SILICON-POLYMER ENCAPSULATION OF HIGH-LEVEL CALCINE WASTE FOR TRANSPORTATION OR DISPOSAL

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ABSTRACT

Engineers at the Idaho National Engineering and Environmental Laboratory (INEEL) are investigating the use of a proprietary silicon-polymer to encapsulate high-level calcine waste stored at the INEEL's Idaho Nuclear Technology and Engineering Center (INTEC). The silicon-polymer-encapsulated waste may be suitable for direct disposal at a radioactive waste disposal facility or for transport to an offsite melter for further processing. In connection with silicon-polymer encapsulation, the University of Akron, under special arrangement with Orbit Technologies, the originator of the Polymer Encapsulation Technology (PET), has studied a simulated waste material from INTEC called pilot-scale calcine that contains hazardous materials but no radioactive isotopes. In this study, Toxicity Characteristic Leaching Procedure (TCLP) and Materials Characterization Center Test 1P were performed to test the waste form for disposal. In addition, a maximum waste loading was established for transporting the calcine waste at INTEC to an offsite melter. For this maximum waste loading, compressive strength testing, 10-m drop testing, melt testing, and a Department of Transportation (DOT) oxidizer test were performed.

INTRODUCTION

At the INEEL, the Department of Energy reprocessed spent nuclear fuel at the Idaho Chemical Processing Plant (now the Idaho Nuclear Technology and Engineering Center INTEC). The reprocessing resulted in a liquid solution considered high level waste that was then treated in a process that resulted in a dry granular high-level waste called calcined waste. This material is not only a mixed waste with heavy metals but also highly radioactive and presently stored in steel bins. The Department of Energy (DOE) is currently considering the final disposition of this material, and the plans include melting the material into a glass waste form for shipment to a permanent federal disposal site. DOE is interested in alternatives to building a glass melter in Idaho and has proposed that the waste be temporarily stabilized for shipment to an offsite melter potentially at Hanford. Another option is to use a nonthermal encapsulation process for the calcine waste such that the resulting waste form satisfies the waste shipping and acceptance criteria at the proposed disposal site. Silicon-polymer encapsulation is a potential candidate technology that could achieve both of these goals. This report presents the results of an experimental study investigating these options.

For waste acceptance (1) at a high-level waste repository the waste must be contained and shipped in a multipurpose canister (MPC) made of austinitic stainless steel with concentric necks and lifting flanges. There has been considerable drop testing and canister design (e.g., 2) for the MPC's and it is assumed that if rendered to practice, the silicon-polymer/calcine mixture would be poured directly into these already developed containers. Other specific disposal (repository) requirements are that the waste must:

- Be a in solid form and placed in sealed containers
- Be consolidated to limit the availability and generation of particulates
- Be noncombustible
- Have no free liquids
- Not be explosive, pyrophoric, or chemically reactive.

These acceptance criteria were examined in the experimental study.

TECHNOLOGY DESCRIPTION/PAST STUDIES USING POLYSILOXANE

The silicon-polymer system is a simple room temperature mixing process in which the base fluid polysiloxane material along with proprietary additives are blended with dry granular waste materials. This mixture is extruded into waste containers while a platinum catalyst is added to start a silicon polymerization process. Polysiloxane is an inorganic thermosetting polymer containing about 50% vinyl-polydimethyl-siloxane, 20% quartz, 25% proprietary ingredients and <5% water. The polysiloxane/ waste mixture sets at low temperatures (essentially room temperature) and thus requires minimal off-gas systems, contains no volatile metals like mercury, and generates no 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 of organic compounds with the chemical resistance of silicone materials. This sturdy formation allows the silicone molecule to be resistant to extreme temperatures, pressures and chemical environments. Specifically PET can resist contact with acids, alkalis, and attack from oxygen.

Orbit's PET was first proposed for use at the Chernobyl plant because of its excellent radiation resistance, Studies (3) show that under gamma irradiation, the compressive strength actually increases as the product changes to a more ceramic form.

INEEL studied polysiloxane encapsulation of Pad-A salt which has plutonium/americium in the pCi/g range and chromium +6 in the 180 ppm range. During this FY 1997 study (4, 5), a pad-A surrogate was formulated with 1044 ppm chromium +6, which is 5.8 times higher than the actual pad-A salt but without the radioactive component. It was determined in that study that at 30% waste loadings, the waste form passed the 1997 Universal Treatment Standard (UTS) at 2.4 ppm in the leachate with a allowable of 5 ppm. It was concluded that if the polysiloxane and actual waste with 5.8 times less chromium were mixed at 30 wt % waste loading, the waste form would most probably pass the current UTS of 0.86 ppm as well.

The INEEL also examined encapsulation of a proposed low-level calcined material that would result from moving the calcine waste through the TRUEX process and then resin columns for Cesium removal in a FY-98 study (6). The surrogate material was made according to formulas provided by INTEC (a dry surrogate with 4500 ppm Cd, 7800 ppm Cr, 2440 ppm lead, 1960 ppm Hg). With proprietary scavengers, at 38wt% waste loading, TCLP leachate results were: Cadmium 3.5 ppm, Chromium 3.5 ppm, lead 2.2 ppm and mercury 0.002 ppm compared to most restrictive treatment standard of 0.11 ppm for cadmium,0.86 ppm for chromium, 0.37 ppm for lead, and 0.025 ppm for mercury. Therefore, only mercury passed the most restrictive standard. In that study, it was recommended that more work on the metal scavengers could lead to better results.

EXPERIMENTAL DESCRIPTION

The Orbit PET material and the nonradioactive but hazardous calcine surrogate (created at the INEEL INTEC during pilot scale operations) were combined in a mixing study and evaluated with several standard waste form acceptance tests. The objective of this study was to evaluate two separate uses of the polysiloxane encapsulation technology. The first part of the study performed testing relating to creating waste forms suitable for disposal at a final high-level repository. The second part of the study examined the potential transportation of the encapsulated calcine material to an offsite melter for processing.

Testing for the disposal option included mixing studies to determine the maximum waste loading that could still pass the Universal Treatment Standard for the Toxicity Characteristic Leaching Procedure (TCLP) and additionally show long-term durability in the Materials Characteristic Center test MCC-1P.

Testing performed for the transportation option included a mixing study to determine the maximum waste loading to be considered a transportable material with compressive strength testing, a 10-m drop test for determining the fragmentation of the resultant material, a Department of Transportation Oxidizer Test to determine flammability and oxidizer potential, and a Thermo-Gravimetric Melting test to determine the melting temperature of transported material. All these tests as well as all testing results are described in detail (7).

RESULTS

Two different Orbit Technologies formulations of polysiloxane were investigated to address two different performance objectives. The commercial formulations were Orbit's PET 99-1 material which was used to investigate final waste storage and disposal, and Orbit's PET 99-2 was used to investigate temporary storage and transportation issues

Baseline Characterization

To obtain baseline waste concentration in the pilot calcine,, Inductively Coupled Plasma-Mass Spectroscopy was performed. Table 1 summarizes the results of that study indicating large quantities of chromium, cadmium and some lead. These values were used in all subsequent calculations involving calcine metal concentrations (e.g., MCC-1P). The greatest metal concentrations were chromium (1036 mg/kg) and cadmium (330 mg/kg).

Table 1. Metal Assay of the Calcine Waste

Metal	Concentration (mg/kg)	Metal	Concentration (mg/kg)
Cd	330	As	< 0.2
Cr	1036	Ba	< 20
Pb	25	Se	< 0.4

Studies Supporting Long-Term Disposal Options

A mixing study was performed in which various combinations of the pilot calcine waste,PET-99-1 and dry and aqueous mixtures of heavy metal scavengers (referred to as JJC1, JJC2, and JJC3) were parametrically evaluated against TCLP and MCC-1P testing protocol to determine leaching of contaminants.

As a baseline, and based on previous success with nitrate surrogate salts (4,5), heavy metal leaching was examined first with an improved Orbit formulation designated as PET 99-1. Cadmium and chromium were selectively monitored in the TCLP testing because they have the greatest metal concentrations in the calcine waste (see Table 1). Table 2 shows the cadmium and chromium TCLP leaching in PET 99-1(no scavengers) encapsulated samples with increasing waste load. Cadmium and chromium concentrations exceeded the Universal Treatment Standards (UTS) levels. In addition, the data shows an expected increase in the leachate metal concentration with an increase waste load.

Table 2. Cadmium and Chromium Leaching from PET 99-1 without pretreatment.

Metal	PET 99-1 40% Load (mg/l)	PET 99-1 75% Load (mg/l)	UTS (mg/l)
Cadmium	0.69 ± 0.01	2.14 ± 0.02	0.11
Chromium	2.15 ± 0.02	7.10 ± 0.06	0.60

Pilot calcine waste was then pretreated with a variety of proprietary pretreatment materials, some of which involved an aqueous mixture of scavenger followed by oven drying at 100°C, and then dry encapsulation of the total mixture with the PET-99-1 material. The pretreatment materials are called JJC1 and JJC2. Table 3 shows cadmium and chromium TCLP results from JJC1 and JJC2 pretreatments without aqueous mixing. Although the metal levels are still greater than the UTS, there was a marked decrease in metal leachate concentration with increasing waste load (41% reduction for Cr and 50% reduction for Cd for a waste load increase from 40% to 50%). Furthermore, JJC2 addition reduced both cadmium and chromium concentrations at comparable waste load (reduced Cr leaching by 75% and Cd leaching by 73%), indicating its potential; however, the UTS was still not passed. Based on the success of JJC1 and JJC2 addition, it was determined that aqueous pretreatment of the calcine waste before encapsulation could also provide a means to further reduce leaching of heavy metals.

Table 3. Cadmium and Chromium Leaching from JJC1 Pretreated Waste in PET 99-1

Metal	JJC1 40% Load (mg/l)	JJC1 50% Load (mg/l)	JJC1[a] 40% Load (mg/l)	UTS (mg/l)
Cadmium	1.24 ± 0.01	0.62 ± 0.004	0.34 ± 0.01	0.11
Chromium	4.55 ± 0.02	2.67 ± 0.02	1.14 ± 0.02	0.60

a) A sample also contains 5.0% by weight of JJC2.

The aqueous pretreatment of the calcine waste was accomplished by mixing the calcine waste, water, and additives (JJC1, JJC2, and JJC3 at 5% wt.) and then evaporating the water in an oven at 100°C. Table 4 shows the leaching results after aqueous pretreatment before encapsulation. Results indicate that aqueous pretreatment of the JJC1-treated waste reduced the leaching of cadmium (by as much as 70%) from the samples. Aqueous pretreatment, however, did not significantly reduce leaching compared to direct material addition to the PET-99-1 system.

Table 4. Effect of Aqueous Pretreatment on Leaching from PET 99-1

Metal	Calcine[a] 40% Load (mg/l)	JJC1[a] 40% Load (mg/l)	Calcine[b] 40% Load (mg/l)	JJC1[b] 40% Load (mg/l)	UTS (mg/l)
Cadmium	0.89 ± 0.01	0.81 ± 0.01	0.99 ± 0.01	0.24 ± 0.004	0.11
Chromium	2.89 ± 0.03	2.80 ± 0.03	2.41 ± 0.02	1.83 ± 0.01	0.60

a Sample also contains 7.0% JJC2 by weight
b Sample also contains 5.7% JJC2 and 5.7% JJC3 by weight

Direct, dry mixing of the JJC2 material was then applied to the PET 99-1/ pilot calcine mixture in increasing doses of the JJC2 material. TCLP results as a function of JJC2 addition for cadmium and chromium are shown in Table 5. JJC2 reduced the leaching of cadmium and chromium, with a 77% reduction in cadmium leaching and 71% reduction in chromium leaching at 5% addition. More importantly, the final TCLP values are less than the UTS levels of both cadmium and chromium. These results also imply that by increasing the proportion of JJC2 beyond 5% it might be possible to reduce the cadmium and chromium leachate concentrations further and thus perhaps allow higher waste loadings. Increasing the mass of JJC2 beyond 5%, however, poisoned the catalyst and prohibited sample curing.

Table 5. Cadmium and Chromium TCLP as a function of JJC2 addition with PET1 at 40% waste load.

JJC2 (wt%)	Cadmium[a] (mg/l)	Chromium[b] (mg/l)
0.0	0.69	2.15
0.8	0.78	2.44
1.6	0.51	1.69
5.0	0.10	0.58

a UTS = 0.11 mg/l
b UTS = 0.60 mg/l

The waste form (40 wt% calcine) using 5 wt% JJ2 additive(dry mixing) was then subjected to MCC-1P testing. This test forms a basis for examining the chemical durability of waste forms. Matrix B of the testing protocol was selected for this test (reference leachants: brine, silicate and de-ionized water). Samples containing 40% waste and 5% JCC2 (note: this combination achieved the lowest TCLP values) of known volume and surface area were immersed without agitation for a period of 28 days in a closed environmental chamber at a fixed temperature of 90°C. The 28 day Total Mass Loss Rate (TMLR) and Normalized Elemental Loss Rates for cadmium and chromium as a function of leachant condition are shown in Table 6. The TMLR for all three leachants was less than four g/m2-day, with normalized elemental loss rates varying from 0 to 27.8 g/m2-day. Leachant characteristic impacts the leaching rate and is metal specific. These numbers compare with values for glass in the less than 1 g/m2-day (8). A parametric study involving different waste loadings would be required to optimize the leaching results from MCC-1P testing.

Table 6. 28 Day Total Mass Loss Rate (TMLR) and Normalized Elemental Leach Rates as a Function of Leachant for a 40 wt% waste loading.

Leachant	TMLR (g/m^2-day)	Cd (g/m^2-day)	Cr (g/m^2-day)
Brine	1.0	6.3	0.0
Silicate	3.9	0.0	19.4
De-Ionized Water	2.0	0.0	27.8

Note: A zero reading indicates a nondetect in the sample.

Studies Supporting the Transportation of Calcine to an Offsite Melter

Several specific tests were performed to examine the maximum waste loading that could be considered a candidate waste form for transportation from INEEL to an offsite melter. Specific tests included compressive strength, 10-m drop test, a DOT oxidizer test, and a minimum melting temperature test.

The mechanical integrity of the waste and its ability to withstand loading pressures in a disposal environment is directly related to compressive strength. Table 7 shows the results of the compressive strength using two different base formulations. Compressive strength for both the base formulations at 80% waste load is much greater than the minimum National Regulatory Commission (NRC) requirement of 50 psi. Neither specimen failed under the maximum load available with the selected apparatus, corresponding to greater than 640 psi with 2" diameter samples.

Table 7. Compressive Strength for Base Formulations.

Material	Waste Loading (wt%)	Compressive Strength (psi)
PET 99-1	80%	> 640
PET 99-2	80%	> 640

A drop test was performed to examine encapsulated sample behavior when dropped from a vertical distance of 10 m onto a stainless steel or concrete surface. For this test, a sample (80% waste loading, PET 99-2 with 5% JCC2) weighing 215 g was dropped from a distance of 10 m (test performed on both a concrete and stainless steel surface). Examination of the drop area for debris and examination of the monolith showed virtually no fracture and no degradation of the material or its original form. In addition, no debris from the sample was observed on the capture cloth.

A DOT Oxidizer test was performed to compare a test substance and three reference substances with regards to their ability to increase the burning rate or burning intensity of a combustible solid. Testing was carried out by Hark Laboratories, Inc. (Barberton, Ohio). Each mixture was arranged in a conical pile and a wire loop placed inside the pile. The wire was then heated to 1000°C until the first sign of combustion or until it was clear that the mixture would not ignite. The time for combustion was then recorded for each substance. At 80% waste loading the PET 99-2 material did not burn after approximately 20 minutes. Based on these results the PET 99-2 waste form would not have a specific packing requirement as an oxidizer (i.e., it did not burn).

Thermal gravimetric analysis was carried out to determine the volatility and melting temperatures of various components of the encapsulated waste sample. Figure 1 shows sample weight loss as a function of temperature using the PET 99-2 formulation at 80% waste load. There was approximately 5% weight loss up to 450°C and ultimately 11% weight loss at 1000°C. The resultant material was a dry powder.

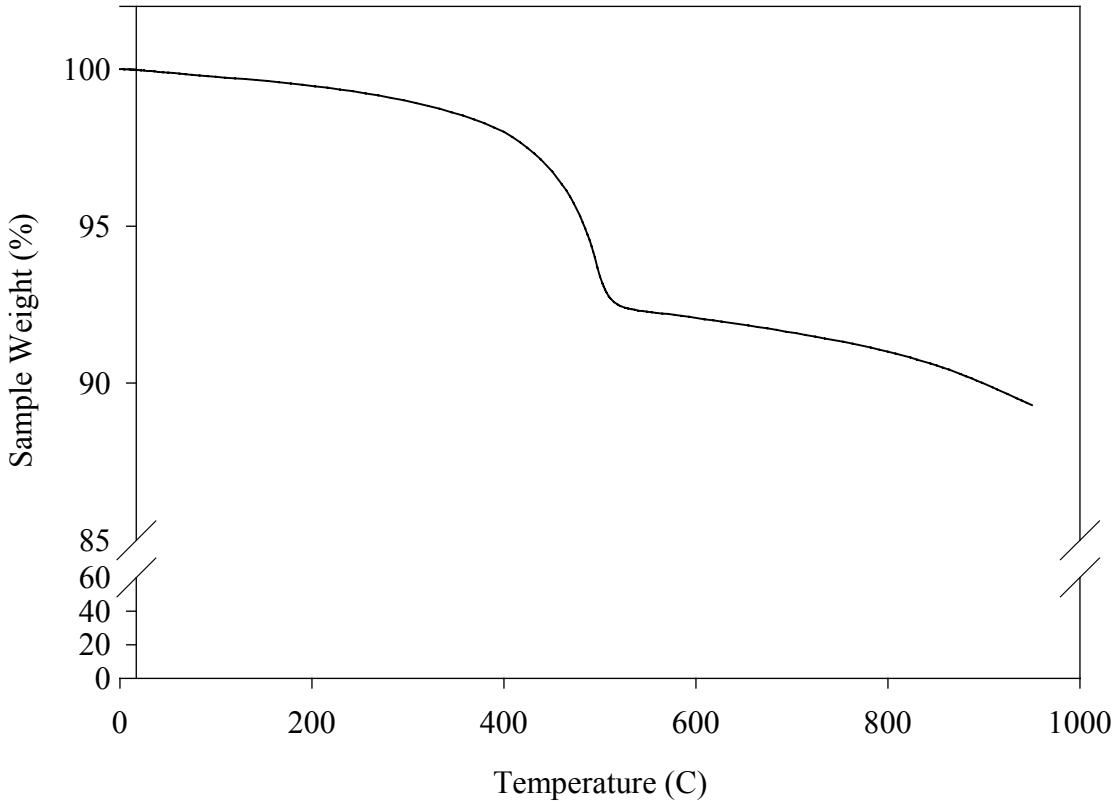

Figure 1. Thermal gravimetric analysis (TGA) of 80% waste load PET 99-2 sample.

DISCUSSION OF RESULTS

The experimental study showed a positive proof of concept for both applications of the silicon-polymer encapsulation process.

Disposal Option: A mixture of 40 wt% calcine waste and 60 wt% Orbit Technologies Polymer PET-99-1, with proprietary heavy metal scavenger "JJ2", resulted in a waste form that could be considered possible for disposal. During Toxicity Characteristic Leach Procedure (TCLP) testing the Universal Treatment Standard was met for both cadmium and chromium using a loading of 5wt% of the "JJ2" scavenger material which is blended as a nonaqueous dry material. By using a higher percentage of the "JJ2" material, it would be possible to accept higher concentrations of cadmium and chromium in the waste and still pass TCLP; however in the present study further addition of the "JJ2" caused a poisoning of the catalyst which prevented the waste form to cure. Further work with other scavengers would be required to achieve a higher waste loading or a higher contaminant concentration in the base material and still cure as well as pass TCLP for the final waste form. Further evidence of a positive proof-of concept is that the MCC-1P test on this waste form at 40 wt% loading showed relatively low concentrations of contaminants in the leachate. The TMLR for all three leachants was less than four g/m2-day, with normalized elemental loss rates varying from 0 to 27.8 g/m2-day. Leachant characteristic impacts the leaching rate and is metal specific. These numbers compare to values for glass in the "less than 1 g/m2-day (8). Additional evaluation of the leaching rate under variable environmental conditions would be needed to adequately characterize these effects. In addition, it would be expedient to perform a parametric study involving waste loading's effect on MCC-1P leaching rate. Even though these initial results do not meet those found in the glass waste form, the initial results suggest a relatively rugged waste form most likely technically adequate for disposal.

Transportation Option: The concept of using the PET process to encapsulate Calcine waste prior to shipment to an offsite melter has shown a positive proof-of-concept. A cohesive monolith suitable for drop testing was formulated at 80wt% pilot calcine material with the PET-99-2 formulation provided by Orbit. The compressive strength of this waste form was above 640psi and the sample did not burn for 20 minutes in a DOT Oxidizer test. Most importantly, during the drop test on both a concrete floor and steel plate, the monolith was essentially unaffected by the drop, rather it simply elastically bounced. When coupled with an approved stainless steel container virtually no spread of contamination would be expected in a transportation accident. In addition, the material was found to melt at 1000C meaning it could be reduced to molten form at an offsite melter without chemical dissolution.

CONCLUSIONS/RECOMMENDATIONS

First, the concept of using silicon-polymer to encapsulate calcine waste for disposal at a permanent high-level waste repository has shown a positive proof of concept. Orbit's Polymer Encapsulation Technology created a sample of the encapsulated calcine waste at 40% loading that passed Universal Treatment Standards for the TCLP testing protocol for the main contaminants of cadmium and chromium present in the pilot calcine material from INEEL. In addition, the first ever test of a polysiloxane waste form based on a 40 wt% pilot calcine showed potential for high durability in the MCC-1P testing.

Second, a positive proof-of-concept was obtained for using PET for creating a maximum loaded waste form suitable for transportation to an off-site melter. Orbit's Polymer Encapsulation Technology created a sample of the encapsulated calcine waste at 80% loading that exceeded 640psi compressive strength. This monolith was dropped 10 m onto a concrete pad and metal plate without mass loss indicating essentially no contamination spread would be expected in a transportation accident. The monolith also passed the Department of Transportation (DOT) Oxidizer Test and could be melted at 1000C.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Assistant Secretary for Environmental Management, under DOE Idaho Operations Office Contract DE-AC07-99ID13727.

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