

Characterization and Leaching Tests of the Fluidized Bed Steam Reforming (FBSR) Waste Form for LAW Immobilization - 13400

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ABSTRACT

Several supplemental technologies for treating and immobilizing Hanford low activity waste (LAW) have been evaluated. One such immobilization technology is the Fluidized Bed Steam Reforming (FBSR) granular product. The FBSR granular product is composed of insoluble sodium aluminosilicate (NAS) feldspathoid minerals. Production of the FBSR mineral product has been demonstrated both at the industrial and laboratory scale. Pacific Northwest National Laboratory (PNNL) was involved in an extensive characterization campaign. The goal of this campaign was to study the durability of the FBSR mineral product and the encapsulated FBSR product in a geopolymer monolith. This paper gives an overview of results obtained using the ASTM C 1285 Product Consistency Test (PCT), the EPA Test Method 1311 Toxicity Characteristic Leaching Procedure (TCLP), and the ASTM C 1662 Single-Pass Flow-Through (SPFT) test. Along with these durability tests an overview of the characteristics of the waste form has been collected using Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), microwave digestions for chemical composition, and surface area from Brunauer, Emmett, and Teller (BET) theory.

INTRODUCTION

The U.S. DOE Office of River Protection (ORP), through its contractors, is constructing the Hanford Site Tank Waste Treatment and Immobilization Plant (WTP) to convert radioactive and hazardous wastes stored in Hanford's underground storage tanks into stable glass waste forms for disposal. Within the WTP, the pretreatment facility will receive waste from the tank farms and separate it into HLW and LLW process streams which will be sent to their respective facilities for vitrification. Presently, the projected throughput capacity at the WTP LAW Vitrification Facility is insufficient to treat the wastes which would extend the River Protection Project (RPP) mission beyond the Tri-Party Agreement milestone date for completing all tank waste treatment. Therefore, supplemental treatment technologies for treating and immobilizing Hanford LAW are being evaluated. One such technology is the Fluidized Bed Steam Reformer (FBSR) granular product, a product composed primarily of sodium aluminosilicate (NAS) feldspathoid minerals.

The FBSR granular product is produced through the use of steam reforming based on the Thermal Organic Reduction (THOR ®) process.[1] The process is capable of incorporating both liquid and solid LLRW into a mineral product. The waste feed may be either basic or acidic.[2] A more detailed description of the dual reformer FBSR design is given elsewhere.[3,4] To produce the FBSR NAS granular product the only necessary ingredients are kaolin clay, the waste stream, steam, and a carbon source, usually coal, which are mixed in the dual reformer.

This process runs at moderate temperatures (625 to 800°C). The ingredients interact in the Denitration and Mineralization Reformer (DMR) steam environment and the clay mineralizing agent becomes unstable as hydroxyl groups are driven out of the clay structure during interaction with the waste.[5] Process gases, consisting mainly of steam, N₂, CO, CO₂, and H₂ are treated to meet specified emission limits. The entire off-gas treatment system provides high-efficiency filtration and oxidation of any residual volatile organics and small amounts of carbon monoxide and hydrogen. The redox environment present in the DMR is controlled in the process to ensure that various redox sensitive elements are in a favorable oxidation state that allows encapsulation. To help assess the suitability and effectiveness of the FBSR process for the treatment of Hanford LAW, a single-reformer laboratory system called the Bench-Scale Reformer (BSR) has been developed at Savannah River National Laboratory (SRNL).[6]

The resulting FBSR granular product is composed primarily of insoluble sodium aluminosilicate (NAS) feldspathoid minerals including sodalite, nosean, and nepheline. Minerals in this group are characterized by an ordered framework of AlO₄ and SiO₄ tetrahedra. These phases may provide a durable waste form for immobilizing the contaminants that are present in the different waste liquids due to their cage- and ring-structures that sequester anions and cations.[7] Contaminants external to the cage-shaped structures are bound ionically to surface oxygen and hydroxide atoms. This allows the mineral to sequester various ions from the waste stream. Nepheline, the major mineral produced from the FBSR process, is a basic NAS mineral with a formula Na₂O-Al₂O₃-2SiO₂. When this phase contains sulfates within the cage structure, the mineral nosean is formed with the formula 3Na₂O-3Al₂O₃-6SiO₂·Na₂SO₄. If chloride is captured in the structure, sodalite forms with the formula 3Na₂O-3Al₂O₃-6SiO₂·2NaCl. Sequestration of cations and anions in nepheline occurs in the eight 9-fold oxygen sites and 6 smaller 8-fold oxygen sites. For the sodalite group minerals (sodalite and nosean), retention of anions and/or radionuclides occurs in the aluminosilicate tetrahedral where the anion is bound to Na. Sodalite cages generally contain two sodium chloride molecules but the chloride ion may be substituted with other monovalent or divalent anions such as OH, SO₄, and CO₃ which are known as basic sodalite, nosean, and natrodavyne, respectively. This flexibility allows the incorporation of ReO₄⁻, and presumably TcO₄⁻, which is the primary radioactive species in the LAW waste stream, directly into mineral products. Feldspathoid minerals can also accommodate sulfur in several oxidation states as either sulfate or sulfide. Even though this occurs with sulfur, in order to incorporate other species with variable oxidation states, such as technetium, the REDOX state must be controlled to force the species into the desired state. This is accomplished through controlling the reducing conditions using a log oxygen fugacity of -20 to -21 atm.[5]

In order to conform to Hanford Integrated Disposal Facility (IDF) requirements the granular product must be encapsulated in a binder and the resulting monolith must have a compressive strength of at least 500 psi. The compressive strength requirement is driven by the need to prevent subsidence, or sinking, of the disposal facility to maintain surface cap and barrier functionality. Encapsulating the granular product also helps reduce the impact of the dispersible materials in human intrusion scenarios. Studies have been performed into possible binder materials. Information on those tests and materials may be seen elsewhere.[4,8]

For a period between from 2010 and 2012 extensive testing was performed at PNNL to investigate the physical properties of the FBSR granular products produced at the engineering- and bench-scale along with these properties of these materials encapsulated into a monolith. An

extensive research campaign on the characterization and durability of this potential waste form has been conducted.

RESULTS

Materials obtained in this study come from the THOR® Treatment Technologies (TTT) Hazen FBSR engineering scale pilot facility and from the Savannah River National Lab (SRNL) Bench Scale Reformer (BSR). The first material was produced at the Hazen Research facility in Golden, Colorado, USA using the Engineering Scale Technology. The waste stream used was non-radioactive Hanford LAW simulant based on the Rassat simulant [9,10] (Lorier et al., 2005; Rassat et al., 2003). Products from the Hazen study are referred to here as P1B. A second granular material, referred to as BSRG, is a chemical shim of Savannah River Site (SRS) LAW (Tank 50) that resembles Hanford LAW. This material was produced at Savannah River National Laboratory (SRNL) using their Bench-Scale Reformer (BSR). Results have shown that the same mineral phases were identified in the pilot-scale and bench-scale reformer.[11] Some radioactive sample batches contain actual Hanford tank wastes which were treated using the BSR. Therefore tests have been completed on radioactive and non-radioactive samples (using Re as a surrogate for Tc-99). An overview of the performance and characteristics of the various products will be given. Treatment of the data for the radioactive tests is still underway.

Scanning Electron Microscopy/Electron Dispersive Spectroscopy

SEM images were obtained for both the P1B and BSR granular particles. A representative particle from the Hazen run can be seen in Figure 1. The micrograph shows blocky grains with dimensions of 10-20 μm on any side with a very porous surface. EDS analysis shows the presence of a roughly 1:1:1 sodium aluminosilicate, which is expected because the FBSR process results in a material with a bulk mass related to NAS feldspathoids.

Williams et al. [12] have also performed cross-sectional analyses of the P1B product. In those micrographs with EDS analysis, one notices the existence of metals present at the interior of the product and not at the surface suggesting that these particles may act as a nucleation site for feldspathoid formation. The existence of titanium, iron and sulfur-rich phases has been observed.

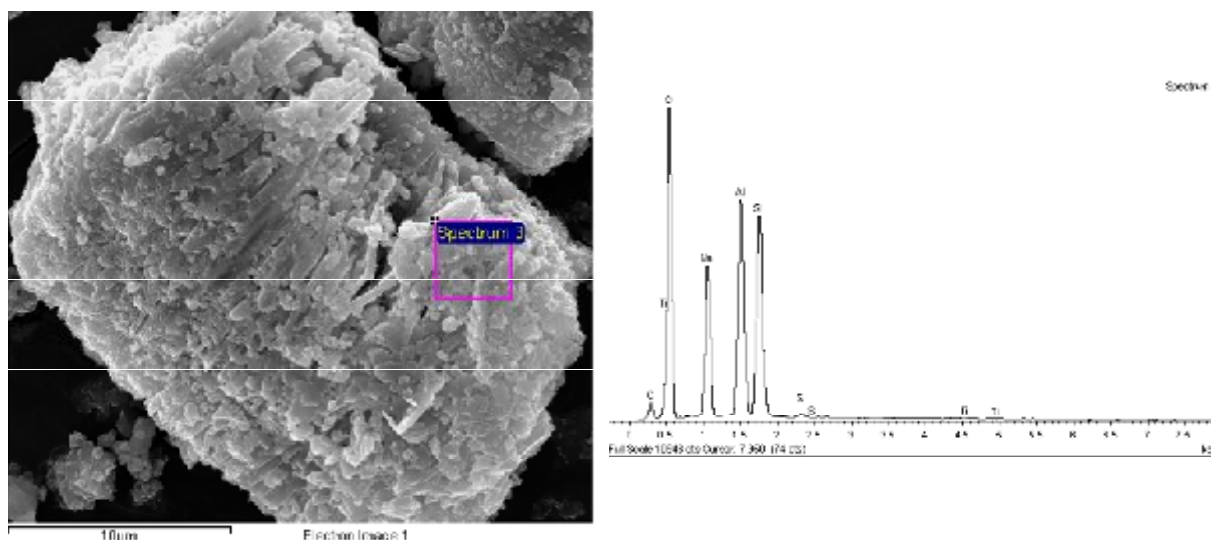


Figure 1. SEM image of the Hazen granular product.

X-ray Diffraction

XRD analyses of the granular and monolith samples have been performed. The various diffractograms obtained demonstrate the inhomogeneity of the FBSR final product. The main differences between the two types of samples are the presence of a large amorphous phase in the monoliths. Therefore, the geopolymer used for FBSR granular material encapsulation leads to a product that is less crystalline than the granular material. Nepheline, quartz and nosean were positively identified for the monolith while nepheline, nosean, and low-carnegeite were identified in the granular product. The initial amorphous content of the granular material was less than 5%.

BET Analysis

BET analyses were performed for the granular and monolith samples from the BSR and P1B samples.[12] It is seen that the monolith samples have a much larger surface area than the granular samples suggesting a much more open porosity. The effect of this porosity is still to be determined. Waste loading is generally 70% by mass of the FBSR granular product in the final monolith. If the geopolymer material adds porosity but the porosity merely manifests itself in the nonradioactive material that makes up the geopolymer additive, this should not have a negative effect on the release of radioactive material if the integrity of the initial granular material is maintained.

Pressurized Unsaturated Flow Tests

Pressurized Unsaturated Flow (PUF) tests have been performed for periods of up to two years. The PUF test was developed to study the performance of waste forms and materials that would corrode under unsaturated conditions for extended periods of time.[13] The systems have been stopped and currently treatment of the data is underway. These data include solution composition, effluent pH, saturation, as well as XRD diffractograms from various levels present in the column.

Leaching Tests (TCLP/C1308/PCT/SPFT)

Extensive leaching tests were performed on the FBSR granular and monolithic product. A first set of tests using the PCT showed that all the different waste forms that were tested performed better than the EA glass commonly used as a baseline for glass corrosion. It should be noted that the calculation of the normalized leaching from the granular and monolith are directly proportional to the measured specific surface area of the product. It should be noted that if the geometric surface area is used instead of the BET surface area, the leaching results are nearly similar to those that result from the leaching of the EA glass. The TCLP and C1308 tests for EPA compliance have also been performed. The TCLP results show that the products pass the requisite release of various RCRA metals. Results from the C1308 tests are still being treated.

Testing was performed using the SPFT test method to determine the intrinsic dissolution rate of the granular and monolith materials from both the Hazen and BSR runs. Tests were first run at varying surface area to flow rate values (q/S). The dissolution rate, r , is calculated through the following (Equation 1):

$$r = \frac{C_{Si} \times \frac{q}{S}}{f_{Si}} \quad (\text{Eq. 1})$$

Where C_{Si} is the steady-state silicon concentration in the outlet solution in g/m^3 , q is the solution flow rate in m^3/d , S is the surface area of the material available for corrosion in m^2 and f_{Si} is the mass fraction of silicon in the original FBSR material. Typical 2σ uncertainties for Si releases were on the order of $\pm 40\%$. Here we present results for the BSR and P1BG monolith samples where the release data for Si as a function of the ratio of the flow rate to surface area. Figure 2 shows these results along with initial data from these tests have already been presented.[14] It can be seen that the granular materials (G) from the two FBSR processes give similar results with the P1BG material showing a slightly higher release. The monolith (M) show slightly lower release rates compared to the granular. The goal of these experiments is to calculate the rate in dilute conditions, i.e. at high q/S values.

Results from this study show the behavior of the P1BG1 and BSRG1 waste forms in flow-through conditions at pH 9 and 40°C in DDI water. The forward dissolution rate of the material at an infinitely dilute silica solution concentration has been calculated. These values were shown to be $1.3 (\pm 0.3) \times 10^{-3} \text{ g/m}^2\text{d}$ for the BSRG1 lab-scale material and $0.4-1.0 \times 10^{-3} \text{ g/m}^2\text{d}$ for all the materials with the granular materials exhibiting slightly higher release rates. These values are similar to Si releases during 14-day SPFT tests conducted on Hanford LAW simulant FBSR bed product in an earlier study.[9]

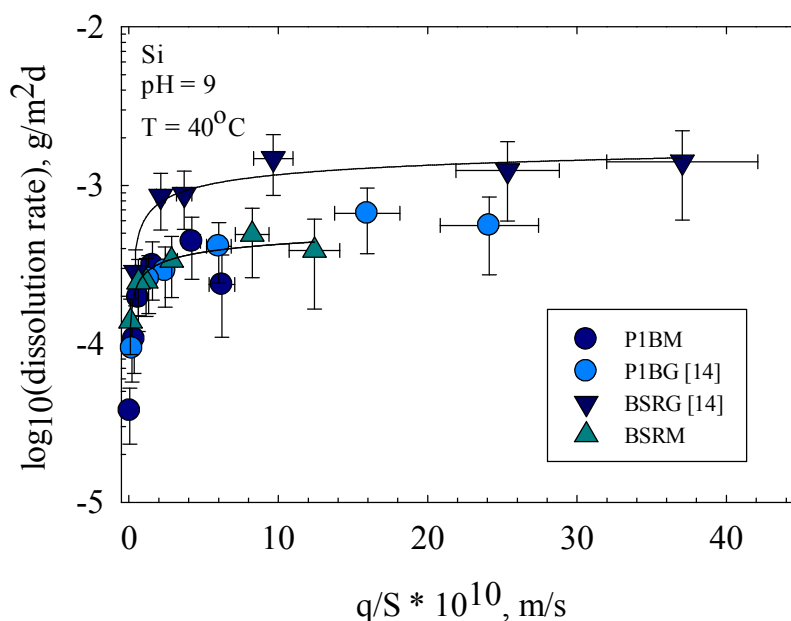


Figure 2. The rate of release of Si for the P1BM, P1BG, BSRG and BSRM samples as a function of q/S (flow rate/surface area). Materials ending with a G are the granular material while those ending in M are the monolith.

CONCLUSIONS

Fluidized Bed Steam Reforming (FBSR) offers a continuous method by which LAW can be processed irrespective of whether they contain organics, nitrates, sulfates/sulfides, chlorides, fluorides, volatile radionuclides or other aqueous components. The technology processes these wastes into a crystalline mineral waste form at moderate temperatures (700-750 °C). In this study, materials produced at the engineering-scale (P1BG1) and with the use of the lab-scale BSR developed at SRNL (BSRG1) have been studied.

Results from the series of studies performed at PNNL show that the FBSR granular product has very rough surface, as observed through SEM imaging as well as results from BET analysis. The XRD diffractograms show that the material is highly inhomogeneous. However, we have been able to positively identify some of the feldspathoid minerals that are expected to be synthesized from the FBSR process.

Results from leaching tests performed on the various FBSR products show promising results. Despite these promising results, further testing of the FBSR mineral product is needed if one is to compare the FBSR waste form to the glass waste form whose durability has been tested for much longer and at a much larger scale. Data must be obtained regarding the impacts of radiation, biodegradation, and water immersion on the compressive strength of the FBSR granular and monolith products. More studies are also needed to understand the mechanisms controlling mineral dissolution and radionuclide release.

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ACKNOWLEDGMENTS

These studies were supported by the U.S. Department of Energy (DOE) through the Office of Environmental Management. Pacific Northwest National Laboratory is operated for the DOE by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830. We would like to recognize the contributions made to this study by other collaborators in this project, including the Geosciences Group at PNNL, Carol Jantzen and the team of scientists at SRNL, Eric Pierce of ORNL, and David Swanberg of WRPS.

The research described in this paper was performed in part in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory in Richland, WA.