Mineral Assemblage Transformation of a Metakaolin-based Waste Form After Geopolymer Encapsulation

Authors

Benjamin D. Williams^{1*}, James J. Neeway¹, Michelle M. V. Snyder¹, Mark E. Bowden¹, James E. Amonette¹, Bruce W. Arey¹, Eric M. Pierce², Christopher F. Brown¹, and Nikolla P. Qafoku¹

Affiliations

1. Pacific Northwest National Laboratory, PO Box 999, MSIN P7-54, Richland, WA 99352 USA; Benjamin.Williams@pnnl.gov, James.Neeway@pnnl.gov, Michelle.ValentaSnyder@pnnl.gov, Mark.Bowden@pnnl.gov, Jim.Amonette@pnnl.gov, Bruce.Arey@pnnl.gov, Christopher.Brown@pnnl.gov, Nik.Qafoku@pnnl.gov
2. Oak Ridge National Laboratory, PO Box 2008, MS-6035, Room 372, Oak Ridge, TN 37831, USA; pierceem@ornl.gov

Corresponding Author

*Benjamin D. Williams, Pacific Northwest National Laboratory, PO Box 999, MSIN P7-54, Richland, WA 99352 USA; Benjamin.Williams@pnnl.gov

Abstract

Mitigation of hazardous and radioactive waste can be improved through conversion of existing waste to a more chemically stable and physically robust waste form. One option for waste conversion is the fluidized bed steam reforming (FBSR) process. The resulting FBSR granular material was encapsulated in a geopolymer matrix referred to here as Geo-7. This provides mechanical strength for ease in transport and disposal. However, it is necessary to understand the phase assemblage evolution as a result of geopolymer encapsulation. In this study, we examine the mineral assemblages formed during the synthesis of the multiphase ceramic waste form. The FBSR granular samples were created from waste simulant that was chemically adjusted to resemble Hanford tank waste. Another set of samples was created using Savannah River Site Tank 50 waste simulant in order to mimic a blend of waste collected from 68 Hanford tank. Waste form performance tests were conducted using the product consistency test (PCT), the Toxicity Characteristic Leaching Procedure (TCLP), and the single-pass flow-through (SPFT) test. X-ray diffraction analyses revealed the structure of a previously unreported NAS phase and indicate that monolith creation may lead to a reduction in crystallinity as compared to the primary FBSR granular product.

Keywords

- Low-Activity Waste
- Fluidized Bed Steam Reformer
- Feldspathoid minerals
- Waste form leach test

1.0 Introduction

The ability to predict the behavior of waste forms (e.g., mineral and glass) over geological time scales constitutes one of the main scientific challenges for evaluating the long-term impacts of nuclear waste storage on public health and environmental resources [1,2]. Hazard mitigation can be improved through conversion of existing waste to a more chemically stable and physically robust waste form. Current research favors waste encapsulation through vitrification or incorporation into cementitious or ceramic matrices [1,4,5]. One example of conversion of hazardous or radioactive waste into a more stable ceramic waste form is the fluidized bed steam reformation (FBSR) process that produces a multiphase sodium aluminosilicate (NAS) ceramic material from high-sodium waste streams [6]. In order to increase the mechanical strength of the waste form and to facilitate transportation and disposal, a monolith can be formed by combination of the FBSR granular product with an encapsulating material that binds the granular product in a largely inert chemical matrix. One such material with a possibility to serve as a binder of the radioactive FBSR product is a geopolymer.

Ceramic waste forms have been studied extensively as a potential host matrix for radionuclides [7,8,9,10]. Some of the most studied multiphase waste forms include SYNthetic ROCK (SYNROC) [11], tailored ceramics [12], pyrochlore [13,14], zirconolite [15,16], and glass-ceramics [17]. For an overview of the these multiphase waste forms see the reviews by Lutze and Ewing [18], Lee et al. [19], Caurant et al. [20], and the NRC [21]. Improving the scientific and technical basis for using multiphase ceramic waste forms in nuclear waste management requires an understanding of the speciation, partitioning, and the release behavior of radionuclides immobilized in the multiphase matrix.

Geopolymers are formed by interaction of solid aluminosilicate minerals with aqueous alkali silicate or hydroxide solutions. Along with previous investigations of geopolymer use in toxic and radioactive

waste immobilization [22,23,24,25], geopolymer materials have recently been the subject of many scientific investigations due to their use in several applications including refractory materials [26], biotechnologies [27], and cements [28,29]. Geopolymers tend to be X-ray amorphous [30] but contain significant microstructure that varies depending on chemical content such as the Si/Al ratio [31,32]. Geopolymer encapsulation suitability is favorable with respect to high pH conditions, relative impermeability, and thermal stability [33,34,35]. Geopolymers can be used for encapsulation of the FBSR granular material, but the phase assemblage evolution as a result of this encapsulation process must be understood to ensure that encapsulation in the geopolymer does not affect the chemical durability of the FBSR product.

In this study, we examine the mineral assemblages formed during the synthesis of the FBSR NAS multiphase ceramic waste form. The objective of the results discussed in this manuscript was to (1) determine the change in mineral assemblages that occur from encapsulating the FBSR NAS granular particles in a geopolymer matrix and (2) the impact of the monolith creation process on the chemical durability of the FBSR NAS material. Information on other characterization and performance testing can be found

2.0 Materials and Methods

2.1 Sample Preparation

2.1.1 Steam Reforming for Fabrication of Granular Material

Granular samples were synthesized with engineering- and bench-scale steam reformers. Production of the engineering-scale granular sample was carried out at Hazen Research Inc. (HRI) in Denver, CO, USA using the THERMAL Organic Reduction (THORSM) Treatment Technologies (TTT) Fluidized-Bed Steam Reformation (FBSR) process (www.thortt.com). The process operates by introducing a high-sodium liquid waste stream, which contains radioactive elements such as Tc, Cs, and I as well as other contaminants, into a fluidized bed where fluidization is maintained with superheated steam at near-

ambient pressure. The waste that is introduced into the fluidized bed is reacted with carbon (coal), clay (kaolinite), and iron-based reductants at temperatures ranging from 650 to 800°C. During the process nitrates and nitrites are converted to nitrogen gas, organic material is converted to CO₂ and water, and a polycrystalline mineral product that encapsulates radionuclides, alkali metals, sulfate, chloride, fluoride, and non-volatile heavy metals is produced. Additional details are given elsewhere [36, 37, 38]. For this study, granular samples created with a non-radioactive simulant waste using the engineering-scale, THOR-TTT FBSR process are referred to as P1BG [37, 39].

The bench-scale steam reformed samples were created at the Savannah River Site (SRS) Bench-Scale Steam Reformer (BSR) with a simulant blend of 68 Hanford tank wastes known as the Rassat simulant [40]. In these samples Re is used as a surrogate for radioactive Tc. The operation of the BSR differs from that of the THOR-TTT FBSR process because the bed in the BSR is not fluidized due to geometric constraints dictated by construction of the BSR in a shielded cell at Savannah River National Laboratory. Construction in the shielded cell was necessary to carry out further tests with actual radioactive waste. Even without fluidization, the BSR process, like the FBSR process, destroys nitrates, nitrites and organic materials present in the waste and results in an alkali aluminosilicate mineral product containing radionuclides and other contaminants present in the initial waste. Previous tests have demonstrated that the lack of fluidization does not impact the gaseous or mineralizing reactions but only impacts particle growth [41]. For this study, granular materials resulting from this process are referred to as BSRG.

2.1.2 Fabrication of Geopolymer Containing Steam Reforming Granular Product

Encapsulation of the granular product, in a geopolymer binder to form monoliths, was investigated as a means to prevent dispersion during transport and to add compressive strength to the potential final waste form. The choice of the geopolymer as binding material was made after testing various cements, hydroceramics, Ceramicrete, and geopolymers and their effects on the release of Cs, I, Re, S, and Na in 7-day leach tests at 90 °C [42]. Geopolymers have an amorphous cross-linked three-dimensional structure and remain amorphous because of insufficient water to crystallize into phases such as zeolites.

For the P1B granular FBSR product and the BSR granular product, geopolymers were made by mixing the granular product and Class F fly ash with a 65% dry basis waste loading based on the mass of the granular product [43,44]. The granular product and Class F fly ash were combined in the mixing bowl of a planetary mixer and this was followed by the addition of a sodium silicate solution (44.1 wt% $\text{Na}_2\text{O} \cdot \text{SiO}_2$). After incorporation of the sodium silicate into the dry powder, a 50 wt% NaOH solution was added with continual mixing. Water was added (~15 wt% of the total mass of the mixture) and a paste was created. After about one minute of total mixing, the paste was transferred into two plastic cylinders, which were capped and left to cure for 28 days at ambient conditions on a benchtop. The resulting geopolymer was known as Geo-7. This composition had undergone studies to optimize FBSR loading, TCLP testing, and compressive strength testing to determine its suitability as an FBSR granular product immobilization agent [34,43].

2.2 Moisture Content, Coal Removal, Brunauer, Emmett, and Teller (BET) Surface Area Analysis and Microwave Digestion (MWD)

The moisture content of sample P1BG was assessed using a 10-gram aliquot dried at 105° C and cooled to ambient temperature at 24-hour intervals. This provided a dryness baseline for future sample preparation.

The moisture content sample was then analyzed for coal content by heating at 525°C for 1, 2, 8, 24, and 36 hours. Residual coal from granular product fabrication was determined through a subsequent loss on ignition test at 950°C for periods up to two hours.

BET samples were prepared by sieving to recover the +200 to -100 size fraction. Where material availability was insufficient, the +325 to -100 mesh size fraction was used. The sample was then washed with ethanol in order to remove any remaining fine particles and heated to remove residual process coal. The BET analysis was performed with a Quantachrome Autosorb using N_2 adsorption.

Microwave digestion was performed on an aliquot of the remainder from the coal removal test. Approximately 0.1 grams of sample was placed in each digestion vessel along with 5 ml of concentrated nitric acid, 2 ml of concentrated hydrochloric acid, and 2 ml of concentrated hydrofluoric acid. The digestion vessels were placed in a CEM MARS5 microwave and heated at 180°C for 60 minutes. The contents of the digestion vessels were transferred to centrifuge tubes, treated with 0.45 grams of boric acid and diluted to 20 ml with DDI. Following dissolution of the boric acid, the contents of the centrifuge tubes were filtered using 0.45 µm PVDF filters and submitted for chemical analysis by ICP-OES and ICP-MS (Table 2b).

2.3 Leaching Tests

Leach testing consisted of the ASTM C1285 Product Consistency Test (PCT) [45], the EPA test method 1311 known as the Toxicity Characteristic Leaching Procedure (TCLP) [46], and the ASTM C1662 Single-Pass Flow-Through Test (SPFT) [47].

The PCT-A was used as a guide with the only deviation being the use of polytetrafluoroethylene (Teflon) containers instead of stainless steel [45]. Briefly, the PCT-A method is a static test where the material of interest is reacted for seven days at 90 °C with a solid-to-solution ratio of 1:10 by mass.

The TCLP was performed on the granular sample materials as they were received. The monolith materials were ground up using an agate mortar and pestle then wet sieved with ethanol to obtain the <74- to >149 µm size fraction. Essentially, the TCLP is a short-term extraction performed at ambient temperature “to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes” [46].

Dynamic SPFT experiments were performed solely on the monolith materials, P1BM and BSRM. Results from the granular materials, P1B and BSR, are given elsewhere [48]. A schematic apparatus of the SPFT system is presented in Figure 1. All solutions were buffered at pH 9 using 0.05 M tris (hydroxymethyl) aminomethane (THAM) pH adjusted with 15.8 M HNO₃. Steady-state was determined when successive effluent concentrations of the analyte of interest differed by less than 10%.

Solutions obtained from the various tests were analyzed for Na, Si, and Al with Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and for Re, Cs, and I using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). The anions SO₄²⁻, PO₄³⁻, NO₃⁻, and NO₂⁻ were monitored using ion chromatography. However, after the first few sampling events, anion concentrations were below the detection limit and therefore the results are not reported in this paper.

Figure 1. Schematic of the single-pass flow-through (SPFT) apparatus for determining reaction rates in continuous flow solution.

2.4 X-Ray Diffraction

All of the samples were suspected of containing substantial quantities of amorphous material. To estimate the quantity of amorphous material, a weighed amount of corundum ($\alpha\text{-Al}_2\text{O}_3$, approximately 10 wt%) was mixed into each sample using a mortar and pestle. The specimens were loaded into traditional well-type aluminum holders with a cavity measuring 20 x 15 x 2 mm. Powder diffraction data were collected with a Panalytical X'Pert Bragg-Brentano diffractometer using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$),

a graphite post-diffraction monochromator, and variable divergence and anti-scatter slits (illuminated length= 10 mm). Patterns were collected between 5 and 75° 2 θ , counting for 2s at 0.04° steps.

Quantitative amounts of crystalline phases and amorphous material were estimated from Rietveld refinements [49] using the program TOPAS (v4.2, Bruker AXS). Crystal structures were obtained from the Inorganic Crystal Structure Database (Fachinformationszentrum Karlsruhe, Germany) and peak shapes were modelled using the fundamental parameters approach [50]. A new structure of NaAlSiO₄ was identified and solved as described in the Supplementary Material. The known quantity of corundum added was used to place the quantities on an absolute scale and the estimate of amorphous material is then established from a difference calculation (i.e., the amount of “missing” material). Uncertainty in the estimates of phase proportions is approximately + 2% for each phase, based on the uncertainty reported by the refinement software and additional uncertainty arising from experimental considerations such as sample presentation and crystal perfection.

Initially, the ability of the method to quantify both crystalline and amorphous phases was tested on a known sample containing a mixture of zincite (ZnO), rutile (TiO₂), eskolaite (Cr₂O₃) and amorphous silica glass powder. The agreement between weighed and analyzed phase composition was excellent, with about 1 wt% accuracy.

2.5 Scanning Electron Microscopy (SEM)/Energy-Dispersive X-ray spectroscopy (EDS)

Scanning electron microscopy (SEM) aided by energy-dispersive X-ray spectroscopy (EDS) was used to investigate the nature of the “as received” P1BG and BSRG samples using an FEI Helios 600 NanoLab FIB-SEM. Operating conditions were typically 5 keV or less for imaging and 20 keV for EDS measurements. EDS spectra were collected using Oxford INCA software with a live count of 100 seconds with a typical dead time of 30%. The P1BG sample was further investigated through preparation and scanning of several sites in a polished cross-section. Elemental mapping was applied to elucidate the distribution of elemental and physical characteristics.

3.0 Results

3.1 Moisture Content and Coal Removal

Moisture content and coal removal tests were performed on multiple aliquots of the PIBG material. Results shown in Table 1 represent total mass loss through the end of that time interval. PIBG moisture content yielded an average of 0.35 ± 0.01 % (Table 1). It can be inferred that any free water available on the granular surface is quickly removed within the first hour of heating.

PIBG coal removal test results are shown in Table 1. The data show that most of the coal is removed within the first hour of ignition; however, residual coal may remain in the sample and may require additional heating for complete removal.

Table 1. Results from moisture content and coal removal test. Moisture content tests were performed at 105 °C and coal removal tests were performed at 525 °C for the indicated amount of time.

Duration (hours)	Moisture Content Sample ID	Relative weight change	Coal Removal Sample ID	Relative weight change
1	MC1	-0.35%	CR1	-1.45%
1	MC2	-0.35%	CR2	-1.41%
2	MC3	-0.35%	CR3	-1.58%
2	MC4	-0.36%	CR4	-1.65%
8	MC5	-0.35%	CR5	-1.67%
8	MC6	-0.34%	CR6	-1.67%
24	MC7	-0.36%	CR7	-1.72%
24	MC8	-0.35%	CR8	-1.72%
36	MC9	-0.37%	CR9	-1.98%
36	MC10	-0.34%	CR10	-1.91%
36	MC11	-0.34%	CR11	-1.90%
36	MC12	-0.34%	CR12	-1.79%

3.2 BET Surface Area

BET surface area for the four FBSR samples is shown in Table 2a. There was a wide variance in surface area between the monolithic and granular forms, suggesting that monolith production adds porosity. At this time, the reason for the difference in surface area for the monolithic and granular materials is unclear. One explanation is that the monolith samples contained coal and the presence of this material may have contributed to the increase in surface area. Additionally, measurements are also required to shed light on the reduced mass loss of the monolith as compared to the granular materials.

Table 2a. Normalized mass loss (NL) values from the Product Consistency Test (PCT) for various elements present in the FBSR and BSR granular and monolith products.

	P1B granular as received	P1B granular roasted	P1B monolith	BSR granular as received	BSR B granular roasted			
			BET	5.95	4.93	38.1	8.16	3.34
			pH	11.4±0.4	11.8±0.1	11.9±0.1	10.1±0.6	9.8±1.
			Al (g/m ²)	1.71×10 ⁻	2.07×10 ⁻	5.54×10 ⁻	8.26×10 ⁻⁴	9.47×10 ⁻
			Re (g/m ²)	3.49×10 ⁻	3.75×10 ⁻	3.45×10 ⁻	1.43×10 ⁻³	3.74×10 ⁻
			Na	1.40×10 ⁻	1.64×10 ⁻	9.15×10 ⁻	4.63×10 ⁻³	2.01×10 ⁻
			Si (g/m ²)	4.27×10 ⁻	5.16×10 ⁻	1.95×10 ⁻	3.30×10 ⁻⁴	9.61×10 ⁻
			I (g/m ²)	---*	3.55×10 ⁻	1.76×10 ⁻	---*	5.21×10 ⁻

* Microwave digestion data is not available for I.

Table 3b. Microwave digestion values from original samples, following coal removal, for various elements present in the FBSR and BSR granular and monolith products.

	P1-B granular as received	P1-B granular roasted	P1-B monolith	BSR granular as received	BSR B granular roasted
Al (ug/g)	1.71x10 ³	1.71x10 ³	2.3x10 ¹	1.16x10 ³	1.19x10 ³
Re (ug/g)	6.9x10 ¹	6.7x10 ¹	2.8x10 ¹	4.10x10 ¹	4.00x10 ¹
Na (ug/g)	1.18x10 ⁴	1.14x10 ⁴	4.63x10 ⁴	5.82x10 ³	5.51x10 ³
Si (ug/g)	4.57x10 ²	4.58x10 ²	1.19x10 ³	4.06x10 ²	4.43x10 ²
I (ug/g)	2.58x10 ²	1.07x10 ²	7.70x10 ¹	1.30x10 ¹	1.30x10 ¹

3.3 X-ray Diffraction

Quantitative XRD analysis was obtained from a variety of FBSR sample types and preparations. The diffractograms are shown in Figure 2 while the distribution of the various phases obtained from these samples are summarized in Table 3. Characteristic peaks corresponding to the major phases are indicated for the low angle peaks; at higher angles the observed peaks are composites from the different phases. Additional peak identification for sample BSR G is shown in the supplemental information.

Table 4. Quantitative XRD results (weight %) for the FBSR P1B samples used in this study.

	BSR		Hazen P1B				
Phase	G²	M³	G	G, EtOH⁴	G, EtOH, no coal⁵	M	M, EtOH
ICSD No. ¹							
Chemical Formula							
Nosean	20.6	11.2	7.1	5.5	6.4	6.2	6.1
ICSD 203102							
Na _{8.08} Al ₆ Si ₆ O ₂₄ - (SO ₄) _{0.98} (H ₂ O) _{0.96}							
Na-Nepheline	26.7	12.6	12.0	10.5	12.0	6.0	5.4
ICSD 155001							
Na ₄ Al ₄ Si ₄ O ₁₆							
NaAlSiO₄	25.1	9.6	14.4	14.5	15.5	5.1	5.1
Quartz	-- ⁶	--	0.3	2.6	1.8	1.2	1.4
ICSD 162490							
α -SiO ₂							
Thermonatrite	--	--	--	--	--	1.0	2.5
ICSD 1852							
Na ₂ CO ₃ ·H ₂ O							

Na-Faujasite ICSD 87850 $\text{Na}_{2.92}\text{Al}_3\text{Si}_3\text{O}_{12}$	--	--	--	--	--	2.6	3.0
Anatase ICSD 63711 TiO_2	--	--	0.4	0.6	0.4	--	--
Hematite ICSD 15840 $\alpha\text{-Fe}_2\text{O}_3$	--	--	--	1.7	2.0	--	--
Illite ICSD 166961 $(\text{K}_{0.60}\text{Ca}_{0.03}\text{Na}_{0.01}) - (\text{Al}_{1.86}\text{Mg}_{0.14}) - (\text{Si}_{3.27}\text{Al}_{0.73})\text{O}_{10}(\text{OH})_2$	--	--	--	1.1	0.8	--	--
Chesnokovite ICSD 250422 $\text{Na}_2\text{SiO}_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	--	12.6	--	--	--	--	--
Amorphous	27.6	54.0	65.7	63.5	61.0	78.0	76.5

¹Entry number in the Inorganic Crystal Structure Database (<http://www.fiz-karlsruhe.de/icsd.html>)

²granular, “as-is”

³monolith, “as-is”

⁴washed with ethanol

⁵residual coal removed by combustion

⁶none detected

Based on the XRD analyses, a high proportion of amorphous material is indicated. In our analyses “amorphous” material is defined by the balance of material not accounted for in the crystalline materials identified (Table 3). This definition includes any unidentified phases below the detection threshold, compounds with a crystallite size less than ~5 nm, and traditional non-crystalline material, thus giving rise to the broad peak seen at ~30° 2θ in the diffraction patterns. In all cases, the peaks associated with

the ~10 wt% internal corundum standard dominate the scan, and support the result showing a very large amorphous content.

Figure 2. X-ray diffraction of various FBSR sample materials. Low angle peaks characteristic of nepheline (Ne), nosean (No), the new NaAlSiO_4 phase (Na), and chesnokovite (Ch) are marked.

A crystalline NaAlSiO_4 phase was found in all seven of the FBSR samples with a diffraction pattern matching that reported previously [51]. The crystal structure of this phase has not been reported, but was solved using the diffraction data collected from the FBSR granular “as-is” sample. The Supplementary Material contains more information about this phase and shows detailed figures of the match with the

database pattern, and of the fit resulting from Rietveld refinement of the structure. Solution of the structure was necessary to carry out the quantitative phase analysis since our method is based on calculating diffraction patterns from crystal structures. The structure of the crystalline NaAlSiO₄ phase is based on the cristobalite structure with paired Na and Al cations substituting for half of the Si cations. This structure is represented in Figure 3. Atomic coordinates are given in Table 4. Si-O and Al-O interatomic distances are 1.66 Å and 1.55-1.68 Å respectively, which are consistent with expected bond lengths for these elements. Na atoms are positioned in cavities in the structure formed from opposing hexagonal rings of (Si,Al)-O tetrahedral with Na-O distances between 2.55 and 3.70 Å. This is reminiscent of the positioning of Na in sodalite cages connected through hexagonal prisms. Sodalite is a desirable product of the FBSR process due to its potential to sequester various radionuclides and contaminants of concern [52,53,54,55,56,57].

Table 4. Crystal structure of NaAlSiO₄ phase solved from powder data. Space group $P3_1$, $a = 5.1164(4)$, $c = 12.5091(18)$ Å. Isotropic displacement parameter $B = 1.39(11)$ applied to all atoms. O atoms were refined as rigid bodies based on tetrahedral SiO₄ geometry and have ESDs derived from refined Si positions and Si-O bond lengths.

Site	x	y	z
Na1	0.661(8)	.086(7)	0.163(3)
Si1	-0.003(7)	0.756(4)	0
Al1	0.342(11)	.400(7)	0.089(4)
O1	-0.048(9)	0.670(9)	-0.123(9)
O2	0.666(9)	0.667(9)	0.054(9)
O3	0.231(9)	0.125(9)	0.013(9)
O4	0.139(9)	0.568(9)	0.062(9)

Figure 3. Representation of the crystalline NaAlSiO_4 structure, created using VESTA crystallography software, identified in all of the FBSR samples. The diffraction data from this structure were previously reported by Nayak and Kutty [34]. The Na interatomic distance along the a-b axis is 5.12 Å. In the above crystal structure the Na atoms are yellow, Si atoms are dark blue, Al atoms are light blue, and O atoms are red.

3.4 Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy

SEM images of P1BG scans revealed discrete blocky, angular grains, on a scale of about 20 μ m, with rough textured surfaces as seen in Figures 4a and b. Incomplete contact between needle and plate components leaves numerous small void spaces. Figure 4c shows another P1B sample with a more plate-like appearance indicating that the morphology of the sample may vary with each particle. The planar surfaces appear to be cleavage or fracture faces that indicate the crystalline nature of the primary particle otherwise obscured by the plate and needle coating.

Figure 5 shows a polished cross section of a P1BG particle. This large particle is roughly five times larger than those in Figure 4. EDS spectra results from P1BG analyses consistently illustrate the similarity in the occurrence and proportions of Na, Al, and Si in these FBSR samples. For all EDS scans we note that the presence of Re, a chemical surrogate for Tc, would not be detected due to the low intensity signal provided by such low concentrations in the original samples (Table 2b). The inner third, or core, of the particle displays distinctly different image intensity than the outer two thirds. EDS are similar to those of the previously mentioned surface scans but have a higher abundance of metals and other analytes of interest such as Ti, Fe, Pb, Cr Ni, I, and Cl. The metals exist as separate phases from the primary NAS mineral, most likely as spinels, created from the iron oxide added to encapsulate these metals [44]. In the SEM/EDS elemental mapping (Figure 6) there is a strong correlation between the presence of Na, Al, and Si while Fe is generally excluded from these areas. There is evidence of potential correlation between S and Ti, while Ni may have some correlation with Fe.

SEM/EDS results of BSRG samples, as seen in Figure 7 and Table 5, reveal greater variation in particle size with fewer angular and planar features. BSRG particles generally appeared to be more rounded, amorphous, and with smooth irregular surfaces. Among the different BSRG sites, EDS profiles for O, Na,

Al and Si were similar to those of P1BG but were distinguished by the greater prominence of contaminant metals such as Ti and Fe.

Figure 4. a) SEM micrograph of P1BG sample demonstrating the porosity of the material, b) the same particle at higher magnification, c) another P1BG material showing a more plate-like morphology.

Figure 6. P1B polished cross section SEM elemental mapping.

Figure 7. SEM micrograph of BSRG sample.

Table 5. BSRG sample EDS corresponding to SEM micrograph in Figure 6.

Element	Wt %	At %
O	43.79	55.85
Na	17.48	15.51
Al	19.06	14.41
Si	19.15	13.91
P	0.26	0.17
S	0.13	0.08
Ti	0.06	0.03
Fe	0.08	0.03
Total	100	100

3.5 Leaching Tests

3.5.1 Product Consistency Test (PCT)

The normalized release values obtained from these tests, including final solution pH, may be seen in Table 1. The normalized released, NL (g/m²) is given through the following equation:

$$NL = \frac{C_i/C_o}{S/V}$$

Where C_i is the concentration of element i measured in solution (g/m³), C_o is the concentration of the element in the starting material (g/m³), S is the surface area of the mineral obtained from BET measurements (m²) and V is the volume of the contacting solution (m³).

To be considered an acceptable waste form, a material should demonstrate a higher chemical durability than the Environmental Assessment (EA) glass [normalized mass loss (NL_{Na}) = 6.81 ± 0.95 g/m²] [48]. In the case of the granular and monolith materials for both the BSR and P1B product, sodium release is near 0.01 g/m², thus falling well below this limit. Lower values were found for Si, Al, I, Cs, and Re used as a chemical surrogate for Tc. A similar trend has been observed in a separate study that reported 7-day PCT values for FBSR product produced at the engineering scale [59]. However, that test shows that the normalized release values are the same or slightly higher than the EA Na release values measured for the EA glass after a one year PCT method experiment.

A critical component in determination of NL values from the PCT is an accurate knowledge of the material surface area available for water contact and subsequent release of elements from the original material. If the geometric surface area, SA_{geo} , of the tested material is used instead of the BET surface area, SA_{BET} , then the NL values increase by two orders of magnitude and are closer to the values measured for the EA glass. The SA_{geo} can be estimated using measured values for the average particle size, and material density, assuming that all particles have a spherical morphology [59]. Previously, it has been noted that the true reactive surface area used in release calculations typically lies between SA_{geo} and

SA_{BET} [59,60]. By using this assumption, the NL values for the results discussed in this manuscript are within an acceptable range even with the uncertainty in the true reactive SA. It should be noted that a similar issue for the surface area of glass, which is considered the best available technology for radioactive waste treatment, is also still under debate [61].

3.5.2 Toxicity Characteristic Leaching Procedure (TCLP)

Results from the TCLP test are listed in Table 6 along with the maximum limits for the US Environmental Protection Agency (EPA) TCLP and the Universal Treatment Standards (UTS). The results pass both the TCLP and the (UTS) for listed wastes. A more detailed discussion of these results can be found in Section 4.

Table 6. Results from the Toxicity Characteristic Leaching Test (TCLP) for the eight Resource Conservation and Recovery Act (RCRA) metals (40 CFR 261.24) as well as the Universal Treatment Standards (UTS) (40 CFR 268.48).

	TCLP Limit	UTS Limit	P1BG (Eng Scale Granular)	BSRG (Bench Scale Granular)	P1BM (Eng Scale Monolith)	BSRM (Bench Scale Monolith)
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Ag	5	0.14	<MDL	$6.5 \pm 5.0 \times 10^{-4}$	<MDL	$3.5 \pm 0.7 \times 10^{-4}$
As	5	5	$4.5 \pm 3.5 \times 10^{-2}$	<MDL	2.0 ± 0.1	2.2 ± 0.1
Ba	100	21	$2.2 \pm 0.2 \times 10^{-1}$	$2.5 \pm 0.1 \times 10^{-1}$	$8.6 \pm 0.7 \times 10^{-3}$	$1.6 \pm 0.3 \times 10^{-1}$
Cd	1	0.11	3.1 ± 0.1	<MDL	$1.8 \pm 1.3 \times 10^{-2}$	$5.5 \pm 0.7 \times 10^{-4}$
Cr	5	0.6	$6.3 \pm 2.1 \times 10^{-2}$	1.2 ± 0.1	$4.6 \pm 1.5 \times 10^{-2}$	$6.5 \pm 1.4 \times 10^{-2}$
Hg	0.2	0.025	$1.9 \pm 1.0 \times 10^{-5}$	<MDL	<MDL	$5.0 \pm 0.0 \times 10^{-5}$
Ni	---	11	1.6 ± 0.0	$2.5 \pm 0.4 \times 10^{-2}$	$2.8 \pm 0.7 \times 10^{-2}$	$1.2 \pm 0.2 \times 10^{-3}$
Pb	5	0.75	$8.6 \pm 3.1 \times 10^{-2}$	$2.9 \pm 3.0 \times 10^{-2}$	$1.5 \pm 0.3 \times 10^{-1}$	$1.5 \pm 0.6 \times 10^{-1}$
Sb	---	1.15	$3.2 \pm 0.2 \times 10^{-1}$	$9.0 \pm 0.0 \times 10^{-3}$	1.1 ± 0.1	$1.8 \pm 0.2 \times 10^{-2}$
Se	1	5.7	$3.8 \pm 0.6 \times 10^{-1}$	1.2 ± 0.1	1.1 ± 0.1	$4.6 \pm 0.2 \times 10^{-1}$
Zn	---	4.3	$1.7 \pm 0.2 \times 10^{-1}$	$3.0 \pm 0.4 \times 10^{-1}$	$6.9 \pm 6.3 \times 10^{-2}$	$8.9 \pm 1.3 \times 10^{-2}$

3.5.3 Single-Pass Flow-Through (SPFT) Test

Figure 8 shows the results of the measured SPFT effluent pH for the P1BG and P1BM samples. The dissolution kinetics of the granular P1B sample has been the subject of another publication [48]. When

comparing effluent pH values from the P1BG and P1BM samples, we note a marked increase in the pH for the early samples from the monolithic material where the P1BM maximum pH was 10.5 at a 10 mL/d flow rate. In contrast, the maximum pH observed at the 10 mL/d flow rate for the granular P1BG was 9.2, similar to that of the blank sample. Monolith effluent pH at the other flow rates tested was also higher than that of the granular form. This suggests that the dissolving species from the monolithic materials have a different chemical composition than the granular materials. As shown in the static, 7-day PCT tests, these materials have exhibited end-of-reaction pH values between 11 and 12. An increase in the pH of the solution is attributed to the release of OH^- from sodium hydroxide that is used as an activator in the production of the geopolymer [62]. Regardless, at longer reaction periods, the effluent pH decreases to a range that is within the experimental error of the inlet buffer solution. A similar trend is observed when comparing results of the BSRG and BSRM materials.

Figure 8. Effluent solution pH from the four non-radioactive test materials.

For the results given in this section, we focus on the results of the P1B samples because it has been shown that the dissolution kinetics of the P1B and BSR samples behave similarly [48,63]. Figure 9 shows the normalized effluent concentration of Al, Si, and Na for P1BM at 300, 150, and 10 mL/d. When the concentration of a particular element is constant as a function of time, the system is assumed to have achieved a steady-state condition. In general, steady-state conditions were achieved after about three

weeks of reaction time. Results indicate that the normalized Na concentration is greater than Al and Si across all the flow rates. The concentration trends for Na and Si follow a similar pattern. Though the normalized concentration of Na is roughly one order of magnitude higher than Si at very short experimental time periods, once the excess NaOH is removed the Na concentrations decrease and converge to a value that is within the experimental error of Si after five days for experiments conducted at 150 and 300 mL/d flow rates and 30 days for the 10 mL/d flow rate experiment. The normalized Al concentration is at least two orders of magnitude lower than Na and Si. The concentration remains low for the first few samplings and then increases to converge with Na and Si. The increased Al concentration is directly related to the pH (Figure 8). During this period of increased pH, Al is not released into solution to the same extent as Na and Si. This trend is not observed with the granular material, P1BG, where Na, Al, and Si are released concomitantly due to the absence of a spike in pH resulting from the excess NaOH release at short time periods [48]. Similar results were observed when comparing the BSRG and BSRM materials; however the results are not shown here.

Figure 9. Waste form P1BM SPFT effluent normalized concentration of Al, Si, and Na at 300, 150, and 10 mL/d at 40 °C given as a function of time. Note the change in scale for the y-axis of the third graph.

The values are not corrected for background. Error from ICP-OES analysis is 10%.

Figure 10 shows the P1BM release of Cs, I, and Re. Cs, Re, and I are of importance because they either represent radioactive isotopes that are present in LAW or act as a surrogate for a radioactive species of

concern [64]. Results show that Re and I follow similar trends whereas Cs follows trends more similar to Na, Al, and Si. This is because cationic species such as Cs can be substituted for Na in the feldspathoid mineral [58]. Release of Re and I in the monolithic material seems delayed, indicating that the aluminosilicate cage in the sodalite structure has to degrade before these species can be released. The presence of Re in the sodalite cage from the FBSR process has previously been confirmed using X-ray absorption spectroscopy (XAS) [53,54,55,65]. Initially high Re and I effluent concentrations decrease and then go through a second maximum with time. The concentration of these elements, at the second maximum, is used to calculate the steady-state dissolution rate because it is similar to the time when a transient steady-state release of Na, Al, and Si is observed. Releases of Cs, Re, and I from the BSRM mineral products show a similar behavior, thus are not given here. The steady-state release rate of the P1BM material based on Si release is $3.4 \pm 1.1 \times 10^{-4} \text{ g/m}^2\text{d}$ while for the BSRM material the value is $4.4 \pm 1.6 \times 10^{-4} \text{ g/m}^2\text{d}$. These results are slightly lower than the values calculated for the B1BG and BSRG materials [48].

Figure 10. Waste forms P1BM SPFT effluent normalized concentration of Cs, I, and Re at 300, 150, and 10 mL/d at 40 °C given as a function of time. Note the change in scale for the x-axis of the third graph.

The values are not corrected for background. Error from ICP-OES analysis is 10%.

4.0 Discussion

The results in Table 1 indicate that over the 6-month time span the material does not appear to be hygroscopic. Additionally, tests where the product was heated at 525 °C for two days show that a 2-hour heating duration is adequate for effective coal removal.

Following coal removal, BET surface area analysis was performed. High porosity in the range of 3.3 to 8.1 m²/g (Table 2a) is in general agreement the results from other sources [38,66]. Overall, the porosity of the material is the most likely explanation for the high measured BET surface area compared to the geometric surface area. It has been noted that an accurate measurement of the surface area is crucial because it is directly related to NL values, which allows for a direct comparison of supplemental waste form performance. At this point, the accurate measurement of the reactive surface area of the FBSR materials remains unresolved (see [59], [60] and [64] for discussion).

XRD indicate up to 65 wt% of amorphous material in the P1B granular “as received” sample. Taken as a whole, these FBSR samples, formed at relatively low process temperatures (650 – 800°C), exhibit a clear predominance of sodium-aluminosilicates existing as separate phases from other metals – particularly iron. Table 3 illustrates the phases identified from XRD of P1B samples. This information, demonstrates the dominant presence of sodium aluminosilicates in the FBSR product material. XRD analysis identified the crystalline NAS phases nosean, nepheline, faujasite, and a new structure related to cristobalite that is represented in Figure 1.

While PCT evaluations are clouded by the uncertainty in surface area, results from the PCT indicate a favorable comparison between the P1B/BSR product and the benchmark standard EA glass. Not only are Na release rates two orders of magnitude lower than for the EA glass when the geometric surface area is used, but other constituents are even lower than that of Na. Based on these PCT results, the FBSR

product is more durable than the EA glass. This improved stability might simplify temporary storage requirements between the time of waste form creation and final disposition.

While results from the TCLP show the release of important contaminants fall below the required final solution concentrations, Cd fails the TCLP test. However, the concentration of this element was greatly increased in the engineering scale test to ensure that measurable quantities of the element could be obtained in the leach tests. This increase was required in order to accurately monitor Cd releases from the waste form. Therefore, this element may comply with test limits at more realistic starting concentrations. When the PIB material is in the monolithic form, the solution concentrations for all contaminants decreased by a factor of 100. A marked performance gain can be realized by converting granular materials to the monolithic form with a geopolymer binder.

SPFT pH studies indicate chemical differences between the monolith and granular product. These differences decrease over time and are thought to be a function of rapid initial dissolution of unreacted NaOH from the monoliths. Correlated to the high pH of monolith early-stage leaching samples, is the relatively low concentration of Al and I. Cs release appears to follow that of Na and Si, and may be accounted for by the tendency of Cs to substitute for Na in feldspathoid structures. Because Na and Si are key components of these structures, their dissolution will also influence Cs release. In contrast to other key elements of interest, Re experiences rapid early release, diminishing to levels comparable to that of I. Subsequently, Re and I seemed to be released at similar rates. This may indicate that Re is present in two phases or may experience co-precipitation after initial release at low flow rates such as 10 mL/day. Results from the PCT and SPFT tests must be combined with other tests, such as Pressurized Unsaturated Flow (PUF) [65,59, 66] in order to fully characterize the durability of this material in a long-term sub-surface repository.

5.0 Conclusion

Solid-state analyses of the P1B and BSR samples confirm the dominant NAS composition targeted as a sequestering waste form for low activity wastes and clarify phase relations in these multiphase waste forms. The BET surface area was similar for both granular products fabricated at the engineering and bench scale. However, the BET surface areas were higher for both the P1B and BSR monoliths fabricated to encapsulate the granular product because of increased porosity created from the geopolymer. The two methods of sample preparation show similar NL values from PCT tests, pass the TCLP, and have the same crystalline phases. However, the P1B and BSR granular material exhibit a slightly different morphology from SEM imaging. XRD analyses have also demonstrated that the granular material has a higher percent of crystalline phases when compared with the monoliths. This may be due to the large amount of amorphous fly ash used to produce the monolith. The FBSR product successfully transforms waste to sodium aluminosilicate minerals that aid in contaminant capture through incorporation into the crystal structure. The dissolution kinetics calculated from SPFT tests further demonstrate the durability imparted through geopolymer encapsulation of the granular material into a monolith.

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Supplementary Material: Identification and structure refinement of the new NaAlSiO₄ phase

X-ray diffraction analysis of all the samples examined in this study showed the presence of peaks corresponding to a phase with the formula NaAlSiO₄ in the ICDD database (pattern 00-52-1342). This compound was reported by Nayak and Kutty (reference 45 in the manuscript) from a sol-gel synthesis. The peaks of this phase match well with our experimental patterns and were strongest for the FBSR granular as-is specimen, shown in figure S1 below.

Figure S1. XRD pattern of FBSR “as-is” sample, with peaks from identified phases overlaid as colored vertical bars. $\text{NaAlSi}_3\text{O}_8$ (red, 00-52-1342) gave the best agreement from an automated search-match.

Figure S2. Enlarged region of diffraction pattern shown in fig S1. A combination of the three phases identified is necessary to account for all the observed diffraction peaks.

The NaAlSiO₄ phase identified is a likely to be a polymorph of nepheline (and other NaAlSiO₄ phases), but has different diffraction peaks and therefore a different crystal structure. The more detailed portion of the XRD pattern shown in Fig. S2 further illustrates how this NaAlSiO₄ cannot be confused with nepheline. It is also distinct from other NaAlSiO₄ phases (e.g. carnegieite) reported in the diffraction database.

Nayak and Kutty reported that the XRD pattern could be indexed using an orthorhombic unit cell, based on an earlier report (Edgar, 1964 *Am. Miner.* 49 1139) of what was believed to be “nepheline hydrate I”.

However, Nayak and Kutty did not observe all the peaks of the earlier report, and the tabulated patterns of the two publications are significantly different. We needed a full crystal structure in order to carry out the quantitative phase analysis from XRD described in the main body of the paper. In the absence of a pure specimen, we solved the structure from the FBSR “as-is” data shown above which contained a high proportion of the new phase.

Indexing of the peaks observed in the present study suggested a hexagonal unit cell, with $a = 5.12 \text{ \AA}$ and $c = 12.51 \text{ \AA}$. Systematic absences were consistent with the space group $P3_1$. After some investigation a likely candidate structure was constructed, starting from the observation that SiO_4 tetrahedra can be arranged in hexagonal sheets with a 2-dimensional lattice spacing of $5.2 \text{ \AA}$. Alternating AlO_4 tetrahedra were substituted into these sheets which were stacked along the c axis. The resulting structure contained cavities above the corner-sharing hexagons of MO_4 tetrahedra suitable for placement of Na. Positioning of Na in these spaces gave the correct NaAlSiO_4 stoichiometry and an encouraging agreement between the observed and calculated diffraction patterns. Rietveld refinement of the structure was carried out using the same software (TOPAS v4.2) used for quantitative phase analysis, with SiO_4 tetrahedra refined as rigid bodies.

The refinement gave a good fit to the experimental data, shown in Fig S3 below. Nosean and nepheline were modeled using the structures reported in Table 3 in the main paper and only scale factors and microstructural parameters were refined for these phases. The Bragg R-factor for the new NaAlSiO_4 phase was 4.5%. This, and the chemically sensible arrangement of $\text{SiO}_4/\text{AlO}_4$ tetrahedra, gave us confidence in the new proposed structure.

Figure S3. Comparison of observed (black) and calculated (red) XRD patterns after Rietveld refinement of new NaAlSiO₄ phase. The contributions of the individual phases are shown below the observed/calculated patterns and the difference is shown at the bottom.