

Immobilization of Radioactive Waste in Fly Ash Based Geopolymers

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INTRODUCTION

The low-level salt waste (LAW) associated with the production of nuclear materials at US Department of Energy (DOE) facilities will be disposed of in shallow land burial sites managed by the DOE. Two of the primary contaminants of interest are Tc-99 and I-129, both soluble and long-lived radionuclides. Cs-137, a short-lived, strong gamma emitter is also a soluble contaminant of concern. In addition to radionuclides, the waste salt solutions can contain toxic quantities of metals as defined by the US Environmental Protection Agency (EPA) Resource Conservation and Recovery Act (RCRA).

One of the proposed LAW treatment methods for the DOE Hanford Site is a thermal treatment of the salt solution mixed with clay to produce granular aluminosilicate minerals that will immobilize the contaminants of concern. To meet the preliminary acceptance requirements of the Hanford Integrated Disposal Facility (IDF), the resulting mineral products were blended with a range of low temperature materials considered for waste forms. A geopolymer comprised of Class F fly ash, sodium silicate, and sodium hydroxide was identified as a candidate to produce a monolith geopolymer waste form¹.

EXPERIMENTAL

A simulated waste salt solution representative of the aggregate LAW at the Harford site was prepared using rhenium as a surrogate for technetium. Stable isotopes of cesium and iodine were used as surrogates for their radioactive form. The concentrations of RCRA metals were augmented in the simulated salt solution to demonstrate the ability of the waste form to immobilize greater than expected quantities of toxic components. Table I is the composition of the salt solution used in this study. As can be seen from the composition, the simulated waste salt solution is primarily a blend of sodium nitrate and sodium hydroxide with a density of 1.25 g/mL.

To prepare the feed, the salt simulant was mixed with metakaolin and coal in a mass ratio of 1:0.51:0.13. The resulting mixture was fed to a reactor operating at 700-750 °C with a continuous flow of steam. In the reactor, the nitrates are reduced to nitrogen, N₂, and the metakaolin reacts with the remaining components to form multiphase mineral assemblage of Na-Al-Si (NAS) feldspathoid minerals (sodalite, nosean, and nepheline) with cage and ring structures that sequester radionuclides and anions such as SO₄, I, F, and Cl.

Table I. Simulated Waste Salt Solution Composition.

Chemical Name	Element	Simulant Recipe (mol/L)
Aluminum	Al	0.06
Silver	Ag	0.002
Arsenic	As	0.001
Barium	Ba	0.008
Cadmium	Cd	0.004
Chromium	Cr	0.01
Cesium	Cs	0.01
Potassium	K	0.01
Sodium	Na	5
Nickel	Ni	0.01
Phosphorus	P	0.05
Lead	Pb	0.006
Rhenium	Re	0.002
Antimony	Sb	0.004
Selenium	Se	0.001
Chloride	Cl	0.04
Fluoride	F	0.03
Iodide	I	0.01
Sulfate	SO ₄	0.09
Oxalate	C ₂ O ₄	0.02
Acetate	CH ₃ COO	0.1
Carbonate	CO ₃	0.5
Hydroxide	OH	0.7
Nitrate	NO ₃	2.6
Nitrite	NO ₂	0.4

The resulting intermediate granular waste form is characterized for composition by dissolution and analysis, phase assemblage by x-ray diffraction (XRD) analysis, and durability by leach testing. The leach testing methods used were ASTM Product Consistency Test² and the EPA Toxicity Characteristic Leaching Procedure³. These analyses are used to confirm the desired products were obtained and the intermediate waste form was durable.

A fly ash based geopolymer composition was selected to encapsulate the granular waste form into a monolith without degrading the existing phase assemblage or reducing the durability of the waste form. The secondary objective is to maximize the waste loading of the granules in the geopolymer to minimize waste volume. The fly ash used was from bituminous coal and contained quartz, mullite, and hematite. Table II is

the composition of the fly ash and Figure 1 is the XRD pattern of the fly ash used. The pattern has the amorphous hump indicating the presence of a glassy phase, required for the geopolymer reaction. The fly ash had a BET surface area of 1.46 m²/g and a particle size distribution with a mean particle diameter of 68 μm with 90% of the particles below 128 μm and 10% of the particles below 5 μm.

Table II. Chemical Composition of Class F Fly Ash.

Oxide	Weight Percent
Al ₂ O ₃	27.68
CaO	1.13
Fe ₂ O ₃	7.40
K ₂ O	3.53
MgO	1.19
Na ₂ O	0.44
P ₂ O ₅	0.34
SiO ₂	56.58
SrO	0.10
TiO ₂	1.42
Total	99.82

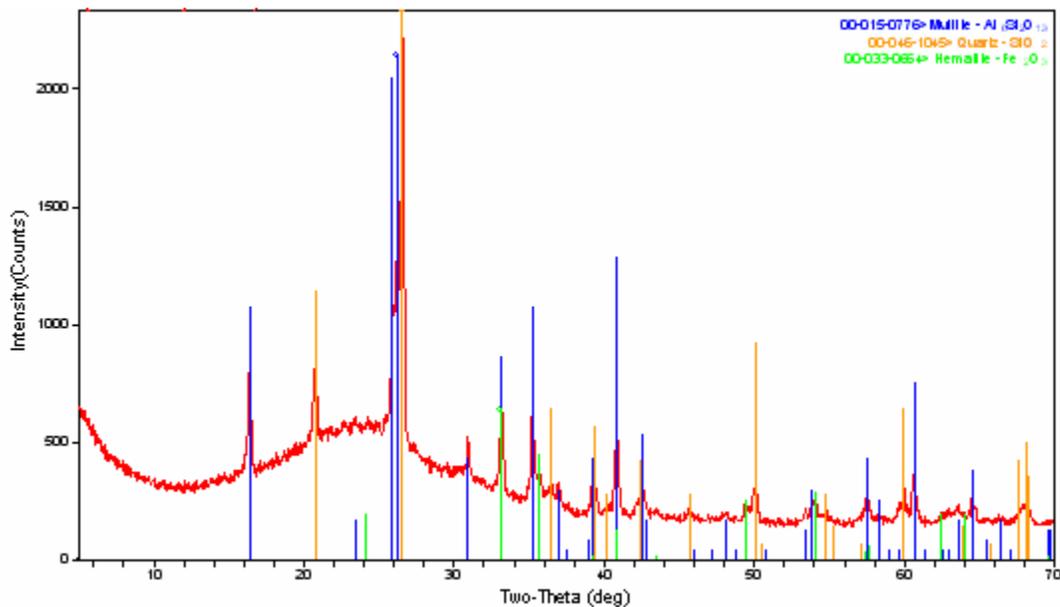


Figure 1. XRD pattern of Class F fly ash used for geopolymers.

To prepare the geopolymer, the granular powder was placed in a planetary mixer. Class F fly ash was added and the powders were blended. The prescribed amount of sodium silicate, sodium hydroxide, and water were added sequentially during mixing. Mixing continued until the liquids were incorporated and the mixture developed into a cohesive mass. Table III is the composition of the geopolymer waste form used in this study.

Table III. Composition of Fly Ash Based Geopolymer.

Component	Weight Percent
Waste Form granules	47.4
Class F fly ash	12.8
Na ₂ O•2SiO ₂ (44.1 wt%)	18.8
NaOH (50 wt%)	12.5
Water	8.6
Total	100.1

After blending the components, the resulting mixture was transferred into two one-inch by two-inch polypropylene cylinders. The capped cylinders were placed on a tapping device to facilitate removal of the entrained air from the mix. The tapped samples were allowed to set for 28 days prior to testing.

Testing of the geopolymer simulated waste form consisted of compression testing, XRD analysis and leach testing. Compression testing was performed using the ASTM method for cylinders modified to test cylinders with a 1-inch diameter (2 inches long)⁴. A portion of the crushed sample was used for XRD analysis. The remaining material was sized for the Toxicity Characteristic Leaching Procedure (TCLP) and the Product Consistency Test (PCT). The TCLP was used to determine the mobility of analytes of interest present in the simulated waste form. TCLP extraction and analysis was performed by GEL Laboratories, LLC, Charleston, SC. The PCT evaluate the chemical durability of waste forms by measuring the concentrations of the chemical species released to a test solution. BET surface area measurements, via gas adsorption, particle size distribution (PSD), via laser light scattering, and density, via gas pycnometry, were performed on the sieved/washed/dried portions of the intermediate waste form granules and geopolymer waste form powders used for PCT. A leachate to sample ratio of 10 cm³/g, test temperature of 90 °C, and test duration of seven days was used for the testing. The PCT results can be expressed as a normalized concentration (NC_i) in g_{waste form}/L_{leachant} or normalized release (NL_i) in g_{waste form}/m². The normalized release is calculated from the normalized concentration and measured surface area by the equations:

$$NC_i = C_i(\text{sample}) / f_i \quad (1)$$

$$NL_i = NC_i / (SA / V) \quad (2)$$

The SA/V ratio is calculated by dividing the measured BET surface area/ gram powder, by the leachant volume, V, via Equation 3:

$$SA / V_{BET} = (SA_{BET} / g_{\text{sample}}) / (g_{\text{sample}} / V) \quad (3)$$

In addition to calculating the PCT release from the simulated waste form. XRD analysis of the leached material was performed and the XRD patterns were compared to the as made waste form to determine if back reactions were occurring to produce alteration phases.

RESULTS

After 28 days of curing^{*}, the geopolymers were removed from the mold and tested for strength. Figure 2 is a typical compression test result. The compressive strength ranged from 650 – 3,550 psi (4.5 - 24.5 MPa). Samples that had reduced compressive strengths were tested promptly after being removed from the mold, whereas samples that were stored in a bag for an additional seven days after demolding exhibited greater compressive strength.

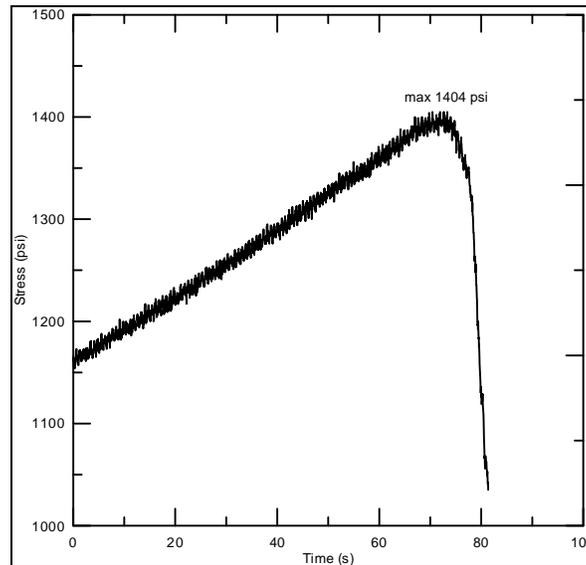


Figure 2. Typical compression result for geopolymer loaded with simulated waste granules.

Figure 3 is the XRD pattern of both the intermediate waste form granules and the resulting geopolymer. As can be seen from the XRD patterns, the primary NAS phases remain prevalent with the addition of quartz and faujasite, a common geopolymer phase created with high sodium hydroxide mixes made with fly ash. The XRD pattern of the geopolymer also has a discernible amorphous hump indicative of the geopolymer gel.

Table IV shows the concentration of the elements in the simulated LAW with the TCLP results for the intermediate granular waste form and the geopolymer waste form. The table also includes the U.S. EPA limits for toxicity and the Ultimate Treatment Standard (UTS) limits. The intermediate granular waste form successfully treated components added at well above expected concentrations. However, the UTS for chromium was exceeded. When analyzed after geopolymer formation, the simulated waste form passed for all of the elements tested.

* Duration of cure time selected for comparison to cementitious materials testing for waste solidification.

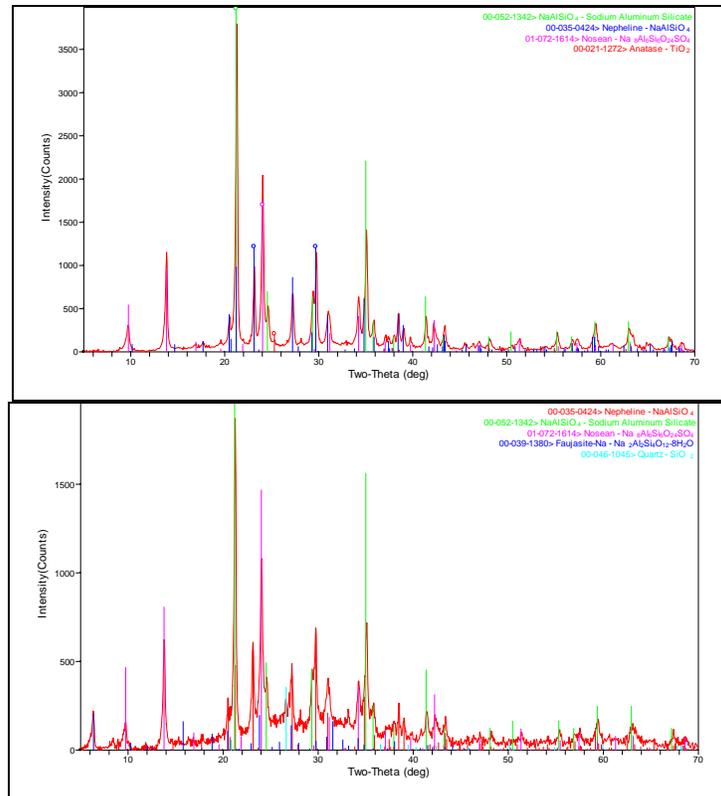


Figure 3. XRD pattern of: Top, the intermediate waste form granules, and Bottom, the geopolymer with the waste form granules incorporated.

Table IV. TCLP Results for the Intermediate Granular Waste Form and the Geopolymer Waste Form Prepared using Simulated LAW.

Element	Simulated Salt Solution	Intermediate Granular Waste Form	Geopolymer Waste Form	TCLP Characteristic of Toxicity	UTS (Non-Waste Water Standard)
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Sb	22.0	<MDL	<MDL	--	1.15
As	113	<MDL	2.48	5	5
Ba	0.5	0.0394 ^J	<MDL	100	21
Cd	<0.1	<MDL	<MDL	1	0.11
Cr	345	1.35	0.053	5	0.6
Pb	395	0.0475 ^J	0.0473 ^J	5	0.75
Se	87.9	1.12	0.385	1	5.7
Ag	0.28	0.0115 ^J	0.0133 ^J	5	0.14
Hg	0	<MDL	<MDL	0.2	0.025
Ni	<0.1	0.0249 ^J	<MDL	--	11
Tl	18.2	<MDL	<MDL	--	0.2
Zn	0	0.0957 ^J	<MDL	--	4.3

^JAnalytical result is above the method detection limit but below the laboratory reporting limit.

Table V is the surface area, particle size distribution and density of the intermediate granular waste form and the geopolymer waste form.

Table V. Properties of Intermediate Granular Waste Form and Geopolymer Waste Form Prepared for PCT.

Property	Method	Intermediate Granular Waste Form	Geopolymer Waste Form
Density (g/cm ³)	Gas Pycnometry	2.39	2.49
Surface Area (m ² /g)	BET	3.33	4.23
Median PSD (μm)	Laser Light Scattering	136.3	138.7

Results of the 7-day PCT are shown in Table VI. All leachate values are shown in mg/L units for Al, Cs, I, Na, Re, S and Si along with the resulting leachate final pH. The surface area to volume ratio of the tests in units of m⁻¹ can be calculated via the equation:

$$SA/V = \frac{g_{wasteform}}{V_{leachate(L)}} \times surface\ area \left(\frac{m^2}{g} \right) \times \frac{1L}{1000\ cm^3} \times \left(\frac{100\ cm}{1\ m} \right)^3 \quad (4)$$

Table VI. PCT Release Expressed as a Normalized Concentration of the Intermediate Granular Waste Form and the Geopolymer Waste Form.

	Intermediate Granular Waste Form	Geopolymer Waste Form
pH	11.40	12.56
Element	Average Release (g/L)	Average Release (g/L)
Al	1.44E-01	2.67E-02
S	5.44E-02	1.82E-01
Cs	8.44E-03	3.29E-03
Re	1.12E-03	2.26E-03
Na	5.95E-01	5.62E+00
Si	6.23E-02	5.71E-01
I	5.00E-04	1.11E-03

As can be seen from the pH values in Table VI, the leachate associated with the geopolymer waste form is greater than that of the intermediate granular waste form. The normalized concentration from the PCT shows that the concentration in the geopolymer waste form is lower than the intermediate waste form for most elements that are either unique to the intermediate granular waste form or participate in the geopolymer reaction.

The normalized elemental release (NL_i) for the 7-day PCT are shown in Table VII. The normalized release is calculated using the equation:

$$Normalized\ Release\ (NL_i)(g/m^2) = \frac{[Leachate\ Concentration]}{(SA/V)/[f_i]} \quad (5)$$

Table VII. PCT Release Expressed as a Normalized Rate of the Intermediate Granular Waste Form and the Geopolymer Waste Form.

	Intermediate Granular Waste Form	Geopolymer Waste Form
Element	Average Release (g/m ²)	Average Release (g/m ²)
Al	2.3E-03	4.53E-04
S	2.9E-02	1.03E-01
Cs	1.1E-02	4.65E-03
Re	8.8E-03	2.01E-02
Na	1.1E-02	7.39E-02
Si	9.8E-04	7.15E-03
I	1.2E-03	3.65E-03

The relatively high surface area of the granular waste form contributes to the reduced release rates of the waste forms. For a typical glass LAW waste form made from a similar simulant composition, the surface area is 0.02 m²/g for the -100+200 mesh powders that were leached and the normalized sodium release rate is 0.1 – 1 g/m². For reference, the proposed acceptance limit for sodium release rate for LAW waste at the Hanford Integrated Disposal Facility (IDF) is <2 g/m².

Figure 4 is the sample of the geopolymer waste form in Figure 3 that has been leached in the PCT.

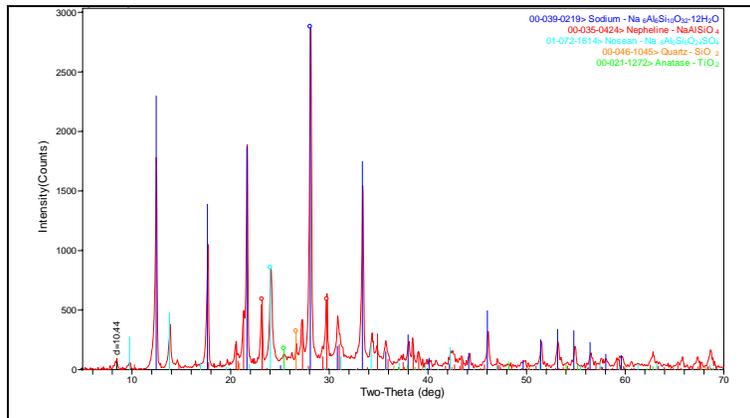


Figure 4. XRD pattern of the geopolymer after PCT leach.

A comparison of the patterns indicates that the mineral phases associated with the intermediate granular waste form persist, while the faujasite, formed as part of the geopolymer, was affected by the leaching.

CONCLUSIONS

A thermal treatment was used to prepare a granular mineral waste form from a simulated LAW salt solution. The mineral waste form was characterized and incorporated into a class F fly ash based geopolymer waste form.

The compressive strength of the geopolymer waste form ranged from 650 – 3,550 psi (4.5 - 24.5 MPa). The difference in performance can be attributed to the exposure to air after the waste forms were removed from the mold.

XRD analysis indicated that the mineral phases produced in the intermediate granular waste form were present in the geopolymer. An additional phase, faujasite, was formed during the formation of the geopolymer. The composition of the Class F fly ash based geopolymer waste form was not optimized and an excess of sodium hydroxide can lead to the formation of faujasite.

The geopolymer waste form passed the U.S. EPA TCLP and UTS standards for shallow land disposal. The geopolymer waste form had a PCT release rate of sodium of 0.074 g/m² compared to the proposed Hanford IDF value of 2 g/m². PCT release rates of surrogate radionuclides of cesium, iodine, and rhenium were comparable to other waste forms for LAW. Mineral phases formed in the thermal treatment of the simulated LAW salt solution to retain the surrogate radionuclides were present after XRD analysis of leached geopolymer waste form.

REFERENCES

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