

Stabilize High Salt Content Waste Using Polysiloxane Stabilization

Mixed Waste Focus Area



Prepared for
U.S. Department of Energy
Office of Environmental Management
Office of Science and Technology

August 1999

Stabilize High Salt Content Waste Using Polysiloxane Stabilization

OST Reference #2045

Mixed Waste Focus Area



Demonstrated at
Idaho National Engineering and Environmental Laboratory
Idaho Falls, Idaho



Purpose of this document

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine if a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at <http://OST.em.doe.gov> under "Publications."

TABLE OF CONTENTS

1	SUMMARY	page 1
2	TECHNOLOGY DESCRIPTION	page 4
3	PERFORMANCE	page 6
4	TECHNOLOGY APPLICABILITY AND ALTERNATIVES	page 10
5	COST	page 12
6	REGULATORY AND POLICY ISSUES	page 13
7	LESSONS LEARNED	page 14

APPENDICES

A	Bibliography
B	TMS Data Elements
C	Acronyms

SECTION 1

SUMMARY

Technology Summary

Throughout the Department of Energy (DOE) Complex there are large inventories of homogeneous mixed waste solids, such as soils, fly ashes, and sludges that contain relatively high concentrations (greater than 15% by weight) of salts. The inherent solubility of salts makes traditional treatment of these waste streams difficult, expensive, and challenging. Many of these materials are in a dry granular form and are the by-product of solidifying spent acidic and metal solutions used to recover and reformulate nuclear weapons materials over the past 50 years. At the Idaho National Engineering and Environmental Laboratory (INEEL) alone there is approximately 8,000 cubic meters of nitrate salts (potassium and sodium nitrate) stored aboveground with earthen cover. Current estimates indicate that over 200 million kg of contaminated salt wastes exist at DOE sites, with over 5 million kg being generated each year.

One of the obvious treatment solutions for these wastes is to immobilize the hazardous components to meet Environmental Protection Agency/Resource Conservation and Recovery Act (EPA/RCRA) Land Disposal Requirements (LDR), thus rendering the mixed waste to a radioactive waste classification only. One proposed solution is to use thermal treatment via vitrification to immobilize the hazardous component and thereby substantially reduce the volume, as well as provide exceptional durability. However, these melter systems involve expensive capital apparatus with complicated offgas systems. In addition, the vitrification of high salt waste may cause foaming and usually requires extensive development to specify glass formulation recipes. As an alternative to thermal treatments, stabilization of these materials in cementitious grouts has also been widely employed. However, salts interfere with the basic hydration reactions of cement, leading to an inadequate set or deterioration of the waste form over time. Sufficient and compliant stabilization in cement can be achieved by lowering waste loadings, but this involves a large and costly increase in the volume of material requiring handling, transporting, and disposal. As a consequence of these stabilization deficiencies associated with salt containing mixed wastes, the Mixed Waste Focus Area (MWFA) (a DOE EM-50 program) sponsored the development of five low-temperature stabilization methods as an alternative to cement grouting. One alternative is microencapsulation by polysiloxane, which in some applications provides higher waste loadings and a more durable waste form than the baseline method of cementitious grouting.

Polysiloxane is part inorganic and part thermosetting polymer. Once formed, the material consists of about 50% vinyl-polydimethyl-siloxane, 20% quartz (used as filler material), 25% proprietary ingredients, and <5% water. The specific material tested as a waste form material (during the development sponsored by the MWFA) was provided by Orbit Technologies of Carlsbad California. Researchers at Akron University with technical support from the INEEL completed the majority of the development tests.

The Orbit product is sold as Ceramic Silicon Foam (CSF). Generally, CSF is formed with a three-part system comprised of the SiH cross-linker (binder), SiOH (the polysiloxane monomer), and a catalyst. Flame resistant platinum is commonly used as the catalyst. Varying the amount of catalyst can vary cure times from a minute upward to hours. The polysiloxane sets at low temperatures and thus requires minimal offgas systems, contains no volatile metals like mercury, and generates little secondary waste.

Upon room temperature reaction of the base materials, a Si-O-Si bond is formed and hydrogen gas is released. When these silicon atoms are further bonded with organic radicals, the resulting material combines the elasticity and water resistance of organic compounds with the chemical resistance of silicone materials. However, the final structure is by definition less than 5% by weight organic. This sturdy formation allows the silicone molecule to be resistant to extreme temperatures, pressures, and chemical environments. Specifically, CSF can resist contact with acids, alkalis, and attack from oxygen. One study showed that after 1-month exposure to 0.1M nitric acid solutions, the CSF exhibited no structural changes.

Common production-scale systems will involve simple mixing apparatus similar to that for the cement based waste stabilization systems. Therefore, there are no substantially increased costs over the



baseline for operations. The polysiloxane encapsulation material is relatively expensive due to the base cost of the chemical compounds. However, high waste loadings can counterbalance this expense.

Orbit's CSF was first proposed for use at the Chernobyl plant in the former Soviet Union because of its excellent radiation resistance. Studies show that under gamma irradiation, the compressive strength actually increases as the product changes to a more ceramic form. It is stable up to 30⁰C, but loses 20% of its mass upon further heating to 110⁰C.

Any properly sized solid or sludge mixed waste material is a potential candidate for this technology. Polysiloxane is suitable for encapsulating mixed waste contaminated with salt, especially the secondary salt wastes generated from the treatment of acid gases from thermal units. It is also compatible with other wastes such as incinerator fly and bottom ashes, failed concrete waste forms, and soils.

Overall benefits of mixed waste microencapsulation using polysiloxane are:

- potential ability to adequately (i.e., comply with disposal requirements) encapsulate/stabilize salt containing wastes at higher waste loadings than conventional Portland cement,
- broad applicability to the many different types of wastes,
- elimination of potential subsidence upon burial,
- low cost treatment that uses no large equipment,
- low temperatures, low emissions, and minimal secondary waste,
- ability to control cure time.

Demonstration Summary

During FY-97 and FY-98, the polysiloxane technology was demonstrated on a surrogate salt waste material simulating the INEEL Pad-A nitrate salts from the Rocky Flats Plant and on two generic salt waste surrogate formulations provided by the MWFA. For the Pad-A waste, the primarily nitrate salts were contaminated with the chromium (+6 oxidation state) RCRA heavy metal at about 1,045 ppm. The results of this study concluded that the salt waste material could be successfully stabilized with waste loadings as high as 50% by mass. The resultant waste forms passed (at the non-UTS levels) the RCRA Toxic Characteristic Leachability Procedure (TCLP) for chromium, the Department of Transportation (DOT) oxidizer test, and a battery of durability testing. These tests included wet/dry cycling effects on the compressive strength, as well as base and water immersion effects on compressive strength. The basic waste form had a compressive strength of over 600 psi at 40% waste loading. For the two MWFA recommended salt containing waste surrogates (one surrogate high in chlorides, the other high in nitrates), the contaminants were oxides of lead, mercury, cadmium, and chromium at 1,000 ppm each. When the salt surrogates were encapsulated with polysiloxane at both 30 and 50% by mass waste loading, the resultant forms passed TCLP limits and in most cases passed the newer lower Universal Treatment Standard (UTS) for the RCRA metals.

Orbit Technologies owns the patent rights to the process and their version of polysiloxane and proprietary ingredients is called CSF. Orbit's objective is to collaborate with polysiloxane vendors to commercialize the technology, train users, and provide it, where applicable, throughout the DOE system.

Contacts

Technical Principal Investigators:

G.G.Loomis
Lockheed Martin Idaho Technologies Company/LMITCO
Idaho National Engineering and Environmental Laboratory/INEEL
P.O. Box 1625-MS 3710
Idaho Falls, Idaho, 84315
(208) 526-9208
FAX: (208) 526-6802
E-MAIL: guy@inel.gov

Dr. Steve Prewett
Orbit Technologies
Palomar Triad One
2011 Palomar Airport Road, Suite 100
Carlsbad, California
(330)-794-2122

Dr. Chris Miller
University of Akron
21 OASEC
Akron Ohio, 44325-3905
(330) 972-5915
FAX: (330) 972-6020

Management:

DOE-ID Program Director
William Owca
Mixed Waste Focus Area
US Department of Energy
Idaho Operations Office
785 DOE Place
Idaho Falls Idaho, 83401-1563
(208) 526-1983
FAX: (208) 526-5964
E-MAIL: owcawa@inel.gov

MWFA Product Line Manager
Vince Maio
Mixed Waste Focus Area
Lockheed Martin Idaho Technologies Company/LMITCO
Idaho National and Engineering Laboratory/INEEL
P.O. Box 1625-MS3875
Idaho Falls, Idaho, 83415
(208) 526-3696
FAX: (208) 526-1061
E-MAIL: vmaio@inel.gov

Other

All published Innovative Technology Summary Reports are available on the OST Web site at <http://em-50.em.doe.gov> under "Publications." The Technology Management System, also available through the OST Web site, provides information about OST programs, technologies, and problems. The OST Reference Number for Polysiloxane is 2045.



SECTION 2

TECHNOLOGY DESCRIPTION

Overall Process Definition

The basic polysiloxane process involves simple mixing of the base polysiloxane materials with the mixed waste in an off-the-shelf paddle wheel mixer. This is followed by extruding the waste blend outside of the mixer while adding a platinum catalyst. The addition of the catalyst starts a silicon polymerization process, which results in a solid waste monolith upon curing.

In terms of basic chemistry principles, polysiloxane is formed not unlike common Room Temperature Vulcanizing (RTV) silicone foam sealants. The basic liquid chemicals SiH and SiOH are thoroughly mixed with the waste and react in the presence of the platinum catalyst to form the desired thermosetting polymer and hydrogen gas. The fundamental chemical formulation is as follows:



The product term in parentheses (vinyl-polydimethyl-siloxane) is the gelled and cured solid structure represented as a repeating siloxane monomer. The goal is to provide sufficient mixing and cure time to allow the polymer chain to form around the waste at a micro level and thereby create a barrier between the waste and the environment. For the applications studied in the MWFA supported development program, the R represented the methyl group, CH₃. However, different types of aromatic and aliphatic R groups can give the polymer different properties. For example, aromatic radical groups add elasticity, improve thermostability, and increase radiation resistance. Since polysiloxane does not possess high strength characteristics, a filler, such as quartz (SiO₂) is usually added to meet the waste form strength criteria.

Polysiloxane is highly durable, passing the National Fire Protection Association (NFPA) 258 smoke emission test, the ASTM-E162 flame spread test, and the ASTM 1171 ozone resistance test. The density of the substance can range from 0.12--0.84 g/cc.

System Operation

Application of the technology is fairly straightforward. A schematic of how the process could be applied at a larger scale is shown on Figure 1. Full-scale operations would involve a high-efficiency particulate air (HEPA) filtered facility with simple paddle wheel mixing systems and screw feeders/extruders. Through one screw feeder the waste material would be metered into the mixing system along with the basic liquid polysiloxane chemicals. The dry granular mixed waste material should be sized to the "hundreds" of micron size to facilitate the encapsulation process. Once in the mixing chamber, the paddle wheel would blend the mix without the onset of polymerization or curing. The blend of base material and mixed waste would then be extruded through a disposable, commercially available nozzle at which point, a platinum catalyst would be added to start the polymerization process. The material upstream of the extruder could be stored temporarily without polymerization. If the process became stalled, the extruder could be replaced and the "set up" extruder treated as secondary waste. For final disposal, the extruder could pour the polymerizing material into waste containers (such as 4 x 4 x 8-foot polyethylene disposable boxes with built-in lifting lugs).

The process can be configured to allow waste forms to set up in 15 minutes to 5 hours to support the required throughput. The process is essentially a room temperature polymerization and there is no accompanying pressure increase. The waste form could be taken directly to a permitted disposal facility for stacking or possibly an approved shallow land burial site.



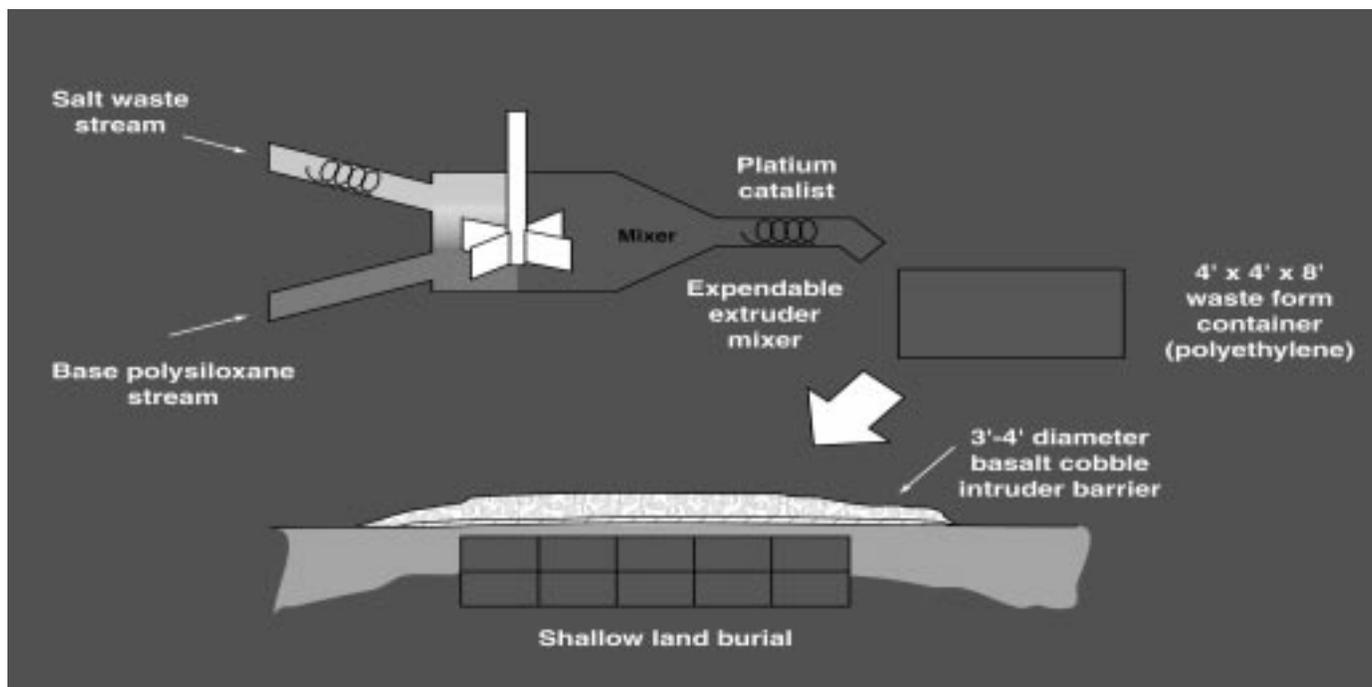


Figure 1. Polysiloxane Process Flow Sketch.



SECTION 3

PERFORMANCE

Demonstration Plan

A proof of concept experimental study was performed to investigate the use of Orbit Technologies polysiloxane grouting material for encapsulation/stabilization of DOE mixed waste salts. The DOE salts are basically evaporator pond material, secondary offgas spent scrub solutions from thermal units, or other solid salt residuals that resulted from acidic metal finishing processes. Presently, the best available technology (basic Portland Cement methods) for stabilizing this waste results in a large volume increase (approximately waste loadings of 15%wt or less). Another option for the salt materials is melting via vitrification. These thermal techniques involve expensive and questionable offgas systems (especially difficult for transuranic materials). Therefore, application of a nonthermal, noncementitious technique has the potential to reduce cost and augment implementability.

The experimental study involved mixing the polysiloxane material with three different surrogate salt materials and performing a variety of leaching, compressive strength, and durability tests on the final surrogate waste forms. The surrogate salts were modeled after several DOE Complex salt materials including: Pad-A salts from the Idaho National Engineering and Environmental Laboratory's Subsurface Disposal Area (INEEL-SDA) at the Radioactive Waste Management Complex (RWMC), and two generic surrogate salt wastes specified by the MWFA. One of the MWFA specified surrogates represents the majority of previously grouted dry solids in the DOE Complex and contains a high level of nitrates. The other MWFA specified surrogate waste contained both chlorides and sulfates and represents an unconcentrated blowdown from the offgas scrubber system of an incinerator or thermal unit. Both MWFA specified surrogates contain RCRA heavy metals in the 1,000 ppm range, thus providing a challenge to the polysiloxane method. The inerts of these surrogates are mostly oxides and hydroxides of common nonhazardous metals. Table 1 provides the detailed compositions of the MWFA specified surrogates.

Table 1. Standard MWFA Salt Surrogate Compositions

	High Chloride wt%	High Nitrate wt%
<i>INERTS</i>		
Fe(OH) ₃ as Fe ₂ O ₃	12.75	6.0
Al ₂ (OH) ₃	8.5	4.0
Na ₂ PO ₄	4.25	2.0
Mg(OH) ₂	8.5	4.0
MicroCel E	17.0	8.0
Portland Cement (Type II)	4.25	2.0
H ₂ O	29.75	14.0
<i>Salts</i>		
NaCl	10.0	0.0
CaSO ₄	5.0	0.0
NaNO ₃	0.0	60.0
<i>Contaminants</i>		
	mg/kg	mg/kg
<i>Toxic Metal Oxides</i>	ppm	ppm
PbO	1,000	1,000
CrO ₃	1,000	1,000
HgO	1,000	1,000
CdO	1,000	1,000
NiO	1,000	1,000
Trichloroethylene	1,000	1,000



The study involved the following tests to assess the polysiloxane process and its resultant waste form:

- 1) A mixing study to optimize the waste loading (salt waste mass to polysiloxane mass) relative to basic compressive strength,
- 2) Durability testing to measure effects on compressive strength. This test included wet/dry cycling, base immersion, and water immersion,
- 3) Leachability testing using EPA's RCRA Toxicity Characteristic Leach Procedure (TCLP) and the ASTM C-1308 accelerated leach test.
- 4) The DOT Oxidizer Test to assess any safety concerns associated with mixing potential oxidizers (nitrate salts) with organic containing material (polysiloxane).
- 5) An evaluation of volatile organic content as determined by zero head space testing.

The samples were also subjected to a Scanning Electron Microscope (SEM) evaluation of encapsulation properties.

For the hazardous metals tested in this project, Table 2 gives the EPA Toxicity Characteristic (TC) levels, Old UTS Levels, and Proposed Revised UTS Levels in effect during the project. Final Revised UTS Levels issued by EPA on May 26, 1998 (FR, Federal Register, -63, p 28556) are also included in the Table. It should be noted that the final UTS levels for cadmium and chromium are significantly lower than the previously existing or proposed revised UTS levels for these two constituents. In addition, before May 26, 1998, existing final EPA rules for D006 – D009 only wastes only required these wastes to be treated to the TC level only, not the UTS level.

Table 2. Various EPA TC and UTS Levels

Waste Code	TC Metal Constituent	EPA Toxicity Characteristic Level (mg/L, TCLP)	Old UTS Level (mg/L TCLP)	Proposed Revised UTS Level (mg/L TCLP)	Final Revised UTS Level (mg/L TCLP)
D006	Cadmium	1.0	0.19	0.20	0.11
D007	Chromium	5.0	0.86	0.085	0.60
D008	Lead	5.0	0.37	0.75	0.75
D009	Mercury	0.2	0.025	0.025	0.025

Results

Testing determined that Orbit Technology's polysiloxane waste forms with INEEL Pad-A salt surrogates result in a cohesive monolith with compressive strengths well in excess of the recommended 60 psi Nuclear Regulatory Commission (NRC) requirement for noncemented waste forms. A basic mixing study was conducted that involved creating 2 x 4-inch cylindrical samples of the surrogates/polysiloxane mixtures. A variety of mixtures were formulated with waste loadings of 65% by weight. The ASTM D-695 compressive test technique was applied since the apparatus only allowed 2 inch diameter x 4 inch long cylinders. Five replicate tests were performed for each of the formulations with the result that the waste form had a compressive strength greater than 637 psi.

A laboratory-scale study of the final waste form showed that one of the formulations was an order of magnitude less than the NRC hydraulic conductivity requirement of 1e-7 cm/s. A hydraulic conductivity test of the two formulations (using ASTM D-5084) resulted in an average hydraulic of 6.4 e-8cm/s. These values are favorable, if the final waste form is to be considered for shallow land burial, since they indicate that little water can enter the waste form for leaching.

A variety of durability tests were performed to investigate the effects on compressive strength (using ASTM D-695) due to water immersion, wet/dry cycling, and base immersion. For the water immersion testing, waste forms remained above the upper limit of the testing apparatus at 637 psi. For the wet/dry cycling testing, polysiloxane waste forms showed only a 1.22-%mass loss and again a compressive strength value above the maximum 637 psi. When subjected to the base immersion test (pH 12.5 for 30 days), the above waste formulation again retained a compressive strength above the maximum value of 637 psi.



The waste forms created by mixing polysiloxane and surrogate INEEL Pad-A salt waste showed adequate chromium leaching resistance to the ASTM C-1308f leach test, but not to the TCLP. At 30% waste loadings, the treated surrogate waste meets the EPA TCLP-based chromium TC level of 5 ppm, but this level was exceeded at 50% loadings. The TCLP extracts at the 30% waste mass loading level ranged from 1.36 to 2.4 ppm chromium. At the 50% waste mass loading level, the TCLP extracts ranged from 5.6 to 5.9 ppm chromium. Therefore at both loading levels, the treated waste did not meet the Old, Proposed, Revised, or Final Revised (May 26, 1998, FR 63, p 28571) chromium UTS levels of 0.86, 0.85, and 0.60 mg/L in the TCLP extract, respectively (see Table 2).

The Pad-A salt surrogate had approximately 1,045 ppm of the highly soluble Cr+6 (1,400 ppm potassium dichromate and 800 ppm chromium trioxide). The Pad-A surrogate waste Cr+6 level was approximately 5.8 times that found in the actual INEEL Pad-A waste. It is therefore possible that surrogates with chromium +6 concentrations, which are more representative of the concentration in actual waste might exhibit lower TCLP extract levels than those found here. Addition of heavy metal scavengers during a pretreatment stage might also improve the chromium retention at the waste loadings of interest.

When subjected to the accelerated leach test defined in ASTM C-1308, there was a nondetect for chromium in the leachate. Using the TCLP protocol the results were 1.36-ppm chromium for the 30% waste loading and 5.6 ppm chromium for waste forms with 50% waste loadings. Based on positive durability testing and preliminary TCLP testing at the University of Akron, the Pad-A waste form was sent to an outside laboratory (Environment and Ecology) for independent TCLP leach testing. The results for Cr+6 were 2.4 to 5.9 ppm, respectively, for 30 and 50% waste loadings (similar to the University of Akron results).

At the 50% loading level, the waste form generated by mixing the suggested MWFA chloride salt surrogate and polysiloxane also met EPA's Final revised TCLP-based UTS levels for mercury and lead, but did not meet the Final Revised UTS levels for cadmium (0.11 ppm) or chromium (0.60 ppm). To meet the Final Revised cadmium level could require a substantial reduction in waste loading and/or cadmium concentration, whereas a small reduction in waste loading or chromium concentration may allow the treated waste to meet the Final Revised chromium level.

Examples of TCLP results at 50% waste loadings of the high chloride waste surrogate were as follows:

- 1) 0.17 ppm cadmium, down from 1,000 ppm cadmium oxide;
- 2) 0.68 ppm chromium, down from 1,000 ppm chromium oxide;
- 3) 0.01 ppm mercury, down from 1,000 ppm mercuric oxide;
- 4) nondetect on lead from 1,000 ppm lead oxide.

The MWFA recommended high nitrate salt waste surrogate was also mixed with polysiloxane at 50% waste loading. The following TCLP results were obtained for the fabricated waste forms:

- 1) 0.04 ppm cadmium, down from 1,000 ppm cadmium oxide;
- 2) 1.3 ppm chromium, down from 1,000 ppm chromium oxide;
- 3) 0.06 ppm mercury, down from 1,000 ppm mercury oxide;
- 4) nondetect for lead from 1,000 ppm lead oxide.

Thus, for the high nitrate salt wastes tested, cadmium and lead were successfully stabilized at the 50% waste mass loading level. Although the chromium TCLP result exceeded all of the Table 2 chromium UTS standards at this loading level, at 30% waste loadings the result was 0.36 ppm, well under the Final Revised chromium UTS of 0.60 mg/L (ppm), the most stringent chromium UTS in Table 2. At the 50% waste mass loading level, the mercury TCLP result exceeded the 0.025-mg/L level of all of the Table 2 mercury UTS standards.

It is important to note that all TCLP prepared samples for this study were ground and/or cut from the original polysiloxane waste form. This is significant in that grinding and cutting to meet the TCLP size criteria can breach the barrier and expose the RCRA hazardous metals to the TCLP leaching environment. In TCLP testing of other microencapsulation techniques, TCLP samples are sometimes specially fabricated or cored to avoid cutting or grinding. Similar sample preparation for TCLP testing of the polysiloxane waste forms may reduce the TCLP levels found.

A mixture of the Pad-A surrogate waste and polysiloxane material passed the DOT oxidizer test (e.g., a mixture of sawdust and the waste form material did not burn after 20 minutes compared with the surrogate salt material alone that burned under similar conditions in 30 seconds). This testing was performed at Hark Laboratories, Inc. (Barberton, Ohio). The result is not surprising in that the polysiloxane material has less than 5% organic content.

A "zero head space" evaluation for trichloroethylene (TCE) was made of the waste form created with the MWFA surrogate high chloride salt to determine the final waste form's ability to retain volatile organics. The result was nondetect for TCE down from a source term in the surrogate of 1,000 ppm TCE.

Scanning Electron Microscope (SEM) studies showed that the simple mixing of polysiloxane material, catalyst, and salt causes a general encapsulation of the salt particles. There is some change (reduction) in the overall size of the salt particles following the encapsulation process suggesting some unknown chemical recombination as part of the polymerization process. The average size of the untreated salt particles is approximately 150 microns. When mixed with the polysiloxane, the size appears to be on the order of 50–100 microns with some particles in the original 150-micron range. It is not clear whether the mixing action breaks up the original salt particles.



SECTION 4

TECHNOLOGY APPLICABILITY AND ALTERNATIVES

Competing Technologies

Competing technologies to polysiloxane include thermal treatment (including vitrification or incineration) and encapsulation by Portland cement. The vitrification option is capital intensive, but can result in an excellent waste form with easy regulatory acceptance. However, this option requires radioactive incineration type permitting, which is difficult to achieve. The basic Portland cement option costs much less than the polysiloxane option for the base ingredients; however, this option results in roughly twice the final waste form volume. This can greatly increase the transporting and disposal costs.

There are many mixed waste stabilization/solidification technologies at various stages of development that could be considered as competing with the Portland cement and polysiloxane process. Numerous tests with low-temperature stabilization techniques involving ceramics and other polymers indicate that greater waste loadings (than those achievable with conventional Portland cement) are possible with even the troublesome salt containing wastes. In addition, alternatives involving thermal-sintering techniques also may lead to acceptable waste forms with considerably more volume reduction compared to that achievable with grouts or polysiloxane. Mixed waste stabilization methods currently in the later stages of development include phosphate-bonded ceramics, enhanced concretes using proprietary additives, and several methods provided by commercial vendors. Low temperature methods like phosphate bonded ceramics not only provide a low porosity ceramic barrier, but render the RCRA metal less hazardous by converting it to the low solubility phosphate salt. Other microencapsulation techniques involving polyesters, polyethylene, and sol-gel technologies have also been demonstrated on surrogate and/or actual wastes.

Sintering differs from vitrification in that only melting at grain phase boundaries occur without the complete amorphous restructuring that takes place in glass formation. Like vitrification, sintering occurs at temperatures over 1,000°C and can emit volatile hazardous metals. Even though densification is possible for some additional volume reduction, slight volume increases usually occur. However, waste loadings as high as 80% are possible. The equipment for sintering is less complex than vitrification, but more complex than grouting. For a typical sintering process, grinding, mixing, and extruding equipment is required as well as ovens, calciners, and offgas treatment systems. For most waste streams, application of sintering methods will require an extensive process development effort involving statistically designed experiments. The experiments are required to identify parameters that avoid the volatility of metals from metal salts existing in the waste stream.

Recently developed polymeric methods using batch mixers or extruder systems are currently available. Like polysiloxane, these low-temperature microencapsulation techniques do not truly stabilize the waste, but create an impermeable barrier between the hazardous components in the waste and the environment. Waste loadings in these organic media are usually on the order of 50% for many troublesome wastes, such as incinerator fly ash or those containing appreciable salts. This value is nearly twice that achievable with conventional cement grout methods.

Technology Applicability

The process may be applicable to any homogeneous solid and/or sludge mixed waste material, but is particularly applicable to mixed waste salts in the DOE Complex. Polysiloxane microencapsulation is applicable for mixed wastes containing moderate amounts of RCRA hazardous metals (i.e., concentrations up to the 500 ppm range), but may require pretreatment (e.g., sulfide addition) steps for higher concentrations to ensure leachability limits are met.



Other solid mixed waste materials, including debris, would have to be size reduced before encapsulation in the polysiloxane system. The process is not applicable to aqueous and organic liquid based wastes, and has not been validated for reactive or other unique waste streams. The primary applicability of this technology is for the establishment of waste forms that meet the requirements for final disposal. However, polysiloxane encapsulation is applicable for waste forms that possess less stringent nondisposal requirements. Examples include temporary storage and transportation, whereas the waste material needs to be encapsulated for enhancing future stabilization or to suppress dust emissions during handling and transport. An example of such an application exists for high-level waste (HLW) calcine material stored at the INEEL.

Patents/Commercialization/Sponsor

An independent company, Orbit Technology of Carlsbad, California, developed the polysiloxane encapsulation material. Orbit's version of polysiloxane is a proprietary mixture of base material, quartz, fillers, and catalysts. INEEL has pursued the possibility of using the polysiloxane material as both an encapsulate for stored and retrieved transuranic (TRU) waste, as well as for mixed waste salt material. In addition, INEEL has considered using polysiloxane as a grouting agent for in situ stabilization of buried waste. Currently, the only sponsor for the work is EM-50.



SECTION 5

COST

Methodology

Cost estimates are based on experience with both cement at the engineering scale and with polysiloxane encapsulation in the laboratory. In addition, discussions with polysiloxane supply companies were used in estimating the cost of the base material as a commodity purchased in bulk amounts. Current price for the base material is \$8/lbm and once a consumer market develops for this material it may drop as low as \$4/lbm.

Cost Analysis and Conclusions

A preliminary cost estimate was performed in which the cost of disposing the polysiloxane based waste form was compared to the cost of mixing salt waste with cement. The estimate assumed that cement could only obtain 10% waste loadings, while polysiloxane could achieve 30%. Final disposal costs were estimated at \$500/ft³ based on information available from the commercial mixed waste disposal facility, Envirocare of Utah. It was further estimated, based on previous development efforts, that each cubic foot of salt material requires 71.7 lb of polysiloxane. For cement based waste forms, each cubic foot of waste becomes 10 ft³ of disposed material. Therefore, if the cost of concrete is assumed negligible, the disposal cost alone is \$5,000 per cubic foot of original waste.

Current pricing on the polysiloxane system is approximately \$8/lb. Therefore, for each cubic foot of salt waste, the mixing/treatment cost would be (\$8 x 71.7 lb) \$573. Based on the 30% waste loading and the higher density of polysiloxane, the disposal only cost is \$1,331 at the \$500 /ft³ rate. The total cost to treat and dispose of a cubic foot of salt via polysiloxane is \$573 and \$1,331, for a total of \$1,904 per cubic foot of salt waste. This compares with approximately \$5,000 per cubic foot of salt for the concrete/salt mixture or a savings factor of 2.6.

An analysis of operating costs and capital costs associated with the polysiloxane encapsulation process has not been performed in detail; however, it is estimated that the basic mixing apparatus and extruder systems can be procured off the shelf. Facility requirements for a polysiloxane system are similar in nature to that required for a cement mixing system.

Based on the above assessments a rough order-of-magnitude (ROM) estimate for installation, start-up, and capital costs is possible. Assuming a system similar to that currently used for low temperature cement and ceramic methods, design, capital equipment, installation, and start-up costs would range between 600K to \$1,000K. This estimate assumes an available facility for housing the equipment with a throughput capacity of ~one 55-gallon barrel per day. The cost estimate also includes those resources necessary to secure the required environmental and operating permits (~200K). These costs are considerably less than those required for a comparable vitrification or high temperature system, where development, design, installation, and capital costs can exceed \$10,000K.

Cost Conclusions

Based on the preliminary cost estimates, the polysiloxane encapsulation is cost competitive with using cement for mixed waste stabilization.



SECTION 6

REGULATORY AND POLICY ISSUES

Regulatory Considerations

The regulatory goal of end users deploying the polysiloxane process is to produce encapsulated waste forms that meet EPA's 40 CFR 268.40 Land Disposal Restriction (LDR) and UTs for the burial of TC RCRA hazardous wastes that are otherwise prohibited from land disposal. For treating RCRA hazardous waste, any polysiloxane full-scale treatment facility will require a RCRA permit or a modification to an existing RCRA permit.

In addition, NRC 10 CFR 61 waste form testing will be necessary if disposal is to be in an NRC licensed facility. Additional requirements for applying the polysiloxane process at a federal facility include a National Environmental Policy Act (NEPA) review (a categorical exclusion is most likely to be applied), and any air emission considerations and/or permits as required under the National Environmental Standards for Hazardous Air Pollutants (NESHAPS) and Prevention of Significant Deterioration standards. Any commercial facility treating radiological waste must secure an NRC permit.

The bench-scale testing and development of the polysiloxane process to date has received NEPA approval through a categorical treatability study exclusion. The cognizant RCRA regulatory authority must be notified 45 days before receiving treatability samples for testing.

Safety, Risks, Benefits, and Community Reaction

Worker Safety Issues

Polysiloxane encapsulation is an inherently safe operation not prone to fire, explosion, or excessive heat of hydration during curing. Simple industrial equipment can be used to implement the technology and standard radiological controls can be applied to avoid the spread of contaminants during processing. Since there is no known offgassing of hazardous or radioactive materials beyond that of hydrogen, there are no airborne safety problems.

Potential Environmental Impacts

Polysiloxane encapsulation does not involve any hazardous materials other than the material being encapsulated. In addition, there is no offgas treatment required other than standard HEPA filtered facilities. The manufacture of the base materials has no environmental impact and application of the encapsulation process is similar in nature to the ongoing operations at other DOE facilities.

Potential Socioeconomic Impacts and Community Perceptions

The only impact on community reaction would come in the disposal of the waste form either in state or out of state for transportation issues. The resulting waste form, however, lends itself to expedited disposal. Regardless of the process applied to the waste, the stakeholder community will have the opportunity to comment on any proposed process. The polysiloxane encapsulation process is so environmentally benign, it is unlikely that this stabilization process will cause concern since its durability could be made greater than concrete and it does not adversely impact quality of life issues. In addition, the increased waste loadings will result in favorable decreases in the final disposed waste volume.



SECTION 7

LESSONS LEARNED

Technology Selection Considerations

Upon choosing polysiloxane microencapsulation as a stabilization treatment option, waste managers and end users in the DOE Complex will have to consider several factors before full-scale implementation. The degree of consideration for these factors will be highly dependent on the waste characteristics and will consist of the following:

Throughput and Total Volume of the Waste to be Treated

These values will determine the size and configuration of the mixer and extruder system, as well as the amount of catalyst material and desired cure time.

Type of Catalyst

Components in the waste stream could prematurely poison the platinum catalyst. Alternatives such as oxides and hydrides may better serve the particular application.

Presizing and Pretreatment Requirements

Large solid materials will require presizing to about 100 microns to ensure homogeneity of the waste mix. If the waste stream contains relatively large quantities of RCRA hazardous components or other incompatible constituents, additional additives to lower the solubility, mobility or toxicity of these components may be necessary. These steps may require additional reactors, vessels, stages, and/or feed ports.

Backend Sampling and Analysis Requirements

To ensure that the polysiloxane encapsulated final waste form meets the specific disposal criteria, the end user will be required to provide the necessary sampling and analytical equipment.

Deployment of the polysiloxane system appears fairly straightforward involving mainly off-the-shelf mixers and feed systems. Treatability and mixing studies are recommended to develop the optimum blend of waste and polysiloxane before any large-scale operations. By far the biggest effort to applying this technology would be the permitting and facility construction issues associated with any mixed waste handling facility.

Technology Limitations and Needs for Future Development

The technology is currently limited to nonaqueous solid materials. It is ideally suited for granular materials such as evaporator pond salts and calcined material; however, the process could easily be applied to any solid mixed waste. For this case, a pretreatment/presizing process would be required such as the cryofracture process. In cryofracture, solid mixed waste such as drums of TRU waste at INEEL or Rocky Flats could be frozen with liquid nitrogen and brittle fractured by crushing (essentially shredded with no contamination spread or threat of fire or explosion). The fractured debris could then be encapsulated with polysiloxane and placed in 4x 4 x 8-ft polyethylene boxes for shallow land burial.

Like many other recently advanced and developed polymeric processes and sol-gel techniques, polysiloxane is only a microencapsulation technique and is not in principle truly or consistently stabilizing the hazardous and toxic components in the waste stream through chemical reactions. Even though TCLP testing may indicate that the RCRA hazardous metals in the polysiloxane waste form leach below the standards set for by the EPA LDRs, no guarantee that these metals will never leach over time is provided. Consequently, long-term durability testing of the polysiloxane based waste forms is needed.



Technology Selection Considerations

Obviously, DOE Complexwide end users with the responsibility of mixed waste management need to consider multiple factors when selecting a low temperature stabilization technology, like polysiloxane. The most important factors are usually total waste volume, waste characteristics and constituents, disposal site criteria, technology versatility, and stakeholder concerns.

Waste Volume

The greater the volume of a relatively homogeneous waste inventory, the greater the benefits of a cement grout alternative, like polysiloxane. Even though the cement grout and polysiloxane processes are similar, the up front capital costs for polysiloxane will be slightly higher due to the more complicated extruder, use of a catalyst, and need to inventory expensive chemical precursors. The more waste that is treated the greater the savings in handling, transportation, and disposal costs as a result of the greater waste loadings polysiloxane can provide. If there is sufficient waste volume these greater savings can more than recover the higher up front costs.

Waste Characteristics and Constituents

Since the polysiloxane method is primarily an encapsulation process, wastes containing high (i.e., >500 ppm) concentrations of RCRA TCLP methods may not be sufficiently immobilized. Depending on how the TCLP samples are prepared from the waste form, these samples may fail, especially at the lower UTS levels. These speculated poor results might require pretreatment steps to lower the solubility of troublesome constituents before the polysiloxane process. Size reduction of the waste feed may also be required to ensure thorough mixing and adequate microencapsulation. Depending on the particular troublesome component and its concentration, these pretreatment steps may be too expensive to implement. As a consequence, investigations into other inorganic based techniques, such as modified cement grouts and low temperature ceramics, may be justified.

Disposal Site Criteria

The criteria and regulatory requirements established for the disposal sites identified for the final waste form can influence the method chosen for stabilization. Many sites only require that LDRs be met for the RCRA hazardous waste components. For RCRA hazardous heavy metals these restrictions are the lower level UTS standards.

Technology Versatility

The primary reason that polysiloxane encapsulation offers an attractive alternative to other treatment/encapsulation options is the straightforward nature of application. Very limited engineering development would be required to build a prototype facility, which could eventually be expanded into a full production operation capable of handling a variety of waste streams. No major investments would be required to perform engineering design studies; rather, the pilot plant could be designed using system integration of existing off-the-shelf systems.

Stakeholder Concerns

In general stakeholders desire low-temperature, nonoffgas producing stabilization technologies that generate no secondary wastes, minimize disposal volumes, and ensure long-term durability. Polysiloxane meets the first four criteria, but very little data exist to support its long-term effectiveness. Critics of the technology question polysiloxane's ability to remain durable over time, especially after encapsulating wastes containing high levels of salts and RCRA hazardous metals.



APPENDIX A

BIBLIOGRAPHY

1. Loomis, G.G., et. al., "Cryofracture as a Tool for Preprocessing Retrieved Buried and Stored Transuranic Waste," Waste Management'93, Tucson, Arizona, February 28–March 4, 1993.
2. Loomis, G.G. and M.J. Sherick, Alternative Disposal Options for Alpha-Mixed Low-Level Waste, 17th Annual DOE Low Level Radioactive Waste Management Conference, Phoenix, Arizona, December 12–14, 1995.
3. Loomis, G.G., et. al., " Mixed Waste Salt Encapsulation Using Polysiloxane-Final Report," INEEL/EXT-97-01234, November 1997.
4. Loomis, G.G., et. al., "Mixed Waste Salt Encapsulation Using Polysiloxane," WM-98 paper Tucson Arizona, March 1–5, 1998.
5. Shvetsov, K., et. al., Determination of the Structural Peculiarities of the Material and the Components Distribution-Cerametalic Silicone Foam Rubber Research Programme-Kurchatov Institute- April 1994.



APPENDIX B

TMS DATA ELEMENTS

Funding Source

This section provides cross-reference information in regards to the EM-50 Mixed Waste Focus Area contract established for development of the Polysiloxane technology. The Department of Energy – Headquarters (DOE-HQ) Technology Management System (TMS) tracking number is provided, as well as the specific Technical Task Plan (TTP).

TMS # 2045 Polysiloxane Encapsulation of Mixed Waste Salts

TTP # ID77MW41 Encapsulation of MW Salts for Final Disposal (TRU & LLW)



APPENDIX C

ACRONYMS

CSF	Ceramic Silicon Foam
DOE	Department of Energy
DOT	Department of Transportation
EM	Environmental Management
EPA	Environmental Protection Agency
FR	Federal Register
HEPA	high-efficiency particulate air
HLW	high-level waste
INEEL	Idaho National Engineering and Environmental Laboratory
ITSR	Innovative Technology Summary Report
LDR	Land Disposal Restriction
LLW	Low-Level Waste
MWFA	Mixed Waste Focus Area
NEPA	National Environmental Policy Act
NESHAPS	National Environmental Standards for Hazardous Air Pollutants
NFPA	National Fire Protection Association
NRC	Nuclear Regulatory Commission
OST	Office of Science and Technology
RCRA	Resource Conservation and Recovery Act
ROM	rough order of magnitude
RTV	Room Temperature Vulcanizing
RWMC	Radioactive Waste Management Complex
SDA	Subsurface Disposal Area
SEM	Scanning Electron Microscope
TC	Toxicity Characteristic
TCE	Trichloroethylene
TCLP	toxicity characterization leaching procedure
TRU	transuranic
UTS	Universal Treatment Standard

