

Single Pass Flow-Through (SPFT) Test Results of Fluidized Bed Steam Reforming (FBSR) Waste Forms used for LAW Immobilization- #12252

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ABSTRACT

Several supplemental technologies for treating and immobilizing Hanford low activity waste (LAW) are being evaluated. One such immobilization technology being considered is the Fluidized Bed Steam Reforming (FBSR) product, which is granular and will be monolithed into a final waste form. The granular component is composed of insoluble sodium aluminosilicate (NAS) feldspathoid minerals. Production of the FBSR mineral product has been demonstrated at the industrial, engineering, and laboratory scales. Single-Pass Flow-Through (SPFT) tests at various flow rates have been conducted with the granular products fabricated using the engineering- and laboratory-scale methods. Results show that the forward dissolution rate for the engineering-scale mineral product is $0.6 (\pm 0.2) \times 10^{-3} \text{ g/m}^2\text{d}$ while the forward dissolution rate for the laboratory-scale mineral product is $1.3 (\pm 0.5) \times 10^{-3} \text{ g/m}^2\text{d}$.

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 177 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 high-level waste (HLW) and low-level waste (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 a portion of the LLW stream. This lack of capacity would extend the River Protection Project (RPP) mission 40 years beyond December 31, 2047, the Tri-Party Agreement milestone date for completing all tank waste treatment. To resolve the issue of throughput capacity and to accelerate the mission at the WTP LAW Vitrification Facility several supplemental waste forms are being considered. One of the potential treatment options is the Fluidized Bed Steam Reforming (FBSR) sodium aluminosilicate mineral product.

Currently the Thermal Organic Reduction (THOR®) steam reforming technology has demonstrated the ability to convert liquid low-level radioactive waste (LLRW) streams into the FBSR mineral product [1]. The THOR® FBSR process creates a mineral waste form by mineralizing the waste in a fluidized bed created with the addition of superheated steam at near-ambient pressure. During mineralization, organic matter is converted to carbon dioxide and steam while nitrates and nitrites are reduced to nitrogen. Non-volatile solids are converted to water-insoluble stable crystalline minerals composed mainly of feldspathoids that incorporate contaminants. Operational temperatures range from 625 to 750°C which is attractive for the treatment of waste streams with species that are volatile at temperatures used to fabricate glass or ceramic waste forms (often 1000-1500°C) [2, 3].

FBSR testing platforms using the THOR® technology have been constructed and used to demonstrate radioactive immobilization in simulant wastes at the bench-, pilot-, and engineering-scale. Currently, an FBSR facility is being designed and constructed at the Idaho National Laboratory (INL) for the treatment of sodium-bearing waste (SBW) to be sent for disposal at the Waste Isolation Pilot Plant (WIPP) in Carlsbad, New Mexico [4,5]. Other such facilities are being considered to treat Savannah River Site (SRS) salt supernate waste [6] and Hanford LAW [7,8].

The FBSR Process

A schematic representation of the dual reformer FBSR design is given in Figure 1 with the second reformer used to oxidize fuel, such as coal, to CO₂. The dual reformer consists of the following primary subsystems [3]: a waste feed, the denitration and mineralization reformer (DMR), a high-temperature filter (HTF), a product receiver (PR), off-gas treatment (typically a second reformer known as the carbon reduction reformer (CRR) which handles organics), and system control and monitoring. Mineralization reactions occur in the DMR and the granular product is collected in the PR. Finer product solids are separated from the process outlet gases by the HTF. Some of these solids can be recycled back to the DMR as seed material, as demonstrated in Figure 1, or they can later be combined with other solids collected in the PR. Outlet gases are treated to meet specified emission limits. 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-top Steam Reformer (BSR) has been developed at Savannah River National Laboratory (SRNL) [7].

The primary granular product from the FBSR process is composed of insoluble sodium aluminosilicate (NAS) feldspathoid minerals. These minerals are composed primarily of sodalite, nosean, and nepheline which all have 1:1 Al:Si ratios and contain cage and ring structures that sequester Tc-99 and ions such as SO₄, I, and F. Cs-137 replaces Na in nepheline. To produce the FBSR NAS granular product the only necessary ingredients are kaolin clay, the waste stream, steam, and a fuel source. The ingredients interact in the 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 [3]. Process gases, consisting mainly of steam, N₂, CO, CO₂, and H₂ exit the DMR through the HTF which may also trap small mineral product particles called fines. 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 from the DMR. Some low levels of NO_x, acid gases, and short-chained organics may also be present. These can be destroyed in the CRR.

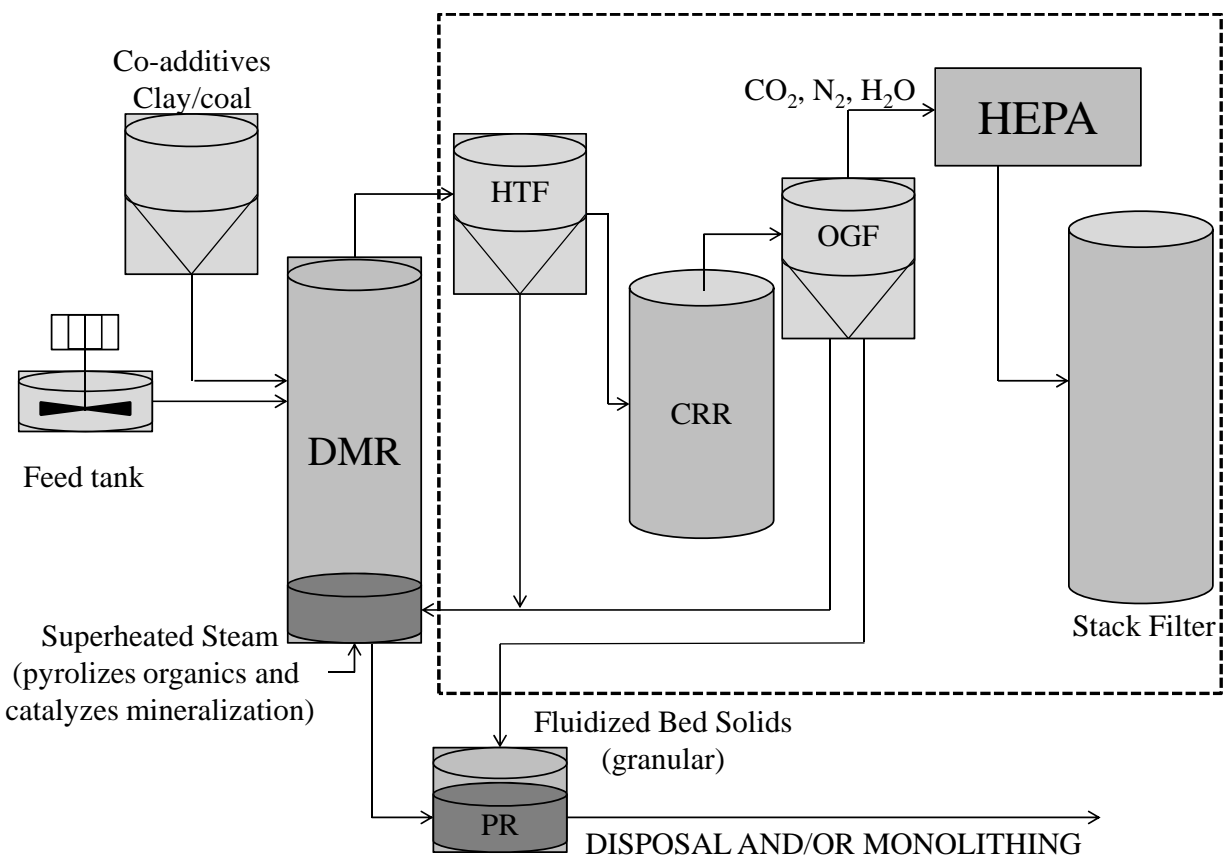


Fig. 1. A flowsheet of FBSR waste form processing which includes the denitration and mineralizing reformer (DMR); product receiver, (PR); high temperature filter (HTF), carbon reduction reformer (CRR), off-gas filter (OGF) and a high-efficiency particulate air (HEPA) filter [3].

Waste form process monitoring and controls are necessary to obtain the desired mineral product. The proper amount of additives and operation in the proper REDUCTION/OXIDATION (REDOX) range ensure autocatalytic heating and pyrolysis. Control of the REDOX potential greatly influences the oxidation state of multivalent elements. Tc (or the Re surrogate) and I in the correct oxidation state are sequestered in sodalite cages while Cr is sequestered in iron oxide spinels.

EXPERIMENTAL METHOD

Materials

Two granular FBSR product materials were used during testing. The first was the mineral product resulting from an Engineering Scale Technology Demonstration (ESTD) test completed in 2008 at the Hazen Research Facility in Golden, Colorado, USA using a non-radioactive Hanford LAW simulant [9]. This mineral product was produced as part of from the DOE Advanced Remediation Technologies (ART) test P1-B and will be referred to as P1BG1 throughout the text. The material is a mixture of 20% PR and 80% HTF fines. A second granular material, referred to as BSRG1, is also a non-radioactive simulant that was chemically shimmed to resemble Hanford LAW. This material was produced at SRNL using the Bench-Scale Reformer (BSR).

Preparation of the P1BG1 material involved wet sieving the received sample to +325 to -100 mesh (0.044 - 0.149 μm) with high purity ethanol to remove adhering fines. The material was dried and placed in a furnace at 525°C for two hours to remove any residual coal remaining from production. The BSRG1 sample was prepared in a similar way, with the only difference being that the +200 to -100 mesh (0.074 – 0.149 μm) size fraction was used. The difference in size fraction used for testing between the two samples was a result of the fine-grained nature of the P1BG1 material, which consisted primarily of material (80%) from the HTF.

Testing has been conducted on the P1BG1 and BSRG1 granular products using the single pass flow-through (SPFT) procedure. The SPFT method is an open system test at a constant temperature and known flow rate. The basic design of the SPFT system used during testing can be seen in Figure 2. A solution is passed through a reaction cell containing the sample and no recirculation of solution occurs. SPFTs are often used to measure the rate of matrix degradation of homogeneous nuclear waste glasses but, in this case, have been extended to characterize the FBSR and BSR materials as has been done previously [13]. Different flow rates were used to measure the release rate of Si as a function of the quotient of the flow rate, q , and the sample surface area, S .

The SPFT experiments were conducted at 40°C and were continuously monitored using a digital thermocouple. Solutions were buffered using a solution of 0.05 M tris (hydroxymethyl) aminomethane adjusted to pH 9 using concentrated HNO_3 . Automated syringe pumps (Kloehn model 55022) transferred the liquid from the pH buffered solution equilibrated at reaction temperature into the Teflon Savillex PTFE reaction cell (60 mL). The fluid entered the cell through ingress ports and exited the cell through the egress ports located at the top of each reactor. The solution was collected at ambient temperature in vessels present outside of the oven. Each pump ran up to six reactors for periods ranging from 28 to 70 days with lower flow rates being run for longer periods. Solution blanks containing only the buffer solution were run at 50 mL/d. Frequency of sample collection varied based on the flow rate. Most samplings were performed daily, though this changed to every third day for the lower flow rates (10 and 50 mL/d). The pH was measured using an aliquot of the effluent. Another aliquot was acidified using 15.8 M grade nitric acid. The elemental concentration of the acidified aliquot was measured using inductively coupled plasma optical emission spectroscopy (ICP-OES). The sample masses and flow rates for each experiment is displayed in Table I.

The goal of these tests is to measure the steady-state Si concentration which is given as the average concentration of Si at the outlet for the last three samplings. The average steady-state concentration is then used to calculate the corresponding dissolution rate, r (Equation 1)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 $\pm 40\%$.

¹ Equation 1 is valid only when there is no measurable Si present in the inlet solution.

The surface area of P1BG1 and BSRG1 samples were measured using N₂-adsorption BET analyses. The P1BG1 granular product had a surface area of 5.7±1.0 m²/g; whereas the surface area of the BSRG1 material was 3.8±0.1 m²/g. It is important to note that the BET measurement provides an estimate of the effective or wetted surface area which is approximately two orders of magnitude greater than the calculated geometric surface area [8]. The discrepancy between the BET and geometric surface area—commonly referred to as surface roughness—is probably the result of intergranular porosity (i.e., porosity between individual grains) that occurs when smaller particles aggregate to form larger grains. The actual rate is suggested to lie between the geometric and the BET surface area [13]. Because of the large difference in surface area, alternative techniques are being explored to improve the estimate.

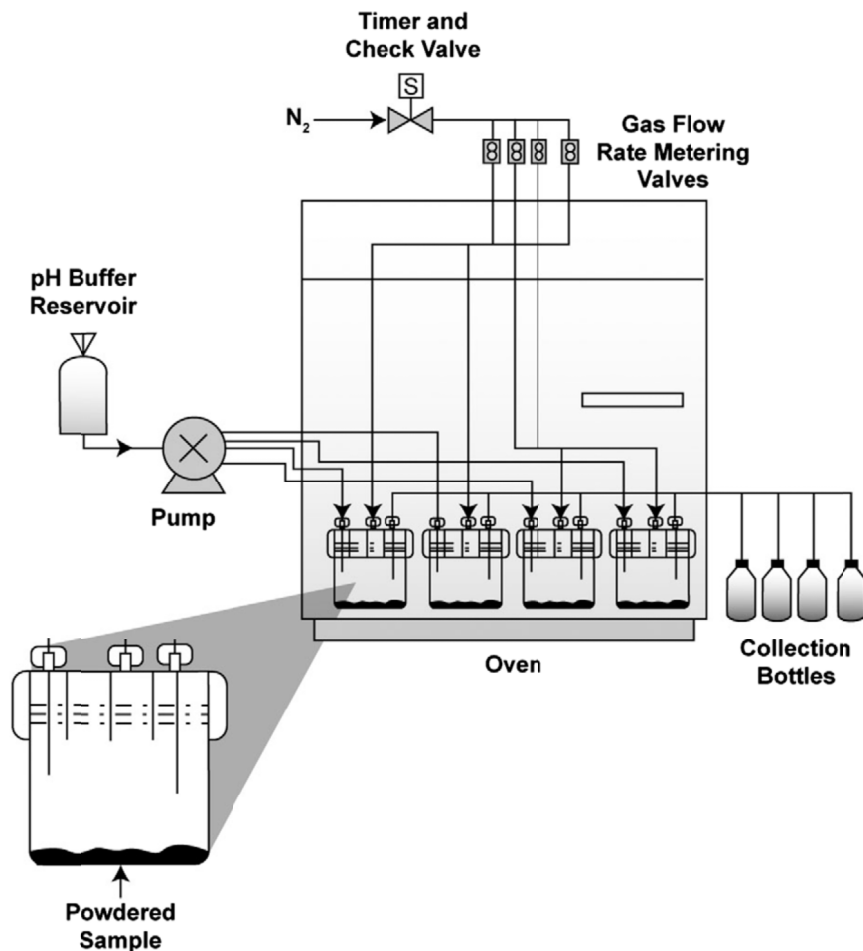


Fig. 2. The single pass flow-through (SPFT) apparatus used in this study (not to scale).

Table I. Nominal Flow Rate and Corresponding Mass Used in the Experiments

Flow rate (mL/d)	mass (g)
300	0.25
200	0.25
150	0.50
90	0.75
50	0.75
10	1.00

RESULTS

The pH versus time for the BSRG1 sample is given in Figure 3. It is seen that the pH does not differ from nominal pH of 9. Results from the P1B material are similar. A pH of 9 is that measured at 23°C.

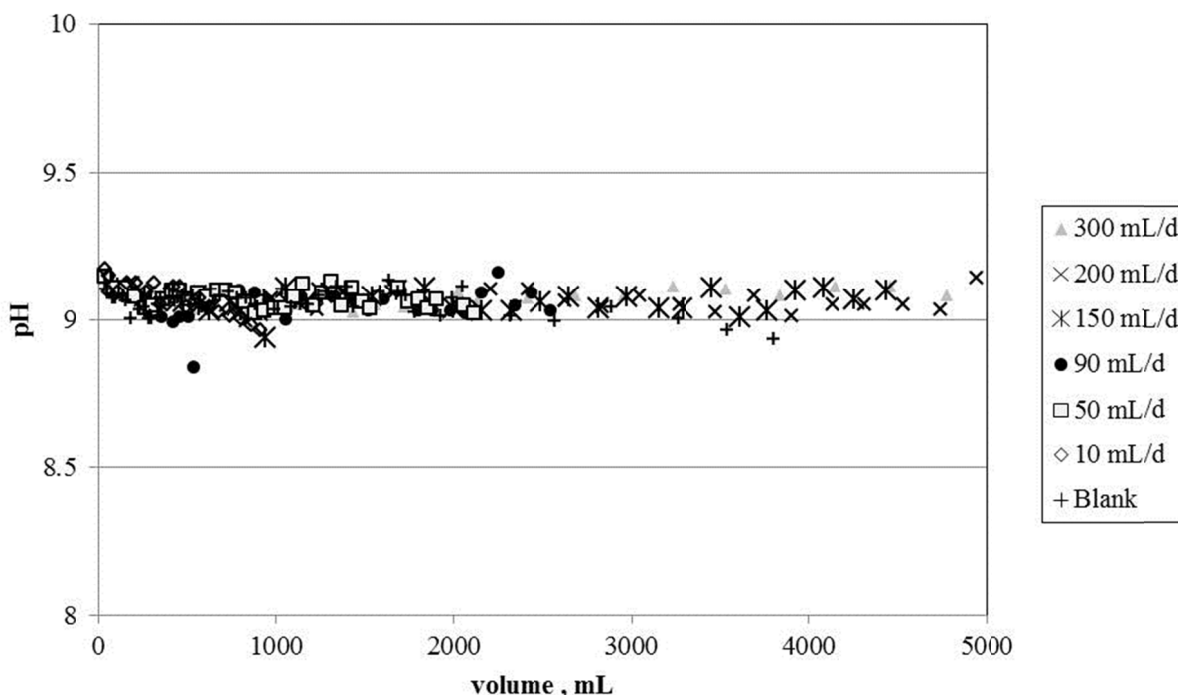


Fig. 3. The pH measured at the outlet solution versus time for the BSR sample.

A graphical representation of the effect of varying the ratio of the flow rate, q , to the sample surface area, S , on the release rates of Si for the P1BG1 and BSRG1 materials is shown in Figure 4. Si is a principle component of the feldspathoid minerals present in the FBSR NAS product and is used here as an indicator for the total dissolution of the waste form. The P1BG1 and BSRG1 samples follow the same general trend where a decrease in the release rates is observed with smaller q/S values. This phenomenon can be explained by a build-up of dissolved mineral components in the contacting solution. If one looks at the right-hand side of

the q/S graph, the rates seem to converge to a single value. This value is considered the forward dissolution rate of the material. The values are $1.3 (\pm 0.5) \times 10^{-3} \text{ g/m}^2\text{d}$ and $0.6 (\pm 0.2) \times 10^{-3} \text{ g/m}^2\text{d}$ for the BSRG1 and P1BG1 materials, respectively.

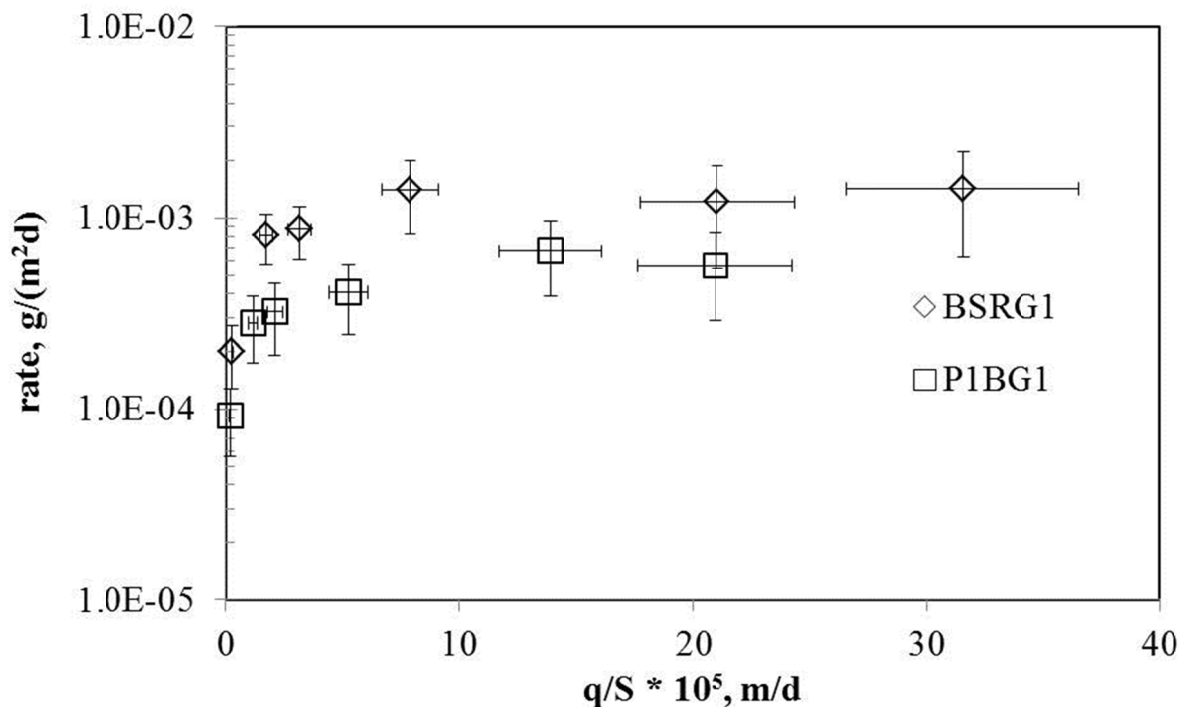


Fig.4. The rate of release of Si for the BSRG1 and P1BG1 samples as a function of q/S (flow rate/surface area).

DISCUSSION

Fluidized Bed Steam Reforming (FBSR) offers a continuous method that can process LAW waste streams that contain organics, nitrates, sulfates/sulfides, chlorides, fluorides, volatile radionuclides or other aqueous components. The technology converts the waste into a crystalline mineral waste form at moderate temperatures (700-750°C). In this study, materials produced at the engineering-scale (P1BG1) and the lab-scale (BSRG1) have been studied.

The results from this study can be used to estimate the forward, or maximum, rate of dissolution of the multi-phase material. A forward dissolution rate of $1.3 (\pm 0.5) \times 10^{-3} \text{ g/m}^2\text{d}$ for the BSRG1 lab-scale material and $0.6 (\pm 0.2) \times 10^{-3} \text{ g/m}^2\text{d}$ for the P1BG1 engineering-scale material. This suggests that the rate of the BSRG1 is nearly double that of the P1BG1 waste form in the SPFT system at pH 9 and 40°C though the values do not differ much if experimental error is taken into account. In fact, release rates of the two minerals would be nearly equal if they had an equal surface area suggesting that methods used to calculate the surface area available for dissolution may need to be reconsidered such as using a geometrical surface area instead of BET. Regardless, these results are similar to Si releases during 14-day SPFT tests conducted on Hanford LAW simulant FBSR bed product in an earlier study [10]. In all cases, both of these values are one order of magnitude below forward dissolution rates of borosilicate and borosilicate glasses measured at the same pH and temperature [11].

Despite these promising results, additional testing of the FBSR mineral product is needed if one is to compare the FBSR mineral durability studied over only 10 years to the glass waste forms whose durability have been studied for the past 30 years. Other remaining unresolved issues are the effects of using a monolith to encapsulate the granular waste form to conform to the Hanford site Integrated Disposal Facility (IDF) standards. Methods to consolidate the FBSR granular product into monolith waste forms are being investigated [10, 12]. Results of 7-day Product Consistency Tests (PCTs) conducted on monolithed samples can be seen elsewhere [8].

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