominal speed of sound in gasoline suggests that longitudinal waves in the product dominate the spectrum of received acoustic energy. The effects of multiple-mode wave propagation and the reflection of acoustic signals within the pipeline were observed as non-random fluctuations in the measured phase difference between sensor pairs. Additional experiments with smaller holes and higher pressures (20 to 50 psi) are required to determine the smallest leaks that can be located over distances of several hundred feet. The current experiments indicate that improved phase-unwrapping algorithms and/or lower noise instrumentation are required to optimize system performance.

ALTERNATIVE TREATMENT TECHNOLOGY INFORMATION CENTER COMPUTER DATABASE SYSTEM

Daniel Sullivan, P.E.
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
2890 Woodbridge Avenue (MS-106)
Edison, New Jersey 08837

The Alternative Treatment Technology Information Center (ATTIC) computer database system was developed pursuant to the 1986 Superfund law amendments. It provides up-to-date information on innovative treatment technologies to clean up hazardous waste sites. ATTIC v2.0 provides access to several independent databases as well as a mechanism for retrieving full-text documents of key literature. It can be accessed with a personal computer and modem 24 hours a day, and there are no user fees.

ATTIC provides "one-stop shopping" for information on alternative treatment options by accessing several databases:

- treatment technology database - this contains abstracts from the literature on all types of treatment technologies, including biological, chemical, physical, and thermal methods. The best literature as viewed by experts is highlighted.

- treatability study database - this provides performance information on technologies to remove contaminants from wastewaters and soils. It is derived from treatability studies. This database is available through ATTIC or separately as a disk that can be mailed to you.

- underground storage tank database - this presents information on underground storage tank corrective actions, surface spills, emergency response, and remedial actions.

- oil/chemical spill database - this provides abstracts on treatment and disposal of spilled oil and chemicals.

In addition to these separate databases, ATTIC allows immediate access to other disk-based systems such as the Vendor Information System for Innovative Treatment Technologies (VISITT) and the Bioremediation in the Field Search System (BFSS). The user may download these programs to their own PC via a high-speed modem.

Also via modem, users are able to download entire documents through the ATTIC system. Currently, about fifty publications are available, including Superfund Innovative Technology Evaluation (SITE) program documents.

For more information, call the ATTIC hotline (703-908-2137), contact EPA (908-321-6677 or fax 908-906-6990), or link your PC to the ATTIC system at 703-908-2138 (at up to 14,4000 band, 8 data bits, no parity).

CLEAN TECHNOLOGY DEMONSTRATIONS FOR THE 33/50 CHEMICALS

Diana R. Kirk
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268
(513) 569-7674

EPA's Risk Reduction Engineering Laboratory (RREL) has a research program to support the 33/50 Program. The 33/50 Program is a voluntary pollution prevention initiative to reduce national releases and off-site transfers to the environment of 17 toxic chemicals. The overall purpose of the 33/50 Program is to study and evaluate substitutes for the 33/50 chemicals to encourage reductions in use and releases of those chemicals. This specific evaluation conducted by the University of Tennessee's Center for Clean Products and Clean Technologies focuses on substitutes such as aqueous wash systems and no-clean technologies for solvent degreasing processes. Calsonic Manufacturing Corporation, located in Shelbyville, Tennessee is the industry partner for this evaluation. Calsonic manufactures automotive parts, including heaters, blowers, cooling units, motor fans, radiators, auxiliary oil coolers, and exhaust systems. Phase-out of 1,1,1-trichloroethane (TCA) degreasing processes at Calsonics is being accomplished through substitution of aqueous cleaning and no-clean technologies (use of a low-boiling-point oil combined with a flash-drying process) for the degreasing processes. The demonstration focused on three cleaning processes used in three of Calsonic's process lines: 1) the aqueous wash system in the radiator line, 2) the no-clean technology in the condenser line, and 3) the hot water wash system in the converter line. The results may be used by industry, state technical assistance programs, universities, EPA and others with an interest in solvent substitutes. The results will help the interested parties understand the overall technical, environmental and economic benefits and costs of switching from solvent degreasing to aqueous cleaning or the no-clean technology.

For more information: Diana R. Kirk, U.S. Environmental Protection Agency, 26 West Martin Luther King Dr., Cincinnati, Ohio 45268, (513) 569-7674.

POLLUTANT ELEMENT FORMS WITHIN SLUDGES GENERATED BY TREATMENT OF TWO ACID MINE WATERS WITH LIME, INORGANIC SULFIDE AND SULFATE REDUCING BACTERIA

Bill Chatham & Frank Diebold
Chemistry & Geochemistry Department
Montana Tech
1300 West Park Street
Butte, MT 59701-8997
(406) 496-4215

One of the research projects within the Mine WAste Technology Pilot Program conducted at Montana Tech under subcontract to MSE, Inc., Butte, MT is entitled "Formation, Properties and Stability of Sludge Generated During Treatment of Acid Mine Water." One area of study within this activity is the determination of the element-solid associations within the three sludges being studied, namely, a lime initiated sludge, an inorganic sulfide initiated sludge and a sulfate reducing bacteria initiated sludge. These sludges are formed from treatment of two acid mine waters; one from an abandoned metal sulfide open pit mine (the Berkeley Pit in Butte, MT) and another from an abandoned metal sulfide underground mine (the Crystal Mine NW of Basin, MT). A sequential leaching scheme has been used to determine the form of the pollutant elements (Cu, Zn, Cd, Fe, Mn, and As) within these sludges. Significant differences are observed between these pollutant elements for each sludge. These data are interpreted in terms of the potential for release of the pollutant elements within a sludge containment pond storage system.

*U.S. Government Printing Office: 1995 — 651-874

United States
Environmental Protection Agency
Center for Environmental Research Information
Cincinnati, OH 45268

Official Business
Penalty for Private Use
$300

EPA/600/R-95/012

Please make all necessary changes on the below label, detach or copy, and return to the address in the upper left-hand corner.

If you do not wish to receive these reports CHECK HERE ☐; detach, or copy this cover, and return to the address in the upper left-hand corner.