Radioactive Benchscale Steam Reformer Demonstration of a Monolithic Steam Reformed Mineralized Waste Form for Hanford Waste Treatment Plant Secondary Waste - 12306

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ABSTRACT

Hanford currently has 212,000 m^3 (56 million gallons) of highly radioactive mixed waste stored in the Hanford tank farm. This waste will be processed to produce both high-level and low-level activity fractions, both of which are to be vitrified. Supplemental treatment options have been under evaluation for treating portions of the low-activity waste, as well as the liquid secondary waste from the low-activity waste vitrification process. One technology under consideration has been the THOR® fluidized bed steam reforming process offered by THOR Treatment Technologies, LLC (TTT). As a follow-on effort to TTT's 2008 pilot plant FBSR non-radioactive demonstration for treating low-activity waste and waste treatment plant secondary waste, TTT, in conjunction with Savannah River National Laboratory, has completed a bench scale evaluation of this same technology on a chemically adjusted radioactive surrogate of Hanford's waste treatment plant secondary waste stream. This test generated a granular product that was subsequently formed into monoliths, using a geopolymer as the binding agent, that were subjected to compressibility testing, the Product Consistency Test and other leachability tests, and chemical composition analyses. This testing has demonstrated that the mineralized waste form, produced by co-processing waste with kaolin clay using the TTT process, is as durable as low-activity waste glass [1]. Testing has shown the resulting monolith waste form is durable, leach resistant, and chemically stable, and has the added benefit of capturing and retaining the majority of Tc-99, I-129, and other target species at high levels.

INTRODUCTION

The 56 million gallons of highly radioactive mixed waste at Hanford's tank farm will be separated into a high-level waste (HLW) stream and a low-activity waste (LAW) stream in a pre-treatment plant. Much of this waste will be treated through the Site's vitrification facility. However, the planned treatment processes generate a significant amount of secondary waste that contains concentrated species such as Tc-99 and I-129 that are volatized during the vitrification process. Various treatment alternatives have been evaluated to treat this secondary waste stream. One of these is the THOR® Fluidized Bed Steam Reforming (FBSR) technology developed by TTT. A non-radioactive pilot plant demonstration of this technology for treating both the LAW and Waste Treatment Plant Secondary Waste (WTP-SW) streams was performed in 2008 using the Engineering Scale Technology Demonstration (ESTD) pilot plant located at the Hazen Research facility (Hazen) in Golden, Colorado [2]. While the 2008 test clearly demonstrated the capabilities of the THOR® process on surrogate waste streams representative of the expected waste to be treated at the Hanford site, additional testing was warranted to confirm the findings from the non-radiological testing using a radiological surrogate. This follow-on WTP-SW work was performed using a bench top test unit in a Shielded Cell Facility (SCF) on a Defense Waste Processing Facility (DWPF) secondary waste sample that was shimmed to represent the expected WTP-SW chemical composition. This work was performed by the Savannah River National Laboratory (SRNL) from June 2009 to December 2011.
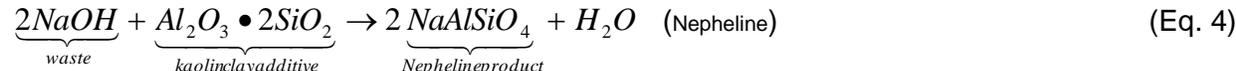
METHOD

THOR® Process Overview

The THOR® process, a fully integrated system, is designed around a core fluidized bed steam reformer and off-gas treatment system. This process can produce a mineralized or carbonate product, and was successfully demonstrated in mineralized pilot plant runs performed in 2007 and 2008. The first reformer, the Denitration and Mineralization Reformer (DMR), operating at approximately 725°C in a chemically reducing mode, evaporates liquids, volatilizes and destroys organics, converts nitrates and nitrites to nitrogen gas, and converts the nonvolatile constituents of the feed into a solid product. The reducing conditions in the DMR are created by the injection of fluidizing steam and granular carbon, which react to produce small amounts of hydrogen, carbon monoxide, and carbon dioxide via the water gas and water gas shift reactions:
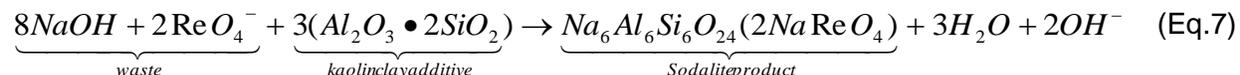
$$H_2O_{(g)} + C_{(s)} \rightarrow H_{2(g)} + CO_{(g)} \tag{Eq. 1}$$

$$CO_{(g)} + H_2O_{(g)} \rightarrow H_{2(g)} + CO_{2(g)} \tag{Eq. 2}$$

The net result of these two reactions is:

$$2H_2O_{(g)} + C_{(s)} \rightarrow 2H_{2(g)} + CO_{2(g)} \tag{Eq. 3}$$

The non-volatile constituents in the waste feed are converted into highly leach resistant forms by reaction with an aluminosilicate clay additive. The mineral species formed are principally alkali aluminosilicates, also referred to as feldspathoid mineral species. These contain unique cage-like structures that retain anions and radionuclides ionically bonded to the aluminosilicate structure and to sodium. These minerals also incorporate other ions elsewhere in their molecular structures. Examples of these minerals are nepheline, nosean, and sodalite, as shown below [3,4]:
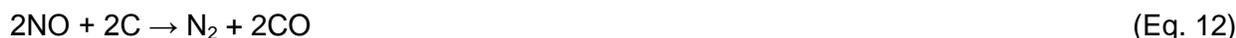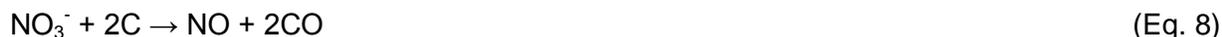
$$\underbrace{2NaOH}_{waste} + \underbrace{Al_2O_3 \bullet 2SiO_2}_{kaolin\,clay\,additive} \rightarrow \underbrace{2\,NaAlSiO_4}_{Nepheline\,product} + H_2O \quad \text{(Nepheline)} \tag{Eq. 4}$$

$$\underbrace{8NaOH + SO_4}_{waste} + \underbrace{3(Al_2O_3 \bullet 2SiO_2)}_{kaolin\,clay\,additive} \rightarrow \underbrace{Na_6Al_6Si_6O_{24}(Na_2SO_4)}_{Nosean\,product} + 3H_2O + 2OH^- \quad \text{(Nosean)} \tag{Eq. 5}$$

$$\underbrace{8NaOH + 2Cl}_{waste} + \underbrace{3(Al_2O_3 \bullet 2SiO_2)}_{kaolin\,clay\,additive} \rightarrow \underbrace{Na_6Al_6Si_6O_{24}(2NaCl)}_{Sodalite\,product} + 3H_2O + 2OH^- \quad \text{(Sodalite)} \tag{Eq. 6}$$

Or (for Re-Sodalite),

$$\underbrace{8NaOH + 2\operatorname{Re}O_4^-}_{waste} + \underbrace{3(Al_2O_3 \bullet 2SiO_2)}_{kaolin\,clay\,additive} \rightarrow \underbrace{Na_6Al_6Si_6O_{24}(2Na\operatorname{Re}O_4)}_{Sodalite\,product} + 3H_2O + 2OH^- \tag{Eq.7}$$

If organics are present in the feed they are steam reformed into carbon dioxide and a small quantity of carbon monoxide, hydrogen, and light hydrocarbons, with methane being the main constituent. These are subsequently treated in the second stage oxidization unit called the Carbon Reduction Reformer (CRR). The major process gases leaving this second stage are steam, nitrogen, and CO_2.

The water gas and water gas shift reactions and evaporation of water are all endothermic processes. A small amount of oxygen is added to the bed to react exothermically in the bed with carbon, hydrogen, and carbon monoxide to maintain the bed temperature (auto-catalytic heating). In addition, several reaction mechanisms convert nitrites and nitrates to nitrogen.

Some examples are shown below:

$$NO_3^- + 2C \rightarrow NO + 2CO \tag{Eq. 8}$$

$$NO_3^- + C \rightarrow NO_2 + CO \tag{Eq. 9}$$

$$2NO_3^- + 4C \rightarrow N_2 + 2CO + 2CO_2 \tag{Eq. 10}$$

$$2NO_2^- + 3C \rightarrow N_2 + 2CO + CO_2 \tag{Eq. 11}$$

$$2NO + 2C \rightarrow N_2 + 2CO \tag{Eq. 12}$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \tag{Eq. 13}$$

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O \tag{Eq. 14}$$

The granular product generated from this process can be further processed for disposal by forming the mineralized granular product into monoliths by mixing it with a binding agent. The agent used during the Benchscale Steam Reformer (BSR) tests was a geopolymer, though other binders have also been evaluated. The resulting monoliths can be evaluated from a disposal standpoint by measuring compressive strength, leachability, and chemical composition.

Benchtop Scale Radioactive Demonstration

Pilot plant demonstrations for the use of the THOR® FBSR process to treat potential Hanford wastes were performed in Golden, Colorado during 2008. Tests were performed on non-radiological simulants of the expected LAW and WTP-SW streams. In order to confirm the findings of the non-radioactive FBSR pilot scale tests, a BSR was designed, constructed, and operated at the SRNL. BSR testing with WTP-SW waste surrogates and associated analytical analyses and tests of granular products (GP) and monoliths began in the fall of 2009, and then was continued from the fall of 2010 through the spring of 2011. The initial non-radioactive tests were followed by processing radioactive simulant commencing in 2010 with a demonstration of Hanford's WTP-SW using Savannah River Site (SRS) High Level Waste (HLW) secondary waste from the Defense Waste Processing Facility (DWPF), which was shimmed with a mixture of I-125, I-129 and Tc-99 to chemically resemble the projected WTP-SW composition. The initial non-radioactive simulants were processed as a basis for comparison with the FBSR product generated during the pilot scale testing.

The principle objective of this activity was to demonstrate, on a bench scale, the production of a radioactive granular product and a final monolithic waste form comparable to that generated using non-radioactive simulant in prior ESTD testing. A non-radioactive simulant was first tested in the BSR in order to provide: (1) optimization of processing parameters for radioactive testing, including the evaluation of multiple potential binders, (2) granular samples for testing the durability response of the BSR product in comparison with the ESTD product, and (3) granular products to monolith and compare (durability and compressive strength) to the monolithic waste forms prepared from the ESTD products.

The granular mineralized waste form products from the BSR tests were characterized and tested. A portion of the granular product was also formed into monoliths. The monoliths were first subjected to compressibility testing to verify they pass a minimum of 500 psi. This value comes from the acceptance criteria for near-surface disposal at the Hanford site. The requirement is derived from an NRC Branch Technical Position on low-level waste (LLW) forms. It also recognizes that a monolithic waste form reduces the impact to human health for the "intruder scenario" in the waste site Performance Assessment.

Crushed pieces of the radioactive monoliths resulting from the compressibility testing were then subjected to ASTM C1285 Product Consistency Test (PCT) analyses. Additionally, the radioactive monoliths were leach tested according to ASTM C1308 using the same temperature

and leaching intervals as the ANSI 16.1 test. Both the granular products and the monolith products were leach tested using the EPA TCLP procedure performed by an EPA certified lab.

BSR Feed Composition

SRNL generated granular product and monoliths using both non-radioactive and radioactive WTP-SW simulants. For mineralized runs, 307 grams of a 55% OptiKasT / 45% Sagger XX kaolin clay mixture per liter of simulant was added to both the non-radioactive and radioactive runs to form the granular product. Analysis was performed on both feed and test product.

Non-Radioactive Simulant: The non-radioactive simulant was selected to match the simulant used during the 2008 FBSR ESTD runs. The composition for this simulant was based on an extensive evaluation of the anticipated chemical composition of the relevant Hanford waste streams [2]. Previous ESTD FBSR testing used spikes up to 10 to 1000 times the expected amounts of various RCRA metals and radionuclide surrogates. Since some of these RCRA/UTS metals are not projected to be in the WTP-SW stream, no Ba, Cd, Tl, Se, and Sb were added to the simulant feed. It was determined these metals would not provide any beneficial information.

Radioactive Simulant: The radioactive feed for the BSR was prepared from the Savannah River Sites (SRS) DWPF Off-Gas Condensate Tank (OGCT) solution. A 20 L sample was evaporated by a factor of 20x and then trimmed with radioactive Tc-99 and mixtures of radioactive I-125 and I-129 to make the DWPF sample match the anticipated WTP-SW composition for Hanford. Re and non-radioactive I-127 were added at the same levels as used in previous non-radioactive campaigns to provide a performance comparison with the Tc-99 and radioactive Iodide (I-125 and I-129), respectively. This provided a confirmation that the Re, used in the non-radioactive simulant, was an appropriate surrogate for Tc-99, which was used in the radioactive tests.

BSR Setup and Operation

The SRNL BSR design is a two-reformer unit that produced the same mineralized products and gas streams as the ESTD FBSR pilot plant (Figure 1&2). Due to spatial limitations, the BSR did not utilize a truly fluidized bed since it had to fit in one of SRNL's shielded cells and the cell did not have sufficient height to allow for product disengagement. Steam was passed through the feed which formed a porous product "biscuit". Steam flowed through the biscuit so the chemical reactions were the same, but the product had to be homogenized manually instead of by fluidization. Because there were no organics in the WTP-SW, only one of the two reformers was used (Fig 2). A Scanning Electron Microscopy (SEM) analysis showed that the final reacted particles in the BSR were substantially similar to those formed in the pilot plant FBSR.

Fig. 2. Photo of DWPF Evaporator and Shielded Cell Benchscale Steam Reformer Setup

Approximately 200 mL of the feed slurry was kept agitated with a stir bar mixer while a peristaltic pump fed the slurry through the center feed port in the lid of the unit at about 1 ml/min. A mineralized product formed in the DMR in the presence of superheated steam, clay, and carbon. The off-gases flowed into a condenser train, which cooled the gas to about 25°C and condensed the steam. A bubbler in the trap section of the condenser removed the remainder of the particulate carry-over. Finally, the gas passed through a 25 µm and 2 µm filter prior to being measured by a Mass Spectrometer (MS) for H_2, O_2, CO_2, N_2, and Ar before being discharged to an exhaust hood. This simplified BSR design made it easier to perform mass balances for the radioactive and non-radioactive constituents of concern.
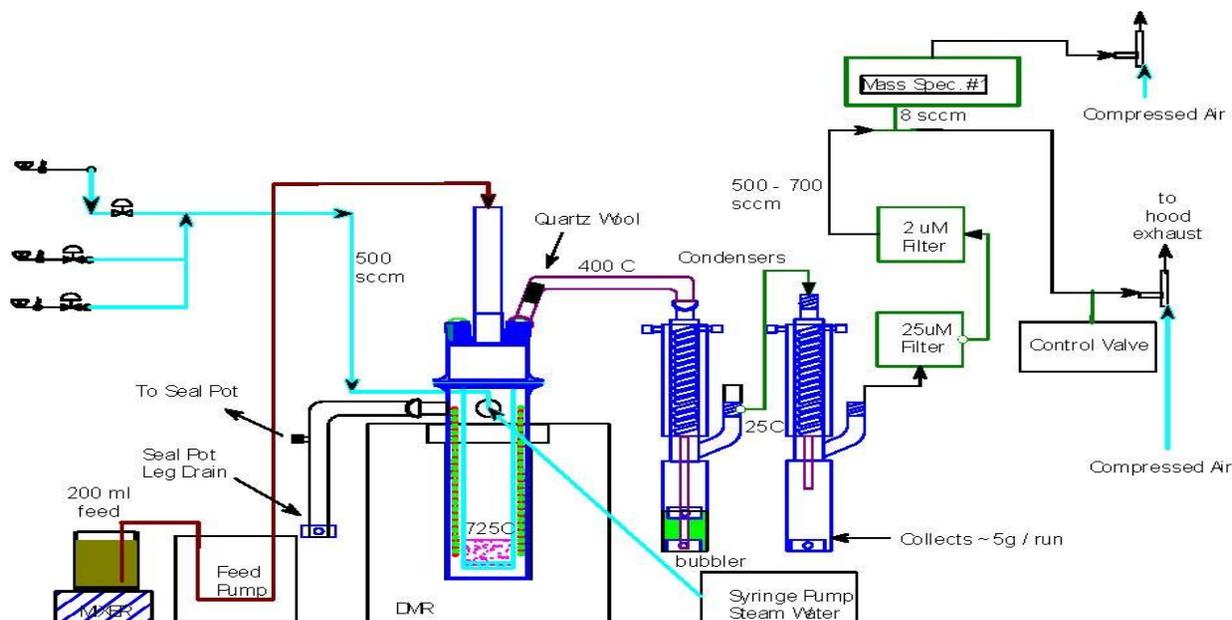
Fig. 2. Schematic of the Benchscale Steam Reformer Setup

The WTP-SW runs were performed in three different campaigns with the process control technology advancing between runs. Campaigns were performed in the Fall of 2009 using surrogate feed and relatively high coal levels. Surrogate feed campaigns were again performed in August 2010 with reduced coal to target lower residual coal levels in the BSR granular product and lower the REDuction/OXidation of the product to ensure that Re and Tc-99 would be in the correct oxidation state to enter the sodalite cage (see Eq.7). Two radioactive feed BSR runs were then performed in September 2010. All of the 2009 and 2010 BSR campaigns used measured H_2 (reductant) gas concentrations as the critical process control parameter. A final set of surrogate feed BSR runs were performed in the Spring of 2011 that used the most recent REDOX control strategy [5]. The purpose of the latter 2011 BSR runs was to produce more granular product for the monolith tasks as the BSR granular product produced previously (Fall 2009 and Fall 2010) had been consumed in previous monolith formulation efforts. An additional goal of these latter Spring 2011 BSR runs was to further investigate the overall mass balance of the BSR runs under the final REDOX control operational strategy.

Table I shows the parameters used in the BSR as compared to typical FBSR parameters. The first two data columns in the table simply show the parameters in different units. The feed rate of approximately 1 mL/min for the DMR was established based on the equipment's ability to pump the clay/coal/waste slurries and the DMR's ability to convert it to a mineral product without the presence of unreacted product. Coal was fed at a rate of 0.20 g/min, which is less than the 0.35 g/min scaled equivalent because the BSR is a hybrid unit that uses coal for auto-catalytic heat augmented by external heating. As such, it doesn't use as much coal as the scaled equivalent

of the pilot plant DMR. Also, excess unreacted coal in the product is undesirable, as it adds unnecessary volume to the product and causes REDOX measurement interferences. Total gas flow was as high as reasonably achievable, but limited based on observed solids carry over. Using nitrogen from a cylinder, the total gas flow was controlled to allow for inert conditions (no air in-leakage with 100% N_2) all the way up to 100% air. The measured H_2 gas concentration was the critical control parameter for the 2008 pilot plant ESTD FBSR and initial 2009 and 2010 campaigns performed with the SRNL BSR. The H_2 concentration was maintained at the nominal range of 1% to 3% (dry basis) by the amount of allowable air in-leakage into the BSR system. The DMR temperatures were the same as for the ESTD runs (see Table I). The BSR ran at a slightly negative pressure, whereas the ESTD FBSR runs operated at a slightly positive pressure. All operational conditions were approved by the testing team and the runs and conditions documented.

Table I. Relative Scaling of Process Operating Parameters for ESTD FBSR vs. BSR Runs

Parameter	ESTD	Scaled BSR	Actual BSR
Feed Rate	757 mL/min (0.2 gpm)	1 ml/min	1 ml/min
Coal Rate	265 g/min (35 lbs/hr)	0.35 g/min	0.2 g/min
Gas Rate	2885 SLM (101.9 scfm)	3.8 SLM	0.7 SLM
Steam Rate	-	--	0.6 mL/min (36 mL/hr)
H_2 Concentration	1% - 2%	--	1% - 3%
DMR Temperature	720 ºC	--	720 ºC
Pressure	14-21 kPa (2 to 3 psig)	--	(-750 Pa (-3 in wc)

The BSR DMR used two thermocouples for measuring the reaction zone temperature. Initially the controlling thermocouple was 1 inch into the bed product solids and the upper thermocouple was positioned 10.16 cm above the ZrO_2 beads holding the bed in place. These locations were later changed to have the controlling thermocouple 6.35 cm above the ZrO_2 beads and the lower thermocouple at the bead surface. This change was made to improve control, as it prevented water and steam from the slurry from contacting the controlling thermocouple. Off-gas conditioning was performed to protect the mass spectrometer, which measured the downstream off-gas composition. The same coal that was used during the ESTD FBSR pilot plant runs was used as the BSR reducing agent. In addition, a small amount of $Fe(NO_3)_3 \cdot 9H_2O$ was added to the BSR runs to act as an analytical indicator of the REDOX potential in the product, typically targeting nominally 1 wt% Fe in the BSR mineral product which forms spinel, Fe_3O_4. The REDOX measurement was used to determine the expected distribution of Tc-99 and other REDOX sensitive species in the product from an Electromotive Force (EMF) series developed at Virginia Military Institute (VMI).

Monolith Fabrication and Curing

Monolith formation for the granular products produced from the BSR were initially formed using the GEO-7 fly ash geopolymer formulation selected during previous SRNL monolith studies on ESTD LAW and WTP-SW products produced in 2008 [6]. The previous work optimized monolith formation based on LAW ESTD products, not the WTP-SW ESTD products. However, as part of that work, several different monolith sizes were fabricated with the WTP-SW ESTD granular products. These WTP-SW GEO-7 monoliths gave the best PCT durability for Re release, TCLP, and compressive strength, so this GEO-7 formulation was specified as the monolith recipe to be used in the follow-on BSR work (WTP-SW is also referred to as module A formation in certain referenced material). However, monoliths had also been made with clay and ESTD granular material. See typical 15¼ cm x 30½ cm (6"x12") GEO-1 monolith in Fig. 3.

Initial attempts to monolith the Fall 2009 BSR granular product using the GEO-7 formulation with 65% dry basis waste loading did not pass the compressibility test target due to excessive

water in the formulation. After the initial monolith attempts, follow-on scoping tests using granular product from earlier BSR runs indicated that longer mixing times were needed to make the GEO-7 formulation using the BSR granular product. These latter tests produced monoliths with compressive strengths above the 3.45E6 Pa (4.07E6 to 1.08E7 Pa) target. It should be noted that the crystalline phases produced in the monolith formation are similar to the starting crystalline phases of the initial BSR granular products. However, follow-on monolith efforts in the Fall of 2010 using BSR WTP-SW radioactive granular product again indicated that even with prolonged stirring/mixing, the mixture did not form a monolithic form using the prescribed water amounts for the GEO-7 formulation.

Fig. 3. **Clay Based 15¼ cm x 30½ cm GEO-1 Monolith for ESTD WTP-SW at 68% FBSR Loading.**

Detailed evaluations of the monolith formation procedures, mix recipes, and a detailed investigation [7] on the initial radioactive monolith process determined that in order to accommodate the high fluoride in the WTP-SW, the monolith formulations should be made with reactive metakaolin clay rather than fly ash. Three important reasons for preferring kaolin clay over fly ash include (1) the unreactive nature of some of the components found in fly ash, such as the minerals mullite and quartz, and (2) the variable nature of fly ash compositions and, (3) clay is more resistant to fluoride attack in an aqueous environment. Accordingly, it was decided to switch geopolymer binder components from the fly ash to the heat-treated clay. Triplicate BSR WTP-SW 2.54 cm (1 inch) diameter x 5.08 cm (2 inch) monolith cylinders made with the clay formulation at 42% FBSR loading and the WTP-SW granular product from the Spring 2011 were prepared and one was compression tested. The crushed monolith was then used for all subsequent testing including chemical composition, PCT and TCLP. A single 2.54 cm diameter x 5.08 cm cylinder was made with the radioactive BSR WTP-SW granular product, along with a smaller 1.27 cm diameter x 2.54 cm 'button'. The radioactive 2.54 cm diameter x 5.08 cm monolith was compression tested and the crushed monolith was then used for subsequent testing including chemical composition, PCT and TCLP. The radioactive button was used for monolith accelerated leach testing (ASTM C1308/ANSI 16.1). The tests met the analytical goals set by the testing team. Note that the GEO-1 formulation in Fig. 3 is 68% FBSR loaded.

Analytical Tests

The granular products and the monoliths for both the non-radioactive and radioactive runs were subjected to several analytical tests.

The granular products (both simulant and radioactive) were tested and a subset of the granular material (both simulant and radioactive) were stabilized in the clay-based geopolymer matrix. Extensive characterization of the granular and monolith material was made, as follows.

- ASTM C1285 Product Consistency Test testing of granular and monolith.
- ASTM C1308 (ANSI 16.1) accelerated leach testing of the radioactive monolith.
- EPA Method 1311 TCLP testing.
- ASTM C39/C39M and ASTM C1231 compressibility testing of monoliths.

PCT Durability Testing: The chemical durability of the BSR products and monoliths were determined using the PCT ASTM procedure C 1285-08 [11]. The BSR granular product and monolith product samples were sized between -100 and +200 mesh (< 149 μm and > 74 μm), which is the same size fraction used to express glass waste form performance. The granular products (simulant and radioactive) were not put through a grinder, but rather wet sieved using an automatic sieve shaker device. The sized material was washed six times (2 with rinse/decant, and 4 with rinse/sonication/decant) with 100% ethanol to remove electrostatic fines, followed by overnight drying in an oven at 90ºC. Water was not used for washing to minimize the potential for water soluble phases being removed prior to leaching as cautioned by the ASTM C1285-08 procedure. Portions of the washed and dried BSR granular product and monolith powders were analyzed for particle size. Brunauer-Emmett-Teller – Surface Area (BET SA) measurements via nitrogen gas adsorption was also performed on the sieved/washed/dried portions of the powders used for PCT. The PCT durability testing was performed on non-roasted samples for all tests in this project, i.e., samples that contained residual BSR coal. The BET SA was performed on a non-roasted PCT sample for the initial Fall 2009 simulant A granular product; however, all subsequent BET SA measurements (radioactive A granular product, simulant A monolith and radioactive A monolith) were performed on roasted powders. Standard glass samples were included in all the PCTs to monitor PCT performance vs. past historical data for the ARM [12] and Low activity Reference Material [13] glasses.

Due to the high surface roughness of ceramic/mineral waste forms such as FBSR products the method for surface area per unit volume determination for this work involves a measurement of the surface area by the BET method. In this method, the amount of an inert gas that condenses on a powdered sample of known mass is measured at a temperature near the boiling point of the gas. The amount of gas condensed on the sample is measured by the pressure change in the system upon exposure to the sample. This method measures all open pores, inclusions, irregularities, etc. that are penetrable by the inert gas. Due to the presence of coal in the sample, several adjustments have to be made in these equations to express the leaching of a particular element on a coal free basis as described in Pareizs et al. [14]. This is done because the coal does not contain any of the constituents of concern (COC) structurally as a separate mineral phase and so it is considered a diluent in the sample when it cannot be removed manually. Coal also contributes to the BET surface area as shown in Pareizs et al. [14] and would cause an abnormally high BET surface area. Therefore, a subset of the PCT prepared sample sieved to -100 to +200 mesh and ethanol washed is roasted at 525°C in air to get a 'coal free' BET surface area, but this subset is not used in the leach testing.

Accelerated Leach Test: The radioactive monolith was leach tested using the ASTM C1308 'Standard Test Method for Accelerated Leach Test for Diffusive Releases from Solidified Waste'. This test is similar to the ANS 16.1 Leach Test. The liquid-to-solid ratio is 10X volume (ml) to monolith surface area (cm^2), giving a 127 mL leachant volume required for the 1.27 cm diameter x 2.54 cm cylinder (total of 12.7 cm^2 surface area). Leaching intervals consist of 2 hours, 5 hours, 17 hours, and 24 hours, and then daily for the next 10 days. An additional leaching interval of nineteen days is also included in this work. The specimen is suspended from the top of the polybottle container lid and the specimen support contacts no more than 1% of the surface area so as to not impede leaching. Leachate concentrations are converted to cumulative amounts of constituents leached using the leachate volume and mass of monolith and measured elemental compositions. The observed diffusivity for each constituent is

calculated using the analytical solution for simple radial diffusion from a cylinder into an infinite bath as presented by Crank [15].

The mean observed diffusivity for each constituent can be determined by taking the average of the interval-observed diffusivity with the standard deviation. The leach index (LI), the parameter derived directly from immersion test results, evaluates diffusion-controlled contaminant release with respect to time. The LI is used as a criterion to assess whether solidified/stabilized waste will likely be acceptable for subsurface disposal in waste repositories.

Durability TCLP: The Hanford LAW is a listed waste under RCRA. The WTP-SW, derived from the treatment of the LAW in a melter, will also be considered a listed waste. When treated, the waste form must retain the hazardous components at the Universal Treatment Standard (UTS) limits [16]. The Land Disposal Restrictions (LDRs) will apply to shallow land burial at Hanford.

All blended granular product samples and crushed monoliths were evaluated for retention of the hazardous metals by EPA Method 1311 (TCLP) [17]. The TCLP method prescribes a 100 g sample sized to < 9.5 mm to 20X leachate ratio; however, in this program the amount of either radioactive BSR granular product or monolith was very limited. Accordingly, only 10-25 gram simulant samples and 3 g to 6 g radioactive samples were submitted to GEL Laboratories, LLC of Charleston, SC, a EPA-certified laboratory. In the standard leaching procedure, samples of < 9.5 mm diameter solids are extracted by a buffered acetic acid fluid for 18 hours. The extraction fluid (leachate) is then filtered and analyzed for elements of interest.

Since organics are destroyed in the FBSR process, only the following RCRA hazardous inorganic species were measured: As, Ba, Cd, Cr, Pb, Se, Ag, Ni, Sb, Tl and Zn. If the concentration of a hazardous inorganic species from the simulated waste form exceeds the UTS limits then it is assumed that the real waste, treated in a similar manner, would also fail the UTS limits and require further remediation. As such, simulant and radioactive BSR granular products and monoliths were submitted for TCLP analyses. None of the materials submitted for TCLP were heat treated to remove carbon. Since TCLP results are reported on an 'mg/L' basis for comparison to the UTS limits, no normalization of the TCLP leachate data was performed, i.e., normalization similar to what is performed for PCT using elemental fractions and measured surface areas. There can be excessive variability in data derived from TCLP testing due to the lack of any specification in lower particle sizes used in this test, i.e., particles can range from < 9.5 mm down to any potential size including submicron sizes.

Compressive Strength Test: All the cylinders were compressibility tested using ASTM C39-04A. These testing procedures and instruments were the same as used in previous SRNL studies on monoliths made using FBSR products [6,8]. Initial monolith compressibility testing on the GEO-7 monoliths prepared in the Fall of 2009 was performed at the SRS by a member of the United Research Services (URS) Company in the SRS N-Area Civil Engineering Test Facility. All subsequent monolith compressibility testing (from 2010 to end of test) used similar instrumentation that had been set up within SRNL. SRNL used a Humboldt Manufacturing model HCM-3000-LXI compression tester. The samples were tested using a modified version of the 2010 reissue of ASTM C 39/C39M [9] to accommodate the sample size. Samples were tested with unbonded caps using ASTM C 1231 [10] modified to accommodate the sample size and lower limit of compressive strength. Compressibility testing of the radioactive monolith was performed by identical equipment using the same methodology in a double plastic bag during testing to prevent contamination of the instrument and lab.

RESULTS

Mass Balance Results

The total mass balance recoveries of the key species were calculated for three of the WTP-SW BSR campaigns. Key species examined in the simulant and test campaigns for the mass

balance include: Radioactive runs: Cs-137, I-125, I-129, and Tc-99; and for non-radioactive runs: Cs-133, Re, I-127, Al, Cl, Cr, Na, Si, and SO_4^{2-}. No mass balance was performed on the original Fall 2009 WTP-SW BSR processing campaign. Percent recovery data for measured and calculated constituents are presented in Table II.

The non-radioactive Cs-133 recovery was 99% for the original Fall 2010 simulant campaign and 77% for the Spring 2011 simulant campaign. The lower recovery in the Spring 2011 simulant campaign was due to the inadvertent low concentration of Cs-133 in the feed for the Spring 2011 run (about 200,000 µg/L) versus that in the Fall 2010 campaign (about 2,000,000 µg/L). For any mass balance, it is more difficult to track a low concentration through a system, as errors and detection limit issues are amplified which impact the overall calculated recovery rates. It is expected that had the Spring 2011 campaign feed levels of Cs-133 been similar to the original module levels, the recovery would have been similar.

Table II. Mass Balance Recoveries for BSR WTP-SW Tests (Total Recovery in %)

Element	Fall 2010 (%)	Spring 2011 (%)	WTP-SW Campaign (%)
	Non-Radioactive		**Radioactive**
Cs-133	99	77	Not Added
Cs-137	Not Applicable		94
I-127	91	106	151
I-125	Not Applicable		93
I-129			98
Tc-99			109
Re	86	95	102
Al	101	107	100
Cr	137	125	181
Na	107	111	151#
Si	114	117	110
Cl	78	99.5	129
SO4	Indeterminate due to low concentration in feed and large contribution from coal.		

High recovery due to as-batched feed value versus measured product value and small amount added in feed

The SO_4 recovery was indeterminate for all WTP-SW runs due to the relatively low amount of sulfate in the feed versus the coal-derived sulfur species. The SO_4 recovery is very dependent on the SO_4 from the coal in the feed mix and the amount of the coal in the feed that is oxidized during treatment.

All total recoveries for the radionuclides in the WTP-SW radioactive campaign were in the range of 93% to 109%. The mass balance data suggests that all analytes remained predominately with the granular product (98-99.4%) in processing the feed slurries in the BSR.

Granular Product and Monolith Characteristics

Table III summarizes the mineralogy as determined by XRD for all the WTP-SW BSR campaigns and the monoliths made from the non-radioactive and radioactive granular products. The mineralogy of the WTP-SW simulants is approximately the same for all three separate BSR campaigns. Sodalite (from the halides) is a major phase and the sulfate sodalite known as nosean is a minor phase since there is less sulfate than halides in this waste simulant. Nepheline is a major phase and low-carnegieite is a minor phase in the Fall of 2009 WTP-SW BSR campaign, and the Spring of 2011 WTP-SW BSR simulant samples appear to have less low-carnegieite than the Fall of 2010 simulant campaign, which has none.

Table III. Mineral Phases Analyzed in FBSR Products

Sample	Low-Carnegieite[ab]	Nepheline[ab]	Nosean[ac] and/or Sodalite[c]	Other Minor Components
Fall 09 (REDOX 0.87 - 0.98)	Y	X	X	SiO_2 & TiO_2
Fall 10 (REDOX 0.65 - 0.78)	N-O	X	X	SiO_2 & TiO_2
Spring 11 (REDOX 0.15 - 0.23)	Y	X	X	SiO_2 & TiO_2
Radioactive (REDOX 0.25 - 0.26)	N-O	X	X	SiO_2
Simulant Monolith	Y	Y	X	SiO_2 & TiO_2
Radioactive Monolith	N-O	X	X	SiO_2 & TiO_2

[a] X = Major Constituent, Y = Minor Constituent, N-O = Not Observed
[b] Nepheline=$NaAlSiO_4$ or $K0.25Na0.75AlSiO_4$ (nominally), Low-Carnegieite=$NaAlSiO_4$ (nominally)
[c] Nosean= $Na_6[Al_6Si_6O_{24}](Na_2SO_4)$; Sodalite=$Na_6[Al_6Si_6O_{24}](2NaX)$, where X=Cl,F,or I

Two different BSR simulant products were analyzed. Simulant 1 is a combination of the three separate runs performed on 8/26/09, 9/2/09, and 9/8/09 and Simulant 2 is a combination of the three separate runs performed on 9/10/09, 9/15/09, and 9/17/09. Chemical composition measurements on the Fall of 2009 Simulant A Batch 1 and Simulant A Batch 2 BSR granular products indicated excellent recovery of all species, as the sums of oxides are all very close to 100%. Chemical composition measurements on the Fall of 2010 radioactive granular product indicated excellent recovery of all species, as the sum of oxides was also very close to 100%.

Chemical composition of the simulant and radioactive monoliths showed similar behavior, as the sum of analyzed oxides was 9 to 12 wt% low. These data suggest that the loss-on-ignition (LOI) measurements to quantify the amount of coal present in the sample were biased low, i.e., not all the moisture and/or residual carbon was removed from heat treatment of the crushed monolith pieces during successive drying from 105 ºC up through 525 ºC. Consequently, the 100% normalized oxide chemical compositions were used in normalizing both the PCT and the ASTM C1308 durability data discussed below, this normalizes out the coal contribution which does not contribute to the durability response.

Table IV shows BET surface area measurements for granular products and monoliths, and compressive strength measurements for the monoliths that pass the 3.45E6 Pa criteria. The BET surface area used is on a coal free basis, as the coal contributes a large factor to the measured BET surface area [14].

Table IV. Data Measured for Granular Products and Monoliths

Monolith	Compressive Strength (Pa)	BET Surface Area w/o Coal (m^2/g)
Sim BSR Granular Product 1	NA	3.87
Sim BSR Granular Product 2	NA	3.87
Rad BSR Granular Product	NA	1.1[a]
Sim Monolith	2.99E7	21.1
Rad Monolith	2.87E7	12.6

[a] A value of 3.87 m^2/g was used to normalize the PCT release.

In the September 2009 tests the BET surface area was determined on the PCT 100/200 mesh powders without pre-roasting of the samples to remove any residual carbon. The presence of residual coal could explain the relatively high measured BET surface areas for these materials in the range of 78 to 123 m^2/g. Accordingly, an average BSR granular product roasted BET surface area of 3.87 m^2/g was used. The observed 1.1 m^2/g BET surface area value for the

roasted radioactive granular product is suspect low, perhaps from the difficulty of remote preparation and handling leading to the powder preparation for the BET SA measurement. Accordingly, as was done with the simulant PCT surface area, an average of BSR granular product roasted BET surface area of 3.87 m^2/g was used. Summary tables of the recovery rates Rad A and SIM A are shown below in Table V and VI.

Table V. Recovery Rates for Rad A Runs

Element	Recovery from All Sources (%)	Product %	Condensate Filtrate %	Condensate Solids %	X-Bar Rinsates %	X-Bar Solids %
Cs-137	94	99.2	0.7	0.01	0.1	0.01
Re	102	99.4	0.5	0.01	0.04	0.002
Tc-99	109	99.8	0.2	0.01	0.02	0.01
I-129	98	98.0	1.9	0.02	0.1	0.02
I-125*	93	98.1	1.8	0.02	0.1	0.01
I-127	151#	93.9	5.8	BDL	0.4	BDL
SO4	Indeterminate due to low amount in feed (527 mg/L) and large amount from coal					

*I-125 values based on half-life decay from when sample pulled and actually analyzed I-125 analytical more accurate than I-129.

Hgh recovery due to as-batched feed value versus measured product value and small amount added in feed.

Table VI. Recovery Rates for Sim A Runs

Element	Recovery From All Sources (%)	Product %	Condensate Filtrate %	Condensate Solids %	X-Bar Rinsates %	X-Bar Solids %
Cs	99	97.8	2.0	0.1	0.1	0.004
Re	86	93.3	6.5	0.1	0.2	0.01
I	91	66.6	30.0	0.1	3.2	0.02
F	73	25.1	41.9	0	33.0	0
Cl	78	80.3	15.1	0	4.7	0
	Indeterminate due to low amount in feed (527 mg/L) and high amount from coal.					

Durability Results

Due to the limited quantity of the available BSR material, only 10 gram duplicate samples of the simulant granular product and a ~3 g single sample of the radioactive granular product were sent to a certified laboratory for TCLP testing. The metals Sb, Ba, Cd, Se and Tl were not requested for testing as they were not shimmed into the BSR simulant feed. The Zn analysis was inadvertently not requested. All other metals shown for the simulant granular product passed the UTS limits. The radioactive granular product passed TCLP for all elements except for Cr and Zn. The radioactive granular product was produced at a much lower REDOX of ~ 0.26 versus the earlier simulant granular product from the Fall 2009 campaign that had a REDOX in the range of 0.87 to 0.98. The behavior of Cr on TCLP testing is known to be REDOX sensitive, with Cr in higher oxidation state, e.g., +6, being more leachable. The use of a mixed oxide iron compound catalyst as an insoluble spinel host for Cr was not used as it was for the ESTD testing. A potential explanation for the failure on Zn could be the excessive remote handling of the granular product in the SRNL SCF using brass (Cu/Zn containing) sieves. For instance, nodules of Cu and Zn from the brass sieves have been observed previously in SEM scans of glass powders prepared for PCT in the SCF.

Due to the limited quantity of the available BSR material, a single 25 gram sample of the simulant monolith and a single ~ 6 gram sample of the radioactive monolith were tested. The simulant and radioactive monoliths passed TCLP for all elements analyzed.

Triplicate PCT testing was performed on the WTP-SW BSR granular products and monoliths formed from the granular products. PCT test results were adjusted for elemental composition, i.e. anhydrous, coal free, and then adjusted for the BET surface area to obtain normalized release values in units of g/m^2. Figure 4 shows the results. In general, the data shows that the monolith normalized releases are comparable to the granular product normalized releases, specifically for the non-monolith binder elements such as Cs, I, Re and S. This suggests that the monolith process is not detrimental to the overall waste form performance. Figure 4 shows that the BSR products and monoliths give similar overall average normalized release of most elements when compared to the results available in Reference 6. The granular FBSR waste form that is produced is as durable as glass based on comparison of normalized releases for glass and FBSR granular product.
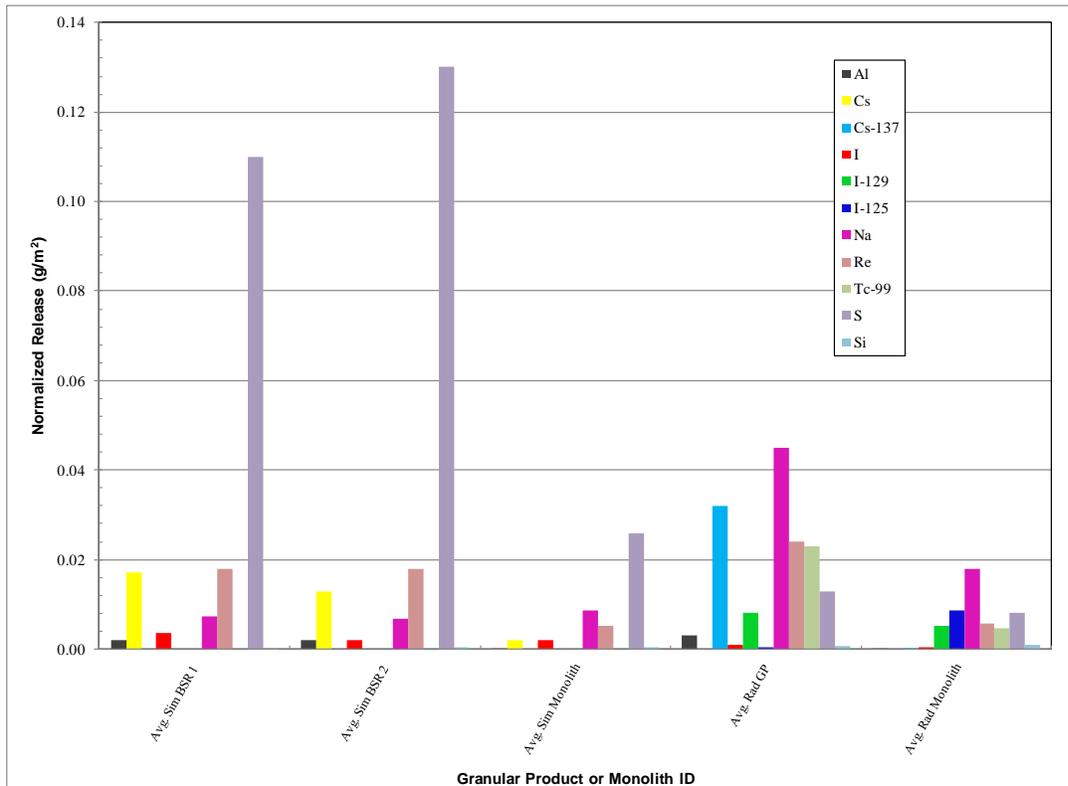
Fig. 4. PCT Results for BSR Granular Products and Monoliths

These are minimum LI target levels associated with the IDF at Hanford, which indicates that this matrix should be acceptable for disposal at the IDF.

The radioactive 1.27 cm diameter x 2.54 cm cylinder monolith was subjected to ASTM C1308 accelerated leach testing at ambient room temperature for the specified intervals. Leachate data was used to calculate the constituent diffusivities. The degree of leaching in these tests is reflected in the diffusivity calculations – the lower the diffusivity, the lower the cumulative fraction leached. The Leach Index (LI) is a negative log of the diffusivity, therefore, the higher LI values indicate a lower leaching (more durable) monolith. Figure 5 shows the calculated leach indexes for the measured constituents. The NRC requirement for the Hanford IDF indicates that waste form Leach Indices (the negative log of the diffusivity) of Na>6, Tc-99>9, and I>11 after 90 days are acceptable [18]. It is clear from Figure 5 that these criteria are all met for the WTP-SW (Module A) monoliths tested to date, even those made from fly ash.
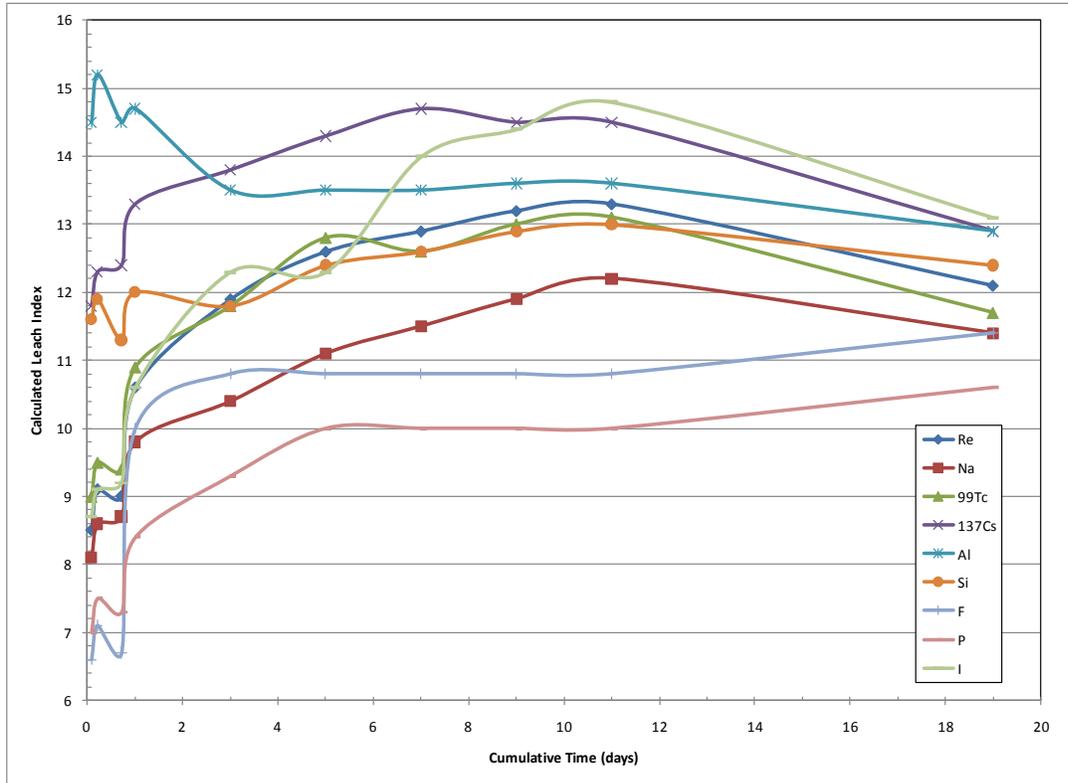
Fig. 5. Calculated Leach Indices for Radioactive Monoliths

Overall Findings

The significant findings of the testing completed on simulant and radioactive WTP-SW are given below:

- Mineralogy features related to the XRD patterns associated with the identified crystalline species and their relative amounts in radioactive and simulant products from the BSR and ESTD are the same.
- Good mass balance closure on Tc, Re, Cs, and I in all WTP-SW BSR tests (radioactive and non-Radioactive).
  - 86-102% recovery of Re in the product streams for simulant and radioactive campaigns. This supports the finding that Re and Tc are essentially completely retained in the mineral product.
  - 109% recovery of Tc-99 in the product streams for radioactive campaigns.
  - 91% recovery of I in the product streams for simulant campaign.
  - 98% recovery of I-129, ~93% recovery of I-125, and 151% recovery of I-127 in the product streams (I-125 has highest analytic sensitivity) for radioactive campaign.
- Data indicates Tc-99, Re, Cs, and I (all isotopes) report primarily to the mineral product and not to the off-gas.
- Tc-99 and Re show similar behavior in partitioning between product (major) and off-gas (trace) so Re is an acceptable surrogate for Tc-99.
- Tc-99, Re, SO_4 and Cr behavior, with respect to their durability in the final granular product, are controlled by the oxygen fugacity in the FBSR/BSR process, i.e. control of the REDuction/OXidation (REDOX) equilibrium.

- TCLP data are acceptable when RCRA metals are not shimmed in excess of their predicted concentrations in actual WTP-SW feeds and REDOX is controlled or a mixed iron oxide additive is present as an insoluble spinel host for Cr.
- Analysis of ESTD FBSR product and monolith TCLP test data indicate that both materials pass TCLP when formed with the actual wastes.
- Evaluation of compressive strength and durability (PCT) data for the larger scale monoliths indicated that a geopolymer binder formulation, designated GEO-7, was the best overall performer when combined with ESTD LAW and WTP SW granular products. BSR testing also indicated that a geopolymer binder with clay instead of fly ash produces a more appropriate monolith recipe.
- ASTM C1285 PCT testing normalized release values were below 2 g/m^2 for the constituents of concern (COC).
  - Use of BET surface area to account for the surface roughness of the mineral granules demonstrates that the FBSR product is 2 orders of magnitude lower than the 2 g/m^2 target for Na.
- All monoliths made from radioactive and non-radioactive (BSR and ESTD) granular products pass compression tests with values greater than the target limit of 3.45E6 Pa (500 psi), maintain PCT leach rates <2 g/m^2, and perform well in ASTM C1308 testing such that the measured Leach Indexes for key components (Na, Re/Tc-99 and I) are all below current Hanford IDF target limits.
  - Na, Re/Tc-99, and I were >10, >11, and >12 respectively after at least the 2-day leaching intervals. These are all above the Hanford IDF target limit Leach Indices of 6, 9, and 11 respectively.
- Good mass balance closure was achieved on Tc, Re, Cs, and I in all BSR tests (radioactive and non-radioactive).
  - SRS DWPF Secondary Waste shimmed to match WTP-SW.

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