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Environmental Monitoring Issues

Results of Workshops Held in July 1992 as Part of EPA's Eighth Annual Waste Testing and Quality Assurance Symposium

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March 1993

ENVIRONMENTAL MONITORING ISSUES:

RESULTS OF WORKSHOPS HELD IN JULY, 1992 AS PART OF EPA'S EIGHTH ANNUAL WASTE TESTING AND QUALITY ASSURANCE SYMPOSIUM

Office of Modeling, Monitoring Systems and Quality Assurance
Office of Research and Development
U.S. Environmental Protection Agency
Washington, D.C. 20460

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FOREWORD

The U.S. Environmental Protection Agency (EPA) has several goals in sponsoring the Waste Testing and Quality Assurance Symposia series. These include serving as a forum for working with the public and other regulatory officials on measurement, monitoring, and quality assurance issues involved with implementing the hazardous waste management program, and exchanging information on new developments in waste and environmental media sampling and testing methods.

As a means of soliciting input from all sectors of the monitoring community, the Agency in 1992 added a series of workshops on monitoring issues important to EPA's regulatory programs. The workshops dealt with four issues:

- Adoption of performance-based methods,
- Predicting the environmental impact of oily materials,
- Characterizing heterogeneous waste, and
- Characterizing mixed wastes.

The Symposium series is cosponsored by EPA's Office of Solid Waste and Emergency Response (OSWER) and Office of Modeling, Monitoring Systems and Quality Assurance (OMMSQA) within the Office of Research and Development (ORD). Due to the importance of issues discussed in the workshops, the Agency is continuing its efforts to address these issues. This document informs persons who were not able to participate in the workshops of the resulting ideas and information, solicits additional information on possible approaches to address the issues, and review activities the Agency has undertaken to followup on the workshops.

Comments on the issues should be sent to the author at the following address:

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ABBREVIATIONS

ASTM	American Society for Testing and Materials
API	American Petroleum Institute
ALARA	As Low As Reasonably Achievable
AEA	Atomic Energy Act
CERCLA	The Comprehensive Environmental Response, Compensation, and Liability Act
CWA	Clean Water Act
CAA	Clean Air Act
DQO	Data Quality Objective
DOE	Department of Energy
DOT	Department of Transportation
EC	Environment Canada
EMMC	Environmental Monitoring Management Council
EMSL-LV	Environmental Monitoring and Support Laboratory , Las Vegas
EP	Extraction Procedure
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
ICP-MS	Inductively Coupled Plasma-Mass Spectrometer
ISO	International Organization for Standardization
INEL	Idaho National Energy Energy Laboratories
LDR	Land Disposal Restriction
NRC	Nuclear Regulatory Commission
NEIC	National Enforcement Investigation Center
OSWER	Office of Solid Waste and Emergency Response
OSW	Office of Solid Waste
OMMSQA	Office of Modeling, Monitoring Systems and Quality Assurance
ORD	Office of Research and Development
OWEP	Oily Waste Extraction Procedure
PCBs	Polychlorinated Biphenyls
QA	Quality Assurance
QC	Quality Control
QAPjP	Quality Assurance Project Plan
RMW	Radioactive mixed waste
RCRA	Resource Conservation and Recovery Act
RSD	Relative Standard Deviation
SDWA	Safe Drinking Water Act
SAB	Science Advisory Board
TDS	Total Dissolved Solids
TCLP	Toxicity Characteristic Leaching Procedure
TSCA	Toxic Substances Control Act
U.S. EPA	U.S. Environmental Protection Agency
WAP	Waste Analysis Plan

1. INTRODUCTION

Each issue workshop consisted of two parts: a plenary session and a working session. During the plenary session, participants heard viewpoints on each issue from:

- A representative of EPA (the regulatory perspective),
- One or more representatives of the regulated industry or the laboratory services industry (the regulated community's perspective), and
- A scientist active in the field to review the state-of-science.

Appendix A contains the text of all presentations.

Following the plenary session, the moderator presented the participants with their charge, and the approximately 200 participants broke into three working groups to address each problem presented. Participants were assigned to different breakout sessions to ensure that all sectors of the monitoring community were represented in each workgroup.

This report highlights the principal points presented by the speakers during the plenary sessions and the results of the working groups. The inputs from each working group on a single issue have been combined to provide a consolidated picture of the information, ideas, and suggestions raised by the participants.

Each workshop provided a forum for members of the environmental monitoring community from industrial, State, Federal, and private sector groups to share ideas and information.

2. PREDICTING THE ENVIRONMENTAL IMPACT OF OILY MATERIALS

2.1. BACKGROUND

Prevention of ground water contamination historically has been one of EPA's highest priorities in implementing the Resource Conservation and Recovery Act (RCRA) hazardous waste management program. To that end, the Agency has developed and promulgated fate and transport models, test methods, and regulatory standards to control the management of wastes whose properties might pose a hazard to ground water. The Agency has further demonstrated its concern for ground water by including the Toxicity Characteristic (40 CFR 261.24) among the hazardous waste identification characteristics.

One type of waste that can pose a hazard to ground water is oily waste, which can, in some cases, migrate like a liquid even though it appears to be a solid. Oily wastes take many forms, including liquids of widely varying viscosity, contaminated soils, sludges, and tarry "plastic" masses. Because oily wastes result from a wide variety of commercial processes and applications, these wastes are broadly distributed and have a large volume.

Over the years, a number of laboratory extraction methods have been applied to the problem of predicting what might migrate from oily wastes managed under landfill conditions. Among the test methods that have been developed and employed to identify those wastes that might pose an unacceptable hazard are: EPA methods 1310 [Extraction Procedure, (EP)], 1311 [Toxicity Characteristic Leaching Procedure, (TCLP)], and 1330 [Oily Waste Extraction Procedure, (OWEP)].

All current approaches have serious deficiencies in predicting the mobility of toxic chemicals from oily wastes. Method 1311 (TCLP) underestimates the mobility of many oily wastes due to filter clogging problems, its degree of precision, and many operational problems. Conversely, Method 1330 (OWEP) probably overestimates mobility, since this method emulates a worst possible case scenario. No available laboratory mobility procedure is truly satisfactory

as each method suffers from one or more problems. The goal of the workshop was to advance the state-of-the-art with respect to techniques for characterizing the leaching potential of oily materials.

Because mobility estimation is such a large and complicated topic, the workshop focused on only one aspect: predicting which substances might leach from oily material that have been improperly placed in a landfill. Participants discussed how to predict either the first or the highest concentration of material that would be released overtime from such waste to the soil immediately below it (the initial source term). This information is used in the fate and transport models that predict the final toxicant concentration at a specified distance from the disposal site.

2.2. SUMMARY OF POSITION STATEMENTS

2.2.1. Regulatory Program Perspective

Mr. David Friedman, ORD, presented the Agency's position that, "Given the importance of this issue, it is imperative that accurate, precise, and usable approaches to characterizing the mobility of oily materials be developed." Predicting a material's leachability requires consideration of the disposal conditions and the fate and transport models for which the characterization is to serve as the release term. No universal test procedure is likely to be developed that will accurately replicate all disposal conditions. There are many disposal scenarios that are of concern. However, for the purposes of this effort, the priority waste management scenario that EPA's Office of Solid Waste (OSW) selected to be modeled in this workshop is placement of the waste into or on the ground (e.g., in an unlined pit, lagoon). This scenario requires considering a number of parameters, including:

- Temperature of the waste,
- Rainfall regime,
- Amount of waste,

- Leachate-waste contact time, and
- Soil types.

The challenge lies in predicting which constituents, at which concentrations, will leave the disposal point and move toward an aquifer. Pollutant migration will result from a combination of movement of the "liquid" phase of the oily waste and from extraction of toxicants by the action of rainwater or landfill leachate. The information obtained from the characterization serves as the input to the fate and transport models being developed as part of other Agency initiatives.

As input parameters, the model requires information on the amount and composition of both the aqueous and non-aqueous phase liquid portions of the waste and the composition of the leachate that might be generated by action of surface waters on any "solid" material present in the waste material. At this time, the Agency does not have a precise way to define either "aqueous-phase liquid" or "nonaqueous-phase liquid."

As a practical matter, it is important that the laboratory test methods selected to predict the environmental impact of oily wastes:

- Be simple to use (not require sophisticated equipment or constant attention by a technician),
- Be inexpensive to perform,
- Take as little time as possible to perform (ideally no more than 24 hours),
- Give consistent results (i.e., RSD $< 50\%$),
- Be rugged, and
- Not generate wastes (e.g., generate little, if any, solvent waste and waste contaminated media).

From a regulatory perspective, it is important that the tests:

- Be accurate (relative to predicting behavior of waste in the environment) and
- Have a high degree of freedom from false negatives (any errors that underestimate the threat to the environment).

The Agency has identified three approaches that may provide the necessary estimate of possible environmental impact of oily wastes under the target disposal scenario:

- One approach defines as mobile all organic materials (e.g., 50+ percent of solvent extractable material is carbon) that have a defined degree of flowability under conditions of moderate temperature (e.g., 20°C) and pressure (e.g., 10 psi).
- A second approach develops a *single generic laboratory procedure* to:

  a. separate the material into that portion of the material that can be expected to flow away from the disposal point (i.e., would behave as a "solid"), and

  b. estimate the concentration in ground water leaving the disposal point that might result from ground water solubilizing the hazardous constituents from both the mobile and nonmobile fraction of the material.
- A third approach relies on a *series of laboratory test procedures* to evaluate the waste material. These procedures would be keyed to the waste properties and could be representative of site specific conditions of the disposal environment.

2.2.2. Regulated Community Perspective

Mr. Clifford Narquist, of BP Research who represented the American Petroleum Institute (API), presented a regulated industry viewpoint.

Many groups, including Environment Canada (EC), American Society for Testing and Materials (ASTM), and EPA, have participated in developing improved leachability and contaminant fate/transport tests and models. Despite this work, predicting the potential

environmental hazard associated with oily wastes remains problematic. TCLP makes the assumption that aqueous and nonaqueous liquids will behave identically, both within the landfill and upon their hypothetical release. Little technical support exists for this position.

The risk from light nonaqueous phase liquids (i.e., oils) appears to result mainly from contaminants partitioning from the oil into the ground water. Free oil, itself, poses little risk because of a lack of exposure. As oil moves through the soil, the soil immobilizes it. Toxic constituents partition into the water phase from this point of immobilization. Because people are highly unlikely to drink free-phase hydrocarbons, leaching the oil fraction along with the solids appears a sensible approach to treating this fraction.

The disposal scenario as depicted by EPA does not reflect current waste disposal management practices. Specifically, an EPA-OSW survey documented that municipal landfills no longer accept liquid-type wastes. New test methods, therefore, should be based on actual waste management scenarios.

With respect to the fate and transport model, the infinite source assumptions currently used are unrealistic. One improvement would be to design transient, declining source terms into the model. Further, the leaching test and model need to consider the processes that transpire in the vadose zone. Among these processes are biodegradation, hydrolysis, volatilization, and soil retardation. These processes are not considered in the current regulatory approach.

Until work on the behavior of nonaqueous materials and the prediction of their movement is more developed, the nonaqueous liquids should be treated like the solid phase of the waste and should be subjected to the same extraction fluid. To the extent that the hazardous constituents are released into the extractant, they should be combined with the aqueous extract generated from the waste solids.

Before developing new test, a consistent and easily applied physical, hydrologic, and geochemical representation should be developed for the waste management scenario of concern.

The development of leach tests and fate and transport models should be coordinated. These new procedures should follow the recommendations of EPA's Science Advisory Board (SAB) Environmental Engineering Committee, Leaching Subcommittee. This approach would place the new tests and models on a firmer scientific basis and lead to better decisions.

2.2.3. State-of-Science Perspective

The state-of-the-science in predicting the environmental impact of oily materials was presented by Mr. Larry Jackson, a private consultant. As with the API presentation, considerable importance was placed on using the rigorous scientific approach of the SAB Leaching Subcommittee.

The presentation proposed a series of evolutionary changes to the current approach based on existing EPA methods, experience gained from using the TCLP, and a reconsideration of some existing models and data on the fate and transport of fuel-derived materials. The presentation also offered four suggestions for improving the current approach:

- Adopt a flowable materials test to separate free liquid phase hydrocarbons from the contaminated solid matrix. Such a test would permit scientists to independently evaluate the potential impact of the free-phase material and the contaminated soil independently. A test similar to EPA's proposed liquid release test was described.

- Modify the TCLP using approaches already allowed in other RCRA methods. These modifications could overcome some mechanical problems associated with the current procedure.

- Adopt a new method of contacting the leach medium with the waste. Descriptions of several column leach testing procedures that are consistent with the SAB recommendations were provided. This approach offers options that allow the evaluation of both lighter-than-water and heavier-than-water materials.

- Use a new model to determine the release potential of oily wastes. The proposed model uses simple well-founded tests and basic physical/chemical parameters of the waste and potential pollutants. With this model, the effect of soils on the fate and transport behavior of individual compounds can be assessed.

2.3. CHARGE TO THE WORKSHOP PARTICIPANTS

Before breaking into three workgroups, the participants were asked to address the following questions:

1. What is the "best" approach to use to predict the nature and concentration of the components that will leach from oily wastes placed in an unlined landfill environment?

2. If the necessary tools are not available, how should such a test method or model be developed and evaluated?

3. What form should a cooperative development program take?
   - How should it be organized?
   - Who might the cooperators be?
   - How long would it require?

2.4. RESULTS OF WORKGROUP DELIBERATIONS

During their deliberations, the workgroup participants dealt with a number of aspects of the problem including the definition of oily waste and analytes of concern. A summary of the discussions follows.

2.4.1 Definition of Oily Waste

Two workgroups felt strongly that the Agency should revisit how "oily waste" is defined and which constituents of an oily waste should be of concern.

Participants discussed two approaches to defining the universe of wastes that should be considered oily wastes. The first classifies wastes based on physical properties such as viscosity

and density. The second approach defines oily wastes by listing wastes or residues resulting from a given industry or waste generation process. The workshop participants believed that developing appropriate testing schemes requires more information about oily wastes than is currently available. Specifically, participants expressed a need for EPA to conduct a survey that will better define the sources of oily wastes, the volumes generated, and the current disposal/treatment options.

2.4.2 Analytes of Concern

Participants voiced concern that whatever future approach the Agency uses to characterize oily wastes that approach should consider more of the compounds listed in Appendix VIII than are currently included in the Toxicity Characteristic. This concern was based partly on the need to protect human health and the environment. In addition, participants stated that the list of regulated compounds will probably grow. This growth in turn will impact the design and conduct of any test. Some participants felt that, unless all analytes likely to be of concern were considered at the beginning, any test developed may require later modification. People objected to spending time developing tests that would rapidly become outmoded.

2.4.3. What Approach Should Be Used in Developing a New Testing Procedure?

This was the central question addressed by the groups, and consideration of this issue occupied most of the discussion time. The participants identified two basic criteria to apply to any new test method development effort:

1. The test must address the procedural problems encountered when applying the TCLP to oily wastes (i.e., time consuming nature of the TCLP, its high cost, its high variability, and its inability to handle materials that are difficult to filter).

2. The new test(s) should be scientifically valid. Where possible, tests should be capable of representing the actual disposal conditions (soil types, rainfall, etc.)

and must simulate the behavior of oily materials in the environment. New tests should consider such properties of the oily waste as amount of flowable material, density of the liquid phase, viscosity, and the material's flow characteristics in a soil environment. Special efforts should be made to validate these models with data from real-world samples disposed in actual landfills.

Members from discussion groups suggested that developing a tiered testing approach would reduce the number of samples requiring leach testing. Specifically, an initial aggressive test, such as compositional analysis of the total waste, would be used to screen the waste. Wastes containing high levels of regulated constituents would be considered as hazardous without mobility testing. Wastes with low levels of contaminants would be considered as nonhazardous. The time consuming, mobility testing procedures would then be applied only to those wastes containing moderate levels of constituents of concern. EPA would establish criteria for each parameter that would initiate the complete leach testing procedure.

Another variation of this approach would employ a quick, relatively inexpensive screening test (e.g., some type of leaching test) to identify wastes that have a high enough potential of posing a leaching hazard to warrant definitive testing for leachability. As before, EPA would have to establish new criteria for each parameter that would initiate further leach testing.

The general consensus favored abandoning the TCLP as a means of characterizing oily wastes. Only one participant wanted to retain TCLP as the principal predictive tool. Attempting to modify the TCLP to improve its performance received support from only two participants. The rest preferred a new approach. Participants discussed two general approaches for predicting leachability: use of laboratory tests and use of mathematical models.

2.4.3.1. *New Laboratory Leach Testing Methods*

Participants considered two approaches to new laboratory methods for evaluating leachability: a multitest approach and column leach testing.

- **Multi-Test Leaching Approach**

  A number of participants supported having a suite of leaching tests to evaluate the environmental impact of oily materials. Given the diverse universe of oily wastes, a single "best" test may not be feasible or scientifically valid. The use of multiple tests will allow analysts to match the characteristics of the waste and/or the management unit to a test designed for the specific situation.

In a related suggestion, some participants proposed a generic testing protocol with a range of options for key testing variables. This approach would allow the selection of the most appropriate test conditions for a particular waste. Variables could include the nature and amount of leaching fluid, particle size of the waste, time, impact of site-specific soils, etc. The concept would apply equally well to either batch- or column-type tests.

- **Column Leach Testing**

  Several people supported the development of a column leaching technique as the best method to simulate the movement of oily material in the environment. The addition of inert materials to the column would immobilize liquid, provide permeability, and allow efficient extraction of the waste material. The column technique also permits determination of the effect of site-specific soils on the waste and its leachate.

In developing new mobility procedures, the workgroup supported validating these procedures against actual field conditions. With column tests, it will also be important to study such factors as particle size and moisture content of the column materials, flow direction and rate, viscosity of materials, etc.

2.4.3.2. *Mathematical Models to Estimate Mobility*

Several participants suggested mathematical models to predict toxicant mobility, because such models can describe the behavior of possible pollutants both in the waste matrix and the disposal environment. The literature contains empirical models for predicting equilibrium partitioning of compounds between oily materials and between aqueous liquids and soils. The key variables in the models are the water solubility of the constituents of concern, the percent carbon in the waste matrix and surrounding soil, and the various partition coefficients.

A modeling approach holds the promise as a means of reducing both the cost and time needed for characterization. In addition, mathematical models can provide site-specific evaluations of environmental impact.

2.4.3.3. *If the Necessary Tools Are Not Presently Available, How Should Such a Test Method Or Model Be Developed And Evaluated?*

A thorough review of existing data from proposed modeling approaches would be useful for directing future efforts. Collecting data from actual field sites would also aid in developing and validating methods.

Participants expressed the opinion that the Agency should work with members of the private sector and universities in developing any new methods. EPA should also involve members of other Agency programs such as the Toxic Substances Control Act (TSCA), the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) programs in the development effort.

Participants recommended additional technology transfer activities similar to this workshop. Suggested activities included symposia and seminars. Possible co-sponsors include ASTM and API. International participation would also be desirable.

The Agency should pursue an evolutionary approach that would bring about incremental modifications in available methodology. Such an approach would lead to improved methods within only 1 to 2 years. However, participants recognized that fully understanding how to predict the mobility of oily material may require up to 10 years of research and development.

2.5. AGENCY FOLLOWUP TO WORKSHOP

Since the workshop, EPA has taken a number of steps to address this problem of predicting the environmental impact of oily materials.

Taking to heart the suggestions that the Agency work with the private sector, EPA has entered into a cooperative agreement with the ASTM Institute for Standards Research. This agreement calls for working with members of the public and private sectors to develop improved protocols for evaluating the mobility of oily materials.

In October SAB met to review the results of the workshop and the Agency's plans for moving forward with the development of improved protocols for oily waste. Appendix A to this report describes the approach under consideration.

As a first step, the Agency plans to use soil column studies to identify those oily wastes for which the TCLP is inappropriate. At the same time, the Agency is determining which management scenarios and subsurface fate and transport models are appropriate for use in assessing the impact of oily waste on ground water. Based on the results of these studies, the Agency will identify the input needs of the models for which the mobility procedures are designed to serve.

3. ISSUES ASSOCIATED WITH ADOPTION OF PERFORMANCE-BASED METHODS

3.1. BACKGROUND

A number of regulatory programs are implemented by EPA that require collection of environmental monitoring data. These include the Safe Drinking Water Act (SDWA); the Clean Water Act (CWA); RCRA; CERCLA; the Clean Air Act (CAA); and FIFRA.

Selecting the appropriate measurement method is a key part of any monitoring program. Over the years, in crafting its monitoring requirements, the Agency has primarily adopted a policy of publishing test methods appropriate for complying with the various regulations. The methods have been written with varying levels of detail. Rather than issuing flexible methods and specifying required performance, the Agency generally has opted to give the analyst mandatory instructions on how to conduct the analysis.

This approach has resulted in several problems:

1. Long delays have occurred in using new technology to cost-effectively analyze samples.

2. In some cases, the required methods either give biased results for some types of samples or do not yield the requisite sensitivity. Since in many cases the methods make no provision for modification by the analyst, the analysis can lead to results that do not meet the data quality needs.

3. Rigid specification of methods rather than data quality, frequently forces laboratories to use expensive technology in place of suitable approaches that are simpler and less costly.

The Agency is aware of these problems and is attempting to solve them. One option entails moving from a system that specifies methods to one that specifies performance and allows flexibility in the methods used to conduct the analysis. Before implementing such an approach, the Agency needs to resolve several questions. These include:

- How will acceptable performance be defined?
- What documentation is needed to verify compliance with performance standards?
- How will the change to performance based methods affect the procurement process, both by EPA and by commercial clients?

The Agency sponsored this workshop to examine this issue and to bring together members of the environmental monitoring community to share ideas and information on ways to increase the utilization of innovative monitoring technologies by switching to performance-based monitoring. This change has the potential to improve both the quality and cost-effectiveness of environmental monitoring. Although many people have ideas on how to implement performance-based monitoring, as yet, there is no agreement on which approach is best.

3.2. SUMMARY OF POSITION STATEMENTS

3.2.1. Regulatory Program Perspective

Mr. Michael Conlon, EPA Office of Ground water and Drinking Water, presented his views on the merits of adopting performance-based analytical methods.

Regulatory data needs to provide accurate information for decision making rather than determining the absolute truth. This is especially true when pursuing absolute truth results in expenditures that bring about little or no additional protection of public health. Limited spending on regulatory data does not mean sacrificing scientific integrity, but rather means obtaining the

needed data at the lowest cost. This need evaluation process has been termed the "data quality objective process."

The control-based approach to obtain regulatory data specifies the exact procedural steps that the analyst must follow. The major advantage of this approach is that one knows in advance what must be done. The disadvantage is that the test results may not meet the acceptance criteria and degrees of certainty normally associated with reliable analytical methods.

As an alternative to the control-based approach to analytical method specification, the Agency is studying a performance-based approach. In a pure performance-based approach, the user can employ any procedure so long as the specified quality of results is achieved. The major advantage of a performance specification is that it assures the desired outcome. The major disadvantage is that performance parameters must be specified to ensure that the results meet minimum standards. In addition, performance must be verified immediately to institute corrective action. Immediate verification may not necessarily be a disadvantage, because total quality management requires monitoring quality at the earliest point in the process rather than waiting until the end to determine if a problem has occurred.

The requirement to produce legally defensible data drives the method specification and documentation process. For a performance-based approach to work, the documentation must assure that the performance criteria were met. The challenge facing the technical community consists of finding a means to have both flexibility of methods and confidence in the results. For the foreseeable future, EPA is likely to rely on both reference and performance-based methods, and the criteria for a performance-based method will likely be driven initially by the reference methods.

3.2.2. Perspective of the In-House Laboratory from the Regulated Community

Mr. Reid Tait, Dow Chemical Company, presented his views of the advantages and disadvantages of using performance-based methods in industrial laboratories. Overall, the concept offers a mechanism to:

- Implement the latest scientific and technological developments in analytical chemistry,
- Minimize costs and paperwork,
- Maximize flexibility of method selection, and
- Improve the quality of results.

Before these benefits can be realized, some important questions must be answered. The first question is primarily institutional in nature: How can industry satisfy the large number of different regulatory program requirements for documentation without being overwhelmed by paperwork? Historically, each program has required considerable documentation to support any method variance. Can reasonable and consistent documentation standards be developed that respect the regulators need to be protective of the environment and yet do not prove unduly burdensome to industry?

Major technical questions are as follows:

- What criteria will be used to judge acceptability of the method, and what are the criteria for rejecting a method? Making this determination entails documentation of performance requirements. Will applying the data quality objective (DQO) process adequately describe the requirements?
- Must the method be capable of yielding comparable results when performed by other laboratories?

- Should the results of the method be confirmed by at least one independent laboratory or should they be compared to existing methods believed to work for the analytes of interest in the sample matrix?

Satisfactory answers to the major technical questions will result in the following benefits being accrued to industry and regulator alike.

- Industry can apply its vast resource of analytical technology and trained personnel to its problems.
- Regulators and other potential users will have immediate access to this technology through the documentation supporting the methods.
- Incentives for industry investment in new, cost-effective technology will be created.
- Both industry and the regulatory community will have a higher level of confidence in the data because the quality assurance/quality control (QA/QC) data accompanying the results will be tailored to prove compliance and control of the analytical process.

The use of performance-based methods will place a premium on effective communication between the industrial laboratory (or its laboratory service providers) and the regulators. A means of determining "acceptable performance standards" expeditiously will have to be developed. Sufficient documentation must to be developed to protect industry from conflict-of-interest claims and the regulator from accusations of inadequate oversight and control. Industry will face the possibility of being required to develop additional methods to meet the new performance requirements.

Mr. Tait's final recommendation was that all methods should be performance-based.

3.2.3. Perspective of the Commercial Laboratory Industry

Ms. Carla Dempsey, Lockheed Engineering and Sciences Company presented her views of the major issues that performance-based standards raise for her industry. This presentation discussed both advantages and disadvantages associated with the change to performance-based methods.

Among the principle advantages is the overall elevation of the level of science in the environmental analytical process. Performance-based methods will make maximal use of the professional chemist's knowledge and experience. As a result, the chemist will improve the quality of data, optimize the time and cost of method performance, and create new methods. Additionally, sound scientific procedures can replace outdated or incorrect ones, improving the overall quality of the environmental decision-making process.

This new approach will attract highly qualified and motivated professionals to environmental chemistry laboratories. Currently, such professionals tend not to pursue careers in environmental chemistry because of both the absence of good science and the boredom associated with strict adherence to prescriptive methods. The competition between laboratories to provide higher quality, more rapid, and cost-effective analysis will benefit the consumer of laboratory services. The ultimate result will be to improve the overall quality of the analytical chemistry industry.

The commercial laboratory industry has many of the same concerns as the in-house industry laboratories. These include:

- How will acceptable performance be defined and measured, and what level of documentation will be required?
- Will it be possible to obtain agreement among the multitude of regulatory groups who are the ultimate end users of the data?

The presentation also raised the following new issues:

- How will analyses be procured? The current prescriptive methods are easy to cost, but how will laboratories establish a fair market price for a performance-based analysis prior to completion of the analysis?

- What will be used as a "benchmark" to establish method performance? Are there existing "scientific performance standards" that can be used as benchmarks or are all current standards method/instrument specific?

- Can current regulations that require use of specific methods be changed in a timely way to allow implementation of a performance-based program for all media?

- Who will select the methods used on projects? How will the laboratory have input into the decision-making process that establishes project objectives?

Ms. Dempsey made some concrete recommendations about specific actions that would aid in the implementation of performance-based methods. They include:

- Defining performance parameters for specific types of environmental decisions (site surveys, clean closure decisions, monitoring, etc.) as part of the DQO process;

- Providing a guidance document so that data users know what types of performance data can be collected and how they are used;

- Defining documentation requirements;

- Promoting the formulation, distribution, and use of appropriate performance evaluation materials (reference materials); and

- Restructuring the procurement process.

The presentation concluded with an endorsement of the shift to performance-based methods and a description of how the commercial laboratory sector could contribute to a joint industry-Agency effort.

3.2.4. State-of-Science-Perspective

Dr. Billy Fairless, EPA Environmental Services Division presented his views on the state-of-the-science position in performance-based methodology at this point in time. He stated that much of the technology necessary to effect the conversion exists, but that it must be organized to promote the use of performance-based methods. The conversion can be implemented quickly and will promote creativity and quality science, produce higher quality data more cost-effectively, and reduce the incentive to commit fraud.

Dr. Fairless supported this latter point with the contention that, when faced with requirements to use prescriptive methods known or believed to be of questionable value, some people may adopt method improvements to try to obtain better data. Such changes may produce data of questionable quality and may even be illegal when viewed in a regulatory sense. Consequently, a person who pursues good science and sound environmental decision may become liable for prosecution. Such a situation is in no one's best interests.

The presentation offered a three-step approach for effecting the conversion to performance-based methods:

1. Fully describe all procedures used to generate data in a quality assurance project plan (QAPjP).

2. Provide documentation that all procedures were in control during the data generation process. Standard QC steps are adequate for the purpose if they are carefully selected and executed.

3. Perform enough replicate sample and spike sample analyses to establish the precision and accuracy of the determinations at the concentration of interest.

At the conclusion of the presentation, the presenters fielded questions from the audience before they broke into discussion groups.

3.3. CHARGE TO THE WORKSHOP PARTICIPANTS

After the four speakers gave their positions, the moderator asked participants to address the following questions:

1. How should performance be defined?

2. What documentation should EPA require to verify compliance with performance standards were met?

3. How will the change to performance standards affect the procurement process by both EPA and commercial laboratories?

3.4. RESULTS OF WORKGROUP DELIBERATIONS

3.4.1. How Should Acceptable Performance Be Defined?

This question received the largest response from each group. The groups identified four principle ways to define acceptable performance. Interestingly, each group independently arrived at the same four approaches. The recommended approaches are:

1. <u>Validation by comparison to reference method.</u>

   With this approach, EPA or some other appropriate standards-setting organization would publish a reference method for the analysis. The performance of the reference method would be defined in terms of precision, bias, sensitivity, or other appropriate criteria. The method that a laboratory opted to use would be compared against the reference

method's performance. As long as this method met the performance criteria, it would be acceptable. Participants agreed that the necessary reference method and performance data do not currently exist for many methods and analytes of interest. If a reference method and performance data are unavailable for a particular method, participants suggested that a laboratory perform a side-by-side comparison with an EPA, ASTM, or other recognized method.

2. Demonstration of compliance with defined, generic QA/QC criteria.

Nearly all participants believed that a sound laboratory QA/QC program is essential for demonstrating acceptable performance for performance-based analyses. Each standard QC criteria (blanks, matrix spikes, duplicates, etc.) applies to this problem. Generic QC criteria for regulatory programs might be set forth in a number of ways including Chapter 1 of SW-846, QAPjPs, and project DQOs. Participants agreed that meeting or exceeding criteria would constitute acceptable performance for a proposed method and that such methods should receive approval. The Agency would specify documentation guidelines that laboratories would have to meet to prove acceptability.

3. Demonstration of compliance with project-specific data quality requirements.

Adherence to project-specific DQOs should be sufficient to define acceptable performance. If properly conducted, the DQO process determines project-specific data quality requirements in terms of acceptance criteria that are independent of the method of analysis. Method substitution cannot occur where data requirements are based on results from an operationally defined procedure, such as TCLP or Total Dissolved Solids (TDS). If the data requirements can be expressed in absolute terms, such as mg/kg or pH units, with applicable acceptance windows, then any method should be acceptable provided that the data meet or exceed the acceptance criteria.

4. Demonstration of performance using performance evaluation materials representative of the material being analyzed.

If the proposed method can produce analytical values within the acceptance range of the certified value using appropriate reference materials, then the method should be considered acceptable. This standard applies to methods that measure absolute properties, such as concentration or pH. This method of defining acceptable performance depends upon the availability of representative performance evaluation samples. The Agency's support for using Performance Evaluation samples is necessary to promote their commercial production.

Two other means of demonstrating acceptable performance drew less discussion. These were:

5. Successful participation in a laboratory accreditation program.

Some participants believed that the Agency should accept data obtained by unapproved methods, provided that the laboratory generating the data was certified under an acceptable laboratory certification program.

6. Successful participation by the analyst in a training and certification program.

Some participants believed that the Agency should accept data obtained by unapproved methods provided that the individual analyst could be certified under an analyst certification program.

Neither proposal found widespread support.

3.4.2. What Documentation Should EPA Require to Verify Compliance with Performance Standards?

Many workshop participants noted that this question was closely related to the first question. The type of documentation required depends on the approach selected to define acceptable performance (See previous discussion.) Several individuals favored global documentation procedures that would apply across all EPA regulatory programs and would greatly simplify documentation problems and also reduce costs.

It was pointed out that establishing the legal defensibility of the data entails Agency-sponsored documentation requirements similar to those in the TSCA and FIFRA programs. Participants expressed considerable concern that laboratory liability is directly linked with adherence to published Agency documentation requirements. Use of International Organization for Standardization (ISO) standards for documentation was suggested as a possible alternative to the Agency developing another set of requirements.

Nearly all participants believe that the documentation requirements should be based on the QA/QC procedures that are commonly used in the laboratory. The documentation requirements should be specified in the QAPjP and be based on the DQO process. In general, participants agreed that developing an achievable and cost-effective DQO requires that the laboratory become involved in the earliest phases of the process. A common complaint raised during the meeting was that the laboratory is currently excluded from the DQO process, sometimes resulting in unrealistic and/or impossible criteria.

Several people supported the recommendation made in the Dr. Fairless' presentation that documentation should include:

- Full descriptions of all procedures used to generate data in the QAPjP.

- Data indicating that all procedures were in control during the data generation process. Standard QC measures are adequate for the purpose, provided that they are carefully selected and properly executed.

- Enough replicate samples and spike samples to establish precision and accuracy of the determination at the concentration of interest.

In addition, several people thought that the documentation should present the reason for not using the "standard method."

3.4.3. How Will the Change to Performance Standards Affect the Procurement Process by Both EPA and Commercial Laboratories?

Only one group discussed this question. The group agreed with the Dempsey presentation that the procurement process would have to change and probably become more complicated. The group believed that the increased complication of the procurement process will impact large and small laboratories differently.

3.5. AGENCY FOLLOWUP TO WORKSHOP

As a followup to the workshop, the Agency's Environmental Monitoring Management Council (EMMC) has undertaken a review of this issue and is currently developing a program to expand the use of performance standards in EPA's regulatory programs.

A specific interoffice committee is working under the auspices of the EMMC, and the committee's recommendation on what performance characteristics need to be monitored is expected in March of 1993. Participation by individual program offices will follow, on a program by program basis over time. The specific requirements for documentation will be contained in individual program rules and regulations.

4. CHARACTERIZING MIXED WASTES

4.1. BACKGROUND

A major challenge facing the Department of Energy (DOE) in its RCRA and CERCLA related cleanup activities is the characterization of mixed waste. Mixed waste is a mixture of radioactive and hazardous waste generally in a liquid or solid form. The presence of radionuclides in a hazardous waste sample increases the procedural problems, the safety precautions, and the cost of analyzing the hazardous component. The presence of radionuclides also reduces or limits the options available for the management, treatment or disposal of the waste. For these reasons, one should know precisely how the data will be used, what and how much data are really needed, and how good that data must be.

In characterizing mixed wastes, samples may be so radioactive that any amount of handling will pose a safety risk. In such cases, special procedures may need to be developed to characterize the waste to determine the proper means of treatment, storage, or disposal. Moreover, careful choice of the properties (in addition to radiological hazards) that need to be determined has to be made to properly characterize the material with respect to the appropriate options for treatment, storage, or disposal.

The goal of the session was to provide a forum for exploring ways to develop waste analysis plans based on the characteristics of the waste materials and the available treatment, storage, and disposal options for mixed waste management; how to balance environmental risk and characterization costs; and potential hazards posed by mixed wastes.

4.2. SUMMARY OF POSITION STATEMENTS

4.2.1. Regulatory Program Perspective

RCRA, Subtitle C, is a hazardous waste management program that emphasizes proper waste characterization by facilities that generate, treat, store or dispose of hazardous waste. Proper characterization is the first step in ensuring the regulator that the waste will be managed under RCRA in a manner protective of human health and the environment. Waste characterization usually requires waste analysis via some testing method. However, waste testing is not always required if background information or process knowledge exists. This is especially true for radioactive mixed waste which poses testing and sampling problems because it contains both radiological and chemical hazards. Testing mixed waste is regulated under two different acts the [Atomic Energy Act (AEA)] for the radioactive component and RCRA for the hazardous component) with two distinct sets of management requirements.

Ms. Susan Jones, OSW, reviewed the RCRA requirements for mixed waste characterization. EPA requires that the hazardous portion be properly identified by process knowledge or testing. In addition to waste identification, waste analysis ensures that incompatible wastes are not stored in the same management unit. Waste analysis also plays an important role in determining land disposal restriction (LDR) requirements. Operators of hazardous waste treatment, storage, and disposal facilities are required to formally document analysis procedures used in a waste analysis plan (WAP) and to accurately identify the hazardous waste by testing using existing published data, or process knowledge.

For mixed waste, EPA will consider reducing testing frequency, modifying testing techniques, and incorporating ALARA (as low as reasonably achievable) practices on a case-by-case basis. The regulated community has communicated to EPA its difficulty in meeting RCRA testing requirements on radioactive mixed waste samples. Some problems include choosing proper sample sizes while maintaining good ALARA principles, determining the number of samples needed to establish the homogeneity of the waste, and obtaining representative samples

of heterogeneous waste. EPA and the Nuclear Regulatory Commission (NRC) recently issued a joint draft guidance document entitled "Clarification of RCRA Hazardous Waste Testing Requirements for Mixed Waste" that provides an overview of the RCRA testing requirements. It addresses concerns such as the potential radiation exposure of employees, elimination of redundant testing and adjusting sample size to reduce radiation exposure while maintaining plausible detection limits.

Many problems exist in characterizing mixed waste, but accurate characterization of mixed waste may be successfully accomplished within the confines of RCRA by using published data and process knowledge. Testing of radioactive mixed waste as a means of waste characterization should only be done when absolutely necessary.

4.2.2. Regulated Community Perspective

Mr. Craig Leasure, of DOE's Los Alamos National Laboratory, reviewed the problem of mixed waste characterization from the perspective of a regulated entity. Characterization of radioactive mixed waste (RMW) is necessary to determine the appropriate treatment options and to satisfy environmental health and safety regulations. Radioactive mixed waste can be classified as contact handled (low-level) or remote-handled (high-level) waste. His paper focused on the characterization of contact-handled RMW.

There are five major issues affecting the sampling and analysis of contact-handled RMW. They are:

- The impact of screening requirements on holding times;
- The management of treatment options;
- The generation of secondary RMW;

- Detection limits; and
- The determination of when material is radioactive.

Radioactive screening of samples can be a time-consuming process that can impact on holding times. The screening process can require such a significant amount of time that analysis can not be successfully completed within the required timeframe. Holding time requirements must be modified to ensure that laboratories have a reasonable amount of time to complete analysis. However, degradation of target compounds must remain minimal during storage. All Government and industrial facilities that handle radioactive material must strictly follow NRC rules or DOE Order 5480.11. The first level of screening is performed with hand-held devices that determine dose rate and the level of personal protection required by field personnel handling samples. The next required screening level ensures that Department of Transportation (DOT) regulations are met and that contract laboratory radioactive material license limits are not exceeded. Screening analysis may include, but is not limited to, gross alpha, gross beta, gamma isotopic, and liquid scintillation counting.

RCRA characterization should not be required on a radioactive mixed waste prior to treatment, if radioactive content is the driver for the type and extent of initial treatment. For example, the only treatment option for a waste that contains significant quantities of fission products may be vitrification. RCRA hazardous waste determination may indicate that the waste contains trace levels of hazardous solvents. However, this information is not likely to change the treatment of the material. The more significant risk would be worker exposure to radiation during sampling and analysis.

Performing RCRA analyses on samples that are known to be radioactive and that are suspected of being hazardous can generate secondary mixed waste. The solvents required to perform extractions are hazardous, and the matrix is spiked with hazardous material. The amount of secondary generated mixed waste can be reduced or eliminated by identifying and

using extraction solvents that are not hazardous and by using process knowledge to minimize the collection of samples and performance of analyses.

EPA requires that relatively large amounts of sample material be taken for analysis to obtain a low detection limit. NRC recommends smaller amounts of sample material to reduce worker exposure. Guidance is needed to optimize sample size and detection limits. If the sample size is reduced by a factor of 50 to reduce worker exposure, then the detection limit will rise by a factor of 50.

One fundamental mixed waste issue that must be addressed is the establishment of a clear definition of what constitutes radioactive material. Presently, the definition of radioactive material ranges from one atom of radioactivity to a material that is greater than 2 nCi/g of radioactivity.

4.2.3. State-of-Science Perspective

Mr. Wayne Griest and Mr. James Stokely, both of DOE's Oak Ridge National Laboratory, reviewed the current state of technology with respect to radioactive waste characterization and discussed promising new developments in the field.

The following mixed waste issues were covered:

- What should be determined and how;
- The applications and limitations of current analytical methodologies;
- Promising new technologies; and
- Areas where further methodology research is needed.

The TCLP developed for disposal of hazardous waste in a landfill, may not be relevant for RWM disposal. Mixed waste will not be disposed of in a municipal landfill. Regulatory

agencies should permit more realistic leaching procedures for RMW, which reflect final waste forms and modes for disposal or storage. Los Alamos National Laboratory is evaluating a brine leaching solution for assessing the suitability of radioactive waste for disposal in the Waste Isolation Pilot Plant.

RCRA allows process knowledge to be used for characterization if a well-defined process generated the waste.

Collection of a representative sample of a waste is critical to generating valid characterization data. For homogeneous low-level wastes, sampling is similar to nonradioactive waste sampling, except additional precautions and constraints are taken to maintain the ALARA principles. Additional research is needed in the sampling and analysis of heterogeneous waste. Heterogeneous waste includes drums containing discrete items such as gloves, bottles, metal items, and towel, and tanks with multiple phases.

More research should be conducted in sample preparation using microwave digestion and EiChroM columns. Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) also seems very promising for radionuclides with long half-lives such as ^{99}Tc, ^{129}I, and ^{227}Np. The development of field analytical methods for the rapid determination of various analytes is under way at Oak Ridge, Los Alamos, and the Nevada Test Site. The development and validation of field analytical methods will be important in minimizing the costs of sample shipment and reducing the number of laboratory analyses.

Idaho National Energy Laboratories (INEL) has adapted TCLP extraction equipment for hot cell use and can perform the procedure using the required amount of sample on high-level samples without significant exposure to workers.

4.3. CHARGE TO THE WORKSHOP PARTICIPANTS

The participants were asked to address the following questions in their workgroup sessions:

1. What kind of information is needed (and what quantity and quality) to safely manage a mixed waste for a series of waste management options?

2. What scientific properties or constituents of the mixed waste should be determined?

The workgroups were asked to focus on the following waste management options:

- Entombment in a below-ground cavern;
- Incineration; and
- Solidification.

4.4. RESULTS OF WORKGROUP DELIBERATIONS

The workgroups discussed each waste management options on which they were asked to focus. Some workgroups extended their discussions to include other waste management options such as:

- Vitrification;
- Reinjection;
- Transmutation; and
- Interim warehouse storage.

Discussions of these options, which may be considered as subsets of the original three options, are also summarized in this report. Each workgroup generated a listing of the essential information that must be collected for the safe handling of mixed waste for the various waste management options. Summaries of the workgroup discussions on these parameters are given below for each waste management option.

4.4.1. Entombment

- Physical matrix or waste type (i.e. sludge, filter cake, clothing, gloves,debris, etc.) is required to provide fundamental information on the waste. This may be obtained through process knowledge or direct testing;
- Offgas monitoring for fixed gases because of the potential danger of explosion;
- Compatibility information for different waste types that may come into contact with each other resulting in adverse interactions;
- Free liquid presence both in the mixed waste and in the underground caverns. Waste with free liquids should be treated to remove the liquid before placement;
- Radiological properties of the mixed waste including daughter products generated; and
- Heat generation from the decaying mixed waste which would have important ramifications concerning the increased mobility of the waste, compatibility of various mixed wastes, and production of gas.

4.4.2. Incineration

- Physical properties of the waste including its BTU content, ash content, moisture, viscosity, and flashpoint;
- Physical form of the mixed waste;
- Chemical content of the waste including the levels of mercury, lead, PCBs (especially tri- and tetra-chlorobiphenyl since they are precursors to dioxins), total halogen content (due to presence of halogenated solvents), total sulfur, NO_x, and volatile radionuclides (e.g. H-3, C-14);

- Specific activity of the waste from gross alpha, beta, and gamma measurements;
- Presence of specific radionuclides and special nuclear materials;
- Presence of materials resistant to incineration, such as teflon or steel pipes, which will require separate disposal for the residues; and
- Any site-specific requirements.

4.4.3. Solidification

- Setting time for the solidification of the waste;
- Compaction strength, leachability, and stability of the stabilization product;
- Total organic content of mixed waste since the presence of organic materials may interfere with the solidification process;
- VOC levels in the offgas generated during the curing phase; and
- Total anion content of the mixed waste since a high level of anions may prevent stabilization or adversely affect the strength of the stabilization product.

In summary, the workgroups felt that general testing guidance outlined in 40 CFR 190 needs to be followed.

4.4.4. Other Issues

Workgroup discussion also included issues related to the information that is required in the safe performance of the waste management options. These are summarized below.

In the case of entombment of waste, the need for performing leaching tests, especially the TCLP test, is questionable. It was suggested that since no salt migration had occurred at the site for tens of thousands of years it is not necessary to perform any leaching tests. If such leaching tests are mandated, however, they should be carried out using a brine solution.

For the incineration process, it was noted that the public would demand the monitoring of all possible air contaminants covered under CAA. It was suggested that a list of target analytes must be developed for mixed wastes or else all possible contaminants would be required. It was also suggested that air monitoring could be made part of the permit process.

One workgroup discussed additional issues associated with incineration that should be considered in deciding to minimize the characterization parameters while protecting the environment and safety of personnel. Protection of workers taking samples may be either a high- or low-cost issue depending on the complexity of the sample. Potentially expensive analyses, such as those for volatile radionuclides and Polychlorinated Biphenyls (PCBs), could be eliminated with process knowledge. Alternative methodologies which are better, faster, and cheaper may become available. Risk of population exposure around the incineration operation and DOT shipping regulations may also impact on the characterization requirements of the mixed waste and the incineration residues.

A possible simpler approach to ensure that solidification is performed in a safe and cost effective manner was suggested. It was proposed to first stabilize the mixed waste and evaluate the stabilization product for compaction strength, leachability, and stability. If a problem is encountered in the stabilization process (i.e the mixture fails to set or has a low-compaction strength), then a detailed chemical evaluation should be performed on the mixed waste. If the stabilized product passed the criteria for strength, stability and leachability, then costly chemical analysis need not be performed.

4.4.5. Other Waste Management Options

Other waste management options were briefly discussed. It was noted that vitrification is probably the best technology in terms of cost and safety, and requires the least characterization; however, it requires the most development before it becomes fully implemented. Deep-well reinjection is a waste management option requiring characterization information similar to that for entombment. Transmutation of actinides and fission products to

stable or more short-lived species may be a practical option, and the cost may not be much greater than the cost for characterization. This will produce a waste that is hazardous only and that may be treated and disposed of by conventional methods. It was suggested that interim warehouse drum storage with an approved monitoring program may be the best management option until we better understand the complexity of mixed wastes is better understood.

4.5. CONCLUSIONS

Generally, the workgroups recommended that the only information needed for characterization is that suggested in 40 CFR 190. Attempts were made to answer the questions posed to the workgroups. Better, more consistent definitions of types of radioactive wastes and de minimis levels are needed. Finally, it was concluded that a well-defined decision tree, including characterization, needs to be prepared initially (i.e. data quality objectives) and be presented to the regulators in developing and implementing a waste management option for mixed waste.

4.6. AGENCY FOLLOWUP TO WORKSHOP

DOE currently has a large amount of containerized mixed wastes in storage at its facilities that need to be cost-effectively characterized prior to treatment. In order to determine the waste properties needed to properly categorize the wastes for treatment, the EPA Environmental Monitoring and Support Laboratory at Las vegas (EMSL-LV) in conjunction with DOE is organizing a workshop to be held in 1993. The workshop will address the issue and attempt to develop specific solutions to the characterization problem.

5. CHARACTERIZING HETEROGENEOUS MATERIALS

5.1. BACKGROUND

In both the RCRA and CERCLA programs, a material often must be characterized to determine if it possesses some property of concern or interest. Types of questions that may require answering include:

- Is the material hazardous?
- Can it be safely or successfully managed using a specified treatment technique?
- How much supplemental fuel must be added to incinerate the waste?

When the material being characterized is homogeneous, conventional sampling and subdividing approaches can be employed. For example, in a truckload of used foundry sand with an average phenol concentration of interest, the material is in the form of relatively fine particles with the phenol uniformly distributed on the surface. Conventional compositing and subsampling can provide representative samples with an average composition very close to that of the entire load. The actual task of obtaining each subsample from the appropriate point in the truck may be very difficult, but the approach used is relatively straightforward.

However, insurmountable problems can develop when faced with a heterogeneous material. Heterogeneity is a relative term and, among other factors, is a function of the objectives of the characterization and the analytical sample size. This workshop was concerned with wastes of such various particle size, waste consistency, or extraordinary concentration gradients that the sampling and analytical objectives could not be met using traditional approaches and standard techniques. This is an important and difficult problem that has been of concern to many organizations involved in waste management.

The workshop goal was to advance the state-of-the-art techniques for characterizing difficult to sample wastes. This covers wastes with a highly variable nature, (e.g. wide ranges of particle size, large concentration gradients, and mixtures of different waste materials (e.g. dredge materials containing sludge, tires, construction debris, bottles, cans, etc.)). These types of materials present challenges that traditional sampling and analysis approaches cannot meet with the level of certainty required for modern waste management decisions.

RCRA has historically taken the position that the sample actually being analyzed does not have to be representative of the material being characterized, but rather that the sum total of the data must represent the property of interest. The problem presented was how to develop practical solutions to characterize these difficult situations. In this session, the participants discussed how to cost-effectively characterize materials that are inherently very heterogeneous and present characterization difficulties.

5.2. SUMMARY OF POSITION STATEMENTS

5.2.1. Regulatory Program Perspective

Mr. Charles Ramsey, EPA's National Enforcement Investigation Center (NEIC), reviewed some issues involved in implementing the RCRA regulatory requirement that a "representative" sample of the waste be collected and analyzed. 40 CFR, Part 260.10 stipulates that a representative sample, '... means a sample of a universe or whole (e.g., waste pile, lagoon, ground water) which can be expected to exhibit the average properties of the universe or whole." This definition has two aspects.

1. What is an average property?
2. How is the universe or whole defined?

The inability to answer these questions in clearly defined scientific terms leads to most of the problems surrounding the characterization of heterogeneous wastes.

Mr. Ramsey Proposed that hazardous waste characteristics are not "averageable" properties. For example, corrosivity is expressed as pH that is a logrithemic function, while ignitibility can be expressed as passing or failing the 60°C ignition test. With these characteristics, the numerical mean is not meaningful; therefore, an average value cannot be obtained.

Using the average value as a measure of hazard with respect to the toxicity and reactivity characteristics may also present potential problems. When the material to be evaluated consists of both a contaminated phase and an inert phase, use of the mean may result in a waste being classified as nonhazardous even though a substantial portion of the waste might be above the regulatory threshold and pose an environmental hazard.

Using "the most likely result" approach (also known as attribute testing) avoids many of the above problems. It requires that a certain percentage (e.g., 50%, 75%, 95%) of the individual sample results fall below the regulatory decision value. This avoids problems associated with determining average values. Use of this approach, however, will require a change in the regulations.

Even when the property of concern is a continuous variable and, therefore, averageable, collecting representative samples of heterogeneous wastes is often extremely difficult. Many heterogeneous wastes are discontinuous in terms of physical/chemical properties and, given the small size of analytical samples relative to the discontinuity, it is not possible to collect (and demonstrate) representative samples of the wastes. Therefore, to ensure that an adequate characterization is conducted, a clear definition is needed of what constitutes the "universe or whole" to be characterized and what constitutes an acceptable level of characterization (i.e., What degree of confidence, that the property is below the regulatory threshold, must be obtained to characterize the waste as nonhazardous.). The universe of the whole must also be defined to determine the period of time and space in which the samples must be collected.

5.2.2. Regulated Community Perspective

An industrial perspective was prepared by Mr. David Reese, Safety-Kleen Corp., and presented by Mr. Gene Klesta, Chemical Waste Management Corp. The presentation focused on the types of samples received at recycle and waste disposal centers and the different types of problems these materials represent relative to heterogeneous wastes found in the field. The industry receives large quantities of containerized wastes from different sources which in the aggregate form a very heterogeneous set.

Industry strongly supports considering the method of management when establishing analytical requirements. The current requirement for full-scale analysis is, in many cases, not necessary and represents a significant financial burden for generators and the waste management industry. The industry recommends that wastes destined for recycling or treatment be exempted from rigorous analysis if the waste management process and end products are thoroughly characterized during operations and prior to disposal.

It is further recommended that the Agency permit the use of methods other than those in SW-846 when conducting acceptance testing of wastes for treatment and recycling. Using proper QA/QC procedures is adequate to ensure that reliable analysis are conducted. Again, process monitoring and end product analysis provide sufficient protection of the environment. The industry will work with the Agency to bring industry-generated methods into the public sector.

The industry position is similar in concept to the Agency's interest in moving towards performance-based methods using sound project QA plans, data quality objectives,and accepted QA/QC procedures as the quality assurance tools to monitor performance.

5.2.3. State-of-Science Perspective

Dr. John Maney, a private consultant, presented a detailed strategy for random and nonrandom sampling of heterogeneous wastes. The presentation, described a unified way of looking at all types of waste based on the source and degree of heterogeneity of the material.

Using flow charts and an extensive set of definitions and examples, the paper presents concrete examples of options available to the field sampling team and the analytical chemist to generate reliable analytical data from complex, heterogeneous materials. However, unless the sample undergoes extensive comminution, Dr. Maney indicated that obtaining an analytical size representative sample of a heterogeneous waste is almost impossible. (See the full paper in Appendix A for details.).

5.3. CHARGE TO THE WORKSHOP PARTICIPANTS

Before breaking into three workgroups, the participants were asked to address three questions:

1. Should EPA change from current practice (average testing) to attribute testing for properties that are not averageable?

2. If so, what is the highest practicable degree of confidence (%) that could be required?

3. Should there be an override that says that if some samples are greater than "X", the waste is hazardous even if the number of such samples are below the percentage established in question 2?

A large part of each workgroup's time was devoted to discussion of the practical definition of attribute testing and how it differs from average property testing. This decreased

the time available to discuss the three issues, so no effort was made to address the third issue within any workgroup.

5.4. RESULTS OF THE WORK GROUP DELIBERATIONS

5.4.1. Should the Agency Change to Attribute Testing for Properties that are Not Averageable?

Approximately 90 percent of the participants believed that attribute testing should be adopted for properties that are not averageable. This approach is more costly than average property testing in those situations where the average property was determined by compositing a series of field samples prior to analysis. There was some discussion that compositing of samples prior to analysis is one way to determine an average property that avoids many of the technical problems associated with averaging the results from a series of discrete sample analyses.

Neither the attribute testing nor the average property testing approach eliminates all the problems associated with the sampling of wastes prior to analysis. The nature of attribute testing can make the sampling in many situations easier. The group agreed that approximately 80 percent of the error in characterizing waste arises from field sampling error that effects both approaches equally.

The Agency should focus its efforts on providing sampling guidance for heterogeneous wastes. Special efforts should be made to provide guidance for specific types of wastes such as tires, telephone poles, construction debris, and military ordinance. Also, knowledge of the process that generated the waste is an important part of the decision to use attribute testing and would be a primary driver in selecting the sampling strategy.

5.4.2. What is the Highest Practicable Degree of Confidence that can be Required?

Several participants felt the answer to this question should take into account the degree of health and ecological risk associated with the material and the amount (mass or volume). Therefore, each site should be considered unique and receive individual consideration. A site-specific degree of confidence should be carefully developed as part of the data quality objective process and be codified in the site-specific QAPjP.

It was generally agreed that a maximum of 10 percent of samples collected should be allowed to fail the regulatory criteria. Sixty-six percent of the participants felt that a 4 to 6 percent failure rate was the most appropriate. All participants felt the Agency should publish clear guidelines on determining if attribute testing should be applied to a specific situation.

5.5. AGENCY FOLLOW TO WORKSHOP

Subsequent to the workshop, Agency staff met to discuss what steps to take to address the issue and the ideas presented during the session. It was decided that quantitative data are needed to determine:

- What the practical effect would be if the attribute testing approach was used instead of the current arithmetic mean.
- How the number of samples needed to achieve a defined degree of confidence would vary across the different types of materials characterized in the RCRA and CERCLA programs.

During the next year, the Agency plans to examine its data in an attempt to answer the above questions. However, the Agency will greatly appreciate receiving any additional information that will help determine if a change in approach will either improve the quality or lower the cost of decision making. If anyone has data that might assist in this effort, EPA will appreciate receiving such information. Such information should be sent to the author at the address indicated in the FORWARD to this report.

APPENDIX A:

ISSUES ASSOCIATED WITH ADOPTION OF PERFORMANCE-BASED METHODS

ISSUES ASSOCIATED WITH ADOPTION OF PERFORMANCE BASED METHODS: INTRODUCTION

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BACKGROUND

EPA implements a number of regulatory programs which require the collection of environmental data. These include SDWA, CWA, RCRA, CERCLA, CAA and FIFRA.

In any monitoring program, selection of the appropriate measurement method is a key part of the process. Over the years, in crafting its monitoring requirements, the Agency has primarily adopted a policy of publishing appropriate test methods for complying with the various regulations. The methods have been written with varying levels of detail. However, rather than issuing flexible methods and specifying required performance, in general, the Agency has opted to give the analyst detailed instructions on how to conduct the analysis.

PROBLEM

This has resulted in several problems.

1. Long delays in bringing new technology to bear for cost-effectively analyzing samples.

2. In some cases the required methods either give biased results for some types of samples or do not yield the requisite sensitivity. Since in many cases the methods do not provide for modification by the analyst, the analysis can lead to results that do not meet the data quality needs.

3. By rigid specification of methods rather than of data quality, laboratories are often forced into using expensive technology when a simpler, less costly approach might be suitable.

PURPOSE OF TODAY'S MEETING

The Agency is aware of these problems and is trying to do something about it. One option being looked at it to move from a system of rigid methods to one where performance is specified and flexibility is given on how the analysis is conducted.

However, implementing this new approach is not easy. A number of problems and issues need to resolved before the system can be changed. These include:

- How will acceptable performance be defined?
- What documentation, etc. is needed to verify compliance with performance standards?
- How will the change to performance based methods affect the procurement process, both by EPA and by commercial clients?

We in EPA are aware of the problems. We agree that something needs to be done. However, while many people have ideas on how such a program can be implemented, not everyone agrees on what is the correct approach. That is where you come in.

The two questions we are asking for your help in answering are:

- How should performance be defined?
- What documentation should EPA require to verify that the required performance standard were met?

We also want your input on how you think a change to performance based methods would affect the procurement process, both by EPA and by commercial clients?

If you think of any ideas, information, or suggestions that you feel the Agency should consider when addressing this issue, please send them to us. Send your comments to:

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We will need to receive your comments by August 21, 1992 in order to incorporate them into the conference final report.

PERFORMANCE-BASED METHODS--one view from the regulators

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ABSTRACT

This paper will offer some definitions of performance based chemistry methods, discuss some of the differences between the performance based and the controlled based methods and describe some of the processes that the Environmental Protection Agency is using to sort through the issues associated with the movement toward the broader use of performance based methods in its regulatory programs. Some of the risks and benefits seen by the regulators will also be described.

INTRODUCTION

As part of its efforts to examine the quality of the information and data underlying its basic regulatory decisions, some parts of the Environmental Protection Agency are taking a closer look at how and why they generate chemistry data. The fashion and form by which it requires others to produce similar information is also being examined. More specifically several programs are examining the question of whether the up-front specification of step by step analytical chemistry methods is the only way, or in fact even the preferable way to cause data to be generated by the regulated community. The step by step procedures articulated in the rules

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and regulations of the last twenty years are being closely examined with an eye toward their being supplemented with the so called performance-based methods; methods whose only specifications might relate to precision, accuracy, sensitivity, precision, and specificity rather than step by step, cook book instructions.

This effort actually goes back a ways and has its roots in the review of the chemistry in the water programs that was directed by amendments to the Clean Water Act in 1987. The results of this review concluded that:

EPA should establish additional performance criteria for EPA chemical methods.

The Office of Water (OW) and the Office of Research and Development (ORD) should agree on ways to improve the process for developing and standardizing methods.

EPA should develop quality control requirements for all test methods promulgated at 40 CFR Part 136.

EPA should establish an Environmental Methods Management Council to coordinate:

common analytical methods,
methods manuals, and
the development of uniform QA/QC requirements within methods.

At the same time, there was a growing concern that a number o the promulgated methods were not necessarily giving us the best answers at the best price. In some cases we were getting inferior information at higher prices and in all too many cases some of us came to realize that we had very carefully crafted a system that fostered duplication and unnecessary redundancy of methods without a clear cut benefit. The only purpose for collecting any of this data is to provide sound, accurate information that can be used in making public policy decisions; that have as their primary purpose the prevention or elimination of disease or damage to people or environmental systems.

Collection of information in search of absolute truth is appropriate for others but not necessarily for those in the environmental protection business. This is especially true if it causes expenditure of monies in pursuit of the ultimate detection level with little or no return in additional protection of the public health. That does not mean that you sacrifice scientific integrity but rather that you focus on the need for which the data are being generated to get the most for your money. Some people have called these data needs data quality objectives.

Concerns over these types of issues as well as a specific examination of the number of the methods that had been promulgated by the various program offices within the Agency caused a number of people to begin to actively search for a mechanism that would help remove some of the confusion. Hopefully this mechanism would also move toward a day when the analyst has greater opportunity to actively improve on basic methods, and in turn improve the efficiency of the overall decision processes if by no other way than making good data some more cheaply.

In the more conventional arenas associated with analytical chemistry on a day to day basis there is a marked increase of interest in the question of how to add efficiency to our efforts to improve the overall quality of the data. Interest in performance-based analytical methods also lies in the problems associated with the development of uniform QA/QC requirements across various methods. The existing suites of analytical methods developed by the various EPA Program Offices do not currently use a consistent set of performance measures, and, where the performance measures are the same in similar methods from different Programs, the performance specifications often vary widely.

Performance versus Control-Based Methods

To understand a performance-based method, one must understand the alternative. The alternative is a control-based method. In a pure performance-based method, the method user would be able to choose any procedure or instrument so long as the specified quality of results is achieved. In a control-based method, the procedural steps are specified and if these steps are

followed exactly, the desired quality of results will be achieved theoretically and the performance does not need to be specified or measured. Control-based methods are required of course when the technique itself defines the parameter. Examples are BOD, TOC, and COD, etc.

The military is a large user of control-based procedures and specifications. Military instruction manuals are written in a terse series of steps that military personnel are expected to follow exactly. In many instances, the person following these steps does not know the performance that is expected and the performance may never be measured.

In practice, most analytical methods are both control-based and performance-based because of the fashion in which methods are developed and edited for publication. A number of agency methods provide procedural steps, and performance specifications that must be met.

EPA 600/1600 wastewater methods (40 CFR Part 136, Appendix A) are mostly performance-based, in that many performance specifications are given in these methods and the analyst must meet these specifications. The analyst is "permitted to modify the method to improve separations and lower the cost of measurements" so long as the performance specifications are met. However, the methods are somewhat control-based, in that the user is not permitted unlimited discretion in modifying the method. For example, an infra-red spectrophotometer cannot be substituted for the gas chromatograph specified in these methods.

The EPA Superfund Contract Laboratory Program (CLP) methods are control-based, in that the procedural steps are specified in great detail and must be followed regardless of the analyst better judgement. The advantage of a control-based approach in the CLP is that it leads to fewer concerns about comparability when data for samples from a single site are generated by a number of laboratories. Unfortunately, on occasion it also has the potential for generating data of legendary quality.

The major advantage of a performance specification is that it assures the desired result. The major disadvantage is that the flexibility of the procedural steps allowed may result in a compromise in performance, unless the performance is completely specified. In addition, performance must be proven nearly immediately in order to institute corrective action. Total quality management and other quality assurance techniques teach that it is better to monitor quality at the earliest point in a process than to wait until the end to find out that problem has occurred.

The major advantage of a control specification is that each step is controlled within a pre-defined limit. In NASA and military hardware manufacturing programs, each step may be witnessed by a quality control officer, thus assuring that the step was followed. The major disadvantage is that when a performance test is finally made, the control may have been insufficient to assure the desired performance.

Performance Specifications Identified by the Workgroup

Because of issues such as these and also in explicit response to recommendations in the 518 Report, EPA formed the Environmental Monitoring Methods Council (EMMC) in late 1989. In turn, the EMMC formed a Panel on Methods Integration that consists of several workgroups, among which is a workgroup on performance-based methods (the Workgroup). This Workgroup is chaired by Orteria Villa, Director of the Central Regional Laboratory in EPA Region III at Annapolis, Maryland.

Initially the workgroup arrived at the following definition for a performance based method:

> "A monitoring approach that permits the use of appropriate analytical methods that meet established, demonstrated method performance standards based on Agency data quality needs. Minimum required elements of performance, such as precision, accuracy,

sensitivity, specificity, and detection limit, must be specified and an available method must be shown to meet the method performance standards."

However, in later discussions a somewhat different view of performance based methods evolved.

A somewhat simpler definition is:

"A procedure containing the necessary methods performance specifications to assure the desired quality of results."

Initially the EMMC Workgroup identified the following list of performance specifications as important to analytical methods. At least one member of the workgroup believed that each was "essential."

Precision

Bias

Sensitivity

Specificity/selectivity

Detection limit

Written method

Performance range

Performance objectives linked to regulatory objectives

QC and performance documentation/initial validation/routine performance documentation

Data review process/internal and external data audits

Performance evaluation samples

Analyst qualifications/proficiency

Several of the items on the list above are not performance specifications, but address the desire to satisfy a particular program need. After further discussions the work group was able to agree that most of these items are related to either precision or bias. Perhaps it should also

be noted that a number of these characteristics are already cited in the 600 and 1600 series methods.

In its most recent deliberations the Workgroup seems to have come to the conclusion that the most appropriate way to proceed toward the adoption of a performance based ethic is more along the lines of establishing not only performance criteria but also dealing explicitly with questions of how much documentation would be required for the use of methods under routine laboratory conditions. In addition, the workgroup also insists on the programs maintaining at least a single reference method that is assured of being able to meet the stated data need.

This group also seems to believe that indicator of method precision include method sensitivity, range of performance, and the ruggedness of a method. Precision criteria should establish numeric, statistically-based quality control requirements related to measurement replication and method calibration and should account for matrix effects.

Limitations of Pure Performance-based Methods

The number of true performance-based methods is limited in part because not every detail of performance can be specified and in part because in a decentralized regulatory program it is much easier to perform comparisons of techniques against a national standard that it to examine the science behind procedures unique to each laboratory. Consider a method for the determination of the 126 Priority Pollutants given in Appendix A to 40 CFR Part 423. The list consists of organics, metals, cyanide, and asbestos. The organics consist of pesticides/PCBs, non-pesticides, and 2,3,7,8-tetrachlorodibenzo-p-dioxin (dioxin).

Consider just the requirements for determining of non-pesticide/non-dioxin organics. A specification can be written for each compound with a required precision, accuracy (recovery), and detection limit. The laboratory making the measurement would then be free to choose the technique used for each compound.

To an extent, this approach to the determination of organic compounds was tried by EPA's Effluent Guidelines Division (EGD), the predecessor division to EAD, in the development of the regulation of discharges from the Organics, Plastics, and Synthetic Fibers (OCPSF) industry. An "Organic Chemicals Verification (OCV) Program" was initiated in the late 1970s to characterize waste streams from OCPSF manufacturing plants. The laboratories were given specifications for precision, recovery, and detection limit.

One of the outcomes of the program was that although the data produced were of a defined quality, the laboratories exercised great latitude in their choice of extraction and cleanup techniques, GC columns, and detectors. EPA's Science Advisory Board (SAB) reviewed the OCPSF program and concluded that the laboratories had been given too much latitude in selection of these techniques and that the program needed to be better controlled.

The Definition of a Method is Changing

The definition of an analytical method is changing from a series of steps performed by an analyst to a series of steps that will result in a data set that will stand up to legal scrutiny. Defendants involved in litigation over environmental measurements will attempt to attack the data produced in order to win their case, and industries subject to regulation will scrutinize data carefully to make sure that the regulation is in their best interest. If it can be shown that the laboratory did not follow the analytical method, or if all of the method specifications were not met, the defendant may prevail. Therefore the data package that results from the method must demonstrate that all of the control- and performance-based specifications were met. This requirement to produce a legally defensible data set changes the way in which performance specifications are developed, in that every specification must be achievable.

Method writers frequently include specifications casually, without studying the consequence of failing a given specification. This places the analyst or laboratory in an unacceptable position. If a specification is failed, and the cause is attributable to a problem

outside of the control of the analyst or laboratory (e.g., a matrix effect), there is no recourse but to continue running the sample (or QC test) over and over.

Similarly, specifications in analytical methods can be so stringent that they are difficult or impossible to meet. Therefore, EPA must ensure that the desire to achieve perfect data is tempered by what is realistically achievable. However, it is essential that the way to the realism is fully documented.

For performance based methods to work with the Environmental Protection Agency there will have to be some agreed upon documentation. The first purpose will be to assure that the performance criteria have been met. To do so, it is likely that the agency will require at a minimum a written description of the method that meets some specified format; results of initial validation studies as well as the maintenance of routine performance information.

The actual values of the performance criteria themselves will of course derive in large measure from the data needs but also from the reference methods. In many cases the reference method will be at the cutting edge and the performance characteristics will be most difficult to achieve using alternatives. However, it is likely that in at least as many cases, the analysts outside the agency will be able to improve on the specified method, or in fact substitute a new method that clearly delivers an equivalent value with a reduction in cost. The movement toward the wider use of performance based methods by EPA will not be without its fits and starts but it will happen. There will be concerns expressed and a number of those are being identified and focused, and it is likely that more will be added to the list in coming months.

For the moment at least the following minimum list of benefits and risk of performance based methods has emerged. This list seems to capture a number of the views and concerns of the regulators who are familiar with the issue, but if you know regulators you know that it will never be complete.

Nonetheless as we see them today, the advantages of performance based methods seem to be:

* *FLEXIBILITY*
* *ALLOWS US TO DEFINE THE QUALITY OF THE DATA*
* *HAS POTENTIAL FOR IMPROVING DATA QUALITY*
* *HELPS ASSURE COMPARABLE (EQUIVALENT) DATA*
* *ALLOWS LABS TO ADOPT NEW TECHNOLOGY RAPIDLY*
* *ALLOWS LABS TO EMPLOY INNOVATIONS/CREATIVITY*
* *MAY MAKE COMPLIANCE MONITORING MORE INTERESTING/ CHALLENGING*
* *SHOULD SPEED METHODS DEVELOPMENT*
* *SHOULD HELP EPA MEET CONGRESSIONAL DEADLINES*
* *SHOULD IMPROVE THE SCIENCE SUPPORTING THE EPA'S MONITORING PROGRAMS*

--and the disadvantages perceived are:

* *MAY PLACE THE SMALL LAB AT A COMPETITIVE DISADVANTAGE*
* *MAY REQUIRE BETTER TRAINED ANALYSTS*

* *MAY REQUIRE MORE EXTENSIVE DOCUMENTATION*

* *MAY REQUIRE MORE FREQUENT AND INDEPTH INSPECTIONS*

* *MAY REQUIRE MORE HIGHLY TRAINED AND SKILLED INSPECTORS*

* *MAY REQUIRE MORE PE CHECK SAMPLES*

* *MAY REQUIRE A DATA BASE TO TRACK METHODS BEING EMPLOYED*

On the other hand, the use of only control-based specifications could result in uncontrolled variability of results because performance would not be tested, thus violating the DQOs of precision and accuracy.

Therefore, EPA will continue to need to use both control- and performance-based specifications in its analytical methods. With prudent use of these specifications, and further method evolution based on improvements in technology, EPA believes that its data quality objectives will met more easily and at a lesser cost.

ISSUES ASSOCIATED WITH ADOPTION OF PERFORMANCE-BASED METHODS: INDUSTRY PERSPECTIVE

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INTRODUCTION

Industry has complained for years about Environmental Protection Agency (EPA) methods that do not work and give data that is at best questionable and costly to obtain. All of us, industry and regulators, want data of known quality based on defensible methodology. The main issue or question regarding any method is: Does it work and how well? The concept of performance based methods can be supported by both industry and the agencies as a way of:

1. Removing road blocks to application of the latest scientific and technological developments;

2. Minimizing paperwork and analytical costs;

3. Maximizing flexibility in method selection;

4. Improving the quality of the results.

Presented on July 13, 1992 at EPA Workshop I on "Performance-Based Methods"

STATEMENT OF THE ISSUE

As we consider the issue of performance based methods, we can briefly review the experience of our Canadian neighbors. They used EPA guidelines as a starting point, but instead of mandating or suggesting methods, they chose to set up performance based guidelines. The Canadian government, contract laboratories, and industrial laboratories soon determined that performance comparison could only be done in a clean matrix. Therefore, specifications were based on clean matrices. The laboratories found that they could meet almost any detection limit if they changed to higher analyte concentrations where better precision allowed them to calculate lower detection limits. Without a definition of a detection limit at a given concentration, almost any answer was possible.

If a laboratory could meet the requirements in a clean matrix, then the system was working and the laboratory could do the analysis. Canadian industry found that the matrix effect issue had to be explained, proven, and negotiated with the government. Does this circle sound familiar? As David Friedman said in the opening remarks, "How will acceptable performance be defined and how will we document it?"

Proving acceptable performance has been difficult in the past. It is one of the major reasons for the high cost of doing business and getting the environmental job done. Much of the work we do to prove acceptable performance is caused by the lack of trust between industry, the public, and government agencies. If a company says it is using EPA method 8270, the company, the contract laboratory, and the Agency know what can be expected from the method. The permit writer feels a certain comfort knowing an EPA method is being used. If a permit writer is asked to accept a method not found in Federal Regulation, EPA manuals, or tested by the EPA, he/she must confer with technical staff and talk with the director. Meanwhile, the much needed permit languishes on the desk. Everyone is afraid that the one being regulated is trying to "put one over on them", or if they accept a company method, that the Agency has "given in".

A broader look at the present situation is that EPA methods (with few exceptions, i.e. land ban requirements) are recommendations, and are to be used as guidance. This means they can be modified to meet the matrix requirements or other data quality objectives. In practice, the recommendations concept has not been applied. If it were, we would not be here having a discussion on performance based methods. In general, all methods are performance based. Industry and agencies alike should support the concept that if a method does not perform, change it so it will, i.e., apply the best available technology (BAT).

Several problem areas which prevent the use of performance based methods need to be considered from the regulated community point of view:

1. How can we minimize the amount of paperwork required to prove a method is adequate in meeting data quality objectives and to present the necessary data in a way that is correct and convincing to the non-technical, non-trusting, and skeptical regulator or permit writer?

2. How can we demonstrate that a company or commercial laboratory method can be performed by any laboratory and get the same results?

3. What criteria will be used to judge the acceptability of the method? What is the criteria for rejection?

4. Should a proposed method be checked by at least one independent laboratory or against existing methods which can be applied to the sample matrix and to the analytes of interest?

5. How cost effective will performance based methods be? Will they save us money or will industry have to pay commercial laboratories to develop a method for each matrix or data quality objectives (DQO)?

6. How can we build trust between industry and the regulator? Will the attitude of the regulators be "this is the level we want you to get to and I do not care how you do it--just do it"; "I want the method to have no bias."; "Don't give me that matrix problem excuse-it is your stuff and it is your problem"?

7. Acceptable performance guidelines need to be defined and documented. Is the DQO concept based on performance methods the answer?

It is not my intent to answer all of the above questions in the limited time allowed for this presentation, but to provide points to explore during the discussion period.

PERFORMANCE-BASED METHODS AND LABORATORIES

The advantages and disadvantages of performance based methods will, to some degree, depend on the company and whether it has or wants to use its own laboratories and methods for analysis. There are companies that have their own laboratory with the latest technology and companies which choose to use one or more commercial laboratory to do their work.

What are some of the advantages and disadvantages of performance based methods from the viewpoint of the regulated community?

Using Industry Laboratories

To the large company which chooses to use its own laboratory, the advantages and disadvantages are:

Advantages:

1. The company has a high experience level with the application of the methods to their compounds of interest. The limitations of the method are usually understood.

2. The methods are already developed.

3. The people are already trained.
4. There is less cost to the taxpayer, since the Agency will not need to develop additional methods.

5. The rate of development of new cost effective methods to meet the performance standards will increase.

6. Manpower intensive and time consuming methods will be eliminated since there are cost incentives for improvement.

7. Less complex methods could be used, since the methods would be designed for the company's compounds of interest (not the universe).

8. The company can submit the results with an appropriate level of QA/QC data and supply a certification of accuracy and responsibility.

9. The Agency can accept the data with a minimum of QA/QC review since it is the responsibility of the data supplier to defend its data.

Disadvantages:

1. The Agency is not familiar with the method, and has historically required a considerable amount of documentation to prove beyond any question, that the method will answer the question and meet the performance criteria or DQOs.

2. The new technology may not be understood by the regulators. A lack of understanding of a technology or a method makes Agency personnel suspicious of the intent of the regulated community and very uncomfortable with any method changes suggested to them.

3. The methodology has come from the very person who is being regulated. Conflict of interest is always a question.

4. Negotiations will require time. Additional time will be needed in order to make sure the data will be accepted by the Agency.

5. Considerable time would be required to compare company developed methods against methods the Agency is familiar with.

6. Intralaboratory studies may not have been done; this makes it difficult to assess the methods ruggedness.

7. Developing matrix specific methods could be more costly to companies.

Using Commercial Laboratories

Companies using commercial laboratories may find several advantages and a few disadvantages. They are:

Advantages:

1. Superior methods or technology will be developed by laboratories to give them a competitive edge.

2. More cost effective methods are available from which to choose.

3. There is more experience with a variety of matrices.

4. It can be less expensive in those cases where the commercial lab has methods already developed.

5. The Agency may be familiar with the commercial laboratory's methods and have confidence in them; thus, less time is required to convince the Agency that the correct methods have been applied.

6. The conflict of interest question is minimized.

Disadvantages:

1. Communications become more difficult between the client and the laboratory. This is and has been a serious problem since the client carries the legal responsibility for the data generated by the laboratory.

2. The regulated company cannot agree to any negotiated performance standards until the contract laboratory has spent some time analyzing the company's samples.

3. Development of a method to meet the performance standards could be very costly.

RECOMMENDATIONS

All methods should be performance based and meet minimal QA/QC requirements instead of the present overkill of redundant standardizations and checks. These increase cost and decrease productivity in an effort to eliminate ALL questions. Data is seldom or ever without qualification; it is seldom or ever absolute.

Let's keep the system simple, get back to the basics, and report the data with the following information:

1. The instrument type
2. Any special sample preparation steps
3. The method for entering the sample into the testing device
4. The instrument operating conditions
5. The tuning requirements have been done and their results (mass spectrometric analyses)
6. Standardization procedures, including linear range
7. Any blank and duplicate data
8. Spike recovery yields for the analytes and surrogates
9. Sample chromatograms
10. Detection and quantitation limits in the matrix of interest
11. Calculation results, including:
    a. Units of measurement
    b. All complete equations used

The amount of detail required will decrease to the following:

1. Report the method used
2. Note any deviation from the method and why
3. Report blank results
4. Report spike, duplicate spike, and duplicate sample results
5. Report calibration checks
6. Note that tuning results were within specifications
7. Report the data and any qualifiers
8. Report detection or quantitation limits of the reported data

The above may need to be modified for the different types of methods used. Most of data that needs to be reported is already being done and should require little or no changes.

CONCLUSIONS

Any method should be acceptable as long as it produces data of known and acceptable quality. The data reported to an Agency should state the method used and the results of spike recoveries, duplicates, blanks, quantification limits, and (where applicable) surrogates.

Performance based methods will allow greater flexibility, and if properly instituted, would be cost effective. The methods will meet the DQOs and answer the question or questions being asked about the site, monitoring wells, etc, without using exotic methods designed for the universe. Performance based methods, used in conjunction with agreed upon data quality objectives, can increase the development of new and better methods, be cost effective, and address environmental needs.

However, the best available technology or performance based technology cannot be effectively applied until mistrust, lack of knowledge, and poor communications between the

regulated community and the regulatory agencies are eliminated, or at least minimized. This will require improved communications, honesty, trust, and the education of each other.

ISSUES ASSOCIATED WITH ADOPTION OF PERFORMANCE-BASED METHODS: INDUSTRY PERSPECTIVE

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INTRODUCTION

Commercial laboratories face different problems in considering how to implement performance-based methods than those which are faced by regulators, EPA and other scientists, and the regulated community. However, the problems that these groups must consider will drive the primary issues and problems faced by the commercial laboratory industry in implementing the program.

The number, type and severity of problems that commercial laboratories will encounter when implementing a program for performance based methods depends almost entirely upon the scientific and policy decisions that are made initially. These decisions include the definition of performance, determining the type, volume, and submittal requirements for information required to demonstrate and document performance, constraints imposed on selection of methods, the role laboratories will have in assisting data users in their planning of the analytical work, and structure of the bidding/costing requirements for competition and completion of work. The ease of implementation will also depend upon how clearly data users define and articulate the types of samples and methods required for data needs of their projects, or alternatively what role the

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laboratory will have in defining the method requirements. Additionally, the availability of quality matrix-specific performance evaluation materials utilized initially to evaluate and optimize methods and then used during ongoing operations to assess performance of methods will impact the ease of implementation and regulatory assessment of laboratory performance.

Science and Policy Questions

Some of the science and policy related questions and problems surrounding this issue that will affect ease of implementation include:

- How will acceptable performance be defined?
- How will acceptable performance be measured?
- How will performance be documented in terms of the report and data that must accompany the sample results?
- How will analyses be procured for sampling and analysis events that have data needs that are not "static?" (e.g. a performance based method may be easily procured, for a process effluent sample can be adequately described for a procurement. In this case, the samples do not change significantly and the decisions based on the use of the data do not change. However, how can procurement be accomplished for many site samples if the samples are from many Superfund sites? In this case the composition of samples differs substantially from site to site. Also the types of decisions that will be supported by sample data vary significantly from site to site and from one phase of the site remediation to another.)
- Is the "performance" of different methods on the same matrix/site/sample significantly different, and if so, what defines the method performance that provides the benchmark to which all other method data will be compared? (This issue is important for consideration in determining how to use data generated from several methods on the same study and in cross-comparisons among studies.) How will method bias be documented and what limits for acceptability for method bias will be established. Will the limits for acceptability vary depending on how the data will be used?

- Do any environmental methods exist that have been evaluated by strictly scientific performance rather than instrument-specific performance measurements that could serve as a prototype performance method for implementation purposes? (An example of scientific performance criteria is the acceptable retention time delta as defined by comparison with a standard and the separation/overlap distance of peaks on a GC trace as defined by comparing standards to samples, rather than requiring use of one particular column and knowing what performance is required for that one column.)

- Can current regulations that require use of specific methods be changed in a timely way to allow implementation of a performance based program for all media?

- Is there a potential for all EPA Program Offices (and other government agencies) that require laboratory data to come to consensus and accept the performance based approach?

- Who will select methods for use on projects? Will the laboratories have any scientific latitude in applying methods to optimize the performance or by substitution of a better performing procedure or will this be precluded by need to define operating parameters so that data from numerous laboratories are comparable and can be utilized on the same study?

Business Aspects of Performance-Based Methods

The questions and problems surrounding this issue that pertain to the business aspects related to change to performance based methods can be relatively simple or extremely complex depending upon the policy and scientific decisions made initially in structuring the program:

- How will the EPA procure laboratory services in a manner that assures that the price and quality of data are fairly evaluated in a competitive process?

- How will the other government agencies and their contractors or other users write contracts to procure performance-based laboratory services?

- What role will the laboratory have in assisting/selecting the methods that can best be utilized for evaluation of particular samples

- Who will specify the type of technical information and documentation requirements that will be considered acceptable format? Will the format be tailored for each method or will it be universal in that requirements for QC information and results?

- Acceptable performance depends on the project objectives. How will performance objectives be stated to the laboratory and how will they be factored into the bid price of the data?

- Will all government agencies, EPA Program Offices and other entities that model their requirements after EPA accept and implement this approach? If this does not occur, the cost of analysis may increase due to implementation of different procedures that add to the complexity of laboratory operations, rather than a decrease in cost based on real cost of the chemistry involved.

Viewpoint from the Commercial Laboratory Perspective

Implementing performance based methods is important for the commercial laboratory industry for several reasons. Many of the reasons are similar to those shared by scientists, regulators and the regulated communities. Some of these reasons for supporting change to performance based methods stem from benefits that may be achieved, including:

- Data that is more useful for its intended purpose will be produced for sound decision making, particularly if laboratories are able to select one of the myriad of methods currently required by regulations and optimize the method both for establishing continual performance and for determining limit of detection and quantitation on a realistic schedule with samples.

- Science will benefit, as the output of the best professional judgments and practices and efforts of professional chemists.

- Better, less costly, and less time-intensive procedures that produce quality data for decisions can be developed and implemented if the field is "deregulated".

- Data will be assessed in a scientifically valid manner instead of basing value on requirements that are not all scientifically valid and/or not useful to data users.

- Sound scientific procedures may promote reason in establishing "holding times" based on scientific data so that sample analyses can be prioritized based on user's needs, not on artificial limits imposed by regulatory or contractual requirements.

- Scientific judgment may be used to optimize method performance to cost-effectively produce useful data, rather than follow rigid protocols exactly as prescribed. (Optimal results on specific samples are not often obtained if methods are not optimized for the samples.)

- Environmental chemistry laboratories, both public and private sector may be better able to attract and retain professional chemists that stay challenged in their positions and advance the collective body of environmental chemical analysis knowledge.

- Per sample cost of analyses may be minimized, allowing for better statistical sampling to occur and more samples to be analyzed at lower cost per sample to allow for more informed decision making.

- Competition would be increased among laboratories based on ability to complete analyses on samples using cost-effective methods and modifications to the methods that are cost-effective and meet customer's needs. Laboratories could then stay competitive based on excellence, based on quality of data as measured by the usefulness of data for decisions, its cost, and overall customer service.

- The current practice of bidding contract work at the price required to win may be eliminated. Therefore, competing with laboratories that complete the analyses to the "letter-of-the-contract but with marginal quality could be replaced with fair competition among laboratories that produce quality data. This change may serve to improve the overall baseline of quality for the industry.

Unfortunately, there are also many apparent advantages in maintaining the status quo, primarily because the potential impact of implementation cannot be understood until the exact nature of the program is defined. Therefore, unless the program is well thought out with industry providing input into it, the change may be viewed as very difficult to implement. Consider some of the advantages to the status quo that occurs because of the competitive bid procedures used to compete for business and conduct business after contracts are awarded:

- Contracting and bidding structure is established, well understood and the primary means of competition for business.

- Customers "order" certain analyses from the laboratory that have clearly defined contract and procedural requirements.

- The evaluation criteria by which the usual analytical data is measured is established.

- The data output requirements and software used to generate this data is in place and well understood by most data users

- The price per sample is based on adherence to specific requirements in methods and delivery of specific data deliverables. Therefore, the competition is based on well understood and conduct of the same methods and delivery of the same data.

Other considerations that have also emerged because of the current way laboratory analyses are conducted but are not generally perceived as positive are:

- Laboratory staff at commercial laboratories has been trained to perform laboratory analyses by rote so the skill level has been established by criteria that currently do not require use of expert professional judgment, as will be required by more analysts in using performance based methods.

- Laboratory equipment purchase has been driven by regulatory method requirements, the ease at which the data systems produce required data formats, and for a myriad of reasons not related to which instruments produce the best data for specific purposes. The laboratory industry may therefore not have purchased the equipment that is most versatile in the laboratory and/or that can perform the best analyses for particular samples, but will have to compromise on optimal performance based on lack of the best equipment until capital equipment expenditures are made.

- In the past, laboratories performed the analyses as specified by the customer with minimal consultation concerning the optimal selection of methods since regulations specified most of the selections. In the future, how will customers decide which methods are optimal? Will the laboratories provide assistance? How will the work be accomplished "optimally" if the bid price dictates how much time the analysis can take? How can fair competition among laboratories occur if the work is not well defined in order to establish the basis of competition?

STATEMENT OF POSITION FROM THE COMMERCIAL LABORATORY PERSPECTIVE

Change must occur so that the chance for data required for sound decision making to be delivered to the data user is maximized. Continuing with the status quo limits the chance that data needed to make sound environmental decisions will be delivered.

Why Labs Want Performance Based Methods

The first reason is that this approach will minimize duplication of methods. Currently, five methods for broad spectrum volatiles analysis are accomplished at the Lockheed Analytical Laboratory (LAL): 624, CLP, 8240, 8260, and 524.2. At least 6 methods for organochlorine pesticides are set up and operational. The differences between the methods are minor and most have no bearing on data quality. However, it is a very large effort to keep standards, procedures, QC requirements, analytical specifics, and reporting requirements separate and accomplish all requirements correctly. The duplication of effort and complications arising from this is a major cost for most environmental laboratories. Further, this expended cost and effort has no discernible benefit on either quality or throughput. In fact, it diverts the expertise in the laboratory from true quality and throughput issues. It prevents the laboratory from expending time on optimizing method performance for an analytical procedure so that bias, limit of detection, quantitation limits and overall performance of the methods are effectively established.

The second reason is that methods remain stagnant in a non-performance based system. As an example of this, consider one pesticides method. Until approximately 1987-1988, the CLP laboratories were required to use 1978 technology (packed columns). When the CLP pesticides method was changed in 1990, the technology was updated to 1985 technology. The procedures in the protocols are written as requirements, so innovation and improvements that may improve performance are prohibited.

Possible Solutions to the Problem, Including Advantages and Disadvantages

Before possible solutions to the problem are discussed, performance based methods must be defined. Some methods that are commonly thought of as performance based are really process based methods even though they include some measures of performance together with a myriad of process requirements. For instance, the CLP currently includes both process and performance requirements. An example of one of the restrictive process based requirements is the requirement for extraction of samples. If a 400 ml beaker is required, it is a violation of the contract to perform the extractions in a different type container. Many parts of some EPA data validation procedures are also largely process based. Much of the focus is not on results of analyses, but on the process used to generate results (e.g. was the DDT retention time greater than 12 minutes?)

Some actions can be taken to solve the problem:

- Defining performance parameters for specific types of decisions is a logical extension of the data quality objective (DQO) process. For example, some data is collected to determine if gross violations or gross level of contamination has occurred. Should performance parameters and requirements on those parameters for data needed for this purpose be the same as that required for data needed to determine if clean-up levels have been reached? Clearly, the decisions are different and therefore we must consider the need for performance parameters and their associated requirements, as well as the needed data documentation requirements that are based on what decisions the data will be used to support. In some instances, such as screening for gross contamination, kit tests may be cost effective and performance parameters may include only a blank check, standard known analyte check and a reading of the samples. Clearly data collected to evaluate effectiveness of clean-up must be supported by more rigorous performance parameters and requirements. Such requirements will include information that allows bias of method to be evaluated, as well as precision and capability of method to perform on the samples. We must be flexible in allowing for differences in performance parameters, requirements, and documentation requirements and assure that all requirements are driven by the needs to evaluate the data with respect to the decisions it is collected to support.

- Provide structure in a guidance document so that data users know what types of performance data can be collected and how it can be used in both very general and very specific examples. Included in this document should be the use of performance evaluation samples and how they can be used both to establish bias of methods and also to evaluate continuing performance. The two uses of evaluation materials must be well understood by data users so that the materials are not misused. An example of their misuse is assuming that acceptable performance on one sample provided to a laboratory assures the data user that the method used by the laboratory has an "acceptable level of bias" or that the data is acceptable for specific decisions. In order to effectively use performance on one evaluation sample, the laboratory must first establish the bias and precision of the method by many replicates of performance evaluation materials of similar matrix to the samples being evaluated. Only after method precision, accuracy and stability are demonstrated can performance evaluation materials be effectively used to predict performance on samples.

- Define what data needs to be collected to document performance for the samples being analyzed by that method. Many performance parameters can be collected to document method performance. However, information that must be documented for any sample includes: (1) methodology used for both sampling and analysis, and supporting information including detection and quantitation limits established for the analytical method, (2) data establishing the response of a blank sample associated with the samples, (3) calibration information showing the method is in control and the standard curve brackets the samples, (4) precision information provided by replicates, and (5) accuracy information provided by control samples and spiked samples.

- Promote the formulation, distribution and use of quality matrix-specific performance evaluation materials for both establishing method bias and day-to-day performance and also to assessing performance of laboratories on an ongoing basis by regulators.

- Restructure procurement process. One alternative to the restructuring can be envisioned to be a two-step process if the need for data of a particular type is large enough to warrant optimizing a method specifically for the samples. Phase one could be called the Development Phase and would consist of developing the optimal method, performance criteria and associated requirements to be used on specific samples. Performance evaluation materials that have qualitative/semi-quantitative to quantitative values associated can be generated for use in evaluating laboratory performance during this phase. The Analysis Phase can then be competitively bid based on specifications for use of a method that can meet very specific performance criteria and requirements that can be met, and specific performance criteria documentation that must delivered. The successful

laboratory then can be "creative", use a method that will produce the quality of data needed, and be assured that the evaluation of data acceptability will be grounded on performance criteria and requirements that are meaningful and achievable for the samples to be analyzed.

- Alternatively, commercial clean-up companies, industries that require RCRA permit-mandated analyses and other industrial clients may elect to award a services contract in order to complete the Development Phase and Analysis Phase in a smooth process. This approach encourages cooperative problem solving and loyalty to a laboratory based on service, price, and quality of resultant data. The approach is attractive, but is complicated in many cases because the requirement for work is to be subcontracted to the lowest bidder.

- Another alternative is for the government to allow award of service contracts instead of firm-fixed price contracts to the laboratories to "perform" quality work on samples rather than use the same methods and same quality for all samples, no matter what the intended use of the data. This approach has been tried and has proven to be very expensive when compared to fixed price laboratory services. However, these comparisons were conducted by only comparing price per sample, and did not measure the usefulness of resultant data to the user. Another argument against this type of approach is that it can foster ineffective use of time and resources.

- A final alternative is for the commercial laboratory community and the regulators to define categories of samples that are cataloged as difficult to easy based on very specific descriptions, such as oily waste to well-water samples. The laboratories could then bid competitively on each type of sample category. If the samples as received in the laboratory failed to meet the definition of the category, the laboratory would then work with the customer delivering the samples to redefine the sample category prior to beginning analysis. Additionally, the laboratories could define charges for additional analytical procedures that may be required on a case-by-case basis for specific types of samples and define with the customers and regulators the justifications based on data quality that would invoke their use and additional charges to be incurred. For this approach to be feasible, it is mandatory that performance requirements for methods used by laboratories be well established and meet well-defined performance requirements on specific sample matrices. Since it is unrealistic to expect all very difficult samples to be able to be effectively analyzed by even the best method available, the implications of this situation must be carefully determined prior to implementing this type of program.

Agency Actions

Agency actions that can be accomplished to implement the suggested solutions include:

- Fully define the program so that it can be implemented based on full understanding of its scope and potential impact.
- Garner the support of all EPA Program Offices and other agencies that now have similar requirements that require regulatory specified methods.
- Define what performance criteria are critical, important and mandatory for any analysis. Prioritize existing criteria based on value in defining the quality of data for different generic an specific purposes. This action was also included in the previous discussion included in the Possible Solutions to the Problem Section.

Implementation Impediments

Impediments to implementing the solution have been implicitly included in the descriptions of the options. However, one impediment that is usually not considered is the dilemma faced in attempting to determine how to utilize past data collected under different requirements. One must use historical data and the lessons learned from generating the data as the baseline for establishing the new system that will be used. Past data must be utilized to the full extent possible based on the decisions to be made and the information content of the data. In evaluating the data for potential use in specific decisions, regulators and other data users may gain insight into what data must be gathered to establish performance and what performance requirements are mandatory for specific decisions. Since history cannot be changed, we must use the past data and past experience to establish more effective means to collect data for future decisions. We must use lessons of the past to craft the best program for the future and not allow past experience and the volume of data generated by past programs to be used as a reason to impede changes and improvements.

Commercial Laboratory Assistance

The commercial laboratory industry can assist EPA in solving the problems in several ways:

- Provide EPA with data demonstrating the within laboratory biases that occur using different methods on the same samples/standards, based on past and future results.
- Assist EPA in defining the set of performance criteria that provides the most information to enable users to assess data fitness for use in particular applications.
- Provide EPA with data for specific methods demonstrating what performance objectives on critical criteria can be met with real waste samples, which has the benefit of producing data that can be used to determine if methods are capable of producing required quality of data on real samples and if laboratories can achieve required performance.
- Assist EPA in structuring the type of competitive bid process that could be used to procure performance-based analyses. Past performance-based schemes were effective in many ways but had several flaws that made it difficult for the system to work, which were discovered and resolved after implementation. These types of lessons learned from the commercial laboratories perspective may help in avoiding relearning the same lessons.
- Provide information on cost impact of selecting different performance indicators and the costs/benefits for frequency of performance data collection.
- Provide general information on the cost/benefit of changing to a performance-based approach based on potential changes in procedures that could allow use of less costly methods than those currently required by regulations

CONCLUSIONS

Change is needed in order to deliver data needed to support sound decisions. Change is also needed to stimulate the industry to use the best new techniques and methods to solve problems that cannot be tackled using the restrictive protocols required today. Therefore,

change must occur and will best proceed if sound scientific and business decisions are the basis for implementation. Industry and government must plan the program cooperatively so that it will be successful.

From our perspective, we prefer that the methods include mandatory surrogate spiking requirements and ongoing verifications of performance, such as laboratory control samples, blanks, and other such information. The resultant program should enable a laboratory to select cost effective methods for analysis if spiking, blank, detection limit and other "science based " performance requirements are met.

OTHER PERFORMANCE BASED METHODS DISCUSSIONS

Laboratories have heard previous discussions of performance based programs which sound like "dial a precision and accuracy number". They seem to be based on the implicit assumption that laboratories have a variety of methods sitting on the shelf where precision and accuracy are directly proportional to price. The client then (1) determines the appropriate precision and accuracy, (2) tells the laboratory to obtain that precision and accuracy, and (3) obtains data that meet the requirements at the lowest possible cost. This sounds wonderful, but it is a simple approach that has no basis in reality. Some reasons follow:

- "Someone once said that the secret to making money in the laboratory business is doing a whole lot of what you are good at." Laboratories like to have single methods set up to accomplish particular analyses. Setting up multiple methods of a single analysis is costly, leads to confusion in the laboratory, and increases the frequency of errors. A laboratory would have to perform multiple methods that produce data with different precision and accuracy, and the precision and accuracy would have to be established for each one of these methods in order to be accomplish the "dial a precision and accuracy" approach.

- The greatest source of variability in environmental measurements is field sampling and environmental heterogeneity. The place to customize precision and accuracy numbers for a project is during the design of the sampling plan. Field duplicates

may add more information than that obtained from more stringent controls on the laboratory in establishing the accuracy of measurements.

- Data quality and laboratory efficiency usually go hand in hand. An ongoing focus of most laboratories is to improve both the quality and efficiency of the analytical procedures. As quality is improved, the number of reruns is lowered. As wasted analytical effort is eliminated, both quality and throughput are improved. With the exception of screening methods, the most cost effective analysis is frequently also the highest quality. If precision and accuracy need to be tightened beyond what is considered reasonable for the most cost-effective analytical procedure, the most cost effective and prudent way may be to conduct duplicate analyses or take duplicate samples.

ISSUES ASSOCIATED WITH ADOPTION OF PERFORMANCE-BASED METHODS: SCIENTIFIC PERSPECTIVE

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INTRODUCTION

I am recommending that the environmental monitoring community and the regulatory agencies should replace existing requirements specifying in detail how data are to be generated with guidelines describing how the quality of data should be documented. This recommendation probably goes beyond what David Friedman had in mind when he asked me to discuss my experiences with performance-based methods. However, I have concluded that it is the performance of the system of methods, rather than a single method, which is only a part of the system, that should be the focus of our attention. This change would give data users the ability to estimate the risk they take when making a decision and it would be more cost effective than current practices. It could be implemented quickly and it would promote creativity and quality science, it would produce higher quality data, it would reduce the incentive to commit fraud and the potential for controversial legal issues.

Because guidelines for documenting the quality of environmental data do not exist, the environmental community has made large time and dollar investments performing actions they assume will improve the quality of the data they generate. Included in this list of actions is the development and use of sample collection, handling, preservation, and analytical methods. These are often specified by a regulatory authority or by an applicable contract. In addition, various options to certify laboratories, field scientists, and analysts also are included or are under

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consideration. One thing that all of these practices have in common is the fact that they will not provide a description of the quality of the data managers use to make their decisions; which is, in my opinion, the most important quality assurance product the scientific community should be providing to environmental managers. Instead, existing requirements are based on unproven assumptions that data quality will both be adequate and will be improved if the actions described above are taken. Although these assumptions may be true part of the time, they are not always true and may not be true for most data collection activities. Why should we continue to base important decisions involving millions of dollars on unproven assumptions, when the quality of the data supporting a decision can be obtained and documented with less time and for fewer dollars than are now being spent?

WHAT IS REQUIRED TO DOCUMENT THE QUALITY OF SCIENTIFIC DATA?

Three kinds of information are needed to document the quality of scientific data. The first of these is done primarily before the samples are taken and are usually contained in what I call an approved Quality Assurance Project Plan (QAPP).

The first kind of information required is a description of all procedures used to generate the data. These procedures should be in sufficient detail that another scientist could reproduce the work described. The documentation (QAPP) should include a description of the decisions to be made with the data to be collected and how the data will be used (perhaps with other existing information) to make each decision. For example, a lawn of a residence might be considered to be contaminated if the average soil lead concentration is above 500 ppm at a 95% confidence level. The documentation should contain a description of the design of the monitoring network, each station in the network, how and when samples are to be collected, handled and analyzed. The QAPP should also include a description of how the precision and accuracy of the data are to be measured.

The second kind of information needed is evidence that all procedures were actually in control during the time that data were being generated. This is usually done by showing the absence of a measurable amount of contamination and by using various performance evaluation standards and sample spikes. The QAPP must describe how the data generator will show that each procedure was in control so it is known that all data were generated under "in controlled" conditions. These quality control data are collected when the environmental data are collected. If control of a procedure is lost, data generation is simply stopped until the problem is corrected.

The third kind of information needed is a measure of the accuracy and precision of the environmental data at the concentration of interest. This information would normally include a knowledge of the distribution (normal,log normal, etc.) of the data and would usually be based on replicate samples or spikes.

REASONS WHY IT IS BETTER TO DOCUMENT DATA QUALITY THAN TO INVEST IN PRACTICES THAT MAY OR MAY NOT PROVIDE USEABLE DATA

It is Cost Effective

My recommendation requires the preparation and acceptance of one guideline. Existing regulations require development of many methods and then tracking compliance with these methods. In addition, such things as good laboratory practices and laboratory certification are required by some programs and states even though there is no evidence that these practices improve data quality by a measurable amount.

It Produces Higher Quality Data

My recommendation includes a measure of data quality. It allows the science to be optimized to the decision and to physical conditions such as sample matrix and other pollutants. If the measure of success is data quality rather than adherence to a specified procedure, those

procedures and practices that most efficiently provide the quality needed will quickly replace procedures and practices that are neither efficient or cost effective.

It can be Implemented Quickly

Implementation does not require that a government or a private Agency establish an elaborate bureaucracy to manage the program. It only needs agreement that the recommendation has merit, preparation of the required guidelines describing how each of us should document the quality of the data we generate and use followed by regulatory approval to use the guidelines rather than existing methods when appropriate to do so.

It Promotes Creativity

Between 5 and 10 years are required to get regulatory approval for the general community to use a "new" method. Therefore, most environmental scientists work 5 to 10 years behind the state-of-the-art in their chosen discipline. As a result, there is less incentive for environmental scientists to develop methods specific to their waste, which reduce waste, that are more efficient, sensitive, accurate or precise because such methods are not easily incorporated into the regulatory system. Should we not provide an incentive for scientists to develop and use the highest quality methods they can and is there any doubt they will do so if that incentive is provided? I expect the fact that environmental regulations effectively prevent environmental scientists from working at the state-of-the-art of their profession has damaged the quality of environmental science more than any other single factor.

It is Consistent with Total Quality Management

The recommendation prevents most data quality problems by requiring better planning with an emphasis on consensus building during preparation and approval of the QAPP. It

includes a measure of the desired product, data quality, that can be used to measure the effectiveness of the different processes that produced the data.

It Reduces the Incentive to Commit Fraud

When scientists are required by regulation or contract to increase their costs by taking actions that do not improve data quality, there is a natural tendency to take shortcuts. Unfortunately, many of these shortcuts are illegal and totally unacceptable even though they would be acceptable to the scientific community. My recommendation provides the flexibility, in most cases, to practice quality science within the recommended guidelines.

**This paper describes the views of the author and does not reflect EPA policy.*

APPENDIX B:

PREDICTING THE ENVIRONMENTAL IMPACT OF OILY MATERIALS

PREDICTING THE ENVIRONMENTAL IMPACT OF OILY MATERIALS: INTRODUCTION AND REGULATORY PERSPECTIVE

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BACKGROUND

Prevention of groundwater contamination has historically been one of the EPA's highest priorities in implementing the RCRA program. To that end, the Agency has developed and promulgated test methods, fate and transport models, and regulatory standards to control the management of wastes whose properties might pose a hazard to groundwater. Scientists are concerned with oily waste due to its volume, toxicity, and potential for causing severe ecological damage. Such wastes take many forms including: liquids of widely varying viscosity, contaminated soils, sludges, and tarry "plastic" masses.

Oily wastes have some unique properties. They can migrate like a liquid but appear to be a solid. Because they result from many commercial processes and applications, they are broadly distributed, of very large volume, and of tremendous commercial importance.

In developing the hazardous waste identification characteristics, EPA highlighted its concerns with protecting ground water resources by developing the Extraction Procedure Toxicity Characteristic (40 CFR 261.24). The characteristic relies on laboratory procedures to predict toxicant mobility.

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Over the years a number of laboratory extraction methods have been applied to the problem of predicting what might migrate from oily wastes managed under landfill conditions. Among the test methods that have been developed and employed to identify those wastes which might pose an unacceptable hazard are: EPA methods 1310, 1311 and 1330 (Extraction Procedure, Toxicity Characteristic Leaching Procedure and Oily Waste Extraction Procedure).

The current approaches all have deficiencies with respect to predicting the mobility of toxic chemicals from oily wastes. Methods 1310 (EP) and Method 1311 (the TCLP) underestimate the mobility of many oily wastes due to filter clogging problems, their precision is less than desirable, and they have certain operational problems. Conversely, Method 1330 (OWEP) probably overestimates mobility since it emulates a worst possible case scenario. None of the available laboratory mobility procedures is thus totally satisfactory.

PROBLEM

Given the importance of this issue, it is imperative that accurate, precise, and usable approaches to characterizing the mobility of oily materials be developed. That is what we are here for today.

The problem of mobility estimation is too large and complicated for us to try and solve all its aspects in a half day. Therefore, we will focus on just one aspect of the problem - predicting the initial source term. To put it another way, we want to predict the highest concentration of material that might be released from the waste to the soil immediately below the point of disposal for some reasonable amount of time. This information would then feed into the fate and transport models used to predict the final toxicant concentration at some distance away from the disposal area.

DISPOSAL SCENARIO OF CONCERN

The priority waste management facility scenario that EPA has selected to be modeled in this workshop is placement of the waste into or on the ground (e.g., landfill or lagoon). Within this scenario a number of parameters need to be considered. These include:

- Temperature (assume temperate conditions),
- Rainfall regime,
- Biodegradation,
- Hydrolysis,
- Soil types (assume soil underlying the waste management unit has a porosity similar to that of sand), and
- Amount of waste (assume amount is large enough so that it can be considered to be infinite).

FATE AND TRANSPORT MODEL CONSIDERATIONS

To properly manage oily wastes to protect ground water sources from contamination by waste constituents, an adequate model to predict the fate and transport in the subsurface environment is needed. The Agency is developing a model to simulate the migration of aqueous and nonaqueous phase liquids and the transport of individual chemical constituents which may move by convection and dispersion in each phase.

As input parameters, the model needs information on the amount and composition of both the aqueous and nonaqueous phase liquid portions of the waste as well as the composition of the leachate that might be generated by action of surface waters on any "solid" material that may have initially been present in the waste material. At this time, the Agency does not have a precise way of defining either an "aqueous phase liquid" or a "nonaqueous phase liquid".

REGULATORY PERSPECTIVE

In an ideal situation, an effective approach to evaluating oily wastes would:

- Be simple to use (not require sophisticated equipment, nor constant attention by a highly trained technician),
- Be inexpensive to run,
- Take as little time as possible to perform (ideally no more than 24 hours),
- Be accurate (relative to predicting behavior of waste in the environment),
- Be precise (i.e., be reproducible),
- Be rugged (capable of characterizing a broad range of waste types and constituents of concern), and
- Not generate wastes (e.g., generate little if any solvent waste and waste contaminated media).

The characteristics that the approach should have (maximum desirable values for each parameter) are:

- A high degree of freedom from false negatives (any errors tend toward overestimation of threat to environment),
- Precision (RSD <50%),
- Relatively low cost ,
- Taking as little time as possible to perform (<24 hours), and
- Ruggedness.

OPTIONS FOR CONSIDERATION

I. Develop a two-component mobility test that determines the fraction of the waste which is flowable (capable of physical movement under the influence of gravity and overburden pressure) under the conditions of the test. Suggested conditions: room temperature and 50 psi. Define as mobile all material that is flowable under terms of the test plus the aqueous extract of the non-flowable fraction. Under this option, the procedures used are independent of waste properties and disposal environment.

II. Develop a single generic laboratory procedure to estimate what disposal point concentration would result from aqueous leaching of the hazardous constituents from both the mobile and non-mobile fraction of the material. Under this option, the procedures used are independent of waste properties and disposal environment.

III. Employ a series of laboratory test procedures to evaluate the waste material. These procedures would be keyed to the fate and transport model to be employed to evaluate the data. The procedure also would be independent of the properties of the material under evaluation.

The questions we would like you to address are:

- What would be the "best" approach to use in order to predict the nature and concentration of the components that would leach from oily wastes if the waste were to be placed in an unlined landfill environment?
- If the necessary tools are not presently available, how should such a test method or model be developed and evaluated?

- What form should a cooperative development program take? How could it be organized? Who might the cooperators be? How long would you expect it to take to develop the necessary tools?

If you think of any ideas, information, or suggestions that you feel the Agency should consider when addressing this issue, please send them to us. Send your comments to:

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US Environmental Protection Agency
401 M St. SW (RD-680)
Washington, DC 20460

We will need to receive your comments by August 21, 1992 in order for them to be incorporated into the conference final report.

PREDICTING THE ENVIRONMENTAL IMPACT OF OILY WASTE: INDUSTRY PERSPECTIVE

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STATEMENT OF ISSUE

Managing solid waste in an environmentally sound manner is a subject of high concern to industry, EPA and the public. However, we must have regulatory tools which accurately reflect the environmental hazard, and analysis tools which accurately assess the potential impact of various management approaches. We need to bring the best science to bear on the evaluation of the potential environmental threat from oily waste disposal, considering the likely management scenarios. One way EPA has decided to regulate certain oily waste in the past is by listing the waste as hazardous under RCRA. This approach identifies a material as an environmental threat based on possible (but not necessarily realistic) mismanagement scenarios. A second way to regulate the waste is to determine if it is hazardous using the toxicity characteristic (TC) and the Toxicity Characteristics Leaching Procedure (TCLP) test. This test is used to determine whether a waste is hazardous or not based upon a specific leachability test and municipal landfill disposal scenario. The options explored in this paper serve to promote thinking about new approaches for identifying the environmental threats and thereby to better focus regulations dealing with the management of these materials. This will be done by introducing and critiquing current most common predictive methods and presenting potential avenues for more accurate methods.

Although it is nearly impossible to precisely define the term "oily waste", the following analysis can provide a basis for further discussion:

Presented on July 14, 1992 at EPA Workshop II on Predicting the Environmental Impact of Oily Materials"

a) An oil is generally an immiscible or relatively insoluble liquid, varying in composition but consisting of organic constituents. Petroleum oils principally consist of hydrocarbons; vegetable and animal oils are glycerides, and fatty acids; and essential oils are terpenes, alkaloids, etc.

b) An oily waste is an industrial process waste or residual bearing oil in visual and/or measurable proportions.

c) Oil in oily wastes can occur in any matrix, including: sorbed to dry solids; in sludges or slurries; multi-phase liquids or sludges/slurries with multi-phase liquids, if water is present. Proper treatment and disposal of all such matrices is a concern of the petroleum industry.

d) Analysis of oils in oily wastes can be accomplished by techniques such as Total Petroleum Hydrocarbons (TPH) (not constituent-specific) or TCLP (constituent-specific). In a number of contexts, the procedures of methods such as these serve to define what is meant by "oil" and "oily waste."

e) Oily wastes possess a wide variety of compositions and physical and toxicological properties.

Some examples of oily waste include petroleum refinery sludges, such as oil- water separator sludge and dissolved air floatation froth, storage tank bottom sludge, used oil and others. Expanded beyond the petroleum community there are many types of oily wastes (POTW sludges, polymer plants, timber processing, iron and steel, pulp and paper, meat packing, slaughterhouse, leather tanning, coil coating,restaurants, and miscellaneous foods including meat, dairy and vegetable based oils and fats, etc.).

Currently there are a variety of state and local programs designed to address potential environmental impacts of the management of various types of oily materials, such as E&P wastes, spill residues and UST wastes. A number of RCRA listed and toxicity characteristic wastes are also regulated under federal programs. EPA is currently evaluating the possible listing of additional petroleum refining wastes.

Unfortunately, the current analytical methods for determination of the environmental threat of petroleum constituents in wastes and oily materials via the TCLP test and model and RCRA listing system remain controversial. USEPA, academia, and the regulated community are continuing efforts to identify a sound, reproducible methodology to accurately assess these threats. In fact, EPA has recently proposed a rule to address the over-regulation of listed wastes created by EPA's "mixture" and "derived-from" rules. This initiative, called the Hazardous Waste Identification Rule, could have major impacts on the classifications and management of hazardous and nonhazardous industrial wastes, including oily waste.

An approach that the American Petroleum Institute (API) has suggested to the Agency is concentration-based exclusion criterion coupled with contingent management. It is a two-tiered process for determining whether wastes captured under the RCRA listing rule should or should not continue to be regulated as hazardous. One tier would allow wastes with constituents below health based levels (with an appropriate multiplier to account for dilution and attenuation) to be deemed nonhazardous provided the waste does not exhibit a RCRA characteristic. A second tier would allow wastes that contain constituents below somewhat higher health based levels to be deemed as nonhazardous, provided these wastes are managed in certain environmentally protective ways. This second approach would alter the current system by basing a waste's classification on how it is actually managed and not how it could be hypothetically mismanaged.

On the test method side, many, including Environment Canada, ASTM and the USEPA, have been involved with the development of improved leachability and contaminant fate/transport tests and models. Despite this work, predicting the potential environmental hazard associated with oily wastes remains problematic.

TCLP APPROACH

The toxicity characteristic leaching procedure (TCLP) was developed as a way to evaluate the threat of solid waste disposal under "...a mismanagement scenario for toxic wastes which constitutes a prevalent form of improper management--namely, the co-disposal of toxic wastes in an actively decomposing municipal landfill which overlies a groundwater aquifer..." (Fed. Reg., May 8, 1990). The TCLP is a leaching and acidic aqueous extraction test. The test was designed to model mismanagement of the disposal of process wastes. The Toxicity Characteristic (TC) rule itself, and constituent-specific limits associated with the TC, define wastes as hazardous on the basis of the concentrations of certain toxic constituents. The TC and its constituent-specific limits were developed in large part to protect human health from contamination of drinking water aquifers. The TCLP test, as currently interpreted, is applicable to those wastes which produce a separate non-aqueous phase as well as those which do not.

Specifically the model system that forms the basis for the regulatory limits imposed by the current toxicity characteristic is one which assumes that the waste is disposed of in a municipal hazardous waste landfill where it is leached by acidic landfill liquids, emerges from the landfill bottom into underlying groundwater whereupon it migrates to an hydraulically down-gradient drinking water well (see Figure 1).

The current Toxicity Characteristic defined-method for determining environmental risks uses a three-part system, consisting of a physical model (TCLP), coupled to a mathematical model (EPACML), coupled to a toxicological model. The TCLP simulates constituent leaching from a landfill, EPACML simulates constituent transport from a landfill to a drinking water well, and the toxicological model relates drinking water concentration to health-effects. The TCLP was not designed as, and fails as, a multi-phase model. This is because the oil phase is simply treated as water. Additionally any multi-phase capability within EPACML was ignored due to the TCLP output.

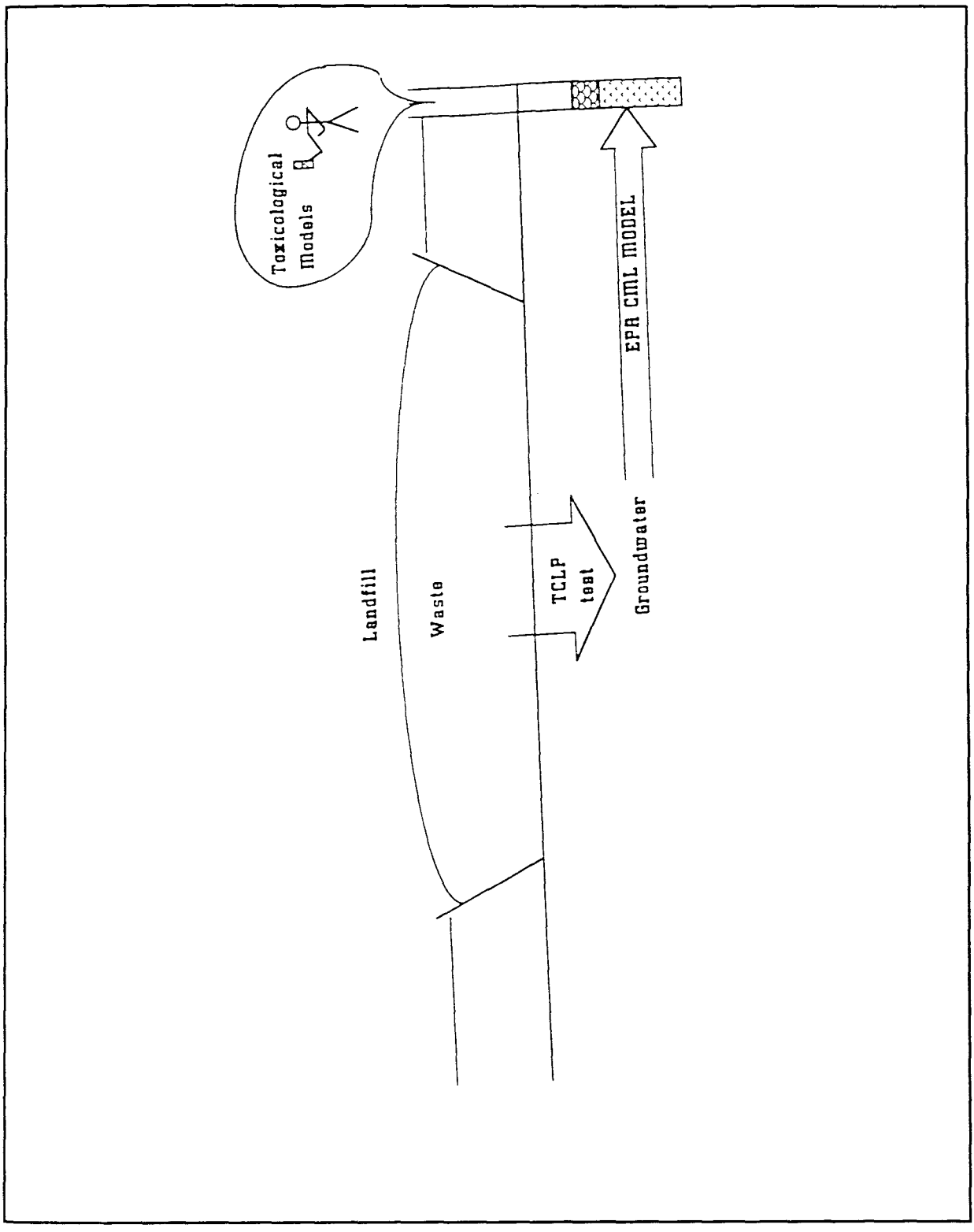

Figure 1: Components of TC "System"

Significant technical aspects of the TCLP simulation can be summarized as follows (see Figure 2).

- No vadose zone-bottom of the landfill is in direct contact with the ground water.
- The disposal of waste liquids (oil and water) are equally mobile.
- The liquids are not leached or diluted but elute directly from the landfill into the ground water.
- Infinite source-liquids continue to be released forever regardless of amount of liquids in the original waste.
- The solids are leached with a 20:1 volume of acidic "landfill leachate" which then enters the ground water.
- Infinite source - the hazardous constituent concentration in the initial 20:1 leachate volume continues to be leached from the material forever, regardless of mass of constituents in the original waste.
- The liquids and leachate travel through the ground water to a drinking water well. Attenuation and dilution reduce concentrations by a factor of 100.
- Oil moves as water.
- Hazardous constituent concentrations achieve steady-state in the well at which time the well-owner drinks two-liters/day for 70 years (oil and all).

VALIDITY OF THE TCLP APPROACH

Oily wastes provide a great challenge to those charged with evaluating their potential impact on the environment. Unfortunately the design of the TCLP test in concept, methodology and fate/transport modeling, inaccurately predicts the behavior of waste containing separate-phase oil and organic constituents. One shortcoming is that it forces a generic disposal scenario which may be reasonable for some cases but impossible for others. Specific problems include operational problems with the test procedure, the assumption that oil behaves identically to water

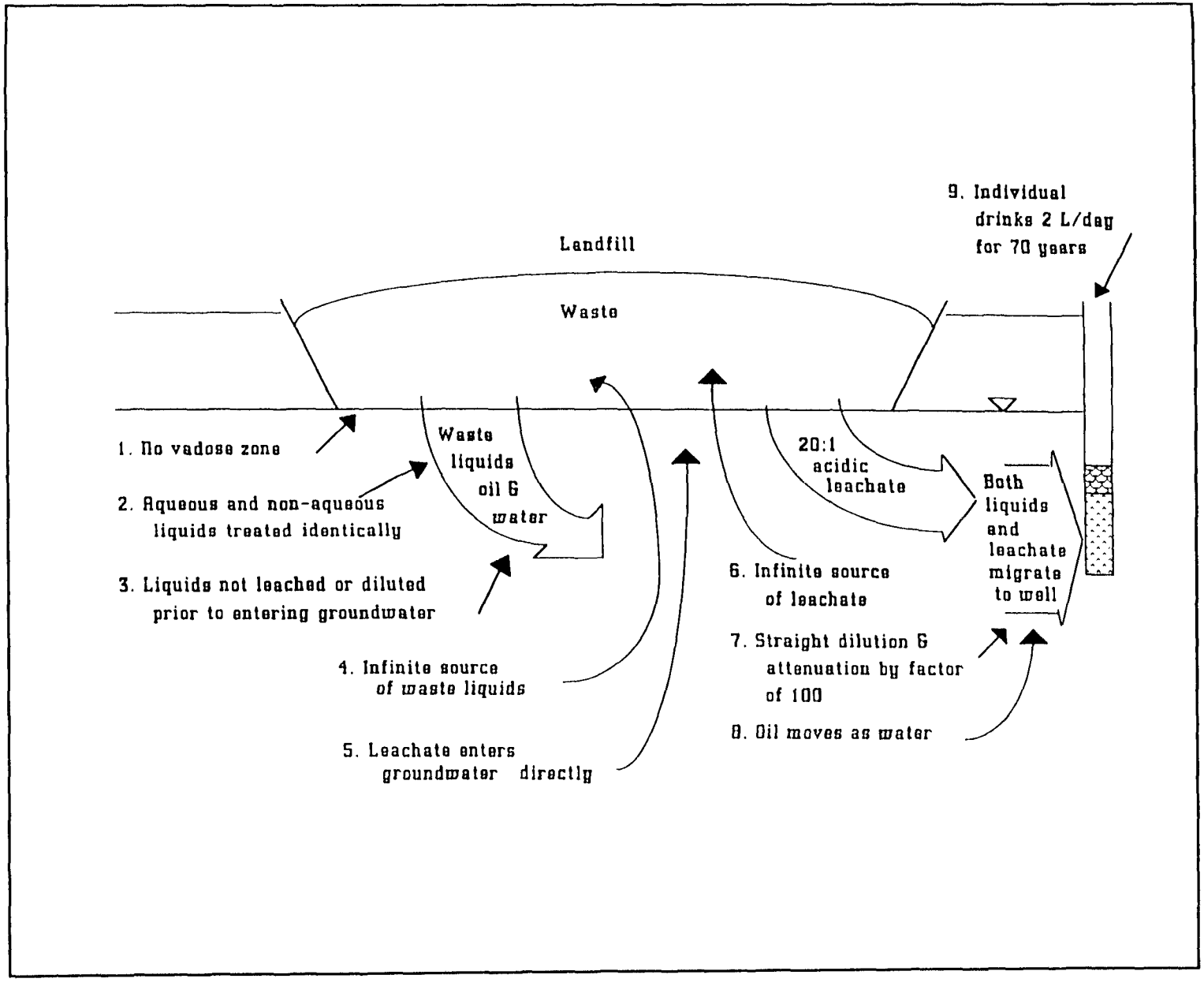

Figure 2: Issues Inherent in TC Scenario Which Work to Introduce Inaccuracy

in the environment, the validity of the disposal scenario, and invalid contaminant fate/transport assumptions.

The test system was not designed for multi-liquid phase materials. This results in operational problems with the TCLP methodology including non-reproducible free oil breakthrough, filter clogging, and difficulties with volatiles equipment. The zero headspace extractor (ZHE) test equipment is difficult to clean. Some volatile chlorinated compounds are transformed within the TCLP extraction (Bricka, et al, 1991). EPA has, to date, not provided approved test methods which are validated for the analysis of metals in non-aqueous liquids (55 Fed.Reg. 4444).

One of the initial steps in the TCLP test is pressure filtration of the waste. For some oily wastes, non-aqueous liquid may be expressed. This liquid is segregated from the remaining solids which are then acid-leached. This acid leachate is combined with the non-aqueous liquid to produce the "TCLP leachate" which is compared to hazardous/nonhazardous criteria.

Implicit in this procedure is the assumption that both aqueous and non-aqueous liquids will behave identically, both within the landfill and upon their hypothetical release. EPA has been able to provide little, if any, support for this critical portion of the TCLP.

"The initial liquid/solid separation problems are due to the tendency for some material, such as certain types of oily wastes, to clog the 0.45 um filter and prevent filtration..... This problem is serious, since materials which do not pass the 0.45 um filter are treated as solids even if they physically appear to be a liquid. These (liquid) wastes are then carried through EP extraction as a solid."

"This is particularly serious for oily wastes, since oils have been known to frequently migrate to ground waters. It is important for the liquid (sic)/solid separation to treat, as liquids, those materials which can behave as liquids in the environment."

"As indicated below, EPA believes that the liquid/solid separation technique.... reduces variability....and that it also provides a more adequate differentiation between those materials that behave as liquids in the environment, and those materials which behave as solids."(51 Fed. Reg. 21658)

As we gain experience with risk evaluations, we see that the risk posed by light, non-aqueous phase liquids (i.e. "oil") appears to be mostly due to dissolved contaminants in drinking water. The calculated risk due to free oil is not great due to the lack of exposure. As it moves through the soil, oil will be immobilized in the soil and from that point may partition into the water phase according to constituent solubilities. Any mobile oil migrating to a water well does not represent a 2L/day, 70 year hazard since it is not realistic to project that anyone will drink free-phase hydrocarbons daily for their entire lives. Therefore, it makes some technical sense to leach the oil fraction with the acidic medium along with the solids.

The disposal scenario as depicted by EPA is not an accurate description of current waste disposal practices. An EPA-OSW survey, several years old already, documents that liquid-type wastes are no longer being accepted by municipal landfills (51 Fed. Reg. 21655). New test methods based upon actual waste management situations would give more accurate results than those based on generic hypothetical scenarios.

Industry has commented upon the shortcomings of the current TCLP/CML model. For example, the infinite source assumptions require contaminant mass to continue to be available for introduction into ground water until steady state is achieved. This is unrealistic. One improvement would be to design transient, declining source terms into the model. Further, there is no consideration of a vadose zone although we know it exists and future landfill regulations will require the presence of a vadose zone. The TCLP is not designed to handle the separate organic phase flow. The current TCLP system does not take into account aerobic biodegradation, volatilization, or retardation. Hydrolysis is apparently being considered at this juncture, but is not currently part of this system.

The unilateral application of TCLP to multi-phase wastes, especially those containing oily materials, is unsupported and inappropriate. There is no evidence that non-aqueous liquids behave as aqueous liquids in a landfill. Indeed, such liquids have an affinity for the solid materials in the landfill which could cause contaminants to be less mobile than predicted by the TCLP.

Until work on the behavior of non-aqueous materials and the prediction of their movement is more mature, the non-aqueous liquids should be treated like the waste itself and be subjected to the same extraction with acidic fluid. To the extent that hazardous constituents are released into the extractant, they should be combined with the aqueous extract generated from the waste solids.

THE EFFECTS OF THE CURRENT TC SCENARIO MODEL - SOME IMPACTS

A number of wastes from the petroleum industry, such as waters from tank drawdowns, ground-water extraction, and hydrotesting, are or may be subject to the TC rule even though there is no conceivable way that these materials would ever find their way into a landfill.

The RCRA Corrective Action Program could potentially generate large quantities of petroleum-contaminated soils. On-site and in-situ management techniques are not accurately represented by the TCLP. In addition, a number of states currently have effective response programs for clean up of spills and other releases of petroleum into the environment. States are concerned that application of the TCLP (particularly if TCLP is a poor estimator of environmental threat) will seriously impact operation and effectiveness of these programs by adding unnecessary and unwarranted hazardous waste handling requirements to wastes which don't pose a threat. We can no longer afford to waste large sums of money handling solid waste in a manner which over estimates the actual environmental threat.

A WAY FORWARD - SAB LEACHABILITY SUBCOMMITTEE

Given the problems with the applicability of the TCLP to multi-phase waste, are there any alternatives? What are the potential ways forward?

Last year, a report was issued by the Science Advisory Board (Environmental Engineering Committee, Leachability Subcommittee), entitled "Recommendations and Rationale for Analysis for Contaminant Release." It contained nine recommendations:

- A variety of contaminant release tests and test conditions which in corporate adequate understanding of the important parameters that affect leaching should be developed and used to assess the potential lease of contaminants from sources of concern.
- Prior to developing or applying any leaching tests or models, the controlling mechanisms must be defined and understood.
- A consistent, repeatable and easily applied, physical, hydrologic and geochemical representation should be developed for the waste management scenario of concern.
- Leach tests and conditions (stresses) appropriate to the situations being evaluated should be used for assessing long-term contaminant release potential.
- Laboratory leach tests should be field-validated, and release test accuracy and precision established before tests are broadly applied.
- More and improved leaching models should be developed and used to complement laboratory tests.
- To facilitate the evaluation of risk implications of environmental releases, the Agency should coordinate the development of leach tests and the development of models in which release terms are used.
- The Agency should establish an inter-office, inter-disciplinary task group, including ORD to help implement these recommendations and devise an Agency-wide protocol for evaluating release scenarios, tests, procedures, and their applications.

- The task group should also be charged with recommending what the appropriate focal point(s), responsibilities, and organizational, budgetary and communication links should be within the Agency for the most effective, continued and ongoing support and pursuit of research, development, and utilization of methods and procedures.

To fully accomplish all of the recommendations will be costly and time- consuming. However there can be no alternate to core research on contaminant release and transport methods. SAB identified approximately 30 leach tests which are used internationally to attempt to evaluate environmental threat of wastes. Unfortunately SAB concludes that each method suffers from shortcomings.

APPLICATION TO OILY WASTE

If we wish to improve upon the system, there are two basic options:

1. Stick with the physical/mathematical model basis of the TCLP and improve accuracy by modeling multi-phase transport and remove assumptions predicated on long-term human consumption of immiscible product.

2. Replace with a single alternative model, either physical or mathematical.

We understand that EPA is exploring various enhanced modeling systems for multi-phase disposal scenarios. These would include multi-phase flow within the unsaturated zone, and partitioning between aqueous, oil, and air phases within the soil. Also included would be saturated zone groundwater pollutant transport models which are more accurate. Industry favors these developments as tools to better understand oily waste disposal impact.

On the other hand, we must currently deal with an inappropriate TC rule. Currently, industry must comply with the TC rule, which means it must run TCLP tests on oily wastes.

This has resulted in a disastrous situation. The TCLP was not designed to accurately assess the environmental threat of oily materials. Therefore it does not. However, decisions on the "proper" management of these wastes are being made on the basis of a flawed test.

Industry has had to deal with the TC for many years. We have modified our waste management approaches and strategies, we have complied with TC and land disposal requirements and we are preparing to fully comply with Corrective Action. Unfortunately, changes to the TC at this point may be just as disruptive and costly as compliance with the TC has been to date. Modifications must be done carefully and deliberately, always using the best possible science to ensure accuracy, not just consistency.

API supports, as mentioned in the Statement of Issue section, a concentration- based exclusion coupled with contingent management for exempting listed hazardous waste from subtitle C requirements. This would address the "inappropriate scenario" dilemma by incorporating elements of actual management approaches instead of one hypothetical approach.

The regulated community has volunteered to work with EPA both as individuals, individual companies, and through trade organizations. We will continue to offer such assistance. For myself, I see continued interaction between EPA- OSW and the American Petroleum Institute. Typical industrial support to EPA includes offering technical comment, procuring wastes, providing waste generation and characterization data, and participating in round-robin testing of new methods.

TABLE 1 - EXTRACTION TESTS

Test Method	Leaching Fluid	Liquid:Solid Ratio	Maximum Particle Size	Number of Extractions	Time of Extractions
I. STATIC TESTS (LEACHING FLUID NOT RENEWED) **A. Agitated Extraction Tests**					
TCLP (1311)	Acetic Acid 0.1 N Acetic Acid Solution, pH 2.9, For Alkaline Wastes 0.1 M Sodium Acetate Buffer Solution, pH 5.0, For Non-Alkaline Wastes	20:1	9.5 mm	1	18 hours
EP TOX (1310)	0.5 N Acetic Acid (pH = 5.0)	16:1 during extraction 20:1 final dilution	9.5 mm	1	24 hours
ASTM DM 3987-85	ASTM Type IV Reagent Water	20:1	As in environment	1	18 hours
California Wet	0.2 M Sodium Citrate (pH = 5.0)	10:1	2.0 mm	1	48 hours
Leachate Extraction Procedure (MOE, Ontario)	Acetic Acid 2 MEQ/G	20:1	As in environment	1	24 hours
Quebec R.S.Q. (MOE, Quebec)	Inorganic 0.02 MEQ/G Organic Distilled Water	10:1	Ground	1	24 hours
French Leach Test (AFMOR, France)	DI Water	10:1	9.5 mm	1	16 hours
Equilibrium Extraction (Environment Canada)	Distilled Water	4:1	Ground	1	7 days

TABLE 1 (continued)

Test Method	Leaching Fluid	Liquid:Solid Ratio	Maximum Particle Size	Number of Extractions	Time of Extractions
Multiple Batch Leaching Procedure (Environment Canada)	Acetic Acid Buffer, pH 4.5	4:1 or 2:1	9.5 mm	Variable	24 hours
Material Characterization Centre-4 (Material Characterization Centre)	Choice	10:1	2 fractions 74-149 mm	1 150-425 mm	20 days to 10 years
Oily Waste (1330)	Soxlet with THF and Toluene EP on Remaining Solids	100 g:300 ml 20:1	9.5 mm	3	24 hours (EP)
Synthetic Precipitation Leaching Procedure (1312)	Variable	20:1	9.5 mm	1	18 hours
Equilibrium Leach Test	Distilled Water	4:1	150 μm	1	7 days
B. Non-Agitated Extraction Tests					
Static Leach Test Method (Material Characteristic Centre-1)	Can be Site-Specific	Vol/Surface 10 μm	40 mm^2 surface area	1	>7 days
High Temperature Static Leach Test Method (Material Characterization Centre-2)	Same as above but at 100°C	Vol/Surface 10 μm	40 mm^2 surface area	1	>7 days
C. Sequential Chemical Extraction Tests					
Sequential Extraction Tests	0.04 m Acetic Acid	50:1	9.5 mm	15	24 hours per extraction
D. Concentration Build-Up Test					
Sequential Chemical Extraction	Five Leaching Solutions Increasing Acidity	Various from 16:1 to 40:1	150 μm	5	Varies from 2 to 24 hours

TABLE 1 (continued)

Test Method	Leaching Fluid	Liquid:Solid Ratio	Maximum Particle Size	Number of Extractions	Time of Extractions
Standard Leach Test, Procedure C (University of Wisconsin)	DI Water Syn Landfill Leachate	10:1, 5:1 7.5:1	As in environment	3	3 or 14 days
II. DYNAMIC TESTS (LEACHING FLUID RENEWED) **A. Serial Batch (Particle)**					
Multiple Extraction Procedure (1320)	Same as EP TOX, then with Synthetic Acid Rain (Sulfuric Acid; Nitric Acid in 60:40% Mixture)	20:1	9.5 mm	9 (or more)	24 hours per extraction
MWEP (Monofill Waste Extraction Procedure)	Distilled/Deionized Water or other for	10:1 per extraction specific site	9.66 or monolith	4	18 hours per extraction
Graded Serial Batch (U.S. Army)	Distilled Water	Increases from 2:1 to 96:1	N/A	>7	Until steady state
Sequential Batch ASTM D4793-88	Type IV Reagent Water	20:1	As in environment	10	18 hours
Waste Research Unit Leach Test (Harwell Laboratory, UK)	Acetic Acid Bufferd pH = 5	1 bed vol 5 elutions 10 bed vol >6 elutions	Crushing	>11	2 to 80 hours
Standard Leaching Test: Cascade Test SOSUV, Netherlands	Distilled Water HNO_3 pH 4.0	20:1	Crushing	5	23 hours
B. Flow Around Tests					
IAEA Dynamic Leach Test (International Atomic Energy Agency)	DI Water/Site Water	N/A	One face prepared	>19	>6 months

TABLE 1 (continued)

Test Method	Leaching Fluid	Liquid:Solid Ratio	Maximum Particle Size	Number of Extractions	Time of Extractions
ISO Leach Test (International Standards Organization)	DI Water/Site Water	N/A	Surface polishing	>10	>100 days
ANSI/ANS 16:1 (American National Standard Institute/ American Nuclear Society)	DI Water	N/A	Surface washing	11	90 days
DLT	DI Water	N/A	Surface washing	18	196 days
C. Flow Through Tests					
Standard Leaching Test: Column Test (SOSUV, The Netherlands)	DI Water HNO_3 pH = 4	10:1	As in environment	7	20 days
Column ASTM D4874-89	Type IV Reagent Water	One void volume	As in environment	1	24 hours
III. OTHER TESTS					
MCC-55 Soxhlet Test (Material Characteristic Center)	DI/Site Water	100:1	Cut and washed	1	0.2 ml/min
Acid Neutralization Capacity	HNO, Solutions of Increasing Strength	3:1	150 μm	1	48 hours per extraction

References:

1. Compendium of Waste Leading Tests, Waste Water Technology Centre, Environment Canada, Final Draft, May 27, 1989.
2. Private discussions with Gail Hansen, Office of Solid Waste, U.S. EPA.

PREDICTING THE ENVIRONMENTAL IMPACT OF OILY MATERIALS: SCIENTIFIC PERSPECTIVE

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Ted Varouxis
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INTRODUCTION

This paper is intended to stimulate discussion into new or better ways to evaluate the potential release of regulated substances from oily wastes. The paper discusses some options to the currently approved procedures to determine the concentrations of regulated organic chemicals released into the groundwater regime from improperly managed oily waste. The paper also describes a proposed method to evaluate the fraction of an oily waste which is flowable under the influence of gravity or overburden pressure if the material is improperly disposed in a landfill. The options presented cover, in part, some of the major technical concerns of the Environmental Engineering Committee of the Environmental Protection Agency's (EPA) Science Advisory Board (SAB) in their October, 1991 recommendations to the EPA Administrator.[1]

This paper is prepared from the perspective that accurate, reliable, and cost-effective analytical procedures can be developed to properly characterize and manage potentially hazardous oily wastes. The paper accepts the premise that the regulatory community must proceed carefully and the "worst case scenario" will be considered in any proposed solutions. The paper seeks to incorporate some of the suggestions of the EPA Science Advisory Board that methods should take into consideration real world factors such as:

Presented on July 14, 1992 at EPA Workshop II on Predicting the Environmental Impact of Oily Materials"

- source matrix properties,
- contaminant properties,
- leachant properties,
- fluid dynamics,
- chemical and physical properties of the waste,
- temporal/spatial dependence,
- measurement methods, and
- physical models.

TECHNICAL ISSUES

Neither the regulatory nor the regulated community has successfully proposed methods to properly characterize the potential for environmental impact for oily wastes. Existing leaching tests are known to be technically and mechanically deficient, and no method exists to measure the amount of flowable, oily material which may be released from a waste. Solutions to these problems have not been discussed to any extent in the published literature nor in the proceedings of symposia and workshops. These issues are recognized as the major unaddressed problems in evaluating the pollution potential of oily wastes. Any scenario which proposes to assess the pollution potential of this class of wastes must address these issues. This section describes the current state of the technology in these areas.

The Oily Waste Extraction Procedure (OWEP, EPA Method 1330A)[2] is designed to evaluate the potential for an oily waste to release metals under aqueous leaching conditions. OWEP separates the solid material from the oil by solvent extraction. The solid phase is then leached by Method 1310A, Extraction Procedure Toxicity Test[2] and the extracted oil analyzed directly for the metals of interest. The results of the analyses of the two fractions are combined mathematically. It is generally conceded that this overestimates the leaching potential of the waste. If the method is applied to the analysis of regulated organic constituents, all of the analyte will be deemed leachable which is incorrect. It should be noted that the OWEP has never been suggested as appropriate for organic constituents.

The current approach for analyzing the leaching potential of solid waste, EPA Method 1311, Toxicity Characteristic Leaching Procedure (TCLP)[2] differs from the OWEP in that TCLP attempts to determine the aqueous leachability of the waste for both inorganic and organic constituents in a single leach test. It is very difficult to conduct in a reproducible manner. Mechanical problems with the test make it time consuming to perform and frequent reanalysis is required. Precision between replicate tests is very poor. Equipment cleanup is a major obstacle to laboratory productivity. Costs can run to several thousand dollars per sample for difficult-to-handle samples. The major problems found in conducting the TCLP are:

- Handling of the sample is messy, effecting weighing of proper amounts into the extraction vessels. Loss of volatiles occurs.
- Proper sub-sampling of multi-phasic materials is difficult. Samples frequently contain oil, water, and solids. Isolation of solids for extraction is arduous.
- The tumbling action of the two liter extraction vessels forms emulsions making isolation of the aqueous leachate difficult.
- Separation of the leachate from the solid residue after extraction is frequently impossible because the oily material clogs the filter. This is especially serious when using the zero headspace extractor (ZHE) since the test must be repeated if this happens.
- Oily wastes frequently yield aqueous leachates and free organic material which must be separated and analyzed separately, doubling or tripling the analytical costs.
- Equipment cleanup is very time consuming, minor amounts of residual organic material can carry over and contaminate succeeding samples.

These problems are sufficiently severe that both regulators and regulated community have lost confidence in the utility of the method to estimate the potential environmental hazard of oily wastes.

PROPOSED APPROACHES

This section discusses four proposed approaches to improving the technical and/or procedural methods for determining the potential environmental impact of oily materials. They are:

- Adopt a flowable materials test
- Modify the TCLP.
- Adopt a new method of contacting the leach medium with the waste.
- Devise a new model for determining the amount of a regulated substance released from an oily waste by aqueous leaching mechanisms.

Approach 1 - Flowable Materials Test

The EPA has laid the groundwork for a Flowable Materials Test (FMT) in the 1991 proposed rule making for the Liquid Release Test (LRT), EPA Method 9096[3]. The Agency has published two reports describing the test for its original application, namely to detect the release of any free liquid from material destined for land disposal[4,5]. The test places a 76mm diameter by 10mm high sample in a confined chamber under a 50 psi load for ten minutes to force the release of free liquids.

If the device is modified to provide an tight fitting piston/barrel arrangement (identical to the design of the zero headspace extractor, the ZHE) and the indicator paper holder is replaced with a reinforced screen and fluid collection vessel, it will be capable of applying the necessary degree of pressure to the sample necessary to simulate overburden pressure. The screen will allow for the effective escape and collection of the flowable material from the solid mass. Both the retained solids and the collected flowable material can be analyzed separately using one or more of the suggested experimental changes described in the following sections.

Approach 2 - Modify the TCLP

Modification 1 - Addition of Inert Substrate.

One basic problem with the ability to conduct TCLP is the physical nature of oily material and the impact that has on the conduct of the test as discussed above. The EPA has addressed this type of problem in Methods 3540 and 3550[2], Soxhlet Extraction and Sonication Extraction respectively, where inert adsorbents are added to the waste to provide a free flowing material with sufficient permeability to allow for efficient extraction. The same approach can be taken with the TCLP.

The addition of a high surface area, inert matrix like silica beads (or sand) will effectively immobilize the free phase organic material and provide a free flowing medium for sample preparation (sub-sampling) and extraction. The increased surface area will promote solubilization of the organic components into the extraction medium. This approach will be effective for both free liquids and oily solids. If an aqueous phase is also present, adsorption of the oily material should facilitate separation of the aqueous material prior to extraction. The presence of the substrate surface as a host site for oily material will minimize the formation of emulsions during tumbling of the waste/leachant mixture, provided the viscosity of the organic material is sufficiently high that the shear forces of the tumbling action do not separate the liquid material from the solid. After the tumbling sequence, the solid substrate and absorbed oily material will settle to the bottom of the leaching vessel and eliminate or minimize the amount of free organic liquid floating at the surface of the solution, making the filtration step much easier and clogging less likely.

This type of sorbent bed closely resembles the real world case of oily material spilled onto or migrating through soil columns until it no longer moves under the force of gravity. This model of oil coated soil represents the most common real world source of potential pollutant release from oily wastes.

Modification 2 - Use of Fritted Stainless Steel Filter.

Regardless of whether or not the method is modified by the addition of an inert substrate to immobilize the oily material, the filtration step of the method can be improved. Agency funded research of improved filtration media led to the development of a sintered stainless steel filter that overcame many of the clogging problems[6]. The modification has not been added to the method at this time, but it has been used without formal regulatory adoption, with some intractable wastes. Other approaches to improve filtering should be examined, such as the use of thick pads (several mms) of non-woven glass or plastic fibers and powdered filter aids as pre-filters. These are physical changes to the filter apparatus; they should be permitted as long as the modifications can be shown not to alter the composition of the filtrate by absorption of analytes or allow for the passage of particles with a nominal size greater than 0.7 micron.

Approach 3 - Adopt a New Leaching Technique

The mechanical forces that act on oily waste during the TCLP tend to separate the oil from the substrate that was part of the original waste material or the inert material added in Approach 2. This leads to the formation of emulsions and/or free liquid phases which coat and clog the filters during the filtration step. Column leaching configurations that are less physically aggressive than tumbling can be used as the leaching model for oily wastes. The permeability of the waste material is the key property of the waste which must be controlled if a column technique is to work (permeability also impacts the efficiency of any extraction process). Use of inert sorbents, as in Approach 2, can provide the necessary permeability to allow for uniform flow of the aqueous medium through the waste bed and promote effective leaching. Uniform flow would be provided by pumping the leachant through the system.

Flow rates can be adjusted to minimize the shear forces which might dislodge oily material from the waste. Flow direction can be changed based on the density of the organic fluids. Downward flow for materials lighter than water and upward flow for materials heavier

than water will minimize the likelihood that oily material will separate from the substrate during testing. If the fluids do separate, they will not find their way into the leachate reservoir without passing through the substrate bed where they will re-deposit on the surface. Minimum flow volumes per unit mass of waste will become the operational control of the test rather than the tumbling time that is now used.

The dynamic flow conditions of the column test also allow for efficiencies in subsequent sample analysis. Modern solid phase sorbents for both organic and inorganic analytes can be placed between the pump outlet and the head of the column to collect and pre-concentrate the analytes for future analysis. The use of these sorbents also allows the introduction of "fresh leachant" to the top of the column of waste in a manner similar to the way fresh ground or surface water would contact the waste in the real world scenario. This would promote maximum release of the target analytes.

The column leach model proposed here resembles the real world case where ground or surface water percolates through oily material that adheres to the soil, more closely than does the tumbling action of the TCLP. The column leach approach can be extended to evaluate the attenuation of solubilized materials by a representative soil, by placing a soil layer in the same extraction column as the waste or by passing the leachate through a second column placed in series with the waste containing column. This allows for the development of a modular test sequence in which the same test used to characterize a waste leachate is used as the source term for attenuation studies, which may be conducted as part of a site-specific risk assessment. This strategy is in keeping with the SAB's recommendation to the EPA.

Approach 4 - Use a Totally Different Leaching Model

The current TCLP and the two options previously discussed are alternative physical models of the leaching process. Most problems resulting from these approaches center around sample handling, leaching, and filtering the leachate. To avoid some of these problems, the

Agency should consider using well-developed, existing theoretical and experimental models of the leaching of materials from oily matrices as well and the migration and interaction of the soluble components with soils. Both the EPA and the American Petroleum Institute (API) have published significant papers on the approach[7,8,9,10,11]. There is ample experimental evidence that these models are a good first order approximation of the amounts material actually found from aqueous leaching of oily materials. They apply to both oily solids and flowable oily materials. The models depend on the amount of the target analyte present in the waste, the analytes physical/chemical properties, and the chemical properties of the soil. Some of the more important features of these models are discussed below.

The American Petroleum Institute (API) published a review of historical data relating fuel composition to the aqueous solubility of its various components[7]. The review investigated the relationship between the solubility of the pure hydrocarbon components in water and the amount found in aqueous solutions that had been allowed to equilibrate with fuels (1:10 fuel/water ratio). The study defined the partition coefficient for this process K_{fw} by equation 1:

$$K_{fw} = \frac{C_f}{C_w} \qquad (1)$$

where: C_f = concentration of the component in the fuel, g/L
C_w = concentration of the component in the water, g/L

This property is related to the solubility of the pure component in water, S, for a group of six aromatic compounds by equation 2 which has a correlation coefficient of $r^2 = 0.99$:

$$\text{Log } K_{fw} = -0.884 \log S + 0.975 \qquad (2)$$

As should be expected, the relationship between S and K_{fw} is a function of the class of organic compounds being considered (aromatic, aliphatic, olefinic, etc.). When six additional compounds, one aromatic, two olefinic, and three aliphatic, were considered, the best fit equation describing the relationship between S and K_{fw} became

$$\text{Log } K_{fw} = -1.018 \log S + 0.706 \qquad (3)$$

and the correlation coefficient, r^2, dropped to 0.87. Table 1 compares the experimental data for eleven of the compounds for which data was experimentally determined with the data derived from equation 3. Most of the data compare favorably with the normal range of allowable differences between replicate analytical determinations.

TABLE 1

Comparison of Observed and Estimated Hydrocarbon Concentrations from a Standard Gasoline in Equilibrium with Water (1:10)

HYDROCARBON	CONCENTRATION	
	OBSERVED	ESTIMATED
Benzene	58.7	58.8
Toluene	33.4	37.8
2-Butene	2.4	3.2
2-Pentene	2.4	1.7
Ethylbenzene	4.3	3.2
o-Xylene	6.9	4.7
m-Xylene	11.0	9.2
Butane	2.7	5.2
1,2,4-Trimethylbenzene	1.1	1.8
2-Methylbutane	3.7	6.2
Pentane	1.0	2.2

This type of model works well for those cases where the oily waste matrix is the primary determinate in the partition coefficient in the matrix/water distribution. The 1984 API report discusses the situation where the amount of oil is very small compared to the total mass of organic carbon in the soil/sediment/waste matrix and in effect represents oil absorbed on soil[6]. Equation 4 applies to these situations.

$$K_p = (K_{oc})(f_{oc}) \tag{4}$$

where: K_p = soil/water partition coefficient
K_{oc} = the organic carbon partition coefficient
f_{oc} = weight percent organic carbon in the substrate.

The organic carbon partition coefficient, K_{oc}, is related to the octanol water partition coefficient, K_{ow}, by equation 5.

$$\text{Log}K_{oc} = \log K_{ow} - 0.317 \tag{5}$$

These models are based on the physical and chemical properties of the target analytes and the substrates with which they are associated, be it a flowable liquid, solid waste, or soil. Accurate and precise methods exist for experimentally determining the input variables to the models. These variables include but are not limited to:

- analyte concentration in total waste,
- percent organic carbon in soil or waste matrix,
- partition coefficients (fuel/water, soil/water, octanol/water), and
- water solubility of target analytes.

As the data base is expanded, relationships among classes of organic compounds, water, soils, and wastes will emerge. These relationships will lead to better empirical and theoretical understanding of the physical and chemical factors controlling the release of materials to the environment. New materials can be evaluated without detailed experimental studies by analogy with similar compounds, wastes, and soils.

Use of this type of approach helps fulfill the SAB's recommendation that more rigorous scientific procedures be used to determine the potential for release as well as environmental impact. This approach also meets the recommendation that rugged tests that are less susceptible to waste matrix effects be used. The approach also uses many of the same parameters used in determining fate and transport and important measures of environmental risk; therefore, a more unified model of environmental impact can be developed.

ROLE OF THE EPA AND PUBLIC SECTOR GROUPS

The EPA can serve as a catalyst for the necessary research studies for needed to improve and develop reliable analytical methods. EPA also can lead in measuring the important physical and chemical properties, of the analytes, wastes, and soils, that define analyte behavior in the environment. Members of the public sector can contribute laboratory support and technical expertise to developing the necessary methodology and demonstrating the applicability and ruggedness of the methods.

These workshops are an ideal expression of how this should work.

APPENDIX C:

CHARACTERIZING HETEROGENEOUS MATERIALS

CHARACTERIZING HETEROGENEOUS MATERIALS: INTRODUCTION

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BACKGROUND

Throughout the RCRA and CERCLA programs, one is faced with the task of characterizing a material to determine if it possesses some property of concern or interest. Types of questions one may be answering include:

- Is the material hazardous?
- Can it be safely or successfully managed using a specified treatment technique?
- How much supplemental fuel might I have to add to incinerate the waste?

PROBLEM

When the material being characterized is homogeneous, conventional sampling and subdividing approaches can be employed. For example, take the case of a truckload of used foundry sand whose average phenol concentration is of interest. The material is in the form of relatively fine particles. Conventional compositing and subsampling will provide relatively small representative samples whose average composition is very close to that of the whole load. The actual task of obtaining each subsample from the appropriate point in the truck may be very difficult, but the approach used is relatively straightforward.

However, what happens when one is faced with a heterogeneous material? When we speak of heterogeneity, we need to keep in mind that this is a relative term and is a function of the objectives of the characterization and the analytical sample size. The concern of today's workshop is generally with wastes of such various particle size, waste consistency or extraordinary concentration gradients that the sampling and analytical objectives cannot be met using traditional approaches and standard techniques. When it is not possible to obtain a representative sample, what shall we do?

This is an important and difficult problem. It is one that has been of concern to many organizations involved in waste management. For example, in March 1991, the Environmental Protection Agency, the Department of Energy, and ASTM's Committee D-34 conducted a workshop to examine how to characterize heterogeneous wastes that were also contaminated with radioactive materials. A report has recently been issued that describes the results of the workshop[1]. However, many problems and issues remain to be addressed and we have convened today's workshop to address some of the issues.

We would like your help with addressing the following specific issues.

Identify characterization situations that present difficult problems (generically identify both the type of material and situation).

- Develop specific guidance laying out the process to be used to adequately and cost-effectively address the problem. Describe what criteria should be used to guide development of solutions/approaches to specific problem situations. Please be as quantitative as possible on when trade-offs may need to be made and how to select among options.

- If research work needs to be done to develop a solution, please identify what work needs to be done.

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[1] Characterizing Heterogeneous Wastes: Methods and Recommendations, EPA/600/R-92/0, February 1992.

- Since EPA would like to solve monitoring problems through cooperative ventures, what form should a cooperative development program take? How can it be organized? Who might the cooperators be?

If you think of any ideas, information, or suggestions that you feel the Agency should consider when addressing this issue, please send them to us. Send your comments to:

David Friedman (RD-680)
US Environmental Protection Agency
Washington, DC 20460

We will need to receive your comments by August 21, 1992 in order for them to be incorporated into the final conference report.

CHARACTERIZING HETEROGENEOUS MATERIALS: REGULATORY PERSPECTIVE

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INTRODUCTION

Characterization is the process used to determine whether solid waste is also a hazardous waste. Characterization is arrived at by following "testing structure." A testing structure is the particular sampling, analysis, and data interpretation steps that are employed to measure a waste. The purpose of this paper is to examine the testing structure used to measure characteristics (ignitability, corrosivity, reactivity, and toxicity) of heterogeneous solid waste that would make it hazardous waste as defined in 40 CFR part 261.21-24.

To date, there has been little progress in developing a testing structure to characterize heterogeneous waste. EPA regulations state that characterizing waste includes determining the average property of the "universe or whole", 40 CFR part 260.10. The problems with the regulations are that "average" lacks scientific validity and "universe or whole" is not defined. These two items are an integral part of the testing structure.

To address these problems, two areas must be explored: 1) policy, regulations, and guidance issues and 2) scientific concerns. This paper focuses on heterogeneous solid waste because it is a worst case scenario. A testing structure that works for heterogeneous solid waste will work for any solid waste.

POLICY, REGULATIONS, AND GUIDANCE ISSUES

Many problems with characterization of heterogeneous materials under RCRA can be traced to the definition of what type of sample must be collected and analyzed. The required sample is a "representative" sample which is defined in 40 CFR part 260.10. "representative sample means a sample of a universe or whole (e.g., waste pile, lagoon, ground water) which can be expected to exhibit the average properties of the universe or whole." At least two problems arise with this definition: what is the average property and what is the universe or whole?

Average

Does average signify the arithmetic average or the "most likely result" of the target population? To illustrate, if the data points are 5.7, 5.7, 5.8, 5.9, and 0.2, the arithmetic average is 4.7. If the regulatory limit is 5.0, the best point estimate of the average is that it is below the regulatory limit. However, if confidence intervals were required, there would be little confidence in this conclusion.

If average, however, signifies the "most likely result" (the point at which one half of the values are above or below--the median) one would conclude that 80% of the data points are above the regulatory limit. This conclusion is also an expression of a higher degree of confidence than the conclusion with arithmetic average. More of the values agree with this conclusion (4 of 5 are above the limit) than agreed with the conclusion based on arithmetic average (1 of 5 were below the limit).

With the arithmetic average approach, it is possible to have well over half the population above the regulatory limit and still achieve compliance. With the "most likely result" approach, not more than one half of the population can be above the regulatory threshold and be in compliance. The "most likely result" is sometimes referred to as "attribute" testing. An

attribute testing structure enables one to conclude if a waste is or is not hazardous--not the degree of hazard.

For clarification of what is meant by average, the Agency provided Chapter Nine of "Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods" (SW-846). This guidance suggests that average signifies the arithmetic average.

A problem with this definition can be illustrated by the following scenarios. One of the RCRA characteristics is ignitability which includes analyzing samples for flashpoint. The characteristic is present when the waste flashes at a temperature less that 60° C. In many cases a number is not recorded, only the presence of a flash. The regulations do not state that a waste which flashes at 10° C is any more hazardous than one that flashes at 59° C. This logic fits well with "most likely result" or percentage (which does not require numeric results), but is inconsistent with the arithmetic average. With ignitability testing sometimes the analysis produces numbers and other times it does not. Without numbers, arithmetic averages can not be calculated, but the "most likely result" can be determined. Another characteristic is corrosivity which can be determined by pH. Several pH values cannot be averaged to determine the average property of a waste. First of all they are log values and adding them to derive an arithmetic average is actually a multiplication, thus yielding the wrong information. Furthermore, from chemical principles, the final pH depends on the buffering capacity of the individual components. If a waste in question has pH measurements of 2 and 4 (the regulatory limit under RCRA is 2.5), it is incorrect to conclude that the average pH is 3 and therefore the waste is not hazardous. Arithmetic average is also not scientifically valid for either toxicity or reactivity.

Alternatively, the "most likely result" approach will produce valid results for each RCRA characteristic test. If five samples were randomly selected from a waste and four flashed, then 80% of the samples exceeded the regulatory limit. If "most likely result" is synonymous with greater than 50%, then the conclusion that the waste is hazardous can be made with confidence.

Universe or Whole

The waste population to be characterized is not defined in the regulations. If the "universe or whole" is undefined with respect to both temporal and spatial requirements, it is not possible to design a valid testing structure. This is illustrated through some of the following scenarios.

If there are several piles of waste, must a decision be made for each pile or for the whole of all the piles. What if one pile is above the regulatory limit and the other pile is below? What if several piles are below the regulatory limit, but a few are above? What if the average is below; are any of the piles hazardous?

What if the average property of a pile is below the regulatory limit? Some portions of the pile could be above the limit, and others below. What if the portion of the pile above the limit was loaded into a truck to be hauled to a non-hazardous waste landfill and this was sampled? Is this waste which was not hazardous in the pile now hazardous when in the truck?

What if the waste produced today is above the regulatory limit, but the waste produced yesterday and the waste produced tomorrow is below the regulatory limit, is the waste below the regulatory limit on average or not?

"Universe or whole" must be defined or it is impossible to know where to sample and how to interpret the results.

SCIENTIFIC CONCERNS

While it is always possible to sample, analyze and produce data for any waste, the problem with heterogeneous materials is the confidence that a correct compliance decision was made based upon a valid testing structure. A compliance decision is affected by the purpose of

the measurement, use of proper sampling and analytical methods, and correct interpretation of the results. The variability within heterogeneous materials exacerbates the bias and imprecision of the results. As bias and imprecision increase and the average approaches the regulatory limit, compliance decisions become more difficult. If, however, the proper testing structure was employed, it would dramatically improve the decision making process and increase the confidence in the results.

A proper testing structure should have the following characteristics:

It must be scientifically valid. Basic scientific principles must not be violated. There are instances where the ideal scientific solution can be adjusted for simplicity, politics, and economics, but the solution must remain scientifically valid. Agency regulations, policy, and guidance must never be inconsistent with basic scientific principles ("Safeguarding the Future: Credible Science, Credible Decisions", EPA/600/9-91/050).

It must be consistent. All elements of the testing structure are dependent on each other for their validity. Sample collection must anticipate the analyses and data interpretation to be performed to ensure that the proper samples are collected. Likewise, without detailed knowledge regarding sample collection, data interpretation is meaningless.

Proper Sampling

Proper sampling primarily depends on the regulatory question (e.g., presence, trends, absence, etc.), the universe or whole (population), and the confidence that the correct compliance decision can be made. These three considerations--question, population, confidence--must be definitively addressed before a sampling plan is developed and implemented.

Proper Analysis

Proper analysis for RCRA characteristics is not an issue, because three of the four characteristics have required test methods referenced in the regulations (reactivity methods are only guidance at this time). The correct analytical result is the one obtained by following the prescribed analytical method.

Proper Data Interpretations

Proper data interpretation is important for making correct decisions. Data interpretation ties the analytical results back to the population with some specified degree of confidence to determine if the sampling and analysis answered the question about the waste. Proper data interpretation includes:

Making the proper type of confidence statement. The statement does not need to be statistical; it can be an expression of professional judgment. If statistical statements are made one must recognize that there are many types (e.g., confidence interval of the mean, tolerance limits, prediction intervals, etc.). Not all statistical statements are valid for any particular compliance problem and care must be chosen to select the correct one.

Establishing degree of confidence in the statistical statement. It is possible that one can make a certain statistical statement (or use professional judgment), but if one is not very confident in the statement it serves no purpose proving compliance or non-compliance.

With many types of statistical statements, certain assumptions are made regarding the distribution of the data. If incorrect assumptions are made, the resulting statistical statement and degree of confidence might not be correct. The guidance given in SW-846 makes certain assumptions regarding the distribution of data (normally distributed) which are usually incorrect. By definition, heterogeneous waste (as well as most environmental data) defies these assumptions

to a degree that can make the decision and confidence statements based on arithmetic average incorrect. The usual indicators of non-normal data are outliers and skewed distributions. With the "most likely result" no distribution is assumed (non-parametric) and therefore the problems with heterogeneous waste do not affect the accuracy and confidence of the decision.

CONCLUSIONS

Characterization of heterogeneous waste depends on the development on a valid testing structure. Currently, only portions of the testing structure are in place. Two items that need to be addressed are:

The "most likely results" (percentage) is the valid statistic for making compliance decisions to characterize waste. The current use of arithmetic average is scientifically invalid for the RCRA characteristics and can lead to wrong compliance decisions. There are at least two percentage options that currently exist in the RCRA regulations. One is the empty drum regulation (40 CFR part 261.7) which states that drums with a capacity of less than or equal to 110 gallons are considered empty if no more than 3% is left (and the contents have been removed using common practices). Drums with a capacity of greater than 110 gallons are allowed 0.3%. The other percentage option is found in the Land Ban regulations (49 CFR part 268) which requires that no more than 1% of the population can be over the treatment standard.

With this new system, the Agency must decide what percentage of the waste it will allow to be over the regulatory limit and still classify the waste as non-hazardous. To be the most protective of the environment, 0% should be adopted although it is probably an unrealistic standard.

"Universe of whole" must be clearly defined. This is not a scientific issue, but rather a policy issue, The term requires clarity and specificity as to both time and space. Some

examples might be: one day of production, one week of production, one pile, all piles currently on the property, 100,000 Kg, etc. Defining "universe or whole" as one waste stream would ignore the temporal problems. Without knowledge of exactly what the waste population is in terms of both time and space, it impossible to develop a testing structure to characterize it.

HETEROGENEOUS WASTE CHARACTERIZATION: INDUSTRY PERSPECTIVE

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INTRODUCTION

Heterogeneous as defined by Webster in the context of a waste is "consisting of dissimilar or diverse ingredients or constituents". The complexity of this issue is illustrated with a drum of heterogeneous waste in figure 1.

Characterization of heterogeneous wastes presents a number of unique challenges for the industrial community. The principal challenges are: sampling, methodology of analysis, frequency of testing, and controlling/ reducing costs.

SAMPLING TECHNIQUES

Routine sampling techniques consisting of sample segregation, compositing,and particle size reduction are often inappropriate when trying to homogenize a heterogeneous waste. Collecting the sample can become a formidable task when the waste is comprised of multiple large particle size components. SW-846 sampling containers often are not suitable for sample containment and larger vessels are required. Loss of volatiles due to headspace in the vessels affects the validity of the results. Present particle size reduction techniques such as grinding only exacerbates the problem by driving off volatiles.

TESTING REQUIREMENTS AND PROCEDURES

State and Federal regulations often require extensive testing protocols in Waste Analysis Plans (WAPs) and permits. Regulators routinely require the use of SW-846 analytical methods. These methods often are not appropriate for a variety of waste streams (organic solvents, oily wastes, by products of recycling such as distillation bottoms). The use of methods other than SW-846 should be accepted for alternative test procedure approval and not rejected on the sole basis they are not SW-846. Most of the quality assurance/ quality control principals and guidelines can be incorporated into alternative test methods resulting in improved data with only procedural and or hardware modifications. Unfortunately these methods are not considered valid by regulators.

The present sampling and testing requirements fail to consider the volume and frequency of the waste being handled. It is extremely costly to test every fifty-five gallon drum according to SW-846 guidelines, while testing every incoming rail car might be feasible. Current sampling frequencies often overlook one of the key issues facing a heterogeneous hazardous waste handler, that being, the end use of the waste. If small volumes of wastes are going to be mixed with other wastes for processing in terms of recycling, and the facility is permitted to handle the waste, the result will have no impact on the process, thus, sampling and testing need to reflect the use of the waste while providing a safe working environment. The product of the process should become the focus of testing.

Continuing the status quo will drive many companies out of business and create large companies which will monopolize hazardous waste handling while passing the costs on to the generator and ultimately the consumer. This is due to the excessive costs associated with testing every handled waste. Multiple testing of the same waste is redundant and provides no greater assurance of safety, process control, product quality.

CONCLUSIONS: DEVELOPING ALTERNATIVES

Recognize Alternative Test Methods

State and federal regulators must become accepting of industry generated methods of analysis for complex waste streams handled on a daily basis.

Develop New Methods

EPA in conjunction with industry should work together to facilitate the rapid development and approval of new methods. This could be accelerated by using industry developed methods.

Encourage Recycling

Recycling needs to be encouraged by minimizing input testing and focussing on by-products of the process. When a facility is fully permitted to handle wastes, analysis does not affect the processing or end use. This adds unnecessary costs to the recycling process through testing of incoming, in process, and final products.

Account for End Use

Prescribing testing must account for the end use of the waste. Some end uses such as alternative cement kiln fuel present minimal hazards, thus testing should be relevant to the waste destination.

Balance Cost with Severity of Hazard

The health and safety models need to be incorporated into the testing protocol by focussing on hazards and not over testing of materials that pose little or no threat.

Obstacle to Implementation

The largest obstacle for implementation of the above alternatives is the magnitude of the number of individual state regulators with differing view points. The result of negotiating fifty different WAPs in fifty states poses limitations on industries ability to comply fully at all times. It is impossible for a business to operate fifty different ways on the same type of waste stream.

REFERENCE

Characterizing of Heterogeneous Wastes: Methods and Recommendations; EPA 600/R-92/033, Feb. 1992

CHARACTERIZING HETEROGENEOUS MATERIALS: SCIENTIFIC PERSPECTIVE

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INTRODUCTION

A discussion of heterogeneous waste characterization is best started with a brief review of definitions.

Sample: a part or piece taken or shown as representative of a whole group. (Webster's Unabridged Dictionary, Second Edition)

Sampling: the act, process or technique of selecting a suitable sample. (Webster's 7th Collegiate Dictionary)

Representative Sample: A sample of a universe or whole (e.g. waste pile, lagoon, ground water) which can be expected to exhibit the average properties of the universe or whole. (CFR 260.10)

Homogeneous: uniform structure or composition throughout. (Webster's 7th Collegiate Dictionary)

After studying the above definitions and applying them to waste characterization, it becomes apparent that sampling of an ideal homogeneous waste will always result in a sample that represents the properties of the waste (assuming that the sampling process itself does not introduce contamination or allows for selective loss of waste components).

Heterogeneous: consisting of dissimilar ingredients or constituents. (Webster's 7th Collegiate Dictionary)

Unfortunately, many of the real-world wastes are not homogeneous, but are heterogeneous, which makes collection of a representative sample a challenging task. Prior to discussing the representativeness of heterogeneous wastes, the following points can be made regarding homogeneity and heterogeneity.

- Homogeneity and heterogeneity are diametric terms.
- Homogeneity and heterogeneity are relative to objectives.
- Homogeneity and heterogeneity are related to spacial and temporal distribution.
- Homogeneity and heterogeneity are sample size dependent.

A determination regarding the homogeneity and heterogeneity of a waste is made by comparing the visual, physical or chemical composition or properties of different samples. The more heterogeneous a waste is, the less homogeneous it is and vise-versa. Thus, when either the homogeneity or heterogeneity of a waste is defined the other is also defined. This relationship should be kept in mind, since for the sake of readability, the remainder of this discussion will often refer to only one term.

Heterogeneity is relative to objectives and perspective. A non-random mixture of fine silver nitrate powder and large crystals of silver nitrate will be considered to be heterogeneous by the analyst performing particle size determination while the analyst performing the TCLP for lead would consider the material homogeneous. Likewise, while the chemical properties of 99.99999% pure uranium are homogeneous, a nuclear chemist may consider it highly heterogeneous on an isotopic level.

The spacial or temporal distribution of dissimilar waste constituents or concentrations gradients can also affect the measured heterogeneity of a waste. If a representative distribution is spread over a greater area or length of time than that represented in a sample, then sample to sample heterogeneity will be greater than when a sample encompasses the distribution of the dissimilar waste components or concentration levels. For example, the measured heterogeneity of an effluent, whose concentration of phenol linearly cycles from 100ppm to 5ppm and back to 100ppm every two minutes, will be a function of what portions, or if the entire cycle is included in sequential samples.

Assuming that the concentration of the target parameter varies with particle size, sample to sample heterogeneity will depend on whether a sample is not only large enough to accommodate all the different sized constituents of a material but will also depend on whether the sample is large enough to accommodate representative amounts of the various sized constituents of a waste. To better understand this concept consider a 2 liter waste container that has one gram nuggets of cadmium randomly distributed through-out an otherwise homogeneous and cadmium free matrix. If one gram samples are collected and analyzed for cadmium, the sample to sample heterogeneity of the waste will vary dramatically and will depend upon whether the sample did or did not contain a cadmium nugget. However, the heterogeneity will appear to be substantially less if 30 gram samples are collected and analyzed in total for cadmium. Thus the measured heterogeneity of the same waste varies according to the size of the sample. That is why for the following discussion, unless otherwise indicated, the sample size used to determine heterogeneity of a waste will be the analytical sample size. Heterogeneity of a waste will be measured according to the ability of an *unaltered analytical sample* to reproducibly represent the average properties and/or chemical constituents of the waste unit of interest. (The *analytical sample* is the mass/volume of sample submitted to analysis not the field sample, e.g. the 1 to 2 gram sample required by the acid digestion specified in Method 3050 . *Unaltered* means that the sample was not subjected to homogenization or pulverization steps. A *waste unit* is the population or unit of waste that is being subjected to evaluation, e.g. drum, a wastepile or landfill).

Representative Database: a database, generated by the collection and analysis of more than one sample, which together represent the average properties of the universe or whole.

It is often impossible to collect a single sample which is representative of a heterogeneous waste. The average properties of a heterogeneous waste are better represented by collecting a number of waste samples such, that all portions of the waste under study have an equal chance of being sampled. Analyses of these samples can be compiled into a database which should be representative of the waste. It is more correct to think of a representative sample in terms of a representative database, which is closer to the statistical use of the term, sample.

In light of all the attention directed towards heterogeneous waste, it is important to note that from a sampling perspective, the significance of heterogeneity is not in this quality, itself, but in the fact, that heterogeneity hinders or prevents the generation of a representative database. The need for representativeness is the driver behind the interest and studies into heterogeneous waste characterization.

Random: being a member of , consisting of, or relating to a set of elements that have a definite probability of occurring with a specific frequency; being or related to a set whose members have an equal probability of occurring. (Webster's 7th Collegiate Dictionary)

Randomness is a critical factor in the characterization of hazardous waste. Accurate characterization requires that the sampling process reflect the randomness or lack of randomness of the waste. If the waste parameter of interest is distributed in a random fashion a proper randomly designed sampling program should generate a representative set of samples. If the waste parameter is not randomly distributed (refer to discussion of strata in the following section) then a simple random sampling plan may not accurately characterize the waste.

TYPES OF HETEROGENEOUS WASTE

If the average properties of the waste unit of interest is not reproducibly represented in analytical samples, then the material is considered heterogeneous. Such heterogeneous wastes can exist in many forms;

RANDOM HETEROGENEOUS

- Randomly heterogeneous in composition/property.
- Randomly heterogeneous in particle size.
- Randomly heterogeneous in particle size and composition/property.

NON-RANDOM HETEROGENEOUS (STRATIFIED)

- Non-randomly heterogeneous in composition/property.
- Non-randomly heterogeneous in particle size.
- Non-randomly heterogeneous in particle size and composition/property.

EXCESSIVELY NON-RANDOM HETEROGENEOUS (EXCESSIVELY STRATIFIED)

- Excessively non-randomly heterogeneous in composition/property.
- Excessively non-randomly heterogeneous in particle size.
- Excessively non-randomly heterogeneous in particle size and composition/property.

Assuming that all particle sizes in the waste can be accommodated by the analytical sample size and that the analytical method is applicable to all waste constituents, then randomly

and non-randomly heterogeneous waste can be characterized by a database generated from the collection and analysis of random or systematic samples. Regarding non-randomly heterogeneous waste a more precise estimate of mean (representative) concentrations can be obtained with a stratified sampling approach.

Excessively non-random heterogeneous wastes are defined as those wastes that have such dissimilar components, that it is not practical to use traditional sampling approaches to generate a representative database. Nor would the mean concentrations reflected in such a database be a useful predictor of a given subset of the waste that may be subjected to evaluation, handling, storage, treatment or disposal, (i.e. the level of uncertainty is too great).

Stratum: a portion or subgroup having a consistent distribution of the target parameter, and a different distribution than the rest of the waste.

Waste strata can be thought of as different portions of a waste population, which may be separated in time or space or by waste component, and each portion has internally similar concentration distributions of the target parameter, through-out. A landfill may display spatially separated strata, since old cells may contain different wastes than new cells. A wastepipe may discharge temporally separated strata, if night shift production varies from the day shift.

There are wastes which do not display any identifiable temporal or spacial stratification, yet the target compound distribution is excessively erratic. For these wastes it may be helpful to consider a third type of stratification - stratification of the waste by waste component.

Component: A waste component is any identifiable article, discrete unit or constituent of the waste, which is randomly or non-randomly distributed through-out the waste.

Stratification by waste component is easily applied to wastes that contain easily identifiable particles such as large crystals or agglomerates, rods, blocks, gloves, pieces of wood, concrete, etcetera. Strata separated by waste component is a different but key concept. Separating a waste into strata according to waste components is useful when a specific kind of waste component is not randomly distributed through-out the waste and when a contaminant or property of interest is correlated with the waste component. This type of strata is different since the components are not necessarily separated in time or space but are usually intermixed and the properties or composition of the individual components are the basis of stratification. For example, automobile batteries which are mixed in an unrelated waste would be a waste component which could constitute an individual strata if lead was a target parameter. If one were to sequester the batteries they would have a consistent distribution which was different from the rest of the waste. However, if the concentration of the target parameter is similar in different components and the particle size is such that all the components are represented in the chosen sample size, then there is no purpose in stratifying by waste component. Strata by component is an important mechanism for understanding the properties of excessively non-random heterogeneous waste and for designing appropriate sampling and analytical efforts for these types of waste.

Table 1 summarizes mechanisms for segregating strata as well as the discriminating qualities of strata. Since the mechanism and qualities are independent of each other there are a total of 9 possible types of stratified wastes.

TABLE 1. Strata Considerations

Mechanism for Segregating Strata	Discriminating Qualities
Spacial	Composition/Property
Temporal	Particle Size
Component	Composition/Property and Particle Size

The contamination in different strata are often generated by different processes. The different geneses of the contamination will usually result in a different concentration distribution and mean concentrations. Thus, each strata will have their own distribution and mean concentration levels. If a waste having strata of distinctly different concentration distributions is sampled using a simple random sampling approach, the concentration distributions of the different strata may result in a bi-modal or multi-modal distribution. Homogeneous and randomly heterogeneous waste, which are not stratified will display a normal unimodal distribution. See Figure 1.

Non-randomly heterogeneous waste will usually have a limited number of strata which can be identified and sampled individually or sampled as one waste. When different strata are sampled as one population, the properties of the different strata are averaged. If the different strata are similar in composition, then the average concentrations will be a good predictor of composition for subsets of the waste and will often allow the program objectives to be achieved. As the difference in composition between different strata increase, the average values become less useful in predicting composition/properties of individual portions of the waste, which may be handled separately. In this later case, it is advantageous to sample the individual strata separately and if an overall average of waste composition is needed, it is best calculated mathematically using statistical information from each strata.

Excessively non-random heterogeneous waste has numerous strata, each of which contain different distributions of contaminants and/or particle sizes, such that an average value for the

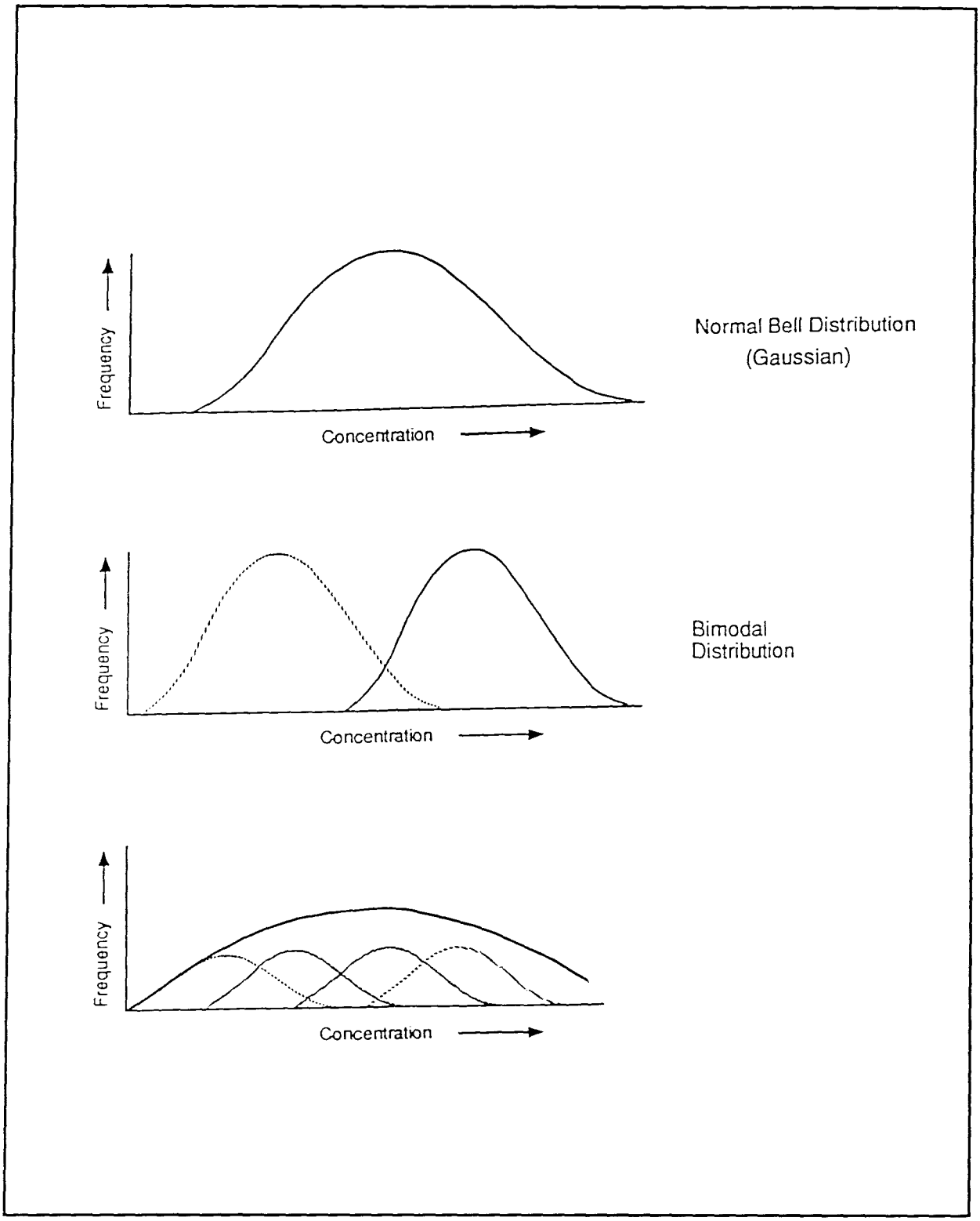

Figure 1: Types of Concentration Distributions

waste would not be useful in predicting the composition or properties of individual portions of the waste (i.e. statistically speaking the variance and standard error of the mean will be large). The line of demarcation between non-random heterogeneous and excessively non-random heterogeneous waste is not hard and fast. A waste can be considered excessively non-random heterogeneous when mean values will not be representative of most portions of the waste and when it is so heterogeneous that the waste cannot be cost-effectively sampled using traditional sampling approaches and meet the project objectives.

A theoretical example of an excessively stratified waste could consists of commingled waste from:

Source A - which generated a waste of varying particle size with a mean antimony concentration of 20ppb and a standard deviation of 7ppb.

Source B - which generated a waste of varying particle size with a mean antimony concentration of 7000ppm and a standard deviation of 5000ppm.

Source C - which generated a waste of varying particle size with a mean antimony concentration of 3% and a standard deviation of 2%.

Source D - which generated a waste of varying particle size with a mean concentration of 81% and a standard deviation of 17%.

To further complicate the above waste, imagine the waste being commingled with other materials of various particle size that may or may not contain various contaminants in addition to antimony.

To improve readability, the remainder of the document will refer to non-random heterogeneous waste as *stratified waste* and excessively non-random heterogeneous waste as *excessively stratified waste*.

Figure 2 presents a graphical depiction of the types of special distributions and heterogeneity. Letters are waste constituents which are identical to other constituents of the same letter in terms of the composition, property, or particle size of interest. Different waste constituents are designated by different letters.

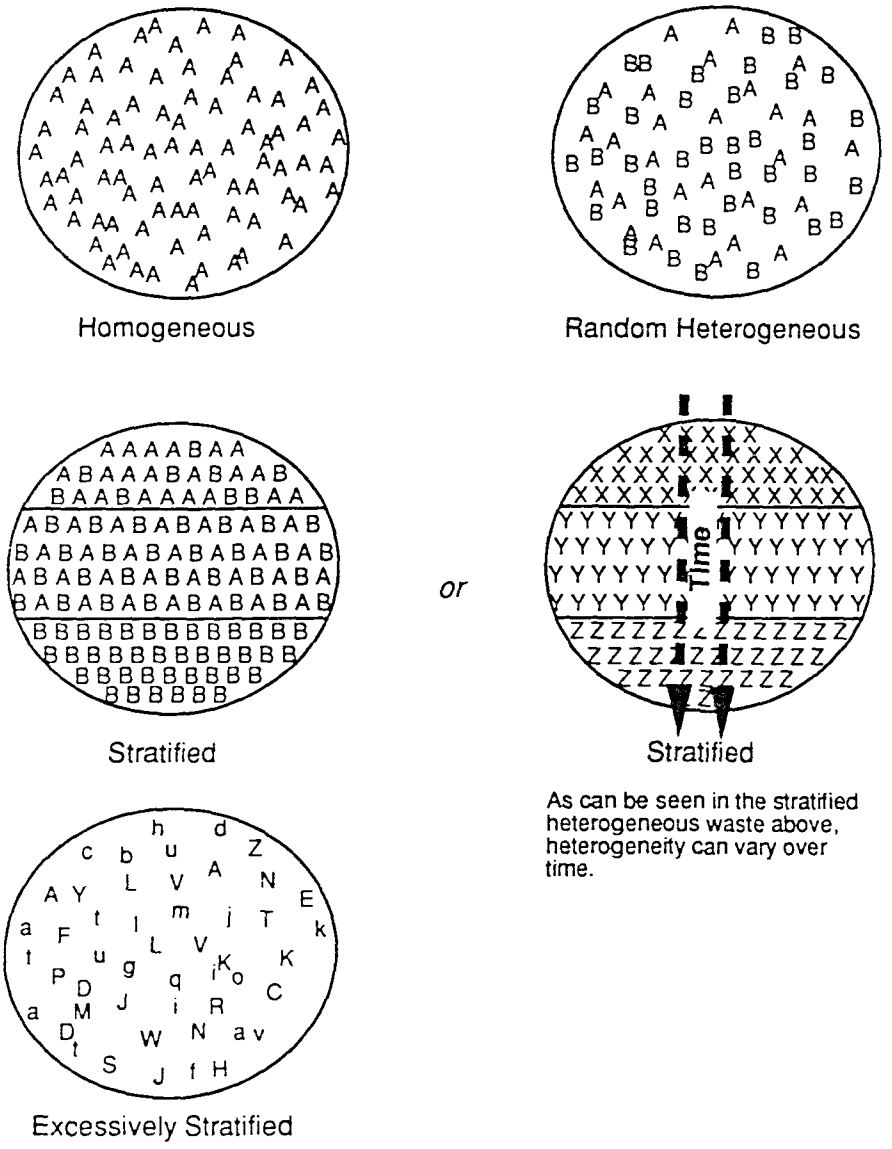

Figure 2: Types of Positional Distributions for a Waste Unit Such as a Landfill

This figure depicts the process by which a waste is classified as a particular waste type. This classification will be based upon knowledge of the waste, observations, or ideally - preliminary sampling of the waste.

If no significant variation is detected between random samples, the waste can be considered homogeneous. The waste is a heterogeneous waste if there is variation between individual samples.

If the waste constituents are randomly distributed through-out the waste, the waste would be a randmoly heterogenous waste. If information describes a correlation between waste variation and time or spatial variations or with certain waste components or particle size, then the waste would be classified as a stratified or excessively stratified waste. Wastes that can be cost-effectively sampled to meet project objectives would be classified as stratified wastes. Those wastes which consist of such strata that they cannot be cost effectively sampled are classified as excessively stratified waste.

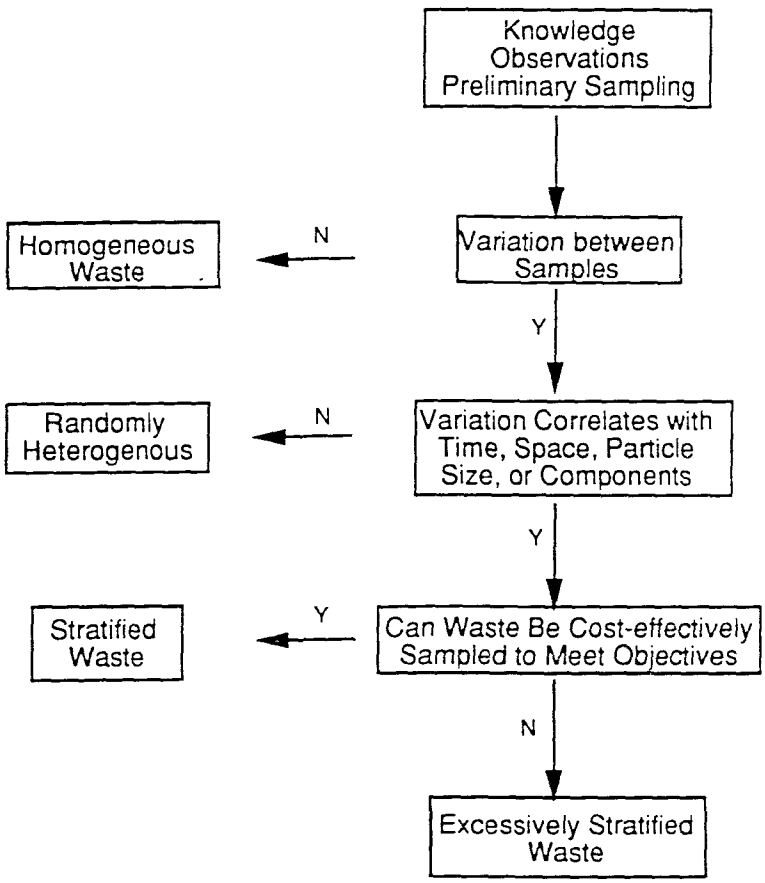

Figure 3: Process for Classifying Wastes

Table 2 details some of the issues and concentration distributions that are pertinent to the different types of heterogeneous wastes. For example, sample size, the number of samples and sample locations are not an issue when sampling a homogeneous waste, while they are critical issues when attempting to collect a representative sample of a heterogeneous waste.

PARTICLE SIZE AND SAMPLING THEORY

As a result of a continuing need to improve environmental data, it has been recognized that sampling is presently the greatest contributor to imprecision and inaccuracy. To minimize this error, many have correctly turned to the mining industry, which has a relative wealth of sampling theory and expertise. The theory and applicable expertise of the mining industry has recently been documented by a recognized expert on sampling, Francis F. Pitard, (Pitard, Francis F., "Pierre M. Gy's Sampling Theory and Sampling Practice, CRC Publishers). This theory, which not only applies to field sampling but also to subsampling performed in the laboratory - determines sample mass/volume as a function of the maximum particle size of the material being sampled..

Based on the maximum particle size of a material, sampling theory suggests minimum sample sizes (refer to Table 3.) and particle size reduction of the sample to minimize sampling error. For example, a waste having a maximum particle size of 0.5 inches would require collection and analysis of a minimum sample size of 2 Kilograms to keep the sampling error less than 17%. Since a 2 kilogram sample is too large to be subjected to analysis, it would have to be subjected to particle size reduction prior to analysis.

It would be very costly to routinely use existing sampling theory to minimize sampling error. These increased costs would be driven by the large sample sizes and the requirement to reduce particle size.

The large sample sizes, specified to minimize sampling error, would increase costs since;

- Sample containers and coolers would be larger and more numerous
- Larger samples would be shipped
- Larger sample storage and sample handling areas would be needed
- Large volume of unused samples would increase disposal costs.
- Health and Safety costs associated with exposure to larger samples.

Particle Size Reduction, (PSR), also has a substantial impact on cost because of the manpower and capital investment for the required crushing and pulverizing equipment. In addition the following are reasons for concern if particle size reduction was to be implemented on a large scale;

- Laboratory contamination from fines.
- Damage to instrumentation from fines.
- Difficulty in cleaning PSR equipment to prevent cross-contamination.
- Loss of volatile and labile compounds and elements.
- Generation of a sample which has different properties and thus yields different analytical results than the original sample.
- Increased Health and Safety Costs

Fortunately, the costs of employing large sample sizes and particle size reduction can often be minimized if the waste history and Data Quality Objectives are communicated to and discussed with the lab staff and field personnel.

TABLE 3. SUGGESTED SAMPLE SIZE BASED ON MAXIMUM PARTICLE SIZE ACCORDING TO PIERRE GY'S SAMPLING THEORY

SUBSAMPLE SIZE (grams)	MAXIMUM PARTICLE SIZE (centimeters)
1	.1
2	.13
3	.14
4	.16
5	.17
10	.21
20	.27
30	.31
40	.34
50	.37
75	.42
100	.46*

*The Toxicity Extraction Procedure and the Toxicity Characteristic Leaching Procedure allow samples to contain particles as large as .95 centimeters.

Waters and soils can be contaminated in numerous ways, the most common **mechanisms** being; direct discharge of the contaminant onto the soil or water and atmospheric fall-out from fires, fugitive emissions, vents and stacks. Soils can also become contaminated from adsorption of groundwater or surface water contaminants while waters can become contaminated by mixing with contaminated waters or by leaching contaminants from contaminated soils or wastes.

Wastes can be contaminated by many mechanisms during generation or by mixing with other wastes or further contaminated by the mechanisms described in the previous paragraph. The different **types of contaminants** are aqueous liquids, non-aqueous liquids, gases, small to large particles and multi-phased mixtures.

How a contaminant will be dispersed in the matrix will be determined by the mechanism of contamination, the type of contamination, the surface area and adsorptive properties of the sample matrix, gravity, physical manipulation and the physical size of the contaminant at the time of contamination. (Eventually, fate and transport will substantially affect dispersion of contaminants.) The physical size of the contaminant can be referred to as the **contaminant** unit and can be measured in centimeters. Liquids, dissolved contaminants and gases have a contaminant unit on a **molecular** or **atomic level**, (e.g. atoms can be on the order of 1 X 10-8 centimeters in diameter). Solids and suspended solids contaminate on a **microscopic** to **macroscopic** level, (i.e. their Contaminant Unit is equal to their particle size).

Particle size can have an impact on sampling error even when the contaminant unit is on the atomic scale, if matrix particles are of different sizes and have different adsorptive properties. If adsorptive properties are similar for different size particles, then the dramatically larger surface area of smaller particles/volume would result in more atomic scale contaminants being adsorbed to smaller particles. (Thus one could eschew particle size reduction, (PSR), and still employ a smaller subsample size by excluding large particles, if the ease of using a smaller sample size out-weighed the chance of a false-high concentration.)

When the contaminant unit is on a larger, particle scale then adsorptive properties of the matrix will not affect contaminant distribution in the sample. For microscopic and macroscopic particles, an accurate representation in the subsample will be affected by the number of particles and the relative size of the particles to the subsample size. Microscopic particles will have a contaminant unit substantially smaller than the sub-sample size and these small particles should not be discriminated against during subsampling.

When the contaminant unit is macroscopic and approaches the size of the sample, the error in sampling will increase, if large sample sizes or PSR is not employed. If the largest particle size in the sample correlates with the contaminant unit, then the large sample size specified by sampling theory pertains to the waste. As the contaminant unit becomes smaller as

compared to the size of the sample, the greater the opportunity to avoid PSR and to selectively exclude larger particles from the sample without introducing substantial error., (If desired the weight of the excluded particles can be used in the calculation of a final concentration. However, this could result in a false low result, since the contamination, if any, associated with the large particles is not accounted for.)

The mechanism of contamination, the type of contaminant and the contaminant unit will impact the complexity and potential error of sampling. These impacts may be better understood by reading the following examples.

Example 1

TYPE OF CONTAMINANT: Particles contaminated with lead

MECHANISM: Direct discharge of particle to soil

CONTAMINANT UNIT: Particles as large as 0.3 centimeters

AVERAGE LEAD CONCENTRATION: 10ppm

HISTORY: A manufacturer of lead-alloy babbitt lining for bearings, stored its machining waste in piles behind it facility. Periodically the machining wastes would be recycled into new babbitt linings. After 50 years of employing this practice, the soil became contaminated with particles of babbitt having a maximum particle size of 0.3 centimeters. The contaminated soil consisted mainly of fine silts with less than 10% consisting of gravel with stones having diameters ranging from 2 to 3 inches. The sampling team uncovered a problem when they referred to the specified "minimum sample size" for 3 inch particles (i.e. 450kg). The problem of large sample size was avoided, since the sampling team was aware of the "Type of Contaminant" and the "Mechanism" of contamination and the "Contaminant Unit". Knowing that lead contaminated particles were discharged directly to the soil, the sampling team was able to discard the large stones with the realization that by discarding the stones, the resulting lead concentrations would be a worst case. (The small lead contaminated particles would preferentially exist in the fine silts as opposed to being adsorbed to the large stones and if lead had dissolved, the dissolved lead would tend to adsorb to the silt which has the much larger surface area.) The sampling team collected approximately 250 mls of soil and delivered them to the laboratory for analysis.

The analyst referred to sampling theory (refer to Table 3.) and determined that the minimum sample size for a sample with a maximum particle size of 0.3 centimeters was 30g. (The small percentage of larger gravel was not used to determine the maximum particle size.)

The analyst split the sample into 30g aliquots and randomly chose one for analysis. Since the analyst did not have particle size reduction equipment and the largest sample volume he could analyze was approximately 10 grams, he split the chosen aliquot in thirds and analyzed all three for lead. After analysis, the concentrations were averaged.

Example 2

TYPE OF CONTAMINANT: Ionic lead dissolved in an aqueous solution (Atomic scale)

MECHANISM: Direct discharge to soil

CONTAMINANT UNIT: Atomic scale, (approximately 1 X 10-8 centimeters for atoms and somewhat larger for ion diameters)

AVERAGE CONCENTRATION: 10 ppm

HISTORY: The above described babbitt manufacturer also employed an acid-treatment process. The aqueous waste was discharged into a tank which allowed the lead contaminated water to leach into the surrounding soils. The surrounding soils consisted of fine silt with 15% of its volume consisting of stones ranging in size from 0.25 to .5 inches. The sampling team collected a 2 Kilogram sample to minimize the sampling error. The samples were sent to the laboratory for analysis. Since the analyst knew that the soil was contaminated by lead on an atomic scale, he discarded the small stones, split the sample and analyzed a 2 gram aliquot. (The analyst knew that the much higher surface area of the silt would have adsorbed orders of magnitude more lead than the stones, so that this approach yielded a worst-case analysis. To check this hypothesis, the analyst performed an acid leach on a few stones and no detectable quantities of lead were measured.)

The above examples show how, with knowledge of the type and mechanism of contamination and the contaminant unit the sampling team and the analyst can decrease the costs of handling large samples and particle size reduction without substantially increasing sampling

error. Without the site history, large sample sizes or particle size reduction would have been required or one would risk the introduction of a substantial error into the measurement process. Thus communication with the analyst regarding the type and mechanism of contamination is an important means of controlling costs and minimizing errors.

The above sampling strategies are not ideal since they allow for assumptions and interpretation and these assumptions and interpretations could lead to substantial intentional and unintentional errors. However, the above sampling strategies are more practical, more likely to be implemented and may be a significant improvement over the alternatives. Lastly, when these sampling strategies are implemented by an experienced personnel who are aware of the DQOs, site history, the types and mechanisms of contamination and the contaminant unit, the errors associated with interpretation and assumptions should decrease substantially.

It is important to note, that application of these sampling strategies to wastes is much more difficult than for soils and subsampling of wastes may frequently require a strict application of sampling theory. Wastes are a more difficult media, since the complexities of waste generation often preclude knowledge of how a contaminant of interest is dispersed within a waste and whether distribution will be a function of particle size.

EXCESSIVELY STRATIFIED WASTES

The remainder of this discussion will concentrate on excessively stratified wastes, the most difficult wastes to characterize. Compositional or particle size heterogeneity or a combination of both compositional and particle size heterogeneity can be the cause of excessive stratification. This discussion will address each of these causes and will concentrate on sampling issues, since sampling is now recognized as the greatest contributor to imprecision and bias.

However, before addressing the different causes of heterogeneity, it will be useful to consider an issue which should be common to all waste characterization efforts.

The first step in characterizing any heterogeneous waste is to gather all available information on the;

- Need for waste characterization,
- Objectives of waste characterization,
- Pertinent regulations, consent orders, and liabilities,
- Sampling, shipping and laboratory health and safety issues,
- Generation, handling, treatment and storage of the waste,
- Existing analytical data and exacting details on how it was generated,
- Treatment and disposal alternatives.

These types of information will be used in the planning of the sampling and analytical effort. The planning process should be detailed and address the issues defined in EPA's data quality objective (DQO) process. The different disciplines (e.g. sampling, chemistry, engineering, statistics needed to properly understand and exploit the above types of information must be present during the planning process. If enough information is available, the planning process will uncover the existence of excessive stratification which will prevent achievement of objectives. If information is lacking, a preliminary sampling effort would be advisable, and if done properly should detect the existence of excessively stratified wastes.

Excessively stratified waste can not be cost-effectively characterized by traditional methods and this fact usually becomes apparent during the planning process. The following discussion will consider approaches which in effect will lessen the level of stratification and allow for more cost-effective characterization. Some of these approaches will require changes in objectives, waste handling or disposal methods, and some will require compromises, but all approaches will require the above types of information.

Of the following types of excessively stratified waste, the difficulty in characterizing a waste increases from those that have strata based solely on particle size, to those which consist of compositional strata to those which have strata of varying composition and particle size. In fact, the difficulty in characterizing waste, which consists of strata of different particle size, is simply a matter of determining that composition is constant across different particle sizes. If the composition is found to be constant across the different particle sizes, the waste should be easily characterized.

The more problematic types of waste, which have enumerable strata of different composition or a combination of different composition and particle size are much more difficult to characterize. The approach to characterizing these wastes usually has to be determined on an individual and unique basis.

Excessive Strata of Different Sized Particles

Wastes having excessive stratification due only to different sized particles will by definition have the same composition or property (i.e. homogeneous or randomly heterogeneous) through-out its different strata. The strata can be separated in space or in time. Unless one is attempting to measure particle size, this waste is the simplest of the excessively stratified waste types to characterize. All particles in these types of wastes are usually generated by the same process, (e.g. smelter slag and the previous example of silver nitrate powder and crystals), which is the reason for similar composition across all particle sizes.

The complexity of dealing with these types of wastes is in proving that the waste has similar composition, (i.e. mean levels and concentration distribution of the parameter of interest) across the varying particle sizes. This determination can be made by using knowledge of the waste or by sampling the different sized particles to determine if there are significant compositional differences. If the determination is made using knowledge of the waste, it is advisable to at least perform limited sampling to confirm the determination.

The characterization process is greatly simplified, once a determination has been made that the waste has similar composition or properties across the various particle sizes. The sampling and subsequent analysis can be performed on particles which are readily amenable to the sampling and analytical process and the resulting data can be used to characterize the waste, in its entirety.

It is important to periodically verify the assumption that the different particle sizes are composed of materials having the same concentration levels and distributions of the contaminant of interest. This verification is especially important when there are any changes to the waste generation, storage, treatment or disposal processes. Similarity of composition between particles has to be verified for each parameter of interest. The effect of different particle size must also be considered when measuring properties such as the Toxicity Characteristic Leaching Procedure (TCLP) .

Excessive Strata of Different Composition or Composition and Particle Size

Wastes having excessive stratification due only to composition or property will have similar particle size through-out its different strata. The strata may be separable in space, time or by component or source. Stratifying the waste should simplify the characterization process.

Wastes having excessive stratification due to both composition/property and particle size are usually the most difficult wastes to characterize. The strata can be separated in space, in time, or by component or source.

Figure 4. summarizes an approach to characterizing these types of excessively stratified wastes. If a waste is excessively stratified, traditional methods of sampling will not allow objectives to be cost-effectively achieved. To cost-effectively sample an excessively stratified waste, one must use a non-traditional approach. The non-traditional approach may involve modification to the sampling, sample preparation or analytical phase of the process. If after

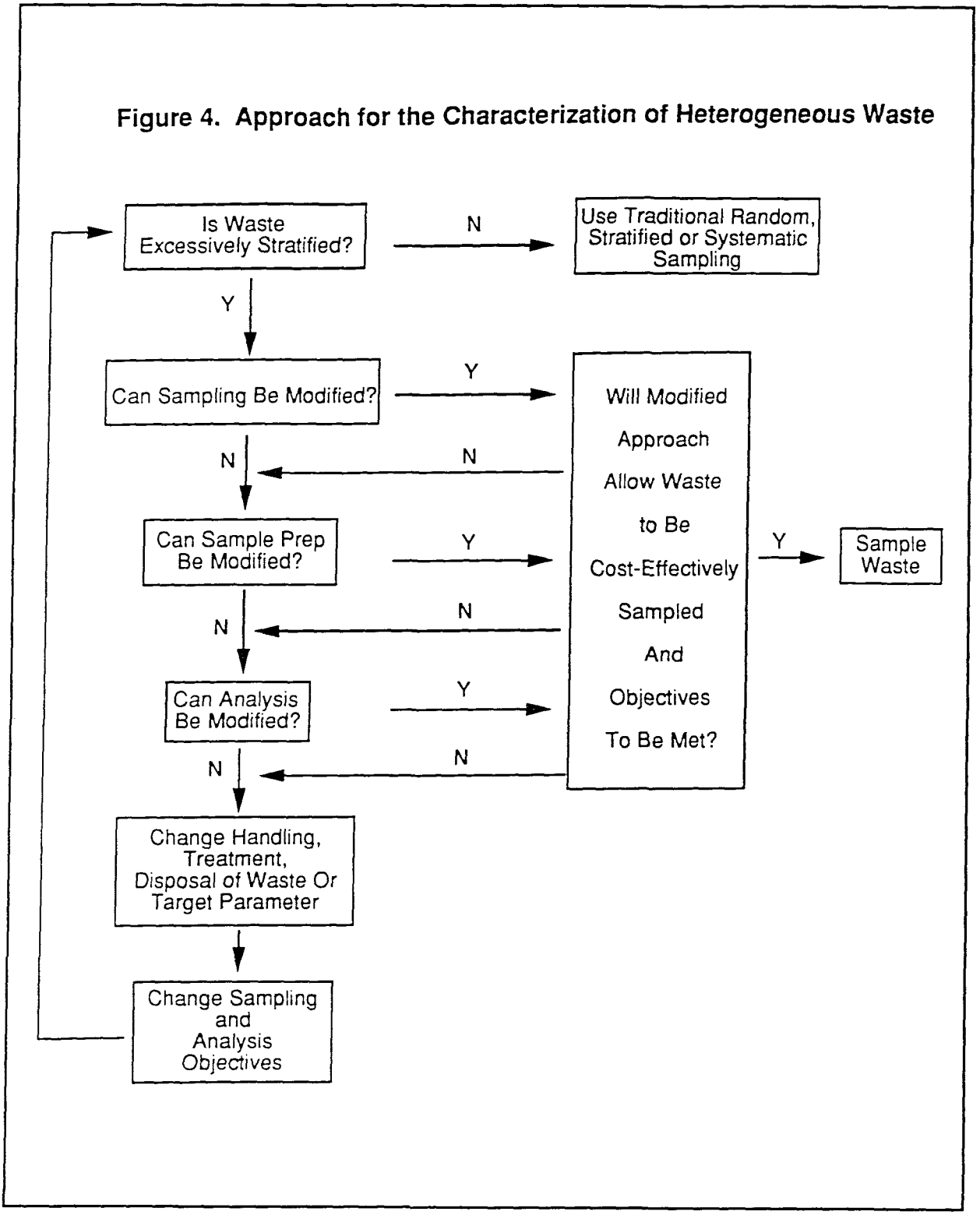

Figure 4: Approach for the Characterization of Heterogeneous Waste

modifying the approach to sampling and analysis the objectives still can not be achieved in a cost-effective manner, then the original plan of waste handling, treatment or disposal has to be examined and changed so the waste can be characterized according to new and achievable objectives.

The following subsections discuss approaches that can be employed to make excessively stratified waste more amenable to a cost-effective sampling approach.

Design of the Sampling Approach

The first efforts to resolve the difficulty in characterizing an excessively stratified waste are usually focused on the sampling aspects of the project. This is a logical place to start and, if a successful sampling approach is designed, the project objectives can be cost effectively achieved.

The difficulty in sampling excessively stratified waste can result from:

1) Various particle sizes and waste consistency which makes sampling difficult and traditional sampling approaches cost prohibitive.

2) Extraordinary concentration gradients between different components or enumerable strata that lead to such excessive variance in the data, that project objectives can not be achieved.

3) Wastes which exhibit both of the above properties.

A strategy for designing a sampling plan for such excessively stratified waste includes the following five steps;

1) Select the target parameters.

2) Determine whether these parameters are correlated with; particle size space time components, or sources.

3) Determine if any waste components or strata can be eliminated from sampling because they do not contribute significantly to the concentration of the target parameter.

4) Determine if small particles in a stratum represent the stratum as well as large more difficult to sample particles. If yes, sample the smaller particles and only track the volume contribution of the larger particles. (See Particle Size and Sampling Theory).

5) Determine if contamination is innate or surface adsorbed. Is the contamination surface adsorbed which would allow the material to be representatively sampled by wipe sampling? Can large particles be wiped and smaller particles extracted, leached or digested. Can waste be stratified according to impervious and non-impervious waste and sampled and analyzed accordingly?

To understand how this strategy would work, consider a hypothetical scenario - a storage area containing 4000 drums of waste generated over a 15 year period. The drum contents are excessively stratified and contain a myriad of wastes from process waste; destruction and construction debris such as wood, concrete; lab wastes including broken glassware, paper, empty bottles; etcetera. The appearance of the combined drum contents could best be described as a municipal landfill in drums which appears impossible to characterize.

1) WHAT ARE THE TARGET PARAMETERS?

None of the waste contents are known to be listed waste so the target parameters are the TCLP and other hazardous waste characteristics. In addition, groundwater modeling has indicated that the storage area is the source of a plume contaminated with solvents and beryllium.

2) ARE THE TARGET PARAMETERS CORRELATED WITH AN IDENTIFIABLE STRATA OR SOURCE?

The source of beryllium is traceable to one process, whose waste should be easily identifiable if drum markings are not legible enough to determine the source. The solvents are likewise traceable to a machine shop which would have disposed of its waste in easily identified drums.

Testing will have to be performed to determine if there is any correlation with particle size, space, time or components in the waste.

3) CAN ANY WASTE COMPONENTS OR STRATA BE ELIMINATED?

Historical information indicated that 400 drums of construction debris were generated during construction of a new warehouse. The information indicates that the virgin nature of the materials may make these drums candidates for not sampling or less intensive sampling.

Likewise, the source of beryllium contamination is a beryllium sludge which exists in drums by itself or in drums commingled with shredded packing material and laboratory wastes that were generated during physical testing of the beryllium product. If the materials commingled with the beryllium waste are known not to be a source of contamination, the commingled

material can be discriminated against during sampling and only the beryllium sludge sampled and the volume contribution of the commingled material noted.

4) ARE CONTAMINATION LEVELS CORRELATED WITH PARTICLE SIZE?

Some of the older beryllium sludge has dried and formed a cementaceous aggregate of different particle sizes. Since the sludge is known to be homogeneous within a batch by process knowledge and preliminary sampling data, sampling can be restricted to the more easily sampled - smaller particles sizes.

5) IS CONTAMINATION INNATE OR SURFACE ADSORBED

The waste from the machine shop consists of varied material from fine metallic filings to large chunks of metal and out-of-specification metal product. Since the only contamination in the machine shop is solvents and cutting oils and the waste matrix is impervious, the contamination is surface adsorbed in nature. Thus sampling of these wastes will consists of the sampling of fines which will be subjected to extraction, wipe sampling of the large metallic objects and notation of the volume contributions of the different particle sizes.

It is essential that all assumptions , (i.e. any correlations), be verified by at least knowledge of the waste and preferably confirmed by exploratory sampling and analyses.

In the above hypothetical case, the proposed strategy for characterizing the 4000 drums resulted in:

The identification of two large strata that constitute the majority of the waste (i.e. the beryllium sludge and the solvent and cutting oil contaminated machine shop waste).

The elimination of the need to sample 10% of the drums, (i.e. the construction debris), if preliminary testing verifies waste disposal information.

Simplified sampling of the beryllium commingled waste by restricting sampling to the beryllium sludge and not the other commingled materials.

Simplified sampling of the cementaceous beryllium sludge by limiting sampling to the more easily sampled small particles.

Simplifying the sampling of the machine wastes since the source of contamination is surface adsorbed and not innate to the waste materials.

A less expensive and doable sampling design which will result in a more precise estimate of the mean and will generate strata specific information which will be valuable if the strata are eventually treated separately.

The following subsections describe additional strategies that can be employed if the above sampling strategies are not applicable to a waste or if they are applicable but by themselves will not allow the project objectives to be cost-effectively met.

Modification of the Sample Preparation Method

As discussed in the Introduction, heterogeneity is analytical sample size dependent. The greater the particle size and the greater the variance of the concentration of the target parameter, the greater the heterogeneity for a given analytical sample size. To minimize the measured heterogeneity and to accommodate large particle sizes, traditional sample preparatory methods can be altered.

In the laboratory, the term "sample preparation" is commonly meant to include two separate steps; 1) the subsampling of a field sample to generate an analytical sample, and 2) the preparation of the analytical sample for subsequent analysis.

Regarding subsampling, the previously discussed logic for field sampling (refer to Section 3.1.1) is also applicable for the generation of analytical samples. That is, knowledge of concentration distributions within the waste can be used to simplify subsampling by:

1) Eliminating any waste components or strata that do not contribute significantly to the concentration of the target compound;

2) Discriminating against large particles and only select small particles if small particles represent the waste as well as large particles; and.

3) Surface wiping larger particles and extracting or digesting fines if surface contamination is the source of the target parameter.

If the above approaches are not applicable to a field sample, the field sample will have to be subjected to particle size reduction (PSR) prior to subsampling or the sample preparation method will have to be modified to accommodate the entire field sample.

PSR is useful for handling field samples, which have particles too large for proper representation in an analytical subsample. The intent of PSR is to decrease the maximum particle size of the field sample so that the field sample can then be split and or subsampled to generate a representative subsample. The difficulties in applying PSR to waste samples are:

1) Not all materials are easily amenable to PSR (e.g. stainless steel artifacts);

2) Adequate PSR capabilities and capacities do not normally exist in environmental laboratories;

3) PSR can change the properties of material (e.g. leachability)

4) PSR can be a source of cross-contamination; and

5) PSR is often not applicable to volatile and labile compounds.

Modification of sample preparative methods can include the extraction, digestion or leaching of much larger sample masses than specified. The advantage of this approach is that the resulting extract, digestate or leachate are relatively homogeneous which simplifies subsampling. This approach is particularly important for volatile organic compounds which may suffer from substantial losses if subjected to PSR. For volatile organic compound analysis, larger portions of the wastes can be subjected to methanol extraction or possibly the entire field sample could be subjected to heated headspace analysis as one sample or as a series of large aliquots.

Prior to modifying a sample preparatory method, especially a method associated with a property such as the Toxicity Characteristic Leaching Procedure (TCLP), it is advisable to consult the end-user of the data and the pertinent regulator if appropriate.

Modification of Analytical Method

The analytical phase of a sampling and analytical program allows another opportunity to simplify the characterization of an excessively heterogeneous waste. Examples of different classes of analytical methods are ;

Screening methods,
Portable methods,
Field Laboratories methods,
Non-intrusive methods,
Innovative methods, and
Fixed laboratory methods.

Screening, portable and field laboratory methods have the distinct advantage that they allow for the cost-effective analysis of more samples. These methods not only generate more precise data but the greater number of samples make it easier to detect correlations between concentration levels and waste strata or components. Also some screening methods may analyze a larger sample volume than what is traditionally submitted to a fixed laboratory.

Non-intrusive methods can be useful when there are health and safety issues regarding exposure to the waste. These methods may also be used to qualitatively or semi-quantitatively evaluate large volume wastes.

An EPA Document entitled "Characterizing Heterogeneous Wastes EPA 600/R-92/033" has a solid discussion of non-intrusive methods and new methodologies that are being developed for the characterization of heterogeneous wastes.

Modification of the Waste Handling, Treatment Disposal Plan

If the modifications discussed in the previous subsections are not applicable to a given waste or when they are applicable but still do not allow the objectives to be cost-effectively met, then the reasoning behind the original program must be examined. The original need behind the waste characterization objectives has to be examined and an approach for simplifying the characterization process must be devised.

For example, assume that the need behind waste characterization objectives for a certain program was the common requirement to determine if a waste is hazardous prior to waste disposal. An initial attempt to characterize the waste; 1) failed to meet the objective, 2) indicated that the waste was excessively stratified, and 3) proved that portions of the waste are hazardous. After reviewing this preliminary information and the costs to attempt a defensible characterization of the waste, it could be decided that all the waste will be assumed to be hazardous and treated as hazardous waste. Under this scenario, the needs change and now compliance with the land-ban requirements may become the issue. Assume that the waste was incinerated, then the less heterogeneous and more easily sampled incinerator ash would be sampled in lieu of the original excessively stratified waste.

An other example would be a large laboratory operation that generates drums of gas-chromatography (GC) vials containing dissolved standards, solvents and numerous contaminants

extracted from samples of different origins. Although, the vial contents were individually analyzed by GC for certain parameters, the contents were not analyzed for enough parameters to characterize the waste. A quick review of this waste would preclude further and cost prohibitive analyses of every vial. Thus, an alternative approach would have to be devised. An alternative approach could require that the vials be crushed and the vial contents and the solvent used to rinse the broken vials would be collected in a receiving drum. This approach would convert drums which contained hundreds of different vials, each of which could have their own independent concentrations of contaminants, into two relatively homogeneous waste strata, i.e. solvent rinsed glass and contaminated solvent.

CONCLUSIONS

The previous discussion reviewed heterogeneity issues and proposed a single and systematic approach to the characterization of hazardous waste. This approach is based upon the evaluation of wastes in terms of their degree and type of stratification - a factor which drives the degree of difficulty in sampling a particular waste.

This discussion also proposed stratification in an additional dimension than the traditional spacial and temporal dimensions. The stratification of waste according to waste components and sources can simplify the characterization process and provide needed strata information.

This systematic approach and the additional mechanisms for stratifying waste is intended to aid in the characterization of wastes especially those that are excessively stratified.

APPENDIX D:

CHARACTERIZING MIXED WASTES

CHARACTERIZING MIXED WASTES: INTRODUCTION

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INTRODUCTION

Certainly, within the Department of Energy's RCRA and CERCLA related clean up activities, mixed waste characterization presents some real challenges. By mixed waste, we mean a mixture of radioactive and hazardous wastes generally in liquid or solid form and combinations thereof. The presence of radionuclides in a hazardous waste sample presents additional handling and procedural problems beyond those presented by non-radioactive hazardous wastes. In addition, their presence limits the options available for managing the waste. This, in turn, dictates the kinds of data needed to select and implement the best option.

The cost of analyzing hazardous constituents in mixed waste samples is considerably greater than that for analysis of the same constituents in non-radioactive waste samples. This increased cost of analysis makes it all the more important to give careful consideration to what samples need to be collected. Determining what samples need to be collected depends on how the data are going to be used. Only when you know precisely how the data are going to be used can you then determine what kind and how much data need to be collected and the necessary data precision, accuracy, and reliability. In most cases, taking extra samples and performing unnecessary analyses is just wasteful, in terms of time and money. In addition, when dealing with mixed waste, one is faced with significant safety problems. Accordingly, we should routinely plan our data collection programs so that, before the first sample is ever taken, we know precisely how we are going to use the data, what and how much data we really need, and how good the data must be.

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CONCERNS

In this session, we will be looking primarily at two concerns.

The first is: if the sample is so "hot" (i.e., radioactive) that any amount of handling would pose a safety risk, then how does one characterize the waste for purposes of determining the proper means of treatment, storage, or disposal?

The second is: given the limitation of possible treatment, storage, and disposal options for mixed waste, there may be only selected types of analyses that need to be performed. If the samples have significant amounts of radioactivity, then what properties (in addition to radiological hazards) need to be determined in order to properly characterize the material with respect to the appropriate options for treatment, storage, or disposal? A sub-part of this concern is: how do we go about minimizing characterization costs while maintaining a high level or environmental protection?

PURPOSE OF TODAY'S SESSION

We will use today's session as a forum for exploring:

- How to develop waste analysis plans tailored to the characteristics of the waste materials and the available treatment, storage, or disposal options,
- How to go about balancing environmental risk and characterization costs,
- Options for mixed waste management (i.e., treatment, storage, and disposal),
- Potential hazards posed by mixed wastes.

The options for mixed waste management that should be considered in the three sessions include:

- Warehouse storage in drums,
- Entombment in a below-ground cavern,
- Incineration,
- High temperature glassification, and
- Solidification using cement, asphaltic, or lime processes.

WORKSHOP ORGANIZATION

This issue session will consist of overview presentations by our three experts. First, Susan Jones will present the regulatory point of view. She will be followed by Craig Leasure, who will give the industrial point of view. Then, Wayne Griest will give us an overview of the current state-of-the-science in the area of mixed waste characterization.

Following these presentations, you will have an opportunity to ask clarifying questions. Then, we will divide into three workgroups to address the issue. The purpose of these workgroup sessions is to solicit your ideas and recommendations that EPA can use in addressing the mixed waste characterization issue.

We would like for each of the three workgroup sessions to focus on the following questions:

1. What kind of information is needed (and what quantity and quality) in order to safely manage a mixed waste for at least each of the following management options:

   - Entombment in a below-ground cavern,
   - Incineration,
   - Solidification using cement, asphaltic, or lime processes?

2. What scientific properties or constituents of the mixed waste should be determined? Examples include:

- Physical form (e.g., liquid content),
- Radiological properties,
- Physical properties (e.g., strength, heat content, flammability),
- Leachability,
- Chemical properties (e.g., corrosivity),
- Metals,
- Organics, and
- Ionic species (e.g., CN, SO_4, Cl).

3. How should one go about balancing risk and characterization costs? Of course, in situations where there are tradeoffs between characterization costs and total project costs, then our concern would be with total project costs. (For example, there have been cases where, by spending an additional $200,000 to do a more precise characterization, the total project costs were reduced by several million dollars). It should be clear to all of you that we are not attempting to balance costs versus benefits - rather we want to explore how to go about minimizing costs while maintaining a high level of environmental protection. The EPA has had considerable success in this area through application of the data quality objective (DQO) process.

Each workgroup has a facilitator and a scribe. After you have completed your deliberations, we will turn over the results to EPA to consolidate the information into a report summarizing the thoughts, ideas, and conclusions presented. We anticipate sending a copy of the report by the end of the year. In addition, EPA will use this information when formulating its approach to the problem. Similarly, DOE will make full use of this information.

CHARACTERIZING MIXED WASTES: REGULATORY PERSPECTIVE

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INTRODUCTION

Subtitle C of the Resource Conservation and Recovery Act (RCRA) is a "cradle to grave" hazardous waste management program (from waste generation to ultimate disposal) that places importance on proper waste characterization by facilities that generate, treat, store or dispose of hazardous waste. Accurate characterization of waste by facilities determines if and/or how wastes will be managed under RCRA. Proper characterization also is the first step in ensuring the regulator that the waste will be managed under RCRA in a manner protective of human health and the environment. A major component of waste characterization is waste analysis. Waste analysis via testing is often the most reliable, accurate and defensible way to characterize hazardous wastes. However, waste testing is not always required, or desirable for certain waste streams. This is especially true for radioactive mixed waste which poses testing and sampling problems because it contains both radiological and chemical hazards. Testing mixed waste is further complicated by virtue of being regulated under two different statues (the Atomic Energy Act (AEA) and RCRA) with two distinct sets of management requirements.

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STATEMENT OF ISSUES

This discussion involves a review of what Environmental Protection Agency (EPA), as a regulator, regards as the essential waste characterization requirements under RCRA, why EPA requires such information, and what concerns EPA has in sampling and testing mixed waste streams.

Hazardous Waste Analysis Requirements for Generators

Waste characterization begins at the point of generation of a solid waste. Initially, a generator is tasked with determining whether his or her solid waste is a hazardous waste that is regulated under Subtitle C of RCRA (see 40 CFR 262.11). This may simply involve applying knowledge of how the waste is generated, knowledge of the hazardous characteristic of the waste, or matching the waste to a hazardous waste listing that describes the waste and, for certain listings, the process that generates it. If the generator lacks data or process knowledge of the generated waste stream, he or she may be obligated to test or send a representative sample off-site for analysis. For purposes of characterizing mixed waste, EPA requires that the hazardous portion is properly identified by process knowledge or testing. If more than one hazardous waste is in the radioactive waste stream, then all hazardous wastes must be identified, and if shipped off-site, reported on the manifest. Any records of such waste identifications, through waste analyses, testing, or determinations made on process knowledge, must be retained for at least three years (40 CFR 262.40) as proof of compliance with RCRA.

Besides waste identification, waste analysis serves to ensure that incompatible wastes are not stored in the same management unit and the composition of the unit is not incompatible with the waste stream to prevent hazards. Waste analysis by generators also plays an important role in meeting the land disposal restriction (LDR) requirements discussed below.

Hazardous Waste Analysis by Treatment, Storage, or Disposal Facility (TSDF) Owner/Operators

Owners/operators of hazardous waste treatment, storage, and disposal facilities also must accurately identify hazardous waste that they manage. However, unlike generators, TSDFs are specifically required to obtain a chemical and physical analysis of a representative sample of the wastes managed on site or received from off-site, and formally document analysis procedures used in a waste analysis plan (WAP). These analyses may include, in part, data developed by the generator, existing published or documented data on the hazardous waste, or data on waste generated from similar processes. The requirements and frequency of such analyses are specified in the waste analysis plan and may be modified to account for hazards presented by the waste stream. For mixed wastes, the waste analysis requirements afford the flexibility to reduce testing frequency, modify testing techniques, and incorporate the principles of *as low as reasonably achievable* (ALARA).

It is important to the regulator that TSDFs gather accurate and current analysis data to ensure that wastes that are analyzed are indeed those the facility can treat, store and dispose as specified by their permit, and are compatible with the processes and units used at the facility. Also important, is the analysis of waste shipments from off-site to verify the identity of the waste on the manifest and verify that the land disposal restriction (LDR) notification of 40 CFR 268.7 is accurate.

Special Waste Analysis Requirements for the Land Disposal Restrictions (LDR)

In addition to the initial waste characterization, RCRA requires some degree of analysis for determinations by generators that their waste is restricted or not restricted under the LDRs, determinations by generators, treaters, or disposers that a land disposal restricted waste meets a required treatment standard, and verifications by off-site facilities through corroborative testing that the hazardous wastes received are in compliance with LDR treatment standards and

prohibitions. Process knowledge may be used for the LDR determinations required of generators (i.e., determinations whether a waste is land disposal restricted and determinations that a waste meets treatment standards). However, some amount of testing is required for treaters and disposers to verify that the treatment standards have been met prior to disposal, unless the treatment standard is a specified technology.

The addition of the land disposal requirements has increased the waste characterization burden on facilities, which in the case of mixed waste, has raised special concerns. In particular, there is concern of increased exposure risk to workers from the additional sampling and analysis of mixed wastes. To address this, EPA has emphasized in the LDR Third Third rule (55 FR 22669, June 1, 1990) and the draft guidance entitled "Clarification of RCRA Hazardous Waste Testing Requirements for Mixed Waste" that the RCRA permit writer has the flexibility in the WAP, on a case-by-case basis, to minimize incremental exposure to radiation by reducing the frequency of testing mixed waste and allowing more reliance by the TSDF on analysis information provided by the generators or treaters of mixed waste.

Purpose and Use of Waste Analysis Information

As mentioned earlier, waste analysis is important in determining whether a solid waste falls within the scope of RCRA and how a waste will be managed once it identified as RCRA hazardous. EPA's primary goal in requiring some level of waste analysis is to ensure that the mixed waste is managed in a safe operating environment and in a manner that is protective of human health and the environment. EPA uses tools, such as the records kept by generators on waste analysis and a facility's WAP, to verify that the data collected and analyzed by facilities is of high quality, to track the movement and management of hazardous waste by ensuring that all parties managing a waste stream have identical information, to determine compliance with RCRA permit conditions and to collect information for enforcement initiatives and legal proceedings. These tools also may benefit generators and facilities to plan waste management activities, provide consistent procedures for analyzing wastes, ensure that information is not lost

during personnel changes or absences, and minimize potential mismanagement of hazardous wastes.

Special Concerns in Sampling and Testing Mixed Waste

The regulated community has communicated to EPA (and the Nuclear Regulatory Commission) their difficulty in meeting RCRA testing requirements. Problems include difficulties in using EPA test methods, choosing sample sizes, obtaining a representative sample for heterogenous waste, determining the number of samples needed to establish the homogeneity of waste, and complying with ALARA in conjunction with complying with RCRA analysis requirements. To address some of these mixed waste testing concerns, EPA and NRC recently issued a joint draft guidance document entitled "Clarification of RCRA Hazardous Waste Testing Requirements for Mixed Waste," which provides an overview of the RCRA testing requirements and addresses concerns related to potential radiation exposure, redundant verification testing, and sample size needed for an accurate test. The guidance emphasizes reliance on process knowledge by generators when feasible, use of surrogate materials for high activity wastes that represent the hazardous properties of the waste, and the use of permit conditions which incorporate ALARA considerations to minimize or eliminate redundant testing by off-site facilities. In addition, the guidance points out that flexibility exists in mixed waste sampling and analysis. For example, choosing a sample size smaller than the 100 gram minimum sample size recommended in a Toxicity Characteristic Leaching Procedure test protocol is allowable if the results show that the test is sufficiently sensitive and measures the constituents of interest at regulatory levels prescribed by the test. EPA and NRC are currently reviewing comments on the guidance which is scheduled for release in the fall.

ADDRESSING THE ISSUES

Much work and coordination with interested parties has to be done to iron out all the issues associated with testing mixed waste. In the near term, EPA is interested in further

investigating the role that reliance on process knowledge might play in limiting exposure from testing, the appropriate types of information that should serve as a basis for the process knowledge determination, and the reasonable limits on using process knowledge so it is not misused. We are also interested in determining the appropriate framework for applying ALARA considerations to adjust or optimize the sampling frequency and waste analysis parameters in a RCRA facility's WAP. Furthermore, we want to gain knowledge of the other ALARA concerns or practical consideration associated with mixed waste testing which are not mentioned here or in the draft guidance. Finally, we hope to explore additional scenarios where surrogate materials may be characterized in lieu of running RCRA tests on specific waste streams that may pose a significant radiation exposure potential.

CONCLUSION

Analysis of hazardous wastes is an integral part of the RCRA program that EPA uses to meet its mission in providing protection to human health and the environment through safe management practices. Although, many problems exist in characterizing mixed waste, EPA feels that accurate characterization of mixed wastes may be successfully accomplished within the confines of RCRA, using minimal testing. Through the waste analysis plan and other regulatory avenues, such as case-specific permit conditions, we should be able to have the flexibility to address mixed waste testing issues as they arise. However, this may only happen through cooperation of the regulators with the regulated community in determining reasonable approaches that offer minimal risk, while meeting the objectives of waste characterization.

CHARACTERIZING MIXED WASTES: INDUSTRY PERSPECTIVE

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INTRODUCTION

Physical and chemical characterization of radioactive mixed wastes (RMW) is necessary for determination of appropriate treatment options and to satisfy environmental regulations. Radioactive mixed waste can be classified as two main categories: contact-handled (low level) RMW and remote-handled RMW. This discussion will focus mainly on characterization of contact-handled RMW.

The characterization of wastes usually follows one of two pathways: 1) characterization to determine necessary parameters for treatment or 2) characterization to determine if the material is a hazardous waste. However, wastes sometimes can be declared as hazardous waste without testing and then treated as hazardous waste.

STATEMENT OF ISSUES

Characterization of radioactive mixed wastes poses some unique issues that will require special solutions. Below, five issues affecting sampling and analysis of RMW will be discussed.

Impact of Screening Requirements on Holding Times

Radioactive screening of samples can be a time-consuming process that can impact holding times. Holding time requirements must be modified to ensure that laboratories handling

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RMW samples can meet holding times without compromising either the health and safety of the workers, Nuclear Regulatory Commission (NRC) regulations, or the ability of the analysis to accurately reflect the bulk concentration of the target analytes. Currently, Environmental Protection Agency (EPA) specified sample holding times may not accurately reflect the amount of time that samples can be stored without compromising the analysis results. However, many regulators will not accept data from an analysis on a sample that misses holding time even though the concentration of target compound that would cause action is one to two orders of magnitude greater than the detection limit of the method. For example, the holding time for water samples for semivolatile organic analysis (Method 8270) is 7 days (1). For a compound such as naphthalene, which has an action level related to land disposal near 60 parts-per-billion (2) and estimated quantitation limit of 10 parts-per-billion, sample degradation must be extensive before reaching a level where a decision is affected. The amount of time for degradation of target compounds to reach one order of magnitude may be months or years when the sample is preserved and stored at low temperature (3).

Radioactive screening can be extensive and time consuming, as discussed below. For samples that are suspected of containing radioactive materials, screening must be conducted to determine the gross amount and type of radioactivity for safe handling and shipping purposes. All government and industrial facilities that handle radioactive materials follow strict rules for their handling, either NRC requirements (4) or Department of Energy (DOE) Order 5480.11 (5). First, screening must be conducted at the sampling site to immediately determine what level of personal protection for field personnel is adequate to handle the samples. This first level of screening usually is performed with hand-held devices with detection levels appropriate only to measure levels of radioactivity that could impact workers. The second level of screening, which cannot be met with hand-held screening devices, is required to ensure that Department of Transportation packaging requirements (6) and offsite contract laboratories' radioactive materials license limits as specified by the NRC are met. This level of screening can entail up to four different analyses (gross alpha/beta, gross gamma, gamma spectroscopy, and liquid scintillation counting) depending on the expected radioactive content of the sample (Knowledge of Process).

Only gamma spectroscopy and liquid scintillation counting can provide definitive isotopic information. Consequently, while the radioactive screening is being conducted, sample cuts for chemical analysis are stored in a fashion to minimize worker exposure (usually a combination of shielding and distance from personnel).

These two levels of screening require time, even when systems are in place to expeditiously perform this screening. Once the data are generated, decisions can be made as to how the samples must be packaged for transport and where the samples can be analyzed (which laboratory, and the impact on radioactive materials license limits). These decisions are dependent on the knowledge of expected isotopes, because even different isotopes of the same element can require different handling or have different license limits. For shipping, the worst case isotope expected can be used in the Department of Transportation packaging determination. A worst case isotope can also be used for the materials license impact determination; however, for the same sample the specific isotope may be different than the worst-case DOT isotope. If the specific isotope or isotopes cannot be estimated, then isotope-specific analyses must be conducted. Isotope-specific analyses generally require significant time (ca. weeks). For example, the analysis of strontium-90 is indirect, meaning that the daughter, yttrium-90, is separated from the sample and yttrium-90 is allowed to grow in for approximately 4 weeks. At that time, the yttrium-90 is again separated from the strontium-90 and the yttrium-90 is analyzed, providing data to calculate the amount of strontium-90 based upon the half-life of strontium-90.

One caution, however, must be made in regard to gross screening of radioactivity. Sometimes the radioactive content in samples can be scattered in a non-uniform manner, which can cause significant problems with the screening data. For example, cores from drilling operations are usually subsampled with a cut from the core selected for radioactive screening. This selection can be done using hand-held devices for guidance to pick the worst-case spot. However, for alpha contamination, a hot spot could be present and not detected. (Alpha particles can be attenuated from the bulk material and that portion of the core could contain several orders of magnitude more radioactive material than was determined from the gross

screening. Therefore, the gross screening data may not always be indicative of the bulk or localized radioactivity. RMW samples that comprise more than one phase are an additional complication.

Even without the added complexity of heterogeneity of the radioactive content in RMW samples, the time required for screening prior to shipment of samples can be as little as several hours to as much as several weeks. For samples requiring analyses where holding times are a requirement (many organic analyses and some inorganic analyses) the impact to the laboratories from reduced holding time windows can be significant. Therefore, for RMW samples, holding times that make technical sense must be determined and assigned.

Management of Treatment Options

For radioactive mixed waste, Resource Conservation Recovery Act (RCRA) characterization should not be required prior to treatment, if the radioactive content is the driver as far as the type and extent of initial treatment. For example, for a waste that contains significant quantities of fission products, the only treatment option may be vitrification. However, if this waste also contains trace levels of RCRA hazardous solvents, a traditional RCRA hazardous waste determination, which will cause exposure of the workers to radiation, will likely not change the treatment of the material. If one were to conduct a risk assessment on this scenario, the significant risk in the entire process would be the exposure of the workers performing the RCRA sampling and analysis. Therefore, a RCRA analysis or analyses prior to treatment would not provide any value-added data. What is likely to be more important from the treatment perspective, in this case, would be the BTU content of the waste. The determination of the BTU content of the waste is a simple process, which can be safely performed on RMW with minimal worker exposure. For RMW where the treatment process is designed for the radioactive material (since the radioactive material is usually the risk driver), RCRA or any other environmental compliance analysis only should be performed on RMW after treatment. One caveat on this statement should be that this is appropriate only if the treatment

process (or facility) is designed to meet requirements for containment of any hazardous or radioactive substances generated, such as offgas.

Generation of Secondary RMW

When performing RCRA or Contract Laboratory Program analyses on samples that are known to be radioactive and that are suspected of being hazardous (suspect RMW), some of the analyses will generate RMW because the required solvents are themselves hazardous or because the matrix is spiked with hazardous materials. One example of this problem is the extraction of semivolatile organics from waste using methylene chloride. If a suspected RMW is extracted with methylene chloride, that suspect RMW is now definitely radioactive mixed waste from the methylene chloride residue. Even if the waste, prior to analysis, was actually radioactive only, and no semivolatile organics were present in the waste before analysis, the material becomes RMW as a result of the analysis. This is a case where more RMW is generated from the analysis than was initially present.

This secondary RMW must then be managed. However, the secondary RMW can take additional forms, such as filters, disposable wipes, gloves, and other consumables generated from not only the analysis, but also from sampling. Currently, the only treatment, storage, and disposal option that may be available to commercial laboratories performing analyses that generate RMW is to capture these wastes and package and ship them back to the source of the samples for ultimate treatment, storage, or disposal. At this time, alternative treatment options for Land Disposal Restricted mixed waste is extremely limited. The added costs to resolve this problem could exceed the actual cost of analysis. Two things are needed to minimize the problem of secondary RMW generation. First, new environmental compliance analyses must be developed that do not themselves use materials that are considered hazardous waste when disposed. Second, Knowledge of Process must be used as much as possible to minimize the collection of samples and performance of analyses, which themselves can create RMW.

Another potential problem, not necessarily a current issue for regulators, but one that could become a significant issue later, may be the question of who will be responsible for the final decontamination and decommissioning of commercial laboratories that perform analyses on RMW.

Detection Limits

Most EPA recommended or required analyses use relatively large amounts of sample material, then digest or extract and preconcentrate to obtain low detection limits. However, the DOE and Nuclear Regulatory Commission ALARA (As Low As Reasonably Achievable) principle requires laboratories to handle as small amount of sample as possible. Consequently, for samples with moderate to high levels of radioactivity, small amounts of sample are handled that satisfy health physics protection requirements but cause detection limits to be higher than for typical hazardous waste samples. For example, Oak Ridge National Laboratory published a method for the determination of semivolatile organics in radioactive tank waste (7). Because of ALARA considerations, they used only 20 mL of sample for extraction rather than the recommended 1000 mL. Hence, their detection limits for most of the target compounds were approximately 50 times higher than for a typical hazardous waste sample. Some latitude in meeting detection limits should be given in cases where ALARA (personnel safety) considerations dominate.

What is needed is guidance on the relative risks posed by hazardous and by radioactive materials. Ultimately, one could foresee a table or graph that one could use to evaluate the risk from the level of radioactive material vis-a-vis the risk from the level of hazardous material so that the true driver of risk could be assessed. Once the true driver is established, one could determine sample designs and analysis schemes that would determine needed actions. However, this is a much more complicated issue than one would first imagine. If one tries to develop the plot, multiple exposure scenarios must be explored. For a single exposure scenario and for a

simple waste that contains one radioactive substance and one hazardous substance, a plot could be developed.

At each end of this plot, either the radioactive substance or the hazardous substance drive the risk. Where this gets very complicated, is in the vicinity where the two lines intersect, where the total risk is a combination of both the radioactive and hazardous substances. As can be seen, this is very complicated when only two components are present; with more components, it becomes a significant problem. Rather than try to provide specific guidance, a better suggestion would be broad guidance such that if the expected risk from the radioactive content of the waste (based upon knowledge of process or screening) is expected to be greater than 10 times the risk posed by the hazardous portion of the waste, the need for strict characterization of the hazardous waste is unnecessary or can be reduced. However, if the risk posed by the hazardous portion of the waste is expected to be less than 10 times or greater than the risk posed by the radioactive portion of the waste, then strict characterization of the waste may be appropriate.

In the case where strict characterization of the hazardous portion is not indicated, allowances should be made for limited characterization that does not adversely impact the health and safety of the workers.

Measurement of Properties Appropriate for Management

When characterizing RMW, only those treatment properties that are appropriate for the management of that RMW should be measured. For example, the Toxicity Characteristic Leaching Procedure was designed with the municipal landfill model in mind. For the Department of Energy (DOE) however, RMW will never be placed into a municipal landfill. RMW will either be incinerated, vitrified, or placed in long-term storage. Therefore, measurements appropriate for the selected treatment scheme or those properties necessary to make a treatment decision should be measured. For vitrification or incineration, the BTU

content, or only those substances that may affect the efficiency of the process or final product should be measured prior to treatment. For long-term storage of wastes that have been vitrified, incinerated, or not treated, only those properties that affect the management of the long-term storage facility (e.g. any mobile substances) should be measured. Since the likely long-term storage option for those materials may be in a salt mine, then the leachability of the materials by brine would be a more appropriate measurement.

WHEN IS A MATERIAL RADIOACTIVE?

All parties involved in the treatment, storage, or disposal of radioactive or RMW materials must agree on a determination as to when a material is considered to be radioactive. A proposal for a definition that could withstand scrutiny both from a risk basis as well as one that is in place already would be 2 nCi/g. One of the fundamental issues that must be addressed when considering radioactive mixed waste is the fact that there are clear definitions and rules regarding when a waste is considered to be hazardous. However, there are currently no clear rules or definitions as to when a waste (or any material) is considered to be radioactive. The definition can range from one atom of added radioactivity (current DOE waste management philosophy) up to 2 nCi/g , which is a Department of Transportation definition of radioactivity as it applies to shipment (8). With the fact that treatment, storage, and disposal options for RMW are extremely limited, it would seem prudent to determine a *de minimis* level for radioactivity for determination that a waste is radioactive.

CONCLUSIONS

The five issues that affect the sampling and analysis of radioactive mixed wastes discussed above are likely only a small part of the overall issues revolving around RMW. However, if some of these issues can be resolved or if we can move toward a successful resolution of these issues, the ultimate goal of protecting our workers, the public, and the environment can come closer to realization.

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CHARACTERIZING MIXED WASTES: SCIENTIFIC PERSPECTIVE*

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INTRODUCTION

This paper is concerned with the following issues concerning the physical and chemical characterization of radioactive mixed wastes (RMW): (1) what should be determined and how; (2) the applications and limitations of current analytical methodologies, (3) promising new technologies, and (4) areas where further methodology research is needed. Constituents to be determined, sample collection, preparation, and analysis are considered. The scope concerns mainly low level and very low level RMW that allow contact handling and analysis by Nuclear Regulatory Commission or Agreement State-licensed commercial laboratories. The paper also discusses high level RMW that will be characterized in laboratories with special shielded or contained facilities.

WHAT SHOULD BE DETERMINED?

The characterization of RMW is driven by regulatory and treatability requirements. Currently, the regulatory requirements are defined jointly by the Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission (NRC) under the Resource Conservation

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and Recovery Act (RCRA) and the Atomic Energy Act, respectively, with enforcement of both delegated to states having EPA Authorizations and NRC Agreements. Specific constituents and concentrations or activities are specified. From a scientific viewpoint, the Toxicity Characteristic Constituents and the toxicity characteristic leaching procedure (TCLP) scenario of waste co-disposal with municipal refuse in a landfill are not necessarily relevant to RMW disposal. The source terms (the wastes or their treated forms) and the localities of release to the environment (leaching and migration to drinking water supplies) are very different for RMW than for the solid wastes that RCRA was intended to regulate. Making radioactivity a Toxicity Characteristic and setting *de minimis* levels of activity would remove the uncertainties leading to current "no added radioactivity" policies which classify all hazardous wastes as RMW until they are proven otherwise.

Regulatory agencies should permit more realistic leaching procedures for RMW which reflect their ultimate forms and modes of disposal or storage. Simultaneously, it should be a high priority in the Department of Energy (DOE) to develop the scientific understanding of the leaching behavior and ultimate fate of the leached compounds in the different waste disposal and treatment options. For high level wastes, this should include evaluations of the changes in waste composition and properties over time which could affect the long-term waste performance (e.g., decay of radionuclides and radiolysis of organics). This knowledge could considerably simplify and "target" the waste characterization needed for evaluation of waste form aging and environmental behavior. A good example is the concentrated brine leaching which will be evaluated at the Los Alamos National Laboratory (LANL) for assessing the suitability of radioactive wastes for disposal in the Waste Isolation Pilot Plant. Leachability and fate are included in the studies.

The constituents and properties that should be measured for waste treatability requirements are complex and not fully understood. The constituents and waste properties that affect the waste form for the major treatment technologies under consideration obviously must be identified, and concentration and property range "windows" acceptable to the treatment

processes must be determined. These will define the RMW characterization requirements from the treatability standpoint. An integrated approach was used by Rockwell International in selecting constituents and establishing detection limits for treatability and regulatory analyses of waste candidates for grouting (1). "Predictor" (or "group indicator") analyses and process knowledge also were included in their approach.

THE ROLE OF PROCESS KNOWLEDGE

The RCRA allows process knowledge to be used for characterization where a well-defined process generated the waste. For RMW, process knowledge is of limited use, because low level wastes generally are not well-defined in composition and data for contaminated environmental samples or for wastes generated from the cleanup or other handling of high level wastes is usually nil. Historical records on old wastes (both low and high level) are usually sketchy at best. The main use of process knowledge in such cases appears to be in assisting characterization efforts by eliminating some constituents from analysis. For example, although many of the inactive nuclear waste storage tanks at the Oak Ridge National Laboratory (ORNL) lack useful source records, herbicides have been excluded from their RMW characterization because the total amount of herbicides used at the lab (estimated from laboratory purchase records) would not exceed the TCLP regulatory levels if disposed entirely in the tanks. This exclusion does not hold for all DOE sites.

HOW CAN THE DETERMINATIONS BE MADE?

The following section discusses sampling and analytical issues, and offers suggestions for resolving some of these problems.

Sample Collection

Collection of a representative sample of a waste is critical to generating valid characterization data. For low level wastes, sampling is conducted similarly to that for non-radioactive wastes but with the additional precautions and constraints of the ALARA principle (keeping radiation exposure and contamination of personnel and facilities as low as reasonably achievable). The main area requiring advances in strategy and technology for low level wastes is in sampling heterogeneous wastes. Drums or bags containing discrete items such as towels, gloves, bottles, and metal parts, or tanks with multiple phases (e.g., oily, aqueous, and sludge layers) are obviously heterogeneous. Other wastes may lack obvious heterogeneity, such as single phases with composition gradients (as observed in an ORNL waste tank)(2). The current options for sampling heterogeneous wastes include segregation and subsampling, multiple sampling, or whole waste homogenizing or compositing and sampling. Heterogeneity also is a problem in sampling high level wastes (e.g., stratified wastes in the Hanford tanks). For situations where there are only a few heterogeneous samples to be analyzed, these approaches are feasible, but laborious. Where there are many samples to be collected and analyzed, current technology is not practical.

Physically collecting the sample, let alone sufficient amounts or representative portions of samples from locations with restricted access is a major technology area requiring development. The presence of high radiation fields (a major problem with high level waste tanks at some DOE sites such as the Hanford reservation) further complicates the problem. Volatile organics are a class of compounds particularly difficult to sample properly under such conditions. Radiation-hardened samplers with articulated arms are under development but are critically needed now. Development of improved sampling equipment and their acceptance by regulatory agencies should be expedited.

General Analytical Consideration

Although low level wastes are not simple to prepare and analyze, there are no unique "show stoppers" in their characterization. Regulatory sample preparation and determination methods such as those listed in the SW-846 manual (3) can be performed essentially without modification in radiochemical hoods, and the measurements can be conducted per the specified protocols with the instruments located in contamination zoned laboratories. The main operational difference from work with nonradioactive samples is the use of appropriate precautions in sample and extract handling and laboratory waste management to observe the ALARA principle and to minimize the spread of radioactive contamination. The major problem in the characterization of low level wastes will be the disposal of contaminated laboratory wastes. Often, secondary laboratory wastes generated in the preparation of RMW for analysis and in the clean-up of hoods after sample preparation can exceed the mass or volume of sample analyzed. This shows the need for the development and regulatory acceptance of "less waste intensive" sample preparation methods to reduce analytical costs.

Sample Handling

Low level samples can be contact-handled in radiochemical hoods. Higher activity wastes require handling and analysis with containment or shielding, which does not limit sample operations and productivity. The permissible activities for radiochemical hood operations currently vary in magnitude as well as units of specification among the DOE laboratories. Generally, they range from about 0.1 to 45 μCi (microCuries) of activity and up to 1 gram of total Pu in solution for alpha emitters, and dose rates of 10 to 500 mrem/hr at contact for beta/gamma emitters. Radiotoxicity and the complexity of the operation (and therefore the potential for a spill or other release of contamination) are also considered in health physics guidelines. For samples containing higher activities than permitted in radiochemical hoods, samples with alpha emitters are handled under containment in glove boxes to prevent the spread of highly radiotoxic nuclides whose radiation has little penetrating power. In contrast, a hot

cells (or, at least, sample shielding with lead bricks) is required for the much more penetrating gamma (and beta) emitters.

Productivity

Almost any operation that can be performed on a bench or in a hood can be conducted in a glove box or hot cell. However, the methods and equipment must be adapted for the latter, highly skilled operators are required to safely perform the work, and productivity is reduced in the much more restricted working environment. With glove boxes, samples and reagents are bagged in, and prepared extracts and wastes are bagged out through sealed bag ports to prevent direct contact of the glove box atmosphere with the laboratory air. Sample manipulations are performed by reaching through heavy walled rubber gloves, which severely restrict manual dexterity and freedom of motion. Sample introduction into hot cells is equally difficult, and in addition, the work is performed using master-slave remote manipulators which require a high degree of eye-hand coordination. Depending upon the complexity of the operation, productivity can be decreased (or conversely, costs are increased) by factors of 2 to 5-hold for glove box operations and up to 10-fold for hot cell operations.

Holding Times

Another consideration is that regulatory holding times designed for environmental samples are very hard, if not impossible, to meet in some instances because of the delays caused by the additional sample characterization needed to define safe handling practices, and the reduced productivity from working under containment or shielding. The relevance of these holding times is highly questionable for RMW materials which in some cases have been in storage or decades. Reconsideration of this issue is needed.

The Toxicity Characteristic Leaching Procedure (TCLP)

Operationally, the TCLP (4,5) consists of two experimental procedures, leaching the wastes and analyzing the leachates for regulated constituents. For low level wastes that can be leached in a radiochemical hood, no major difficulties are anticipated in conducting the leaching. Cleaning the leaching equipment (especially the zero headspace extractor [ZHE]) will cause a waste disposal problem because of the generally messy nature of equipment cleanup operations and the radioactive contaminated lab wastes generated from the cleaning operations.

Because of the relatively large sample sizes (25 - 100g) and bulky, complex apparatus and equipment (e.g., the ZHE and tumbler) specified in the regulations, few laboratories have adapted the TCLP leaching procedures to glove box or hot cell operations for high level RMW. The nonvolatile leaching has been adapted to glove box and hot cell operations in only five DOE laboratories, with the main deviation from the EPA protocol being a reduction in scale. The Idaho National Engineering Laboratory (INEL) is the only laboratory conducting the full-scale non-volatile leaching in a hot cell. The ZHE is much more complicated and difficult to adapt to glove box or hot cell use, but work in this area is underway. At least two companies are designing full-scale, lower cost ("disposable") ZHEs for hot cell use, and ORNL and INEL are designing ZHEs from alternate apparatus such as gas syringes. Reductions in TCLP sale to accommodate ALARA, limited sample availability, or more practical hot cell equipment for high level waste leaching must be developed and accepted by regulatory agencies. The recent draft of the joint EPA/NRC guidance on mixed waste testing (6) suggested a regulatory agency realization of this need. Until such equipment and procedures are developed and approved, the direct analysis option makes the most sense for RMW from both a scientific and a practical standpoint.

A final problem with the TCLP that is not specific to RMW is the interference of acetate with the analytical procedures. In particular, acetate from the leaching fluids is carried into the semivolatile organics analysis (SVOA) extracts, where it seriously degrades the performance of

the capillary GC-MS determinative method. Acetate also comes derivatizing agents in the preparation for herbicides determination by GC-ECD. The use of SW-846 GC methods 8040 (for phenols), a combination of 8121/8091/8081 (for hexachlorobenzene, dinitrotoluene, and the pesticides), a modification of HLPC method 8123 (for herbicides), and 8260 (volatiles plus the remaining extractable organics) allow determination of all TCLP organics without interference from the acetate (7). The HPLC method is being further adapted to include all of the acidic extractable TCLP organics without any required sample preparation. Regulatory agency acceptance of HPLC methods for these compounds would permit faster and cheaper analyses with less laboratory waste and personnel exposure.

No difficulties are anticipated with the determination of the characteristics of corrosivity, flammability, or reactivity in low level RMW. Flammability determinations can be a problem when high level RMW samples require shielding or containment. INEL is developing a flash point apparatus with a pressure-sensing membrane to allow this determination to be conducted in a hot cell or glove box.

Organic Chemical Analysis

Problems dealing with organic chemicals in RMW are discussed in this section.

Sample Preparation

For low level RMW, current ultrasonic or soxhlet (solids) or separatory funnel or continuous extractor (aqueous liquids) SW-846 or Contract Laboratory Program methods can be used with little modification and careful handling and containment to minimize personnel exposure and prevent spread of contamination. However, considerable laboratory waste that is contaminated with radioactivity (therefore a low level waste and possibly RMW from toxic solvents or spikes) can be generated and will have to be disposed. With higher activity RMW,

these problems are compounded with the difficulties of working in a glove box or hot cell, often with smaller sample amounts than specified in SW-846 protocols (which raises detection limits).

Several extraction technologies may be useful in low and high level RMW analysis, and expedited acceptance of them by regulatory agencies will help to alleviate these difficulties. Work at several laboratories (including EPA-sponsored studies) has demonstrated that a variety of analytes can be efficiently recovered form solids by supercritical fluid extraction (SFE). LANL recently has shown that carbon dioxide with a water modifier can efficiently extract many semivolatile organics (including phenols) from simulated RMW. The ability to extract relatively small masses of sample (in a glove box or hot cell, if need be) and analyze the extracts on-line via transfer lines to a GC-MS outside the box or cell greatly reduces lab waste generation, radiation exposure of staff, labor, and sample preparation/analysis time. For liquids samples, solid phase extraction using packed columns (as in some EPA 500 and 600 series methods), extraction membranes, and open plastic tubing (as at LANL) promise rapid and reproducible methods with far less solvent usage and operator exposure than current solvent extraction methods. Both of these technologies can be conducted relatively easily under shielding or containment, and they could be readily automated to further improve productively. Further development and optimization of these powerful tools, and their acceptance by regulatory agencies clearly should be a priority.

For higher level wastes, the presence of high concentrations of nitrite has caused problems in aqueous liquid sample preparation for the SVOA. Foaming during acidification and release of oxides and nitrogen, which creates artifacts by nitrating organic compounds (Westinghouse Hanford has observed nitration of at least two SVOA surrogate standard phenols), are some of the problems caused by nitrite (2). A means of selectively removing or lowering the nitrite, or of avoiding the need to acidify before extraction would be helpful in improving sample handling and reducing potential artifacts. Other problems encountered with high level wastes include high alkalinity of sludges and also unidentified interferences in Hanford tank wastes which quickly degrade volatile organic analysis (VOA) and SVOAS GC-MS performance.

The latter is not removed by CLP purification methods. Clearly, there are major technology needs for clean-up of high level samples.

The automation of sample preparation and analysis will increase laboratory productivity and reduce operator exposure to radioactive samples. In the near term, only segments of procedures are automated (e.g., VOA purge and trap or gel permeation chromatography and fraction concentration), but in the long term, efforts such as the DOE contaminant Analysis Automation Program should provide the methods and equipment. This effort should be continued.

Determination of Regulated Organic Compounds

Low level RMW do not present major problems in the organics determination steps, and regulatory agency protocols can be followed as prescribed. The instruments preferably should be located in contamination zoned laboratories to contain any radionuclides which may be carried over into sample extracts. The concentrated extracts are usually decontaminated by several orders of magnitude and thus could be analyzed in non-zoned laboratories (if the extracts are analyzed for gross alpha and gross beta activities to confirm decontamination), but it cannot always be assumed that complexing agents will not be present in the samples. Complexing agents would facilitate the transfer of radionuclides into the SVOA or PCB/pesticide extracts. The volatile organics analysis (VOA) must be conducted in a zoned laboratory because the sample preparation (purge and trap) is best carried out on-line with the GC-MS.

For high level RMW, sample amounts are often limited by compliance with the ALARA principle or by sampling constraints. This increases analysis reporting limits. Means of increasing the fraction of the SVOA extract for example, injected into the GC-MS would offset the smaller sample sizes. Application of the SVOA extract to an adsorbent, evaporation of the solvent and thermal desorption into the GC-MS are being evaluated at ORNL. On-line SFC-GC-MS as being developed at LANL also may overcome this problem. Use of more sensitive MS

instrumentation (i.e., the ion trap mass spectrometer) also should be examined. Validation of these methodologies and regulatory agency acceptance of their use is needed. Alternatively, it would be more reasonable for regulatory agencies to relax organic and inorganic compound regulatory limits for samples whose primary hazard is a high level of radioactivity.

DOE-Unique Organics

A major area requiring methods development is the determination of compounds that are unique to DOE RMW in their complexity and concentrations, i.e., chelators, extractants, decontamination agents, their radiolytic/chemical/thermal decomposition products, and chelated radionuclides. The organic matter suggested to be present in some DOE RMW by total organic carbon measurements is rarely accounted for by regulatory organics determinations (2,8), and in some cases is accounted for by these compounds. Although these compounds are not currently regulated, they are important for their influences upon treatment (e.g., grouting behavior) and mobility of radionuclides (e.g., environmental transport of radionculides from leaks of radioactive wastes). These compounds are not determined using current regulatory GC-MS methods because of their high polarity, water solubility, and thermal instability. At present, analysis of these compounds is performed by an incompletely evaluated method including waste drying and derivatization followed by GC or GC-MS. High performance liquid chromatography and capillary zone electrophoresis interfaced with mass spectrometry appear to be good candidates for identifying and measuring DOE-unique compounds. The very small sample volume requirements (microliter volumes for nanoliter injections), high efficiency (up to one million plates per meter of column), and natural applicability to polar, water-soluble, ionic species make the latter particularly attractive. Development and validation of methods will be needed for these specialized constituents.

Inorganic and Radiochemical Analyses

This section presents the problems that are unique to the analysis of inorganic and radiochemical analytes of RMW.

Sample Preparation Methods

Low level RMW sample preparation (where radiochemical hood containment is sufficient) for inorganic and radiochemical analyses presents few additional problems over nonradioactive samples. Analyses of low level wastes are readily feasible with current technologies, although there are areas where methodology improvement is desirable to facilitate their turn-around.

One problem unique to RMW is the spectral interferences caused by the presence of uranium, thorium, plutonium, and other actinides in sample digests analyzed for metals by inductively coupled plasma - atomic emission spectrometry (ICP-AES). The concentrations of actinides in the sample digests can be reduced using tri-n-octylphosphine oxide extraction or extraction chromatography on the unique EiChroM TRU-Spec chelator columns (9) developed at Argonne National Laboratory (ANL). Evaluation of these preparation methods is nearly complete at ORNL. Regulatory acceptance of these clean-up methods would improve ICP-AES performance with samples heavily contaminated with actinides.

A second problem unique to RMW, but limited to high level wastes, is the requirement to conduct the metals analyses of sample digests under containment or shielding. Many DOE laboratories have placed the ICP-AES, ICP-MS, or flame-AA burner, and the GF-AA or electrothermal vaporization ICP-MS furnace in glove boxes, and INEL has the only x-ray fluorescence source in a hot cell. It would greatly facilitate metals analyses of high level samples if methods were available to reduce the radionuclide content of the digests. Transuranics can be removed from the sample digest with essentially no effect upon RCRA and EPA Target Analyte List metals using TOPO extraction or the EiChroM columns, but a major

technology development need is for methods to isolate or remove beta- and gamma-emitting radionculides from regulated metals.

Sample dissolution/digestion preparation methods improvements would benefit both metals and radiochemical analyses. These include high pressure sealed tube dissolution methods, improved microwave dissolution methods, and methods for obtaining clean digests or organic matrices. Removal of salts from the digests is also highly desirable. The high solids content they contribute to digests interferes with metals analyses and especially gross alpha activity determinations. Salts also interfere with alpha spectrometry unless lengthy separations are performed. One promising method, the isolation of alpha emitters by extraction chromatography with the EiChroM TRU-Spec columns, should be validated for RMW and accepted by regulatory agencies.

With high level RMW samples, high concentrations of alkali metal nitrates in the sample digests cause corrosion of the graphite furnace in the GF-AA analysis of metals, and probably also of the electrothermal vaporization furnace of ICP-MS. A means of separating the heavy metals from nitrates would reduce graphite furnace corrosion and maintenance. Interferences in As and Se determinations by the hydride method have been observed at Westinghouse Hanford in samples with high Bi concentrations, possibly indicating the need to remove Bi (which also can consume hydride) from the digest.

The colorimetric determinations of cyanide and sulfide are subject to interferences from co-distilled compounds such as oxides of nitrogen and elemental chlorine and iodine. Methods to reduce the concentrations of these species would increase the reliability of colorimetric anion analyses. Preferably, however, regulatory agencies should accept ion chromatography for cyanide and sulfide analysis determinations in RMW because it is not subject to these interferences. Several laboratories are using this method successfully.

Inorganic and Radionculide Determinations

No major problems exist for the inorganic and radiochemical determinations of low level wastes. However, laboratory operations would be considerably facilitates by more rapid, high sample load methods to measure gross alpha and gross beta activities. This would speed up sample turn-around because these are generally the first analyses conducted upon sample receipt in the laboratory, and they are also usually the highest sample load. Automation of these determinations if called for. Sample preparation and transfer to counters (which already have automated sample changers) is a good candidate for robotics, and the prognosis for a near-term payoff is very good.

Both radiochemical and inorganic analyses of wastes would benefit considerably from the evaluation and regulatory agency acceptance of ICP-mass spectrometry (ICP-MS), particularly for multielement scanning and for the determination of long-lived, low specific activity radionuclides . Traditional sample preparation and long counting times lengthen turn-around times for determinations of radionuclides such as ^{99}Tc, ^{237}Np, and ^{129}I. Among the attractive features of ICP-MS are multielement capability, high sensitivity, small sample requirements (at least with electrothermal vaporization), direct analysis of solids and slurries with laser ablation or electrothermal vaporization, and its ease of automation. Also, RCRA metals probably could be determined with high accuracy using isotope dilution techniques. ICP-MS analytical technology should be a high priority for validation and acceptance by regulatory agencies.

For higher level RMW, determination methods for total fissile material by ICP-MS or by delayed neutron counting after neutron activation need to be evaluated and accepted.

Field Analytical Methods

Certainly, RMW characterization would benefit from the development, validation, and acceptance of methods for rapid sample screening and analysis in the field. These methods

would eliminate sending samples with little or no organics, metals, or radionuclide content back to the laboratory for expensive analyses. Work is underway at ORNL and LANL with ion trap mass spectrometry, immunoassay, and other fieldable techniques for organics determinations. Field methods for rapidly screening samples in the field for selected metals and gross alpha and beta activity would be a useful adjunct to the organics screening methods. The latter also could reduce the time for laboratory radiochemical analyses needed for health physics protection. Examples of important work in this area include the method adaptation work which will be underway shortly at LANL for field gross alpha and gross beta measurements using the Protean system, and gross gamma and ^{3}H measurements by other methods. A field test or a portable x-ray fluorescence screen for selected metals (10) was supported by the Army. The Nevada Test Site is also supporting work adapting the Frisch grid detector for alpha spectroscopy in the field.

CONCLUSIONS

The main conclusions from the scientific perspective are that, although there are difficulties working with low level and very low level RMW, there are no major problems or "show stoppers" preventing their characterization in appropriately equipped and licensed commercial laboratories. The main problem probably will be the disposal of secondary laboratory wastes generated in the analysis of low level wastes. However, validation and regulatory agency acceptance of new technologies or adaptations of current technologies would greatly facilitate the characterization of the large sample load expected for DOE. Development and validation of field analytical methods also will be important in minimizing the costs of sample shipment and laboratory analyses and may help in meeting currently very restrictive holding time requirements. Higher level RMW requiring more stringent containment or shielding pose much greater characterization problems in their own right.

Two roles will be important in successfully meeting this challenge. DOE and other agencies must identify and adapt new laboratory and field analytical technologies, evaluate their performance, and transfer these technologies among the DOE sites and to the commercial sector.

The EPA must facilitate the means of gaining regulatory agency acceptance of new and adapted methods. It also must officially recognize the limited applicability of the TCLP to RMW, and the high desirability of minimizing the characterization required of highly radioactive wastes.

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APPENDIX E:

LEACHABILITY PHENOMENA: Recommendations and Rationale for Analysis of Contaminant Release by the Environmental Engineering Committee

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

EPA-SAB-EEC-92-003

OFFICE OF
THE ADMINISTRATOR

October 29, 1991

Honorable William K. Reilly
Administrator
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460

Subject: Leachability: Recommendations and Rationale for Analysis of Contaminant Release

Dear Mr. Reilly:

The Leachability Subcommittee (LS) of the Science Advisory Board's Environmental Engineering Committee (EEC) has prepared the attached recommendations and rationale on leachability, an important release term related to solid wastes and contaminated soils, for your consideration.

Over the past decade, the EEC has reviewed a number of EPA issues involving leachability phenomena and noted several problems relating to this release term that were common to a variety of EPA offices. The Committee believed that these common problems would be best called to the Agency's attention through a general review of leachability phenomena.

Drafts of this report on leachability have been reviewed at a series of Subcommittee, Committee, and Executive Committee meetings over the past 18 months. This included both a session on February 26, 1990, devoted to assessing the Agency's varied needs on leachability-related information, and a Technical Workshop on May 9, 1990. The workshop assisted in determining how leachability phenomena should be used to determine how a waste will leach when present under various scenarios in the environment.

The following recommendations have been developed. First, in regard to leachability test development we recommend:

a) incorporation of research on processes affecting leachability into EPA's core research program to better define and understand principal controlling mechanisms,

b) development of a variety of contaminant release tests, rather than focusing on mimicking a single scenario,

c) development of improved release and transport-transformation models of the waste matrix to complement the leaching tests, and

d) field validation of the tests and models, and establishment of release-test accuracy and precision before tests are broadly applied.

Next, in regard to the application of such tests and models, we recommend:

e) use of a variety of contaminant release tests and test conditions which incorporate adequate understanding of the important parameters that affect leaching in order to assess the potential release of contaminants from sources of concern. A medical analogy is that no physician would diagnose on the basis of one test showing only one aspect of the problem,

f) development of a consistent, easily applied, physical, hydrologic, and geochemical representation for the phenomenon or waste management scenario of concern,

g) identification and application of appropriate environmental conditions for tests in order to evaluate long-term contaminant release potential as required under varying statutes, and

h) coordination between the Agency's programs which develop leachability tests with those that develop the environmental models in which the release terms are used.

Finally, we recommend:

i) establishment by the Agency of an inter-office, inter-disciplinary task group, including ORD to help implement these recommendations, and

j) development of an Agency-wide protocol for evaluating release scenarios, tests, procedures, and their applications.

These recommendations are made with the anticipation that an improved understanding of the fundamental scientific principles that control contaminant release and transport within a waste matrix will allow better regulatory and technical decisions to be

made in cases where the potential exists for leaching of contaminants into the environment.

We are pleased to be of service to the Agency, and hope that you will find this effort useful. We look forward to your response to the recommendations cited above.

Raymond C. Loehr

Dr. Raymond C. Loehr, Chairman
Executive Committee

Richard A. Conway

Mr. Richard A. Conway, Chairman
Environ. Engineering Committee

Calvin H. Ward

Dr. C. H. Ward, Chairman
Leachability Subcommittee

United States Environmental Protection Agency
Science Advisory Board (A-101F)
EPA-SAB-EEC-92-003
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EPA

Leachability Phenomena

Recommendations and Rationale for Analysis of Contaminant Release by the Environmental Engineering Committee

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ABSTRACT

The Leachability Subcommittee (LS) of the Environmental Engineering Committee (EEC) of the EPA Science Advisory Board (SAB) conducted a self-initiated study and prepared a report on the topic of leachability phenomena. The intent of this report is to provide recommendations and rationale for analysis of contaminant release to the staff in the various offices of the Environmental Protection Agency (EPA). The nine recommendations from the report are highlighted as follows:

1) A variety of contaminant release tests and test conditions which incorporate adequate understanding of the important parameters that affect leaching should be developed and used to assess the potential release of contaminants from sources of concern.

2) Prior to developing or applying any leaching tests or models, the controlling mechanisms must be defined and understood.

3) A consistent, replicable and easily applied, physical, hydrologic, and geochemical representation should be developed for the waste management scenario of concern.

4) Leach test conditions (stresses) appropriate to the situations being evaluated should be used for assessing long-term contaminant release potential.

5) Laboratory leach tests should be field-validated, and release test accuracy and precision established before tests are broadly applied.

6) More and improved leach models should be developed and used to complement laboratory tests.

7) To facilitate the evaluation of risk implications of environmental releases, the Agency should coordinate the development of leach tests and the development of models in which the release terms are used.

8) The Agency should establish an inter-office, interdisciplinary task group, including ORD to help implement these recommendations and devise an Agency-wide protocol for evaluating release scenarios, tests, procedures, and their applications.

9) Core research on contaminant release and transport within the waste matrix is needed.

Key Words: leachability, leachability phenomena, leach tests and methods, leaching chemistry, leaching models

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I. EXECUTIVE SUMMARY

In waste management, including managing the effects of spills or other releases which are sources of underground contamination, a critical issue is the assessment of the potential for constituents to leach to the environment. The Environmental Engineering Committee (EEC) of the Science Advisory Board (SAB) undertook a study of this issue because it noted several common problems relating to this release term as it reviewed, over the past decade, various leaching tests and risk models for several EPA offices. Tests such as the Extraction Procedure (EP) and the Toxicity Characteristic Leaching Procedure (TCLP) had, and continue to have, scientific limitations, yet were being inappropriately and in some cases widely used. Often tests were developed without rigorous review. A self-initiated study seemed appropriate to define the leachability problem better and to offer advice on its resolution.

The EEC established a Leachability Subcommittee (LS) that addressed:

1) Needs of the Agency and regulated communities to quantify leachability (releases) of contaminants to the environment.

2) State-of-the-art and science related to fundamental principles and practice in predicting leaching of constituents from wastes, contaminated soils, and other sources.

3) Recommendations to improve the scientific understanding and application of leaching tests.

Workshops were held, literature was analyzed, and findings were discussed over an 18-month period leading to the preparation of this report.

The various needs for tests and models to predict leaching are defined. Tests developed and used in the U.S. and Canada are summarized. The scientific considerations important in design and interpretation of leachability tests are presented. This information, expert advice and analysis by workshop participants, and reviews by SAB members, resulted in guidance which should, if progressively implemented, significantly strengthen the Agency's ability to assess appropriately leaching of contaminants from hazardous wastes, contaminated soils and other sources.

This guidance, in the form of nine recommendations, is summarized as follows:

1) A variety of contaminant release tests and test conditions which incorporate adequate understanding of the important parameters that affect leaching should be developed

and used to assess the potential release of contaminants from sources of concern.

2) Prior to developing or applying any leaching tests or models, the controlling mechanisms must be defined and understood.

3) A consistent, replicable and easily applied, physical, hydrologic, and geochemical representation should be developed for the waste management scenario of concern.

4) Leach test conditions (stresses) appropriate to the situations being evaluated should be used for assessing long-term contaminant release potential.

5) Laboratory leach tests should be field-validated, and release test accuracy and precision established before tests are broadly applied.

6) More and improved leach models should be developed and used to complement laboratory tests.

7) To facilitate the evaluation of risk implications of environmental releases, the Agency should coordinate the development of leach tests and the development of models in which the release terms are used.

8) The Agency should establish an inter-office, inter-disciplinary task group, including ORD, to help implement these recommendations and devise an Agency-wide protocol for evaluating release scenarios, tests, procedures, and their applications. The task group should also be charged with recommending what the appropriate focal point(s), responsibilities, and organizational, budgetary and communication links should be within the Agency for the most effective, continued and ongoing support and pursuit of the research, development and utilization of methods and procedures.

9) Core research on contaminant release and transport within the waste matrix is needed.

II. INTRODUCTION

In both hazardous and non-hazardous waste management, one of the most critical issues is the assessment of the potential for constituents contained in the source material to leach or otherwise be released to the environment. Approaches to estimate potential release of organic and inorganic constituents and their subsequent environmental migration and associated health risks are important in many situations (e.g., pollution prevention, risk reduction, restoration-remediation and hazard identification).

This review has been initiated by the Environmental Engineering Committee of the Science Advisory Board because 1) the Committee has been reviewing Agency actions which require definition of the potential for releases from wastes and their transport to human and environmental receptors where exposure can occur, and 2) the Committee has previously reviewed the scientific and technical basis for two tests for leaching potential intended for particular uses: the Extraction Procedure (EP) and the Toxicity Characteristic Leaching Procedure (TCLP) (See for instance, US EPA, Science Advisory Board, Report of the Environmental Engineering Committee, Report on the Review of EP-III, A Procedure for Determining the Leaching Potential of Organic Constituents from Solid and Hazardous Wastes, July 19, 1984). In addressing and reviewing Agency proposals, the Committee has repeatedly observed and commented on the scientific limitations of the EP and TCLP tests. Many of the proposed uses for the tests have been inappropriate because the waste management scenarios of concern were not within the range of conditions used in the development of the tests themselves.

In most cases of inappropriate use of the EP or TCLP tests, the justification given was that it is necessary to cite "standard" or "approved" methods. Even if it is acknowledged that the tests cannot be applied without significant change in the test protocol itself, the need to use a previously "approved" test has been cited.

In a contradictory set of pressures, some offices have devised new tests to suit particular needs, e.g., the "oily waste extraction test," when it was considered necessary. Only rarely have such new or modified leaching tests been subjected to a rigorous review of their precision, accuracy or technical bases comparable to that applied to the EP and TCLP tests.

There are many laboratory tests that have been devised to obtain estimates of the potential for contaminant release. These tests are generally characterized as either static or dynamic. In all instances, aqueous solutions have been utilized as the leaching fluid. Solid-to-liquid ratios of 2:1 to 20:1 have been prescribed. Leaching times of 18 hours to several days, and in some tests, years are required. Various tests specify single to over 20 extractions, and particle sizes from 2 mm to monolith proportions. Table 1 (page 20), provides a summary of over 30 tests designed to help determine the potential for contaminant release. Although a wide range of leaching tests exist, a conceptual framework for their application is generally lacking.

In preparing this report, the Committee has sought the best technical input available on "state-of-the-art" knowledge of the leaching phenomenon. It has also sought and received extensive information on the needs of regulatory and enforcement programs for reliable leaching predictions and their interpretations.

Building on its previous experience in technical reviews, on outside input, and on its own expertise, the Committee offers advice on ways to resolve the conflict between the need for "standard" tests and the need for tests better adapted to the circumstances to which the data are to be applied.

This self-initiated study focused on the following three questions:

1) What are the needs of the Agency and regulated community to quantify leachability or release of contaminants to the environment?

2) What is the state-of-the-art and science dealing with the fundamental principles that should be considered in predicting leaching of chemicals from wastes, contaminated soils, and other sources?

3) What should be or could be done to improve the scientific understanding and application of leaching tests in future risk analysis?

III. WHAT ARE THE NEEDS OF THE AGENCY AND REGULATED COMMUNITY?

The Subcommittee convened a one-day session on February 26, 1990, in Washington, D.C., devoted to assessing the Agency's and other's (private sector and citizen groups) varied needs for leaching tests and information. The findings are summarized in Table 2 (page 25) and are detailed in Appendix C (pages 35-45). Table 2, summarizes the Subcommittee's understanding of the wants, uses, and needs for leachability tests/data within the Agency. At least six program offices have expressed interest in such information. The wants, or what the program offices would like, are varied. Most focused on a means to predict field conditions. All offices expressed a desire for a method(s) to appropriately classify a waste. Given that such a test(s) did exist, the offices would use it such as to set standards, primarily through simulating risk. The Office of Toxic Substances appears to have the broadest uses. Just as the wants and uses are varied, so too are the needs. Consistently, all offices see leachability tests as a means of demonstrating compliance; a use for which most leaching tests were not originally intended.

The EPA, through mandates of the RCRA, CERCLA, CWA and associated regulatory programs, has required chemical testing and other laboratory procedures to predict the possible hazards of chemicals potentially released into the environment. The intent of leaching/extraction tests is to reliably estimate the potential amount and/or rate of contaminant release under worst case environmental conditions, thus enabling remedial, prevent-ative

and anticipatory management actions to be taken to protect human health and the environment.

IV. ASSESSMENT OF CURRENT PRACTICE

The Committee assessed the state-of-the-art in leachability determinations through several means:

a) Participation in a Workshop on Contaminant Migration at Rice University on December 15-16, 1989, organized by the National Center for Ground Water Research for the EPA Robert S. Kerr Environmental Research Laboratory in Ada, OK., in cooperation with the University of Texas at Austin and the Electric Power Research Institute.

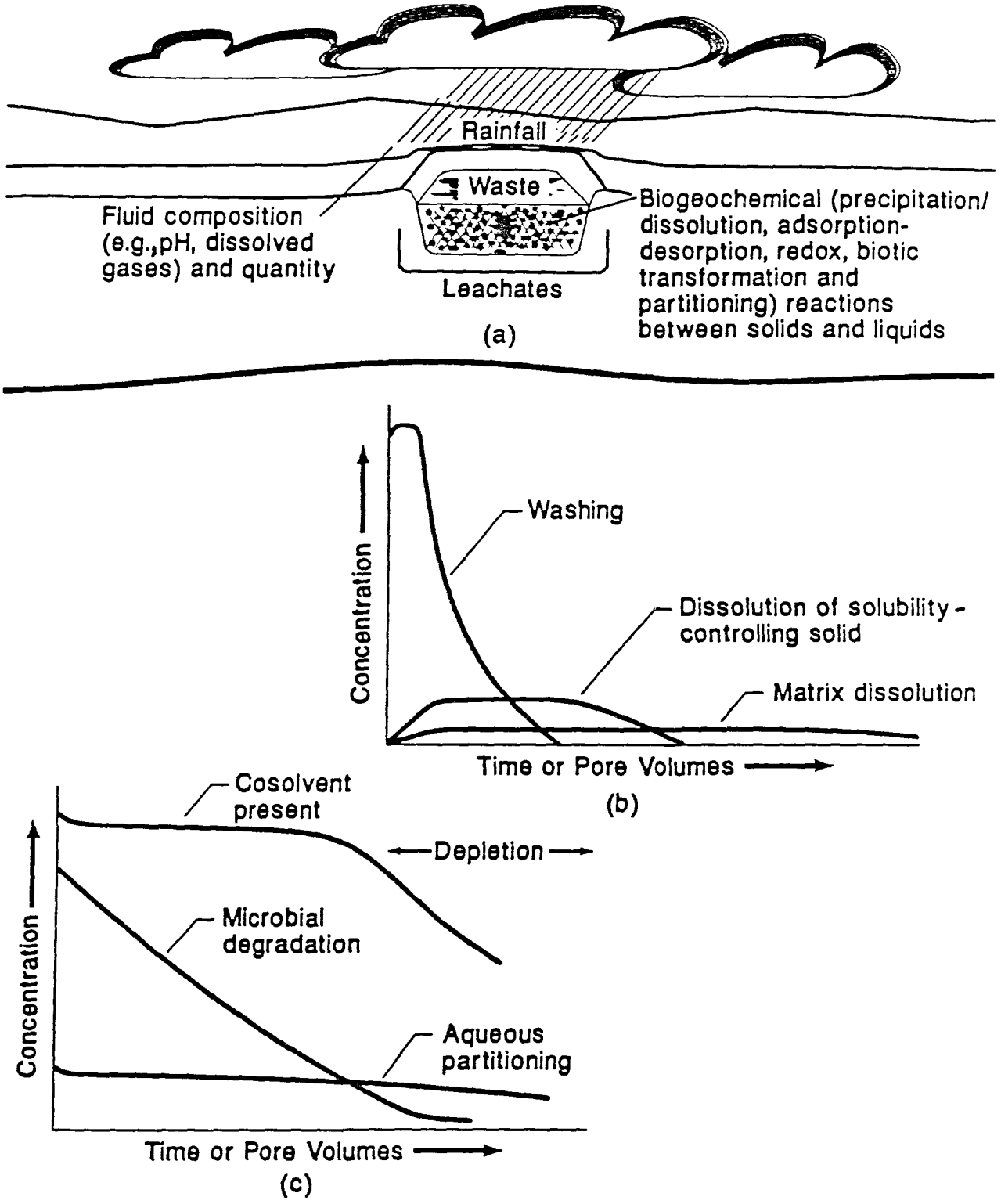
b) Holding a Leachability Workshop under the auspices of the US Environmental Protection Agency, Science Advisory Board on May 9, 1990 in Washington, D.C. The Workshop Program and list of speakers are given in Appendix B, page 34.

c) Review of key references assessing current leachability tests, e.g., Compendium of Waste Leaching Tests, Wastewater Technology Centre, Environment Canada, May 27, 1989 (See Table 1, page 20 for summary of extraction tests).

The findings reported also reflect the personal experiences and expertise of the members of the Leachability Subcommittee.

The Leachability Workshop was conceived as a vehicle for knowledgeable scientists, engineers and practitioners in the field to focus on the scientific principles and issues relating to leachability. The purpose of the Workshop was to conduct a review of the scientific principles involved with leachability phenomena. Various experts discussed relevant topics such as test methods, their descriptions and capabilities for application to the leaching of organics and inorganics, the leaching of stabilized materials, physical-chemical mechanisms, leaching chemistry of organics and inorganics, and alternative approaches to laboratory tests.

The Workshop assisted the Leachability Subcommittee in summarizing the fundamental scientific principles that control leachability (Appendix B, page 34, and Figure 1 page 6), and determining how they can be applied to predict the extent to which contaminants will leach when disposed under various potential environmental scenarios. The Contaminant Migration Workshop, the Leachability Workshop, and the review and assessment of key references, provided the background for formulation of recommendations on how basic principles can be



FIRGURE 1. Conceptual View of Leaching in a Waste Unit.
(a) Generation of leachates;
(b) Potential leaching stages for inorganic contaminants;
(c) Generation of organic leachates.

used on a consistent basis for improving or developing decisions related to leachability.

A conceptual view and summary of the major processes and interactions that can occur in leaching of a waste matrix is presented schematically in Figure 1, page 6. The generation of leachates is depicted (Figure 1a) and is the sum of several geochemical processes involving reactions within a physical mixture of different forms of the same element. For example, in fly ash, an element such as cadmium may occur as simple oxide salts accumulated on the surface of ash particles, as an element within the glass matrix, and as a post-combustion product of aqueous reaction such as $CdCO_3$. Potential leaching stages areillustrated for an inorganic contaminant in Figure 1b. Reaction of the readily available and highly soluble fraction, such as the surface oxide salts, provides high solute concentration during initial washing or leachate generation. This stage is followed by considerably decreased concentrations of solutes as the readily available fractions have been leached or transformed into less soluble forms (such as the $CdCO_3$). These transformed solids are referred to as solubility-controlling solids. Dissolution and depletion of these solubility controlling solids and the bulk matrix are important determinants of the temporal change and characteristics in leachate generation following initial washing.

The generation of organic leachates (Figure 1c) also involves several biogeochemical processes. For example, the leachate concentration of an organic compound may be controlled by its water solubility (aqueous partitioning). However, in the presence of a cosolvent, the leachate concentration is usually controlled by the solubility of the constituents in the organic phase rather than in water and may be substantially increased. Microbial degradation, abiotic transformations and physical partitioning to gaseous and solid phases can further alter the pattern of leachate generation.

V. RECOMMENDATIONS FOR IMPROVED LEACHABILITY DETERMINATIONS TO FILL GAPS BETWEEN NEEDS AND CURRENT PRACTICES

Based on a broad-ranging review and analysis of needs and information available on leaching phenomena, the Leachability Subcommittee has developed the following recommendations:

1) A variety of contaminant release tests and test conditions which incorporate adequate understanding of the important parameters that affect leaching should be developed and used to assess the potential release of contaminants from sources of concern.

In scientific and technical terms, no "universal" test procedure is likely to be developed that will always produce

credible and relevant data for input to all decision making exercises. There is nothing inherently bad about having a wide variety of test conditions and methods, to cover the range of needs, if each is defensible in view of the scientific and technical understanding of the basic processes involved. Provisions for adequate margins of safety and varied scenarios should be made. A wealth of knowledge already exists which can form the essential basis for quantitative determinations of the release of contaminants. Appropriate physical, chemical and biological factors should be selected for a specific test or model to reliably estimate contaminant releases. Important information includes: waste characteristics, mobilizing fluid characteristics, intrinsic behavior of chemicals, and most likely reactions to occur under varying hydrologic, chemical and atmospheric conditions (Table 3, page 27).

Chemical and physical characteristics of a waste are significant determinants of leachate composition. The nature and conditions of occurrence of leachable constituents, rather than the total amounts, often dictate the consequential release of contaminants from the waste. Moreover, the speciation of constituents of concern, for example, heavy metals, cannot or has not in most cases been reliably quantified. This can confound reliable anticipation of potential contaminant release, further contributing to uncertainty in contaminant release assessment. Waste or matrix heterogeneity is another complicating factor.

In addition to waste and matrix characterization, it is similarly important to characterize the leaching medium (i.e.,the fluid) which contacts the waste material. Terrestrial porewaters, including groundwaters, have broadly defined fluid parameters and show tremendous diversity in those characteristics which influence solubility and chemical behavior of mobilized waste chemical constituents. Also, fluid which contacts the waste can be influenced by the presence of contaminants from other wastes, such as at a Superfund site where waste oil has been codisposed with PCBs.

2) Prior to developing or applying any leaching tests or models, the controlling mechanisms must be defined and understood.

Contaminant release (and eventual fate) in a field environment is an extremely complex phenomenon involving multiple phases and multiple constituents. In order to provide a proper conceptual framework for a leachability scenario, a recommended first step in any leaching test or model should be to identify all significant mechanisms that can ultimately determine release and environmental fate of the contaminants.

After identifying mechanisms, an understanding of how they (directly or indirectly) influence release and environmental fate

should be established. Past experience suggests that identifying the principal controlling mechanisms is often straightforward. However, anticipating the interrelationships among concurrent and often competing mechanisms can be much more difficult, yet critical in the characterization of leachability.

In developing the conceptual framework for a leachability scenario, attention should be given to accounting for all significant phenomena -- be they physical, chemical, or biological --and their potential interactions. At a minimum, the following phenomena should be considered: fluid characteristics and flow dynamics, source matrix morphology and chemistry, chemical reactions (equilibrium or kinetic), biotic reactions, and temporal and spatial dependence. These are discussed in relation to the principles identified throughout this report (see also Figure 1 and summary Tables 1, 2 and 3 for overview information).

To understand and predict the leaching of organic constituents of concern, it is important to consider the presence of organic solubilizers such as solvents and oil in addition to wastes. Under the conditions of codisposal with solubilizing agents, the extent of leaching is usually controlled by the solubility of the constituents in the organic phase rather than in water. However, dissolved solvents can, to a lesser extent, affect constituent solubility in the aqueous phase.

Experimental data obtained over the last decade indicate that the solubilizing effect of some agents can dramatically increase the concentrations of normally insoluble organic constituents. In some instances, organics have been shown to enhance the mobility of inorganic constituents, most likely through complexation. In these cases, aqueous extractions to estimate the extent of leachability of the waste may seriously underestimate the magnitude of release for constituents of concern.

Biotic reactions are known to be important in some circumstances and should be considered to fully simulate leachability. Both inorganic and organic constituents frequently undergo biological transformations within a source matrix. These transformations can directly change the chemical environment and composition of the leachate, and contribute to other secondary effects such as changing the nature of the leaching fluids and the setting within which leaching occurs.

The effect of biotransformation has been considered in some instances. The EP, the TCLP and other tests use an organic acid in an attempt to simulate codisposal with degradable materials. The oily waste extraction procedure requires extraction of oil from the solids prior to leaching, because biodegradation in

nature will remove the oily film allowing more intimate contact with the leaching fluid.

It is often difficult to reproduce or simulate in batch extraction procedures, biotransformations which occur in field situations, in part because the temporal and spatial considerations for each are so different. Batch extractions are designed to evaluate equilibrium processes, while biotransformations are rate-limited. However, biotransformation studies are not inherently incompatible with column or dynamic leaching tests, and as such should be incorporated in those cases where they could be important. In attempting to integrate the assessment of biotransformation phenomena into a leaching test, it is critical to consider rate limitations in choosing the test's duration. The effects of biotransformation should be considered in interpreting or applying leachability results in cases where it can occur.

3) A consistent, replicable and easily applied , physical, hydrologic and geochemical representation should be developed for the waste management scenario of concern.

Central to devising leaching tests and models is the development of a sound conceptual framework of the physical system which is to be simulated. This framework requires proper and relevant identification of the precipitation-dissolution reactions by systematically examining the fluid and waste characteristics as well as the intrinsic chemical behavior of the constituents. This includes the equilibrium or steady state conditions as well as the reaction rate representing the dynamics of the leaching process. Reaction rate is an important, yet poorly understood, factor.

The complexities of fluid-solid waste interaction dynamics can occur in "real world" field conditions in which fluid parameters can change spatially and temporally with corresponding shifts in constituent release behavior. A constituent may initially occur in a highly soluble form, but may subsequently be transformed to highly insoluble precipitates, thereby rendering it immobile. Similarly, a constituent may be leached at a greater rate due to the very acidic or very alkaline pH of the leaching fluid. Dissolution of the protective matrix material may increase the potential for transport of the leaching fluid and the release of contaminants.

The Subcommittee believes that rate-limiting chemical and microbial reactions often play a pivotal role in governing leaching rate and contaminant fate. Consequently, situations can occur in which equilibrium concepts may not apply to some (and probably even to the majority) of the contaminant release (and transport) scenarios. It is expected that, in numerous instances, equilibrium-based projections of leachate levels can

only provide an asymptotic (e.g., upper or lower limit) estimate of leachability that is not experienced at actual disposal sites during the management period of interest. In addition, hydrologic conditions and their spatial and temporal variations can impact on rates of dissolution and precipitation, mass transfer, and disequilibria. These effects and their impacts are not well understood, despite their important contributions to leaching of constituents to the environment. Despite these limitations, determinations of hazard for various contaminant release (and transport) scenarios are a necessity in order to accommodate the realities of statutory requirements and the attendant regulatory requirements.

If the intent is to match a test to an environmental situation with respect to contact time, a distinction could be made between situations where the waste is contained within a lined landfill (long contact time), or where the waste is underlain by a very porous medium or is in a flowing surface water (short contact time). Likewise, the leaching liquid-to-solid ratio at a waste management site is functionally (dynamically) related to rainfall, infiltration rates, the presence or absence of a cap over the waste, the quantity of waste, and other site-specific factors. Exceptions do occur based on site-specific factors. For example, if porous media have been plugged, this would increase contact time. Because of plugging phenomena, significant retention of waste leachate has been observed in some municipal landfills (such as in the Long Island, New York area), despite the fact that they are unlined and underlain by a very porous medium (sandy soil).

Explicit selection of leachate tests to best match repeated or continual leaching may require a determination of whether the particular management scenario involves wastes in a lined and/or capped landfill, or in more open systems in which greater contact exists with the surrounding environment. In the former case, the leachate may only be drained from the waste once. In the latter case, multiple leaching and contact times can reasonably be expected to occur. In most cases, multiple leaching can probably be expected, although contact times, liquid-to-solid ratios, pH and other environmental factors may vary, not only for different scenarios, but also for successive leaching events in a given environmental setting. This variability can be difficult to predict and simulate.

The nature and influence of physical dimensions (e.g., particle size and shape) of the waste matrix is difficult to predict for test development purposes. As a general principle, accuracy and reliability should be improved if the waste is leached in the form that is present in the environment, if it can be expected and demonstrated that the form of the waste will remain relatively unchanged with time. In other words, waste matrix dimensions should simulate what is expected in the

environment over the time period of concern. It also follows that the dimensions range in test samples should reflect that of the wastes of concern.

A noteworthy issue is that some wastes in the environment clearly have dimensions which are too large to be examined with a particular laboratory test apparatus. Depending on accommodations to particular requirements of the test apparatus, this may or may not be a serious problem. If only a modest size reduction is required, such as reduction of a football-sized object to an average of one inch diameter, this is likely not to be a serious problem with respect to the development of leachability information, because the surface to volume perturbation is much less severe than had the requirement been to reduce the football-sized mass to milled wastes of a millimeter or less size range. The surface-to-volume ratio between large particles and those of an inch or so in size is not greatly different. However, diffusion limitations are intimately related to grain size and matrix uniformity, and the time scale is proportional to the square of the length scale. Size reduction may also cause changes in surface chemistry, redox conditions and availability of reaction sites.

One practical way to limit the size problem in batch tests is to mill or crumble wastes which do not have strengths appreciable enough to survive in the environment. Accurate predictions of leaching potential from wastes with intermediate strength may be better handled by subjecting them to sequential leaching accompanied by sequential particle size reduction. At the other extreme, exceptionally durable materials are best handled by leaching in an "as is" condition. Column tests, provided that channel effects are minimized or eliminated, are more amenable to testing wastes "as is" with respect to waste matrix size than are batch tests. Secondary tests which evaluate strength in waste management environments include, for example, the Toxicity Characteristic (TC) structural integrity test, unconfined compressive strength, freeze-thaw (ASTM Method 4843-88) and wet-dry (ASTM D4842-89) tests. Most batch leachate tests require wastes to be tumbled. It has been shown that if wastes are tumbled "as is", those which are not strong enough to survive in the environment will, in fact, break up during tumbling, while only strong materials will survive and remain intact (Bone et al, "Modification of the TCLP Procedure to Accommodate Monolithic Wastes," Fifth Annual Waste Testing and Quality Assurance Symposium, July 24-28, 1989). Additional testing may be necessary to determine whether the stabilized waste will remain a monolith under varying environmental conditions. Thus it is generally best to limit sample size reduction even in batch tests.

4) Leach test conditions (stresses) appropriate to the situations being evaluated should be used for assessing long-term contaminant release potential.

The best way to estimate the extent of contaminant release from a waste matrix of interest is to have a test that reflects realistic field conditions (Table 3, page 27). However, the regulatory and statutory framework for decision makers often seems to require that estimates be made for the maximum potential for contaminant release in a specific scenario (Table 2, page 25). This involves testing under extreme conditions or stresses, employing physical parameters such as fine particle size, temperature and pH set at high contaminant solubility, high ratio of leaching fluid to sample, high degree of mixing, and long fluid/particle contact time. But, while it may seem necessary from a regulatory and compliance perspective to use maximums in leach tests, every effort should be made to design realistic tests which simulate those actual worst case field leaching conditions that can be reasonably postulated to occur at some frequency in relevant waste management conditions.

In order to adequately characterize any particular field scenario for leach tests, the relevant environmental conditions postulated, and the degree to which they should be applied to samples undergoing contaminant release testing, should be carefully established and should take into consideration the nature of the regulatory decisions that are required. Moreover, any extrapolation of a set of conditions or stresses appropriate for one purpose should not be applied for other applications without reasonable verification of relevance. Extrapolation of tests designed for one purpose to another purpose should be scientifically defensible. A suggested approach to development of an array of leach tests follows:

a) First, identify the set of regulatory decisions that will be made with the test results.

The decision set could include (but is not limited to): (1) a decision whether or not a waste should be classified as hazardous; (2) the extent of leaching from a large volume waste in order to determine suitability for waste utilization or alternative management with or without restriction; (3) a determination of release potential to support an estimate of risk to human health or the environment; (4) a determination of solidification/stabilization effectiveness to provide a basis for a containment design; and, (5) selection of containment, treatment or remediation technologies.

b) Convene a panel of individuals that represent a cross-section of the regulatory community, the regulated community, academia, and environmental/public interest groups for the

purpose of defining the array of conditions for each type of test.

Inputs should be sought from the broad technical (expert) community, for example, ASTM Committee D-34 on Waste Management and other technically credible groups of scientists, engineers and practitioners in the field. Consideration should be given to obvious stress factors such as: the appropriateness of sample size reduction, leaching fluid pH and buffering capacity, leaching temperature, waste-to-leaching fluid ratio, number and sequence of leaching steps, contact time, agitation mode, biological action, and exposure to freeze/thaw as well as wet/dry cycles.

c) Develop a hierarchial framework for reasonable stresses.

The set of possible stresses can be ranked from moderate to severe, and identified with appropriate regulatory decisions, depending on the conditions to which they are applied and the importance of the decisions.

Using the above rationale, as the need for a new decision is identified, its placement within and relevance to the decision-making framework of prescribed stresses (and extant leach tests) should be clear. While some procedures must be developed to make decisions in direct compliance with regulations, and require either site-by-site or type of application assessments, this recommended exercise could help to avoid the inappropriate application of a leach test or related test that has been developed for another purpose.

5) Laboratory leach tests should be field-validated, and release test accuracy and precision established before tests are broadly applied.

Numerous tests have been developed by the EPA, ASTM and others in order to estimate contaminant release and subsequent transport through soil matrices (Table 1, page 20 and Appendix C, page 35). Some of the test methods have been subjected to extensive precision studies involving multiple laboratory samples and analysis, while other tests have clearly only been subjected to minimal or very limited evaluation, as in single laboratory precision studies. Furthermore, the accuracy of leaching test results has not been, for the most part, subjected to field verification. Anecdotal evidence suggests that the accuracy and reliability of laboratory test results for field application are questionable, primarily due to the simplifications or approximations utilized. In principle, the accuracy and precision of contaminant release predictions can be improved by matching the controllable test variables more closely to the environmental conditions that actually are encountered under field conditions. But it is questionable whether many leaching

tests are adequately predictive of some reasonable worst case scenarios.

The number and types of analytes for which the tests have been evaluated and applied are likely to evolve continuously. Currently, all of the tests are designed for metals, semi-volatile, and non-volatile organics, and only a few are valid for volatile organics. Consequently, there are considerable data to determine the precision of the tests for metals. This is fortunate, since metals leachability is much more sensitive to factors which are difficult to control, such as pH, ionic strength and particle size. Thus, in view of current knowledge about metals leachability, much can be inferred about the fundamental processes involved in leaching of inorganic constituents from wastes.

As was suggested in the SAB EEC Leachability Workshop and technical briefing of May 9, 1990, review of the reliability and precision of metals leachability test results leads the Subcommittee to conclude that test precision is probably satisfactory, particularly in comparison to the reliability of test methods and variables associated with other factors which are used in conjunction with leachability to arrive at environmental risk assessments. Although the precision of any test used for regulatory decisions or environmental risk assessments should always be evaluated, test accuracy is more important than test precision.

The state of scientific capability for leaching test interpretation indicates that, in order to provide a realistic estimate of the leachability of a specific waste in a given environment, site-specific conditions must be fully considered. Consideration must be given to all factors that have the potential to impact leachability in either a positive or a negative fashion. For example, cosolvent effects can greatly facilitate the movement of contaminants out of the waste matrix, while biological activity can increase or decrease the release of contaminants as well as transform contaminants prior to their release into the environment.

Therefore, the Subcommittee recommends that, through the Office of Research and Development, EPA carry out a comprehensive "field validation" of leaching tests and establish laboratory accuracy and precision. The results should then be factored into guidance for the improvement of leaching tests.

6. More and improved leach models should be developed and used to complement laboratory tests.

Unlike the advances in models for transport and fate predictions, development of mathematical models to predict contaminant leaching is in its infancy. Only a small number of

"leachate generation" models are proposed (e.g., HELP, FOWL™, UNIFAC), and to date these have had limited use.

While various laboratory tests can, in principle, be used to physically "model" a contaminant release scenario, more and improved "mathematical" models for leaching predictions should be developed and employed to complement laboratory tests.

Simple equilibrium (or as warranted, more comprehensive dynamic) models could be utilized to analyze data obtained from various leaching tests. These investigations could then be used to evaluate the applicability of such models as a leach test adjunct, or in more direct application, as an approach to estimating field leachability.

Contaminant release and transport models currently play an important role in the Agency's regulatory decision-making process. For example, the HELP model is used in the delisting regulation to project hydraulic flux through landfills. Further, the HELP model, in conjunction with the EPACML, is used to predict the dilution attenuation of contaminants from the bottom of a landfill to the nearest well. This and other models hold the promise of significant utility if: (1) they are sufficiently comprehensive and reliable for predicting the transport and fate of contaminants of concern; and (2) the data base necessary (including leachate composition) for model use is adequate and reliable. These criteria limit the conditions under which a model can be applied.

Potential pitfalls in the use of models should be examined prior to their application, to ensure that their results are reliable (Refer to the SAB Resolution on Use of Mathematical Models by EPA for Regulatory Assessment and Decision-Making (EPA-SAB-EEC-89-012), January 1989). Generally, such a review can proceed consistent with principles outlined in prior SAB deliberations on the generic use of models. Examples of concern to be addressed include: Agency over-reliance on models to the exclusion of the acquisition of needed data; the extent to which models are based on a fundamental representation of the relevant physical, chemical and biological processes that can affect environmental systems; the extent to which models have been validated with laboratory and field data; the analysis of sensitivity and uncertainty impacts on models and model predictions; and, the need to ensure adequate peer review of model development and utilization. In circumstances where laboratory and field data fail to confirm the adequacy of a model, it is inappropriate to use the model for decision making until improvements of an acceptable nature can be implemented.

Laboratory and field tests should be utilized to establish the conditions under which model simulations can be used to extrapolate laboratory and field data. A model should not be

used to predict leachability or transport in scenarios that are outside the scope of the model applicability.

The sensitivity of a model to specific input data parameters should be established; this indicates the level of effort needed in the determination of the parameters for model evaluation. Pertinent questions include: How accurate should the input data be? Can input data be estimated by analogy rather than obtained from actual field measurements? Following these judgments, an appropriate data base can be developed for a model input.

Analysis should attempt to identify whether a different outcome might have been realized had more representative data been available, i.e., the expected model outcomes associated with varying degrees of data uncertainty should be established. Consistent with input data requirements, a model can then be used to predict leachability behavior in a specified field scenario.

7) To facilitate the evaluation of risk implications of environmental releases, the Agency should coordinate the development of leach tests and the development of models in which the release terms are used.

Leaching tests characterize the "source terms" for transport and fate models. Yet almost all transport and fate models assume that leachates are of constant concentration and of infinite duration and quantity. In reality, source terms (leachates) are a function of time, space, waste properties, and leaching fluid characteristics.

Numerous models presently are available to describe the transport of chemicals through porous material, including both the saturated and unsaturated zones. The hydrologic or fluid flow models (such as EPACML, HELP) could be improved to consider the chemistry and microbiology of contaminant release within the source waste matrix. The resulting leaching predictions would then be dynamically included in the transport analysis. The Subcommittee recommends that models used by the Agency be modified to couple source leaching masses with the transport and fate predictions. Such linked models would more accurately and precisely predict environmental concentrations to quantitatively evaluate risk implications, albeit at the cost of greater computational and data collection effort.

8) The Agency should establish an inter-office, inter-disciplinary task group, including ORD to help implement these recommendations and devise an Agency-wide protocol for evaluating release scenarios, tests, procedures, and their applications. The task group should also be charged with recommending what the appropriate focal point(s), responsibilities, and organizational, budgetary and communication links should be within the Agency for the most effective, continued and ongoing support and pursuit of

the research, development and utilization of methods and procedures.

The Subcommittee's discussions on Agency "needs" with the various program offices pointed out that a variety of applications and regulatory decisions depend on appropriate "release" tests and waste matrix transport and fate analyses (Table 2, page 25 and Appendix C, page 35). Therefore, it is recommended that an inter-office, inter-disciplinary task group be established to aggressively formulate implementation plans for the development of scientifically defensible leaching tests and models for the many contaminants and applications. This task group should include experts in the field of hydrology, soil science, analytical chemistry, environmental chemistry and biology, mathematical modeling and environmental engineering.

9) Core research on contaminant release and transport within the waste matrix is needed.

Consonant with the underlying concept of EPA's core research initiative and its intent to provide and sustain knowledge and expertise responsive to both current and future risks to human health and the environment, it is apparent from the preceding discussions that issues associated with leachability, and specifically methods to adequately measure and predict leaching from an assortment of waste matrices, are and should remain a priority focus.

Unfortunately, consensus with respect to the use of leachability testing protocols has yet to be attained. It appears that methods currently advocated neither fully satisfy short-term or long-term needs, nor do they withstand the rigors of scientific scrutiny to an extent that scientifically supportable management decisions can be made.

Therefore, the present state-of-knowledge concerning leaching phenomena under a broad range of waste management scenarios of regulatory and scientific interest should be fully analyzed and reported. Based on the outcome of this task, an integrated, active program of research, including exploration of potential and actual risks associated with leaching of constituents, should be developed.

The core research program regarding leachability should embrace, to the maximum extent feasible, all underlying issues pertinent to leachability. This should include, but not be limited to the following: basic mechanisms, potential test procedures, analytical methods, predictive model development, performance standards, and regulatory initiatives. Accordingly, a complementary understanding of the scientific and operational issues of various waste management options, as well as the intricacies of the associated environmental settings, is

required. For instance, a possible approach may be to develop a waste management matrix which defines both current and potential future treatment, storage, use or disposal practices and associated environmental circumstances, and then develop companion testing protocols to simulate each situation. These tests should consider the operational phase as well as the pre-installation and post-closure periods.

Such an approach as recommended above should provide better correspondence between the results of testing protocols intended to simulate actual conditions under both short-term and long-term conditions. Whether these objectives can be accomplished with laboratory, pilot or field-scale simulations would be part of the challenge of the core research initiative. However, it could be anticipated that both short-term or accelerated screening and long-term field-scale simulations may need to be developed as an essential adjunct to each selected waste management alternative. The ultimate goal would be to provide operational as well as regulatory (and remedial) control, thereby enhancing the potential for more meaningful assessments of environmental and health risks.

TABLE 1 - EXTRACTION TESTS

I. STATIC TESTS (LEACHING FLUID NOT RENEWED)

A. AGITATED EXTRACTION TESTS

TEST METHOD	LEACHING FLUID	LIQUID:SOLID RATIO	MAXIMUM PARTICLE SIZE	NUMBER OF EXTRACTIONS	TIME OF EXTRACTIONS
TCLP (1311)	ACETIC ACID	20:1	9.5 mm	1	18 HOURS
	0.1 N ACETIC ACID SOLUTION, pH 2.9, FOR ALKALINE WASTES				
	0.1 N SODIUM ACETATE BUFFER SOLUTION, pH 5.0, FOR NON-ALKALINE WASTES				
EP TOX (1310)	0.5 N ACETIC ACID (pH=5.0)	16:1 DURING EXTRACTION 20:1 FINAL DILUTION	9.5 mm	1	24 HOURS
ASTM D3987-85	ASTM TYPE IV REAGENT WATER	20:1	AS IN ENVIRONMENT	1	18 HOURS
CALIFORNIA WET	0.2 M SODIUM CITRATE (pH=5.0)	10:1	2.0 mm	1	48 HOURS
LEACHATE EXTRACTION PROCEDURE (MOE, ONTARIO)	ACETIC ACID 2 MEQ/G	20:1	AS IN ENVIRONMENT	1	24 HOURS
QUEBEC R.S.Q (MOE, QUEBEC)	INORGANIC 0.02 MEQ/G ORGANIC DISTILLED WATER	10:1	GROUND	1	24 HOURS
FRENCH LEACH TEST (AFNOR, FRANCE)	DI WATER	10:1	9.5 mm	1	16 HOURS
EQUILIBRIUM EXTRACTION (ENVIRONMENT CANADA)	DISTILLED WATER	4:1	GROUND	1	7 DAYS
MULTIPLE BATCH LEACHING PROCEDURE (ENVIRONMENT CANADA)	ACETIC ACID BUFFER, pH 4.5	4:1 OR 2:1	9.5 mm	VARIABLE	24 HOURS

TABLE 1 - EXTRACTION TESTS (Continued)

TEST METHOD	LEACHING FLUID	LIQUID:SOLID RATIO	MAXIMUM PARTICLE SIZE	NUMBER OF EXTRACTIONS	TIME OF EXTRACTIONS
MATERIAL CHARACTERIZATION CENTRE-4 (MATERIAL CHARACTERIZATION CENTRE)	CHOICE	10:1	2 FRACTIONS 74 - 149 mm 150 - 425 mm	1	20 DAYS TO TO YEARS
OILY WASTE (1330)	SOXLET WITH THF AND TOLUENE EP ON REMAINING SOLIDS	100G:300ML 20:1	9.5 mm	3	24 HOURS (EP)
SYNTHETIC PRECIPITATION LEACHING PROCEDURE (1312)	VARIABLE	20:1	9.5 mm	1	18 HOURS
EQUILIBRIUM LEACH TEST	DISTILLED WATER	4:1	150 μm	1	7 DAYS

B. NON-AGITATED EXTRACTION TESTS

TEST METHOD	LEACHING FLUID	LIQUID:SOLID RATIO	MAXIMUM PARTICLE SIZE	NUMBER OF EXTRACTIONS	TIME OF EXTRACTIONS
STATIC LEACH TEST METHOD (MATERIAL CHARACTERISTIC CENTRE-1)	CAN BE SITE SPECIFIC	VOL/SURFACE 10μm	$40mm^2$ SURFACE AREA	1	> 7 DAYS
HIGH TEMPERATURE STATIC LEACH TEST METHOD (MATERIAL CHARACTERIZATION CENTRE-2)	SAME AS ABOVE BUT AT 100°C	VOL/SURFACE 10μm	$40mm^2$ SURFACE AREA	1	> 7 DAYS

C. SEQUENTIAL CHEMICAL EXTRACTION TESTS

TEST METHOD	LEACHING FLUID	LIQUID:SOLID RATIO	MAXIMUM PARTICLE SIZE	NUMBER OF EXTRACTIONS	TIME OF EXTRACTIONS
SEQUENTIAL EXTRACTION TESTS	0.04 M ACETIC ACID	50:1	9.5 mm	15	24 HOURS PER EXTRACTION

TABLE 1 - EXTRACTION TESTS (Continued)

D. CONCENTRATION BUILD-UP TEST

TEST METHOD	LEACHING FLUID	LIQUID:SOLID RATIO	MAXIMUM PARTICLE SIZE	NUMBER OF EXTRACTIONS	TIME OF EXTRACTIONS
SEQUENTIAL CHEMICAL EXTRACTION	FIVE LEACHING SOLUTIONS INCREASING ACIDITY	VARIES FROM 16.1 TO 40.1	150 μm	5	VARIES FROM 2 TO 24 HOURS
STANDARD LEACH TEST, PROCEDURE C (UNIVERSITY OF WISCONSIN)	DI WATER SYN LANDFILL LEACHATE	10:1, 5:1 7.5:1	AS IN ENVIRONMENT	3	3 OR 14 DAYS

II. DYNAMIC TESTS (LEACHING FLUID RENEWED)

A. SERIAL BATCH (PARTICLE)

TEST METHOD	LEACHING FLUID	LIQUID:SOLID RATIO	MAXIMUM PARTICLE SIZE	NUMBER OF EXTRACTIONS	TIME OF EXTRACTIONS
MULTIPLE EXTRACTION PROCEDURE (1320)	SAME AS EP TOX, THEN WITH SYNTHETIC ACID RAIN (SULFURIC ACID: NITRIC ACID IN 60:40% MIXTURE)	20:1	9.5 mm	9 (OR MORE)	24 HOURS PER EXTRACTION
MWEP (MONOFILL WASTE EXTRACTION PROCEDURE)	DISTILLED/DEIONIZED WATER OR OTHER FOR SPECIFIC SITE	10:1 PER EXTRACTION	9.5 mm OR MONOLITH	4	18 HOURS PER EXTRACTION
GRADED SERIAL BATCH (U.S. ARMY)	DISTILLED WATER	INCREASES FROM 2:1 TO 96:1	N/A	>7	UNTIL STEADY STATE
SEQUENTIAL BATCH ASTM D4793-88	TYPE IV REAGANT WATER	20:1	AS IN ENVIRONMENT	10	18 HOURS
WASTE RESEARCH UNIT LEACH TEST (HARWELL LABORATORY, UK)	ACETIC ACID BUFFERED pH=5	1 BED VOL 5 ELUTIONS 10 BED VOL >6 ELUTIONS	CRUSHING	>11	2 TO 80 HOURS
STANDARD LEACHING TEST: CASCADE TEST SOSUV, NETHERLANDS	DISTILLED WATER HNO_3 pH 4.0	20:1	CRUSHING	5	23 HOURS

TABLE 1 - EXTRACTION TESTS (Continued)

B. FLOW AROUND TESTS

TEST METHOD	LEACHING FLUID	LIQUID:SOLID RATIO	MAXIMUM PARTICLE SIZE	NUMBER OF EXTRACTIONS	TIME OF EXTRACTIONS
IAEA DYNAMIC LEACH TEST (INTERNATIONAL ATOMIC ENERGY AGENCY)	DI WATER/SITE WATER	N/A	ONE FACE PREPARED	>19	>6 MONTHS
ISO LEACH TEST (INTERNATIONAL STANDARDS ORGANI-ZATION)	DI WATER/SITE WATER	N/A	SURFACE POLISHING	>10	>100 DAYS
ANSI/ANS 16.1 (AMERICAN NATIONAL STANDARDS INSTITUTE/ AMERICAN NUCLEAR SOCIETY)	DI WATER	N/A	SURFACE WASHING	11	90 DAYS
DLT	DI WATER	N/A	SURFACE WASHING	18	196 DAYS

C. FLOW THROUGH TESTS

TEST METHOD	LEACHING FLUID	LIQUID:SOLID RATIO	MAXIMUM PARTICLE SIZE	NUMBER OF EXTRACTIONS	TIME OF EXTRACTIONS
STANDARD LEACHING TEST: COLUMN TEST (SOSUV, THE NETHERLANDS)	DI WATER HNO_3 pH=4	10:1	AS IN ENVIRONMENT	7	20 DAYS
COLUMN ASTM D4874-89	TYPE IV REAGENT WATER	ONE VOID VOLUME	AS IN ENVIRONMENT	1	24 HOURS

TABLE 1 - EXTRACTION TESTS (Continued)

III. OTHER TESTS

TEST METHOD	LEACHING FLUID	LIQUID:SOLID RATIO	MAXIMUM PARTICLE SIZE	NUMBER OF EXTRACTIONS	TIME OF EXTRACTIONS
MCC-5S SOXHLET TEST (MATERIAL CHARACTERISTIC CENTER)	DI/SITE WATER	100:1	CUT AND WASHED	1	0.2 ML/MIN
ACID NEUTRALIZATION CAPACITY	HNO_3 SOLUTIONS OF INCREASING STRENGTH	3:1	150 μm	1	48 HOURS PER EXTRACTION

REFERENCES:

1. Compendium of Waste Leading Tests, Waste Water Technology Centre, Environment Canada, Final Draft May 27, 1989
2. Private discussions with Gail Hansen, Office of Solid Waste, U.S. EPA

TABLE 2 - TEST REQUIREMENTS, USES OF TESTS, AND PROGRAMATIC NEEDS FOR LEACHABILITY TESTS BY THE AGENCY AS PERCEIVED BY THE SCIENCE ADVISORY BOARD's ENVIRONMENTAL ENGINEERING COMMITTEE

	PROGRAM OFFICE *					
TEST REQUIREMENTS	SF	SC	OSW	OTS	RSKERL	OMMQA
Simple method	O	X	X	O	O	X
Field Analog	X	X	O		O	O
Model Source Term	X	O	X	O	X	X
Predict Leaching	X		X	O	X	X
Method Validation	X		X	O	X	X
TIE Compatible		X		O		
Surface Water Interface	X	X	O		O	O
Mismanagement Predictor	X	X	X		X	X
Waste Classification	X	X	X	X	X	X
"No Reasonable Risk" Determination				X	O	O
USES OF TESTS						
Demonstrate Federal/ State Compliance	X	X	X	X	O	X
Simulate Risk	X	X	X	X	X	X
Set Standards	X	O	X	X	O	O
Compare Waste Management Strategies	X	O	X	X	O	X
Compliance/ Clean-Up Goals	X	O	O	O	O	X
Examine "Worst Case"	X		X	O	X	X
Apply to Human Health	O	X	O	O	O	O
Identify Toxicants	O	X	X	X	X	X
New Product Information				X		O
Establish "Equivalency" To Thermal Destruction				X		O
Evaluate Lined and Unlined Units	X		X	O	O	O

TABLE 2 - (Continued)

PROGRAMATIC NEEDS FOR TESTS	PROGRAM OFFICE *					
	SF	SC	OSW	OTS	RSKERL	OMMQA
Flexibility	X	X	O		O	O
Multiple Tests	X	X	O		X	X
Standardized Protocols		X	X	O	O	O
Compliance	X	X	X	X	X	X
Remedial Design	X	O	O	O	X	O
Biological Response	O	X	O	O	O	O
Matrix Data	X	X	X	O	X	X
EP/TCLP	X		X	O	X	O
Acid Rain Leaching	O	O	X		X	O
Multiple Extraction	O	O	X	X	X	X
Oily Waste Extract	O	O	X	X	X	X
Equivalent Tests				X		O
Non-Destructive Tests	O	O	O		O	O

* SF = Superfund Program, US EPA
SC = Office of Water, Sediment Critria Program, US EPA
OSW = Office of Solid Waste, US EPA
OTS = Office of Toxic Substances, US EPA
RSKERL = R.S. Kerr Environmental Research Lab, US EPA
OMMQA = ORD/Office of Modeling, Monitoring, and Quality Assurance, US EPA
X = Yes, a Blank Signifies No
O = Sometimes or Occasionally

TABLE 3 - SCIENTIFIC CONSIDERATIONS IN DESIGN AND INTERPRETATION OF LEACHABILITY TESTS

PROPERTIES/CHARACTERISTICS	IMPORTANCE AND TEST RAMIFICATIONS
1. Source Matrix Properties	Matrix properties affect availability and accessibility of contaminants.
Chemical composition (functional groups, carbon content, etc.)	Relates to containment and leaching environment.
Morphological structure (amorphous vs. crystalline)	Affects access and containment.
Surface area (surface-to-volume ratio)	Determines interface for sorption; can affect pH.
Surface physics (e.g., charge, tension)	Controls access and flow in the pores matrix.
Matrix heterogeneity	Creates morphological and chemical differences.
Pore structure (volume, distribution)	Constricts flow, retains gas, serves as "small" reactor.
Pore liquid volume (degree of saturation)	Contributes to effective leachate volume.
Pore liquid composition	Modifies leachate composition.
Permeability	Affects flow regime and residence time.
Ease of saturation (time, pressure required)	Leachant/waste interface may be limited by the rate and extent of saturation.
Pooling (micro- and macro-reservoirs, field capacity)	Extracting fluid ("leachant") and leachate retention; provides *in situ* reaction opportunity.
Biodegradability	Matrix can change properties due to biodegradaton.
Toxicity	May limit biodegradation of the contaminants or matrix property changes.

TABLE 3 (continued)

PROPERTIES/CHARACTERISTICS	IMPORTANCE AND TEST RAMIFICATIONS
Buffer capacity	Availability of buffer capacity affects leachability and diffusion, and regulates efficiency and nature of biodegradation.
2. Contaminant Properties	Leachability is a function of the nature of the contaminants.
Chemical composition	Different chemicals or the same contaminant in a different physical or chemical form exhibit distinct differences in leachability.
Concentration	Concentration gradients affect leaching rate and equilibria.
Toxicity	Reduces efficiency of concurrent biotransformation.
Biodegradability	Compound structure and environmental conditions affect biodegradability.
Heterogeneity	Affects containment and availability for reaction and/or leaching.
Diffusivity	Determines transport via diffusion.
Solubility	May affect mass transport and limit removal and/or reaction.
Volatility (boiling point, Henry's constant)	Controls liquid/vapor phase transport and loss of contaminants during leaching and analysis.
3. Leachant Properties	Leachant properties control solubilization/dissolution and mass transport processes.
Initial chemical composition	Could contain contaminants, may be aggressive, may change as the leaching process proceeds.
Aqueous/non-aqueous	Normally water (distilled, tap, or site) as modified by test protocol.

TABLE 3 (continued)

PROPERTIES/CHARACTERISTICS	IMPORTANCE AND TEST RAMIFICATIONS
Hydrophobic-hydrophilic nature **	Surfactants or hydrophobic solvents could enhance leaching.
Gas (oxygen, carbon dioxide content, etc.)	Affects pH and nature of biological, physical and chemical interactions.
Density	Contributes to hydraulic gradient effects and hydraulic conductivity.
Buffer capacity	Controls pH change.
Viscosity	Affects flow regime, saturation, and hydraulic conductivity.
pH	May or may not control the leaching process.
4. Fluid Dynamics	Fluid dynamics in a given system dictate contact time and opportunity, which affect reaction extent and mass transfer. Fluid dynamics have important ramifications to the selection of leaching mode, e.g., continuous column, batch, sequential batch; equilibrium (intended to represent specific, worst case scenarios), non-equilibrium; dynamic (mixed), static.
Flow gradient	Affects transport of contaminants by dispersion, convection, and advection. Also affects mechanism of mass transport. Agitation may be used to generate a maximum gradient. Flow path could lead around or through the waste. Cracks or interconnected pores would short-circuit flow.
Flow regime (laminar vs. turbulent)	Affects contaminant transport and gradient. Restricts the applicability of Darcy's Law.

** NOTE: This is also a contaminant characteristic which determines affinity to leach or to be bound in a matrix.

TABLE 3 (continued)

PROPERTIES/CHARACTERISTICS	IMPORTANCE AND TEST RAMIFICATIONS
Flow pattern (intermittent vs. continuous)	Could weather and/or disintegrate waste matrix. Impacts on the concentration gradient and transport.
5. System Properties	Operationally determined by the leachant/waste interaction.
Precipitation/dissolution/ reprecipitation	Potential removal/release process.
Solubilization (capacity, limits)	Ability to remove contaminants by dissolution.
Other chemical reaction and reversibility	May change contaminant behavior and/or structure.
Complexation	Affects transport, solubilization and possible surficial binding of metals and organometallic compounds.
Sorption/desorption	Contributes to the retention or removal of solutes.
Partitioning	Affects equilibrium opportunity and spatial and temporal distribution.
Cosolvency	Enhanced removal by solvent mixtures, affects distribution of solutes.
Common ion effect	Could delay the removal of contaminants associated with more than one anion.
Redox environment	Could affect opportunity for biological or chemical transformations and reactivity.
pH	Major influence on biological, physical and chemical transformation processes.
Temperature	Affects reaction rates, solubility, pore pressure, etc.
Mass transfer or equilibrium limitations	Need to determine which dominates.

TABLE 3 (continued)

PROPERTIES/CHARACTERISTICS	IMPORTANCE AND TEST RAMIFICATIONS
6. Temporal/Spatial Dependence	Temporal and spatial limitations may accelerate or retard leaching.
Contaminant recharge	Important element of tests involving site-specific simulations.
Aging dynamics	Physical and chemical properties may change in time.
Weathering effects (dissolution surface washing, wet/dry, freeze/thaw)	Long-term humidity and temperature changes affect matrix integrity.
Biodegradability	Aerobic and anaerobic transformation of and within the matrix.
Barometric fluctuation	Impact gradients, dispersion, and groundwater movement, and behavior of gases and volatiles.
Leachant volumes (contact time)	Major consideration when selecting the leachant/waste (or source matrix) ratios. Leachant/source-matrix interface over an extended period of time could result in the depletion of the contaminant or in the erosion of the matrix.
7. Monitoring methods	Method of monitoring could influence the test and their results.
Precision/accuracy (overall)	To be defined by the data quality objectives.
Environmental sampling, sample preservation/holding time (environmental samples and leachate test samples)	Affects results; plans and standards may be available.
Leaching test	Selected in accordance with objectives. Considers time, environmental conditions, and site specifity.
Leachate preservation/storage	Sample components change with time.

TABLE 3 (continued)

PROPERTIES/CHARACTERISTICS	IMPORTANCE AND TEST RAMIFICATIONS
Analytical (sample preparation and test method)	Reproducible, specific, and efficient methods are available. Analytical procedures need to be appended with appropriate protocols.
Testing schedule (time)	Could affect reproducibility, interpretation, and comparability of data.
8. Physical Modeling	
Comparability with scenario to be simulated	Similar in form and arrangement.
Congruence with scenario	Governs applicability of results.

APPENDIX A - BACKGROUND ON LEACHABILITY AS A SELF-INITIATED ACTIVITY OF THE SCIENCE ADVISORY BOARD

Over the past decade, the Environmental Engineering Committee (EEC) of the Science Advisory Board (SAB) has reviewed a number of EPA subjects and issues involving leachability phenomena either as a major or minor factor in the review. In these various reviews, the Committee has noted a number of problems and issues, relating to leachability phenomena that were common to a variety of programs, rules and Agency procedures. The Committee believed that these common problems and issues, would be best called to the Agency's attention through a general set of recommendations on leachability phenomena, rather than in the specific, individual reviews.

Believing that the scientific principles of contaminant leachability need broader understanding and exposition, the EEC has undertaken the initiative, with the concurrence of the Executive Committee, to conduct this self-initiated review to:

1) Consider the fundamental scientific principles that can reliably describe contaminant release/transport. In particular, to consider the controlling characteristics of the source, the leaching media and the importance of dynamic considerations; and

2) Suggest how the scientific principles can be applied to determine how a waste will leach when present in the environment, according to a prescribed scenario.

The Leachability Subcommittee (LS) was formed by the EEC. The group convened a project scoping and planning session in Houston, Texas on December 15-16, 1989, immediately following a Workshop related to this topic. The LS then followed this with a one-day session in EPA's Headquarters Office in Washington, D.C. on February 26, 1990, devoted to assessing the Agency's varied needs for leachability-related information. The day's activities and findings were then discussed with the full EEC on February 27, 1990. This was followed by a Workshop on Leachability on May 9, 1990 in Washington, D.C. The Workshop was conceived as a vehicle for distinguished scientists, engineers and practitioners in the field to focus on the scientific principles and issues relating to leachability phenomena. The Workshop was video taped, so that those unable to attend from EPA or any other interested parties could have the benefit of this exchange of information.

The Leachability Workshop assisted the LS of the SAB's EEC to better define the fundamental scientific principles that control leachability. Further, the workshop assisted the SAB and the attendees in ascertaining how leachability phenomena and tests can be applied on an appropriate and consistent basis to determine how a waste will leach when present under various scenarios in the environment.

APPENDIX B
LEACHABILITY WORKSHOP PROGRAM
May 9, 1990

Welcome and Administrative Remarks	Dr. C.H. Ward Mr. Richard A. Conway
Statement of Issues and Needs	Dr. Raymond C. Loehr
Test Methods: Descriptions, Capabilities, Organics-Inorganics	Dr. Pierre Côte'
Leaching of Stabilized Materials	Dr. Paul Bishop
Physical-Chemical Mechanisms: Concepts on Interactions of Solids-Liquids, Liquid-Liquid, Solids-Liquids-Gases	Dr. Marvin Dudas
Technical Problems and Challenges for Regulators and the Regulated	Mr. Robert L. Huddleston
Leaching Chemistry of Inorganics	Dr. John M. Zachara
Leaching Chemistry of Organics	Dr. P. Suresh Rao
Alternative Approaches to Laboratory Tests (Modeling)	Dr. Carl Enfield
Concluding Remarks	Dr. C.H. Ward Dr. Ishwar P. Murarka

CONVENERS AND SPEAKERS

Dr. C.H. Ward, Chairman, Leachability Subcommittee, Rice University, Houston, Texas

Dr. Ishwar P. Murarka, Vice-Chairman, Leachability Subcommittee, Electric Power Research Institute, Palo Alto, California

Mr. Richard A. Conway, Chairman, Environmental Engineering Committee, Union Carbide Corporation, South Charleston, West Virginia

Dr. Raymond C. Loehr, Chairman, Science Advisory Board, University of Texas, Austin, Texas

Dr. K. Jack Kooyoomjian, Designated Federal Official, US EPA, Science Advisory Board

Dr. Donald G. Barnes, Director, US EPA, Science Advisory Board

Mr. A. Robert Flaak, Assistant Staff Director, US EPA, Science Advisory Board

Dr. Pierre Côte', Zenon Environmental, Inc., Burlington, Ontario, Canada

Dr. Paul Bishop, University of Cincinnati, Cincinnati, Ohio

Dr. Marvin Dudas, The University of Alberta, Edmonton, Alberta, Canada

Mr. Robert L. Huddleston, Conoco, Inc., Ponca City, Oklahoma

Dr. John M. Zachara, Battelle Pacific Northwest Laboratories, Richland, Washington

Dr. P. Suresh Chandra Rao, University of Florida, Gainesville, Florida

Dr. Carl Enfield, R.S. Kerr Environmental Research Laboratory, Ada, Oklahoma

APPENDIX C - LEACHABILITY NEEDS, USES, TESTS, CONCERNS, AND ISSUES

C-1 - SUPERFUND REMEDIAL AND REMOVAL PROGRAMS

NEED FOR USE OF LEACHING TESTS

- Need to comply with Federal and State laws that are applicable, or relevant and appropriate (e.g., RCRA)

- Need to approximate real world conditions

- Need for methods which provide input to groundwater modeling

- Need for standardization of Leaching methods (including K_d for specific applications and data uses

- Need for methods development for predicting long-term Leaching potential

- Need for validation of Leaching methods

- Leaching, extraction and other chemical test are typically needed to provide a variety of data on either untreated or solidification/stabilization (S/S)-treated wastes for the following purposes:

  - To identify principal threats which indicate mobility of contaminants (e.g., in untreated or S/S-treated waste) when they are in the environment (e.g., in contact with leaching medium and each other)

  - Determine compliance with regulations, such as CERCLA, RCRA (e.g., if Land ban BDAT has been met)

- To show that reduction in mobility of the hazardous components has been achieved between untreated and treated wastes, or that treated waste is protective (i.e., that it meets National Contingency Plan expectations, such as passing a specific test, such as the TC test)

  - To assess the effectiveness of a technology (e.g., S/S technology)
  - To estimate source terms and/or boundary conditions for ground-water modeling
  - To look for "hot-spots," and in many cases, locate with model instead of acquiring (sometimes extensive) data

USES OF LEACHABILITY AND LEACH TESTS

- To demonstrate compliance with Federal and State Laws (e.g., RCRA, TSCA, etc.)

- To model risk to:
  - Assess potential for groundwater and surface water contamination
  - Establish clean-up standards

- Selection of Remedy:

- To differentiate among various waste management regimes for modeling and assessing risk
  - In situ management/disposal (modeling)
  - Delisting
- To ensure that waste management alternatives address environmental concerns
- To predict long-term environmental behavior (e.g., such as for "mixed" waste, radioactive, RCRA hazardous waste, debris and/or large objects)

- To determine chemical characteristics of wastes

- To identify possible interference with treatment (e.g., immobilization)

- To evaluate treatment (e.g., treatment residuals) compliance with clean-up goals
- Input data to modeling, such as fluxes into saturated zone (e.g., ANSI 16.1)
- For organics, such as immobile constituents, Low concentrations to examine:
  - "Worst case" Leaching
  - Total waste extraction
  - Non-polar solvents for PCB's

TYPES OF DATA REQUIRED, SPECIAL CONCERNS, ISSUES AND CONSTRAINTS (e.g., variables that can affect test results.)

- Superfund allows flexibility in choice of Leachability test based on site specific conditions and needs

- National Contingency Plan (NCP) outlines program goals and expectations which drive the remedy selection process. Some of the expectations are:
  - EPA expects to use treatment to address principle threat wastes (e.g., highly toxic, mobile, etc.)
  - EPA expects to use engineering controls (e.g., containment) to address wastes which pose a relatively low long-term threat or where treatment is impracticable
  - EPA expects to return usable ground waters to their beneficial uses whenever practicable

- Parameters that can affect test results include:

  - Sample heterogeneity
  - Curing time
  - Liquid-to-solid ratio
  - Extraction time, number and frequency
  - Leaching medium

- Superfund is unique in that the program can use flexibility on a site-by-site and case-by-case technical basis for selection of remedy:

  - Additional goals in the NCP aim to treat waste that are the principal threat (e.g., highly mobile, toxic, etc.)
  - Probably will not excavate and treat non-mobile wastes which are not the principal threat
  - Generally, there is an expectation goal to reduce toxicity, mobility and volume of the waste by 90% to 99% (whether or not this presumption is valid)

- Superfund may use multiple tests. Various leach tests (e.g., 18 hours versus 90 days or more) are employed. There is a large variety, depending on the waste and the disposal scenario:

  - The more agreement and consensus on appropriateness of tests, the more important are the tests to the program (e.g., decisions in New Jersey and California should be consistent.)

- Superfund waste removal activities have more flexibility than remedial activities. However, the science and technical decisions must withstand scrutiny.

- For Superfund, RCRA protocols may not be appropriate because:

  - The Superfund application is a different purpose than for what the RCRA protocol was originally devised.
  - Lack of standardized protocols in Superfund
  - Many methods exist with a lot of variability
  - Technical uncertainty on making sense of the varied forms of data to make a decision.

TYPE OF TESTS

- Note that all treated wastes (not just solidified/stabilized (S/S) treated wastes) need to be evaluated to determine how protective they are in specific management scenarios

- While Superfund program must comply with Federal and State regulatory requirements (e.g., RCRA TCLP methodology), other tests may be utilized to approximate real world conditions. Single or multiple methods may apply to a site. Additional methods may include the following listed below:
  - Short-term extraction tests (hours to days)

  - Leaching tests (weeks to years)

  - Column Leach Test

  - EP (Method 1310) (Was used in the past, but is superseded by the TCLP)

  - TCLP (Method 1311)

  - TCLP with cage modification (This has never been promulgated and appears to have reproducibility problems)

  - California Waste Extraction Test (Cal WET)

  - Multiple Extraction Procedure (MEP)

  - Synthetic Acid Precipitation Leach Test

  - Monofilled Waste Extraction Procedure (Method 1312) (MWEP)

  - Materials Characterization Center Static Leach Test

  - American Nuclear Society Leach Test

  - Dynamic Leach Test (DLT)

  - Shake Extraction Test

  - Others

NEEDS FOR USE OF LEACHING OR OTHER TESTS

- Simple methods that can be simply used by field people for all types of sediment and water environments to address the toxicity of sediment:
  - Need for an in-the-field practical method where each method is not turned into a "research project"
  - The AET (Apparent Effects Threshold) method uses a preponderance of evidence approach
  - The AET method has no relevance to sediments that are exposed to leaching conditions
  - Addresses the toxicity of in-place sediments
- Methods to provide sediment criteria decisions to evaluate the following:
  - Most likely scenario
  - Methods to be applicable to human health, aquatic life or wildlife protection
  - Ability to generate numerical criteria for specific chemicals
- Toxicity Identification Evaluation (TIE) procedures to identify and quantify chemical components responsible for sediment toxicity, such as:
  - Techniques for the identification of toxic compounds in aqueous samples containing mixtures of chemicals
  - Interstitial water toxicity method TIE procedures are implemented in three phases to evaluate:
    - Pore water toxicity,
    - Identify the suggested toxicant, and
    - Confirm toxicant identification.

USES OF LEACHABILITY AND LEACH TESTS

- Sediment criteria decisions for:
  - Applicability of method to human health, aquatic life or wildlife protection
  - Predicting effects on different organisms
  - Suitability for in-place pollutant control
  - Suitability for source control
  - Suitability for disposal actions
  - Suitability for different sediment types
  - Suitability for different chemicals or classes
  - Ability to generate numerical criteria for specific chemicals
- Toxicity Identification Evaluation (TIE) potential uses:
  - Use of pore water as a fraction to assess sediment toxicity
  - In conjunction with TIE procedures, can provide data concerning specific compounds responsible for toxicity in contaminated sediments
  - Ability to identify specific toxicants responsible for acute toxicity in contaminated sediments

TYPES OF DATA REQUIRED, SPECIAL CONCERNS, ISSUES AND CONSTRAINTS (e.g., variables that can affect test results.)

- Types of data required:
  - Biological response data (either acute or chronic)
  - Choice of Test Organism
- Practical concerns of method choices:
  - Ease of use
  - Relative cost
  - Tendency to be conservative
  - Level of acceptance
  - Ability to be implemented by laboratories with available/typical equipment and handling facilities
  - Degree to which results lend themselves to the following:
    - Interpretation
    - Environmental applicability
    - Accuracy and precision
- Concern for leaching of hazardous substances or hazardous materials to food, plants, groundwater and sediment
- Concern for monofilling and impacts on groundwater:
  - There are differences in sorptive capacity (reductions) observed in monofill versus an increase in sorptive capacity in well-aerated soil (plow zone)
- Groundwater to surface water issues
- All current sediment criteria development efforts address the toxicity of <u>in-place</u> sediments. As a result, research activities have not focused on what happens to sediment-bound chemicals when exposed to leaching conditions:
  - Some research suggests that for non-ionic organic contaminants, the presence of organic carbon in leaching materials may be responsible for some binding of contaminants, as well as mobility
  - For metals, it is possible that the leaching conditions might provide for the release of significant levels of metals, because of the expected reduction of the acid volatile sulfide (AVS) content of many sediments
    - AVS binds up significant levels of metals and is lost when exposed to oxidizing conditions

TYPE OF TESTS

- Aeration tests
- Bioassays
- Equilibrium Partitioning Approach
- Solid phase extraction tests
- Graduated pH test
- Filtration tests
- Reversed phase, Solid Phase Extraction (SPE) tests
- Oxidant reduction test
- EDTA addition test (The EDTA - Ethylene diamine tetraacetic acid test)
- Hollow block with a semi-permeable membrane, which is inserted into the sediments

C-3 - OFFICE OF SOLID WASTE

NEEDS FOR USE OF LEACHING TESTS:

- Statutory requirement of RCRA to look at reasonable worst-case mismanagement and maintenance scenarios to assess:

  - Landfill scenarios (sanitary and monofill)
  - Maintenance scenarios
  - "Mismanagement" scenarios
  - Acid leaching scenarios
  - Pump and treat systems
  - Effect of covers
  - Effect of Liners

- To characterize the leachate source term, such as:

  - Finite versus infinite source of waste
  - Effect on leachate quantity
  - Effect on leachate quality

- To determine if a waste is hazardous or non-hazardous. (Such determinations are built into RCRA.):

- To determine how a particular material needs to be managed:

  - Need a decision-making tool to evaluate leachability
  - Need to examine various scenarios and their validity

USES OF LEACHABILITY AND LEACH TESTS:

- To model and simulate risks
- To assess risks
- To direct regulatory decisions
- To come to grips with the complexities of leachability phenomena (i.e., the source term itself is very difficult and complex)
- To answer questions pertaining to what kind of contaminant levels are appropriate to be left in the soil or removal from the soil (e.g., clean closure)

TYPES OF DATA REQUIRED, SPECIAL CONCERNS, ISSUES AND CONSTRAINTS (That is, variables that can affect test results.):

- Factors affecting leachability include, but are not necessarily limited to the following:

  - Size of materials
  - Permeability of solid
  - Time dependency of leaching
  - Contact time (a crucial issue_
  - Type of contact (tumbling versus stirring)
  - Ratio of leaching fluid to waste (i.e., solubility versus mass-limited; also, infinite source versus finite source)
  - Changes in the waste <u>itself</u> (e.g., due to biodegradation, chemical changes, anaerobic versus aerobic, hydrology, and climate changes)

- Issue of scenarios where organics may be bound better under acid, rather than neutral or basic circumstances (Many industrial landfills are highly on the <u>basic</u> side)

TYPE OF TESTS

- EP (Extraction Procedure) (Method 1310)
- TCLP (Toxicity Characteristic Leaching Procedure) (Method 1311)
- TCLP with cage modification
- Acid rain leaching tests for large volume wastes (Method 1312)
- Multiple Extraction Procedures (MEP) for delisting
- Oily Waste Extraction Procedure (OWEP) for delisting

C-4 - OFFICE OF TOXIC SUBSTANCES

NEEDS FOR USE OF LEACHING TESTS

-TSCA is a "No Unreasonable Risk" Statute

- The only alternative technologies acceptable, for instance for PCB's, must demonstrate that they are equivalent to thermal destruction of PCB's (e.g., solidification of PCB's would cause a problem under these TSCA criteria.)

- TSCA is also a cost-benefit statute:

  - Possible use of waivers by EPA Regional Administrators
  - With this (cost-benefit) constraint, there could be a problem between what the Superfund and the Office of Toxic Substances programs says are "low" and/or acceptable concentrations
  - Need some tests to determine the long-term effectiveness of these problems

USES OF LEACHABILITY AND LEACH TESTS

- Particularly interested in leachability data, especially for new product information in the PMN (Pre-Manufacturing Notification) program for new and existing chemicals

- OTS is in need of information on leachability for establishing the equivalent comparison in a chemical waste landfill, which is the only non-destructive method that is authorized (that is not to say that treatment processes that are non-destructive would not be examined)

TYPES OF DATA REQUIRED, SPECIAL CONCERNS, ISSUES AND CONSTRAINTS (This is, variables that can affect test results.)

- Equivalency test data, for alternative technologies to thermal destruction

- Cost-benefit data on alternative technologies to incineration:

  - The Office of Toxic Substances is in need of information that examines the alternative technologies to incineration
  - The alternative technologies to incineration must demonstrate equivalency
    - Need to know what kind of leachability criteria would be needed to obtain a revised equivalent to incineration
    - Also, need to know what kind of laboratory testing should be required to give results equivalent to incineration

- R&D is needed to answer above.

TYPE OF TESTS

- Equivalency tests (as compared to the incineration alternative) need to be developed

- At present, disposal of waste in chemical waste landfill is the only non-destructive method that is authorized

- Other treatment processes that are non-destructive could be possible, but to date, no research has occurred to develop such non-destructive tests which demonstrate the equivalence to incineration

- Need some tests to look at the long-term effectiveness of these problems

C-5 - R&D PERSPECTIVE OF THE R.S. KERR LAB. IN ADA, OKLAHOMA

NEEDS FOR USE OF LEACHING TESTS

- The RCRA statute requires development and use of Leachability data and tests

- Mission of the Lab. and the technical support center is to further understanding of subsurface media to:

  - Remediate contaminated vadose and saturated zones
  - Provide a technical support bridge between the Lab. and the EPA regional and state regulators

  - R.S. Kerr Lab. is primarily a user and not a developer of different Leaching test methods and alternative procedures:

  - EPA ORD, EPA OSW, ASTM, NRC and others develop leaching tests

USES OF LEACHABILITY AND LEACH TESTS

- To answer questions pertaining to what kind of contaminant levels are appropriate to be left in the soil, so that there will not be a problem later (i.e., so that leachate through the soil will be protective of groundwater). Hence, this leads to the following questions:

  - What kind of leaching test can be used to develop criteria for "safe levels?"
  - What site specific processes must be considered in the criteria development process?
  - What kind of vadose zone models should be used?

TYPES OF DATA REQUIRED, SPECIAL CONCERNS, ISSUES AND CONSTRAINTS (That is variables that can affect test results.)

- To develop a "family of procedures" and to determine when it is appropriate to use each procedure to answer site-specific questions

- Ability to get source term in model is a problem

- Need to act conservatively, particularly with organics, but need to use "common sense"

- There is considerable competition between different tests

- To date no evaluation has been made as to what, in fact, are the reasonable stresses, such as:

  - When to grind or not to grind a waste
  - When to apply acid and at what strength and duration

- Issues with appropriate tests for radionuclides and mixed wastes:

  - What kind of test will be applicable to low-level radioactive material?
  - Is EP Tox. or TCLP appropriate? Under what circumstances?

- There are no "standard" R&D leaching tests or migration potential evaluation protocols for Superfund on-site remedies

- For the combustion residue area, the following issues illustrate special concerns and constraints:

  - The ability to get the appropriate source term is usually a basic problem
  - The R&D program uses a lot of different procedures to develop a credible data base
  - In this context, ORD is primarily a user, and not a developer of methods for leaching tests
  - The R&D staff are using a lot of different procedures to develop a credible data base

TYPE OF TESTS

- EP (Method 1310)
- TCLP (Method 1311)

C-6 - R&D PERSPECTIVE OF THE OFFICE OF MODELING, MONITORING, AND QUALITY ASSURANCE, WASHINGTON, D.C.

USES OF LEACHING TESTS

- Determining regulatory status of waste
- Determining effectiveness of treatment processes which are designed to reduce Leachability
- Determining leachability of waste under different management scenarios

TYPES OF TESTS NEEDED (SCENARIOS TO BE MODELED)

- Sanitary Landfill co-disposal:
  - Lined unit
  - Unlined unit
- Monowaste disposal
- Dedicated, mixed waste unit
- Uncontrolled contaminated soil

USES OF TRANSPORT TESTS

- Predicting transport through media as input to fate and transport models (i.e., serve as the source term for the models)

TYPES OF TESTS NEEDED (ENVIRONMENTS TO BE MODELED)

- Vadose Zone:
  - Moist
  - Dry
- Saturated Zone:
  - Sandy
  - Clay
  - Loam
  - Calcarious
  - Acidic
- Effect of waste on Leachability/transport of material from other wastes

C-7 - CRITERIA AND OBJECTIVES OF LEACHING TESTS AND MODELING CONSIDERATIONS FOR PARTITIONING TESTS FROM THE PERSPECTIVE OF REGULATORS VERSUS INDUSTRY

INDUSTRY VIEW OF THE PERSPECTIVE OF THE REGULATORS

- Simplicity (e.g., simplicity of test protocol)
- Reproducibility
- Conservatism, if realism is not practical
- One/few tests to fit most wastes
- Use to delineate "non-hazardous" versus "hazardous" wastes (e.g., differentiating between wastes needing RCRA "C" standards management and wastes that only need "D" controls.)

  [NOTE: The above is in contrast to a large part of the Agency's response, particularly Superfund and the Kerr Lab.]

PERSPECTIVE OF INDUSTRY

- Simplicity only where appropriate,
- Reproducibility
- Realism in approximating site and waste specific conditions
- Test variations to account for waste differences
- Suitable for differentiating between different disposal conditions
- Use to define acceptable disposal conditions

TYPICAL CURRENT PRACTICES OF INDUSTRY IN LEACHATE TESTING

- Determine regulatory status of waste, such as hazardous waste e.g., Subtitle C which is subject to land ban), EP, TCLP and SPLP (e.g., Method 1312)
- Determine reasonable worst-case releases from waste residual oils, and contaminated media
- Determine effectiveness of waste treatment process (e.g., solidification/stabilization)
- Provide basis for landfill design
- Account for biological activity (rarely) in soil column effects
- Deal primarily with large volume, mono-filled wastes

DISTINCTIONS TO BE MADE BETWEEN LEACHING TESTS AND MODELING CONSIDERATIONS FOR REGULATORS AND INDUSTRY

- There is a distinction between leaching tests and partitioning tests:
  - Current leaching tests are standardized regulatory tests not requiring site-specific analyses (e.g., modeling)
  - Partitioning tests are used for data input into mathematical models for site-specific subsurface migration analysis
  - Leaching tests are not for site-specific analysis of contaminant transport

- Regulators and Industry do not want to spend time, money and resources applying leaching tests which are not:

  - Applicable for given conditions
  - Realistic, given site specific conditions type and strength
  - Cannot be used to identify prudent waste management and disposal activities

- "False positives" and "false negatives" are costly from both the regulator and industry point-of-view

PERSPECTIVE OF PUBLIC

- Desire for conservatism
- Tests subject to public review
- Reflective of reasonable worst-case environmental transformation

C-7 - CRITERIA AND OBJECTIVES OF LEACHING TESTS AND MODELING CONSIDERATIONS FOR PARTITIONING TESTS FROM THE PERSPECTIVE OF REGULATORS VERSUS INDUSTRY (Continued)

BASIC NEEDS

- o A Rational Construct of the Leaching Phenomenon
  - Avoid regulatory expediency, conservatism
  - Aim for well founded approach

- o Understand and Clearly Define the Role of Basic Mechanisms
  - Weathering, Dissolution
  - Desorption
  - Diffusion, Permeation
  - Mechanics/Chemistry of Stabilization/Solidification

- o Develop a Leachate Test/Model Interface
  - Tests representative of important phenomena
  - Test results usable in diffusion, flow models

- o Validate Model Results through Field Studies
  - Realistic Test Cells
  - Actual Disposal Situations

BASIC BELIEFS

- o All Materials Leach

- o Our Goal Should be an Acceptable Rate of Release To The Environment

- o Leachate Tests Provide a Useful Measure of Environmental Availability
  - Excellent predictor of water borne contamination
  - Of Secondary value for volatile emissions

- o Leachate Tests Should Fairly Represent the Actual Mechanics in the Field

- o Properly Constructed Leachate Experiments Coupled With Technically Sound Analysis of Flow Phenomena Can:
  - Provide environmentally acceptable disposal
  - Define risks posed by contaminated media

C-7 - CRITERIA AND OBJECTIVES OF LEACHING TESTS AND MODELING CONSIDERATIONS FOR PARTITIONING TESTS FROM THE PERSPECTIVE OF REGULATORS VERSUS INDUSTRY (Continued)

EFFECTS OF SOME LEACHATE TEST PARAMETERS

- o Waste/Liquid Ratio
  - Most allow equilibrium/saturation
  - Worst case for total dissolved materials
  - Saturation might suppress relative solubility of some constituents

- o Leaching Time
  - Most approach equilibrium
  - No residence time/advection relationship unless a column test

- o Number of Extractions
  - Single extractions tell little of leaching phenomena
  - Multiple extractions can provide more information
    - o Surface Effects
    - o Diffusional Fluxes
    - o Compositional Changes

- o Particle Size
  - Size reduction provides rapid equilibrium, most conservative, but unrealistic results
    - o Ignores permeation, diffusion rate
    - o Defeats solidification/stabilization mechanisms

- o Leaching Medium (Eluant) Composition
  - Organic acids represent specialized case
    - o To simulate municipal co-disposal
    - o To provide buffered system, stable Ph
    - o Acetates, citrates preferentially extract metals
    - o May confuse analysis
  - Inorganic acids to represent "acid rain"
    - o More realistic for mono-wastes
  - Total acidity
    - o Often high to counteract high alkalinity wastes
    - o Overestimates rate and amount of neutralization

- o Agitation
  - Speeds Equilibrium
  - Not representative of actual conditions

APPENDIX D - CREDITS AND ACKNOWLEDGEMENTS

The Leachability Subcommittee (LS) of the Science Advisory Board's (SAB) Environmental Engineering Committee (EEC) wishes to acknowledge the many people and offices for their numerous contributions to this self-initiated study to arrive at recommendations and rationale for analysis of contaminant release. While listing names provokes the opportunity to miss contributors by omission, we believe that the following contributors to the efforts of the LS and its parent EEC deserve a special "thank-you" and acknowledgement for their time, energies and efforts toward improving this product and the perspective of the SAB members and consultants in this very complex area.

With respect to an information gathering session conducted on February 26, 1990 in which the LS attempted to assess the varied needs of the Agency, the following persons are recognized for their participation in this exercise, as well as participation in the follow-up activities after this session:

Mr. Harry Allen, EPA, Office of Emergency and Remedial Response (OERR), Emergency Response Division (ERD), Edison, New Jersey

Ms. Robin Anderson, EPA, OERR, Hazardous Site Control Division (HSCD), Washington, D.C.

Ms. Joan Blake, EPA, Office of Toxic Substances (OTS), Exposure Evaluation Division (EED), Washington, D.C.

Mr. David Friedman, EPA, Office of Research and Development (ORD), Modeling, Monitoring Systems and Quality Assurance Office, Washington, D.C. (Formerly with the Office of Solid Waste (OSW), Characterization and Assessment Division (CAD))

Ms. Gail Hansen, EPA, OSW, CAD, Washington, D.C.

Mr. Alexander C. McBride, Chief, Technical Assessment Branch, EPA, OSW, CAD, Washnigton, D.C.

Ms. Lynnann Hitchens, EPA, ORD, Office of Environmental Engineering and Technology Demonstration (OEETD), Washington, D.C. (Now with ORD's Waste Minimization, Destruction and Disposal Research Division (WMDDRD) within the Risk Reduction Engineering Laboratory (RREL), Cincinnati, Ohio)

Mr. M. R. Scalf, EPA, ORD, R.S. Kerr Environmental Research Laboratory, Ada, Oklahoma

Mr. Carlton Wiles, Chief, Stabilization Section of the Municipal Solid Waste Residuals Branch,WMDDRD, RREL, ORD, EPA Cincinnati, Ohio.

Mr. Christopher Zarba, EPA, Criteria and Standards Division (CSD), Office of Water Regulations and Standards (Now known as the Health and Ecological Criteria Division, Office of Science and Technology), Washnigton, D.C.

Dr. Linda E. Greer, Natural Resources Defense Council, Washington, D.C. (At the time she was with the Hazardous Waste Treatment Council (HWTC), but represented herself at the meeting, and not the HWTC)

Mr. Phillip A. Palmer, E. I. duPont DeNemours & Co., Engineering Department, Newark, Delaware

The above participants in the February 26, 1990 information gathering session deserve special recognition for helping develop Appendix B which summarizes the various uses and needs of leaching tests. Dr. K. Jack Kooyoomjian of the SAB Staff and Designated Federal Official to the EEC and its LS deserves particular recognition for synthesizing the above information. Additionally, Mr. Samuel Rondberg's assistance in setting up Appendix B and assisting in the numerous and often tedious edits is greatly appreciated.

With respect to the Leachability Workshop and Technical Briefing which the LS held on May 9, 1990, the following persons are recognized for their contributions as participants in briefing the LS members and consultants:

Dr. Paul Bishop, Department of Civil and Environmental Engineering, University of Cincinnati, Cincinnati, Ohio

Dr. Pierre Côté, ZENON Environmental, Inc., Ontario, Canada

Dr. Marvin Dudas, Department of Soil Science, The University of Alberta, Edmonton, Alberta, Canada

Dr. Carl Enfield, R.S. Kerr Environmental Research Laboratory, Ada, Oklahoma

Dr. Robert Huddleston, Conoco, Inc., Ponca City, Oklahoma

Dr. P. Suresh Chandra Rao, Institute of Food and Agricultural Sciences, Soil Science Department, University of Florida, Gainesville, Florida

Dr. John Zachara, Battelle Pacific Northwest Laboratories, Geochemistry Section, Richland, Washington

With respect to Figure 1 in the text which depicts a conceptual view of leaching in a waste unit, the following person deserves recognition:

Dr. Ishwar Murarka, Program manager for Land and Water Studies, EPRI, Palo Alto, California

With respect to the development of information on Extraction Tests (Table 1), the following persons deserve particular recognition:

Dr. Larry I. Bone, Environmental Quality, Dow Chemical, Midland, Michigan

Ms. Gail Hansen, EPA, OSW, Characterization and Assessment Division, Washington, D.C.

With respect to the development of Table 3 which lists the scientific considerations in design and interpretation of leachability tests, the following persons deserve particular recognition:

Mr. Richard Conway, Senior Corporate Fellow, Union Carbide Corporation, South Charleston, West Virginia

Mr. Peter Hannak, Union Carbide Chemicals and Plastics Company, Inc., South Charleston, West Virginia (Formerly of Alberta Environmental Centre)

And last, but not least, we would like to offer a special thanks to Mrs. Marcy Jolly, Secretary to the Leachability Subcommittee, for typing and retyping the numerous drafts of this report.

Of course, this report would never have materialized without the perseverance of the LS and the EEC after the need for a self-initiated report on leachability was recognized. Special recognition is made to Dr. Ward, Chairman of the LS and to Dr. Murarka, Vice-Chair of the LS for guiding the report to a successful conclusion.

APPENDIX E - GLOSSARY OF TERMS AND ACRONYMS

AET ----- APPARENT EFFECTS THRESHOLD
ANS ----- AMERICAN NUCLEAR SOCIETY
ANSI ---- AMERICAN NATIONAL STANDARDS INSTITUTE
ARARSs -- APPLICABLE OR RELEVANT AND APPROPRIATE
ASTM ---- AMERICAN SOCIETY OF TESTING MATERIALS
AVS ----- ACID VOLATILE SULFIDE
BDAT ---- BEST DEMONSTRATED ACHIEVABLE TECHNOLOGY
C ------- CENTIGRADE
CERCLA -- COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION AND LIABILITY ACT (ALSO KNOWN AS "SUPERFUND")
CWA ----- CLEAN WATER ACT
DI ------ DEIONIZED
DLT ----- DYNAMIC LEACH TEST
EDTA ---- ETHYLENE DIAMINE TETRAACETIC ACID
EEC ----- ENVIRONMENTAL ENGINEERING COMMITTEE (SAB/EPA)
EP ------ EXTRACTION PROCEDURE TOXICITY
EPA ----- U.S. ENVIRONMENTAL PROTECTION AGENCY (US EPA, or "THE AGENCY")
EPACML -- EPA COMPOSITE MODEL FOR LANDFILLS
FOWL™ -- FOSSIL FUEL COMBUSTION WASTE LEACHING
HELP ---- HYDROLOGIC EVALUATION OF LANDFILL PERFORMANCE
IAEA ---- INTERNATIONAL ATOMIC ENERGY AGENCY
ISO ----- INTERNATIONAL STANDARDS ORGANIZATION
K_d ------ DISTRIBUTION COEFFICIENT
LS ------ LEACHABILITY SUBCOMMITTEE (EEC/SAB/EPA)
M ------- MOLE (MOLARITY)
MCC ----- MATERIAL CHARACTERISTIC CENTER
MEP ----- MULTIPLE EXTRACTION PROCEDURE
MEQ/G --- MILLI EQUIVALENT PER GRAM
MIN ----- MINUTE
ML ------ MILLILITER
MM ------ MILLIMETER
MWEP ---- MONOFILL WASTE EXTRACTION PROCEDURE
OMMQA --- ORD/OFFICE OF MODELING, MONITORING, AND QUALITY ASSURANCE, US EPA
N ------- NORMAL (NORMALITY)
N/A ----- NOT APPLICABLE
NCP ----- NATIONAL CONTINGENCY PLAN
NRC ----- NUCLEAR REGULATORY COMMISSION
OMMQA --- OFFICE OF MODELING MONITORING AND QUALITY ASSURANCE, ORD/EPA
ORD ----- OFFICE OF RESEARCH AND DEVELOPMENT, US EPA
OSW ----- OFFICE OF SOLID WASTE, US EPA
OTS ----- OFFICE OF TOXIC SUBSTANCES, US EPA
OSW ----- OFFICE OF SOLID WASTE, US EPA
OTS ----- OFFICE OF TOXIC SUBSTANCES, US EPA
OWEP ---- OILY WASTE EXTRACTION PROCEDURE
PCB's --- POLYCHLORINATED BIPHENYLS
pH ------ NEGATIVE LOG OF HYDROGEN ION CONCENTRATION
PMN ----- PRE-MANUFACTURING NOTIFICATION
R&D ----- RESEARCH AND DEVELOPMENT
RCRA ---- RESOURCE CONSERVATION AND RECOVERY ACT
RSKERL -- R.S. KERR ENVIRONMENTAL RESEARCH LABORATORY, US EPA

SAB ----- SCIENCE ADVISORY BOARD (EPA)
SC ------ OFFICE OF WATER, SEDIMENT CRITERIA PROGRAM, US EPA
SF ------ SUPERFUND PROGRAM, US EPA
SPE ----- SOLID PHASE EXTRACTION
SPLP ---- SYNTHETIC PRECIPITATION LEACHING PROCEDURE
S/S ----- SOLIDIFICATION/STABILIZATION
SYN ----- SYNTHETIC (IN REFERENCE TO SYNTHETIC LANDFILL LEACHATE)
TC ------ TOXICITY CHARACTERISTIC
TCLP----- TOXICITY CHARACTERISTIC LEACHING PROCEDURE
THF ----- TETRAHYDROFURAN
TIE ----- TOXICITY IDENTIFICATION EVALUATION
TSCA ---- TOXIC SUBSTANCES CONTROL ACT
µM ------ MICRO MOLES
UNIFAC -- UNIVERSAL FUNCTIONAL ACTIVITY COEFFICIENT MODEL
WET ----- WASTE EXTRACTION TEST

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