EPA 402-R-96-014
June 1996

STABILIZATION/SOLIDIFICATION PROCESSES FOR MIXED WASTE

Center For Remediation Technology and Tools
Radiation Protection Division
Office of Radiation and Indoor Air
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, DC 20460

Prepared under:
Contract No.
2W-7520-NASA

Office of Environmental Restoration
U.S. Department of Energy
Germantown, MD 20874

DISCLAIMER

Mention of trade names, products, or services does not convey, and should not be interpreted as conveying, official EPA approval, endorsement, or recommendation.

PREFACE

This report contains information and data for four Stabilization/Solidification (S/S) processes: Grout/Portland Cement Stabilization, Sulfur Polymer Encapsulation (SPE), Polymer Encapsulation (PE) and Phoenix Ash Technology (PAT). The majority of the information and data in this report were furnished by the companies that own the processes. These data are informative and adequate for a preliminary understanding of each process; however, these data cannot render a true comparison from one process to another due to the independent tests that these companies have performed.

Our next project is to design and develop a test matrix for testing the four S/S processes at independent laboratories using the same procedures and techniques. The subject should be tested under different conditions in a controlled, monitored and otherwise uniform environment to provide unbiased data and information for a more accurate and comparable analysis. That project is to present an objective point of view, and no recommendations or endorsements of a S/S process will be finalized in that report.

ACKNOWLEDGMENTS

Tri T. Hoang of ORIA's Remedial Technology and Tools Center is the EPA project manager for this report. EPA/ORIA wishes to thank the following individuals for their technical assistance and review comments on the drafts of this report:

Lawnie Taylor, DOE-HQ, Environmental Restoration
Ed Barth, EPA Office of Research and Development
Andrea Faucette, Kaiser-Hill Company, L.L.C.
Gary Fox, Technical Innovation Development Engineering
Steve Hoeffner, Clemson Technical Center
Paul Kalb, Brookhaven National Laboratory
Christine Langton, Westinghouse Savannah River
Roger Spence, Oak Ridge National Laboratory
John Thies, Pressure Systems, Inc.
Irma McKnight, ORIA Product Review Officer

In addition, the following staff from ORIA's Radiation Protection Division assisted in the development and review of this document:

Nicholas Lailas, Director, RTTC
Robin Anderson, RTTC
Michael Boyd, RTTC
Michael Eagle, Center for Waste Isolation Pilot Program
Ed Feltcorn, RTTC
Carey Johnston, RTTC
Scott Monroe, Center for Waste Isolation Pilot Program
Hari Mukhoty, RTTC (EPA SEE Program)
Ronald Wilhelm, RTTC

ABSTRACT

The Environmental Protection Agency's (EPA) Office of Radiation and Indoor Air (ORIA) has entered into an agreement with the Department of Energy's (DOE) Office of Environmental Restoration (EM-40) to investigate technical issues related to treatment processes for low-level radioactive and mixed wastes. In accordance with this agreement, EPA proposed to assemble a panel of experts on waste stabilization and solidification processes in order to consider the appropriateness of several processes for specific low-level mixed waste (LLMW) categories.

On September 6-7, 1995, EPA/ORIA hosted a conference in Arlington, Virginia, to assemble data on these processes into a form that will be readily comprehensible to decision makers. This document contains a prose summary to describe the status of each process that was presented during the conference.

ACRONYMS

ANS	American National Standards
APC	Air Pollution Control
ASTM	American Society for Testing and Materials
BDAT	Best Developed Available Technology
BNL	Brookhaven National Laboratory
BWR	Boiling Water Reactor
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CFR	Code of Federal Regulations
CRADA	Cooperative Research and Development Agreement
DOE	U.S. Department of Energy
DSSI	Diversified Scientific Services, Inc.
EPA	U.S. Environmental Protection Agency
ETEC	Energy Technology Engineering Center
FUETAP	Formed Under Elevated Temperature And Pressure
HEPA	High-Efficiency Particulate
HDPE	High Density Polyethylene
HQ	Headquarters
IAW	In Accordance With
IDC	Item Description Code
INEL	Idaho National Engineering Laboratory
LDPE	Low Density Polyethylene
LI	Leachability Index
LLMW	Low-Level Mixed Waste
LLNL	Lawrence Livermore National Laboratory
LLW	Low-Level (Radioactive) Waste
LDR	Land Disposal Restrictions
MCC	Material Control Center
METC	Morgantown Energy Technology Center
MSO	Molten Salt Oxidation
MVST	Melton Valley Storage Tank
ND	Non Detect
NRC	Nuclear Regulatory Commission
ORIA	Office of Radiation and Indoor Air
ORNL	Oak Ridge National Laboratory
PAT	Phoenix Ash Technology
PE	Polymer Encapsulation
PSI	Pressure Systems Incorporated
QA	Quality Assurance
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RPD	Radiation Protection Division

ACRONYMS *(Continued)*

RREL	Risk Reduction Engineering Laboratory
RTTC	Remediation Technology and Tools Center
SEG	Scientific Ecology Group
SPC	Sulfur Polymer Cement
SPE	Sulfur Polymer Encapsulation
S/S	Stabilization/Solidification
TCLP	Toxicity Characteristic Leaching Procedure
TCA	Total Constituent Analysis
TIDE	Technical Innovative Development Engineering
TSCA	Toxic Substance Control Act
UCS	Unconfined Compressive Strength
USBM	U.S. Bureau of Mines
UTS	Universal Treatment Standard
VES	Vinyl Ester Styrene
WAC	Waste Acceptance Criteria
WERF	Waste Experiment Reduction Facility
WSRC	Westinghouse Savannah River Company

TABLE OF CONTENTS

LIST OF TABLES

1. COMPARATIVE SUMMARY OF PROCESSES

EPA's Office of Radiation and Indoor Air (ORIA) has entered into an agreement with the Department of Energy's Office of Environmental Restoration (EM-40) to investigate technical issues related to treatment processes for low-level radioactive and mixed wastes. In accordance with this agreement, EPA assembled a panel of experts on waste stabilization and solidification processes in order to consider the appropriateness of several processes for specific low-level mixed waste (LLMW) categories. As a first step, on September 6-7, 1995, ORIA hosted a conference in Crystal City, Virginia, to assemble data on these processes into a form that will be readily comprehensible to decision makers. The processes considered, along with the experts presenting them, are:

- **Phoenix Ash Technology:** John Thies, Pressure Systems, Inc. (PSI) and Steve Hoeffner, Rust-Clemson Technical Center

- **Grout/Portland Cement Stabilization (Grout):** Roger D. Spence, Chemical Technology Division, Oak Ridge National Laboratory, and Christine Langton, Westinghouse Savannah River Co.

- **Sulfur Polymer Encapsulation:** Paul D. Kalb, Environmental and Waste Technology Center, Brookhaven National Laboratory

- **Polymer Encapsulation:** Andrea M. Faucette, Kaiser Hill Company, and Paul D. Kalb, Environmental and Waste Technology Center, Brookhaven National Laboratory

In addition to the data presented by the above experts, more detailed background information on each of the four processes taken from the references presented and other information in the literature and elsewhere was assembled and is also presented in this document. The information so developed, along with the detailed write ups given later in this document, are summarized in Tables A-1 through A-4 of Appendix A. These summaries are made for each process, waste stream by waste stream, using the set of criteria described below. They are also used as the raw data for the final comparative tables in this section.

In this section, Tables 1-2 through 1-7 summarize the information as concisely as possible using "better/average/worse" comparative ratings for each criterion. In doing so, Tables 1-2 through 1-4 compare the basic properties of waste forms produced in the four processes from six different waste types of primary interest to EM-40, all low-level mixed waste (LLMW). In addition to waste form properties, various engineering parameters are compared for each process in Tables 1-5 through 1-7. Each table provides the comparative information for a particular regulatory/disposal scenario as described below.

1.1 WASTE TYPES

The six waste types considered in this document are:

- **Fine grained soils (e.g., clays and silts)**
- **Coarse grained soils (e.g., sands and gravels). This includes residuals from concrete decontamination.**
- **Metal sludges (e.g., electroplating residues)**
- **Nitrate salts from processing operations**
- **Chloride salts from off-gas treatment systems (e.g., incinerator scrubbing systems)**
- **Incinerator fly and bottom ash**

Each of these waste types is assumed to be contaminated with heavy metals (e.g., lead, chromium and/or cadmium) and radionuclides (e.g., cesium, strontium, uranium, and/or plutonium), since these are mixed waste. However, in some cases, there is process experience with RCRA wastes (i.e., no radionuclides) of the same type; here data are given as available and is so noted in the table. It is assumed that organic contamination is not present, or not an issue, in these waste types. Since these are generalized waste types, rather than specific actual process streams or remedial projects, specific numerical data cannot be given in most cases. Rather, data ranges, pass-fail criteria, better worse, and other evaluations are used.

1.2 REGULATORY/DISPOSAL SCENARIO - TREATMENT LEVEL

Each waste type/stabilization process combination can be further categorized according to one of several treatment levels based on regulatory regimes/disposal scenarios that are applicable now or might be in the near future. The three categories are:

- **Treatment Level A:** Treatment to present commercial mixed waste disposal facility requirements. Since there is only one such facility presently operating in the Envirocare of Utah - the requirements for disposal at that facility are used in this document. These requirements comply with present RCRA LDRs and with NRC's Class A LLW minimum requirements.
- **Treatment Level B:** Treatment to typical RCRA requirements (present or future) that might be applied to mixed waste disposal facilities at some time in the future, based on proposed or pending regulations, as well as developments in the RCRA Corrective Action and CERCLA areas. This includes more stringent metals leaching levels (Table 1-1 and Appendix B), and higher strength specifications.

- **Treatment Level C:** Treatment to NRC requirements or recommendations for low-level radioactive waste solidification waste form stability requirements (Classes B and C LLW) for cement and noncement waste forms. More stringent ANS 16.1 leachability standards may be required at specific site, for example, Westinghouse Savannah River Company (WSRC).

The reasoning behind this further sort of classification is that all of these processes have been developed with some set of criteria in mind, but not the same set for all processes. For example, the PAT, SP, and PE processes were designed to produce moderate to high strength monoliths that would meet NRC requirements, while most Grout processes produces low to moderate strength waste forms that may be either granular and soil-like to meet the Envirocare Waste Acceptance Criteria (WAC) (Class A LLW), or monolithic to meet NRC Classes B and C LLW cement waste form requirements. The criteria used for each scenario are given in Table 1-1. Appendix B provides more detail on the present and possible future RCRA criteria based on TCLP leachability (Treatment Level B).

Table 1-1
Criteria for Different Waste Disposal Scenarios
LLMW

Criterion	Regulatory/Disposal Scenario			
	Treatment Level A Envirocare WAC	Treatment Level B RCRA	Treatment Level C NRC **(3)**	
			Cement	Noncement
Free liquid	None	None	IAW ANS 55.1: ≤ 0.5% (vol.); free liquid pH ≥ 9.	IAW ANS 55.1: ≤ 0.5% (vol.)
Particle size	Granular, not dusty, preferred maximum size of 10 inches.	No spec.	Monolith	Monolith
Strength (UCS)	None	Varies, often 50 psi	IAW ASTM C39: 500 psi	IAW ASTM C39 or D695: 60 psi
Permeability	No spec.	Varies	No spec.	No spec.
Leachability (TCLP)	Present LDR Standards	Proposed LDR Standards **(1)(2)**. See also Appendix B.	LDR Standards	LDR Standards
Chemical Durability - Leachability	No spec.	No spec.	IAW ANS 16.1: LI ≥6.0, and retain UCS after 5-day test. At WSRC, LI≥12 for metals, ≥9 for soluble ions.	IAW ANS 16.1: LI ≥6.0, and retain UCS after 90 days
Containment of Salts	No spec.	No spec.		
Immersion	No spec.	No spec.	Retain UCS after 28 TO 180 days immersion	Retain UCS after 90-day immersion
Radiation stability	No spec.	No spec.	No spec. unless dose exceeds 10^9 Rads	Retain UCS after 10^8 Rads
Resistance to Thermal Degradation (Thermal Cycling)	No spec.	No spec.	IAW ASTM B553: Minimum of 60 psi after 30 cycles. Also, no evidence of cracking, spalling or disintegration for cement forms	IAW ASTM B553: Minimum of 60 psi after 30 cycles.
Resistance to Biodegradation	No spec.	No spec.	IAW ASTM G21 & G22: Retain UCS, no visible growth	Not required unless form contains carbonaceous material

(1) *Federal Register 60, No. 162*. Aug. 22, 1995. pp. 43654-43699.
(2) *Federal Register*. Dec. 21, 1995. p. 66344.
(3) *Final Waste Form Development Project: Performance Criteria for Phase I Treatability Studies*. 1992. ORNL.

1.3. EVALUATION CRITERIA

The first set of comparative tables in this section (Tables 1-2 through 1-4) gives the waste form property criteria (strength, leachability, etc.) of typical waste forms made from the various waste by each process. Each table provides this comparison for one of the three specific treatment levels. Only those properties or criteria applicable to LLMW are considered. The second set of tables (Tables 1-5 through 1-7) gives engineering criteria (cost, scale proven, etc.) for each combination in the same way.

The criteria used for evaluation are:

Waste Form Criteria:

- **Meets Waste Form/Size Optimal Requirement:** Different requirements apply here, depending on the regulatory/disposal scenario. Envirocare prefers waste particle sizes within a certain range. NRC regulations require monoliths for most waste. RCRA regulations do not specify either in general, but may in individual disposal scenarios, especially in remediation projects. While all processes considered can, in principle, meet any of the requirements, comparison is based on ease with which this is accomplished; e.g., does it require special equipment or techniques.

- **Strength:** Usually measured as unconfined compressive strength (UCS) by one of several ASTM standards.

- **Long-Term Durability:** Generally determined as one of a variety of physical tests: resistance to immersion in water; resistance to freeze/thaw; resistance to thermal cycling; resistance to biodegradation. Performance in the ANS 16.1 leaching tests is also a measure of long-term stability, but is considered separately here.

- **Radiation Stability:** Also a long-term stability test, the stability of the final waste form to radiation, either internally or externally, is of importance in mixed waste disposal.

- **Leachability of RCRA Metals and Radionuclides:** Two types of leaching tests are used: the Toxicity Characteristic Leaching Procedure (TCLP) required for regulatory purposes under the RCRA land Disposal Restrictions (LDRs); ANS 16.1, required under NRC regulations. Comparison is based upon the degree of difficulty/cost encountered in meeting RCRA or NRC requirements.

- **Containment of Salts:** Applies to the leachability of soluble species such as chlorides, sulfates, and nitrates. Waste forms that have good metal leaching properties may exhibit poor containment of salts.

- **Waste Loading:** The percentage of the final waste form that comprises the original waste. The higher the value, the better, since higher loadings mean less stabilizing reagent or polymer and less total waste to package, ship and dispose. This is especially important in mixed waste stabilization processes, because the packaging, shipping and disposal of the waste is generally much more costly than the stabilization process per se.

- **Volume Increase:** Important in the packaging, shipping, and disposal of the waste. Volume increase is a function not only of the process, but of the physical form and properties of the waste and the pretreatment operations that may be used. It is especially important in comparing processes and waste types to understand that these comparisons cannot be made unless sufficient information is given about the nature of the waste before and after stabilization. Unsaturated waste, such as most soils, ashes and some salts, have bulk densities that are variable depending on the prior handling of the waste; this is also true of some stabilized waste forms, especially those from grout/Portland cement processes. These materials are compressible and, therefore, the degree of compaction before and/or after treatment will strongly affect the observed volume increase.

Engineering Criteria:

- **Cost:** Where data are available, treatment costs for capital, processing, chemicals/materials and the total cost are compared. Cost in the mixed waste field is complicated by the high packaging, shipping and disposal costs. This is discussed in more detail below.

- **Complexity:** This refers to operating the process - ease of operation, degree of training required, etc.

- **Robustness:** Refers to the degree to which process equipment is strong and durable, and the process itself is forgiving in its operation.

- **Availability of Equipment and Process Technology:** Equipment refers to whether the equipment is commercially available or easy to adapt, as opposed to the requirement for non-standard, custom-built equipment. Process refers to whether the process can be acquired; i.e., is it generic or must it be licensed, are licenses available, etc.

- **Pretreatment:** Is pretreatment required to effectively operate the process on the waste in question?

- **Residuals:** Does the process produce any residual streams, other than the waste form, that may need to be treated or disposed?

- **Through-put Potential:** Are there practical and important limitations on the process rate that can be achieved?

- **Scale-Proven:** At what scale has the process been operated successfully?

- **Ease of Permitting and Public Acceptance:** What will be the comparative level of difficulty in obtaining regulatory permits to operate the process at a given location. Same for public acceptance - for example, incineration currently has a high degree of public opposition.

1.4. RATING SYSTEM

The following notes and codes apply to Tables 1-2 through 1-7:

- Metals Considered: lead, chromium, cadmium, cesium, strontium, uranium, and plutonium

- General Rating Codes:

■	Better
□	Average, Typical, Intermediate
♦	Worse
I	Inadequate information
Light shaded	Property is not applicable in this regulatory/disposal scenario
Dark Shaded	Process cannot be used with that waste type.

  It must be remembered that the ratings are relative within the framework of the processes under consideration here. For the different regulatory/disposal scenarios, the relative situation may change from one to the other, not only for the waste form parameters, but also for the engineering parameters in some cases, such as permitting/public acceptance.

- Process Scale Proven: (may be footnoted where special circumstances apply)

C	Commercial
P	Pilot
B	Bench

- Costs:

  For uniformity, costs are given in dollar/yd^3 for all processes wherever possible, with other units in parentheses where applicable. Conversions from $/unit volume to $/unit weight are made based on actual densities where that information is given. In some cases, data given in $/unit weight are not converted to $/unit volume where densities are not given and not easily estimated.

  Cost comparisons among processes are made on the basis of the <u>minimum</u> required waste form properties for that regulatory/disposal scenario. For example, all of the processes except grout tend to produce high strength, durable waste forms in any case; but in Treatment Levels A and B, this is not required and is of no present commercial advantage.

Therefore, the minimal strength and durability values obtainable with grout at high waste loadings are comparable, cost-wise, with the other processes' waste loadings, rather than the property-by-property comparisons often used by those promoting the other processes, where grout is assumed to have low waste loadings. Conversely, the low grout waste loadings necessary to meet the more stringent strength and durability standards of Treatment Level C present a very different cost comparison picture. An analogous situation occurs with waste containing large amounts of soluble salts. In the case of RCRA metals, however, PAT and grout processes are capable of yielding leachability results at least as good as the other processes at their normal, low waste loadings regardless of the Treatment Level required.

- Availability:

  For equipment, ratings are based on:

  - ■ Available off the shelf at full-scale
  - □ Standard equipment, but may require modification, special order, etc.
  - ♦ Not standard equipment, or not widely available

  For process, ratings are based on:

  - ■ Generic process, no license required, well known
  - □ Patented or proprietary process, but license, license-with-purchase-of-reagents, or licensed vendors widely available
  - ♦ Patented or proprietary process, not widely available or only limited vendors

- Waste Loading/Volume Increase:

  - ■* For the PAT Process, these parameters may be strongly affected by the high compression achieved in the process when particulate or granular wastes such as soils and ash are treated. In such cases, actual volume decreases may be observed, sometimes of large magnitude (up to 80 percent reduction has been achieved).

Table 1-2

Product Properties vs Waste Type and Stabilization Process
Treatment Level A: Treatment to Present Mixed Waste Disposal Facility Requirements; i.e., Envirocare

Waste Type	Process	Meets Waste Form/ Size Opt.	Strength	Long Term Durabil.	Radiation Stability	Leachability of RCRA Metals and Radionuclides*		Contain-ment of Salts	Waste Loading	Volume Increase
						TCLP	ANS 16.1			
Fine-grained soils	PAT	□			■	□			■*	■*
	Grout	■			■	■			■	■
	SPE	□			■	□			□	□
	PE	□			■	■			□	□
Coarse-grained soils	PAT	□			■	□			■*	■*
	Grout	■			■	■			■	■
	SPE	□			■	□			□	□
	PE	□			■	■			□	□
Metal Sludges	PAT	□			■	□			□	□
	Grout	■			■	■			■	■
	SPE	□			■	□			□	□
	PE	□			■	■			□	□
Nitrate Salts	PAT	□			■	□			□	□
	Grout	■			■	■			□	□
	SPE									
	PE	□			■	■			■	■
Chloride Salts	PAT	□			■	□			□	□
	Grout	■			■	■			□	□
	SPE	□			■	□			□	□
	PE	□			■	■			■	■
Incinera-tor Ash	PAT	□			■	□			■*	■*
	Grout	■			■	■			■	■
	SPE	□			■	□			□	□
	PE	□			■	■			□	□

Table 1-3

Product Properties vs Waste Type and Stabilization Process
Treatment Level B: Treatment to Typical RCRA Requirements, Present or Future.

Waste Type	Process	Meets Waste Form/ Size Require.	Strength	Long Term Durabil.	Radiation Stability	Leachability of RCRA Metals and Radionuclides*		Contain-ment of Salts	Waste Loading	Volume Increase
						TCLP	ANS 16.1			
Fine-grained soils	PAT	□	■		■	□			■*	■*
	Grout	■	□		■	■			■	■
	SPE	□	■		■	□			□	□
	PE	□	■		■	■			□	□
Coarse-grained soils	PAT	□	■		■	□			■*	■*
	Grout	■	□		■	■			■	■
	SPE	□	■		■	□			□	□
	PE	□	■		■	■			□	□
Metal Sludges	PAT	□	■		■	□			□	□
	Grout	■	□		■	■			■	■
	SPE	□	■		■	□			□	□
	PE	□	■		■	■			□	□
Nitrate Salts	PAT	□	■		■	□			□	□
	Grout	■	♦		■	■			□	□
	SPE									
	PE	□	■		■	■			■	■
Chloride Salts	PAT	□	■		■	□			□	□
	Grout	■	♦		■	■			□	□
	SPE	□	■		■	□			□	□
	PE	□	■		■	■			■	■
Incinera-tor Ash	PAT	□	■		■	□			■*	■*
	Grout	■	□		■	■			■	■
	SPE	□	■		■	□			□	□
	PE	□	■		■	■			□	□

Table 1-4

Product Properties vs Waste Type and Stabilization Process
Treatment Level C: Treatment to NRC Requirements/Recommendations for Low-Level Radioactive Waste

Waste Type	Process	Meets Waste Form/ Size Require.	Strength	Long Term Durabil.	Radiation Stability	Leachability of RCRA Metals and Radionuclides*		Contain-ment of Salts	Waste Loading	Volume Increase
						TCLP	ANS 16.1			
Fine-grained soils	PAT	■	■	■	■	□	I	I	■*	■*
	Grout	□	□	□	■	■	■	♦	♦	♦
	SPE	■	■	■	■	□	I	I	I	I
	PE	■	■	■	■	■	■	I	□	□
Coarse-grained soils	PAT	■	■	■	■	□	I	I	■*	■*
	Grout	□	□	□	■	■	■	♦	♦	♦
	SPE	■	■	■	■	□	I	I	I	I
	PE	■	■	■	■	■	■	I	□	□
Metal Sludges	PAT	■	□	■	■	□	I	I	□	□
	Grout	□	□	□	■	■	■	♦	♦	♦
	SPE	■	■	■	■	□	I	■	I	I
	PE	■	■	■	■	■	■	I	□	□
Nitrate Salts	PAT	■	■	■	■	□	I	I	□	□
	Grout	□	♦	♦	■	■	I	♦	♦	♦
	SPE									
	PE	■	■	■	■	■	■	■	■	■
Chloride Salts	PAT	■	■	■	■	□	I	I	□	□
	Grout	□	♦	♦	■	■	I	♦	♦	♦
	SPE	■	■	■	■	□	□	I	□	□
	PE	■	■	■	■	■	■	■	■	■
Incinera-tor Ash	PAT	■	■	■	■	□	□	I	■*	■*
	Grout	□	□	□	■	■	■	♦	♦	♦
	SPE	■	■	■	■	□	■	I	□	□
	PE	■	■	■	■	■	■	■	□	□

Table 1-5

Process Engineering Parameters vs Waste Type and Stabilization Process
Treatment Level A: Treatment to Present Mixed Waste Disposal Facility Requirements; i.e., Envirocare

Waste Type	Process	Cost				Complex-ity	Robust-ness	Availability		Pretreat-ment *	Residuals **	Through-put Potential	Scale Proven	Ease of Permit./ Public Accept.
		Capital	Process	Chemical /Materials	Total			Equip-ment	Process					
Fine-grained soils	PAT	♦	□	■	■	□	□	□	♦	■*	■ **	□	C	■
	Grout	■	■	■	■	■	■	■	■	■	■	■	C	■
	SPE	□	□	♦	♦	□	□	□	□	□ *	♦ **	□	P	□
	PE	♦	□	♦	♦	□	□	□	□	□ *	♦ **	□	P	□
Coarse-grained soils	PAT	♦	□	■	■	□	□	□	♦	■ *	■ **	□	C	■
	Grout	■	■	■	■	■	■	■	■	■	■	■	C	■
	SPE	□	□	♦	♦	□	□	□	□	□ *	♦ **	□	I	□
	PE	♦	□	♦	♦	□	□	□	□	□ *	♦ **	□	P	□
Metal Sludges	PAT	♦	□	■	□	□	□	□	♦	□*	□**	□	P	■
	Grout	■	■	■	■	■	■	■	■	■	■	■	C	■
	SPE	□	□	♦	♦	□	□	□	□	♦	♦	□	I	□
	PE	♦	□	♦	♦	□	□	□	□	♦	♦	□	P	□
Nitrate Salts	PAT	♦	□	■	■	□	□	□	♦	□ *	□ **	□	P	■
	Grout	■	■	□	□	■	■	■	■	■	■	■	C	■
	SPE													
	PE	♦	□	♦	♦	□	□	□	□	□ *	♦ **	□	P	□

Table 1-5 *(Continued)*

Process Engineering Parameters vs Waste Type and Stabilization Process
Treatment Level A: Treatment to Present Mixed Waste Disposal Facility Requirements; i.e., Envirocare

Waste Type	Process	Cost				Complex-ity	Robust-ness	Availability		Pretreat-ment *	Residuals **	Through-put Potential	Scale Proven	Ease of Permit./ Public Accept.
		Capital	Process	Chemical /Materials	Total			Equip-ment	Process					
Chloride Salts	PAT	♦	□	■	■	□	□	□	♦	□ *	□ **	□	P	■
	Grout	■	■	□	□	■	■	■	■	■	■	■	C	■
	SPE	□	□	♦	♦	□	□	□	□	□ *	♦ **	□	P	□
	PE	♦	□	♦	♦	□	□	□	□	□ *	♦ **	□	P	□
Inciner a-tor Ash	PAT	♦	□	■	■	□	□	□	♦	■	■	□	P	■
	Grout	■	■	■	■	■	■	■	■	■	■	■	C	■
	SPE	□	□	♦	♦	□	□	□	□	■	■	□	P	□
	PE	♦	□	♦	♦	□	□	□	□	■	■	□	P	□

* Required pretreatment depends on the moisture level in the waste stream. If below process requirement, rating would be ■. Incinerator ash is assumed to have low moisture content. PAT Process can tolerate more moisture SPE or PE - up to 15% -which would not require pretreatment for most soils.

** Amount and type of residuals depends on the particular waste stream. If moisture and volatile contents are very low, rating would be ■. Incinerator ash is assumed to have low moisture and volatiles contents. Nonheated processes, such as Grout and PAT would not normally have volatiles residuals.

Table 1-6

Process Engineering Parameters vs Waste Type and Stabilization Process
Treatment Level B: Treatment to Typical RCRA Requirements, Present or Future.

Waste Type	Process	Cost				Complex-ity	Robust-ness	Availability		Pretreat-ment *	Residuals **	Through-put Potential	Scale Proven	Ease of Permit./ Public Accept.
		Capital	Process	Chemical /Materials	Total			Equip-ment	Process					
Fine-grained soils	PAT	♦	□	■	■	□	□	□	♦	□ *	□ **	□	C	■
	Grout	■	■	■	■	■	■	■	■	■	■	■	C	■
	SPE	□	□	♦	♦	□	□	□	□	□ *	♦ **	□	P	□
	PE	♦	□	♦	♦	□	□	□	□	□ *	♦ **	□	P	□
Coarse-grained soils	PAT	♦	□	■	■	□	□	□	♦	□ *	□ **	□	C	■
	Grout	■	■	■	■	■	■	■	■	■	■	■	C	■
	SPE	□	□	♦	♦	□	□	□	□	□ *	♦ **	□	I	□
	PE	♦	□	♦	♦	□	□	□	□	□ *	♦ **	□	P	□
Metal Sludges	PAT	♦	□	■	□	□	□	□	♦	♦	□	□	P	■
	Grout	■	■	■	■	■	■	■	■	■	■	■	C	■
	SPE	□	□	♦	♦	□	□	□	□	♦	♦	□	I	□
	PE	♦	□	♦	♦	□	□	□	□	♦	♦	□	P	□
Nitrate Salts	PAT	♦	□	■	■	□	□	□	♦	□ *	□ **	□	P	■
	Grout	■	■	□	□	■	■	■	■	■	■	■	C	■
	SPE													
	PE	♦	□	♦	♦	□	□	□	□	□ *	♦ **	□	P	□

Table 1-6 *(Continued)*

Process Engineering Parameters vs Waste Type and Stabilization Process
Treatment Level B: Treatment to Typical RCRA Requirements, Present or Future.

Waste Type	Process	Cost				Complex-ity	Robust-ness	Availability		Pretreat-ment *	Residuals **	Through-put Potential	Scale Proven	Ease of Permit./ Public Accept.
		Capital	Process	Chemical /Materials	Total			Equip-ment	Process					
Chloride Salts	PAT	♦	□	■	■	□	□	□	♦	□ *	□ **	□	P	■
	Grout	■	■	□	□	■	■	■	■	■	■	■	C	■
	SPE	□	□	♦	♦	□	□	□	□	□ *	♦ **	□	P	□
	PE	♦	□	♦	♦	□	□	□	□	□ *	♦ **	□	P	□
Inciner a-tor Ash	PAT	♦	□	■	■	□	□	□	♦	■	■	□	P	■
	Grout	■	■	■	■	■	■	■	■	■	■	■	C	■
	SPE	□	□	♦	♦	□	□	□	□	■	■	□	P	□
	PE	♦	□	♦	♦	□	□	□	□	■	■	□	P	□

* Required pretreatment depends on the moisture level in the waste stream. If below process requirement, rating would be ■. Incinerator ash is assumed to have low moisture content.

** Amount and type of residuals depends on the particular waste stream. If moisture and volatiles contents are very low, rating would be ■. Incinerator ash is assumed to have low moisture and volatiles contents.

Table 1-7

Process Engineering Parameters vs Waste Type and Stabilization Process
Treatment Level C: Treatment to NRC Requirements/Recommendations for Low-Level Radioactive Waste

Waste Type	Process	Cost				Complex-ity	Robust-ness	Availability		Pretreat-ment *	Residuals **	Through-put Potential	Scale Proven	Ease of Permit./ Public Accept.
		Capital	Process	Chemical /Materials	Total			Equip-ment	Process					
Fine-grained soils	PAT	♦	□	■	■	□	□	□	♦	□ *	□ **	□	C	■
	Grout	■	■	□	□	■	■	■	■	■	■	■	C	■
	SPE	□	□	□	■	□	□	□	□	□ *	♦ **	□	P	■
	PE	♦	□	□	■	□	□	□	□	□ *	♦ **	□	P	■
Coarse-grained soils	PAT	♦	□	■	■	□	□	□	♦	□ *	□ **	□	C	■
	Grout	■	■	□	□	■	■	■	■	■	■	■	C	■
	SPE	□	□	□	■	□	□	□	□	□ *	♦ **	□	I	■
	PE	♦	□	□	■	□	□	□	□	□ *	♦ **	□	P	■
Metal Sludges	PAT	♦	□	■	■	□	□	□	♦	♦	□	□	P	□
	Grout	■	■	□	□	■	■	■	■	■	■	■	C	□
	SPE	□	□	□	■	□	□	□	□	♦	♦	□	I	□
	PE	♦	□	□	■	□	□	□	□	♦	♦	□	P	■
Nitrate Salts	PAT	♦	□	■	■	□	□	□	♦	□ *	□ **	□	P	□
	Grout	■	■	♦	♦	■	■	■	■	■	■	■	C	♦
	SPE													
	PE	♦	□	□	■	□	□	□	□	□ *	♦ **	□	P	■

Table 1-7 *(Continued)*

Process Engineering Parameters vs Waste Type and Stabilization Process
Treatment Level C: Treatment to NRC Requirements/Recommendations for Low-Level Radioactive Waste

Waste Type	Process	Cost				Complex-ity	Robust-ness	Availability		Pretreat-ment *	Residuals **	Through-put Potential	Scale Proven	Ease of Permit./ Public Accept.
		Capital	Process	Chemical /Materials	Total			Equip-ment	Process					
Chloride Salts	PAT	♦	□	■	■	□	□	□	♦	□ *	□ **	□	P	□
	Grout	■	■	♦	♦	■	■	■	■	■	■	■	C	♦
	SPE	♦	□	□	■	□	□	□	□	□ *	♦ **	□	P	■
	PE	♦	□	□	■	□	□	□	□	□ *	♦ **	□	P	■
Inciner a-tor Ash	PAT	♦	□	■	■	□	□	□	♦	■	■	□	P	■
	Grout	■	■	♦	♦	■	■	■	■	■	■	■	C	□
	SPE	♦	□	□	■	□	□	□	□	■	■	□	P	■
	PE	♦	□	□	■	□	□	□	□	■	■	□	P	■

* Required pretreatment depends on the moisture level in the waste stream. If below process requirement, rating would be ■. Incinerator ash is assumed to have low moisture content.

** Amount and type of residuals depends on the particular waste stream. If moisture and volatiles contents are very low, rating would be ■. Incinerator ash is assumed to have low moisture and volatiles contents.

2. PHOENIX ASH TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

The Phoenix Ash Technology (PAT) process involves the conversion of a mixture of fly ash, volcanic ash or kiln dust and other materials into a solid form, typically a brick. This stabilization process is similar to typical solidification/stabilization (S/S) processes that depend on high pH (from the pozzolan added to the waste material) to precipitate and stabilize the contaminants such as RCRA metals. The PAT is unique from those more typical processes in that it relies on mechanical compression during the initial onset of hydration, and uses moisture levels below that normally experienced in cementitious slurry or hydraulic form processes. This compression, associated with the pozzolanic quick/flash set provides a compact mass that can be manipulated.

The PAT process is simple to implement and applicable to a wide variety of materials but is particularly viable for fine inorganic materials. The equipment can be provided in a mobile configuration so that materials can be treated onsite. Typical volume reductions of 25-50 percent are experienced with a resultant durable material.

2.2 EXPERIENCE WITH HAZARDOUS AND MIXED WASTE STREAMS

Because the PAT process is relatively new, the number of waste streams which have been treated using PAT are limited. The list of successful treatments include waste water treatment sludges, pond sludges, industrial sludges, tank wastes, incinerator ashes, medical waste ash, contaminated soil, mine tailings, salts from blowdown scrubbers, and nitrate salts.

Hazardous

The first significant use of the PAT process was on lead contaminated soil from a battery reclamation site (Versar, 1992) . This material was subjected to treatability tests after stabilization using the PAT process. Lead was present at 15,600 mg/Kg (206 mg/L TCLP) in the untreated soil. After treatment, TCLP lead was <0.04 mg/L. Compressive strengths of 3,400 psi were achieved.

Radioactive

A scrubber blowdown high in sodium chloride and containing 12 nCi/g cobalt-60 and trace amounts of heavy metals was obtained from the DSSI incinerator located near Oak Ridge (Rust Federal Services, 1995). The material was dried, treated and compressed into bricks. Compressive strengths of 250 to 1,500 psi were attained. Cadmium solubility was reduced.

Other metals were not present in sufficient leachable concentrations (i.e., above quantitation limits) to determine the effect of the PAT.

Mixed Wastes

A nonhazardous surrogate of the sludge from the West End Treatment Facility at the Oak Ridge Y-12 plant was prepared by mixing calcium carbonate, water and 10,000 ppm of lead, cadmium, chromium and selenium (Rust Federal Services, 1995). The resulting material was dried, treated, and compressed into bricks. The resulting bricks lacked the characteristic structural integrity of similar previous tests. In fact, the bricks crumbled indicating a complete lack of pozzolanic material. No further tests were conducted to determine the cause of the failure. There is no reason to believe that the PAT will not work as well on mixed wastes as it does on hazardous and radioactive wastes.

An F006 pond sludge from K-25 at Oak Ridge was dried, treated, and compressed into bricks (Siegrist, 1994). Compressive strengths of 290 to 530 psi were attained. Metal leachate concentrations were below TCLP limits in both the untreated and treated material. Samples spiked with 1,000 and 10,000 ppm of silver and nickel oxide were also stabilized. Nickel solubility was reduced to below TCLP limits by stabilization alone. Further treatment was required to reduce silver solubility to an acceptance TCLP LDR level. Other metals were not present in sufficient leachable concentrations to determine the effect of the PAT.

A nonrad surrogate waste salt solution, representative of the saltcrete waste from the Rocky Flats Environment Technical Site main aqueous waste treatment facility, was prepared by mixing sodium nitrate, potassium chloride, sodium sulfate, calcium carbonate, sodium fluoride, magnesium chloride, and water. To test the ability of the PAT process to treat this material, the surrogate was spiked with 10,000 ppm of lead, cadmium, chromium, and selenium (Rust Federal Services, 1995). The material was dried, treated, and compressed into bricks. Compressive strengths of 990 to 1,580 psi were attained. Cadmium, lead, and selenium solubility were reduced from 243, 2.8 and 2.7 ppm to 19, <0.14 and 1.7 ppm respectively. Pretreatment with ferrous sulfate and lime was required to reduce cadmium and chromium leachate levels below TCLP limits (from 19.0 and 2.7 ppm to 0.03 and 0.9 respectively).

A nonhazardous surrogate of the liquid waste from tanks at the Idaho Chemical Processing Plant was prepared by mixing sodium nitrate, water bismuth, manganese, and zinc as surrogates for lead, chromium, cadmium, and mercury, respectively. This nitrate salt surrogate was also spiked with cesium (^{137}Cs), strontium (^{90}Sr) and natural uranium. Studies are in process at the Clemson Technical Center to subject stabilized samples to compressive strength, freeze/thaw, wet/dry, immersion, and ANSI/ANS 16.1 leach testing.

A bottom ash from the K-25 TSCA incinerator at Oak Ridge was dried, treated, and compressed into bricks (University of Pittsburgh Applied Research Center, 1993) (Spence, 1993). Compressive strengths of 1,650 to 2,600 psi were attained. After immersion, compressive

strengths of 1,800 to 3,300 psi were attained. Metals were not present in sufficient concentrations to determine the effect of the PAT (lead solubility was reduced slightly). Samples spiked with 10,000 ppm of chromium were also stabilized. Chromium leachate concentrations were below TCLP limits in both the untreated and treated material. Chromium solubility was reduced slightly by the PAT. An ANSI/ANS 16.1 Leach Indices of 6.6 to 6.9 was obtained from a technetium-spiked ash.

Additional work was done at Oak Ridge with the participation of the Energy Technology Engineering Center (ETEC) of Canoga Park, CA, on final waste form salt produced from Molten Salt Oxidation (MSO) unit treatment of contaminated materials (US Department of Energy, 1993). During this effort, bricks with high strengths were produced.

An additional evaluation was performed by the Los Alamos National Laboratories for Oak Ridge National Laboratory at Rocky Flats (Siegrist, 1994) for the purpose of identifying, evaluating, and screening options for treatment and disposal of the containerized sludges through the information available from previously published work. It examined nine potential treatment options in light of three feasible burial options for final disposal. The PAT process scored well in many categories of this screening.

2.3 TESTING STAGE

The testing to date of mixed waste is reflected by the references noted in the previous section. The testing to date has been primarily bench scale efforts with real and surrogate materials. Additional tests have been performed by PSI using contract laboratories. These additional tests indicate a broad range of waste may be effectively stabilized/solidified using the PAT. However, confirmatory testing by independent laboratories is necessary to validate these results.

2.4 DEGREE OF TECHNICAL DEVELOPMENT

Experience to date indicates that the PAT has the potential to acceptably treat a wide variety of waste streams. The only materials that have not been stabilized successfully are organic materials which have a memory effect and rebound back to original size after compression (e.g. wood chips and rubber crumbs), and a sludge that contained high levels of calcium carbonate. In such instances, stabilization may be possible after pretreatment of the waste.

The performance of materials treated with the PAT process varies based on the constituents in the waste stream. Waste loading is most sensitive to moisture content. If waste streams are dry or have a moisture content such that the final mixture of constituents prior to compression can be held at 8-12 percent wt., waste loading can be as high as 80 percent wt.

The brick forms immediately but is fragile for the first few minutes and continues to cure over an extended period of time. After one day the compressive strength of the brick is about one half of the 28-day strength and after seven days the brick is about 80 percent of the 28-day strength. The 28-day strength is assumed to be about 95 percent of the full strength achievable. This is an estimate because extended period tests have not been performed. The final products are generally very durable with one indicator being the unconfined compressive strength (UCS). Although this does not guarantee long-term durability, UCSs of a few hundred to as high as 7,000 psi. have been experienced. The UCS and the associated durability will vary with the chemical reactions in the process which will be dictated by the constituents of the waste stream. Pretreatment may contribute to these characteristics. Thermal characteristics of a fully cured block indicate a relatively high specific heat and the material typically behaves as a ceramic or refractory. The bricks usually exhibit extreme resistance to freeze/thaw cycles and have low rates of absorption. Immersion test results indicate the brick product appears to be durable. Additional testing is required in this area. Resistance to radiation studies have yet to be performed. TCLP and ANSI/ANS 16.1 leach results indicate reduced leaching similar to other stabilization processes. Pretreatment may be required for chromium, silver, and cadmium.

Volume reductions of the original waste materials, assuming the moisture content criteria has been satisfied, is always experienced. Volume reduction of the combined waste and pozzolan, as measured by free fall volume of the mixture, is experienced in varying degrees unless the pozzolan percent volume exceeds 50. Work at the Clemson Technical Center has experienced volume reductions from 10 to 50 percent with final densities in a range of 1.6 to 2.1 g/cc. Leachability of the original waste streams is generally reduced by a significant amount and in many cases to a nondetect (ND) level. Results will vary with chemistry experienced in the combining of the waste and pozzolan and typical of cementitious processes.

An additional consideration is that there may be residual loose material on the surface of the blocks or dust expelled from the compression operation. To control dust, protect the environment and operations personnel from airborne exposure when processing radioactive materials, simple process design modifications utilizing containment and HEPA filtration will be incorporated.

The PAT process, being a stabilization process, is considered Best Developed Available Technology (BDAT) for many waste types.

2.5 DEGREE OF COMMERCIAL DEVELOPMENT

The PAT process is currently being used on a commercial level both in the United States and Europe to remediate hazardous waste sites. Equipment design and manufacturing to meet specific waste stream and waste site requirements is provided by Pressure Systems, Inc. of Albuquerque, New Mexico.

2.6 COST CONSIDERATION

Cost of implementing the PAT process for any given waste stream at any given site will vary based on costs for pozzolan, labor, operating safety requirements, etc. For waste streams that do not require pretreatment and do not have extreme hazards associated with handling the waste materials, the costs will fall in a range of $40 to $60 per ton. The cost of pretreatment, containment, and HEPA filtration will be incremental additions to the cost of normal operations.

2.7 DATA GAPS

Additional testing is needed in several areas. More tests need to be performed on mixed waste with a full regimen of durability and leachability tests. This should include samples that significantly exceed TCLP limits and challenge the PAT process. Testing of additional types of waste streams are required. Comparative studies on identical wastes using competing processes, would be useful in trading off different approaches. In addition, basic studies on the chemical reactions that occur within the treated material are required to better understand the process.

2.8 ASSESSMENT

The fact that the PAT is new to the remediation industry, and that few exposures to field application are available, has hindered wider acceptance of this process. The primary benefits of the PAT process are its simplicity, low cost, and volume reduction. Other benefits include high waste loading, high strength, and low leachability. Within the overall cost considerations, the process attribute of volume reduction will have a positive impact on handling/transportation costs as well as long-term disposal costs. Advantages often achieved include waste loadings of 40 to 60 percent and volume reductions of 10 to 50 percent, compressive strengths of up to 7,000 psi, and low leachability.

Limitations associated with the process include the pretreatment requirements of low moisture and a granular size $\leq$ 0.375in. For hazardous or mixed wastes, particle size $\leq$ 0.25 in. is desirable to achieve proper brick formation and adequate stabilization.

2.9 LIST OF REFERENCES

Rust Federal Services. 1995. *Evaluation of TIDE Solidification Technology for Mixed Waste Salts.* Clemson Technical Center, Anderson, SC. Draft Report. September.

Siegrist, R.L., K.S. Dickerson, M.I. Morris, M.J. Wilson-Nichols, R. Juhlin, L. Cummins. 1994. *Evaluation and Screening of Treatment and Disposal Options for the Solar Pond Sludges at Rocky Flats*. LA-UR-94-4414, Los Alamos Technology Office/Oak Ridge National Laboratory/RUST Geotech. December 23.

Spence, R.D., C.L. Francis, I.L. Morgan, D.R. Trotter. 1993. *TIDE Stabilization of the K-25 Incinerator Ash,* Letter Report, October.

University of Pittsburgh Applied Research Center. 1993. *Evaluation of TIDE Solidification Technology for Mixed Waste Incinerator Bottom Ash,* National Environmental Technology Applications Center (NETAC), Pittsburgh, PA. Environmental Restoration, Department of Energy (DOE) and Office of Radiation and Indoor Air, US Environmental Protection Agency (EPA), Washington, DC. November.

U.S. Department of Energy, Office of Environmental Restoration. 1993. *Molten Salt Oxidation Technology Progress Report,* DOE/ID/12584-119, GJPO-112 Part 3. October.

Versar Inc. 1992. *Onsite Engineering Report for the Bench-Scale Solidification/Stabilization of Soil Washing Fines Using the TIDE Encapsulation Technology*. Springfield, VA. Contaminated Soil and Debris Program, US Environmental Protection Agency, Office of Solid Waste, Washington, DC. June.

3. GROUT/PORTLAND CEMENT STABILIZATION

3.1 TECHNOLOGY DESCRIPTION

Cementitious stabilization/solidification (S/S) is one of the most widely used techniques for the treatment and ultimate disposal of hazardous waste and low-level radioactive waste. In the latter waste field, this technique is commonly called grouting, and the mixtures so obtained, grouts. Cement-based "grout" systems have been used for so many years, in so many instances for S/S of RCRA, radioactive waste of all levels, and now LLMW, that it is impossible here to discuss individual cases for the most part. Private companies such as Chem-Nuclear Inc. have been using cement-based systems on low-level waste from nuclear power plants for decades. Large volumes of solutions, sludges, salts, and solids, containing a wide variety of hazardous and radioactive constituents, have been treated by cement-based S/S at government-owned plants, both from on-going processes and from remedial activities. Much of this waste would have been considered LLMW under current regulations. A huge volume of testing data is available in the open literature, in government reports, and in Topical Reports submitted by S/S vendors. Not all of these efforts have been successful, at least with the more difficult to treat waste.

As a result of the large amount of information available, this section of the report discusses the basic chemistry and properties of cement-based systems in a more general way than do the other sections that deal with much more specific technologies. Therefore, the comparative tables in the Appendix for this process consist of summarized information, rather than specific project data.

Cementitious materials are the predominant materials of choice because of their low associated processing costs, compatibility with a wide variety of disposal scenarios, and ability to meet stringent processing and performance requirements. Cementitious materials include cement, ground granulated blast furnace slag, fly ash, lime, and silica fume. Various clays and additives are used to help immobilize contaminants or otherwise enhance the waste form properties. Soluble constituents in the waste chemically interact with the cementitious materials to form low solubility products at the high pH and the E_h prevailing in the waste form. These interactions usually affect the cementitious hardening and properties to some degree. Testing with a specific waste or waste stream is required to tailor the formulation to the desired properties. Sufficient attention must be given to characterizing the waste, developing the formulation to treat the waste, and to implementing this formulation in the field to assure correct mixing of the formulation. Adding these dry ingredients usually increases the volume of the waste treated, which can add significantly to the lifetime disposal costs. The volume decrease claimed by some processes come from evaporation of the water and encapsulation of the solids. The same evaporation pretreatment could be used with cementitious S/S to obtain a net volume decrease, but some of the simplicity of the cementitious S/S would be lost. The cementitious waste forms are porous making the interior more accessible than for polymeric or glass waste forms. The key has been controlling leachability by pH, E_h, and/or absorbents for a simpler and cheaper treatment.

3.2 EXPERIENCE WITH HAZARDOUS AND MIXED WASTE STREAMS

Aqueous Liquids

Liquid waste, even with high dissolved solid contents, can be and are solidified into grout waste forms, particularly low-level radioactive waste [e.g., Oak Ridge National Laboratory (ORNL) Melton Valley Storage Tank (MVST) supernate, Hanford phosphate-sulfate liquid waste, and WSRC saltcrete]. Often, waste water treatment (e.g., precipitation, flocculation, filtration, ion exchange, evaporation) is performed to produce "clean" water with grout stabilization of the resulting sludges, resins, or evaporator concentrates.

Other techniques require evaporation of the water and encapsulate the solids originally dissolved in the aqueous liquid waste. Removing the water decreases the volume of the aqueous liquid waste, which is claimed as one of the advantages of these encapsulation techniques. Water removal, with the resulting volume decrease, could also be done prior to stabilization in grout, if desired.

Aqueous Sludges

Sludges resulting from wastewater treatment, incinerator air pollution control systems (APC) and other processes are among the physical waste types often stabilized with grout systems. In general, sludges are easier to stabilize than liquids containing only dissolved solids.

Acids

Corrosive acids react strongly and consume Portland cement and other grout additives. This does not prevent S/S of such waste, it just increases the amount of additives required in order to neutralize the acid before solidification can occur. It may be more economical to neutralize the acid with cheaper reagents prior to S/S. The resulting grout waste form is not resistant to corrosive acids, so exposure to acid after S/S can destroy the cementitious matrix and release the stabilized contaminants. Grouts are designed to withstand the acetic acid extraction of the TCLP test by neutralizing the acid, resulting in a high final extract pH and low RCRA metal concentration.

Bases

Grouts are high pH waste forms and are generally compatible with corrosive bases. Calcium hydroxide is a byproduct of the hydration of Portland cement, implying a pH of about 12.5. The presence of alkalies in cement paste may increase paste pH to 13.0 or 13.5. Strong bases react with and activate ground granulated blast furnace slag, fly ash, silica fume, and other pozzolans (consuming the base in the process of forming calcium and sodium silicates). Grouts have been developed for S/S of the strong base solutions stored in DOE tank wastes (some of these supernates have high sodium hydroxide concentrations).

Cyanides

In general, destruction of cyanide is preferred prior to S/S of a waste, although small quantities of cyanide may not justify expensive destruction techniques. Conner (1990) discusses destructive techniques for cyanide, as well as listing references for S/S using cement in combination with aluminum hydroxide, anion exchange resin, calcium polysulfide, lime, iron salt, iron sulfate, calcium chloride, iron chloride, aluminum chloride, and/or surfactant.

Metals

In general, the BDAT for the RCRA metals is S/S. Interestingly, metals in aqueous solution may be desired because they can be precipitated as the species of choice; e.g., lower soluble sulfide rather than hydroxide (Conner, 1990). The natural high pH of grout offers a satisfactory low solubility environment for many metals, although most solubility curves pass through a minimum in the pH range of 9-11 (i.e., metals become more soluble at the extremely high pH range). For this reason, pure cement pastes, with their pH environment of 12.5 to 13.5, do not always make the best waste forms. Tailoring the grout with slag or pozzolans is desirable for a lower matrix pH and better stabilization. Conner (1990) indicates that the pH of most grout waste forms are initially 11. Conner (1990) lists information on the solubility of different species of the metals as well as examples of stabilization of the metals. Even if straightforward hydroxide chemistry has problems meeting the regulatory limits, the metal may be stabilized using other anions; e.g., chloride may be added to a grout to stabilize silver. Chromium is the notable exception to this general approach. Chromium (VI) (chromates) must be reduced to chromium (III) for stabilization. Such reduction can be done in a treatment prior to S/S, but adding reducing agents to the grout has also been used (Spence et al, 1995). One of the grout additives, ground granulated blast furnace slag, is an effective reducing agent because of the iron sulfide naturally present in this slag. This natural reducing capability of slag has proven effective in stabilizing technetium by reducing the soluble pertechnetate anion [Tc(VII)] to the more insoluble cation [Tc(IV)] (Spence et al, 1989). WSRC has been using slag formulations since 1984 for reduction of Tc^{+7} and Cr^{+6}, as well as for improved nitrate retention and better durability. Typical formulations use 0-10 percent cement, 20-40 percent slag, and 20-40 percent flyash, and have waste loadings of 40-55% (Langton, 1995).

Mercury

Conner (1990) discusses the S/S of metals, including mercury, in hazardous waste. He indicates that most of the references discuss wastewater removal techniques that precipitate soluble mercury, usually as relatively insoluble mercuric sulfide, but lists reported S/S of mercury wastes. Treatment of the waste to precipitate soluble mercury as the sulfide may be desirable prior to S/S. Some DOE facilities have significant amounts of elemental mercury waste. Amalgamation is the suggested stabilization technique. It is desirable to remove and recycle (preferable) or amalgamate metallic mercury from contaminated waste. In general, high

temperature stabilization techniques (e.g., vitrification, thermoplastic encapsulation) must remove mercury prior to stabilization or risk contaminating the offgas with mercury.

Organics

Organics are generally incompatible with cement, sometimes interfering with the hydration reactions and preventing or delaying set. Aqueous liquids or sludges slightly contaminated with organics can usually be solidified with little or no problem. Oily sludges and pure organic liquids generally may coat cement particles preventing hydration and set. Special additives have been developed to allow solidification of even these difficult wastes (Trussel and Spence, 1994) (Trussel and Spence, 1993) (Spence and Osborne, 1993). In general, grouts encapsulate, rather than stabilize, the organics. They require special additives to stabilize or destroy organics. These additives are claimed to stabilize organics, albeit with limited effectiveness (Conner, 1990) (Spence et al, 1992) (Spence et al, 1990).

The regulatory situation with respect to organics requires some explanation. Several older guidelines under "Superfund" (CERCLA) and two recent final regulations under the Resource Conservation and Recovery Act (RCRA) mandate treatment of all hazardous organics contained in "contaminated debris" and of 26 compounds contained in other waste. Under CERCLA, a variance procedure in remedial actions allows immobilization of organics as an alternative to removal or destruction (U.S. EPA, 1990) and a draft guidance document from EPA Risk Reduction Engineering Laboratory (RREL) (U.S. EPA, 1991) recommends total constituent analysis be used as a means of judging the success of immobilization. Under RCRA, the 1992 "debris rule" (U.S. EPA, 1992) and the new rule dealing with EPA Waste Codes D018 - D043 ("Characteristic" or "D-Code" waste) (U.S. EPA, 1994) require the treatment of hazardous constituents in debris and other waste. Most importantly, now two different test methods are used to judge the effectiveness of the treatment in meeting the regulatory requirements: the Toxic Characteristic Leaching Procedure (TCLP) and Total Constituent Analysis (TCA). TCA has replaced TCLP in the case of organics for most purposes under RCRA, and is recommended (U.S. EPA, 1991) as the primary test in CERCLA and other remedial actions. It is also the basis for EPA's Universal Treatment Standards (UTS) (U.S. EPA, 1994). TCLP is used in the case of debris (U.S. EPA, 1992) and as an additional test in remedial work. Due to the test procedures, meeting the present and forthcoming TCA standards is much more difficult than passing the old TCLP test in the case of organics. The latest regulation proposed by EPA (Federal Register, 1995) would change the rules again, proposing two levels for organics that would allow exit from RCRA LDRs. One is a TCA level, the other a TCLP leaching level.

The advent of the new rules and testing protocols has made necessary the development of innovative stabilization techniques. Previously, the use of additives such as activated carbon in S/S systems to immobilize organic constituents was based on the TCLP test method. However, with the TCA test method, such additives are often not very effective (Lear and Conner 1991). As a result, a number of other reagents have been developed or adapted from other processes to meet the new requirements. Furthermore, immobilization of organic constituents is not

necessarily dependent on alkaline binders; in fact, high alkalinity may be detrimental in some cases. Conner and Smith (1993) described the results of an extensive development effort in this area.

Macroencapsulation

Debris, large solids, and other heterogeneous waste may be macroencapsulated in grouts, including crucibles, bricks, resins, carcasses, plastic, rubber, paper, cloth, rags, asphalt, lab packs, equipment, gloveboxes, and filters. Macroencapsulation may not necessarily prevent degradation (e.g., biodegradation) of such materials, which may lead to large voids inside the grout waste form. The grout consolidates such material, offers a physical barrier, and stabilizes metals and radionuclides contaminating such debris.

3.3 TESTING STAGE

Grout/Portland cement stabilization of hazardous, radioactive, and mixed wastes has been practiced in the field for decades and several commercial vendors offer this service. The regulatory gray area of mixed waste is a recent phenomenon. Under currently applicable regulations, large quantities of mixed waste are currently stored at DOE sites across the country. The Federal Facility Compliance Act is specifically designed to bring these facilities into compliance using Federal Facility Compliance Agreements among DOE, EPA, and the relevant states. These agreements identify mixed waste for which treatment/storage/disposal exists and those for which treatment/storage/disposal do not exist. Under these plans, studies would identify suitable treatment/storage/disposal for this category of waste. Bench (hot and cold) and pilot testing has been underway at these DOE sites, including grout/Portland cement stabilization. Some field operations have been planned or conducted in recent years. Privatization of these efforts is currently a major objective of DOE. Currently, Envirocare is the only licensed commercial mixed waste disposal facility, but DOE is also interested in privatization of treatment and disposal onsite. Vendors are interested in supplying this service.

3.4 DEGREE OF TECHNICAL DEVELOPMENT

The grout properties are a function of the chemistry and microstructure of the grout matrix. One must change the chemistry and/or microstructure to improve a given grout property; but, in general, this changes the other grout properties. For example, the compressive strength can be improved by increasing the cement content, but this decreases the waste loading and increases the volume of the final waste form. In addition, the contaminant retention and waste form durability are usually improved by such compositional changes. Although the waste form physical and chemical properties usually improve with higher binder (e.g., cement) contents, it must be remembered that the intent is to stabilize a waste for disposal, not create a strong cement structure slightly contaminated with waste. One must balance the desired grout properties

against the ever increasing final waste form volume as the additive content increases. Eventually, a point of diminishing returns is reached, in which improvements in grout performance are not worth the increased volume. One strategy is to add the minimal amount of additive to meet the performance criteria, minimizing the volume increase.

The regulatory criteria do not necessarily require the formation of a monolithic waste form with a high compressive strength. Historically, the compressive strength requirement has been 50 or 60 psi, i.e., strong enough to support the expected overburden. The U.S. NRC has recommended an average compressive strength of 500 psi, pretty much guaranteeing solidification into a monolith. However, the Envirocare mixed waste disposal facility prefers granular waste and charges extra for large monoliths, which they must break up for burial.

The radioactive waste form leach tests (e.g., ANSI/ANS-16.1, MCC-1) are generally designed to leach small monoliths of the waste form and the physical barrier of the monolith is credited with assisting in contaminant retention. Such is not the case for the hazardous waste leach test, the TCLP. For this test, if the waste has been solidified into a monolith, it must undergo size reduction prior to leach testing. No incentive exists in this case to solidify the waste into a monolith, unless there is a criterion for a significant compressive strength.

Grouts interact with the waste to stabilize the contaminants. The chemical interaction of the grout with the waste stabilizes the contaminants, so that the waste form does not depend on the physical integrity to retain the contaminants. If the waste is never solidified into a monolith, physical properties such as compressive strength and durability have no meaning. For this reason, much of the work with hazardous waste does not concentrate on, or measure, compressive strengths or durability.

On the other hand, all things being equal, monoliths offer higher mass transfer resistance than a bed of rubble. If the retention required depends on this physical integrity, then the weathering of the monolith into a particulate form can be viewed as a failure. Typically, radioactive waste forms have been subjected to compressive strength and durability testing.

Compressive Strength

Generally, the compressive strengths of solidified monoliths range from a few hundred psi to several thousand psi, depending on the waste loading, water content, and interferences with the hydration reactions. The strength of neat Portland cement paste depends on the water content of the paste, so the water content is an important parameter. In general, higher waste loadings lead to lower grout strength. Sometimes the waste interferes with the set, usually only delaying the set and the eventual strength achieved. In extreme cases, set has been prevented for simple grout recipes, requiring tailoring with different binders, pozzolans, and/or admixtures to achieve the desired set. Sometimes the interferants cause lower compressive strengths than would otherwise be observed, but usually acceptable strengths can be attained.

Durability

Usually, grout monoliths can be prepared that pass freeze/thaw, wet/dry, immersion, and radiation testing. Excessive water content can cause freeze/thaw failure in grouts, if the excess water is retained in the grout during the test (the recommended NRC test requires testing bare without controlling humidity, allowing drying of the grout at the highest temperature). Solidifying aqueous waste does lead to grouts with excess water, since high waste loadings are desirable (evaporating some of this water will reduce the final volume of waste solidified). Air entraining admixtures can be used to provide freeze/thaw resistance for high water grouts or grouts stored outside, above ground.

The waste that have caused problems in these tests generally involve some form of expansion under these changing conditions, because the grout sets in a rigid three-dimensional structure and volume increases after set can be destructive. Ion exchange resins have typically caused such problems for grout, because these resins do shrink during drying and swell during wetting. Grouts have been developed to encapsulate ion exchange resin and survive wet/dry, freeze/thaw testing (Morgan and Bostick, 1992).

Sulfate attack of Portland cement paste is a well known phenomena and sulfate containing waste can lead to the growth of expansive minerals. This can be a problem for high salt waste, especially those containing high sulfate waste. This problem is exacerbated in wet/dry or freeze/thaw testing, because the loss of water concentrates the soluble salts in the grout. Expansive minerals that have been observed in grout waste forms are ettringite, calcium chloroaluminate hydrate, and darapskite. On the other hand, grouts have been developed for aqueous waste with high salt concentrations, including sulfate (Sams and Gilliam, 1992) (Sams et al, 1986) (Gilliam et al, 1987) (Spence et al, 1993). The Westinghouse Savannah River Co. (WSRC) solidifies a concentrated brine (5M salt solutions) into "saltcrete" after pretreatment for hexavalent chromium (Cr^{+6}) and technetium (Tc^{+7}).

Radiation testing of grouts usually subjected grout samples to a high gamma field to obtain a total dose of 10^8 Rad. Grouts have proven to be relatively insensitive to this type of radiation exposure and are generally considered durable waste forms under exposure to radiation. The problem with stabilizing radioactive waste, especially highly radioactive waste, is self-radiolysis, leading to build up of hydrogen over long times if the waste form contains much water. Typical grout does contain much water, which may limit the concentration of radioactivity that may be stabilized. A grout was developed specifically to combat this problem, FUETAP.

3.5 DEGREE OF COMMERCIAL DEVELOPMENT

Stabilization in grout is a mature process that has been practiced for decades. Many vendors practice this technology, especially for hazardous waste. Fewer vendors stabilize radioactive waste. There has been much less experience with treatment and disposal of currently defined

mixed waste. There is currently only one licensed commercial facility in the United States for final disposal of mixed waste, Envirocare in Utah. Their license restricts the radionuclides that can be disposed and requires the waste to meet LDR limits. Ostensibly, Envirocare does have grout stabilization capability.

Presently, with the regulatory uncertainties, mixed waste is going in one of several routes:

- Decharacterization or delisting to remove it from the RCRA hazardous waste classification, leaving only a low-level radioactive waste;

- Shipment to Envirocare for treatment and disposal;

- Treatment and storage onsite, especially for remedial actions.

WSRC is looking at delisting of certain waste (Langton, 1995) and disposal at a radioactive waste site or onsite in a concrete vault, at a ten-fold cost reduction. WSRC also has done a CERCLA closure, with solid material compacted into place. At present, delisting is a difficult process under EPA's rules, but newly proposed rules (Federal Register, 1995) may change this situation. At other sites, such as Rocky Flats, mixed waste is currently stored onsite awaiting other disposal options, and this is probably the most common situation.

3.6 COST CONSIDERATION

The costs for cementitious waste forms from Dole and Trauger (1983) and Kessler *at al.* (1984) are 10$/yd^3-$30/yd^3 ($0.05-$0.15/waste gal.) for the materials cost and $20/yd^3-$100/yd^3 ($0.10-$0.50/waste gal.) total disposal cost (including material, capital, and operating costs) (Dole and Trauger, 1983) (Kessler et al, 1984). At the other end of the spectrum, Myrick *et al.* (1992) had a total estimated project cost of $23,230/yd^3 ($115/gal. concentrated low-level liquid waste) for solidifying 47,000 gal. of waste. This cost is unusually high for S/S, even for such a small quantity of waste. The cost of an alumino-silicate stabilization was estimated by Bates *et al.* (1992) at $190-$360/yd^3 ($0.94-$1.78/gal) to treat 15,000 yd^3 of a SITE demonstration waste (Bates et al, 1992).

In making a case for vitrification of low-level waste, Gimpel (1992, 1992a), Diggs (1992) and Diggs and Gimpel (1992) have made economic assessments and published several papers together or separately either claiming the costs for vitrification is comparable with that of S/S or that the costs for making the glass waste forms is higher, but the total life cycle costs (including the disposal costs and monitoring costs for 100 y after disposal) are comparable between the two options because of the higher volumes that must be disposed and monitored from S/S. They estimate the direct costs to be $69/yd^3 ($90-$220/m^3) ($0.34-$0.83/gal) for S/S and $306/yd^3 ($400/m^3) ($1.51/gal) for vitrification, but total costs (including disposal) at $907/yd^3-$1598/yd^3 ($1186-$2090/m^3) ($4.49-$7.91/gal) and $705/yd^3-$1147/yd^3 ($922-$1500/m^3) ($3.49-

$5.52/gal), respectively. The assumptions made regarding S/S appear reasonable, but are more questionable regarding vitrification. However, the authors make a valid point that most cost estimates are the direct costs of making the wastes and do not include the disposal costs. The cost deficit from increasing the waste volume should be estimated for S/S; or, the cost benefit estimated from the volume decrease for vitrification.

The disposal costs estimated in a progress report to the Savannah River Laboratory (1989) ranged from $381/yd^3 to $1282/yd^3 ($14.10/ft^3 to $47.50/ft^3) (Waste Management Program, 1989). Estimated total costs depend on the assumptions made for direct costs of making the waste form and the assumptions made for disposal costs, including the final waste form volume compared to the initial waste volume.

Jacobs et al. (1984) estimated the costs for treatment (including transportation and burial) of 12,700 ft^3/y for 30 y of concentrated BWR waste for the following five options:

	$/yd^3	$/ft3	$/gal
1. Crystallization followed by S/S	999.	37.00	4.95
2. Drying followed by S/S	781.	28.93	3.87
3. Evaporation followed by encapsulation in asphalt	950.	35.20	4.71
4. Drying followed by encapsulation in DOW binder (VES)	664.	24.60	3.29
5. Evaporation followed by S/S	2409.	89.21	11.93

3.7 DATA GAPS

Grout/Portland cement stabilization has been extensively tested with a wide range of waste over a wide range of contaminants and their concentrations. Through hard-earned experience, the areas where difficulties can be expected have been identified. In addition, 150 years of research have revealed much about Portland cement paste chemistry and microstructure. The survival of cement structures for millennia gives hope for the lasting durability of cementitious waste forms. Nevertheless, only a few studies have been conducted on the fundamental chemistry and microstructure of waste contaminants in cementitious waste forms. Cement, without the complication of encapsulating and stabilizing waste, is a complex heterogeneous material and source of much investigation. The addition of waste changes the chemistry and microstructure of the final product in ways that are not well understood, but highly effective for stabilizing certain species. The adoption of the Universal Treatment Standards continues the regulatory trend of ever more stringent standards that is beginning to approach, or fall below, the solubility limits of certain species. Such strict standards may require low solubility (as in the interaction of the waste with the cement) combined with mass transfer resistance (as in the microencapsulation with thermoplastics).

Durability of all waste forms, not just grout, is not well defined as a property or test. The tests, by necessity, are short term, while the time of interest is on the order of 20 years, 100 years, 500

years or 10,000 years. Portland cement structures are routinely designed for 50-year life spans and cement chemists feel that the cement matrix can survive for the time spans of interest if properly protected from aggressive environments (usually associated with being immersed in water and the soluble species that attack the matrix). It is not clear how to prove such assertions in short-term tests to the satisfaction of all protagonists. Durability usually means the retention of the physical structure of a waste form over time or under adverse conditions. In general, the TCLP test removes this physical barrier to releasing the contaminants; thus, durability may have little meaning for a waste form that depends on the chemical stabilization of the contaminants (as does grout), especially if the original waste form is not designed as a strong monolith (as is the case for some hazardous waste treatments). The same cannot be said of waste forms that depend on microencapsulation (such as thermoplastics) for the retention of the waste species. Clearly, in such cases the stability of the binding matrix over time is important since, when it fails, the contaminants are released.

8. ASSESSMENT

Cementitious stabilization/solidification is one of the most widely used techniques for the treatment and ultimate disposal of hazardous waste and low-level radioactive waste. Cementitious materials are the predominant materials of choice because of their low associated processing costs, compatibility with a wide variety of disposal scenarios, and ability to meet stringent processing and performance requirements. The interaction of the cementitious materials with the waste has proven to be a double edged sword. The interaction has been cited as a deterrent because of the possible interaction effects which interfere with setting. Although such interferences do occur, they can usually be overcome. In addition, it is this interaction that changes the chemistry of the waste and stabilizes many of the constituents. For this reason, stabilization can be achieved, even if the waste form is broken up for testing in the TCLP test.

Stabilization/solidification is the Best Demonstrated Available Technology (BDAT) for most of the inorganic species (RCRA metals). Incineration is the most common BDAT for the organics, and is often a "specified technology," meaning that it must be used under the Land Disposal Restrictions (LDRs). While grouts have only a limited capability to stabilize organics in waste with high organic contents, cementitious stabilization has been used in a number of remedial projects where organic constituents of concern are present at low levels. Oily materials in waste can severely interfere with hydration and set in simple cement-based formulations. However, additives have been developed to allow the solidification of grout even when mixed with oily sludges. In waste with high concentrations of RCRA metals that are slightly contaminated with organics, grout stabilization without incineration may be justified as the most effective and least expensive alternative. Otherwise, organic destruction or removal is desired.

Vitrification is "specified technology" BDAT for high-level radioactive waste containing arsenic, but otherwise stabilization/solidification is usually BDAT and has proven effective without the use of special additives in most cases. Chromium (VI) (chromate) is not directly stabilized by

pH control, the main means of cement stabilization of metals. Chromates must be reduced to the less soluble chromium (III) valence state, prior to being stabilized. This can be accomplished in grouts using blast-furnace slag and/or special additives. Mercury may be a more problematic species, but amalgamation of the element and precipitation of the ion as a sulfide has been done extensively. Grout stabilization of both elemental mercury and the soluble compounds has been demonstrated at the bench level using special additives. Mercury currently cannot be vitrified and poses a volatility problem even at the low temperatures of thermoplastic encapsulation. Under the LDRs, mercury removal by retorting is a specified technology for certain levels of mercury in certain waste, while organic mercury-containing waste have incineration as the specified technology.

The most frequently cited problem with grout stabilization/solidification is the associated volume increase. Volume increase can be minimized by adding the minimal amount of additive to pass the TCLP test at the expense of strength and physical stability of the final waste form. Hazardous waste stabilization/solidification has used this strategy to achieve waste loadings of 80 to 90 percent by weight, and volume increases of less than 10 percent by volume. Evaporation prior to grout stabilization/solidification would also result in volume decreases, but S/S of solid salts can interfere with the set and result in low strengths. The concentration of sulfate, in particular, must be limited if the waste form is to be judged by physical stability and/or durability. In general, waste loadings of 40 to 60 percent by weight with volume increases of about 50 percent by volume are not unusual. Small waste loadings can result in many fold volume increases.

Unlike glass or thermoplastics, grout waste forms are solid bodies with accessible porosity, reducing their effectiveness as a mass transfer barrier to soluble species such as many salts. For this reason, soluble species (not stabilized in the grout) may have a leachability index (ANSI/ANS 16.1) of only 6 to 8, compared to values of 9, 10 or higher that have been measured for thermoplastics and glass. These effective mass transfer barriers, of course, depend on the stability and durability of the corresponding physical matrix and the area available for leaching.

3.9 LIST OF REFERENCE

Bates, E.R., P.V. Dean, and I. Klich. 1992. "Chemical Stabilization of Mixed Organic and Metal Compounds: EPA SITE Program Demonstration of the Silicate Technology Corporation Process." *J. Air Waste Management Association*, 42(5: 724-728. May.

Conner, J.R. 1990. *Chemical Fixation and Solidification of Hazardous Wastes.* Van Nostrand Reinhold, New York. 1990.

Conner, J.R. and F.G. Smith. 1993. "Immobilization of Low-Level Hazardous Organics Using Recycled Materials". In *Third International Symposium on Stabilization/Solidification of Hazardous, Radioactive, and Mixed Wastes,* Williamsburg, VA, November 1-5.

Diggs, I.W. 1992. "Integrating Innovative Technology into Remedial Action at a U.S. Department of Energy Facility." Presented at the *ECO WORLD '92 Conference and Exhibit,* FEMP--2248, Washington, D.C. June 14-17.

Diggs, I.W. and R. F. Gimpel, 1992. "Maws' - A Development Program and Demonstration to Reduce Vitrification Remediation Treatment Costs." Presented at the *Spectrum '92 Conference, ANS Topical Meeting on Nuclear and Hazardous Waste Management,* FEMP--2263, Boise, Idaho, August 23-27.

Dole, L.R. and D. B. Trauger. 1983. Presented at the *1983 Mid-South Conference on Hazardous Waste*, CONF-8311125--1, Memphis, Tennessee. November .

Federal Register. 1995. December 21. p.66344.

Gilliam, T.M., E. W. McDaniel, L. R. Dole, H. A. Friedman, J. A. Loflin, A. J. Mattus, I. L. Morgan, O. K. Tallent, and G. A West. 1987. *Summary Report on the Development of a Cement-Based Formula to Immobilize Hanford Facility Waste*, ORNL/TM-10141, Oak Ridge National Laboratory.

Gimpel, R.F. "Solidification and Vitrification Life-Cycle Economics Study." 1992. Presented at the *Federal Environmental Restoration '92 Conference & Exhibition*, FEMP--2249A. January 24.

Gimpel, R.F. 1992a. "Choosing Solidification or Vitrification for Low-Level Radioactive and Mixed Waste Treatment." Presented at the *85th Annual Meeting and Exhibition of the Air & Waste Management Association*, FEMP--2256, Kansas City. June 21-26.

Jacobs, M.H., C. C. Miller, and L. G. Young. 1984. *Low-Level Radwaste Engineering Economics*, EPRI NP-3577. July.

Kessler, J.H., L. R. Dole, and S. M. Robinson. 1984. "Radwaste Grouting Technologies Applicable to Hazardous Waste Management." *Proceedings of the Second Conference on Management of Municipal, Hazardous, and Coal Wastes*, DOE/METC/84-34, edited by S. Sengupta. September. P. 219-229.

Langton, C. 1995. At *EPA/ORIA Conference on Treatment Technologies for Low-Level Radioactive and Mixed Wastes.* Crystal City, VA.

Lear, P.R. and J. R. Conner. 1991. "Immobilization of Low-Level Organic Compounds in Contaminated Soil. In *Sixth Annual Conference on Hydrocarbon Contaminated Soils.* Amherst, MA , September 23-26.

Morgan, I.L. and W. D. Bostick. 1992. "Performance Testing of Grout-Based Waste Forms for the Solidification of Anion Exchange Resins." *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes, 2nd Volume*, STP 1123, ASTM, Philadelphia. pp 133-145.

Myrick, T.E., S. P. du Mont, R. E. Helms, F. J. Homan, M. V. Keigan, T. H. Monk, R. W. Morrow, T. F. Scanlan, R. M. Schultz, C. B. Scott, L. C. Williams, S. D. Van Hoesen. 1992. *The Emergency Avoidance Solidification Campaign of Liquid Low-Level Waste at Oak Ridge National Laboratory*, ORNL/TM-11536. January.

Sams, T.L., E. W. McDaniel, and T. M. Gilliam. 1986. "Immobilization of Neutralized Cladding-Removal Waste in a Cement-Based Grout." *Proceedings of the Second International Conference on Radioactive Waste Management*, Canadian Nuclear Society, 1-11. September.

Sams, T.L. and T. M. Gilliam. 1992. "Systematic Approach for the Design of Pumpable, Cement-Based Grouts for Immobilization of Hazardous Wastes." *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes, 2nd Volume*, STP 1123, ASTM, Philadelphia. pp 15-20.

Spence, R.D. and S. C. Osborne 1993. *Literature Review of Stabilization/Solidification of Volatile Organic Compounds and the Implications for Hanford Grouts*, ORNL/TM-11824. September.

Spence, R.D., W. D. Bostick, E. W. McDaniel, T. M. Gilliam, J. L. Shoemaker, O. K. Tallent, I. L. Morgan, B. S. Evans-Brown, and K. E. Dodson. 1989. "Immobilization of Technetium in Blast Furnace Slag." Presented at the *Third International Conference on the Use of Fly Ash, Silica Fume, Slag & Natural Pozzolans in Concrete in Trondheim*, Norway. June 19-24.

Spence, R.D., T. M. Gilliam, I. L. Morgan, and S. C. Osborne. 1990. *Immobilization of Volatile Organic Compounds in Commercial Cement-Based Waste Forms*, ORNL/TM-11251. December.

Spence, R.D., T. M. Gilliam, I. L. Morgan, S. C. Osborne. 1992. "Stabilization/Solidification of Wastes Containing Volatile Organic Compounds in Commercial Cementitious Waste Forms", *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes, 2nd Volume*, STP 1123, edited by T. M. Gilliam and C. C. Wiles, ASTM, Philadelphia. pp 61-72.

Spence, R.D., E. W. McDaniel, C. M. Anderson, R. O. Lokken, and G. F. Piepel. 1993. *Development of Grout Formulations for 106-AN Waste: Mixture Experiment Results and Analysis*, Vol.s 1&2, ORNL/TM-12437/V1&2, Oak Ridge National Laboratory. September.

Spence, R.D., T. M. Gilliam, and A. Bleier. 1995. "Cementitious Stabilization of Chromium, Arsenic, and Selenium in a Cooling Tower Sludge." Presented at the *88th Annual Meeting of the Air & Waste Management Association*, San Antonio, TX. June 18-23,

Trussell, S. and R. D. Spence. 1993. *Feasibility Study on the Solidification of Low-Level Radioactive Mixed Waste in the Inactive Tank System at Oak Ridge National Laboratory, Oak Ridge, Tennessee*, ORNL/ER-142. January.

Trussel, S. and R. D. Spence. 1994. "A Review of Solidification/Stabilization Interferences." *Waste Management.* 14 (6):507-519.

U.S. Environmental Protection Agency. 1990. *Superfund LDR Guide #6B*. Superfund publication: 9347.3-06BFS. Washington, DC., September.

U.S. Environmental Protection Agency. 1991. *Engineering Bulletin: Solidification/Stabilization of Inorganics and Organics (draft)*. Washington, DC., November.

U.S. Environmental Protection Agency. 1994. *Land Disposal Restrictions Phase II -- Universal Treatment Standards, and Treatment Standards for Organic Toxicity Characteristics Wastes and Newly Listed Wastes, Final Rule*. Washington, DC, August.

Waste Management Program Technical Progress Report January-June, 1987, DP-87-125-1/2, BEI-SRL-8655-1/87. 1989. Prepared for Savannah River Laboratory. March.

4. SULFUR POLYMER ENCAPSULATION

4.1 TECHNOLOGY DESCRIPTION

Interest in sulfur cement as an alternative to hydraulic cements dates back to the early 20th century. Its corrosion resistant properties made it a candidate for potential use as a construction material in the chemical industry. Product failures were encountered during the use of these early formulations, which have been attributed to internal stresses set up by changes in the crystalline structure upon cooling. Attempts to improve product durability by the addition of modifying agents were either unsuccessful or uneconomical.

Pollution abatement regulations, which require sulfur dioxide removal from combustion stack gases, have resulted in increased volumes of by-product sulfur. Sulfur is also recovered from the refining of natural gas and petroleum. By the year 2000, as much as 85-90 percent of all sulfur production will result from these cleanup operations, yielding over 30 million tons per year. In an attempt to develop new, commercially viable uses for this by-product material, the U.S. Bureau of Mines (USBM) initiated a Sulfur Utilization Program in 1972. Through their research efforts, a sulfur polymer cement (SPC) was developed employing readily available and relatively inexpensive chemical modifiers which significantly improve product durability. Elemental sulfur is reacted with 5-wt% dicyclopentadiene, which suppresses a solid phase transition responsible for the instability (Sullivan and McBee, 1976) (McBee et al, 1981). The product is manufactured commercially under license from the USBM, and is marketed under the trade name Chement 2000 (Martin Resources, Odessa, TX).

Despite its name, SPC is a thermoplastic material, not a hydraulic cement. It has a relatively low melting point (120°C) and melt viscosity (about 25 centipoise), and thus can be processed easily by a simple heated stirred mixer. Compared with hydraulic Portland cements, sulfur cement has a number of advantages. Sulfur concrete compressive and tensile strengths twice those of comparable Portland cement concretes have been attained. Full strength is reached in a matter of hours rather than several weeks. Concretes prepared using sulfur cements are extremely resistant to most acids and salts. Sulfates, for example, which are known to attack hydraulic cements have little or no effect on the integrity of sulfur cement. Because of these properties, modified sulfur cement has been proposed for use as a paving material, and for the production of tanks, pipes, and other structures where durable concretes are required.

Based on its superior properties for construction applications, a process using sulfur polymer for treating radioactive, hazardous, and mixed wastes was developed at BNL and it has been applied to a wide range of waste types including evaporator concentrates, ash, and sludges. Improved waste loadings have been achieved while still exceeding waste form performance standards specified by the NRC and EPA. A process flow diagram of the sulfur polymer microencapsulation process is shown in Figure 4.1.

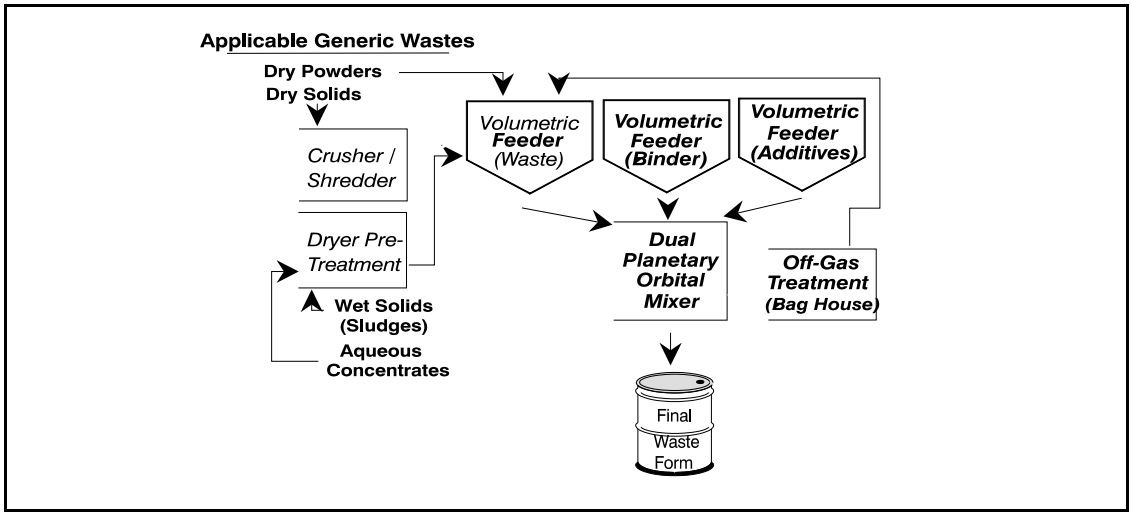

Figure 4.1. Sulfur Polymer Microencapsulation Process Flow Diagram

4.2 EXPERIENCE WITH HAZARDOUS AND MIXED WASTE STREAMS

Bench-scale process development work has been conducted at BNL using both surrogate and actual hazardous, radioactive, and mixed wastes (Kalb and Colombo, 1985) (Kalb et al, 1991) (Kalb and Adams, 1994) (Adams and Kalb, 1995). For example, mixed waste surrogates representing generic DOE incinerator ash and chloride, sulfate, and nitrate salts were prepared according to DOE waste characterization data (Bostick et al, 1993). Compounds of chromium (Cr), nickel (Ni), lead (Pb), and cadmium (Cd) were added to the baseline formulation for purposes of providing a source term for waste form leach characterization. Other surrogate waste types examined in bench-scale studies at BNL and at the Energy Research Foundation in the Netherlands include evaporator concentrates (sodium sulfate, boric acid), sludge, ion exchange resins, and off-gas scrubber blowdown solution (Kalb and Colombo, 1985) (Kalb et al, 1995) (Van Dalen and Rijpkema, 1989). Actual mixed waste incinerator ash generated at the INEL WERF was also successfully treated in BNL bench-scale studies. The actual fly ash contained extremely high concentrations of Pb (7.5 wt%) and Cd (0.2 wt%), as well as about 1.5 Bq/g (40 pCi/g) of mixed fission products (primarily ^{137}Cs) and activation products (primarily ^{57}Co and ^{125}Sb) (Kalb et al, 1991) (Kalb et al, 1991a). Potential use of SPC for mixed waste encapsulation is also currently being evaluated at ORNL (Mattus and Mattus, 1994).

4.3 TESTING STAGE

Scale-up process feasibility was investigated using surrogate waste materials by researchers at INEL (Darnell et al, 1992) (Darnell, 1993). Nonhazardous coal-fired fly ash and simulated metal debris waste were used in their testing. BNL is planning to conduct bench- and scale-up testing

in FY 1996 on actual hazardous wastes generated in the production of petroleum. Currently, SEG is utilizing sulfur polymer encapsulation at production-scale for treatment of their mixed waste incinerator fly ash, which is similar in composition to WERF ash.

Bench-scale development has been accomplished using a variety of mixers including simple heated vessels with a single stirring blade and double planetary orbital mixers. The latter uses two independently rotating paddles to provide stirring action while the blade assembly rotates around the vessel to assure complete mixing. Scale-up testing has been conducted using several types of paddle mixers including solid core and heated hollow core paddles. SEG has adapted a heated high shear mixer for processing sulfur polymer. Each processing technology has advantages and disadvantages and continuing scale-up testing is being conducted to determine optimal processing methods.

4.4 DEGREE OF TECHNICAL DEVELOPMENT

Process development studies conducted to date have demonstrated improved waste loading efficiencies (more waste encapsulated per drum) using sulfur polymer encapsulation compared with conventional hydraulic cement processes (Kalb et al, 1990). For example, a maximum of only 16-wt% INEL WERF incinerator ash was successfully solidified in conventional Portland cement, due to chemical interferences associated with the high concentrations of chlorides, sodium, zinc and lead. Monolithic waste forms containing as much as 55-wt% incinerator fly ash have been formulated with sulfur polymer, and as much as 43-wt% WERF ash was encapsulated in sulfur polymer while still maintaining the ability to pass regulatory performance criteria. Maximum waste loadings for sulfur polymer waste forms are compared with hydraulic cement on a mass basis (Figure 4.2) and volume basis (Figure 4.3).

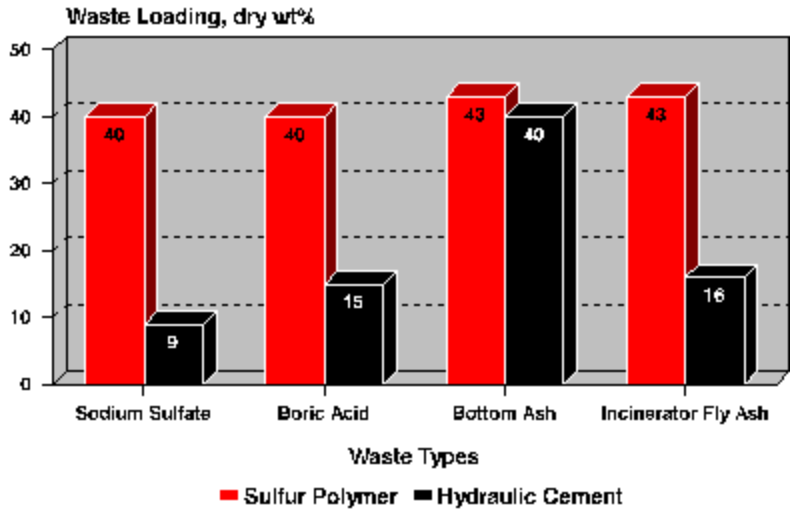

Figure 4.2. Maximum waste loadings for sulfur polymer and hydraulic cement final waste forms on a mass basis.

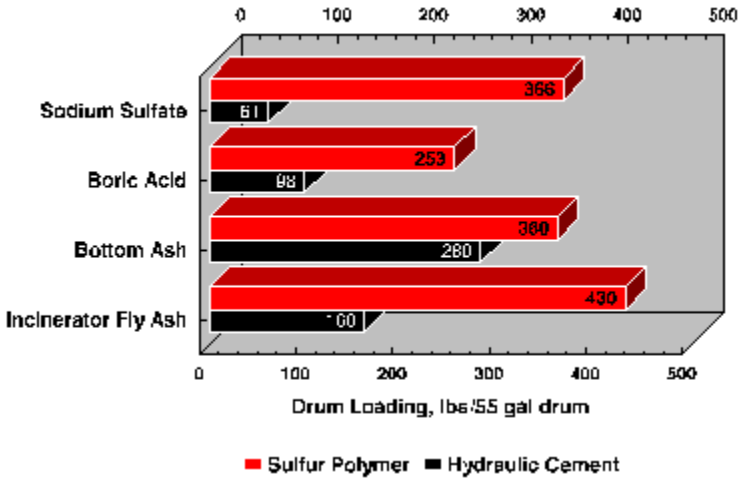

Figure 4.3. Maximum waste loadings for sulfur polymer and hydraulic cement waste forms on a volume basis.

Sulfur polymer waste forms have been subjected to numerous performance tests to determine durability and leaching properties under anticipated storage and disposal conditions. Testing was conducted at BNL in accordance with NRC guidance in support of 10 CFR 61 for commercially generated low-level radioactive waste (U.S. Nuclear Regulatory Commission, 1991). Final waste form performance testing included compressive strength, water immersion, thermal cycling, radiation stability, biostability, and radionuclide leaching. Typical performance data for sulfur polymer waste forms are provided in Tables 4.1 and 4.2. Data indicate that for each property tested, results far exceed minimum test criteria recommended by the NRC.

Table 4.1. Typical final waste form performance data for sulfur polymer waste forms

Test Protocol	Results[a,b]
Compressive Strength	4,250 psi
Water Immersion	3,870 psi
Thermal Cycling	3,830 psi
Biodegradation	2,620 psi
Radiation Stability	1,950 psi

a) Data for waste forms containing 30-wt% ash. Biodegradation and Radiation Stability testing conducted on neat sulfur polymer specimens (no waste).
b) Minimum compressive strength recommended by NRC is 60 psi.

Table 4.2. Average Leachability Index Values for Modified Sulfur Cement Waste Forms Containing Incinerator Ash[a]

Ash Waste Loading, wt%	Co-60 Leachability Index	Cs-137 Leachability Index
20	14	11.2
40	14.6	11.1

a) Conducted as per procedures outlined in ANS 16.1 Standard Leach Test Method. Minimum Leach Index recommended by NRC is 6.0.

Leachability testing of characteristic toxic constituents under EPA TCLP have been conducted. Studies have shown that sulfur polymer test specimens are physically abraded by the 18-hour end-over-end tumbling required by the TCLP method, and thus suffer reduction in their ability to microencapsulate contaminants. TCLP results are dependent on the concentration of toxic metals in the waste and the chemical and physical characteristics of the waste itself (e.g., solubility, pH, particle size). However, BNL has been successful in using additives to enhance the ability of sulfur polymer waste forms in retaining toxic constituents. For example, incinerator ash containing 7.5-wt% lead and 0.2-wt% cadmium encapsulated in sulfur polymer with additives resulted in leachable levels of 1.5 ppm Pb and 0.2 ppm Cd, below existing allowable concentrations of 5.0 and 1.0 ppm, respectively.

4.5. DEGREE OF COMMERCIALIZATION

Scientific Ecology Group and BNL are working together under a Cooperative Research and Development Agreement (CRADA) to commercialize the sulfur polymer encapsulation technology. SEG has begun scale-up and limited production capacity for treatment of mixed waste incinerator ash. Under a pending process patent, BNL has also issued licensing agreements for the technology. As with other emerging treatment technologies, commercial availability is dependent on demonstrating the site- and waste-specific technical and economic feasibility.

4.6 COST CONSIDERATION

Detailed life-cycle cost data for sulfur polymer encapsulation are not available. The current cost of commercially available sulfur polymer binder is relatively inexpensive ($0.12/lb for quantities of several tons). Larger quantities and the availability of low-cost by-product sulfur are expected to bring the cost even lower. Capital costs for mixing equipment are equivalent

or lower than those of competing technologies (e.g.,polymers, vitrification). From a processing perspective, simple mixing equipment and relatively low process temperatures are factors that minimize operating and maintenance costs, thus reducing overall system costs.

A key consideration in determining processing costs is the loading efficiency; i.e., how much waste can be incorporated per unit volume processed. For "problematic" waste such as those containing high metals and chloride salt content, SPC can successfully incorporate significantly higher waste loadings than conventional hydraulic cement processes when it is necessary to meet NRC (Treatment Level C) requirements. For example, for INEL WERF ash containing high chlorides, zinc and lead concentrations, SPC can solidify up to 43-wt% ash compared with a maximum of 16 wt% for conventional Portland cement processes. The improvement in waste loading of > 2.5 times, greatly reduces the number of drums for processing, storage, transportation, and disposal where the more stringent NRC requirements must be met.

Sulfur polymer encapsulation process temperatures are 130 - 140°C. At these temperatures, moisture or other volatile compounds contained in the waste are driven off. Small quantities of moisture (e.g., < 5 wt%) can be effectively volatilized during the heating/mixing cycle. For larger quantities of moisture or volatile, pretreating the waste to dryness would provide a more efficient means of removal and would improve overall processing efficiency. Thus, for waste streams containing significant quantities of moisture or volatile, (e.g., aqueous concentrates, sludges) a suitable dryer system is required. Unlike polyethylene extrusion processing, minimum particle size constraints are not problematic for SPC processing. Various dryer technologies including, spray dryers, vacuum dryers, rotary drum dryers, and fluidized bed dryers could be used. Additional capital, operating, and maintenance costs associated with this additional step must be considered in the overall life-cycle cost analysis. For some waste streams containing high concentrations of contaminants and/or expansive salts, additives may be required to enhance final waste form performance, but these are not expected to significantly impact overall costs. Wastes containing ion exchange resins would require pretreatment prior to encapsulation with SPC to reduce the tendency of the resins to swell on contact with saturated conditions.

4.7 DATA GAPS

Limited R & D studies have been completed to date investigating the effectiveness of the SPC encapsulation process for specific types of waste and specific waste streams. Waste- and site-specific treatability studies to confirm process applicability for additional waste streams are required prior to implementation of any emerging technology such as SPC encapsulation. Such studies investigate specific waste-binder compatibility, processing parameters (e.g., waste loadings), and key final waste form performance issues (e.g., leachability). Since EPA is proposing much stricter release limits for toxic metals, additional work is recommended to evaluate the ability of SPC to meet the new standards. In some cases, additional process modifications may be required. Since SPC is a relatively new engineering material, additional

testing to examine long-term durability under anticipated disposal conditions is needed. For example, current standard test methods for biodegradation testing (ASTM G-21, G-22) were not designed for testing sulfur matrices. These tests should be appropriately modified to include sulfur attacking microbes and conducted to confirm product durability under disposal conditions. Optimization of full-scale processing design and equipment is needed to "fine-tune" the technology. Examination of SPC for macroencapsulation of debris is an another area of potential use for this technology that has not been adequately explored.

4.8 ASSESSMENT

Sulfur polymer encapsulation is a thermoplastic process amenable to both for microencapsulation and macroencapsulation of hazardous, radioactive, and mixed wastes. It hardens and cures to full strength rapidly and has significantly higher strength than conventional cement materials. It is extremely durable and resistant to attack from acidic and corrosive environments. Unlike hydraulic cement processes, it does not rely on a chemical reaction for setting and curing. Thus it is not susceptible to interference between compounds present in the waste and the solidification mechanism. Slight changes in waste chemistry over time do not adversely affect this process. SPC is less sensitive to minimum particle size constraints than other thermoplastic processes such as polyethylene. To date, it has been demonstrated to be effective for several types of waste including incinerator fly ash, bottom ash and combined ash, sludges, and blowdown solutions. A major advantage is its ability to successfully handle high-waste loadings while still meeting or exceeding regulatory and disposal site acceptance criteria. Due to low material costs and high-waste loading efficiency, the process is expected to be economically attractive with certain waste types.

One disadvantage of SPC encapsulation (especially for waste containing a high moisture content) is the need to pretreat the waste to dryness. If the waste stream contains a significant percentage of moisture (>5 wt%) and is amenable to conventional hydraulic cement grout processing (i.e., does not contain significant concentrations of compounds known to interfere with the hydration process), SPC may not prove to be an advantage. SPC may be incompatible with some waste streams. For example, in the presence of waste containing high concentrations of nitrate (oxidizer), and carbon the mixture may become unstable and is not recommended. For untreated ion exchange resins encapsulated in SPC, rapid degradation of the waste form has been observed due to expansion of the resin beads. This problem was reportedly (Spence, 1995) overcome in Europe. Pretreatment of the resins may provide improved processing for this waste stream. Literature indicates that SPC is incompatible with high alkalinity and phenols (Spence, 1995). Strong caustic waste such as Hanford tank waste would be incompatible. It is unclear whether waste water treatment sludges would present a problem. Also, such encapsulation techniques require casting tiny (<3/8 inch) sample material to pass TCLP, because they do not interact directly with the waste to stabilize contaminants (Spence, 1995).

Most of the testing on SPC has been conducted with various LLMW and surrogate incinerator ashes, containing high chloride and sulfate levels (Anderson, 1994). SPC is effective in solidifying and retaining chloride, sulfate and nitrate salts and boric acid; however, the use of SPC with highly concentrated nitrates is not recommended (Darnell, ca. 1992 and 1992a). SPC is not compatible with highly alkaline waste. Because of its natural high strength, in the range of 4000 psi, and its water resistance, SPC is especially effective in meeting the highest NRC regulatory level of 500 psi, as well as in meeting all NRC-required durability tests - freeze/thaw, biodegradation, thermal cycling, immersion, and irradiation.

Little information is available on the cost of SPC treatment. The basic material costs about $0.12/lb, or $240.00 per ton. This is 3 to 4 times the cost of Portland cement, and about 10 times the cost of Type C flyash. Sodium sulfide, used as an additive for metal stabilization, costs about $700.00 per ton. Based on the loadings given for incinerator ash, SPC material cost would be about $100/yd^3 of ash treated (density of ash = 0.23 g/cm^3) or about $445/ton of ash treated. Where NRC Classes B and C LLW requirements (strength and durability) must be met on waste with high salt content, the high-waste loadings relative to cement grout make SPC a good choice on a total life-cycle cost basis. However, to meet only the present LLMW disposal criteria at Envirocare or the probable future RCRA LDR requirements, SPC stabilization would likely be uncompetitive.

4.9 LIST OF REFERENCES

Adams, J.W. and P.D. Kalb. 1995. "Thermoplastic Stabilization of a Chloride, Sulfate, and Nitrate Salts Mixed Waste Surrogate." In: Proceedings of the *I&EC Special Symposium, Emerging Technologies for Hazardous Wastes*, American Chemical Society, Atlanta, GA. September 19- 21.

Anderson, W.C., ed. 1994. *Innovative Site Remediation Technology: Solidification/Stabilization*. American Academy of Environmental Engineers. Annapolis, MD.

Bostick, W.D. et al. 1993. "Surrogate Formulations for Thermal Treatment of Low-Level Mixed Waste: Part II: Selected Mixed Waste Treatment Project Waste Streams." *DOE/MWIP-16, Rev 0.3, Martin Marietta Energy Systems, Inc.* September.

Darnell, G.R. ca. 1992. "A New Stabilization Agent for Mixed and Low-level Radioactive Waste." Idaho National Engineering Laboratory, Idaho Falls, ID.

Darnell, G.R. ca. 1992a. " Sulfur Polymer Cement, A Solidification and Stabilization Agent for Hazardous and Radioactive Wastes." Idaho National Engineering Laboratory, Idaho Falls, ID.

Darnell, G.R., W.C. Aldrich, and J.A. Logan. 1992. *Full-Scale Tests of Sulfur Polymer Cement and Non-Radioactive Waste in Heated and Unheated Prototypical Containers*, EGG-WM-10109. Idaho National Engineering Laboratory, Idaho Falls, ID. February.

Darnell, G.R. 1993. *Progress Report: Full-Scale Tests with Sulfur Polymer Cement," GRD-73-93*. Idaho National Engineering Laboratory, Idaho Falls, ID. August.

Kalb, P.D., and P. Colombo. 1985. *Modified Sulfur Cement Solidification of Low-Level Wastes*, BNL-51923. Brookhaven National Laboratory, Upton, NY. October.

Kalb, P.D., J. Heiser, and P. Colombo. 1990. "Comparison of Modified Sulfur Cement and Hydraulic Cement for Encapsulation of Radioactive and Mixed Wastes." In: Proceedings of the *12th Annual DOE Low-Level Waste Management Conference*. Chicago, IL. August 28-29.

Kalb, P.D., J.H. Heiser, and P. Colombo. 1991. "Modified Sulfur Cement Encapsulation of Mixed Waste Contaminated Incinerator Fly Ash." *Waste Management* 11(3):147-153. Pergammon Press, New York.

Kalb, P.D., J. Heiser, R. Pietrzak, and P. Colombo. 1991a. "Durability of Incinerator Ash Waste Encapsulated in Modified Sulfur Cement." In: Proceedings of the *1991 Incineration Conference.* Knoxville, TN. May 13-17.

Kalb, P.D., and J.W. Adams. 1994. "Mixed Waste Treatability Using Polyethylene and Sulfur Polymer Cement Encapsulation Technologies." In: Proceedings from *Spectrum '94*, Atlanta, GA. August 14 -18.

Kalb, P.D., J.W. Adams, M.L. Meyer, and H.H. Burns. 1995. "Thermoplastic Encapsulation Treatability Study for a Mixed Waste Incinerator Off-Gas Scrubbing Solution." *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes,* ASTM STP1240, T. M. Gilliam, and C.C. Wiles, eds. American Society for Testing and Materials, Philadelphia, PA.

Mattus, C.H., and A.J. Mattus. 1994. *Evaluation of Sulfur Polymer Cement as a Waste Form for the Immobilization of Low-Level Radioactive or Mixed Waste, ORNL/TM-12657*. Martin Marietta Energy Systems, Oak Ridge, TN. March.

McBee, W.C., T.A. Sullivan and B.W. Jong. 1981. *Modified Sulfur Cements for Use in Concretes, Flexible Pavings, Coatings and Grouts*, RI-8545. Bureau of Mines, U.S. Dept. of the Interior, Washington, DC.

Spence, R.D. 1995. Private Communication.

Sullivan, T.A., and W.C. McBee. 1976. *Development and Testing of Superior Sulfur Concretes*, RI-8160. Bureau of Mines, U.S. Dept. of the Interior, Washington, DC.

U.S. Nuclear Regulatory Commission. 1991. *Technical Position on Waste Form, Revision 1," Final Waste Classification and Waste Form Technical Position Papers*. U.S. NRC, Washington, DC. January.

Van Dalen, A., and J.E. Rijpkema. 1989. "Modified Sulphur Cement: A Low Porosity Encapsulation Material for Low, Medium, and Alpha Waste" *Nuclear Science and Technology*, EUR 12303EN. Commission of the European Communities, Luxembourg.

5. POLYMER ENCAPSULATION

5.1 TECHNOLOGY DESCRIPTION

The U.S. Department of Energy has supported over the past 12 years the development of polymer encapsulation processes for treatment of low-level radioactive, hazardous, and mixed wastes. Tests completed to date using both surrogate and actual waste indicate that polymer microencapsulation is a viable treatment option for variety of mixed waste streams including evaporator concentrate salts, sludges, incinerator ash, ion exchange resins, blowdown solutions, and molten salt oxidation residuals. Furthermore, polymers have been successfully used to macroencapsulate radioactive lead and debris wastes. This discussion emphasizes polymer microencapsulation applications.

Mixed waste stabilization using polymers is adopted from existing processes widely used in the polymer industry. Although the application of polymers to mixed waste differs from private sector applications in the areas of product acceptance criteria and operating conditions, the two applications are very similar. Two classes of polymers, thermosetting and thermoplastic, have been applied to waste encapsulation.

Thermoplastic polymers, such as polyethylene, can be heated above their melting temperature (110°C), mixed with powdered waste, and poured into a disposal container, where solidification occurs as the melt cools. No interaction occurs between the waste and the polymer. Most of the emphasis for polymer encapsulation of mixed waste within the DOE complex is on thermoplastic extrusion using low-density polyethylene.

Waste requiring stabilization to meet TCLP standards is dried and then encapsulated in polyethylene using a commercially available compounding extruder (Rauwendaal) (White) (Mack 1990). Electrical resistance heaters in the extruder barrel and friction introduced by the rotation of the screw melt the polyethylene pellets. Dried waste is fed into the extruder using a down stream side feeder, at which point the waste encounters molten polyethylene. Kneading blocks and/or pin mixers downstream of the waste feed port mix the waste with the molten polyethylene. A vent port can be used to remove excess moisture and reduce the porosity of the final waste form. The molten mixture is output into the final disposal container, where solidification occurs as the mixture cools.

Thermoset polymers, such as epoxies, are formed by the chemical reaction of a liquid monomer and a curing agent. Powdered waste is mixed with two components. As the liquid monomer and curing agent react, solidification occurs. A major disadvantage to using this process for stabilizing waste is that waste constituents can react with the monomer and curing agent, thus interfering with solidification. Although thermoset polymers are a good option for macroencapsulation of debris and radioactive lead wastes, the potential for interference of the solidification reaction makes thermoset polymers a less desirable solution than thermoplastic

extrusion for particulate waste such as salts and sludges. For this reason, most of the emphasis for polymer encapsulation of mixed waste within the DOE complex has been on thermoplastic extrusion using low density polyethylene.

5.2 EXPERIENCE WITH HAZARDOUS AND MIXED WASTE STREAMS

Although polymer macroencapsulation processes are permitted for treatment of hazardous debris, lead, and medical waste, no polymer microencapsulation processes are currently permitted for treatment of mixed waste requiring stabilization to meet TCLP standards. Recently, however, extensive testing has been completed which indicates that the process is a viable alternative to conventional stabilization processes for a variety of mixed waste.

Extensive testing of both actual and surrogate mixed waste has been completed at several DOE facilities. A list of the waste streams tested, volume of waste treated during the testing process, toxic constituent treated, and the treatment standard met is provided in Tables 5.1 and 5.2.

5.3 TESTING STAGE

Bench scale testing using actual low-level mixed waste has been completed on waste streams that required stabilization to pass the EPA TCLP. Waste forms produced during these tests met the applicable characteristic or universal treatment standards. Waste loadings producing compliant waste forms varies from 20-wt% to 55-wt% (Armentrout, 1996) (Faucette and Getty, 1995) (Faucette, 1995) (Kalb et al, 1993) (Lageraaen et al, in press).

Bench scale testing using surrogate waste has also been conducted at several facilities. Polyethylene extrusion tests for microencapsulation of particulate waste have been conducted at Oak Ridge National Laboratory, Brookhaven National Laboratory, and Rocky Flats Environmental Technology Site. Polymer microencapsulation tests using thermosetting polymers have also been conducted at several DOE facilities, universities, and private sector companies (Powell and Mahalingham, 1992) (Subramanian and Mahalingham, 1979) (Tyson and Schwendiman, 1995). If properly controlled, thermosetting polymers can have wide application to mixed waste treatment, including solidification of wet waste, stabilization of a wide variety of contaminants including organics, and increased radioactive stability. A major disadvantage is the relatively high cost of the resins.

Pilot scale testing using surrogate waste has also been conducted (Kalb and Lageraaen, 1994) (Logsdon et al, 1994). Although the cold pilot scale tests verified scale up feasibility, the surrogate materials used were not spiked with toxic constituents, so TCLP testing was not performed on the final waste forms.

Table 5.1

Rocky Flats Polymer Encapsulation Accomplishments as of May 19, 1995
Nonradioactive and Surrogate Wastes Treated

Waste Streams	Resin Used, Volume Treated	Toxic Constituent Treated	Treatment Standard Met
Nitrate salts from aqueous waste treatment	Low density polyethylene, 470 gallons (2)	D006, D007, D008, D011, F001, F002, F003, F005, F006, F007, F009, F039	UTS (1)
Incinerator ash	Low density polyethylene, 30 gallons	D006, D007, D008, D011, F001, F002, F003, F005, F006, F007, F009, F039	UTS (1)
Debris (IDC 330, Mixed IDCs)	Low density polyethylene, 135 gallons	D006, D007, D008, D011, F001, F002, F003, F005, F006, F007, F009, F039	MACRO
Debris contaminated with beryllium fines	Epoxy resin, 175 gallons	Beryllium	MACRO
DETOX solution	Low density polyethylene, 5 gallons	F006	UTS (1)
Leaded gloved (0.050 inch lead thickness)	Low density polyethylene, 5 gallons	F008	MACRO
C-018 hydroxide precipitation sludge (WRAP2A from the Hanford site)	Low density polyethylene, 1.5 gallons	D006, D007, D008, D009, Copper	UTS (1)
Ammonium sulfate (WRAP2A from the Hanford site)	Low density polyethylene, 1.5 gallons	D006, D007, D008, D009, Copper	UTS (1)
Basins 3 and 4 sludge (WRAP2A from the Hanford site)	Low density polyethylene, 1.5 gallons	D006, D007, D008, D009, Copper	UTS (1)
Crystalline solids (WRAP2A from the Hanford site)	Low density polyethylene, 1.5 gallons	D006, D007, D008, D009, Copper	UTS (1)
Hydroxide precipitation bypass sludge from aqueous waste treatment	Low density polyethylene, 5 gallons	D006, D007, D008, D011, F001, F002, F003, F005, F006, F007, F009, F039	UTS (1)
Ground glass	Low density polyethylene, 1 gallon	D008, D009, F001, F002, F003, F005	MACRO
Lead metal	Epoxy resin, 10 gallons	D008	MACRO
Lead metal	Low density polyethylene, 1 gallon	D008	MACRO

Table 5.1 *(Continued)*
Rocky Flats Polymer Encapsulation Accomplishments as of May 19, 1995
Nonradioactive and Surrogate Wastes Treated

Waste Streams	Resin Used, Volume Treated	Toxic Constituent Treated	Treatment Standard Met
Analytical Lab solutions	Low density polyethylene, 5 gallons	D006, D007, D008, D011, F001, F002, F003, F005, F006, F007, F009, F039	UTS (1)
Sodium chloride salts	Low density polyethylene, 5 gallons	D006, D007, D008, D011, F001, F002, F003, F005, F006, F007, F009, F039	UTS (1)
Molten salt oxidation salts (LLNL)	Low density polyethylene, 2 gallons	D006, D007, D008, D011, F001, F002, F003, F005, F006, F007, F009, F039	UTS (1)
Crucibles	Epoxy resin, 8 gallons	F001, F002, F003, F005	MACRO
Light metal	Low density polyethylene, 5 gallons	F001, F002, F003, F005, D007	MACRO

(1) Universal Treatment Standard
(2) 300 gallons treated at offsite vendor's.

Table 5.2

Rocky Flats Polymer Encapsulation Accomplishments as of May 19, 1995

Radioactive Waste Treated

Waste Streams	Resin Used, Volume Treated	Toxic Constituent Treated	Treatment Standard Met
Debris (IDC 330, Dry burnables)	Low density polyethylene, 135 gallons	D006, D007, D008, D011, F001, F002, F003, F005, F006, F007, F009, F039	MACRO
Nitrate salts from aqueous waste treatment	Low density polyethylene, 10 gallons	D006, D007, D008, D011, F001, F002, F003, F005, F006, F007, F009, F039	UTS (1)
Clarifier bottoms (soil from bench-scale washing facilities)	Low density polyethylene, 1 gallon	D006, D007, D008, D011, F001, F002, F003, F005, F006, F007, F009, F039	UTS (1)
Incinerator ash (oils, paper, coveralls, etc.)	Low density polyethylene, 3 gallons	D006, D007, D008, D011, F001, F002, F003, F005, F006, F007, F009, F039	UTS (1)
Debris (IDC 870) & lead (321)	Epoxy, 165 gallons	D008, F001, F002, F025	MACRO
Lead	Low density polyethylene, 10 gallons	D008	MACRO
Sludge	Low density polyethylene, 1 gallon	F006, F039	UTS (1)

(1) Universal Treatment Standard

Pilot scale testing of large quantities of actual low mixed salts, sludges, and ash is in progress at the Rocky Flats Environmental Technology Site. This work is being conducted under a Research, Development, and Demonstration (RD&D) permit. Pending successful completion of these tests, the system used for the RD&D tests will be permitted for production operations.

5.4 DEGREE OF TECHNICAL DEVELOPMENT

The treatability studies completed indicate that waste loadings of 30 to 80-wt% are possible with polyethylene extrusion while still producing an LDR compliant waste form. Waste loadings of 50-wt% are typical for the majority of mixed waste tested. Depending on the physical characteristics of the waste stream and the maximum achievable waste loading, volume expansion factors vary from -0.5 to +l.5.

Because polyethylene is resistant to most chemicals, polyethylene extrusion is a good option for mixed wastes that are difficult to stabilize using other methods, such as cementation or vitrification. Sodium chloride salts, for example, are not soluble in glass and severely inhibit the cement hydration reaction. Since there is no reaction between the sodium chloride and the polyethylene, high-waste loading of sodium chloride is achievable in polyethylene. Other salts that are difficult to stabilize in cement or glass, but that are compatible with polyethylene extrusion, include sodium sulfate, ammonium sulfate, and sodium nitrate.

Although the polyethylene extrusion process is resistant to most chemical constituents in the waste stream, it is sensitive to moisture content. Wastes containing more than 3 to 10 percent moisture require an additional drying step prior to extrusion. Size reduction of agglomerations in the waste may also be required to meet tolerance requirements in the extruder.

Through its wide usage, the durability of polyethylene has been clearly demonstrated. Particularly significant is the fact that polyethylene does not degrade in municipal landfills. Durability testing at BNL included the complete suite of tests recommended by the NRC for commercial low-level radioactive waste in support of 10 CFR 61 (Kalb et al, 1993). These include compressive strength, water immersion, thermal cycling, biodegradation, radiation stability and radionuclide leaching.

Also of particular concern to radioactive waste forms is the potential for degradation and hydrogen gas generation as a result of radiation-induced reactions. A literature review concluded that radiolysis effects for low-level radioactive (<100 nCi/gram) waste encapsulated in polyethylene are insignificant (Faucette et al, 1992). In terms of the mechanical properties, low level waste does not have a sufficiently high specific activity to deliver the 100 megarads required to degrade the polyethylene. Testing with surrogate waste forms exposed to gamma radiation doses up to 10^8 rad demonstrated increased compressive strength and lower leachability (Kalb and Fuhrmann, 1992). Hydrogen gas generation is insignificant with these waste types.

Another area of concern is the issue of the thermal stability of sodium nitrate waste encapsulated in polyethylene. Encapsulating sodium nitrate, an oxidizer, with polyethylene, an organic, could potentially result in a chemically reactive mixture. Such a mixture of fuel and oxidizer could burn if exposed to sufficient thermal energy, and consequently release additional energy and gases.

Experiments conducted to evaluate the issue of the thermal stability of the sodium nitrate/polyethylene waste form conclusively demonstrated that no exothermic reaction hazards exist. A wide variety of tests have been conducted, including calorimetry, ignition, time-to-explosion, thermal decomposition, gas evolution, detonation, and thermal runaway. None of the experimental results indicate any tendency to detonate or explode, even under wide variations in the waste-to-polyethylene ratio (Block-Bolten et al, 1991).

The most significant waste form performance criterion for mixed waste is the Toxicity Characteristic Leaching Procedure (TCLP). Studies conducted using both surrogate and actual wastes have demonstrated both successes and failures. Polyethylene may have improved TCLP performance for chromium in the hexavalent state compared to cementation, where reduction to trivalent chromium is usually necessary as a pretreatment. Cemented waste forms also require more careful control of pH for amphoteric metals, compared to polyethylene. Metals that are not amphoteric, such as cadmium, typically leach less from cemented waste than from polyethylene encapsulated waste. The leach performance from both technologies can be enhanced through the use of additives to reduce metals solubility under TCLP leaching conditions.

5.5 DEGREE OF COMMERCIAL DEVELOPMENT

No polyethylene extrusion processes are currently permitted for mixed waste treatment. Extrusion technology is available from the private sector; however, no private sector vendors are currently advertising mixed waste treatment capability using polyethylene microencapsulation. This situation may change shortly as DOE works with private sector treatment vendors to commercialize this process.

5.6 COST CONSIDERATION

Materials and equipment costs for polyethylene encapsulation are higher than materials and equipment costs for cementation processes. Equipment costs for a fully integrated extrusion system (extruder, control system, feeders) are approximately $300,000. If a dryer is required, total equipment costs would be significantly higher.

Virgin polyethylene costs approximately $0.30/lb and post industrial recycle material costs up to $0.19/lb (including transportation costs). The post consumer market for low density polyethylene is still relatively undeveloped. Rocky Flats has been collecting donated low density

polyethylene (LDPE) from the public and employees, and has recently identified several potential onsite sources of waste polyethylene (Beattie et al, 1996). Even if sufficient material can be collected through these methods to meet site needs, overall material costs are likely to be higher than cement because of collection and processing costs. Also, such sources are notoriously unreliable, and may not be available at all locations. A private study of encapsulation of hazardous waste incinerator ash to meet RCRA LDR standards (Chemical Waste Management, 1991) in 1991 found that clean, chipped, recycled high density polyethylene (HDPE) prices ranged from $0.21 (mixed color) to $0.28 (natural). The study found that, in a cost comparison between HDPE encapsulation and cement stabilization at large scale (20 tons/hr), polyethylene would cost $95 - $112 per ton of ash treated, vs $50 - $60 for cement. These numbers would likely be much the same, on a relative basis, today and for LDPE as well as HDPE.

Materials and equipment costs for treating radioactive waste, especially waste contaminated with transuranics, are relatively insignificant compared to operations costs, including storage, shipping, and disposal. A detailed cost estimate developed by Rocky Flats as part of a compliance document (U.S. DOE, 1992) calculated high unit costs of $18,744/m^3 for polymer microencapsulation compared to $65,707/m^3 for cementation. These costs include facility, pre-operations, operations, storage, shipping, disposal, and process development. The primary reason for the reduced polymer encapsulation costs compared to cementation is because the higher waste loading achievable with polymer encapsulation results in reduced final waste form volume. This reduces the costs of storage, shipping, and disposal.

5.7 DATA GAPS

Favorable results have been achieved on bench-scale treatability studies and limited cold pilot-scale testing. However, no pilot-scale tests have been conducted to date on polyethylene microencapsulation of actual low-level mixed waste. This is critical to demonstrating the process' performance. Extended hot pilot scale tests are planned at Rocky Flats in mid-1996 to meet this need.

5.8 ASSESSMENT

Although not as widely used as cementation, polymer encapsulation offers several advantages, including increased waste loadings, increased waste form durability, and insensitivity to variations in waste stream chemistry. Polymer encapsulation is a simple, low temperature process that is relatively easy to permit and implement. Furthermore, waste plastics can be used as the encapsulating medium. This has cost benefits and provides an opportunity to put to beneficial use material that might otherwise be landfilled.

A comprehensive process evaluation conducted by Rocky Flats concluded that a lack of definitive waste characterization requires that both cementation and polymer microencapsulation

be pursued for immobilization of the low level mixed waste inventory at Rocky Flats (U.S. DOE, 1993). The two processes complement each other with respect to treating certain waste forms. Polymer encapsulation is a good solution for waste that is difficult to cement, such as soluble salts. Heavy metals that are difficult to stabilize by direct cementation, such as chromium, can be effectively immobilized in polyethylene. Conversely, cementation is more effective than polyethylene extrusion at immobilizing other heavy metals, such as cadmium. Also, wet sludges can be stabilized directly in cement, whereas a drying step is required prior to polyethylene extrusion.

Polyethylene extrusion is not a feasible option for high specific activity waste due to the potential for radiolysis effects. This is not an issue, however, for low-level waste forms.

5.9 LIST OF REFERENCES

Armentrout, D.M. 1996. *Treatability Study: Polymer Microencapsulation of Low-Level Mixed Bypass Sludge*, Rocky Flats Environmental Technology Site Report No. TI-96-003.

Beatty, J.R., J. Navratil, and A. Faucette. 1996. "Use of Consumer Waste Plastics for Encapsulation of Mixed Waste." *Waste Management '96.* Tucson, AZ. March.

Block-Bolten, A., D. Olson, P. Persson, and F. Sandstrom. 1991. *Polyethylene Waste Form Evaluation of Explosion and Fire Hazards, Final report FR-91-03.* Center for Explosives Technology Research, Socorro, NM, 87801, New Mexico Inst. Of Mining and Technology.

Chemical Waste Management Technical Note 91-218. 1991. CWM Geneva research Center, Geneva, IL. December 30.

Faucette, A.M., B. Logsdon, and J. Oldham. 1992. "Thermal and Radioactive Stability of Polyethylene Encapsulation Nitrate Salt Waste." *Waste Management '92.* Tucson, AZ. March.

Faucette, A.M. et al. 1992. "Thermal and Radioactive Stability of Polyethylene Encapsulated Nitrate Salt Waste." *Waste Management 92.* Tucson, AZ. March.

Faucette, A.M. and R.H. Getty. 1995. "Stabilization of High Salt Wastes by Polymer Extrusion." In: Proceedings of the *Emerging Technologies in Hazardous Waste Management VII*. American Chemical Society, Atlanta, Georgia. September 17-20.

Faucette, A.M. 1995. *Polymer Encapsulation of Clarifier Bottoms*., EG&G Rocky Flats, Internal Report. February 24.

Kalb, P.D. and P.R. Lageraaen. 1994. *Polyethylene Encapsulation Full-Scale Technology Demonstration, Final Report, BNL-52478.* Brookhaven National Laboratory, Upton, NY. October.

Kalb, P.D., J. Heiser and P. Colombo. 1993. "Long Term Durability of Polyethylene for Encapsulation of Low-Level Radioactive, Hazardous and Mixed Wastes." *Emerging Technologies in Hazardous Waste Management*, D.W. Tedder and F.G Pohland, eds, Chap. 22. American Chemical Society, No. 518. April.

Kalb, P.D., J.W. Adams, H.H. Burns, and M. Meyer. 1993. "Thermoplastic Encapsulation Treatability Study for a Mixed waste Incinerator Off-Gas Scrubbing Solution." At: *Third ASTM International Symposium on Stabilization/Solidification of Hazardous, Radioactive and Mixed Wastes*. Williamsburg, VA. November 1-5.

Lageraaen, P.R., B.R, Patel, P.D. Kalb and J.W. Adams. In-press. "Treatability Studies for Polyethylene Encapsulation of INEL Low-Level Mixed Wastes." *Brookhaven National Laboratory.* Upton, NY.

Logsdon, P.R., A. Faucette, J. Oldham, and R. Jantzen. 1994. "Pilot-Scale Extrusion Testing of Surrogate Nitrate Salt Waste." *Topical Report, TD-94-035.* Rocky Flats Environmental Technology Site, Golden, Co. September.

Powell, M.R. and R. Mahalingham. 1992. "Continuous Solidification/Stabilization Processing of Hazardous Waste Through Polymeric Microencapsulation." *J. Ind. Eng. Chem. Res. V. 31.*

Subramanian, R.V. and R. Mahalingham. 1979. "Immobilization of Hazardous Residues by Polyester Encapsulation." *Toxic and Hazardous Waste Disposal*, R.B. Pojasek, ed., Chap. 14. Ann Arbor Science.

Tyson, D.R. and G.L. Schwendiman. 1995. "Treatability Studies Involving Epoxy Solidification for Various Mixed Wastes at the Idaho National Engineering Laboratory." *Mixed Waste Proc. Of the Third Biennial Symp.* ASME, Baltimore, MD. August 7-10.

U.S. DOE. 1992. *Comprehensive Treatment and Management Plan.* Rocky Flats Plant, Golden, CO. March.

U.S. DOE. 1993. *Technology Evaluation Framework.* Rocky Flats Plant, Golden, CO. April.

APPENDIX A

COMPARATIVE DATA TABLES BY TECHNOLOGY TYPE

Table A-1

PROCESS: P.A.T. (Type C Flyash + High Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
Meets Waste Form/ Size Requirement?	Yes: Monolithic waste forms can be made in a variety of sizes, from 2.5"x3.5"x7.6" standard bricks to 14"x14" tiles.					
Strength	Pb-containing fines from soil washing at lead battery reclaiming remediation site: 3,400 psi		ORNL K-25 Sludge: 290 to 530 psi	Dewatered surrogate salt waste [NaNO3, KCL, $Na_2(SO_4)_3$, $CaCO_3$, NaF, $MgCl_2$] salt spiked with Pb, Cd, Cr and Se (1,000ppm): 990 to 1,580 psi --- Molten salt oxidation waste salt: "high strength"		Radwaste incinerator scrubber blowdown w/ Co60 and metals (Cd): 250-1,500 psi --- ORNL K-25 incin. ash: 1,650 to 2,600 psi
Long-Term Stability	Little data available except for one instance of ANS 16.1 leach testing and water immersion. Water immersion tests indicate no effect of immersion. Heating at 1,000°F has no effect. No deterioration after freeze/thaw testing.					ORNL K-25 incin. ash: 1,650 to 2,600 psi before immersion, better after.
Radiation Stability	No data.					
Waste Loading	Generally 40 to 60%					
Volume Increase	Minus 10 to minus 50%, depending on waste type.					

Table A-1 *(Continued)*

PROCESS: P.A.T. (Type C Flyash + High Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
TCLP Leachability of RCRA Metals and Radionuclides	Pb-containing fines from soil washing at lead battery reclaiming remediation site, with 15,600 mg/kg Pb: Reduced TCLP from 206 to <0.04 mg/l @ 20% waste loading		ORNL K-25 sludge spiked with Ni and Ag: Metal TCLPs below RCRA limits.	Dewatered surrogate salt waste [NaNO3, KCl, $Na_2(SO_4)_3$, $CaCO_3$, NaF, $MgCl_2$] salt spiked with Pb, Cd, Cr and Se (10,00ppm): With pretreatment, metal TCLPs reduced to below RCRA limits.		ORNL K-25 incinerator ash with 10,000 ppm Cr: Metal TCLPs reduced to below RCRA limits.
ANS16.1 Leachability of RCRA Metals and Radionuclides						ORNL K-25 incinerator ash: LX = 6.6 - 6.8 in Tc-spiked ash.
Containment of Salts	No Data					
Pretreatment	Remove large organic matter such as wood chips, etc. Dewater if necessary to <20% moisture. Reduce particle size to ≤ 0.25" for LLMW Pretreat for Cr^{+6}, Cd, Ag		Dewater if necessary to <20% moisture. Reduce particle size to ≤ 0.25" for LLMW Pretreat for Cr^{+6}, Cd, Ag			
Residuals	None, except for water removed in dewatering to <20% moisture.					
Throughput	Maximum of 10 tons per hour for a single unit. Units may be set up in parallel for increased output.					

Table A-1 *(Continued)*

PROCESS: P.A.T. (Type C Flyash + High Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
Cost: Capital	$30 to $50 per ton	$40 to $60 per ton	Data not available	Data not available	Data not available	$30 to $50 per ton
Process	No data given					
Chemicals/ Materials	No data given					
Total	$30 to $50 per ton	$40 to $60 per ton	Data not available	Data not available	Data not available	$30 to $50 per ton
Availability: Equipment	Commercial grade equipment provided by Pressure Systems, Inc. Of Albuquerque, New Mexico. Equipment is available in fixed plant, trailer, or skid-mounted units.					
Process	PSI owns the patents to the Phoenix Ash Technology. Teaming, joint venture, and licensing agreements are all negotiable to obtain access to the technology.					

Table A-1 *(Continued)*

PROCESS: P.A.T. (Type C Flyash + High Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
Complexity	Chemically, the process is simple, involving only mixing of flyash and additives with waste and compressing. Mechanically, high pressures involve a more complex reaction.					
Robustness	Equipment is robust, and well proven in commercial use. High pressures suggest that it will require more maintenance and repair than a simple mixing process.					
Scale Proven	Remedial Project: Mine tailings at Oregon site, 900 tons. Full-scale plant: Installed in Czech Republic for treatment of Uranium mine tailings and ash. On-line in Sep. 1995, no data yet available.		Bench and pilot scale only; no commercial installations.			
Ease of Permit & Public Approval	Should be better than average for waste treatment facilities. No high temperature processes, no air emissions, minimal water effluents. Product is in a very acceptable form in terms of public attitude, especially with volume reduction aspect. Beneficial reuse not possible for LLMW, but high strength monolithic form is likely to be well received.					
Comments	Process transforms waste and flyash into various small monolithic forms: bricks, tiles, paver tiles. Waste forms are high strength, developing about 75% of ultimate strength in 7 days, 95% in 28 days, to about 7,000 psi maximum. Meets ASTM and UBC standards for structural materials. Excellent resistance to high temperature, water immersion, freeze/thaw. Some volume reduction is always obtained. Process is commercial and available. More data is needed for use on LLMW of different types, and waste form properties under standard RCRA and NRC testing protocols. Testing done at: Los Alamos National Lab. (for ORNL); Versar, Inc. (for EPA/OSW); Waste Management Educational and Research Consortium (DOE funded); National Environmental Technology Application Center (for EPA/ORIA and DOE Environmental Restoration); Rust Federal Services, Clemson Technical Center.					

Table A-2

PROCESS: GROUT (Portland Cement Based, Aqueous, Ambient Temperature and Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
Meets Waste Form/ Size Requirement?	Yes: Can be formulated to meet any required particle size requirement and low to moderate strength waste form.					
Strength	Monolithic forms have strengths in the range of 25 psi to 500 psi or more. Strength generally varies inversely with waste loading and water content, and directly with cement content.					
Long-Term Stability	Durability is generally good, depending on waste loading, water, and cement content.			Durability generally poor with concentrated salt solutions and solids		Durability generally good if salt content is not too high.
Radiation Stability	Excellent with doses up to at least 10^9 rads					
Waste Loading	Up to about 90%, depending on strength and durability requirements		Up to about 80%, depending on strength and durability requirements	Up to about 50%, depending on strength and durability requirements, and form and concentration of salt.		Up to about 90%, depending on strength and durability requirements
Volume Increase	5% to 20%		10% to 20%	25% to 50%		5% to 20%

Table A-2 *(Continued)*

PROCESS: GROUT (Portland Cement Based, Aqueous, Ambient Temperature and Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
TCLP Leachability of RCRA Metals and Radionuclides	Can be formulated to meet virtually any RCRA LDR requirement for RCRA metals, and low leaching levels for radionuclides.					
ANS16.1 Leachability of RCRA Metals and Radionuclides	Can generally meet NRC requirements for radionuclides and other metals.					
Containment of Salts	Fair to good for low levels of soluble species. Special formulations can improve performance.			Poor. Special formulations may improve performance somewhat.		Fair to good for low levels of soluble species. Special formulations can improve performance.
Pretreatment	Usually none required. Cr^{+6} and Tc^{+7} usually require reduction to lower valence states. With high moisture content waste, dewatering may be recommended to increase waste loading and reduce cost.					
Residuals	None, except contaminated water if dewatering is used.					
Throughput	Typical throughput rate in large-scale remedial projects is 100 tons or yd^3/hr for ex-situ treatment systems. Fixed installations can be of virtually any size.					

Table A-2 *(Continued)*

PROCESS: GROUT (Portland Cement Based, Aqueous, Ambient Temperature and Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
Cost: Capital	Based on experience with hazardous wastes, amortized capital costs are low, generally less than 5% of total vendor price in large-scale projects. Capital cost of LLMW would likely be considerably higher. Actual process equipment cost for treatment units varies from $10,000 to $500,000, depending on scale and not including special handling requirements for LLMW.					
Process	Based on experience with hazardous waste, labor, utilities, etc. are typically about 20% of the total vendor price in remedial projects.					
Chemicals/ Materials	Based on experience with hazardous wastes, chemical costs are typically 40% of the total vendor price in remedial projects.					
Total	Based on experience with hazardous wastes, total vendor prices range from $40/yd^3 to $200/yd^3, exclusive of excavation, handling and disposal. Treatment of small quantities of waste will be much higher. Large-scale treatment mixed wastes can be expected to cost $100/yd^3 or more. These costs are for as-received waste, and do not include any benefit or cost from dewatering.					
Availability: Equipment	Equipment is readily available in all sizes and scales. Most equipment is off-the-shelf, and available on short notice.					
Process	Nearly all process formulations are available generically. Some proprietary versions exist, but are usually not necessary, and are generally available as formulated additives.					

Table A-2 *(Continued)*

PROCESS: GROUT (Portland Cement Based, Aqueous, Ambient Temperature and Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
Complexity	Processes are simple and easily carried out with normal industrial equipment and personnel skills. Hazards, other than the waste itself, are primarily those of moving mechanical devices - mixers, conveyors, etc. Maintenance and repair are conventional and routine.					
Robustness	Equipment is very robust. Processes are generally forgiving in operation, not requiring any high or unusual degree of control to meet QA/QC standards.					
Scale Proven	Proven at commercial scale on virtually every type of hazardous and radioactive waste, and on many LLMW types.					
Ease of Permit & Public Approval	Should be about average for waste treatment facilities. No high temperature or pressure processes, no air emissions, no water effluents. Environmental release very unlikely. Product is in an acceptable form in terms of public attitude.					
Comments	Process is well proven, commercial, and available at low cost. As with all stabilized waste forms, long-term durability is not defined as a property or test, but long-term experience with concrete gives an added measure of confidence.					

Table A-3

PROCESS: SULFUR POLYMER CEMENT (Modified Sulfur at Low-Moderate Temperature and Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
Meets Waste Form/ Size Requirement?	Yes: Can be produced to meet minimum and maximum particle size requirements, and a high-strength monolithic waste form.					
Strength	No data available on these waste types. Expected to be similar to incinerator ash in general properties and parameters if soil is dry. May not be competitive with grout and PAT processes, especially if waste contains large amounts of water and/or volatile organics.			Not recommended at high nitrate levels.	2000 - 4500 psi	4250 psi
Long-Term Stability					Excellent resistance to thermal cycling, immersion, freeze/thaw, and biodegradation. Resistant to acid attack. Attacked by strong alkalies.	
Radiation Stability					Tested and OK at $\geq 10^9$ Rads	
Maximum Waste Loading					40%	43%
Volume Increase					Not stated, but probably in the range of minus 50% to +50%, depending on waste physical characteristics and maximum waste loading. Large variability is due primarily to variations in the water content of the original waste.	

Table A-3 *(Continued)*

PROCESS: SULFUR POLYMER CEMENT (Modified Sulfur at Low-Moderate Temperature and Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
TCLP Leachability of RCRA Metals and Radionuclides	No data available on these waste types. Expected to be similar to incinerator ash in general properties and parameters if soil is dry. May not be competitive with grout and PAT processes, especially if waste contains large amounts of water and/or volatile organics.			Not recommended at high nitrate levels.	No data given	Tested at 7.5% Pb, 0.2% Cd level: 1.5 mg/l Pb, 0.2 mg/l Cd with 7% Na_2S addition. $Ca(OH)_2$ addition required to reduce Zn to 0.1 mg/l.
ANS16.1 Leachability of RCRA Metals and Radionuclides					No data given for chloride salts. Test results with Na_2SO_4 salt: LI = 10.7 for Co-60 LI = 9.7 for Cs-137	LI = 14.6 for Co-60 LI = 11.2 for Cs-137
Containment of Salts					Good, but no specific data given.	
Pretreatment					Requires drying, if necessary, to ≤ 5% moisture. Cost and waste loading data do not include drying operation, if required. Size reduction may be required.	
Residuals					Any vaporized and condensed water and volatile, if present in waste. SO_2 and H_2S emissions are below allowable TLVs.	
Throughput					No data given.	

Table A-3 *(Continued)*

PROCESS: SULFUR POLYMER CEMENT (Modified Sulfur at Low-Moderate Temperature and Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
Cost: Capital	No data available on these waste types. Expected to be similar to incinerator ash in general properties and parameters if soil is dry. May not be competitive with grout and PAT processes, especially if waste contains large amounts of water and/or volatile organics.			Not recommended at high nitrate levels.	No data given.	
Process					No data given.	
Chemical Materials					No data given.	SPC costs ~$0.12/lb ($240./ton). Na_2S, when required, costs ~ $0.35.lb. ($700./ton). At 43% waste loading, with 7% Na_2S added: $90/yd^3; $390/ton.
Total					No data given	$90/yd^3 ($390/ton) plus capital amortization and processing cost.
Availability: Equipment					Standard industrial equipment available at various process sizes. Variations possible to meet specific waste and throughput requirements.	
Process					Available at bench and pilot levels. License may be required from BNL for pending process patent.	

Table A-3 *(Continued)*

PROCESS: SULFUR POLYMER CEMENT (Modified Sulfur at Low-Moderate Temperature and Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
Complexity	No data available on these waste types. Expected to be similar to incinerator ash in general properties and parameters if soil is dry. May not be competitive with grout and PAT processes, especially if waste contains large amounts of water and/or volatile organics.			Not recommended at high nitrate levels.	More complex than grout processes. Operating temperature of 120°-140°C, max. of 150°C to prevent emissions. Hot, melt requires safety precautions.	
Robustness					Good. Melt can be held for long periods if necessary. Product can be re-melted. No chemical reactions required. Equipment is robust, industrially proven. Melt viscosity increase with high waste loadings may be a limitation.	
Scale Proven					Bench and small pilot scale proven at BNL and INEL. Production scale in process at SEG.	
Ease of Permit & Public Approval					Elevated temperatures and possible toxic gas emissions if temperature excursions occur may make permitting and public approval more difficult than ambient temperature processes. However, strong, durable waste form is a plus.	
Comments:					SPC process is probably not competitive with grout and PAT systems for high moisture waste, especially those not containing high soluble salt levels. Problemattic use on ion exchange resins. Not usable for high alkalinity wastes, high nitrate or carbon content wastes, or those containing phenols. For optimum TCLP performance, may require casting to <3/8 inch particle size.	

Table A-4

PROCESS: POLYMER ENCAPSULATION (Polyethylene at Moderate Temperature and Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
Meets Waste Form/ Size Requirement?	Yes: Can be formulated to meet minimum and maximum particle size requirements, and a high-strength monolithic waste form.					
Strength	No specific data are given for this waste, but strengths would likely be in the 2,000 psi range.		CIF blowdown surrogate sludge: 2,000 psi	2,000 psi	No specific data are given for this waste, but strengths would likely be in the 2,000 psi range.	
Long-Term Stability	Although complete long-term durability testing has not been completed on all waste types, test results with incinerator ash, salts and metal-containing wastes indicates generally excellent resistance to thermal cycling, immersion, freeze/thaw, and biodegradation. Resistant to attack by virtually all acids, alkalies and solvent under any expected environmental conditions. PE does not degrade in landfills.					
Radiation Stability	May not be appropriate for highly active waste > 10,000 nCi.gm. PE degraded at $>10^8$ Rads.					
Waste Loading	Mixed waste soils successfully treated at 50%. Higher waste loadings likely, but not tested		CIF blowdown surrogate sludge: 35% . Ferric hydroxide sludge: 80%. Cadmium plating sludge: 20%	50%. Samples failed TCLP at higher waste loadings	59%	30-40%.
Volume Increase	Minus 50% to +50%, depending on waste physical characteristics and maximum waste loading. Large variability is due primarily to variations in the bulk density of the original waste. Removing water from waste tends to reduce the bulk density and, in some cases, increases the waste volume prior to encapsulation. Rocky Flats usually calculates volume change based on feed to the extruder and does not consider volume increase/decrease due to evaporation.					

Table A-4 *(Continued)*

PROCESS: POLYMER ENCAPSULATION (Polyethylene at Moderate Temperature and Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
TCLP Leachability of RCRA Metals and Radionuclides	Mixed waste: Met Cd, Cr, Pb, Ag, F001-3, F005-7, F009, F039 UTS levels		Mixed waste: Met F006, F039 UTS levels. Surrogate waste: Met Cd, Cr, Pb, Hg, Ag, Cu, F001-3, F005-7, F009, F039 UTS levels CIF blowdown surrogate: Met all TC and listed limits with pretreatment additive	Mixed waste: Met Cd, Cr, Pb, Ag, F001-3, F005-7, F009, F039 UTS levels. Surrogate waste: Met Cd, Cr, Pb, Ag, F001-3, F005-7, F009, F039 UTS levels	Surrogate waste: Met Cd, Cr, Pb, Ag, F001-3, F005-7, F009, F039 UTS levels	Mixed waste: Met Cd, Cr, Pb, Ag, F001-3, F005-7, F009, F039 UTS levels. Surrogate waste: Met Cd, Cr, Pb, Ag, F001-3, F005-7, F009, F039 UTS levels
ANS16.1 Leachability of RCRA Metals and Radionuclides	Although no ANS 16.1 data is given for this waste, very good to excellent LIs would be expected for metals and salts.			LI = 7.8 for Na @ 70% loading; 11.1 @ 30% loading	Although no ANS 16.1 data is given for this waste, very good to excellent LIs would be expected for metals and salts.	
Containment of Salts	No specific information given. Probably very good.			LI = 7.8 for Na @ 70% loading; 11.1 @ 30% loading	No specific information given. Probably very good.	
Pretreatment	Requires drying, if necessary, to 3 - 10% moisture. Cost and waste loading data do include drying operation, if required (Rocky Flats). Size reduction may be necessary to meet extruder tolerance requirements.					
Residuals	Any vaporized and condensed water and volatile, if present in waste.					
Throughput	Process uses standard industrial equipment. Equipment can be sized for any conceivable throughput rate.					

Table A-4 *(Continued)*

PROCESS: POLYMER ENCAPSULATION (Polyethylene at Moderate Temperature and Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
Cost: Capital	$300,000 for a fully integrated extrusion system.					
Process	No data given. Processing cost should be less, assuming little or no pretreatment.		No data given. Probably similar to nitrate salts.	$960/ton of waste treated (including pretreatment).	No data given. Probably similar to nitrate salts.	No data given. Processing cost should be less, assuming little or no pretreatment.
Chemical Materials	Virgin polyethylene costs range from approximately $0.30/lb (Kalb and Faucette, this report) to $0.45 (Anderson, 1994) and recycle material costs up to $0.19/1b, including transportation costs. Assume $0.40/lb. ($800/ton) for these cost estimates.					
	Loading = 40-70%: $1200 to $344/ton of waste treated.		Loading = 35%: $1488/ton of waste treated.	Loading = 50%: $34/ton of waste treated.	Loading = 59%: $552/ton of waste treated.	Loading = 40%: $1200/ton of waste treated.
Total	No data given. Total cost will depend primarily on waste loading. Does not include packaging, shipping, and disposal.			$1304/ton of waste treated, not including capital amortization. Does not include packaging, shipping, and disposal.	No data given. Total cost will depend primarily on waste loading. Does not include packaging, shipping and disposal.	
Availability: Equipment	Standard industrial equipment available at various process sizes. Variations possible to meet specific waste and throughput requirements.					
Process	Process is available and there is presently a CRADA between RFETS and Rust Federal Services.					

Table A-4 *(Continued)*

PROCESS: POLYMER ENCAPSULATION (Polyethylene at Moderate Temperature and Pressure)

	Fine-grained soils	Coarse-grained soils	Metal Sludges	Nitrate Salts	Chloride Salts	Incinerator Ash
Complexity	More complex than grout processes. Operating temperature of 125°-190°C. High pressure only in localized zones in extruder. Hot melt requires safety precautions. Design modifications may be required for specific waste streams, based on testing to date.					
Robustness	Good. Melt can be held for long periods if necessary. Product can be re-melted. No chemical reactions required. Equipment is robust, industrially proven. Melt viscosity increase with high waste loadings may be a limitation.					
Scale Proven	Bench and pilot scale proven at BNL and RFETS.					
Ease of Permit & Public Approval	Elevated temperatures may make permitting and public approval slightly more difficult than ambient temperature processes. However, strong, durable waste form and excellent resistance to chemicals are pluses.					
Comments:	PE and cement-based grouts are complementary processes. PE can tolerate only up to 12% moisture. Overall, 30 - 80% waste loadings can be used, with 50% being typical. PE process is probably not competitive with grout and PAT systems for high moisture wastes, especially those not containing high soluble salt levels. Waste loading and cost comparisons were based on NRC waste form criteria due to lack of DOE performance criteria.					

APPENDIX B

PRESENT AND PROPOSED RCRA LDR REQUIREMENTS OF METALS

Table B-1

Present and Proposed RCRA LDR Metals Leaching Levels, TCLP Test

TC Metal	RCRA Code	Present TC Level (mg/l, TCLP)	Proposed UTS TC Level (mg/l, TCLP) Federal Register 60, No. 162. Aug. 22, 1995. pp. 43654-43699.	Proposed TC LDR Exit Level (mg/l, TCLP) Federal Register. Dec. 21, 1995. p. 66344-.
Antimony			2.10	0.53
Arsenic	D004	5.00	5.00	
Barium	D005	100.00	7.60	16.00
Beryllium			0.014	0.00032
Cadmium	D006	1.00	0.19	0.11
Chromium	D007	5.00	0.86	0.48
Lead	D008	5.00	0.37	12.00
Mercury (retort residues, D009)	D009	0.20	0.20	0.14
Mercury (all others, D009)	D009	0.20	0.025	0.14
Nickel			5.00	5.00
Selenium	D010	1.00	0.16	0.36
Silver	D011	5.00	0.30	
Thallium			0.078	0.019
Vanadium			0.23	4.00
Zinc			5.30	38.00