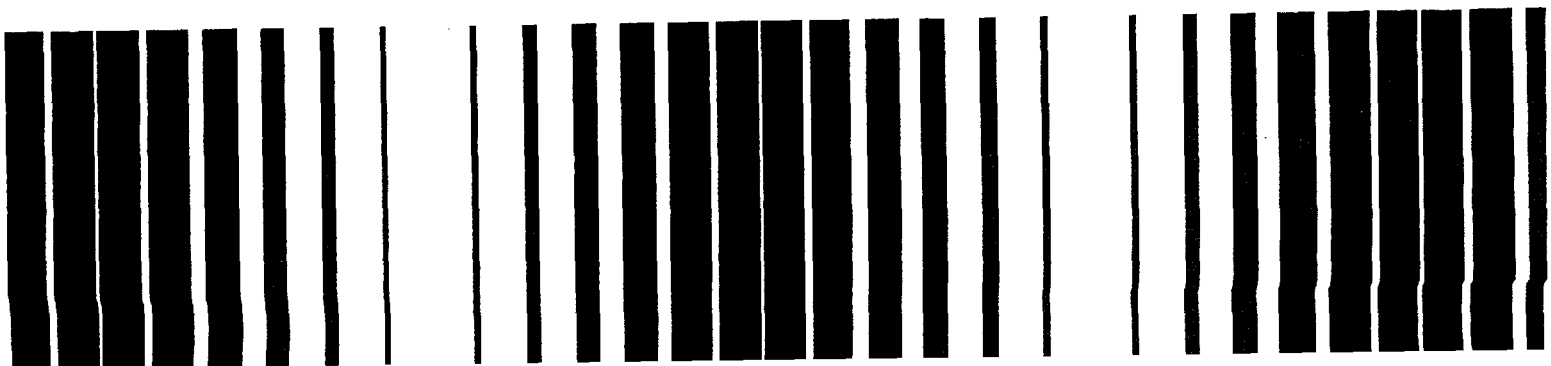




# Volatile Organic Compounds (VOC) Recovery Seminar

September 16-17, 1998  
Cincinnati, OH



EPA/625/R-99/005  
July 1999

**Volatile Organic Compounds (VOC)  
Recovery Seminar**  
September 16-17, 1998  
Cincinnati, OH

Sustainable Technology Division  
Technology Transfer and Support Division  
Air Pollution Prevention and Control Division  
National Risk Management Research Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Cincinnati, OH 45268



Printed on *Recycled Paper*

## **Notice**

This document has been reviewed in accordance with US. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

# Contents

Notice .....	ii
Contents .....	iii
List of Tables .....	v
List of Acronyms .....	vi
Introduction .....	viii
<b>Risk Management: Strategic Issues for Volatile Organic Compounds (VOCs) in the Environment</b> by Subhas Sikdar .....	1
<b>VOCs: Sources, Definitions, and Considerations for Recovery</b> by Carlos Nunez .....	3
<b>Overview of VOC Recovery Technologies</b> by Kamaiesh Sirkar .....	5
<b>Industrial Research Programs</b> by Edward Moretti .....	10
<b>VOC Recovery Research at EPA Office of Research and Development (ORD)</b> by Teresa Harten .....	12
<b>Short Flow Path Pressure Swing Adsorption - Lower Cost Adsorption Processing SHERPA™</b> by William Asher .....	14
<b>Solvent Recovery Applications at 3M</b> by James Garmaker .....	16
<b>The Economics of Recovery: Using the Office of Air Quality, Planning, and Standards (OAQPS) Cost Manual as a Tool for Choosing the Right Reduction Strategy</b> by Daniel Mussatti .....	18
<b>Rotary Concentration and Carbon Fiber Adsorption</b> by Ajay Gupta .....	21
<b>Zeolite Absorption and Refrigeration - CONDENSORB™ VOC Recovery System</b> by Jon Kostyzak .....	23
<b>A Novel Fluidized Bed Concentrator System for Solvent Recovery of High Volume, Low Concentration VOC-laden Emissions</b> by Edward Biedell .....	25
<b>Recovery of VOCs by Microwave Regeneration of Adsorbents</b> by Philip Schmidt .....	27
<b>Removal and Recovery of Volatile Organic Compounds for Gas Streams</b> by Hans Wijmans .....	30

## Contents (Cont'd)

<b>Synthetic Adsorbents in Liquid Phase and Vapor Phase Applications</b> by Steven Billingsley . . . . .	32
<b>Cryogenic Condensation for VOC Control and Recovery</b> by Robert Zeiss . . . . .	34
<b>Brayton Cycle Systems for Solvent Recovery</b> by Joseph Enneking . . . . .	35
<b>Control of VOCs in Refinery Wastewater</b> by Mike Worrall . . . . .	37
<b>Separation of Volatile Organic Compounds from Water by Pervaporation</b> by Richard Baker . . . . .	39
<b>Dehydration and VOC Separation by Pervaporation for Remediation Fluid Recycling</b> by Leland Vane . . . . .	41
<b>Polymeric Resins for VOC Removal from Aqueous Systems</b> by Yoram Cohen . . . . .	43
<b>The New Clean Process Advisory System™ (CPAS™) Separation Technology and Pollution Prevention Information Tool</b> by Robert Patty. . . . .	47
<b>Comparative Cost Studies</b> by Edward Moretti . . . . .	51
<b>Availability of Technology Information, Including Internet-Based Sources</b> by Heriberto Cabezas . . . . .	53
<b>Paint Spray Booth Design Using Recirculation/Partitioning Ventilation</b> by Charles Darwin . . . . .	56
<b>Summary and Concluding Remarks/Seminar Follow-Up Efforts</b> by Scott Hedges . . . . .	59
<b>Breakout Session Summaries</b> . . . . .	60
<b>Appendix A - List of Seminar Attendees</b> . . . . .	63
<b>Appendix B - Breakout Group Notes and Members</b> . . . . .	70

---

## **List of Tables**

<b>1.</b>	<b>Process Options for Removing VOCs from Vent Streams .....</b>	<b>7</b>
<b>2.</b>	<b>Typical VOC/Water Separation Factors in Pervaporation .....</b>	<b>9</b>
<b>3.</b>	<b>Polymer Resins Versus Activated Carbon .....</b>	<b>45</b>

## List of Acronyms

ACA	Air Compliance Advisor	°F	degrees Fahrenheit
AERP	Air Emission Reduction Program	gpm	gallons per minute
AIChE	American Institute of Chemical Engineers	HAPs	hazardous air pollutants
BACT	Best Available Control Technology	IPA	isopropyl alcohol
BCA	beaded carbonaceous adsorbent	kcal/mole	kilocalories per mole
BRU	Benzene Removal Unit	KOH	reaction rate constant for the reaction of a compound with an hydroxyl radical
BTUs	British Thermal Units	kW	kilowatt
BTEX	benzene, toluene, ethylene, and xylene	lbs/hr	pounds per hour
BTX	benzene, toluene, and xylene	LEL	lower explosive limits
CenCITT	Center for Clean Industrial and Treatment Technologies	LNAPL	light non-aqueous phase liquid
CERI	Center for Environmental Research Information	m <sup>2</sup> /g	square meters per gram
cfm	cubic feet per minute	m <sup>3</sup> /hr	cubic meters per hour
CPI	The Construction Productivity Institute	MACT	Maximum Achievable Control Technology
CRADA	Cooperative Research and Development Agreement	mg HC/liter	milligrams hydrocarbon per liter
CWRT	Center for Waste Reduction Technologies	mg HC/Nm <sup>3</sup>	milligrams of hydrocarbon per normal cubic meter
DNAPL	dense non-aqueous phase liquid	mg/L	milligrams per liter
DOD	Department of Defense	mg/m <sup>3</sup>	milligrams per cubic meter
DOE	Department of Energy	MIR	maximum incremental reactivity
°C	degrees Celsius	mm Hg	millimeter of mercury
EPA	Environmental Protection Agency	MS	Molecular Sieve
		NAPLs	non-aqueous phase liquids

## List of Acronyms (continued)

NESHAPs	National Emission Standards for Hazardous Air Pollutants	PVC	poly vinyl chloride
		R&D	research and development
NJIT	New Jersey Institute of Technology	RIA	Regulatory Impact Analysis
NO <sub>x</sub>	nitrogen oxides	SAB	Science Advisory Board
nPA	n-propyl alcohol	scfm	standard cubic feet per minute
NRMRL	National Risk Management Research Laboratory	SEE	Senior Environmental Employee
O&M	operation and maintenance	SERDP	Strategic Environmental Research and Development Program
OAQPS	Office of Air Quality, Planning, and Standards	SIP	State Implementation Plan
OH	hydroxyl	SITE	Super-fund Innovative Technology Evaluation
ORD	Office of Research and Development	SO <sub>x</sub>	sulfur oxides
		TRI	Toxic Release Inventory
P2P	Pollution Prevention Progress	TTN	Technology Transfer Network
PM	particulate matter	TWA	time weighted average
ppb	parts per billion	UCLA	University of California, Los Angeles
ppm	parts per million		
ppmv	parts per million by volume	UT	University of Texas
ppmw	parts per million by weight	uv	ultraviolet
PPPS&D	Pervaporation Performance Prediction Software and Database	VCM	vinyl chloride monomer
		v o c	Volatile Organic Compound
PSA	pressure swing adsorption	%	percent
psia	pounds per square inch area		



## Introduction

The Volatile Organic Compounds (VOC) Recovery Seminar was held September 16 - 17, 1998, in Cincinnati, Ohio. The seminar was cosponsored by the U.S. Environmental Protection Agency's (EPA's) National Risk Management Research Laboratory (NRMRL), the U.S. Department of Energy (DOE), the American Institute of Chemical Engineers (AIChE), and the AIChE-affiliated Center for Waste Reduction Technologies (CWRT). Representatives from industry, academia, consulting firms, and government attended.

The purpose of the seminar was to bring researchers, technology developers, and industry representatives together to discuss recovery technologies and techniques for VOCs. The seminar focused on the specific VOC recovery needs of industry and on case studies that summarize effective VOC product recovery techniques applicable to air, water, and solid waste. The case studies highlighted examples in which existing and new recovery technologies resulted in significant cost savings to industry.

The seminar focused on the following key issues:

- Status and future direction of EPA, DOE, and other major research programs.
- What are the latest technology innovations in VOC treatment and recovery?
- Performance and cost effectiveness of VOC recovery techniques.
- How are recovery techniques applied to air, water, and solid wastes?

Presenters were from industry, academia, EPA, and various consulting firms. The presentations were followed by several facilitated breakout sessions; these sessions allowed participants an opportunity to discuss their needs and opinions on VOC recovery trends, research, and other issues.

This document contains summaries of the presentations and discussions during the seminar. It does not constitute an actual proceedings, since the presentations were informal and no written versions were required. The list of participants and contact information are included in Appendix A.

# **Risk Management: Strategic Issues for Volatile Organic Compounds (VOCs) in the Environment**

Presented on September 15, 1998 by Subhas Sikdar, U.S. Environmental Protection Agency (EPA) National Risk Management Research Laboratory (NRMRL)

VOC recovery technologies are of particular interest to U.S. EPA NRMRL. The Cincinnati laboratory needs to be familiar with both current and upcoming VOC recovery technologies in order to support its technical role in EPA and to serve as a technical advisor to the regulatory offices on these technologies.

The strategic issues associated with managing VOCs in the environment are: 1) what emissions data tell us; 2) industrial emission sources; 3) where the problems are most evident; and 4) strategies for reducing risks.

## **“What Emissions Data Tell Us” -Toxic VOCs in the Environment**

VOC data indicate that the majority of VOC emissions are anthropogenic and dilute (i.e., man-made and at low concentrations). While this information indicates that the majority of VOC emissions can potentially be controlled (i.e., the man-made portion), the prevalence of low concentration streams indicates that control may be difficult to accomplish since few technologies are currently available to control/recover low concentration streams effectively. Since VOC contamination in the air and water is a major health and ecological risk that can lead to tropospheric ozone formation, stratospheric ozone depletion, lung disease, and cancer, promising technologies capable of treating low concentration streams need to be developed.

Before Toxic Release Inventory (TRI) data were available, EPA and industry did not fully comprehend industry's contribution to VOC releases. After TRI data were released, EPA was able to comprehensively assess where pollution was originating and develop a strategy for its reduction. TRI data resulted in the development of a number of programs to reduce emissions, including the 33/50 Program for 17 chemicals, Project XL, and the Common Sense Initiative. TRI data also helped make industry and citizens aware of the seriousness of the pollution issue. This new awareness resulted in company-specific emission reduction programs, Responsible Care® programs in the chemical industry, and the wide-scale acceptance of pollution prevention programs.

## **“Industrial Emission Sources” and “Where the Problems Are Most Evident”**

Based on 1998 emission projections, the chemical, primary metals, petroleum, paper, and food industries generated the most production-related waste, with the chemical industry serving as the largest emitter. A comparison with 1996 data indicates that the paper and primary metals industries experienced emission reductions of 0.5 and 2.0 percent (%), respectively, and that petroleum industry releases remained unchanged during this period. The chemical and food industries, however, showed emission increases of 6.8% and 83.1%, respectively, from 1996 to 1998. It should be noted that many of the controls implemented by the chemical industry from 1996 to 1998 were overshadowed by the tremendous growth experienced by the industry during that period.

A review of production-related waste data indicates that, on a pound-per-pound basis, methanol (245 million pounds), toluene (126 million pounds), and xylene (88 million pounds) were the VOCs emitted in the largest quantities in 1996. Other high level or volume production-related waste chemicals included: zinc compounds (209 million pounds), ammonia (193 million pounds), nitrate compounds (169 million pounds), chlorine (67 million pounds), and hydrogen chloride (66 million pounds).

#### **“Strategies for Reducing Risk”**

Three strategies can be employed to reduce VOC-related risk. The first strategy entails remediating the contaminated media (land or groundwater) using a treatment/destruction technology such as bioremediation. In general, recovery technologies are not considered for remedial efforts because the recovered contaminant rarely has reuse value.

The next strategy for reducing VOC-related risk involves the use of control technologies, like incineration or catalytic oxidation, to treat pollution (e.g., VOC emissions). In general, destruction technologies are employed to deal with “end-of-pipe” emissions.

The third strategy involves using pollution prevention techniques to prevent the generation of a pollutant. This can be accomplished by: 1) employing material substitution, material avoidance, and process changes (e.g., substitute an aqueous solvent for a chlorinated solvent); or 2) recycling/reusing materials (e.g., methylene chloride recovery from polycarbonate manufacture, solvent recovery from paint spray booths, or in-process recycling of reactants/byproducts/solvents).

All three strategic avenues are important for VOC management. Unfortunately, few conventional technologies can efficiently remove, capture, or recover/reuse VOCs from low concentration streams. The technical challenge faced by technology developers today is the development of highly efficient, cost effective VOC recovery methods (e.g., low-cost designer sorbents with high capacity or pervaporation, which are capable of transforming dilute streams into highly concentrated streams). To support this effort, seminar participants were encouraged to identify currently available technologies, technologies that appear promising, and technologies that are coming in the near future.

# VOCs: Sources, Definitions, and Considerations for Recovery

Presented on September 16, 1998 by Carlos Nunez, U.S. EPA NRMRL

This presentation gives an overview of major VOC sources and general considerations for product recovery, including several basic and pertinent definitions.

## Definitions

VOCs are defined as “any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.” If, however, the photochemical reactivity of an organic compound is negligible (e.g., less than the reactivity of ethane), it can be excluded from classification as a VOC. Furthermore, once a compound is classified as a VOC, its specific reactivity becomes irrelevant from a recovery/control perspective since the regulatory mandates (and the resulting recovery/control systems) focus on total VOC reduction goals, which fail to weight individual compounds based on their reactivities.

Originally four compounds were classified as negligibly reactive (methane, ethane, methyl chloroform, and trichlorotrifluoroethane). Since 1977, 42 compounds or classes of compounds have been classified as negligibly reactive and added to the exempt list. Most of the exemptions were determined by comparing the  $k_{OH}$  value of the compound of interest to the  $k_{OH}$  of ethane. [Note:  $k_{OH}$  is the reaction rate constant for the reaction of a compound with an hydroxyl (OH) radical.] In 1993, however, EPA began evaluating exemption petitions based on the maximum incremental reactivity (MIR) of a compound. MIRs, which focus on the mechanistic aspects of atmospheric reactions, are calculated based on the grams ozone produced per gram of compound reacted; acetone was the first compound evaluated for exemption using MIR. Currently 15 exemption petitions are being processed.

## Major VOC Sources

Based on 1996 data, processes that involve solvent utilization are responsible for 33% of the VOCs released to the atmosphere. The remaining 67% is provided by the following sources: 29% from on-road vehicles, 13% from non-road vehicles, 7% from storage and transport activities, 3% miscellaneous, and 15% from other sources (i.e., fuel combustion, chemical and allied product manufacturing, metals processing, petroleum and related industries, waste disposal and recycling, and other industrial processes). Since approximately half of the releases associated with solvent utilization can be attributed to various coating operations, EPA Research Triangle Park has targeted this area for further research.

It should be noted that the VOC levels in 1996 represent total estimated reductions of 7% and 38%, respectively, from 1995 and 1970 levels. This can be attributed in part to significant emissions reductions in the mobile sector due to uniform nationwide controls. (Note: Vehicle emission rates were reduced by approximately 90%, compensating for population increases and the two-fold increase in the number of vehicle miles traveled.) It should also be noted that VOCs from natural sources are almost equal to anthropogenic emissions; however their atmospheric impacts are unknown.

## Considerations for Product Recovery

Technical feasibility and economic feasibility must be accounted for when considering product

recovery. In order to determine the technical feasibility of a process, the following parameters need to be evaluated: 1) recovery efficiency (regulatory requirement); 2) product quality (process requirement); 3) the product's physical and chemical characteristics (e.g., vapor pressure, molecular weight, polarity/solubility, and molecular size); and 4) emission stream characteristics (e.g., flow rate, concentration, temperature, moisture, contaminants). The economic feasibility of a process can be determined by: 1) identifying the capital and operating costs (recovery, destruction, and new); and 2) comparing annualized costs to virgin material costs and the costs of other treatment or disposal options. To be considered economically feasible, recovery costs must be less than disposal/destruction and makeup material costs. Ultimately, the process chosen to control a VOC stream will need to balance technical and economic goals/limitations to meet environmental and corporate requirements.

# Overview of VOC Recovery Technologies

Presented on September 16, 1998 by Kamalesh Sirkar, New Jersey Institute of Technology (NJIT)

After providing some background information on recovery technologies, vapor- and aqueous-phase VOC recovery processes were discussed. Emphasis was placed on vapor-phase processes, since the majority of aqueous-phase systems are well known.

## Background Information

References - Although there is a lack of consolidated sources of VOC recovery studies, the following references were identified as useful resources:

- J.L. Humphrey and G.E. Keller, II, "Separation Process Technology," McGraw Hill, New York, Chapter 7 (1987).
- N. Mukhopadhyay and E. C. Moretti, "Current and Potential Future Industrial Practices for Reducing and Controlling Volatile Organic Compounds," Center for Waste Reduction Technologies (CWRT), American Institute of Chemical Engineers (AIChE) (1993).
- Papers Presented in "Zero Discharge Manufacturing: Removal of Organics from Air I, II, III," Sessions 26, 27, and 28. Preprints of Topical Conference on Sep. Sci. and Tech., AIChE Annual Mtg., Part II, Los Angeles, CA, Nov. 16-21 (1997).

Definition - VOCs can be defined as organic chemicals with a vapor pressure of more than 0.1 millimeter of mercury (mm Hg), at 20 degrees Celsius ("C) and 760 mm Hg, which participate in atmospheric photochemical reactions. This definition excludes carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate. Over 318 compounds have been classified as VOCs. These compounds contribute to an annual VOC emission rate of 8.5 to 17 million metric tons per year (from stationary sources) and an annual energy loss of 450 to 900 trillion British Thermal Units (BTUs) per year (approximately 3% of the total net U.S. industry usage).

Industry Perspective-A CWRT study by Mukhopadhyay and Moretti (1993) yielded the following:

- Information on process vents, wastewater operations, storage tanks, transfer operations, air-stripping operations, purge streams, devolatilization operations - Maximum Achievable Control Technology (MACT) standards.
- Information on the reduction of aliphatic, aromatic, and halogenated hydrocarbons as the primary VOCs emitted; also significant amounts of alcohols, ethers, glycols, etc., were emitted
- User survey results indicating that users spend 40% of their capital expenditures on streams with flows near 500 standard cubic feet per minute (scfm). This indicates that it is time to redirect research towards small flow streams since lower flow streams apparently command a substantial portion of the market. Additionally, the CWRT study notes that 80% of user capital expenditures are for streams with flows less than 5,000 scfm, an area which most developers are focusing on.
- User survey results indicating that users spend 90% of their capital expenditures on VOC streams with VOC concentrations from 500 to 10,000 parts per million (ppm). Additionally, 50% of their capital expenditures are for VOC streams with concentrations from 1,000 to 5,000 ppm and 8% of their capital expenditures are for lean VOC streams with concentrations less than 500 ppm.

- Supplier surveys indicating that 40% of their total sales are attributed to adsorbers.

Basic Principles - In-plant gaseous stream sources (air/nitrogen) are often too numerous for collection and treatment by a central facility/process. In-plant liquid sources are also numerous; however, these streams are usually collected for centralized cleanup. Additionally, when gaseous streams are treated, aqueous streams are often produced (and vice versa); thus a clear-cut distinction between treatment of gaseous and liquid streams is not always possible.

### **Vapor-Phase Systems**

Gas-phase VOC recovery is typically accomplished using phase change processes (e.g., distillation or condensation) or mass separating agent-based processes, including equilibrium-based processes (e.g., adsorption, absorption, and membrane-based absorption) and rate-governed membrane processes (e.g., vapor permeation). Generally, however, most processes are hybrid processes, consisting of at least two separation techniques.

Adsorption and Regeneration Processes - Activated carbon, synthetic resin beads (styrene divinylbenzene polymers), zeolites, and aerogels (which are regenerable at 50°C) are among the different types of adsorbents available for VOC recovery. Although activated carbon provides excellent adsorption, regeneration can be difficult. Furthermore, activated carbon has poor stability, humidity control problems, and is chemically reactive with certain contaminants (e.g., causing bed fires from ketones, aldehydes, etc.).

When adsorption is used for VOC removal, the adsorbent can be regenerated using thermal regeneration, pressure swing adsorption (PSA), or with purge gas. A variety of thermal regeneration processes are available, including steam, hot nitrogen [450 degrees Fahrenheit (OF) - BOC - AIRCO], microwave, infrared (for fixed beds), rotary wheels (for traveling beds), and fluidized beds. A schematic of a fixed-bed adsorption process for recovery of acetone for air and an adsorbent wheel with monolithic adsorbent were presented as examples of adsorption systems.

Fluidized Bed Systems - The Polyad® Process was presented as an example of a continuous fluidized bed process. This process utilizes a separate adsorber and desorber and a highly abrasion resistant, macroporous, polymeric pellet called Bonopore. During operation, particles are pneumatically transported from the adsorber to the, desorber, where they are regenerated using steam-heated, air-based desorption. The recovered VOCs are condensed using cooling water. These units typically treat 35,000 cubic meters per hour (m<sup>3</sup>/hr) vapor streams, but have a 500 to 500,000 m<sup>3</sup>/hr range. Additionally, special hydrophilic adsorbents (Optipore®) can be used for streams containing water vapor for adsorbing formaldehyde.

A schematic of a Sorbathene®-DOW PSA process was presented to highlight some of the characteristics of a PSA system. Although activated carbon PSA processes have been used in 90% of all gasoline vapor recovery systems installed at fuel loading terminals, including 1,000 locations in the U.S. and 500 international locations there is a general misconception that PSA has to be performed using polymeric adsorbent. Because only adsorbents with high butane working capacities can be used (e.g., greater than 0.065 grams per cubic centimeter), only 4 of 150 activated carbon adsorbents have appropriate retentivity (i.e., two wood-based and two coal-based). Typically these systems have to meet 10 milligrams hydrocarbon per liter (mg HC/liter) and demanding regeneration vacuum requirements, [Note: The German limit is 150 milligrams of hydrocarbon per normal cubic meter (mg HC/Nm<sup>3</sup>), 65 times lower than the U.S. EPA limit] Furthermore, they primarily adsorb non-(CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) VOCs, such as C<sub>4</sub>H<sub>10</sub>, C<sub>5</sub>H<sub>12</sub>, C<sub>6</sub>H<sub>14</sub>, etc.

Absorption - Absorption processes should be selected based on the characteristics of the VOC to be treated. Since water can act as an absorbent as long as an azeotrope is not formed, conventional towers should be used to treat hydrophilic VOCs. If a hydrophobic VOC requires treatment, membrane-based absorption and stripping using heavy hydrocarbon absorbents is probably appropriate. A schematic of an absorption process for recovering acetone from air was presented,

Membranes - During membrane permeation, the VOC permeates through a VOC-selective, rubbery membrane composed of polydimethylsiloxane or polyoctylmethylsiloxane, leaving the nitrogen and air behind. These membranes come in a number of configurations, including spiral-wound modules (from MTR, Inc.), round flat sheet membranes in a membrane envelope (from GKSS, Inc.), and hollow fiber membranes having plasma-polymerized silicone membranes (from AMT, Inc.). Typically, membrane systems contain a condenser, compressor, and a membrane. The flow diagrams developed for these systems are determined by compression, condensation, and membrane hybrid configurations. Three membrane process schematics highlighted some of the different configurations possible with membrane systems: 1) membrane-based absorption and stripping process; 2) flow swing membrane permeation; and 3) vacuum driven vapor permeation process.

Condensation - A schematic of a condensation system for removing acetone from air and a schematic of the Kryoclean™ VOC control system served as an aid to visualize condensation systems.

Process options for removing VOCs from vent streams are summarized in Table 1.

**Table 1. Process Options for Removing VOCs from Vent Streams**

<b>Process</b>	<b>Maximum Pollutant Concentration (mole % in feed, except where indicated)</b>	<b>Maximum Removal (%)</b>
Membranes	nearly unlimited	90 to 98
PSA	20 to 40	greater than 99
Temperature swing Adsorption/Fixed Bed	a few %	greater than 99
Moving/Fluidized Beds	a few %	90 to 98
Wheel-Based	1,000 to 5,000 ppm	98
Absorption	nearly unlimited	90 to 98
Refrigeration/Cooling	unlimited	50 to 75
Freezing with Liquid Nitrogen	unlimited	greater than 99

A comparison of vapor-phase VOC recovery technologies, based on air feed rates and acetone concentrations, indicates the following:

- Membranes are appropriate for high concentration (greater than 2% acetone), low flow rates (from 100 to 1,000 scfm)
- Absorption technologies are appropriate for high concentration (greater than 2% acetone),



medium to high flow rates (from 1,000 to 10,000 scfm), and for low to medium concentration (0 to 2% acetone), high flow rates (greater than 2,000 scfm)

PSA is appropriate for low concentration (less than 0.3% acetone), low to medium flow rates (from 100 to 2,000 scfm).

This comparison also indicates that a number of technologies (e.g., membranes, PSA, etc.) are competing against each other for the medium concentration (0.3 to 2% acetone), low to medium/high flow (100 to 2,000 scfm) streams.

### **Aqueous-Phase Systems**

Aqueous-phase VOC recovery is typically accomplished using phase change processes, filtration processes, or mass separating agent-based processes. Appropriate mass separating agent-based processes include equilibrium-based processes (e.g., adsorption and stripping) and rate-governed membrane processes (e.g., pervaporation). Like gas phase systems, most processes are generally hybrid processes, consisting of at least two separation techniques. An aqueous VOC recovery which employed a combination of several processes (stripping, adsorption, etc.) was shown to illustrate prevalence of hybrid systems for dealing with aqueous phase VOC recovery.

**Stripping** - A schematic of an open- and a closed-loop stripping/adsorption system was used as an introduction to stripping processes. Steam- or air-stripping effectiveness can be evaluated using the following equation:

$$K^{\infty} = \frac{y}{x} \Big|_{\text{inf. dil}} = f^{\circ} g^{\infty} / P$$

where,

$K^{\infty}$  = the dimension less Henry's Law constant

$y$  = gas phase mole fraction

$x$  = liquid phase mole fraction

$f^{\circ}$  = fugacity, which can be approximated by the vapor pressure

$y^{\infty}$  = infinite dilution activity coefficient

$P$  = total pressure.

Contaminants with a  $\log_{10} K^{\infty}$  which is greater than -2 and less than 2 tend to be highly hydrophilic, low molecular weight compounds which are difficult to strip (e.g., ethylenediamine, ethylene glycol, formaldehyde, acetic acid, phenol, methanol, acetone, 1-butanol, and ethyl acetate). Contaminants with a  $\log_{10} K^{\infty}$  greater than 2 are usually easier to strip (e.g., methylene chloride, chloroform, benzene, toluene, carbon tetrachloride, vinyl chloride, and 1-hexane).

Surfactant-enhanced carbon regeneration is an interesting technology in which the organic-saturated column is regenerated first with surfactant and then with water. The surfactant rinse produces a surfactant/organic stream; the water rinse produces a water/surfactant stream.

**Pervaporation** - Pervaporation processes are also used to remove organics from aqueous streams. Table 2 contains typical VOC/water separation factors for pervaporation. Surfactant enhanced aquifer remediation for surfactant recovery can also be employed during soil remediation. This application of the technology was discussed by Leland Vane in another session.

**Table 2. Typical VOC/Water Separation Factors in Pervaporation**

<b>VOC/Water Separation Factors</b>	<b>Volatile Organic Compounds</b>
greater than 1,000	Benzene, ethyl benzene, toluene, xylenes, trichloroethylene, chloroform, vinyl chloride, ethyl dichloride, methylene chloride, perfluorocarbons, hexane
100 to 1,000	Ethyl acetate, ethyl butyrate, hexanol, methyl acetate, methyl ethyl ketone
10 to 100	Propanol, butanol, acetone, amyl alcohol, acetaldehyde
1 to 10	Methanol, ethanol, phenol, acetic acid, ethylene glycol, dimethyl formamide, dimethyl acetamide

Hybrid Process - A variety of hybrid processes can be used for wastewater treatment including: 1) air-stripping followed by activated carbon adsorption of the stripping air; 2) steam-stripping followed by condensation; 3) activated carbon adsorption followed by steam-stripping; and 4) solvent extraction followed by distillation. Additionally, wastewater from stream-stripping can be treated by reverse osmosis and concentrated for recovery by pervaporation.

A comparison of aqueous-phase VOC recovery technologies, based on feed rates and VOC concentrations, indicates the following:

- Chemical oxidation, ultraviolet (UV) destruction, or air stripping/carbon adsorption are appropriate for low concentration (from 0.001 to 0.01% VOC), low to high flow rates (from 0.1 to 1,000 gallons per minute, or gpm)
- Pervaporation is appropriate for medium concentration (from 0.01 to 10% VOC), low to medium flow rates (from 1 to 100 gpm)
- Steam stripping is appropriate for medium concentration (from 0.01 to 10% VOC), medium to high flow rates (from 10 to 1,000 gpm)
- Distillation and incineration are appropriate for high concentration (from 10 to 100% VOC), low to high flow rates (from 0.1 to 1,000 gpm).

### **Conclusions**

- Need comparative economics and evaluation for air/nitrogen streams having: 1) large flow rates, 2) hydrophobic VOCs, and 3) hydrophobic and hydrophilic VOCs
- Need comparative economics and evaluation for aqueous waste streams utilizing different processes (e.g., stripping, reverse osmosis, pervaporation, solvent extraction, and distillation) and combinations of processes
- Need compact and flexible devices for vents from small-scale equipment
- Need more VOC-selective pervaporation membranes for polar VOCs
- Need membrane-based, compact and cheaper steam strippers
- Need selective and stable adsorbents that are strippable using small temperature changes
- Need to continue to improve PSA processes.

# Industrial Research Programs

Presented on September 16, 1998 by Edward Moretti, Baker Environmental

This presentation gives an overview of new applications, developments of existing technologies and innovative technology developments. Although the seminar emphasizes VOC recovery, both recovery and destruction technologies were presented. This was done to ensure that the seminar participants were aware of the technologies that recovery processes compete against, both technically and economically. Volume reduction technologies were not discussed, since these technologies have moved from research to application.

## **New Applications of Existing Technology**

Membrane Separation - During membrane separation, contaminants are recovered from waste process streams using permeable membranes. Membrane separation has been used in the past for water quality management and has recently been used for air management, particularly VOC recovery. Membrane separation is used to recover compounds that are not efficiently recovered using adsorption and condensation, Membrane separation is increasingly being used for halogenated solvents and is a good alternative for recovering expensive solvents.

Biofiltration - Biofiltration has been used frequently in Europe for odor control and is currently expanding into a number of other areas. During biofiltration, VOCs are destroyed in biologically active filter beds. The technology has a 50% success rate for sustained operation and some success with gasoline and benzene, toluene, and xylene (BTX) vapor streams. It also has low operating costs and energy usage.

Photochemical Destruction Technologies - Photochemical destruction technologies destroy VOCs using UV radiation and oxidants. In general, this technology has limited commercial application.

## **New Developments Using Existing Technologies**

New Adsorbents - Adsorbents other than granular activated carbon are currently being developed including zeolites, polymers, and carbon filters. In addition to treating a larger number and range of VOCs, these adsorbents offer improved performance for high boiling point compounds, humid vapor streams, and exothermic adsorption.

Newer Bed-Regeneration Options - A number of newer bed regeneration options have been developed, including the following:

- Refrigeration (e.g., Brayton Cycle Systems)
- Solvents (e.g., acetone, methanol)
- Vacuum (e.g., PSA)
- Inert gases (e.g., nitrogen)
- Resistive electrical heating
- Microwave heating.

Resistive electrical heating and microwave heating both use the electrical characteristics of the adsorption material (carbon or other) to regulate the temperature of both the adsorption material

and adsorbed compounds.

New Packing Materials and Cryogenic Fluids for Condensation - Research continues on new packing materials to reduce fouling and on cryogenic fluids for condensation (e.g., liquid nitrogen and liquid carbon dioxide).

### **Innovative Technology Developments**

Totally New Concepts and Market Drivers - The destruction of VOCs using ionized gas (e.g., plasma) is a relatively new concept. The plasma is a high temperature ionized gas that reacts with VOCs to form carbon dioxide, hydrogen, and water. Corona discharge plasma reactors and electron beam reactors are also being developed. The VOC innovative technology market has been driven by the type and concentration of VOCs encountered in exhaust streams, exhaust stream flow rates (e.g., high concentration, low flow rate streams are well suited), and regulatory pressure. Emphasis has been placed on developing technologies capable of treating more difficult streams (e.g., multiple VOC streams, halogenated VOCs)

Benefits and Risks of Innovative Technologies - The benefits of using innovative technologies include permit waivers (to accommodate these technologies as they are developing) and demonstration co-funding. The risks associated with using innovative technologies include unknown operation and maintenance (O&M) costs, scale-up problems (from bench to pilot to commercial applications), unacceptable process changes, unknown waste generation costs, unknown long-term operational reliability, and unknown long-term reliability to meet regulatory performance standards. These challenges can be met by technologies capable of demonstrating technical feasibility and attractive economics.

# VOC Recovery Research at EPA Office of Research and Development (ORD)

Presented on September 16, 1998 by Teresa Hat-ten, U.S. EPA NRMRL

The Clean Products and Processes Branch at U.S. EPA NRMRL uses the risk management/risk assessment paradigm to prioritize its research efforts. This approach was recommended by the Science Advisory Board which is responsible for reviewing EPA's research. EPA NRMRL in Cincinnati, Ohio focuses on the risk management facet of the paradigm, while the other three laboratories in ORD focus on risk assessment.

EPA NRMRL in Cincinnati, Ohio is currently concentrating its research efforts on pervaporation, temperature swing sorption, and pollution prevention tools. These efforts are summarized below.

## **Pervaporation**

Pervaporation combines permeation and evaporation to transfer contaminants from a liquid stream through a non-porous VOC-selective membrane to an inert gas vapor stream. Pervaporation research at EPA NRMRL in Cincinnati originated from a joint EPA/Department of Defense (DOD) effort to identify/develop a technology capable of remediating contaminated groundwater at DOD sites. EPA NRMRL has begun an industrial pollution prevention pervaporation research project designed to investigate regeneration of cleaning alcohols using dehydration. (Note: Cleaning alcohols are being used by a number of facilities as an alternative to chlorinated solvents.) Other EPA NRMRL research projects are described in the following subsections.

Remediation Fluid Recycling - A DOD-sponsored effort that is discussed in detail in Leland Vane's presentation "Dehydration and VOC Separation by Pervaporation for Remediation Fluid Recycling."

Pervaporation Performance Prediction Software and Database (PPPS&D) Development - Version 1 of the software program contains a tutorial to educate the user, a research database developed using research and commercial data, and numerical and other models which can be used to predict bench-scale performance. Version 2, which will be used to predict pilot-scale performance, and Version 3, which will be used to estimate pilot unit costs, will be developed under a Cooperative Research and Development Agreement (CRADA) with Mempro, a privately owned software company.

Polymer/Ceramic Composite Membrane Development - These membranes can potentially operate at separation factors of 3,000 to 10,000.

Conductive Membranes and Films for Separation Processes - Electric currents are used to heat the separation membranes using resistive heating, thereby encouraging contaminant vaporization.

## **Temperature Swing Sorption**

Like pervaporation, temperature swing sorption research at EPA NRMRL in Cincinnati started as a DOD-funded effort. In this case, however, the DOD was interested in identifying/developing a technology which would be capable of recovering VOCs from paint spray booth streams (which typically contain water vapors). Temperature swing sorption uses a polymeric sorbent material

instead of carbon to separate contaminants from a process stream. Unlike traditional adsorption (during which the contaminated air is heated and cooled cyclically), only the sorbent, not the air stream, is cooled during the sorption phase; this increases both capacity and efficiency. Also, regeneration is completed in place and the presence of water vapor should not affect capacity.

The technical objective of this research is to develop a cost-effective technology for recovering VOCs from paint spray booth exhausts. Recovery becomes viable when low VOC coating formulations can not be used or when reductions are mandated by a State Implementation Plan (SIP).

#### **Pollution Prevention Analytical Tools Development**

EPA ORD is currently developing process simulation software (waste reduction algorithm) which can be used as an add-on package to commercial software programs. This software can be used to predict waste generation from various process configurations, which can be modified by the user. EPA ORD is also developing a number of life cycle tools for inventory and impact assessment. These tools can be used during technology development to assess relative environmental impacts of various chemicals/wastes (e.g., ozone depletion, global warming, and human and ecological toxicity).

# **Short Flow Path Pressure Swing Adsorption - Lower Cost Adsorption Processing SHERPA™**

Presented on September 16, 1998 by William Asher, SRI International

SHERPA™ is a short flow path PSA process which can be used for lower cost adsorption processing. With this process, the flow path is reduced from several feet to a fraction of an inch. By reducing the flow path, the size of the unit used to remove VOCs is decreased by a factor of 100. This results in lower capital costs and space requirements.

The PSA cycle has three steps: 1) pressurization, 2) high pressure flow, and 3) depressurization. During the pressurization step, VOC adsorption begins as process air (usually at a vacuum) flows into the adsorber through an open valve at the bottom of the unit. Since the outlet valve located at the top of the unit is closed, pressure continues to build as process air enters the unit. Once atmospheric pressure is achieved, the outlet valve is opened and the second step in the cycle, high pressure flow, begins. During high pressure flow, both the inlet and outlet valves remain open. During this step, contaminated air enters the unit, is cleaned by the adsorber, and exits through the outlet valve. Step 3, depressurization, begins after the adsorbent has become saturated with contaminants. During this step the exit valve is closed, and contaminants are removed from the adsorbent through the valve at the bottom of the adsorber. As depressurization continues, the pressure in the adsorber decreases to vacuum levels and the feed and adsorbate flows decrease to close to zero.

Conventional PSA beds are approximately 5 to 20 feet long and contain evenly distributed adsorbent particles. They can be as large as one eighth of an inch in diameter in order to limit the pressure drops across the beds. Prior hollow fiber PSA contactors use hollow fibers to lower the pressure drop across the length of the 'bed. As a result, smaller particles can be used with this configuration.

Although these prior hollow fiber systems are more efficient than conventional PSA beds, their efficiency is limited by the diffusion of contaminants from the hollow fibers to the external surface of the adsorbent particles. To address this limitation, every other fiber has been blocked in newer hollow fiber systems, causing process air to enter the bed through one set of fibers/tubes and flow through adsorbent particles to the adjacent fibers, where the process air is transferred out of the system. With this configuration, the most distant particles are utilized and there is no selectivity for the fibers. As a result, the flow path drops from several feet to a fraction of an inch.

The reduction in flow path experienced using the newer hollow fiber configuration results in tremendous cost and performance advantages. In addition to being able to use particles as small as 20 microns in diameter, both the cycle time and the bed size are reduced by a factor of up to 100. This results in a much smaller and lower cost unit. Also, diffusion to the adsorbent is no longer the limiting step in the process. (Note: Bed size is directly proportional to cycle time.) According to the developer, the new paradigm is different in kind and concept from all previous hollow fiber adsorbers and all previous rapid cycle PSAs. Additionally, the feasibility of the new contactor has been experimentally established.

The contactors are composed of a woven "mat" which is rolled up and placed within a case. The

mat is composed of sorbent, solid filaments, porous hollow elements with sealed ends, and an impermeable layer. The contactors can be manufactured using Celgard® fiber, fabric, a center tube with a central plug, and resin.

The newer PSA systems can be used for the removal and/or recovery of VOC (using established and new adsorbents) and natural gas (using natural gas liquids, water, and acid gases). It can also be used for separations on petrochemical light ends and to remove and/or recover a number of other gases. As SRI approaches commercial application of this system, they have recently entered into discussions with hollow fiber producers/module fabricators and valve manufacturers for less than 1-second valves. The system is particularly applicable to new sorbent systems under development.



# Solvent Recovery Applications at 3M

Presented on September 16, 1998 by James Garmaker, 3M Corporation

This presentation is divided into two main components: an overview of solvent recovery applications at 3M and a **case** study based on real data.

## Solvent Recovery Applications at 3M

3M has 110 VOC air pollution control systems worldwide: 85 thermal oxidizers and 25 solvent recovery units. The first systems were installed in the 1970s. In 1987 the Air Emission Reduction Program (AERP) became global corporate policy. Under this policy all sources which emit more than 100 tons per year must meet local government standards and AERP requirements of 81% control for existing sources and 90% control for new sources. Since AERP's adoption, emissions have dropped from over 100,000 tons per year in 1990 to just over 20,000 tons per year in 1997.

To date, 3M has invested approximately \$260 million in VOC control systems and received the following awards:

- 1996 - President's Sustainable Development Award for 3P Program
- 1995 - Environmental Champions Award for Air Emission Reductions (U.S. EPA)
- 1995 - Energy Efficiency Award for Brayton Cycle Solvent Recovery Systems (Alliance to Save Energy).
- 1991 - Stratospheric Ozone Protection Award (U.S. EPA)
- 1991 - Winner of the President's Environment and Conservation Challenge Award Citation.

3M currently uses 15 carbon adsorption systems (13 which employ steam regeneration and 2 which use inert gas regeneration), 10 inert gas condensation systems (which condense solvents on cooling coils), and 5 liquid wet scrap distillation systems (which recover solvents from hazardous waste). The carbon adsorption process air flows range from 6,000 to 102,000 scfm and the inert gas condensation process solvent rates ranges from 5 to 900 pounds per hour (lbs/hr). Hexane, heptane, toluene, naptha, ethanol, isopropyl alcohol, ethyl acetate, methyl ethyl ketone, cyclohexanone, and carbon disulfide are among the solvents recovered with 3M's solvent recovery systems.

In general, 3M favors solvent recovery applications with the following characteristics:

- High VOC usage rates
- Fixed solvent blends (to ensure cross-contamination does not occur)
- Reuse solvent in process
- High solvent value
- Continuous operation (to provide enough payback to justify the higher costs).

## Solvent Recovery Case Study (3M Hutchinson, Minnesota)

The 3M Hutchinson, Minnesota facility is an audio/video tape manufacturing facility which utilizes methyl ethyl ketone, toluene, and cyclohexanone during production. In 1990, 3M installed a solvent recovery plant at this facility which uses carbon adsorption, steam regeneration, and solvent distillation.

The solvent recovery plant is a continuous process which operates, with the help of two operators, 24 hours a day, 360 days per year. The plant is designed to process 102,000 scfm of

contaminated process air and recover 5,100 pounds of solvent per hour. The recovered solvent is composed of methyl ethyl ketone (55%), toluene (30%), and cyclohexanone (15%). The system is designed to yield a recovery efficiency of 99% and to produce a recovered solvent which is 99% pure.

During adsorption (which lasts 132 minutes) 75,000 scfm of solvent-laden air is typically processed. Once the adsorption cycle is complete, the regeneration cycle begins. During regeneration (which lasts 40 minutes) 16,500 lbs/hr of steam are introduced to the adsorbers. The regeneration phase is then followed by a cooling phase (which lasts 23 minutes), during which 14,000 scfm of ambient air is introduced to the adsorbers.

The adsorption plant performance can be summarized as follows:

- Processes 75,000 scfm of solvent-laden air with a temperature of 95°F and 45% R.H.
- Produces 2,800 pounds of solvent per hour
- 99.5% adsorption efficiency
- 4 to 10% carbon working capacity
- Generates 5 to 8 pounds of steam for every pound of recovered solvent.

The reaction chemistry of the system also results in the formation of diacetyl and adipic acids (from methyl ethyl ketone oxidation) and the potential for a ketone-related fire at carbon monoxide concentrations below 5 ppm.

The distillation process employed at the 3M Hutchinson, Minnesota facility generates 67,000 pounds of solvent per day. During the distillation process, water/solvent separation is performed using decanters and wastewater stripping columns. The separated solvent is then neutralized using a wash column and distilled using dehydration, methyl ethyl ketone, toluene, and cyclohexanone columns.

As of May 1998, 1,610,751 pounds of methyl ethyl ketone, toluene, and cyclohexanone were recovered by the plant's solvent recovery system. Overall, 99.4% of the recovered solvents were later applied at the plant. The net percent of recovered solvent applied was 101.7%, 99.9%, and 90.1% for methyl ethyl ketone, toluene, and cyclohexanone, respectively.

The solvent recovery system was started in 1990 and temporarily shut down in 1991 following an adsorber carbon bed fire and adsorber implosion. The process was later reformulated in 1993 to reduce chloride production. In 1997 the MACT modifications were installed. These modifications included 41 mixing kettle vents, 3 wash tank vents, and 20 solvent recovery vents (15 tanks/vessels and 5 distillation columns).

Capital costs for this system totaled \$23,400,000. This total includes \$19,500,000 for installation, \$2,500,000 in recommissioning, and \$1,400,000 in MACT modifications. Annual operating costs averaged \$3,300,000. Approximately 13,200,000 pounds of methyl ethyl ketone; 7,200,000 pounds of toluene; and 3,600,000 pounds of cyclohexanone were recovered per year. The total value of the recovered solvent equaled \$7,968,000 (i.e., \$5,016,000 for methyl ethyl ketone; \$1,152,000 for toluene; and \$1,800,000 for cyclohexanone).

# **The Economics of Recovery: Using the Office of Air Quality, Planning, and Standards (OAQPS) Cost Manual as a Tool for Choosing the Right Reduction Strategy**

Presented on September 16, 1998 by Dan Mussatti, U.S. EPA OAQPS

The OAQPS Cost Manual is one of the principal engineering tools for predicting/assessing control costs. It was developed by the Innovative Strategies and Economics Group within the Air Quality Strategies and Standards Division in OAQPS. The manual is available on the Technology Transfer Network (TTN) web page at <http://www.epa.gov/ttn/catc/products.html#cccinfo>.

The OAQPS Cost Manual frequently serves as a reference and template for other cost manuals produced within and outside the EPA. It is designed to be general in nature, rather than control- or vendor- specific. It provides information on "how" a control works and costs incurred using the control. The level of detail contained in the OAQPS Cost Manual is rigorous and complete, particularly in regard to smaller costs that are easily overlooked. The OAQPS Cost Manual is designed for estimating costs for regulatory development [Regulatory Impact Analysis (RIA) etc.]. Although it does not cover every situation, it contains default assumptions that can be customized to fit a specific situation better.

The OAQPS Cost Manual is an evolving document which is presently under review/revision. It currently contains eleven chapters, with two new chapters forthcoming:

- Introduction
- General discussion of costs
- Nine chapters on control devices (incinerators, flares, adsorbers, filters, precipitators, condensers, hoods, ducts, and stacks).
- Nitrogen oxide (NO<sub>x</sub>) control devices (forthcoming)
- Permanent total enclosures (forthcoming).

Plans have been made to include a chapter on compliance assurance monitoring and to also add text throughout the document addressing the costs associated with retrofitting and process uncertainty.

In addition to discussing traditional accounting costs (e.g., the types of costs seen on a financial or profit/loss statement), the manual accounts for social costs, both tangible and intangible. Social costs are more difficult to quantify than accounting costs and are frequently forgotten in traditional cost evaluations. They consist of both tangible costs which can be measured to some extent (increased morbidity/mortality due to pollution, property damage due to pollution, productivity losses, and crop and livestock damage), and intangible costs (habitat loss, diminished biodiversity, aesthetic loss, option values, and existence values) which are very difficult to place a monetary value on. Accounting costs, on the other hand, are relatively easy to address and consist of annual costs (direct and indirect, fixed and variable, and recovery and salvage) and investment costs (land, capital, and salvage value).

Most firms are concerned with maximizing profits/revenues in the long-term and minimizing costs in the short-term. Thus, in the short-term many firms want to select a control strategy that has the lowest marginal cost of operation (i.e., the lowest cost of the next increment removed) over the relevant range, while in the long-term they are more likely to choose a control strategy with the

highest “net present value.” Unfortunately, when comparing the marginal costs associated with different “control” alternatives (e.g., a recovery process versus incineration), many companies fail to account for the social costs associated with the alternatives (Resource Conservation and Recovery Act costs, recycling revenues, etc.). This may cause a company to choose a non-recovery-based system (e.g., incineration) based on an analysis which underestimates the alternative’s true and full cost.

The experiences of a graphics printing enterprise highlight how social costs impact control strategy selections. This company originally used four different solvents as part of its operation, resulting in a waste stream that could not be recovered for reuse and causing the owners to favor incineration over traditional disposal alternatives (due to disposal-related regulatory liabilities). In response to these issues, the printing company chose to reformulate its process so that only one solvent was used (i.e., hexane). It then installed carbon adsorbers to recover the solvent for in-plant reuse. Not only did it essentially become a net supplier of hexane, but the company was also able to meet the discharge standards at a reduced compliance cost.

In this and other approaches being applied, a reduction strategy was selected after first examining the facility outputs with regard to the following:

- Identify the compounds in the effluent stream to be controlled
- Determine whether the effluent stream has value
- Determine whether the effluent stream contains toxic substances and, if so, whether those toxic substance are valuable and identify their disposal requirements.

If the effluent stream contains toxic substances that have no value, then incineration is probably the most cost-effective alternative. If, however, the effluent stream contains substances that have salvage value (e.g., reuse potential), then alternative technologies for recapturing the substances should be considered and their costs (i.e., net of salvage value) compared to the cost of incineration.

Ultimately a system is chosen based on how much control is needed. The “bad news” is that “The cost of reduction (control) is directly related to the level of reduction, and the level of reduction is highly correlated to how many regulations apply to the industry.” The “good news” is that there is a new tool available, called the Air Compliance Advisor (ACA), that can be used to help end-users solve complex air management problems.

ACA is a customizable decision support tool consisting of an integrated package of databases, algorithms, and models. End-users can modify ACA by resetting the default values (e.g., formulas and labor costs) to mimic specific situations. It is also a framework in which many models operate (and many more can be added).

ACA was developed by the Strategic Environmental Research and Development Program (SERDP) under a joint agreement between DOD, EPA, and DOE. It is composed of: data and analysis algorithms; data libraries; chemical properties; regulatory data; a hierarchy of source types; emission control technology information; pollution prevention information; and “suggestions” data. It contains information on the following control technologies:

- Carbon adsorbers (single bed and multiple bed)
- Thermal incinerators (catalytic, recuperative, and regenerative)
- Flares (self-supported, guy-supported, and derrick-supported)
- Gas absorbers
- Refrigerated condensers

- Wet scrubbers for particulate matter (PM) (venturi, impact)
- Baghouses (pulse-jet, reverse air, shaker).

Plans are currently being made to also include information on other common VOC and NO<sub>x</sub> controls.

ACA uses algorithms from AP-42, Water 8 documentation, and AQUIS. It can be used to calculate actual and potential emissions rates and as a means of documenting emission factor ratings and references (approximately 75% complete). ACA is available free of cost on the TTN web site at <http://www.epa.gov/ttn/catc/>.

# Rotary Concentration and Carbon Fiber Adsorption

Presented on September 16, 1998 by Ajay Gupta, Dürr Environmental

## Rotary Concentration

Rotary concentrators are a variation of conventional adsorption technologies which simultaneously perform adsorption, desorption (using hot air), and cooling. They use a rotating cylindrical honeycomb element that has been impregnated with adsorbent (carbon, zeolite, or a combination) to separate contaminants from process streams.

Before entering the rotating honeycomb element, process air is first treated to remove particulate (using a filter house, venturi scrubber, or electrostatic precipitator) and then forwarded through a static adsorption unit (usually containing granular activated carbon). The majority of the process air (approximately 90%) proceeds directly through the rotating element where approximately 95% of the VOCs are removed by adsorption. A small portion (e.g., 5 to 10%) of the process air is used to cool the honeycomb element. After exiting the element, the cleaned air is heated and re-circulated through the rotating wheel in order to desorb VOCs from the element. The solvent-laden air is then forwarded to a thermal oxidizer (recuperative, regenerative, or catalytic) for thermal treatment for VOC destruction.

Rotary concentrators are typically used to treat high volume (5,000 to 600,000 scfm), low concentration streams [less than 1,000 parts per million by volume (ppmv)] produced by paint spray booths (automotive and others), printing operations, semiconductor applications, and fiberglass plastic manufacturing operations. They have been used to concentrate/control a wide range of VOCs, including alcohols, aliphatics, ketones, glycols, and chlorinated compounds. Since process streams with less than ten or more organic components are rare, opportunities to use rotary concentrators to recover solvents have been limited.

Rotary concentrators normally operate at process temperatures of less than 100°F and humidities of less than 65% for carbon and less than 95% for zeolite. They are generally used to treat process streams with concentrations of less than 1,000 ppmv in order to ensure that lower explosive limits (LEL) are not exceeded. (Note: Typically the desorption air exiting the rotating element is ten times more concentrated than the untreated process air entering the cylinder.) These systems also operate at VOC removal efficiencies of 95% or greater.

Rotary concentrators can potentially be used for the following solvent recovery applications:

- Pre-concentrator for a conventional solvent recovery system
- Solvent recovery for VOCs with high LELs (e.g., for trichloroethylene at a concentration of up to 80,000 ppmv)
- In series to achieve concentrations which are 100 times greater than pretreated process air concentrations. In addition to yielding much higher concentrations, these systems will also be compact, light weight, have low pressure drops (4 to 5 inches water), and perform continuous solvent recovery, (Note: A new design, which uses concentrators in series, has been developed but has not yet been patented.)

## Carbon Fiber

Carbon fiber solvent recovery systems are batch systems which sequentially perform adsorption, desorption (with steam), and cooling. These systems use high capacity carbon fiber non-woven

mats setup in a baghouse-like configuration to separate contaminants from process streams. They have been used for the last 15 to 20 years in Germany and Japan; however, cost concerns have limited their use in the U.S.

Carbon fiber systems are typically used to treat high concentration streams (greater than 1,000 ppmv) produced by chemical manufacturing operations, pharmaceutical facilities, printing operations, and the painting and coating industry. They have been used to concentrate/control a wide range of VOCs, including alcohols (excluding methanol and ethanol), aliphatics, aromatics, ketones, glycols, and chlorinated compounds (including trichloroethane, methylene chloride, and trichloroethylene). Carbon fiber systems can also effectively treat flows of greater than 1,000 scfm, with the average single unit treating up to 15,000 scfm. (Note: Carbon fiber systems are not able to treat methanol and ethanol cost-effectively because carbon has a low capacity for these compounds.)

Carbon fiber systems normally operate at process stream temperatures of less than 150°F and humidities of less than 95%. They are generally used to treat process streams with concentrations that are greater than 1,000 ppmv and generally operate at removal efficiencies of 90 to 98%. Although the pressure drops and system removal efficiencies are similar to packed bed systems, steam consumption is lower and the units generally weigh less and are smaller in size (i.e., smaller footprints). The quality of the recovered solvent is also very high, in part because the carbon fibers are relatively free of impurities.

Activated carbon fiber matrices also have far more micropores than granular activated carbon pellets. This contributes to much faster adsorption and desorption kinetics experienced by carbon fiber systems as compared to traditional granular activated carbon systems.

# Zeolite Adsorption and Refrigeration - CONDENSORB™ VOC Recovery System

Presented on September 16, 1998 by Jon Kostyzak, M&W Industries

The Condensorb™ System combines high control efficiency, mechanical simplicity, low maintenance, low space requirements, and flexibility (e.g., changing solvents and flow rates) to cost-effectively recover concentrated dry solvent.

The Condensorb™ System is a combination of fixed bed zeolite adsorption and mechanical refrigeration condensation. This configuration allows the Condensorb™ System to treat large volumes of process air with low solvent loadings cost-effectively. The system typically removes 95 to 100% of the VOCs and hazardous air pollutants (HAPs) (including alcohol, acetate, and other water soluble solvents) from high flow rate process exhausts.

During treatment, process air is sent through a prefilter (as needed) to remove particulates before entering the concentrator. The concentrator is composed of a number of zeolite cells/bed which are responsible for removing the VOCs/HAPs from the process stream. During regeneration, warm air is sent through the concentrator (one to two zeolite beds only) in order to recover the VOCs/HAPs adsorbed by the zeolite beds. The ultra-low flow warm air used to regenerate the zeolite beds produces a regeneration air stream highly concentrated in VOCs. Although relatively dry, the regeneration air is sent through a drying stage after it leaves the concentrator to remove any moisture which may have entered the concentrator with the process air. The regeneration air is then forwarded to a mechanical refrigeration condenser, where it is chilled to 20 degrees below zero. The recovered VOCs and HAPs are collected and the residual air forwarded to the concentrator for final treatment.

Since steam is not used to regenerate the zeolite cells, the Condensorb™ System does not use a boiler. This saves on space, capital investment, and energy costs. Boiler-related tasks, like decanting and pH adjustment, are also avoided. Also the recovered solvent is relatively dry, making it a more usable product.

Power costs are also lower than for traditional recovery or destruction systems since the Condensorb™ System consumes little power and no fuel. Additionally, VOC or HAP recovery allows the unit to achieve a return on the investment.

The Condensorb™ System has the following advantages and disadvantages as compared to a traditional solvent recovery system:

## Advantages

- Recovered VOC/HAP adds economic benefit
- No fuel consumption
- No NO<sub>x</sub> production
- Very low pressure drop
- Relatively quiet
- 95% minimum recovery
- Adsorption media easily replaced/updated



- Very high uptime reliability
- Existing solvent recovery system can be retrofitted

#### Disadvantages

- Particulate filtration may be needed
- Inlet temperature is limited to 140°F (maximum).

A case study involving a flexographic printing operation demonstrates the economic payback that can be achieved using the Condensorb™ System. This company currently has a 45,000 scfm carbon solvent recovery system which needs to be updated to achieve an ethanol removal efficiency of 95% or greater. With the present system, it currently costs \$3.34 to recover a gallon of solvent. This cost includes \$1.57 per gallon to neutralize the recovered solvent.

By replacing the traditional solvent recovery system with the Condensorb™ System, a control efficiency for ethanol of greater than 95% will be achieved at a lower recovery cost that is less than \$1.25 per gallon of recovered solvent. Also, at least 50 gallons of ethanol lost per day using the traditional system can now be recovered using the Condensorb™ System.

An analysis of the cost and recovery estimates yielded the following “payback” results using the Condensorb™ System:

- Greater than 95% control of ethanol
- 132,000 gallons solvent recovered per year
- \$275,880 saved in annual recovery cost
- \$585,900 to install Condensorb™ System
- 25 month payback schedule.

# **A Novel Fluidized Bed Concentrator System for Solvent Recovery of High Volume, Low Concentration WC-laden Emissions**

Presented on September 16, 1998 by Edward Biedell, REECO

Technologies are needed which can economically and effectively recover or capture/destroy dilute concentrations of VOCs contained in relatively large air flows emitted by industrial and manufacturing facilities. A number of destruction and recovery technologies are available that can potentially fulfill this need (e.g., thermal oxidation, catalytic oxidation, carbon adsorption, and hybrid systems consisting of pre-concentration followed by oxidization or solvent recovery). This presentation focuses on the applicability of fluidized bed pre-concentrators.

In general, a recovery technology like fluidized bed pre-concentration is selected if the solvents requiring control are valuable and if they can be recovered economically. To determine this, the following factors need to be considered:

- VOC composition in the process exhaust
- Value of the recovered solvent (i.e., is it greater than \$0.30 per pound?)
- Capital, operating, and maintenance costs.

Fluidized bed pre-concentrators are synthetic carbonaceous beds used to adsorb VOCs/solvents. They are used to treat high volume (e.g., 10,000 to 500,000 scfm) process exhausts with VOC concentrations of less than 300 ppm and temperatures of less than 120°F. Although less common, fluidized bed pre-concentrators can also be used to treat exhausts with very low VOC concentrations (10 to 20 ppm), as well as concentrations near 1,000 ppm. Their ability to treat relatively high and low concentration streams effectively is strongly dependent, however, on the characteristics of the stream and system design.

Fluidized bed pre-concentrators typically achieve 95 to 98% VOC destruction or solvent recovery. They are also able to effectively handle lower inlet concentrations than regenerative thermal oxidation (RTO) and can be used for solvent recovery, unlike fixed carbon beds or rotary wheels. Fluidized bed pre-concentrators typically exhibit much higher air volume reduction factors (800 to 1,000:1) than fixed bed or rotary systems (10 to 30:1). The dramatic difference in volume reduction factors is attributed to the use of inert desorbing gases (steam or nitrogen) instead of air.

From a capital cost perspective, fluidized bed pre-concentrators consist of an adsorber and a desorber. Adsorber size (and cost) is dependent on air flow; desorber cost is based on the concentration of VOCs. In general, fluidized bed capital costs are close to the capital costs associated with regenerative thermal oxidation, but less than rotary wheel systems. Their operating costs, which are mainly limited to fuel and power costs, are much lower than regenerative thermal oxidation (approximately 20%) and the same as, or lower than, rotary wheel systems.

The beaded carbonaceous adsorbent (BCA) used in these units is a synthetic form of activated carbon with the following characteristics:

- Smooth, hard beads

- High surface area
- Carbonaceous composition
- Particle sizes ranging from 0.3 to 1 millimeter
- Less than 2% per year attrition rates
- Capable of on-site regeneration
- Able to easily handle (adsorb/desorb) chlorinated VOCs and hexamethyldisilanes without any adverse effects.

During treatment, process exhaust passes through a blower and enters the adsorber at the base of the unit. The process exhaust is cleaned as it flows through the BCA pellets contained in the upper portion of the adsorber. As process air flows up the adsorber, spent BCA pellets (i.e., saturated with organic compounds) exit the adsorber near its base. These pellets are gravity-fed through a desorber where organic compounds are removed by a counter-current flow of steam or nitrogen gas. The desorber is operated at or below the boiling point of the VOCs being removed, usually between 400 to 500°F. The cleaned pellets are returned to the top of the adsorber and the organic-laden air is forwarded to an oxidizer for destruction or to a solvent recovery system for condensation.

Fluidized bed pre-concentration systems can potentially be used at semiconductor chip manufacturing facilities, surface coating facilities (e.g., automotive, aerospace, furniture finishing, and metal decorating), soil remediation sites, and solvent recovery locations/sites. They also provide the following advantages for high flow, low VOC concentration applications:

- High capture and destruction recovery potential
- Lower energy consumption
- Smaller footprint
- Reduced weight (this allows them to be placed on rooftops)
- High reliability
- Safety.

---

# Recovery of VOCs by Microwave Regeneration of Adsorbents

Presented on September 16, 1998 by Philip Schmidt, University of Texas (UT) at Austin

There is a lot of interest in recovering VOCs from low-concentration air streams. Currently many companies use destruction technologies to treat low-concentration streams because they are more cost-effective than commonly available recovery technologies (e.g., direct condensation, hot inert gas regeneration of adsorbents, and steam-stripping of adsorbents). Unfortunately, when destruction technologies are used, valuable materials and energy are often wasted. Microwave regenerated adsorption systems may prove to be an appropriate, non-destructive alternative for recovering VOCs from low-concentration streams.

Compared to the more common heat-based alternatives, microwave regeneration provides improved recovery, enhanced heat/mass transfer rates, and improved control. The technology requires little to no purge gas to produce a highly concentrated off-gas that can be easily condensed. Unlike carbon bed systems which utilize steam regeneration, microwave regeneration systems do not need to perform liquid-liquid separation, eliminating the difficulties associated with separating water-soluble solvents. Because microwave energy does not require a medium for transfer (it can heat in a vacuum), heat transfer rates depend solely on the available generator power and are not limited by surface area or heating medium. VOC transport out of the adsorbent is also dominated by pressure-driven flow and is not limited by molecular diffusion. The enhanced heat/mass transfer rates achieved by microwave regeneration result in higher throughputs and shorter cycle times.

UT at Austin has performed numerous microwave regeneration bench scale, process design, and comparative cost design studies over the past 7 to 8 years. These studies followed the following research approach:

- Bench-Scale Experiments: For proof-of-concept and to obtain kinetics and sensitivity to operating parameter data.
- Process Design Studies: To evaluate alternative configurations, adsorbent selection, and to estimate costs and equipment size.
- Comparative Economic Feasibility Studies: To evaluate cost-effectiveness in selected applications. These tests were performed at the pilot level, although a field test is planned.

UT at Austin is also planning a number of lab pilot column and field demonstrations to obtain scale-up information and to **assess** compatibility with commercial environments.

## Bench-Scale Experiments

Over 100 bench-scale experiments have been performed **as a** proof-of-concept and to explore the desorption kinetics of microwave regeneration. In general, these tests were conducted using stripping gas or under vacuum conditions (25 to 150 torr) and the desorbed solvents were recovered by condensation. The following solvents and adsorbents were tested during these experiments:

- Solvents: Methyl ethyl ketone, toluene, n-propyl alcohol (nPA), water
- Adsorbents: Molecular Sieve (MS) 13X, Dowex Optipore, MHSZ (a registered trademark product of UOP).

A review of the bed temperature profiles for a conventional regeneration process (e.g., inert gas

stripping in conventional adsorbent beds) versus microwave regeneration indicates that microwave regeneration heats more uniformly and more rapidly than conventional systems. Microwave regeneration systems also tend to reach higher temperatures. The desorption effluent concentration profiles indicate that microwave regeneration leads to a much faster evolution of the solvent from the adsorbent.

UT at Austin also performed bench-scale experiments to determine how well microwave regeneration works using a number of different adsorbents. During these tests, UT at Austin measured the dielectric loss factor of a number of different adsorbents and solvents. (Note: The dielectric loss factor measures how effectively a material can convert electromagnetic energy to heat. Materials that do not absorb microwaves and convert them to heat are considered “transparent” to microwaves.) A review of the data from these experiments indicates that if either the adsorbent or the solvent has a high dielectric loss factor, then microwave regeneration can generally be used. The experiments also demonstrated that microwave regeneration is generally not subject to heat and mass transfer. The following conclusions were also reached:

- Volumetric heating minimizes thermal gradients
- Mass transfer of VOCs out of the adsorbent is enhanced by a significant pressure-driven flow (“expulsion”)
- The vacuum minimizes external film resistance to mass transfer
- No nitrogen counter-diffusion occurs.

### **Process Design Studies**

During the process design studies, UT at Austin also examined the following parameters from an economic feasibility standpoint: 1) adsorbent selection; 2) desorption thermodynamics, desorption kinetics, and capital and operating costs (e.g., make-up inert cost, microwave power requirements, and refrigeration/vacuum power requirements) for vacuum and gas purge systems; 3) system configuration; and 4) microwave applicator configuration. The following conclusions were reached:

Adsorbent Selection - Although the cost per pound for polymeric resins may often be much higher than lower cost alternatives, the cost per pound of VOC treated was lower. In fact, recovery costs increased as follows: polymeric resins (lowest), high silica zeolite, activated carbon, and MS 13X (highest).

Vacuum Versus Gas Purge - Vacuum purge systems cost less (\$0.206 per pound of VOC) than gas (inert) purge systems (\$0.271 per pound of VOC). Vacuum heating also has some attractive features for fixed bed systems.

System Configuration - In general, somewhat unconventional configurations (e.g., axial flow columns and horizontal rectangular bed columns) are suitable for microwave regeneration, in part due to penetration depth limitations and other microwave-related issues.

Microwave Applicator Configuration - Configurations were investigated for both fluidized bed systems (to replace steam or electronically heated units) and moving bed applications. Of the two recommended for moving bed applications, the resonant cavity applicator is more sophisticated and more efficient than the multimode applicator, which is essentially a microwave oven with piping.

### **Comparative Economic Feasibility Studies**

Comparative economic feasibility studies of various incineration technologies (i.e., thermal oxidation, catalytic oxidation, regenerative thermal oxidation, rotary concentrated oxidation, and fluidized bed oxidation) and solvent recovery technologies (i.e., fluidized bed adsorption recovery, fluidized bed microwave regeneration, fixed bed stream regeneration, fixed bed hot gas regeneration, and fixed-bed microwave regeneration) indicate that the solvent recovery technologies are fairly competitive without even accounting for the cost of the recovered material. Additionally, among the recovery technologies examined, fixed bed microwave regeneration was the least expensive for the specific case studied (\$0.099 per pound of VOC removed for a counter-current stream with a VOC concentration of 3,220 ppm and a flow of 22,500 cubic feet per minute or cfm).

### **Lab Pilot Column and Field Demonstrations**

UT at Austin plans to use the following configurations for the proposed lab pilot and field demonstrations:

- Pilot Desorption Column
  - Multimode microwave applicator
  - Column: 6" glass process pipe
    - 100 to 200 pound-mole per hour adsorbent throughput
  - 25 pound-mole per hour recovered solvent
  - 3 to 5. kilowatt (kW) microwave heating rate
- Field Test Unit
  - Fluidized bed adsorber/steam regeneration system from EC&C, Inc.
  - Retrofit with compact microwave desorber unit
    - 1.5 kW microwave generator
  - Rated stream flow of 70 cfm
  - Planned field test at a 3M site in Austin, Texas.

During these tests, UT at Austin plans to collect information on the validity of the process simulation models, uniformity of heating, uniformity and depth of regeneration, purity of the recovered solvent, adsorbent behavior, and controllability.

# Removal and Recovery of Volatile Organic Compounds for Gas Streams

Presented on September 16, 1998 by Hans Wijmans, Membrane Technology and Research, Inc.

MTR was founded in 1983 and was dedicated to the commercialization of membrane-based separation technologies. MTR develops novel technologies based on innovative research and development (R&D) funded largely through U.S. government contracts.

In 1995, 27.7 million tons of VOCs were emitted in the United States: 13 million tons from industrial processes, 8.5 million tons from transportation activities, 0.7 million tons from fuel combustion, and 0.5 million tons from other sources. Of the 13 million tons of VOCs emitted by industrial processes, 3.8 million tons were produced by the chemical, petrochemical, and pharmaceutical industries and 3.2 million tons were produced by coating and degreasing operations. In order to control these emission, a number of VOC control technologies, including the VaporSep process, have been developed.

The VaporSep technology separates and recovers VOCs from air or nitrogen. The first system was installed in 1992 and there are currently over 50 systems in operation. The major application of the VaporSep system is for monomer recovery in polymer production operations: poly vinyl chloride (PVC), polyethylene, and polypropylene.

The VaporSep technology consists of a multilayer membrane composed of a selective layer, a microporous layer, and a support web. The membrane is rolled around a collection pipe to form a spiral-wound module. During treatment, the process stream (e.g., hydrocarbon in nitrogen) is passed through a compressor and a condenser before entering the membrane. The compressor removes the majority of the contamination (e.g., hydrocarbon) in the process stream; this material exits the compressor in liquid form. A diluted process stream is then forwarded to the membrane where the majority of the remaining contaminants are removed by the selectively permeable membrane and concentrated in a permeate (hydrocarbon enriched). The treated air is exhausted from the membrane through a vent and the permeate is forwarded to the condenser, where it is combined with incoming process air. One of the advantages of this approach is that the concentration does not depend on condenser pressure; therefore, high pressures and/or low temperatures are not needed.

The system's performance at a PVC manufacturing plant highlights the material and costs savings that can be obtained with the VaporSep process. This company typically lost 700,000 pounds of vinyl chloride monomer (VCM) per year in its PVC reactor purge gas, losing usable VCM and creating a need for emission controls. By forwarding the purge gas through the VaporSep process, this company was able to reduce the amount of VCM forwarded to the incinerator by over 95%. The recovered VCM was then recycled for in-plant reuse, resulting in a significant cost savings. The recoveries experienced at this plant concur with results obtained during vinyl chloride recovery tests at eight different plants, during which the VaporSep Process yielded an average- percent recovery of 93%. Capital costs at the eight plants ranged from \$50,000 to \$250,000 and annual savings ranged from \$85,000 to \$900,000.

The VaporSep process was first installed for monomer recovery in polyolefin production in 1996 in the Netherlands. Since then, 15 additional systems have been ordered and the process received the 34<sup>th</sup> Kirkpatrick Chemical Engineering Achievement Award in 1997. During polyolefin production, a monomer supply and other raw materials are processed through a polymerization reactor, followed by resin degassing where nitrogen is added. In the past, off-gases from the resin degassing step were sent to a flare where recoverable nitrogen and monomer were lost. By sending the off-gas through the membrane system, however, the recovered nitrogen and monomer (C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub>) can be recycled (in-process) for reuse. A benefits analysis of the plant showed a net payback in less than 2 years. This conclusion was based on the following costs and savings: \$1,500,000 for installation; \$300,000 per year for operation; and \$1,100,000 per year from recovered propylene.

A comparison of the VaporSep and other membrane systems with condensation and adsorption (using both steam regeneration and off-site regeneration) indicates that: 1) unlike their competitors, membranes are able to treat moderate to very high concentrations (0.1 to 99% VOC streams) at low to moderate flow rates (from 1 to 10,000 scfm); and 2) that membranes lose their competitive advantage when treating very high flow rates or low concentration streams.

In closing, since 1992, systems have been installed with a total capacity to remove over 30,000 tons of VOC per year and save over 3 trillion BTUs per year of energy. Given the number of systems currently in design and under construction, these values are expected to increase to over 50,000 tons per year and over 5 trillion BTUs per year in 1999.



# Synthetic **Adsorbents** in Liquid Phase and Vapor Phase Applications

Presented on September 16, 1998 by Steven Billingsley, Ameripure, Inc.

This presentation gives an overview of synthetic resins, some typical system flow schematics, and technology applications for both liquid and vapor phases.

## **Advantages of Synthetic Adsorption Resins**

Synthetic resins are engineered compounds with large surface areas, high adsorptive capacities, physical integrity, and fast adsorption/desorption kinetics. They also have no capacity loss from repeated regenerations and support very little catalytic activity, making them suitable for alcohol recovery. They can be used to adsorb aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, aldehydes and ketones, alcohols and acetates, pesticides and herbicides, chemical agents, and siloxanes.

## **Liquid Phase Regenerative Adsorption Systems**

During liquid phase treatment using a regenerative adsorption system containing synthetic resins (e.g., carbonaceous or polymeric), process water enters the packed beds after being pre-filtered to remove excess particulate. As the process water flows up the bed, contaminants are adsorbed on the synthetic resins contained within, before exiting the unit for discharge. After the bed has become saturated with organics, it is regenerated using countercurrent steam. During steam regeneration, the steam proceeds down the bed and exits through the bottom of the bed. The recovered material is cooled and sent to a phase separation tank, where the recovered organic is forwarded for recycle and the aqueous phase is forwarded back through the resin beds. Typically, these systems can be applied to landfill leachate, for groundwater remediation, for wastewater treatment, and for resource recovery.

## **Vapor Phase Regenerative Adsorption Systems**

During vapor phase treatment using synthetic resins (e.g., polymeric), two types of adsorbent bed designs are typically used: packed bed systems (for flows less than 500 scfm) and fluid bed systems (for flows greater than 500 scfm). During treatment, contaminants are removed from the process air as it flows up through the adsorbent. After the bed has become saturated with organics, it can be regenerated using microwave energy. During the microwave regeneration, an inert gas such as nitrogen is forwarded through the bed as it is heated using microwave energy. The desorbed contaminants exit the bed with nitrogen gas and proceed to a condensor, where the organics are recovered for reuse. Typically, these systems can be applied to landfill gas clean-up, soil vapor extraction, solvent recovery, vapor recovery, and industrial off-gas. If used to recover high-value solvents, the cost of recovered material can defray initial capital costs. Furthermore, in addition to being very efficient, microwave regeneration offers the following advantages over other regeneration systems: it creates no chemical or catalytic waste; recovered products have low water content; it is energy-efficient; it heats uniformly and has reduced regeneration times; and operating costs are low.

## **Study Results**

The following pilot, treatability, and field study results were presented to demonstrate synthetic adsorbent performance at different facilities and using different configurations.

Pilot Testing and Proof of Principle Demonstration - Pilot testing took place at a refinery site with an influent concentration of 140 to 160 parts per billion (ppb) methyl tertiary butyl ether. In addition to methyl tertiary butyl ether, other gasoline components were present in the process stream. During the test, 1,250 gallons were treated at a rate of 0.5 gpm. The concentration of organics in the effluent from the synthetic resin (i.e., L-493) was non-detectable by U.S. EPA "Test Methods for Evaluating Solid Waste," SW-846, Method 8240. Steam regeneration produced less than 5 gallons of condensate, with a concentration of 38.7 ppm methyl tertiary butyl ether.

Treatability Study: Pilot Demonstration - Combined liquid- and vapor-phase adsorption was used during a pilot demonstration at a US Army groundwater site with an influent contaminated with 1,500 to 2,500 ppb of various halogenated aliphatics (e.g., 1,1,2,2-tetrachloroethane; trichloroethylene; vinyl chloride). During the study, approximately 200,000 gallons were treated at a rate of 10 gpm. The concentration of contaminants in the effluent was non-detectable using EPA SW-846 Method 624. Steam regeneration produced 80 gallons of condensate. Utility costs for the system were \$0.08 per 1,000 gallons and total O&M costs were \$0.74 per 1,000 gallons. Vinyl chloride and 1,1,2,2-tetrachloroethane breakthrough started to occur at 6,000 and 7,000 bed volumes, respectively, and the desorption cycle lasted approximately 350 minutes.

Field Scale System: Service Station - A fixed bed vapor adsorption system was used to separate BTEX and other aliphatic hydrocarbons from a soil vapor recovery system (250 scfm) installed at a service station. Approximately 4.8 gallons of contaminants were recovered per day. The recovered product (7% water by volume) was desiccated and delivered to the customer's low-grade fuel tank for resale. Utility costs for the system were \$0.15 per pound of recovered hydrocarbon.

Field Scale System: Chemical Process Plant - A fixed bed vapor adsorption system is currently in the start-up phase to treat a 250 scfm stream at a chemical process plant. Ameripure estimates that up to 6 pounds of hexamethyldisiloxane, trimethylsiloxanol, benzene, and toluene will be recovered per hour using this system. The project is in the data acquisition phase.

## **Conclusions**

As demonstrated by Ameripure and other companies' results, synthetic resins offer an excellent means of VOC recovery due to their high capacities and rapid kinetics. Lab-scale, pilot-scale, and full-scale data confirm the technical viability and cost effectiveness of these systems.

# Cryogenic Condensation for VOC Control and Recovery

Presented on September 16, 1998 by Robert Zeiss, BOC Gases

This presentation gives an overview of cryogenic condensation and offers a case study highlighting the advantages of the Kryoclean system.

## **Cryogenic Condensation**

Cryogenic condensation is an extension of typical condensation which uses lower temperature refrigerants to reduce system temperatures. Unlike traditional nitrogen gas condensation systems, the Kryoclean VOC control system functions as a vaporizer and utilizes the cooling value of the liquid nitrogen to provide cooling during abatement. The flexibility of the Kryoclean VOC control system gives it the ability to handle increased loads at a high level of compliance, without the need for additional add-on equipment. This is accomplished by lowering the temperature when an increased load needs to be processed. Commercial test results using methylene chloride streams and an average nitrogen flow and inlet solvent load of 20.4 scfm and 20.3 lbs/hr, respectively, yield an average VOC recovery efficiency of 99.43%, and an average outlet temperature of -91.33°F. Additionally, preliminary outlet emission test results indicate that emissions went from approximately 210 ppmv at -88°C to 7 ppmv at -109°C.

## **Case Study**

A specialty chemical manufacturing company needed to control VOC emissions from storage tanks, including acetone, methanol, heptane, ethyl acetate, and acetic acid. The company hired an environmental consultant to evaluate VOC control technologies on both a technical and an economic basis. The following technologies were evaluated: thermal oxidizer, catalytic oxidizer, flare, carbon adsorption, scrubber, and cryogenic condensation. EPA OAQPS cost estimation techniques were used to evaluate the different technologies. The following capital and installation costs were accounted for: primary control device cost, auxiliary equipment, instrumentation, freight, foundation supports, handling and erection, electrical, piping, insulation and painting. The following operating costs were also accounted for: operator costs (based on labor rates), utility costs of consumables, interest, control system life, taxes, insurance, and administration.

Based on this evaluation, the environmental consultant determined that cryogenic condensation had the lowest annual operating costs of all the technologies evaluated (e.g., from \$65,000 to \$445,000 less per year than the other alternatives). Capital costs, which were only \$156,000 less than the least expensive alternative (from a capital cost perspective), were also less than three of the other technologies studied.

## **Conclusions**

Field study results indicating 99.6% recovery at -94°F and laboratory test results showing treated concentrations of less than 10 ppmv at -164°F demonstrate the technical potential of the Kryoclean system. These results, combined with the system's flexibility, low operating costs (which can be attributed to the reuse of the vented nitrogen for blanketing or inerting), and low mist/fog formulation (due to controlled surface temperatures), make the technology an attractive option for VOC control. There is also the potential that, in the future, cryogenic condensation systems could be used to cool VOC-laden streams to -250°F.

# Brayton Cycle Systems for Solvent Recovery

Presented on September 16, 1998 by Joseph Enneking, NUCON International, Inc.

The Brayton Cycle Process is a low temperature condensing technology used to recover solvents for reuse. The technology, which is based on the Brayton thermodynamic cycle, was developed and patented by 3M in the mid-1980s and licensed to NUCON International Inc.

During treatment, process gas is transferred from a turbo-compressor to a recuperator (e.g., heat exchanger), where the air is cooled. The cooled air is then forwarded to an expander, where isentropic expansion results in a large temperature drop. The chilled gas is then forwarded to the recuperator, where it is used to cool gas entering the recuperator. The condensed solvent is separated in vertical cylindrical vessels fitted with mist eliminators. The pressure change responsible for the isentropic expansion of the gas can be developed by a compressor at the inlet side of the process or a vacuum on the outlet side.

The basic process can be applied in a wide variety of solvent recovery or pollution control applications. However, different process air characteristics (e.g., solvent types, concentrations, and flow rates) along with different emission control requirements have resulted in a variety of equipment configurations. When the concentration is below 5,000 ppmv, a concentrator is needed for the condensation process to be effective.

## **Case Study #1: Tape Coating Process, Greenville, South Carolina**

During this project, the Brayton Cycle Process was used to treat a low concentration (2,500 ppm of heptane), high flow (7,000 scfm) stream. During treatment, the process air was forwarded through a filter before entering two activated carbon beds prior to being exhausted to the environment. When a bed became saturated with hydrocarbon, it was taken off-line for regeneration. During regeneration, inert nitrogen gas was processed through the beds to desorb the contaminant (e.g., heptane). After exiting the beds, this gas was forwarded through the Brayton Cycle Process. The regeneration air was forwarded through an expander, where it was cooled. The condensed solvent was separated for reuse (at a temperature of -20°F and atmospheric pressure) and the lean gas was then forwarded through a compressor, where it was heated before being recirculated through the carbon beds. The same closed loop process was used to cool the bed before it was returned to the adsorption mode. The use of two beds in the system permits continuous operation.

The residual amount of solvent on the bed at the end of the heating cycle was less than 5% while the capacity of the carbon bed to hold solvent during the adsorption cycle was over 25%. The process achieved over 95% recovery of the heptane, which was then recycled to the manufacturing plant. The capital cost of the system was \$1.64 million. Since the equipment operates automatically, little or no operator supervision was required.

## **Case Study #2: Tablet Coating Process, Pfizer, Puerto Rico**

During this project, a medium concentration (10,000 ppm of methylene chloride and methane), low flow (1,700 scfm) stream was treated. During treatment, the process air (100°F) was cooled and then forwarded through the turbo-compressor and an after-cooler. Any condensed water was then separated and the process air was forwarded through a desiccating dryer bed to prevent freeze-up

in the low temperature sections of the process. After exiting the desiccator, the process air was forwarded through the recuperator, where it was cooled. After separating the condensed solvent, the process air [- 70°F and 23 pounds per square inch area (psia)] was forwarded to the turbo expander, where it was cooled to less than - 150°F (6.5 psia). After passing through the recuperator, the process air was forwarded through the vacuum pump (+230°F) and back to the process.

Over 90% of the air was recycled back to the process. The overall efficiency of the process was 98%. The capital cost of the system was \$1 million. Since the equipment operates automatically, little or no operator supervision was required.

### **Case Study #3: Medical Product Manufacturing, Carter Wallace, Indirect BRAYCYCLE® System**

The Braycycle® Process was used at this site to treat a high concentration (100,000 ppm of tetrahydrofuran), low flow (500 scfm) stream. Since cooling and condensing could not be supplied by the process stream, an indirect Brayton cycle system was used that consisted of separate process air and Brayton cycle loops. The high pressure version of the Brayton cycle process was chosen to reduce the size of the equipment.

During treatment, process air was forwarded through a pair of recuperators, followed by a pair of separators where the condensed solvent was removed. After passing through the second recuperator (#2), the process air was re-routed through the original recuperator (#1) and then a blower before being exhausted. In addition to the "process gas loop", a separate "Brayton cycle cooling loop" consisting of the following elements (in order) was used: recuperator #1a, pre-compressor, turbo compressor, heat exchanger (for process heat), cooler, recuperator (#1a), expander, and recuperator (#2). (Note: The second recuperator, #2, was shared with the process gas loop.) Dehumidification was not needed because the gas stream in the Brayton cycle cooling loop was composed of dry nitrogen. The solvent volume was reduced to 0.05% by volume. The overall removal efficiency of the process was 99%. The capital cost of the system was \$1 million.

# Control of VOCs in Refinery Wastewater

Presented on September 17, 1998 by Mike Worrall of AMCEC Inc.

This presentation briefly discusses aromatics and their regulation in wastewater. Numerous control technologies are broadly discussed before a more detailed discussion of AMCEC's Benzene Removal Unit (BRU) is provided, complete with a case study.

## **Aromatics and their Regulation in the Refinery Industry**

Aromatic hydrocarbons, which are present in petroleum, are a wastewater problem for the refinery industry. Many aromatics are partially soluble in water, as demonstrated by the following solubilities: benzene -1800 parts per million by weight (ppmw); toluene - 470 ppmw; ethyl benzene -150 ppmw; and xylene - 150 ppmw. (Note: These solubilities are measured when the organics are present in water and there is not an excess of oil or hydrocarbon fluids.) These contaminants enter the wastewater during various process steps and activities.

A typical refinery discharges between 100 to 2,000 gpm of wastewater. Under the National Emission Standards for Hazardous Air Pollutants (NESHAPs), any refinery emitting over 10 metric tons per year of HAPs must control its wastewater concentrations to less than 1 ppmv, with at least 98% captured/destroyed. Since many refineries are very large, and their wastewater facilities can be located a distance from the source (e.g., up to 2 miles), this can create serious processing difficulties.

Refinery wastewater is typically produced by the desalter (which removes corrosive salts from the oil with hot water flushes), aromatic units, chemical units (which frequently leak), and the general process area (from leaks, spills, and drainage). In general the desalter is the major source for contaminated process wastewater and is typically the largest contributor to total benzene, toluene, ethylene, and xylene (BTEX) discharges. Since NESHAPs does not permit open process drains, where possible the HAP treatment unit is located adjacent to the HAP source since enclosed drainage systems are often very expensive.

To highlight the wide-scale applicability of this problem, the yearly wastewater discharge from a "typical" refinery (e.g., with a flow rate of 100 to 2,000 gpm and contaminant concentrations of 50 ppmw of benzene and 50 ppmw of toluene, ethylene, and xylene) was calculated. Assuming an average flow of 500 gpm and an average concentration of 50 ppm benzene, approximately 54 metric tons of hydrocarbons (e.g., benzene) would be released per year, well over the 10 metric tons per year limit.

## **Control Technologies**

There are several techniques/technologies available to prevent or control HAPs and VOCs in wastewater discharges. Some of the advantages and disadvantages of these techniques/technologies are described below:

Desalter Emulsion Breaker - Although this technology has low capital and operating costs, its impact is limited. For example, if aromatics originated from sources other than the desalters, this technology would not be effective.

Activated Carbon - Liquid Phase - This method has a low capital cost but a very high operating

cost. The high operating cost is not only due to fuel costs to run the kiln, but also to high transportation costs associated with transporting the carbon for reactivation in a high temperature kiln which could be 500 miles away. For a recent 500 gpm project, capital costs ranged from \$0.25 to \$0.50 million and operating costs ran from \$1.2 to \$1.5 million.

Steam-Stripping - Although this method is very effective, it has a high capital cost and a high operating cost due to use of extreme temperatures. In addition, these systems are easily fouled with other contaminants.

Air-Stripping - This technology has only moderate capital costs but high operating costs associated with carbon reactivation. Also, this process can easily foul the wastewater with biological slime created from oxygen exposure. Potentially explosive conditions in the stripper may also be a safety concern.

#### **AMCEC's BRU**

AMCEC's BRU nitrogen stripping procedure performs vapor-phase carbon adsorption with in situ regeneration. In addition to being safer and less likely to foul than air stripping (since there is no oxygen present), the carbon in the BRU does not require expensive transportation to a high temperature kiln for regeneration. Instead, regeneration takes place on site using a closed loop nitrogen process.

When used to treat a refinery wastewater with a flow rate of 500 gpm and concentrations of 50 ppm for benzene and 50 ppm for toluene, ethyl benzene, and xylene, the process required 1500 lbs/hr steam, 50 kilowatt per hour electric power (which did not include power for the wastewater pumps), 300 standard cubic feet per hour nitrogen, and an equipment cost of \$1,250,000. When the hydrogen sulfide load is more than a few ppm, the hydrogen sulfide will load up on activated carbon. Although this is a concern, since the system has very little oxygen, it is not a huge problem.

There are currently 12 BRU systems operating at various refineries. These units are currently treating flows ranging from 100 to 3,000 gpm. These systems have proven to be effective and reliable (e.g., wastewater streams with BTEX concentrations of 1,000 ppmw are typically reduced to concentrations of less than 0.5 ppmw). Additionally, since BRUs are recovery systems, they do not get the HAPs attention that wastewater treatment requires.

# Separation of Volatile Organic Compounds from Water by Pervaporation

Presented on September 17, 1998 by Richard Baker, Membrane Technology and Research, Inc.

This presentation discusses what pervaporation is, its effectiveness, how it can be applied, and when it is most useful.

## **The Pervaporation Process**

During pervaporation, contaminants are transferred from a liquid feed stream (e.g., 500 ppm toluene in water) through a selective membrane to an inert vapor stream. The purified air (e.g., less than 1 ppm toluene) is exhausted and the permeate (e.g., toluene and water vapor) is forwarded to a condenser, where it is cooled to liquid form (e.g., 5 to 10% toluene). The success of this process is based on the fact that the membrane is much more permeable to the contaminant (e.g., toluene) than water.

A comparison of feed velocities to separation factors (i.e., the measure of the selectivity of a membrane as a function of feed velocity) indicates the applicability of pervaporation for VOC separation. The comparison also shows that hydrophobic compounds such as trichloroethylene and toluene are better candidates for pervaporation than their more hydrophilic counterparts (e.g., ethyl acetate or 1-propanol). This is because the more hydrophobic a compound is, the greater is the separation factor. Unfortunately, a stagnant solution layer often forms next to the membrane which depletes the organic component by up to 90%. The feed velocity can be increased to reduce the stagnant layer; however, depletion is still a factor.

## **Once-Through Pervaporation**

During processing using a "once-through pervaporation" system, the liquid stream is forwarded from a feed pump and heater, where it is heated to 150°F, and then through the membrane modules. The treated water is forwarded for discharge and the permeate is cooled in a condenser responsible for creating the vacuum used to drive the entire process. These systems can be used to separate isopropanol because membrane performance is independent of the feed rate.

## **Batch Pervaporation**

During batch pervaporation, a surge tank is used to contain the feed solution until there is enough to start the system, which is about 50 to 100 gallons. During processing, the feed is transferred from the surge tank, through a filter to the feed/process tank. The feed is then recirculated through feed pump, heater, and membrane modules until treatment is completed. After treatment is completed, the treated water is drained from the feed/process tank. Permeate from the membrane modules is cooled in the condenser and collected for discharge from the system. The entire system is controlled by a simple PLC.

A comparison of percent toluene remaining in the feed over time for three batch runs shows that the first run was a little slower at 110 minutes than the last two runs, which took less than 90 minutes. The last two runs had an average treating rate of 0.5 gpm.



## **Applications**

As described below, pervaporation is being used in the food and flavor industry, for fine chemicals/process streams (e.g., pharmaceuticals), and for pollution control, including groundwater and industrial wastewater. Examples of these applications are included below.

**Food and Flavor Industry** - In an application in which permeation was used to treat a peppermint oil decanter run-off, the permeate was diluted 20-fold. Since peppermint oil is very valuable, the use of pervaporation was driven completely by the value of the recovered product.

**Pollution Control** - Pervaporation was used to remediate groundwater contaminated with 800 ppm methylene chloride. During treatment, the concentration methylene chloride in the groundwater was reduced to less than 3 ppm in under 2 hours. The resulting permeate had a concentration of 800,000 ppm. Unfortunately the groundwater contained iron which built up and fouled the system. Treatment was discontinued as a result.

**Fine Chemicals/Process Streams** - Pervaporation was used to reduce wastewater concentrations in a 300 gallon per day flow. During treatment, concentrations were reduced from 30 ppm methylene chloride to 35 ppb methylene chloride, which qualified the wastewater for discharge. Prior to the installation of the pervaporation system, the company was trucking the water for disposal off-site at \$0.34 per gallon.

Ideally pervaporation should be used to treat small volume streams such as those in the flavor production industry with moderate concentrations of contaminants. Distillation or incineration should be used to treat very concentrated streams (greater than 5%), and air stripping or carbon adsorption is much more economical for the treatment of low concentration streams (less than 100 ppm).

# Dehydration and VOC Separation by Pervaporation for Remediation Fluid Recycling

Presented on September 17, 1998 by Leland Vane, U.S. EPA NRMRL

This presentation provides a brief background discussion of pervaporation and dehydration followed by a pilot-scale study highlighting soil remediation successes and a description of current EPA pervaporation efforts.

## **Background of Pervaporation and Dehydration**

Pervaporation combines permeation and evaporation to remove organic contaminants from liquid streams. During treatment, organic contaminants pass from a contaminated liquid phase through a hydrophobic, VOC-selective membrane to an inert vapor phase which is under vacuum. When used as a dehydration system, alcohol and water in a liquid phase is pushed under pressure through a water-selective membrane to the vapor phase. Dehydration systems are more frequently used in industry, especially in Europe.

During soil remediation at DOE and DOD sites, a flushing solution containing VOC-solubilizing agents is pumped through an injection well to an aquifer contaminated with non-aqueous phase liquids (NAPLs). The solubilized light non-aqueous phase liquids (LNAPLs) and flushing solution are extracted from the subsurface through a withdrawal well. Economics dictate that the surfactant then be recovered for reuse.

Current soil flushing options include aqueous surfactant solutions for solubilization, mobilization, and foam flood, and pure solvents for pure alcohols, mixed alcohols, and alcohol and water. Mixed surfactants and alcohols are also an option.

## **Pilot Demonstration at Hill Air Force Base**

A pilot demonstration was performed at Hill Air Force Base near Ogden, Utah, which at one point was contaminated with 100,000 to 1,000,000 gallons of chlorinated solvents. Currently this site is contaminated with 50,000 gallons of chlorinated solvents.

During treatment, injectate was added to the subsurface at a rate of 6 gpm. The injectate contained 8% by weight surfactant, 4% by weight isopropyl alcohol (IPA), and 1% by weight sodium chloride to control the surfactant properties. The injectate was mixed in a tank prior to injection into the contamination plume. The surfactant was extracted, along with recovered NAPL (e.g., VOCs) and groundwater, through a withdrawal well at a rate of 11 gpm. The extracted fluid contained 4% by weight surfactant, 2% by weight IPA, and 5,000 milligrams per liter (mg/L) VOC (trichloroethylene, trichloroethane, and tetrachloroethene). This fluid was forwarded to a pervaporation unit, where the NAPL and IPA were removed. The diluted surfactant solution was then forwarded to an ultrafiltration unit where water and residual IPA were removed before returning the recovered surfactant to the mixing tank.

Since the injectate had a solubilization capacity of 200,000 to 500,000 ppm, the source could theoretically be cleaned up in a matter of years rather than the decades needed if pump-and-treat was being used. Additionally, since approximately 89% of the surfactant was recovered for reuse, over \$4,700 was saved each day (i.e., 81% of the surfactant cost without recycling). This is a

major benefit since most sites want to limit remediation costs.

If the injectate contained higher alcohol concentrations, alcohol recovery may be warranted. For example, if the injectate contained 4% by weight IPA, over 2,880 pounds of IPA would be injected per day. This corresponds to a material cost of approximately \$1,150 per day or almost \$400,000 per year.

#### **Alcohol Recovery and Dehydration**

Pervaporation was not originally intended for alcohol treatment. However, necessity dictated its use for this purpose. During dense non-aqueous phase liquid (DNAPL) separation and alcohol recovery, a two-step pervaporation process can be used. During the first pervaporation step, DNAPL is removed and the aqueous stream (surfactant, alcohol, and water) is forwarded to an ultrafiltration unit where the alcohol and water are removed and the surfactant is recovered for reuse. The alcohol and water are then forwarded to a second pervaporation unit, where the recovered alcohol is forwarded for reuse and the water is processed for treatment/discharge. If warranted, the DNAPL could be removed using an alternate process, such as steam-stripping, and the alcohol and water could then be separated using pervaporation. Additionally, if surfactant is not present in the aqueous stream (e.g., an alcohol flushing stream consisting of NAPL, water, and alcohol), the ultrafiltration step can be eliminated from the process.

#### **Technical Approach/Current Status**

EPA is currently concentrating on bench-scale and pilot-scale experiments with surrogate solutions. Bench-scale studies are typically used for process modeling and pilot-scale demonstrations are performed with actual remediation fluids. To date, the EPA has performed bench-scale experiments on two surfactants: Triton X-100 (nonionic) and sodium dodecyl sulfate (anionic). Pilot-scale tests have been performed on DowFax 8390 (an anionic surfactant composed of hexadecyl diphenyl oxide disulfonate) and Coptic Aerosol MA 80 (an anionic surfactant composed of sodium diehexyl sulfosuccinate with IPA and sodium chloride as modifiers). Pilot-scale demonstrations have shown that performance degrades slightly with the addition of surfactant. This was determined based on trichloroethane and toluene percent removals; however, this is not a major problem and can be accounted for during system planning.

EPA is currently designing and constructing a field pervaporation unit to treat a tetrachloroethene/surfactant stream at Camp LeJeune AFB; treatment should start in January 1999. EPA is also considering IPA recovery at the same AFB. Technical personnel are also trying to relate Henry's Law constants to surfactant properties and concentrations. EPA is also attempting to model the effect of micelles on mass transport in pervaporation.

#### **Conclusions**

In situ soil-flushing can result in reductions in both remediation times and remediation expenditures. Surfactant and IPA recycling with pervaporation can also lead to significant material and cost savings. In fact, a 10-gpm installation can expect to save more than \$1,000,000 per year by using surfactant and IPA recycling. Based on this information, it can be concluded that VOC separation and recovery are critical to cost-effective in situ soil flushing. Additionally, pervaporation can be used to separate VOCs from the following streams: VOC-NAPL/surfactant solutions, alcohol/water solutions, and water/alcohol solutions.

# Polymeric Resins for VOC Removal from Aqueous Systems

Presented on September 17, 1998 by Yoram Cohen, University of California (UCLA), Los Angeles

UCLA's industrial affiliates questioned whether polymeric resins can be regenerated and whether they merit consideration if they cannot withstand multi-cycle use. Polymeric resins were initially used in chemical analyses as a means for concentrating a specific chemical in a sample. As early as the mid-1960s, research was done on the application of ion exchange resins for the removal of organics from aqueous streams. Commercial polymeric resin applications date back to the early- to mid-1970s. With new resins, not only adsorption but also absorption is important, opening the door for other types of applications.

A 1979 paper from Chemical Engineering Progress showed the adsorption of a mixture of chlorinated pesticides in a packed bed. In this article, activated carbon was compared to XAD-4 (a polystyrene resin produced by Rohm and Haas). XAD-4 exhibited very low leakage compared to the activated carbon, and this provided motivation for continued research.

The main questions that were addressed included:

- Are the surface area and pore size distribution suitable for VOCs?
- Can solute-polymer affinity be controlled?
- Can polymeric resins be readily regenerated?
- Are polymeric resins stable for cyclic operation?
- Are there severe mass transfer limitations?

When discussing the pore size and volume distribution of polymeric resin, the available volume, rather than the actual pore size/volume, needs to be addressed. Inaccessible pore volume may range from 5 to 30%. When dealing with hydrophobic resins, the loss in accessible pore volume due to wetting becomes a very important issue. The manner in which resins are pretreated will determine what percentage of the resin's volume will be accessible. It is important to note that the accessible volume of some polymeric resins can increase with continued use. This improvement in performance can be attributed to resin swelling. It can also indicate that pretreatment was not complete.

Some newer resins have a surface area which is comparable to that of activated carbon. Before 1990, resins were made with free-radical polymerization; after 1990 resins were made using the Friedel-Crafts reaction. Resins made using the Friedel-Crafts reaction have much smaller cross-linking distances between chains and a higher degree of cross-linking, resulting in much larger surface areas. In addition to the smaller pore sizes, many newer resins are no longer macroporous. With these changes, mass transfer limitations may need to be studied in more detail in the future. Moreover, resin pretreatment is important in determining the working adsorption capacity of the resin. Pretreatment often involves the use of a water-soluble aliphatic alcohol (e.g., methanol) to displace air or wet the resin, then water to displace the solvent.

Because a polymeric resin is made with few functional groups (often it is the single dominant functional group which gives the surface its adsorption characteristics), one can ascertain the affinity (e.g., Hansen solubility parameter) and predict the adsorption capacity based on thermodynamics. Various studies have shown that adsorption capacities of a variety of solutes

and polymeric resins can be correlated with solubility parameters. Such an approach is not feasible with activated carbon, which has more functional groups.

Affinity can be evaluated by testing whether the adsorption capacity varies (i.e., whether it scales) with surface area. Trichloroethylene adsorption capacities over six orders of magnitude of concentration were plotted against adsorption capacities over five orders of magnitude. A good correlation was observed for five resins, indicating that the adsorption capacity scales with surface area for the five hydrophobic resins in question. Activated carbon results plotted on the same graph indicated that activated carbon had a higher adsorption capacity than the five resins.

Affinity can also be evaluated by recognizing that fugacity is the driving force for adsorption. As an example of the approach, adsorption onto XAD-4 resin of phenol and a number of hydrophobic chlorinated solvents (tetrachloroethene, trichloroethene, chloroform, and methylene chloride) was plotted versus the solute fugacity (concentration multiplied by Henry's Law constant) in the solution phase. XAD-4 exhibits an affinity for hydrophobic compounds, but a higher adsorption capacity for phenol, which is slightly more polar. On activated carbon, chain formations or multiple layers can be adsorbed. Polymeric resins adsorbed all of the compounds at concentrations up to their respective solubility limits; at these high concentrations the capacity of some resins can approach or even exceed that of activated carbon.

Methanol was selected for polymeric resin regeneration. Methanol is used to displace the water and regenerate the column after breakthrough is experienced. In situ regeneration using methanol occurs under very mild conditions. If required, higher temperatures or microwave regeneration can be used. When chlorobenzene is treated with XUS resin (Dow), breakthrough occurs at about 1200 bed volumes. Regeneration with methanol takes about 15 bed volumes, resulting in a net concentration factor of about 50. Economics dictate how long the regeneration step is run. Plotting fractional recovery versus methanol bed volumes indicates that greater than 90% of the chlorobenzene is recovered after about 10 bed volumes. After 15 bed volumes the recovery rates of 95% are achieved. Equilibrium dictates that a very high volume of methanol is required to get complete chlorobenzene recovery.

Benzoic acid was adsorbed on MN-170 resin. Breakthrough occurred at approximately 1000 bed volumes (with 2500 bed volumes to saturate the resin). Benzoic acid was tested in part because volatility problems in the laboratory could be avoided. A curve was plotted for methanol regeneration of columns saturated with benzoic acid at different concentrations (100 to 400 mg/L). Nearly complete regeneration occurred at around 40 bed volumes or less, resulting in a concentration factor of approximately 25 to 50. Because methanol is soluble in water and water is present in the column when regeneration begins, this relationship was of particular interest. Adsorption (milligrams per gram) was plotted against concentration of methanol-water mixtures (20%, 40%, 60%, 80%, and 100% methanol). Water and methanol adsorption capacities differed by more than an order of magnitude. By using multiple regenerant passes, the concentration factor was increased from 50 to 250. The number of regenerant passes utilized on-site will be determined based on economics.

Solute recovery and solvent regeneration can be summarized as follows:

- The solute is concentrated in the regenerating stream
- Concentration factors range from 10 to 250
- Solvent can be recycled up to 3 to 4 cycles
- Solvent can be regenerated using appropriate separation methods.

Resin stability was evaluated by examining the dynamic adsorption capacity over repeated adsorption/regeneration cycles. The deviation of the above ratio from unity was within about +/- 2%. This difference can be attributed to either experimental error or to adsorption capacity fluctuations related to: 1) multiple passes of water and methanol through the bed; and 2) the degree to which methanol is removed after regeneration. Plots of up to 80 cycles with the XUS resin showed no decrease in the stability or adsorption capacity of the resin.

The mass transfer limitations of benzoic acid were compared with literature data for three adsorbents: activated carbon (Takeuchi and Suzuki, 1984), macroreticular adsorbent (Huang et al., 1994), and macronet (this study). The reported intraparticle diffusivities for the three adsorbents were:  $0.41 \times 10^{-11}$ ,  $2.71 \times 10^{-11}$ , and  $1.9 \times 10^{-11}$  square meter per second, respectively. The mass transfer limitation of the newer resin was significantly less than the activated carbon. However, the older macroreticular resin used by Huang et al. exhibited a somewhat lower degree of mass transfer limitation, as expected for this higher pore size resin.

Table 3 summarizes the properties of activated carbon and polymer resins. When comparing the properties of activated carbon to polymeric resins, the following issues need to be considered: 1) the high heat of adsorption (requiring significant energy input) of the carbon; 2) the degradation of carbon during repeated regeneration cycles; and 3) the relative cost.

**Table 3. Polymer Resins Versus Activated Carbon**

POLYMER RESINS	ACTIVATED CARBON
High surface area (greater than 1000 square meters per gram or $\text{m}^2/\text{g}$ )	High surface area (greater than 1000 $\text{m}^2/\text{g}$ )
Low heat of adsorption (less than 4 kilocalories per mole or $\text{kcal}/\text{mole}$ )	High heat of adsorption (greater than 10 $\text{kcal}/\text{mole}$ )
Solvent regeneration (e.g., using aliphatic alcohols)	Thermal regeneration (e.g., steam regeneration)
No loss in performance over many cycles	5 to 10% degradation per cycle
Limited choice and high cost (approximately \$20 per kilogram)	Readily available, low cost (less than or equal to \$2 per kilogram), general adsorbent material
	Spent carbon may have to be treated as hazardous waste

In summary:

- Polymeric sorption resins can be regenerated in situ by solvent regeneration or thermal recovery.
- Cyclic adsorption/regeneration processes are feasible.
- Solvent regeneration and solute recovery from the solvent may be the more expensive

portion of the process.

- The dominance of low-cost activated carbon is an important reason for the small market share of polymeric resins and this in turn explains their high cost.
- Capital costs for polymeric resin packed-beds should be similar to granular activated carbon adsorption systems.
- Operating costs for polymeric resin packed beds should be lower for the following reasons:
  - Virtually no resin attrition
  - Resin stability is maintained over many cycles
  - Regeneration can be performed in situ under mild conditions.
- There is a need for design data (adsorption/regeneration) and a better understanding of adsorption/regeneration coupled with polymeric resins.

# The New Clean Process Advisory **System™ (CPAS™)** Separation Technology and Pollution Prevention Information Tool

Presented on September 17, 1998 by Robert Patty, The Construction Productivity Institute (CPI)

CPAS is a set of pollution prevention process and product design tools containing design information regarding new and existing clean technologies and design for constructability. EPA is concerned with constructability because of the micro-environment that exists on a project site in which we throw some 5 to 8% of our workforce during the process of construction itself.

According to Cheremisinoff and Ferrante (1989), "The most significant technical barrier to waste minimization may be a lack of suitable engineering information on source reduction and recycling techniques." Although the situation has improved, designers lack a tool which provides pertinent information as attested to by the following statement. "There is a large dearth of pertinent information and guidance techniques to accomplish source reduction - design process changes. For example, pollution prevention options for process effluent streams already installed by other organizations, are not well documented." (U.S. Congress, Office of Technology Assessment, 1994).

According to Buckminster Fuller, "If you want to change a person's way of thinking, don't give (him) a lecture, give (him) a tool." In this case, the required "tool" is an information system that can easily be used to begin assimilating the issues involved and developing solutions to explore.

Of those tools, the separation technologies and pollution prevention information tools are a set of four individual but interconnected relational knowledge bases in which project teams can identify viable pollution prevention options during stream-by-stream analysis of process facilities. These CPAS tools include brief summaries of 518 new or emerging source reduction, recycling, and end-of-pipe treatment technologies and methods. The user can very quickly sort through the knowledge bases and summaries based on process stream characteristics and desired separation or waste minimization performance criteria. This is not new information. It is the existing knowledge base of the industry, or a significant portion of it, in an organizational structure that is easier for the design engineer to understand.

There are several developers involved in the first version of these tools include:

- The CWRT
- The M.W. Kellogg Company (a large engineering and design firm for oil refineries and chemical processes)
- The National Center for Clean Industrial and Treatment Technologies (CenCITT) based at Michigan Technological University
- The Department of Energy - Office of Industrial Technologies
- ENSR Consulting and Engineering
- The Bechtel Corporation.

Quite a number of organizations also contributed to the knowledge base:

- HazTECH Publishing, Inc.



- High Tech Resources International, Inc.
- Chemical Manufacturers Association
- Texas Natural Resource Conservation Commission
- Hydrocarbon Processing Magazine (Gulf Publishing Company)
- AIChE and Chemical Engineering Progress Magazine
- U.S. EPA - Superfund Innovative Technology Evaluation (SITE) Program
- CWRT sponsors and over 450 other organizations.

Significant funding was also provided by EPA under a cooperative agreement with CPI.

Why was the knowledge base developed?

- No such compendium of information exists today. Much of this information may be available on the Internet, but it is not organized in a fashion that facilitates easy retrieval.
- Innovative separation technology information is crucial to economic pollution prevention.
- To improve technology transfer between industries and within large organizations. People often become pigeon-holed; they need to have a source of information to cross-link to other organizations to find out what they are doing.
- To accelerate the consideration of capable separation technologies outside of the industry sectors where they have been primarily deployed.

Simply getting more information is not the answer. Between 1985 and 1995, the publications cataloged included:

- 5,708 on distillation
- 23,108 on extraction
- 52,726 on adsorption
- 111,520 on membranes.

There is also vendor technology data, unpublished information from conferences, corporate information, and patent literature.

The benefit of this approach is that it provides guidance to accomplish source reduction and design process changes. It also provides consideration of other companies' innovative waste reduction techniques, such as gas-gas and liquid-liquid separation technologies which minimize or eliminate end-of-pipe streams. It also provides a sizable knowledge base of water reuse, enabling quicker incorporation of waste and/or energy reduction into operations.

The expected mode of operation in design is to use these tools in the conceptual design phase or earlier to provide:

- Stream by stream flowsheet reviews for alternative technology options
- Information based on separation performance or function desired
- Alternate searches based on technology group or licensor or vendor name
- Quick reviews of many separation options for separation and recovery of contaminants in lieu of end-of-pipe treatment.

Information typically needed during this early design phase includes:

- Phase of the contaminant and carrier stream (gas, liquid, or solid)
- Chemical group of the contaminant and carrier stream
- Applicable temperature and pressure ranges
- Applicable flow rate and contaminant concentration
- Contaminant recovery desired
- Commercial status desired.

The pollution prevention tool was released as Version 1.0 in July 1998. Version 2.0 is currently under development.

Two of the tools were demonstrated (the Gaseous Pollution Prevention Design Options Tool and the Separation Technologies Tool) and the following scenario was presented.

#### **Scenario - Methanol Production Process**

You are an experienced process engineer at a world-scale methanol plant. Your assignment is to identify and evaluate the two best options for increasing plant production. Because cost is a very important factor, the two options must take into account all of the current and near-future safety, health, and environmental requirements for methanol production. The most important gaseous process effluent streams are:

- The synthesis loop purge, and
- The refining column overhead gas.

The most important aqueous process effluent streams are:

- The fusel oil side-draw from the refining column,
- Refining column bottoms, and
- Process condensate.

The best process information indicates that the synthesis loop purge is fairly large and contains hydrogen, carbon monoxide, carbon dioxide, argon, nitrogen, and some methanol. The refining column overhead gas contains acetone, methanol, dimethyl ether, formaldehyde, and methyl formate. These two streams are now fed to the boilers for steam generation.

In your data gathering for the aqueous effluent streams, you have found the fusel oil stream to contain 36% methanol, 6.3% ethanol, 1.5% i-propanol, 0.6% i-butanol, and 55.3% water. This stream now goes to the boilers as fuel for gathering steam. The refining column bottoms is almost entirely water with a very low concentration of methanol present and is currently routed to biological treatment. The process condensate is also mostly water with a small amount of dissolved gases and some methanol. This stream currently is stripped with steam and recycled back to the boiler feed waste steam system with the stripping steam recycled to the reformer inlet.

Once the best two options are identified, you intend to use a process simulator, as always in design, to verify the effects (or lack thereof) on the rest of the production process.

One would go into the gaseous pollution prevention tool in several ways. For instance, in this case, select first a stream-by-stream analysis. Then select a contaminant, in this case an organic contaminant such as methanol. Next select a carrier stream: hydrogen. Finally, select "OK" and the computer will search the database and provide results for the selected parameters. In this case five technologies were selected; these included: alternative reaction pathways (1), stock pre-treatment technologies (1), and recycle with (1) and without separation (2). The list includes the company name and, in some cases, the product name. Simply select the technology of interest to get more product information, including process information, process diagrams, reported results, and point of contact.

The organic compounds were changed to phenol and the feed stream to air. Ten technologies were identified: alternative feedback (1), feedstock pre-treatment (1), recycle with separation (4),

recycle without separation (3), and consolidated vent and relief systems (1).

CPAS can define the contaminant streams based on the engineering properties of the contaminant and carrier: nine combinations were listed. Select "gas-gas", choose the carrier (air), define the feed conditions (temperature of 0 to 100 °C), pressure range (14.7 to 50 psia), range of recovery (greater than 99.9%). The list of potential technologies has been narrowed to four. Now, say you decide that the recovery can be lower (less than 1,000 ppm) - this is mutually exclusive with the percentage selected earlier. Then select a commercial status (pilot-plant testing). The field now includes 24 potential technologies.

This tool is a rather simple concept. By input of basic process information such as pressure, temperature, carrier gas, etc., the list of technologies can be searched and narrowed. The plan is to collect and update information from vendors. Version 2.0 will be more ergonomic, especially in its use. The tool is CD-based. Version 1.0 cannot be updated by the vendors. Version 2.0 will use a shadow file that will be reviewed by a technical committee before inclusion in the database.

# Comparative Cost Studies

Presented on September 17, 1998 by Edward Moretti, Baker Environmental

VOCs can be abated through prevention (e.g., material substitution, process optimization, and work practices), recovery (e.g., adsorption, adsorption/distillation, condensation, membrane separation, and volume reduction), and destruction (e.g., thermochemical destruction, photochemical destruction, plasma/electron beam destruction, and biofiltration). To select an appropriate reduction strategy, the following steps should be followed:

- 1) Characterize the emissions by pollutant type and emission rate.
- 2) Identify appropriate environmental objectives. If regulatory-driven emission control is being targeted, identify the applicable VOC regulations and VOC abatement options that meet the regulatory requirements. If emissions control is being targeted in order to comply with waste minimization efforts, define the corporate culture and business objectives and the VOC abatement options that eliminate or reduce waste sources.
- 3) Evaluate VOC abatement options. Assess applicability relative to various operating conditions and parameters (exhaust stream flow rates, VOC concentrations, and VOC categories - ketones, alcohols, halogens, and hydrocarbons). Also assess energy requirements and environmental issues (e.g., secondary environmental impacts, opportunities for recycle, and fugitive emissions). The following economic factors also need to be considered: pretreatment considerations (e.g., dilution, preheating, pre-cooling, humidification, dehumidification, particulate removal, entrained liquid removal), maintenance requirements, and capital, annualized, and social costs.
- 4) Select the most cost-effective option which meets the environmental objectives.

## **VOC Abatement Options-Applicability Table**

The costs of VOC abatement options **vary** based on customer specifications, although in general industrial applications are the most expensive, followed by commercial and then municipal efforts. VOC abatement costs also vary based on the following: site preparation, instrumentation and controls, energy costs (fuel and electricity), solvent recovery value, operating/maintenance costs, VOC concentrations, exhaust stream flow rates, the number of VOCs in the exhaust stream, the type of VOC, materials of construction, operator requirements, and the number of hours the system is operated.

Abatement costs can be estimated by using best engineering judgement, published guidance, and vendor assistance. The following guidance is available on TTN's web page at <http://www.epa.gov/ttn>: U.S. EPA CO\$T-AIR, U.S. EPA HAP-PRO, and U.S. EPA OAQPS Cost Manual. Additional cost guidance can also be obtained from the technical associations and state/local agencies. U.S. EPA has also developed a number of documents which can serve as valuable background information sources.

The following comparative costs were developed based on industrial experience and are consistent with U.S. EPA cost programs.

- Natural gas = \$2.10 per million BTU
- Electricity = \$0.04 per kilowatt hour

- Water = \$0.08 per 10,000 gallons
- Catalyst life = 5 years
- Wastewater treatment = \$0.50 per pound of VOC
- Value of recovered solvent = \$0.50 per pound of VOC
- Membrane life = 3 years.

A comparative analysis of capital costs for various exhaust abatement options (e.g, catalytic oxidation, regenerative adsorption, condensation, volume reduction, regenerative thermal oxidation, adsorption, and membranes) indicates that as gas flow rates rise near 10,000 scfm, costs drop to the \$50 to \$350 per scfm range. This analysis also indicates that catalytic oxidation and adsorption (at gas flow rates over 10,000 scfm) are the most cost-effective. The comparative annualized costs (without social costs) for catalytic oxidation, regenerative adsorption, condensation, regenerative thermal oxidation, and adsorption also drop to a relatively narrow range (\$5 to \$25 per year per scfm) at flows over 10,000 scfm. In this comparison regenerative adsorption appears to be the most cost-effective alternative.

The strong public support for environmental protection is leading many companies to consider waste minimization for VOC abatement. Stockholder pressures on industry to demonstrate responsible care and strongly held sustainable development/green design values also contribute to increased interest in waste minimization approaches to VOC abatement. In the future, innovative technologies that combine pollution abatement with manufacturing process improvements will probably be more likely to experience commercial success. In fact, according to the U.S. Commerce Department, corporate spending on so called "integrated technologies" has more than doubled since 1983.

## Availability of Technology Information, Including Internet-Based Sources

Presented on September 17, 1998 by Heriberto Cabezas, U.S. EPA NRMRL

There are a number of useful technology information sources currently available, including Internet-based sources. Five of these sources/tools are discussed below. These tools include:

- Three software applications for finding or designing solvent substitutes
- One software application for quantifying pollution prevention progress
- One software application for modifying design parameters to reduce pollution in chemical processes.

The five tools discussed should not be viewed as a comprehensive list of information sources, but rather as a subset of the available sources.

### **SAGE: Solvents Alternatives Guide**

SAGE is an Internet-based tool developed by the Surface Cleaning Program at Research Triangle Institute in cooperation with the U.S. EPA's Air Pollution Prevention and Control Division. It is available at: <http://clean.rti.org/>

SAGE works as both an expert system for evaluating various process and chemistry alternatives for a particular situation and as a hypertext manual on cleaning alternatives. The expert system, or advisory portion of SAGE, will ask a series of questions about the particular part(s) that need to be cleaned. These are the same questions that a process engineer would have to answer when changing a process (e.g., questions on size, part volume, nature of the soil to be removed, production rate, etc.).

After the question and answer session is complete, the system produces a list of processes and "chemistries", together with a relative score ranking those alternatives most likely to work for a particular situation. The relative score will help the user rank the commercially available solvent alternatives. SAGE can also be used as a reference source. Each alternative will also act as a hyperlink to further information on the general use of the process or chemistry, safety data, and case studies.

The Solvent and Process Alternatives Index can be used to access information directly on the various alternatives listed in SAGE. Ideally this index can be used to retrieve information on a specific alternative; it will not, however, provide ranking information based on the process requirements. SAGE also does not assist in the design of new solvents.

### **CAMD: Computer-Aided Molecular Design**

CAMD was developed by R. Gani and P. Harper at the Computer-Aided Process Engineering Centre, Department of Chemical Engineering at the Technical University of Denmark (DK-2800 Lyngby, Denmark). It can be used to select and design new solvents. CAMD applies the following "Generate and Test" methodology:

- Compounds of the desired type are generated
- The generated compounds are screened against the property constraints.

CAMD contains the relevant rules on numbers and types of atoms that can bond to form

molecules. Compounds are generated based on thermodynamic properties (vapor pressure, etc.) of the molecules requiring replacement. When an existing molecule is known, the process is relatively straightforward - there are thousands of chemicals in existence from which to choose. In cases where the desired molecule does not exist, CAMD uses reasonably sophisticated computational chemistry to optimize the isomeric configuration of the selected chemical.

The following tools are needed to use CAMD:

- Structure generation algorithm
- Property prediction methods (usually by a group contribution method or a computational chemistry method)
- Selection/search algorithms (to match the generated molecules to the required properties).

There are five steps during the application of CAMD:

- Step 1: Problem formulation (identify solute properties, target properties, and build a knowledge base)
- Step 2: Generation/testing of fragments (develop group description and estimate primary properties)
- Step 3: Generation/testing of final structures (generate isomers and estimate primary, secondary, functional properties)
- Step 4: Generate an atomic description and search database (develop an atomic description of candidates)
- Step 5: Final selection and analysis (sort candidates for specified properties and structural properties)

### **PARIS II: Program for Assisting the Replacement of Industrial Solvents**

PARIS II was developed by H. Cabezas, R. Zhao (Research Associate, National Research Council), and J. C. Bare of the U.S. EPA NRMRL (the core program and theory) and S. R. Nishtala of Research Triangle Institute (Windows interface). PARIS II performs tasks similar to CAMD, but works in a different manner. Paris has a database of 1,500 chemicals developed by the Design Institute for Physical Properties Research under the auspices of the AIChE and a Consortium of Industries.

PARIS II is a second generation solvent design software system. The program finds or designs a chemical or chemical mixture that matches desired solvent properties. It uses the static, dynamic, performance, and environmental solvent properties. Various properties can be adjusted to fine-tune the selection. The software yields application-independent substitute solvents or mixtures and optimizes the solvent to ensure that a single-phase material is developed and meets other design requirements. The substitute solvent should act as a "drop-in replacement" - it should do essentially everything the original solvent did.

Properties that are evaluated by the PARIS II software are:

- Static (molecular mass, density, boiling point, vapor pressure, and six activity coefficients)
- Dynamic (viscosity, thermal conductivity)
- Performance (flash point)
- Environmental [air index, total environmental index (eight environmental categories are evaluated - ozone depletion, global warming, smog formation, acidification, human toxicity-ingestion, human toxicity-exposure, ecological-aquatic toxicity, and ecological-terrestrial

toxicity)).

A slide show demonstrating an early version of PARIS is located on the Internet at [www.rti.org/units/ese/p2/PARIS1.html](http://www.rti.org/units/ese/p2/PARIS1.html)

### **Pollution Prevention Progress (P2P)**

P2P was developed by Greg Carroll, David Pennington (Post-doctoral Research Associate, ORISE), Robert Knodel [Senior Environmental Employee (SEE) Program Associate], and David Stephan (Retired, 2/96) of the U.S. EPA NRMRL. P2P is a user-friendly, computer-based tool for assessing pollution prevented (or sometimes increased) as a result of product redesign, reformulation, or replacement. There are two versions of the software: Mark I, released February 1995, and Mark II, released July 1997. The software provides:

- Before and after snapshots and reports describing pollution prevention accomplished with respect to media (water, soil/groundwater, and air); categories of pollution (human health, environmental use impairment, disposal capacity, and life-cycle stages)
- Classification for 22 classes of pollution prevented (toxic organics; toxic inorganics; carcinogens, teratogens, mutagens; fine fibers; heavy metals; radioactives; pathogens; acid rain precursors; aquatic life toxics; global warmers; biological oxygen demand; chemical oxygen demand; nutrients; dissolved solids; corrosives; ozone depleters; particulates; smog formers; suspended solids; odorants; solid wastes; hazard wastes).

P2P also accounts for energy-related pollution associated with pollution prevention. P2P - MARK II includes the following improvements over Mark I:

- A database containing almost 3000 pollutants
- Ability to search by CAS No. and synonym
- Ability to deal with incompletely-classified pollutants
- Ability to report potential regulatory impact.

P2P - MARK III is currently under development. The proposed improvements over the Mark II version include:

- Windows-based program
- Accounts for "potencies" of pollutants (i.e., characterization) with respect to environmental and health impacts
- Restructuring of impact categories to improve comprehensiveness, consistency with other Science Advisory Board (SAB) tools.

### **WAR: Waste Reduction Algorithm**

WAR was developed by D. Young, H. Cabezas, and J. C. Bare of the U.S. EPA, NRMRL and by G. Pearson of Chemstations, Inc. The WAR algorithm is a design tool for chemical manufacturing processes which evaluates the environmental impacts of proposed process flow sheets and assists in reducing pollution. It uses a process simulator along with an associated methodology, i.e., theory, and a database of chemical environmental impact information to compute indexes representing the generation of potential environmental impacts inside the process plant, and the emission of potential environmental impact from the process plant. As changes are made in an attempt to reduce pollution generated and emitted, these indexes are used to make comparisons for evaluating the environmental impact of those changes. Whereas P2P tracks pollution prevention progress, the WAR Algorithm is a manufacturing process design tool for use with computer process simulators. WAR will be available as part of ChemCAD simulator.



# **Paint Spray Booth Design Using Recirculation/Partitioning Ventilation**

Presented on September 17, 1998 by Charles Darwin, U.S. EPA NRMRL

This presentation addresses process modifications to reduce air flow in paint spray booths and thus control equipment size and cost. The presentation included background information on paint spray booth design, particularly recirculation issues. The information presented was obtained over a number of years during a multi-agency effort between the EPA, Department of Defense, and U.S. Marine Corps. Results from the demonstration of a novel recirculation/flow partitioning paint spray booth were also included.

## **Flow Management and Reduction**

Both the technical and economic feasibility of various options have to be evaluated when choosing an emission control strategy. Although it is generally understood within the engineering field that almost any emission source can be controlled if the necessary funding is available, few facilities have the wherewithal to pay for expensive control strategies. Since emission control costs are typically dependent on the volume of air requiring treatment, strategies to reduce and manage air flow were targeted by EPA and its partners during this effort.

Paint booths use process air to support a reaction and provide a safe environment during painting/surface cleaning operations. Since the volume of air requiring treatment is dependent on process air throughput, EPA and its partners first focused their efforts on techniques to reduce direct air input. Based on tests performed on 20 to 30 conventional spray booths, EPA knew that typically more air is processed through conventional systems than is needed to maintain safe operating conditions. Since spray booth design is regulated under OSHA, EPA also investigated whether design changes to reduce direct air input would impact compliance with applicable regulations (e.g., regarding air velocity and internal pollutant concentrations). EPA and its partners also considered including air recirculation, which has been used to a limited extent since the late 1970's.

## **Air Recirculation in Paint Spray Booths**

The recirculation concept can reduce control equipment and operating costs (due to smaller equipment and air volume reductions), thus allowing for the continued use of high concentration solvent (VOC) coatings. Although recirculation is not a control technology, it is a booth design concept that enhances emission control alternatives.

Since both capital and operating costs for spray booth emission treatment vary based on air flow, and since economical control options for controlling these flows are not readily available, the goal of this effort was to develop a design that reduces exhaust flow rates to air pollution control systems or the atmosphere.

## **What is Recirculation?**

In conventional, horizontal-flow spray booths, the inlet air flows through the booth in a straight path and is exhausted through the front of the booth for treatment or to the atmosphere. After examining these booths, it quickly becomes obvious that to control emissions the total volume

of air entering and exiting the booths needs to be controlled.

When recirculation is used, a portion of the process exhaust is recirculated in the booth, reducing fresh intake air and process exhaust volumes. The fresh intake air combines with the recirculated air to form a homogenous, dilute mixture which complies with safe operating levels.

### **Interpreting Government Agency Regulations**

When evaluating that a recirculating spray booth could be designed, the following health and safety issues were researched and addressed:

- Does recirculation violate the intent of OSHA regulations 1910.94 and 1910.107?
- Does recirculation, as recommended and presently used, present an added safety burden?

OSHA 1910.107, which covers spray painting using flammable and combustible materials, is intended to provide a safe operating environment (from a fire hazard perspective) and can be interpreted to forbid recirculation. However, since most booths operate at combustible element concentrations that are lower than concentrations needed to sustain combustion (e.g., at 20 to 50 ppm rather than 9,000 to 10,000 ppm), combustion is unlikely.

OSHA 1910.94 (C)(3) on ventilation covers the design and construction of paint booths. Although this rule does not place restrictions on recirculation, it refers to OSHA 1910.1000 for health and safety issues associated with toxic and hazardous substances. OSHA 1910.1000 contains concentration limits for toxic and hazardous substances. Under this regulation, if the concentration(s) in the booth exceeds a specified limit(s), the booth is not deemed acceptable for human occupation.

After working with EPA on the recirculation issue, in 1994 OSHA determined that recirculated booths could be used as long as the equivalent toxicity of the stream, as calculated using the below equation, was less than 1:

$$\sum_{i=1}^n \frac{[\text{concentration}]_i}{TWA_i} \leq 1$$

where,

$[\text{concentration}]_i$  = concentration of each hazardous constituent

$TWA_i$  = TWA (time weighted average) of each hazardous constituent (as defined by OSHA or AIChE).

As a result of this decision, this equation has driven recent paint booth designs.

### **Concentration Distributions and Their Impact on the Design of Partitioned Booths**

Studies of the vertical distribution of contaminants in paint booth exhausts show that contaminant concentrations formed a gradient in the vertical direction, with concentrations decreasing with the distance from the floor. By plotting these concentrations (x-axis) versus height (y-axis) and integrating the area under the graph at a specific height, the amount of pollution in the air at a given height can be calculated.

These findings led to the conceptualization of split-flow ventilation systems, which separate the lean air from the concentrated portion at the bottom of the booth. The end result was a design for a partitioned/recirculating paint booth, which was capable of recirculating the less concentrated exhausts (e.g., the leaner flow) and forwarding the more concentrated exhaust for treatment.

### **Projections for the Partitioned/Recirculating Paint Booth**

Projected recirculated concentrations from a 55,000 cfm air flow contaminated with 5.5 milligrams per cubic meter ( $\text{mg}/\text{m}^3$ ) toluene,  $4.9 \text{ mg}/\text{m}^3$  butyl acetate,  $0.206 \text{ mg}/\text{m}^3$  xylene,  $0.0046 \text{ mg}/\text{m}^3$  naphthalene,  $0.014 \text{ mg}/\text{m}^3$  diethyl phthalate, and  $0.08 \text{ mg}/\text{m}^3$  di-n-butyl-phthalate yielded the following results:

- At a recirculation rate of 25%, the equivalent toxicity was 0.03 and the exhaust rate 41,000 cfm.
- At a recirculation rate of 75%, the equivalent toxicity was 0.05 and the exhaust rate was 13,750 cfm.
- At a recirculation rate of 90%, the equivalent toxicity was 0.139 and the exhaust rate was 5,500 cfm.

A comparison of pre- and post-modification booth flows and costs (with no recirculation and 63% recirculation) revealed the following:

- Exhausted flows dropped from 55,000 scfm to 20,210 scfm.
- Estimated costs dropped from \$1.1 million to \$400,000.
- Operating costs dropped from \$130,000 to \$50,000.

### **Demonstration Results**

Under this project, a partitioned/recirculating paint spray booth was used to paint tanks at the Marine Corps Logistics Base in Barstow, California. During this demonstration, air flow was reduced from 55,000 scfm to 20,210 scfm. Although the concentrations in the booth increased significantly over original levels, the equivalent toxicity factor was 0.72 before dilution (with intake air) and 0.4 after dilution.

### **Why it Works**

Partitioned recirculating paint booths work for the following reasons:

- Pollutants are typically heavier than air and will, therefore, fall towards the bottom of the booth
- Heavier solid and gaseous pollutants fall to lower levels of the booth prior to exhaust
- Pollutants follow flow streamlines from release point or fall to the booth floor
- Recirculated air is relatively clean of paint pollutants
- Recirculated concentrations do not approach health and safety limits
- Health and safety limits are based on the concentration, not the total volume, of paint used.

# Summary and Concluding Remarks/Seminar Follow-On Efforts

Presented on September 17, 1998 by Scott Hedges, U.S. EPA NRMRL

Following the breakout sessions, summary and concluding remarks were presented, along with a brief outline of follow-on efforts.

## **Summary and Concluding Remarks**

There is a need for more guidance documents and information on source reduction - process design and VOC recovery technologies. There is also a need to incorporate pollution prevention/waste minimization into VOC recovery/source reduction issues, to improve recovery cost-effectiveness (in part through flow VOC concentration and flow reduction), and to continue to convert promising/emerging recovery technologies into viable commercial applications.

## **Follow-On Efforts**

In addition to this seminar summary report, an edited videotape of the seminar presentations will also be distributed as a technology transfer aid through the U.S. EPA Center for Environmental Research Information (CERI).

## Breakout Session Summaries

### introduction

The purpose of the breakout sessions was to have the VOC Recovery Seminar attendees identify VOC recovery research needs and barriers preventing companies from employing recovery strategies. The sessions were also designed to get feedback on technology transfer needs (e.g., guidance documents and handbooks)

A questionnaire was sent to each attendee prior to the seminar focusing on three main areas: barriers, research needs, and technology transfer. The attendees were asked to fill out the questionnaire and bring it with them to the breakout sessions for discussion. Each breakout session had a facilitator as well as a note-taker to assist the progression of the discussions. After the breakout sessions were completed, Seminar attendees reconvened to discuss and highlight points made in the individual groups. A copy of the questionnaire is included in Appendix B.

Session highlights are summarized below. Individual session notes are included in rough outline form in Appendix B. A list of each group's participants, along with their affiliation, is also provided in Appendix B. Each group conducted discussions in different manners, as is seen in this report and Appendix B. Group B adhered strongly to the prepared questionnaire; Groups A and C, on the other hand, applied the questionnaire more loosely to their discussions.

### Group A

Mr. Daniel Mussatti of U.S. EPA OAQPS summarized Group A's session. He opened by stating that the three main barriers to VOC recovery technology innovation are: 1) lawyers; 2) government (EPA); and 3) society.

He first addressed the impact lawyers had on blocking the use and development of innovative VOC recovery technologies. He noted that, in the absence of regulatory drivers, more incentives are needed to encourage the use of new technologies. Additionally, barriers that limit technology innovators from recouping the cost of recovery research need to be removed/reduced. As an example, he noted that patented technologies dropped significantly in cost after the patent expires. He suggested, that tax incentives could be given to companies to reduce the cost of a patented technology to encourage wider use.

He also attributed some of the responsibility for innovation barriers to the "command and control" attitude common to government officials and regulators. He noted that this attitude resulted in proven (older) technologies being used more often than new innovative technologies.

He then noted that society's short-term, bottom-line attitude prevents companies and other organizations from taking the long view on environmental issues. With accountants making most major decisions, recovery technologies, which at best can be seen as a "cost savings" option, can never rise to the forefront of organizational agendas.

He concluded by summarizing his group's recommendations for overcoming barriers to innovative VOC recovery development and use. The following recommendations were made:

- Show a cost benefit
- Provide tax incentives for investors/developers/users of innovative (risky) technologies (e.g., for patent relinquishment)

- Consider increasing regulatory flexibility; focus on the spirit of the law rather than the letter of the law
  - Give variances where variances are needed
  - Examine on a situation by situation basis
- Provide performance bonuses to facilities for reducing emissions from stacks, etc.
- Increase collaboration between industry/government/academia.

### **Group B**

Dr. Kamallesh Sirkar of NJIT summarized Group B's session. His group started by asking industry representatives from Intel and Owens Corning to identify what they thought were the biggest barriers to the use and development of VOC recovery technologies. They responded that solvent recovery is not profitable due to the low values associated with the recovered materials and because solvent mixtures (which are more common than a single solvent stream) are more difficult to recover. As a result, industry is more likely to employ destructive practices (e.g., incineration), even though they will need to deal with NO<sub>x</sub> and sulfur oxides (SO<sub>x</sub>). Session members suggested that in addition to needing cheaper recovery technologies, industry also needs to receive recognition for using an 85% effective recovery process instead of a 95% effective incineration process.

Dr. Sirkar then suggested that recovery be employed at every point of use in a process. He noted that in the current regulatory environment, however, a permit is needed for every point in the process. This presents a significant regulatory barrier to VOC recovery use as compared to incineration, which often requires one control permit for one stream.

Dr. Sirkar then noted the following R&D needs:

- Chemical adsorbent performance, cost, and other data need to be compiled and made available to the public. Material capabilities and behavior with various compounds or combinations of compounds should be included.
- Technologies/media capable of treating low molecular weight polar organic compounds need to be developed/improved.
- Research to identify the operational and performance characteristics of a variety of VOC recovery technologies/media (i.e., concentration ranges, temperature ranges, percent removals).
- More compact technologies ("unit ops") for small source use.

Dr. Sirkar closed by noting the following technology transfer needs:

- Develop a comprehensive data base containing operational and performance characteristics (i.e., concentration ranges, temperature ranges, percent removals) of a variety of VOC recovery technologies/media. This database will be particularly useful to facilities and companies with a combination of VOC recovery needs/situations.
- Develop a manual containing standard test methods or test conditions to compare different techniques.

### **Group C**

Mr. Stephen Adler of CWRT summarized Group C's session. His group started by defining the biggest problems VOC recovery technologies need to address, namely: 1) low flow, high concentration streams; or 2) high flow, low concentration streams. He noted that past improvements treating/reducing stream concentrations, had increased the difficulties faced by current VOC recovery developers as they try to treat lower and lower concentration streams.

He discussed the R&D needs identified by Group C. He noted that some of the needs were more research-oriented and other more development-oriented. The following R&D needs were identified:

- "Real-world" process demonstrations are needed
  - There is less need for new ideas to tackle a familiar problem except when costs are "excessive"
- Demonstration funding is needed (e.g., DOE)
- Academia, national labs, etc., focus on areas where existing technologies are not cost-effective
- EPA/national labs should focus on helping industry commercialize technologies and not on basic research
- Technology developers need to work with EPA on demonstration sites (testing is expensive)
- Government funding for "not-for-profit" efforts is drying up and other sources of funding are also difficult to obtain (industry is uninterested because the incentives are low)
- Funding is going to the wrong places.

Adler then noted the following barriers to VOC recovery development and use:

- Must be able to recycle materials for in-plant use, not off-site use. Also, the recycled material needs to have a recovery value at least \$100,000 per year, and a rate of return less than 2 years, for the technology to be used.
- Must be able to recycle materials for in-plant use
- Many systems are "on-off"
- Many technologies are not adaptable to small scale systems ("mom" and "pop" operations without the means, staff, or knowledge to operate complicated systems). Since technology providers cannot provide as much service to small providers (a marketing barrier), these products must be robust, reliable, and require little technical attention.
- Lack of funds for commercial "real-world" demonstrations
  - EPA does not have significant funding to support this
  - Lack of data prevents technologies from succeeding in the market
- Small point sources often do not have the funding to install recovery systems
- "White shoe salesman" syndrome - Does the technology really work?
- Regulatory uncertainty (e.g., "Any day now" regulations) and State and Federal regulations which keep being pushed back
- Lower cost systems are needed for low concentration streams
- Lack of readily available sources of information (e.g., databases) on existing technologies.

Adler concluded his summary by briefly presenting the following suggestions for overcoming technology barriers:

- Better identification of barriers to VOC recovery technology use and development
- Provide incentives for new technologies
- Eliminate the short term bottom-line mentality
- Address hazardous waste issues which present a barrier for establishing new markets for VOC recovery
- Address the fact that a social conscience is not profitable
- Tax incentives
- Increase regulatory flexibility
- Performance bonuses
- Trading programs
- Increase collaboration between industry and government for demonstration programs.

## Appendix A - List of Seminar Attendees

Stephen Adler Office: (203) 750 0219 Fax: (203) 750 02 19 E-mail: <a href="mailto:stephen.adler@compuserve.com">stephen.adler@compuserve.com</a>	Center for Waste Reduction Technologies 16 Grey Hollow Road Norwalk, CT 06850
Frank Alvarez Office: Fax: E-mail:	U.S. EPA, NRMRL 26 W. Martin Luther King Drive Cincinnati, OH 45268
Jimmy Antia Office: (513) 556 3637 E-mail: <a href="mailto:jimmy.antia@uc.edu">jimmy.antia@uc.edu</a>	University of Cincinnati Dept. of Civil & Environmental Engineering, ML 007 1 Cincinnati, OH 4522 1-007 1
William Asher Office: (650) 859 2823 Fax: (650) 859 3678 E-mail: <a href="mailto:bill.asher@qm.sri.com">bill.asher@qm.sri.com</a>	SRI International 333 Ravenswood Ave Menlo Park, CA 94025
Richard Baker Office: (650) 328 2228, ext 111 Fax: (650) 328 6580 E-mail: <a href="mailto:mtr@mtrinc.com">mtr@mtrinc.com</a>	Membrane Technology and Research 1360 Willow Road, #103 Menlo Park, CA 94025
Kathy Baldock Office: (513) 333 4704 E-mail: (513) 651 9528 <a href="mailto:kathy.baldock@does.hamilton-co.org">kathy.baldock@does.hamilton-co.org</a>	Hamilton County DOES 1632 Central Parkway Cincinnati, OH 452 10
Michael Barrasso Office: (908) 233 2882 Fax: (908) 233 1064 E-mail: <a href="mailto:mbarrasso@csmsystems.net">mbarrasso@csmsystems.net</a>	CSM Environmental Systems 200 Sheffield Street, Suite 305 Mountainside, NJ 07092
Satish Bhagwat Office: (740) 321 5265 Fax: (740) 321 7567 <a href="mailto:satish.bhagwat@owenscorning.com">satish.bhagwat@owenscorning.com</a>	Owens Corning 2790 Columbus Road Granville, OH 43023
Dibakar Bhattacharyya Office: (606) 257 2794 Fax: (606) 323 1929 E-mail: <a href="mailto:db@engr.uky.edu">db@engr.uky.edu</a>	University of Kentucky Department of Chemical Engineering Lexington, KY 40506-0046
Edward Biedell Office: (908) 685 4238 Fax: (908) 685 4181 E-mail: <a href="mailto:edward_biedell@reeco.r-c.com">edward_biedell@reeco.r-c.com</a>	REECO P.O. Box 1500 Somerville, NJ 08876
Steven Billingsley Office: (805) 833 9200 E-mail: (805) 833 9300 <a href="mailto:amerpure@lightspeed.net">amerpure@lightspeed.net</a>	Ameripure, Inc. 6701 McDivitt Drive, Suite A Bakersfield, CA 933 13
Paul Bishop Office: (513) 556 3675 E-mail: (513) 556 2599 <a href="mailto:pbishop@boss.ccc.uc.edu">pbishop@boss.ccc.uc.edu</a>	University of Cincinnati Department of Civil & Environmental Engineering Cincinnati, OH 4522 1-007 1



Karen Borel	U.S. EPA, Region 4
<u>Office:</u> (404) 562 9029	61 Forsyth Street
<u>E-mail:</u> (404) 562 90 19	Atlanta, GA 30303
<u>borel.karen@epa.gov</u>	
Heriberto Cabezas	U.S. EPA, NRMRL
<u>Office:</u> (513) 569 7350	26 W. Martin Luther King Drive
<u>Fax:</u> (513) 569 7111	Cincinnati, OH 45268
<u>E-mail:</u> <u>cabezas.heriberto@epamail.epa.gov</u>	
Richard Carter	Science Applications International Corporation
<u>Office:</u> (714) 793 7600	655 Metro Place South, Suite 745
<u>Fax:</u> (614) 797 7620	Columbus, OH 43017
<u>E-mail:</u> <u>george.r.carter@cpmx.saic.com</u>	
Bor-Yann Chen	U.S. EPA, NRMRL
<u>Office:</u>	27 W. Martin Luther King Drive
<u>Fax:</u>	Cincinnati, OH 45268
<u>E-mail:</u> <u>chen.bor-yann@epamail.epa.gov</u>	
Yoram Cohen	University of California, Los Angeles
<u>Office:</u> (310) 825 8766	553 1 -E Boelter Hall
<u>Fax:</u> (310) 645 5269	Los Angeles, CA
<u>E-mail:</u> <u>yoram@ucla.edu</u>	
Vern Corbin	Trotter Equipment Company
<u>Office:</u>	Cincinnati, OH
<u>Fax:</u>	
<u>E-mail:</u>	
James Dale	NUCON International
<u>Office:</u> (614) 846 5710	7000 Huntley Road
<u>Fax:</u> (614) 43 10858	Columbus, OH 43229
<u>E-mail:</u> <u>jimdale@nucon-int.com</u>	
Charles Darwin	U.S. EPA, NRMRL
<u>Office:</u> (919) 541 7633	MD-61 U.S. EPA Mailroom
<u>Fax:</u> (919) 5417891	Research Triangle Park, NC 277 11
<u>E-mail:</u> <u>darwin.charles@epa.gov</u>	
John Davison	Intel Corporation
<u>Office:</u> (503) 613 9262	5200 N.E. Elam Young Parkway
<u>Fax:</u> (503) 613 9299	Hillsboro, OR 97124
<u>E-mail:</u> <u>john.davison@intel.com</u>	
Frank Desantis	REECO
<u>Office:</u> (908) 685 4248	P.O. Box 1500
<u>Fax:</u> (908) 685 4181	Somerville, NJ 08876
<u>E-mail:</u> <u>frank_desantis@reeco.r-c.com</u>	
Jean Dye	U.S. EPA, NRMRL
<u>Office:</u> (513) 569 7345	26 W. Martin Luther King Drive
<u>Fax:</u>	Cincinnati, OH 45268
<u>E-mail:</u>	
Joe Enneking	NUCON International
<u>Office:</u> (614) 846 5710	7000 Huntley Road
<u>Fax:</u> (614) 431 0858	Columbus, OH 43229
<u>E-mail:</u> <u>joeenneking@nucon-int.com</u>	
James Gallagher	Chevron Products Co.
<u>Office:</u> (770) 984 4136	2200 Windy Ridge Parkway, Suite 800
<u>Fax:</u> (770) 984 4107	Atlanta, GA 30339-5673
<u>gpja@chevron.com</u>	

Sowmya Ganapathi-Desai Office: (513) 569 7232 Fax: (513) 569 7677 E-mail: ganapathi-desai.sowmya@epamail.epa.gov	U.S. EPA 26 W. Martin Luther King Drive, MS 443 Cincinnati, OH 45268
James Garmaker Office: (651) 778 4307 Fax: (651) 778 6745 E-mail: jgarmaker@mmm.com	3M Company Bldg 42 2W-09 P.O. Box 3333 1 St. Paul, MN 55133
Emma Lou George Office: (513) 569 7578 Fax: (513) 569 7585 E-mail: george.emmalou@epamail.epa.gov	U.S. EPA, NRMRL 26 W. Martin Luther King Drive Cincinnati, OH 45268
Jayant Gotpagar Office: (502) 564 4797 Fax: (502) 564 5096 E-mail: jayant@engr.uky.edu	University of Kentucky - FFOU 18 Reilly Road Frankfort, KY 40601
Margaret Groeber Office: (513) 569 5865 Fax: (513) 569 5864 E-mail: mgroeber@pol.com	Science Applications International Corporation 2260 Park Avenue, Suite 402 Cincinnati, OH 45206
Doug Grosse Office: (513) 569 7672 Fax: E-mail:	U.S. EPA, NRMRL 26 W. Martin Luther King Drive Cincinnati, OH 45268
Lee Gruber Office: (513) 333 4716 Fax: (513) 651 9528 E-mail: lgruber@hamilton-co.org	Hamilton County DOES 1632 Central Parkway Cincinnati, OH 45210
Ajay Gupta Office: (313) 207 8500 Fax: (313) 207 8930 E-mail:	Durr Environmental, Inc. 14492 Sheldon Road, Suite 300 P.O. Box 701608 Plymouth, MI 48170
Terry Harris Office: (513) 467 2470 Fax: (513) 467 2137 E-mail: terry-a.harris.b@bayer.com	Bayer Corporation 356 Three Rivers Parkway Addyston, OH 45001
Teresa Harten Office: (513) 569 7565 Fax: (513) 569 7677 E-mail: harten.teresa@epamail.epa.gov	U.S. EPA, ORD, NRMRL, STD 26 W. Martin Luther King Drive Cincinnati, OH 45268
Scott Hedges Office: (513) 569 7466 Fax: (513) 569 7585 E-mail: shedges@epamail.epa.gov	U.S. EPA, ORD, NRMRL 26 W. Martin Luther King Drive, MSG77 Cincinnati, OH 45268
Lynn Ann Hitchens Office: (513) 569 7672 Fax: E-mail:	U.S. EPA, NRMRL 26 W. Martin Luther King Drive Cincinnati, OH 45268
John Hofmann Office: (513) 467 2321 Fax: (513) 467 2137 E-mail: john-f.hofmann@bayer.com	Bayer Corporation River Road Addyston, OH 45001

William Jones	U.S. EPA
<u>Office:</u> (3 12) 886 6058	77 W. Jackson Boulevard
<u>Fax:</u> (3 12) 886 5824	Chicago, IL 60604
<u>E-mail:</u> <a href="mailto:jones.william@epamail.epa.gov">jones.william@epamail.epa.gov</a>	
Sumana Keener	University of Cincinnati Environmental Training Institute
<u>Office:</u> (513) 556 2542	1275 Section Road
<u>Fax:</u> (513) 556 2522	Cincinnati, OH 45237
<u>E-mail:</u> <a href="mailto:skeener@uceng.uc.edu">skeener@uceng.uc.edu</a>	
Jon Kostyzak	M&W Industries, Inc.
<u>Office:</u> (714) 374 7459	
<u>Fax:</u> (714) 374 7469	
<u>E-mail:</u> <a href="mailto:jkostyzak@mw-industries.com">jkostyzak@mw-industries.com</a>	
Walter Koucky	Science Applications International Corporation
<u>Office:</u> (513) 569 5860	2260 Park Avenue, Suite 402
<u>Fax:</u> (513) 569 5864	Cincinnati, OH 45206
<u>E-mail:</u> <a href="mailto:wkoucky@pol.com">wkoucky@pol.com</a>	
Rolf Laukant	Prism Environmental Equipment
<u>Office:</u> (630) 279 3464	531 S. Monterey
<u>Fax:</u>	Villa Park, IL 60181
<u>E-mail:</u> <a href="mailto:prismjr@msn.com">prismjr@msn.com</a>	
Wayne McDaniel	Trotter Equipment Company
<u>Office:</u>	Cincinnati, OH
<u>Fax:</u>	
<u>E-mail:</u>	
Hugh W. McKinnon	U.S. EPA, NRMRL
<u>Office:</u> (513) 569 7689	26 W. Martin Luther King Drive, MS 225
<u>Fax:</u> (513) 569 7549	Cincinnati, OH 45268
<u>E-mail:</u> <a href="mailto:mckinnon.hugh@epamail.epa.gov">mckinnon.hugh@epamail.epa.gov</a>	
Alberta Mellon	Hamilton County DOES
<u>Office:</u> (513) 333 4730	1632 Central Parkway
<u>Fax:</u> (513) 651 9528	Cincinnati, OH 45210
<u>E-mail:</u> <a href="mailto:alberta.mellon@does.hamilton-co.org">alberta.mellon@does.hamilton-co.org</a>	
Edward Moretti	Baker Environmental
<u>Office:</u> (412) 269 6055	420 Rouser Road
<u>E-mail:</u> (412) 269 6097	Coraopolis, PA 15108
<a href="mailto:emoretti@mbakercorp.com">emoretti@mbakercorp.com</a>	
Dan Murray	U.S. EPA, ORD, NRMRL
<u>Office:</u> (513) 569 7522	26 W. Martin Luther King Drive
<u>Fax:</u> (513) 569 7585	Cincinnati, OH 45268
<u>E-mail:</u> <a href="mailto:murray.dan@epamail.epa.gov">murray.dan@epamail.epa.gov</a>	
Daniel Mussatti	U.S. EPA, OAQPS, ISEG
<u>Office:</u> (919) 541 0032	MD-15
<u>Fax:</u> (919) 541 0839	Research Triangle Park, NC 27711
<u>E-mail:</u> <a href="mailto:mussatti.dan@epa.gov">mussatti.dan@epa.gov</a>	
Ion Nicolaescu	Owens Corning
<u>Office:</u> (740) 321 6392	2790 Columbus Road
<u>Fax:</u> (740) 321 7567	Granville, OH 43023-1200
<u>E-mail:</u> <a href="mailto:ion.nicolaescu@owenscorning.com">ion.nicolaescu@owenscorning.com</a>	
Carlos Nunez	U.S. EPA, NRMRL
<u>Office:</u> (919) 541 1156	MD-61 U.S. EPA Mailroom
<u>Fax:</u> (919) 541 7891	Research Triangle Park, NC 27711
<u>E-mail:</u> <a href="mailto:cnunez@engineer.aeerl.epa.gov">cnunez@engineer.aeerl.epa.gov</a>	

Stephen Opperman Office: (616) 845 6679 Fax: (616) 845 6749 E-mail: <a href="mailto:ranger@t-one.net">ranger@t-one.net</a>	Ameripure, Inc 84 North Dennis Road Ludington, MI 4943 1
Dave Polachko Office: (419) 248 8878 Fax: (419) 325 4878 E-mail: <a href="mailto:david.palachko@owenscorning.com">david.palachko@owenscorning.com</a>	Owens Corning One Owens Corning Parkway Toledo, OH 43659
Craig Patterson Office: (513) 569 7359 Fax: (513) 569 7707 E-mail: <a href="mailto:itcorp.te@epamail.epa.gov">itcorp.te@epamail.epa.gov</a>	IT Corp c/o T&E Facility 1600 Gest Street Cincinnati, OH 45204
Robert Patty Office: (801) 766 8075 Fax: (801) 766 8076 E-mail: <a href="mailto:rmpatty@burgoyne.com">rmpatty@burgoyne.com</a>	The Construction Productivity Institute 568 West 2280 North Lehi, UT 84043
Paul Randall Office: (513) 569 7673 Fax: (513) 569 7677 E-mail: <a href="mailto:randall.paul@epamail.epa.gov">randall.paul@epamail.epa.gov</a>	U.S. EPA, NRMRL 26 W. Martin Luther King Drive Cincinnati, OH 45268
Priya Rangarajan Office: (606) 323 2976 Fax: (606) 323 1929 E-mail: <a href="mailto:prang01@engr.uky.edu">prang01@engr.uky.edu</a>	University of Kentucky 177 Anderson Hall, Chemical Engineering Lexington, KY 40506
Joseph Rogers Office: (212) 591 7727 Fax: (212) 591 8895 E-mail: <a href="mailto:jorogers@aiche.org">jorogers@aiche.org</a>	Center for Waste Reduction Technologies 3 Park Avenue New York, NY 10016-5901
Steven Rosenthal Office: (312) 886 6052 Fax: (312) 886 5824 E-mail: <a href="mailto:rosenthal.steven@epamail.epa.gov">rosenthal.steven@epamail.epa.gov</a>	U.S. EPA 77 W. Jackson Boulevard Chicago, IL 60604
Brad Russell Office: (847) 375 7418 Fax: (847) 375 7982 E-mail: <a href="mailto:bprussel@uop.com">bprussel@uop.com</a>	UOP 50 E Algonquin Road, P.O. Box 5016 Des Plaines, IL 60017-5016
Philip Schmidt Office: (512) 471 3118 Fax: (512) 471 1045 E-mail: <a href="mailto:pschmidt@mail.utexas.edu">pschmidt@mail.utexas.edu</a>	University of Texas at Austin Department of Mechanical Engineering, MC C2200 Austin, Texas 78712
Chris Schnetzer Office: Fax: E-mail:	Trotter Equipment Company Cincinnati, OH
Brian Schumacher Office: (702) 798 2242 Fax: (702) 798 2107 E-mail: <a href="mailto:schumacher.brian@epamail.epa.gov">schumacher.brian@epamail.epa.gov</a>	U.S. EPA, NERL, ESD-LV P.O. Box 93478 Las Vegas, NV 89193-3478
Mohamed Serageldin Office: (919) 541 2379 Fax: (919) 541 5689 E-mail: <a href="mailto:lin.mohamed@epamail.epa.gov">lin.mohamed@epamail.epa.gov</a>	U.S. EPA QAQPS-MD-13 Research Triangle Park, NC 27711

Larry Shaffer	NUCON International
<u>Office:</u> (614) 846 5710	7000 Huntley Road
<u>Fax:</u> (614) 4310858	Columbus, OH 43229
<u>E-mail:</u> lshaffer@nucon-int.com	
Richard Sharp	U.S. EPA, NRMRL
<u>Office:</u> (513) 569 7393	26 W. Martin Luther King Drive
<u>Fax:</u>	Cincinnati, OH 45268
<u>E-mail:</u>	
Subhas Sikdar	U.S. EPA, NRMRL
<u>Office:</u> (513) 569 7528	26 W. Martin Luther King Drive
<u>Fax:</u>	Cincinnati, OH 45268
<u>E-mail:</u> sikdar.subhas@epa.gov	
Guy Simes	U.S. EPA, NRMRL
<u>Office:</u> (513) 569 7845	26 W. Martin Luther King Drive
<u>Fax:</u> (513) 569 7677	Cincinnati, OH 45268
<u>E-mail:</u> simes.guy@epamail.epa.gov	
Kamalesh Sirkar	New Jersey Institute of Technology
<u>Office:</u> (973) 596 8447	136 Bleeker Street
<u>Fax:</u> (973) 596 8436	Newark, NJ 07102
<u>E-mail:</u> sirkar@admin.njit.edu	
Johnny Springer	U.S. EPA, NRMRL
<u>Office:</u> (513) 569 7542	26 W. Martin Luther King Drive
<u>Fax:</u>	Cincinnati, OH 45268
<u>E-mail:</u>	
Anand Srinivasan	Bayer Corporation
<u>Office:</u> (412) 777 7735	100 Bayer Road
<u>Fax:</u> (412) 777 7447	Pittsburgh, PA 15205
<u>E-mail:</u> andy.srinivasan.b@bayer.com	
Jim Strahan	Ameripure, Inc.
<u>Office:</u> (616) 845 6679	84 North Dennis Road
<u>E-mail:</u> (616) 845 6749	Ludington, MI 49431
<u>E-mail:</u> ranger@t-one.net	
Frank Stoy	Hamilton County DOES
<u>Office:</u> (513) 333 4716	1632 Central Parkway
<u>E-mail:</u> (513) 651 9528	Cincinnati, OH 45210
Vivek Utgikar	U.S. EPA
<u>Office:</u>	26 W. Martin Luther King Drive
<u>Fax:</u> (513) 569 7105	Cincinnati, OH 45268
<u>E-mail:</u> utgikar.vivek@epamail.epa.gov	
Leland Vane	U.S. EPA, NRMRL
<u>Office:</u> (513) 569 7799	26 W. Martin Luther King Drive, MS 443
<u>Fax:</u> (513) 569 7677	Cincinnati, OH 45268
<u>E-mail:</u> vane.leland@epamail.epa.gov	
Jerry Waterman	U.S. EPA, NRMRL
<u>Office:</u> (513) 569 7834	26 W. Martin Luther King Drive
<u>Fax:</u> (513) 569 7585	Cincinnati, OH 45268
<u>E-mail:</u> waterman.jerry@epamail.epa.gov	
Jack Watson	AIChE Research, New Technology Committee
<u>Office:</u> (423) 574 6795	P.O. Box 2008
<u>Fax:</u> (423) 576 7468	Oak Ridge, TN 37831-6178
<u>E-mail:</u> watsonjs@ornl.gov	

Nan Wei	Amoco
<del>Office:</del> (630) 420 598 1	150 W. Warrenville Road
<del>Fax:</del> (630) 420 4678	<b>Naperville, IL 60563</b>
E-mail: <b>nwei@amoco.com</b>	
Jim Wessels	Trotter Equipment Company
<del>Office:</del>	Cincinnati, OH
<del>Fax:</del>	
<del>E-mail:</del>	
Hans Wijmans	Membrane Technology and Research, Inc.
<del>Office:</del> (650) 328 2228, x 118	1360 Willow Road
<del>Fax:</del> (650) 328 6580	Menlo Park, CA 94025
E-mail: <b>wijmans@mtrinc.com</b>	
John Williams	EPS
Office: (2 19) 277 2577	P.O. Box 6034
Fax: (2 19) 277 3775	South Bend, IN 46660
E-mail: <b>eps@asme.org</b>	
Walter Wilson	Hill Air Force Base
<del>Office:</del> (801) 775 6902	<b>00-ALC/EMC</b>
<del>Fax:</del> (801) 777 4306	Ogden, UT 84015
E-mail: <b>wilsonw@hillwpos.hill.af.mil</b>	
Mike Worrall	AMCEC. Inc.
<del>Office:</del> (630) 577 0400	2525 Cabot Drive
F a x : (630) 577 0401	Suite 205
E-mail: <b>mworrall@amcec.com</b>	Lisle, IL 60532
Qingzhong Wu	University of Cincinnati
<del>Office:</del> (513) 556 2498	Department of Civil & Environmental Engineering
<del>Fax:</del> (513) 556 2599	Cincinnati, OH 4522 1-0071
E-mail: <b>wugg@email.uc.edu</b>	
Robert Zeiss	<b>BOC Gases</b>
<del>Office:</del> (908) (908) 508 771 3911 1709	<del>Mountain Hill, NJ Avenue 07974</del>
E-mail: <b>bob.zeiss@us.gases.boc.com</b>	

## Appendix B - Breakout Group Notes and **Members**

The purpose of the breakout sessions was to address each of the questions summarized in the following questionnaire. Participants were asked to complete the below questionnaire in advance of the seminar.

### **B.I Questionnaire - Trends/Issues/Research Needs By industry**

#### To Be Answered By Consultants, Government Employees, University Representatives, Non-Governmental Organization Representatives

- 1) What types of organic (volatile or non-volatile) destruction and recovery technologies and applications have you evaluated/permited during the course of your work?
- 2) What are the relative differences in capital, operating, and maintenance costs between destruction and recovery systems that you have encountered (if known)?
- 3) Are there potential cost differences if one uses a life cycle assessment view (i.e., cradle to grave considerations of materials consumed and byproducts/wastes generated)?
- 4) Can you identify the barriers for switching from a destruction to a recovery process?
- 5) Do you have suggestions as to how to minimize or eliminate these barriers?
- 6) Are there any special problems inherent in the destructive processes that are overlooked because they are "known or established technologies"?
- 7) What issues/problems have you encountered with the recycle/ reuse of organics?

#### To Be Answered By Industry Representatives and Manufacturers/Designers/Distributors of Technologies

- 1) Do you have any organic (volatile or nonvolatile) streams presently treated by destruction that might be candidates for recovery (if uncertain, assume they may have a potential for recoverability)?
  - a) If so, describe each of these streams.
  - b) What are the chemical constituents in each of these organic streams (if possible, include % volume or weight of each chemical)?
  - c) What are the organic concentrations in these streams, and what are the stream flow rates?
- 2) What types of destruction processes do you use to treat your organic streams?
- 3) What are the approximate capital, operating, and maintenance costs for these processes?
- 4) Are there potential cost differences if one uses a life cycle assessment view (i.e., cradle to grave considerations of materials consumed and byproducts/wastes generated)?
- 5) Can you identify the barriers for switching to a recovery process?
- 6) Do you have suggestions as to how to minimize or eliminate these barriers?
- 7) Who is the individual or what is the corporate function in your organization that is key in getting recovery processes evaluated to replace destructive processes?

- 8) Have you evaluated any recovery process, and, if so, what have been your experiences?
- 9) Are there any special problems inherent in the destructive processes that are overlooked because they are "known or established technologies"?
- 10) What issues/problems have you encountered with the recycle/ reuse of organics?

To Be Answered By All Seminar Participants

- 1) What organic recovery research programs do you think should be undertaken and why?
- 2) What modifications/additions to existing research programs do you think are needed and why?
- 3) What types of economic/compliance incentive programs are needed to encourage the use of innovative organic recovery technologies?
- 4) What improvements in recovery technologies are needed to increase the use of these technologies (in your facility, with your stakeholders, in industry as a whole)?
- 5) What sources of information (e.g., how-to manuals, guidance documents, technology handbooks, etc.) do you think are needed to improve the general understanding of organic recovery technologies as well as to encourage their use?

## **8.2 Breakout Group A**

### **B.2.1 Session Participants**

The following individuals were members of Group A:

Leland Vane	U.S. EPA NRMRL
Joseph Enneking	NUCON International
James Garmaker	3M Company
Daniel Mussatti	U.S. EPA OAQPS
Philip Schmidt	UT at Austin
James Gallagher	Chevron Products Co.
Paul Randall	U.S. EPA NRMRL
Steven Billingsley	Ameripure, Inc.
Scott Hedges	U.S. EPA NRMRL.

### **B.2.2 Session Notes**

The following text contains the detailed session notes for Group A in rough outline form.

#### Can new streams be recovered?

- Styrene
- Butadiene
- Refinery streams
- Methyl ethyl ketone from paint spray...point source recovery
- Polymeric adsorbents
- Gasoline remediation... consider economics
- Jet methyl tertiary butyl ether out of groundwater
- Vapor transfer in tankers



### 3M

- 110 control units - only 25 to address recovery problems
- Issues
  - Different solvents
  - Whether the separation unit can be changed to control (or recover) valuable solvents at the source
- When the process is changed, can quality assurance be guaranteed?
- Tremendous resources are needed to change a process
- The price of recovered material dictates any changes
- The command control attitude of the Best Available Control Technology (BACT) approach discourages innovative technologies
- Industries which have emissions just above regulation levels could have a major incentive to go below the regulatory levels by using VOC recovery measures
- New control techniques may not be widely available because the patents are held by the inventor
  - Can tax advantages be given to the inventor to make the technology widely available?
- Can the rules be changed so that hazardous waste materials are not "arbitrarily labeled"?
- Intangible costs need to be taken into account (like social costs)
- Social conscience is not profitable; special tax incentives are needed to encourage the use of recovery technologies
- Short sighted versus long term thinking
- Technology is forcing regulation

### Recovery Decision Making Process in Industry

- Economic justifications are needed
- Starts at the plant level, gradually winds up
  - The level at which authorization is obtained depends on project size
- Often a quick return on investment is required
- Proven technologies are usually preferred
- Retrofitting is more difficult than new construction

### Research Needs

- The effect of EPA regulations (often anticipated) were underestimated
  - New control technologies sources dried up due to underestimates - NUCON comment
- New markets need to be identified
- New technologies should be able to selectively extract desired components
- Reduction in capital costs of recovery systems
- More support is needed for universities

## **8.3 Breakout Group B**

### **B.3.1 Session Participants**

The following individuals were members of Group B:

Jack Watson	AIChE CWRT
Teresa Harten	U.S. EPA NRMRL
Walter Koucky	Science Applications International Corporation
John Davidson	Intel Corporation
Kamalesh Sirkar	NJIT
Yoram Cohen	UCLA

### B.3.2 Session Notes

The following text contains the detailed session notes for Group B in rough outline form. As noted in the session report, Group B strongly adhered to the questionnaire.

1) Do you have any organic (volatile or nonvolatile) streams presently treated by destruction that might be candidates for recovery (if uncertain, assume they may have a potential for recoverability)?

a) If so, describe each of these streams.

- Yes, Intel and Owens Corning
- Intel's response
  - Semiconductor
    - Low to high volatility
    - Methanol
    - Ethanol
    - IPA - ethyl acetate
    - Propylene glycol
    - Xylene
    - Monomethyl ether acetate
    - Recovery but not onsite
    - Currently six recovery units
- Owens Corning's response
  - Painting
    - Xylene
    - Ethylene glycol
    - Toluene (most common)
  - PVC based streams
    - Toluene
    - Ethylene glycol
    - Methanol
  - One incinerator per plant
  - Multiple lines

b) What are the chemical constituents in each of these organic streams (if possible, include percent volume or weight of each chemical)?

- Owens Corning's response
  - 40,000 cfm flows
  - High purity streams
  - One central control is easier to permit
  - Collected solvent (potential barrier)
  - Large streams (50,000 cfm)
  - No recovery is currently being performed by Owens Corning

c) What are the organic concentrations in these streams, and what are the stream flow rates?

See response for question 1 b.

2) What types of destruction processes do you use to treat your organic streams?

- Incineration at both Owens Corning and Intel

3) What are the approximate capital, operating, and maintenance costs for these processes?

- No response provided

4) Are there potential cost differences if one uses a life cycle assessment view (i.e., cradle to grave considerations of materials consumed and byproducts/wastes generated)?

- Recoup to regenerate
  - Self sufficient
  - Reduced fuel costs
- Looking at novel technologies
- Concerns about NO<sub>x</sub> (thermal treatment)

5) Can you identify the barriers for switching to a recovery process?

- Intel's response
  - Recovery for incineration has some value
  - Mixed streams and low-value solvents are barriers
  - Destruction generates NO<sub>x</sub>
  - Silicon in products
    - Creates particulate
    - Contaminates catalysts
  - Semiconductor industry
    - Lower percent efficiency but low NO<sub>x</sub> and PM
- Owens Corning's response
  - Capital costs
  - Low solvent values

6) Do you have suggestions as to how to minimize or eliminate these barriers?

- Intel's response (less focused on capital costs)
  - Recovery can be cost effective but currently has lower percent capture than destruction technologies – improve percent capture
- Owen Corning's response
  - Reduce capital costs
  - Energy balance issues
    - Process streams are warm and need less energy for thermal treatment than to cool/condition for recovery
  - Address humidity issues
  - Concentration expansive
    - Low VOC streams
  - Reduce potential for dilution
  - Use lower velocity hoods/pick-ups/ovens

7) Who is the individual or what is the corporate function in your organization that is key in getting recovery processes evaluated to replace destructive processes?

- Intel's response
  - Corporate level decision (e.g., senior vice president)
- Owens Corning's response

---

  - Corporate level decision

8) Have you evaluated any recovery process, and, if so, what have been your experiences?

- Owens Corning's response
  - Evaluated and rejected recovery applications
  - Paint lines need cleanup solvents
  - May have on-site uses for recovered solvents (need to investigate)
- Dr. Yoram Cohen's response (UCLA)
  - Petroleum products (Port Valdez oil tanker)
    - 40,000 tons per year to atmosphere
  - Chlorinated hydrocarbons
    - Low values solvents: economics may not justify recovery, but risk (especially perceived risk) and public concern regarding incineration should be considered
  - VOCs from tanker loading - incinerate?
    - Opted for recovery - economics and public opinion opted for recovery
- NUCON's response
  - NUCON sells recovery; does not do economics
  - Customer prefers to do economics
  - Bigger companies are sophisticated at evaluating the cost
  - Regulations are feared (perception of regulation)
  - 50% non chlorinated/50% chlorinated VOCs streams
  - Corrosion increases prices; greater incentive for recovery

9) Are there any special problems inherent in the destructive processes that are overlooked because they are "known or established technologies"?

- NO<sub>x</sub>
- SO<sub>x</sub>
- PM
- Methyl ethyl ketone
- Secondary pollutants

10) What issues/problems have you encountered with the recycle/reuse of organics?

- Intel's response
  - Needs to be high purity - has low value
- Owens Corning's response
  - Low value solvents - need market for recovered product

11) What organic recovery research programs do you think should be undertaken and why?

- Kamallesh Sirkar's response (NJIT)
  - Polymeric sorbents (printed literature)
  - Third party comparisons
  - Polar organics - sorbent problems
  - Formaldehyde - hydrophilic sorbent claims it works, problem for carbon
  - Organics
    - More selective membranes
    - In plant VOC recovery devices
    - Dilute air streams (250 ppm, 1000 cfm flows)
- Yoram Cohen's response (UCLA)
  - Polymeric resins - should not be magic
  - Which sorbent (known chemistry) is used should not be just a vendor decision - resins not

- made for all compounds (use correct polymers)
- Performance not established
- Rate data - tons of data on carbon (e.g., pH, metals, interferences) but not on polymers, at least in the "OPEN" literature

12) What modifications/additions to existing research programs do you think are needed and why?

- Barriers can impede small and large systems
- Rules can be barriers too
- Small systems - "record keeping" and "monitoring"
- Stringency of regulation
- Small, compact, hydrophilic, low molecular weight systems - also point of use systems for wastewater
- Teflon membrane destruction technologies
  - ozonation of 100 ppm streams
  - 2-3 companies in the market

13) What types of economic/compliance incentive programs are needed to encourage the use of innovative organic recovery technologies?

- Government incentives

14) What improvements in recovery technologies are needed to increase the use of these technologies (in your facility, with your stakeholders, in industry as a whole)?

- Technologies for dilute streams (100 ppm), process integration, and optimizing new technologies
- Combined short bed absorption with pervaporation - small scale application
- Information on process design as well as chemistry
- Smaller scale processes for special applications - large companies sell finished products, this limits creativity
- Turnkey system versus active media companies is economical
- Sell systems not membranes
- Standard tests (American Society of Testing and Materials) to compare media on equal ground
- Standard tests for evaluating performance -- can be used to bring more systems to market

15) What sources of information (e.g., how-to manuals, guidance documents, technology handbooks, etc.) do you think are needed to improve the general understanding of organic recovery technologies as well as to encourage their use?

- Owens Corning's response
  - More pilot scale research
  - Database containing available information and knowledge
  - Manual to help integration of technology and provide alternatives when one choice does not solve the problem

## B.4 Breakout Group C

### B.4.1 Session Participants

The following individuals were members of Group C:

Stephen Adler	AICHE CWRT
Joseph Rogers	AICHE CWRT
William Asher	SRI International
Charles Darwin	U.S. EPA NRMRL

Richard Baker	Membrane Technology Research, Inc.
Carlos Nunez	U.S. EPA NRMRL
Bob Patty	CPI
Satish Bhagwat	Owens Corning
Mohammed Serageldin	U.S. EPA OAQPS
Nan Wei	Amoco
Walter Wilson	Hill Air Force Base
Larry Shaffer	NUCON International.

#### **B.4.2 Session Notes**

The following text contains the detailed session notes for Group C in rough outline form.

##### Research and Development Needs

- "Real-world" demonstration of processes are needed
  - There is less need for new ideas to tackle a familiar problem except when costs are "excessive"
- Demonstration funding is needed (e.g., DOE)
- Academia, national labs, etc., focus on areas where existing technologies are not cost effective
- EPA/national labs should focus on helping industry commercialize technology and not on basic research
- Technology developers need to work with EPA on demonstration sites (testing is expensive)
- Government funding for "not-for-profit" efforts is drying up and other sources of funding are also difficult to obtain - industry uninterested because the incentives are low
- Funding is going to wrong places

##### What are the Problems?

- Aluminum coating solvents
- Blowing hydrochlorofluorocarbons from warehouses - a high flow/low concentration issue
- High flow, low concentration streams (50,000 cfm/few ppm)
- Streams with concentrations near 500 ppm and flows less than 5000 cfm
- Styrene
- High flow, low concentration streams (200,000 cfm/less than 100 ppm)

##### Some Conflict Between EPA and OSHA Interests and Concerns

- EPA wants to push towards concentration/recovery
- OSHA wants to push towards dilution for worker safety
  - Therefore, need to find balance between the two forces
  - Balance is more difficult to obtain due to the small size of many manufacturers

##### Barriers

- Must be able to recycle materials for plant use, not off-site use - needs a recovery value of at least \$100,000 per year and a rate of return less than 2 years
- Many systems are "on-off"
- Many technologies are not adaptable to small scale systems because of marketing barriers - product must be robust, reliable, and require little technical attention
- Small point sources often do not have the funding to install recovery systems
- White shoe salesman syndrome - Does the technology really work?
- Lack of funding for commercial demonstrations
  - EPA does not have the funding to support this

- “Any day now” regulations - State, Federal regulations keep getting pushed back
- Lower cost process systems for low concentration streams
- Lack of readily available sources of information (e.g., a database) on existing technologies

#### How to overcome barriers?

- Identify the barriers
- Provide incentives for new technologies
- Eliminate the short term bottom-line mentality
- Address hazardous waste issues which present a barrier for establishing new markets for VOC recovery
- Address the fact that a social conscious is not profitable
- Use tax incentives
- Increased regulatory flexibility
- Performance bonuses
- Trading programs
- Increased collaboration between industry and government for demonstration programs

United States  
Environmental Protection Agency  
Center for Environmental Research Information  
Cincinnati, OH 45268

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.

PRESORTED STANDARD  
POSTAGE & FEES PAID  
EPA  
PERMIT No. G-35

Official Business  
Penalty for Private Use  
\$300

EPA/625/R-99/005