Properties of Vitrified Rocky Flats TRUW with Different Waste Loadings

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ABSTRACT

Leach rates, phase structures, and mechanical properties of simulated Rocky Flats Plant 1st and 2nd stage sludge vitrified in an arc melter are described as a function of waste to soil fraction and method of devitrification to produce the glass-ceramic waste form. Volatile, hazardous, and transuranic (TRU) surrogate metals were added to assess dissolution effects. Zirconia and titania were also added to confirm their ability as transuranic-surrogate getters.

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INTRODUCTION

One of the major waste streams at the Idaho National Engineering Laboratory (INEL) is a

combination of the Rocky Flats Plant 1st and 2nd stage sludges (hydrated metal oxides or H-series), which constitutes about 20 wt% of the buried waste. A similar mass fraction is in interim storage.

The buried waste is commingled with about five times as much soil that has become contaminated as the containers have deteriorated. There are six or seven different major input waste streams that will probably be fed into a treatment system with minimum sorting; some waste stream limits will be

required to obtain appropriate tolerances on final waste form properties. Properties and compositions of various types of waste forms are provided in a treatise edited by Lutze & Ewing.¹ The waste form compositional range considered here is that of an iron-enriched basalt (IFB), discussed in detail

elsewhere.^{2,3}

A number of studies have shown that vitrification of the transuranic-contaminated mixed waste (TRUW) results in a stable waste form with life cycle costs lower than cementation.^{4,5,6} It has also been shown that high-temperature plasma arc melters are required to melt the waste/soil mixtures and the structural metals in the buried waste, as well as to handle the heterogeneous feed composition robustly.^{7,8}

The purpose of this paper is to report on waste form property variations of the H-series waste melted with various fractions of soil, plus volatile and hazardous metals and transuranic surrogates. Optimally, the waste form will minimize the bulk leach rate, maximize the volume reduction, minimize the additives needed, and stabilize the transuranic nuclides. Topics to be discussed include the input and final compositions, the melting and crystallization processes, the test results, and conclusions.

WASTE STREAM AND FORM COMPOSITION

The H-series waste stream may be either a 1st stage sludge (H1) or a mix of 1st and 2nd stage sludges (H2). The H1-series is studied here because its higher alkali concentration will have a greater effect on the tolerance limits of the leach rate. The composition of the H1-series waste (after dehydration of 60% as water) is shown in Fig. 1 as a function of wt% of soil.⁹

Soil fractions from 0% (H1-0) to 100% (H1-100) were investigated. Cd, Cr, Pb and Zn (1% each) were added as hazardous metals with various degrees of volatility. Cesium (1%) was added to simulate the Cs-137 nuclide; the Ca in the waste stream should be a reasonable Sr surrogate. Cerium and samarium (1% each) were used as TRU surrogates. All were added as oxides.

The Synroc additives, zirconia and titania, had been found to act as getters for both transuranics¹⁰ and TRU surrogates.¹¹ Five wt% of each were added to give sufficient quantities for analysis, based on the aforementioned experiments. Later it was found that an additional 1-3% ZrO_2 dissolved into the melt from the refractory. Ti and Zr are Group IVB elements in the Periodic Table; hence, the waste form is designated IEB4.

Fig. 1 H-series waste composition.

PROCESSING METHODS

The processing methods are thermal desorption and/or combustion of organics, melting in an arc melter, and a devitrification process. It was assumed that the waste had previously been oxidized. The appropriate mixture of oxides plus INEL soil was added to the melter in batch mode, melted in approximately one hour, and then cooled by various methods.

The arc melter system schematic is shown in Fig. 2. The melter is a water-cooled stainless steel crucible with a multiport top. Two 1-in. graphite electrodes are lowered through the top and are usually operated very close to, but above, the melt so that Joule heating dominates (>90%). Typical operating conditions are 100-200 A and 150-250 V. The present tests were made without a cold cap of feed material. The crucible is either unlined, lined with a coating of Sauereisen cement, or lined using a 0.5 inch-wall ceramic pot made mostly of ZrO_2 (54%), SiO_2 (27%), Al_2O_3 (16%) and CaO (3.3%).

Three cooling or devitrification methods are available. If fast-cooled (FC), the melt remains in

Fig. 2 Schematic of bench-scale arc melter system.

the water-cooled crucible lined with cement and cools through the 1250-1100°C crystallization range in about 5 min. If slow-cooled (SC), the melt remains in the crucible, but the water is turned off and drained, lengthening the crystallization period to 10-20 min. The third method is devitrification (DV) by core drilling samples from a FC or SC process, remelting in quartz tubes in an oven at 1400-1500°C, then lowering to 1200°C for 16 h, as per References 10 and 11, then annealing at 600-700°C, and cooling to room temperature.

EXPERIMENTAL RESULTS

Photomicrographs from the scanning electron microscope (SEM) for the SC and DV waste forms at 1000X-2000X magnification are given in Figs. 3 and 4, respectively. The amount of soil goes from 0% on the upper left to 100% on the lower right corner in 20% increments. It is apparent that as soil was added, fewer and smaller crystals formed. The crystals are usually smaller in the SC case than in the DV case. For H1-100/SC (Fig. 3), the slag is very reducing, resulting in iron spheres. In the DV case, some additional oxidation probably occurred when remelting, thus no obvious iron spheres. Phase and overall compositions were determined using energy dispersive x-ray spectroscopy (EDXS).

The crystals in Figs. 3 and 4 are of similar phase composition, irrespective of soil fraction or cooling method. The lightest colored crystals are either zirconia or a Zr-rich zirconolite, $(\text{Ca,Fe})_2(\text{Ti,Zr})_2\text{O}_7$. A few at 100% waste loading contain a mainly-Cs nepheline, $(\text{Cs,Na,K})(\text{Fe,Al})\text{SiO}_4$. The next lightest crystals or borders are either a Zr-rich zirconolite adjacent to zirconia or a more complex mineral or solid solution that also includes (Al,Cr). To get a better description, analysis is continuing. The Mg/Al/Fe/Cr spinels are gray and blocky. Some spinels include ulvoespinels (because of the reducing conditions) which are less chemically stable.¹² In Fig. 4, H1-100/DV, the light-gray blocky crystals are zircon, ZrSiO_4 . The feathery crystals are pyroxenes, and the background is composed of feldspathoids, feldspars and glass.

The TRU surrogates, Ce and Sm, are almost totally in the Zr-zirconolite phases with the balance in the glass/feldspar. Without a cold cap, essentially all of the Cd and Pb left the melt. Some Zn, most of the Cs, and essentially all of the Cr remained in the melt. The Zn and Cr are in the spinels and the Cs in the Cs-nepheline.

Leach tests and redox measurements were done by Cels-Laboratory Services, Corning, New York. The leach test used is the PCT, Method A, 7-day, static test of a crushed sample (74-149 μm) in deionized water at 90°C. Much data exists in the literature based on MCC-1 mass flux leach tests¹ using 28-day, static, monolithic samples in deionized water at 90°C. A method to convert from PCT-A data to MCC-1 for glass-ceramics had been developed¹³ using actual densities, volume to surface area, and normalizing with overall compositions from EDXS measurements. The method was calibrated for glass-ceramics over more than 5 orders of magnitude, with results equivalent to the

Fig. 3 IEB4/H-series slow-cooled waste form magnified 1000X-2000X.

Fig. 4 IEB4/H-series devitrified waste form magnified 1000X-2000X.

scatter in the original data. Apparently other attempts to convert PCT-A to MCC-1 values for the more narrow range of interest for glass have been unsuccessful.

Averaged PCT-A leach data from duplicate measurements are given in Table 1. Test methods were flame emission spectroscopy (Cs, Na), ICP (Ca, Si) and ICP/MS (Ce, Sm). The data show that the alkali elements leach more than the alkaline earths, which leach more than the TRU surrogates. Table 1 also includes the equivalent Environmental Assessment (EA) Glass normalized mean leach rates reported by Jantzen, et al.¹⁴ for comparison. The leach rates for IEB4/H1-40 are approximately an order of magnitude lower than obtained for the EA Glass. Figure 5 shows the converted normalized PCT-A leach rates as a function of soil wt%. Na leaches the most, with Cs second, followed closely by Si (the bulk rate indicator used here). Ca is a factor 10 lower, and Ce and Sm 10 to 100 times lower yet. There does not appear to be any significant difference between the SC and the DV leach rate values. Apparently in the SC case, the crystals are of similar fraction but are smaller and more difficult to see. Prior studies¹⁵ of IEB with coarse and fine grain crystals reported a similar result.

The leach rates of Na, Cs, and Si decrease with increased soil fraction, but Ca, Ce, and Sm rates are statistically flat. Na-nepheline apparently increases leach rates in glass, but here the Cs-nepheline results in lower Cs leach rates than found in other glass-ceramics.¹ Similar results were reported by others.¹⁶ Prior IEB studies had found a simple relationship between the bulk leach rate

Table 1. PCT-Method A 7-day leach rates in normalized mg/L.

Species	H1-0	H1-20	H1-40	H1-60	H1-80	H1-100	EA Glass
Si SC	2.16E+01	8.34E+02	2.35E+02	1.74E+02	9.08E+01	6.95E+01	3.92E+03
DV	1.92E+03	1.18E+03	2.76E+02	1.95E+02	1.41E+02	7.89E+01	
Ca SC	3.89E+00	6.67E+00	8.53E+00	4.34E+00	1.63E+01	5.93E+01	
DV	<1.73E-02	3.74E+00	4.01E+00	3.43E+00	6.51E+00	5.91E+01	
Na SC	2.87E+04	5.55E+01	2.50E+03	1.63E+03	3.78E+02	4.59E+02	1.33E+04
DV	2.21E+04	8.34E+03	7.54E+01	1.63E+03	1.03E+03	4.98E+02	
Cs SC	7.56E+04	4.50E+02	9.54E+02	5.49E+02	2.06E+02	6.07E+01	
DV	5.49E+04	1.95E+03	1.40E+03	5.80E+02	2.95E+02	9.26E+01	
Ce SC	<2.04E-02	1.00E+00	2.05E-01	1.62E+00	1.22E-01	6.05E-01	
DV	<4.76E-02	1.28E-01	7.59E+00	3.69E+00	9.56E-01	2.02E-01	
Sm SC	<5.66E-02	1.43E+00	1.92E-01	4.76E-01	1.43E-01	4.43E-01	
DV	<6.90E-02	1.47E-01	1.06E+01	5.34E+00	9.82E-01	2.08E-01	
Fe ²⁺ /Fe ^{tot}	0.38	0.71	0.93	0.96	0.93	0.86

Fig. 5 PCT-A leach rates for the (a) slow-cooled and (b) devitrified samples (converted).

and the Fe/Si ratio in the glass-ceramic for the A-series (average TRUW) as shown in Fig. 6.¹⁷ Also plotted and fitted in Fig. 6 are the SC and DV data for the IEB4/H1-series, using the Si rate as the bulk rate. Later IEB measurements,¹⁵ as well as some taken recently with the IEB/A-series¹⁸ indicate a shift down to the proximity of the IEB4 data is appropriate. The conclusion is that IEB and IEB4 data lie close together on this plot, possibly on a "universal" curve.

Fig. 6 Bulk leach rate for IEB/IEB4 as $f(\text{Fe}_3\text{O}_4/\text{SiO}_2)$.

The redox ratio, $\text{Fe}^{2+}/\text{Fe}^{\text{total}}$, for the SC samples is given in Table 1. A value of unity is fully reduced (all FeO). The values show that the high waste loadings are much more oxidizing. The DV samples were additionally oxidized during remelting.

Mechanical tests were made to compare the H1-series with other waste forms. Compressive strengths were measured using ASTM C39. Table 2 shows that the compressive strengths of the glasses and glass-ceramics are much higher than those of cement/concrete and all are higher than a typical requirement of 10 MPa, for a deep geologic repository. Respirable-fine tests were based on the impact test procedure of Jardine, Reedy and Mecham.¹⁹ Table 2 shows that the glass-ceramics generated no respirable fines under either the 10 or 15 μm size criteria.

Table 2. Mechanical tests of different waste form materials.

Waste Form	Compressive Strength (MPa)	Respirable Fines (wt%)			Smallest	Ref.
		<10 μm	<15 μm	<96 μm		
PCC	21-55	0.32	0.40	---	---	1,18
SPC	34-69	0.15	0.33	---	---	18
BSG	550	0.17	---	---	---	1
ASG/S-40	119	None	None	0.088	26 μm	18
IEB/A-40	430	None	None	None	>200 μm	18
IEB4/A-40	403	None	None	0.008	16 μm	18
IEB4/H-40	440	None	None	None	124 μm	18

DISCUSSION

The effects of soil addition on the waste form are the following. When the waste loading is increased (soil is decreased), the phase structure is more crystalline, the redox state is more oxidizing, the bulk leach rate (based on Si) increases, the Cs leach rate increases, but the TRU-surrogate leach rate is statistically flat. There is no significant difference between the leach rates of the slow-cooled (SC) and the devitrified (DV) waste forms over the range of soil added. The crystals are smaller in the slow-cooled waste form. This suggests that a special cooling process is probably not necessary for the H-series waste stream.

Optimum soil loading to minimize the bulk leach rate, maximize the waste loading (volume reduction), and minimize variations in waste form structure appears to be 30-50 wt% soil (50-70 wt% waste loading), or IEB4/H1-40. This is identical to the result obtained in prior IEB research for the average TRUW, i.e., IEB/A-40.²

On an absolute basis, the H1-series waste form quality is indicated by its ability to dissolve toxic metals or radionuclides. Mercury, chlorine, and sulfur will be in the offgas and require a secondary waste form, as will the extremely volatile heavy metals like Cd. This will be similar to most other thermal treatments. Zn, Pb and almost all of the Cr have been found dissolved in the very stable spinels. Most of the Cs is found dissolved in a mineral more stable than if it were in a borosilicate glass (BSG).

The effect of the Synroc additives (Ti, Zr) is to create a much higher concentration of very stable phases than in IEB or BSG. Some perform as TRU-surrogate (Ce, Sm) getters, as shown elsewhere for several actinides (Pu, Am, Np, Cm),¹⁰ as well as hosts for Sr (Ca). These crystals are surrounded by stable spinels, and less stable pyroxenes, feldspars and glass. The less stable phases are the hosts for the highest leaching species (Na, Cs, Si), even though their leach rate decreases with increasing glass fraction.

The bulk leach rate in glass-ceramics is misleading because much of the waste form is essentially insoluble, and would be partially excluded from leaching via the availability factor in performance assessments. As it is, the IEB/IEB4 bulk leach rate is about five times smaller, and most other leach rates are a factor of ten or more smaller, than typical BSG leach rates.^{1,17} The Cs leach

rate is about five times larger than the IEB/IEB4 bulk rate, but the TRU-surrogate leach rate is more than 1000 times smaller.

CONCLUSION

The IEB4/H1-40 waste form is extremely stable and a superior waste form for transuranic nuclides. The leaching characteristics did not vary significantly with the crystallization method, indicating that a special devitrification procedure is probably not required. The bulk properties of IEB4/H1-40 and IEB/A-40 are equivalent, with an apparently "universal" bulk leach rate function. IEB4 provides additional mechanisms for long-term stability for the actinide and fission surrogates investigated.

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