Accelerated Weathering of Fluidized Bed Steam Reformation Material Under Hydraulically Unsaturated Conditions

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Abstract

To predict the long-term fate of low- and high-level waste forms in the subsurface over geologic time scales, it is important to understand the behavior of the corroding waste forms under conditions that closely mimic the open flow and transport properties of a subsurface repository. Fluidized bed steam reformation (FBSR), a supplemental treatment technology option, is being considered as a waste form for the immobilization of low-activity tank waste. To obtain the fundamental information needed to evaluate the behavior of the FBSR waste form under repository relevant conditions and to monitor the long-term behavior of this material, an accelerated weathering experiment is being conducted with the pressurized unsaturated flow (PUF) apparatus. Unlike other accelerated weathering test methods (product consistency test, vapor hydration test, and drip test), PUF experiments are conducted under hydraulically unsaturated conditions. These experiments are unique because they mimic the vadose zone environment and allow the corroding waste form to achieve its final reaction state. Results from this on-going experiment suggest the volumetric water content varied as a function of time and reached steady state after 220 days of testing. Unlike the volumetric water content, periodic excursions in the solution pH and electrical conductivity have been occurring consistently during the test. Release of elements from the column illustrates a general trend of decreasing concentration with increasing reaction time. Normalized concentrations of Na, P, Re (a chemical analogue for Tc-99), and S are as much as 1 × 10^2 times greater than Al and 1 × 10^4 times greater than Si. After more than 300 days of testing, the solution chemistry data collected to-date illustrate the importance of understanding the long-term behavior of the FBSR product under conditions that mimic the open flow and transport properties of a subsurface repository.

Introduction

The accelerated cleanup mission at Hanford is a strategic initiative for acceleration of tank waste treatment by increasing the capacity of the Waste Treatment Plant (WTP) and utilizing supplemental technologies for waste treatment and immobilization of as much as 70% of the low-activity waste (LAW). The use of a supplemental treatment technology is expected to accelerate the overall cleanup mission at the Hanford site by at least 35 years. In 2003 DOE evaluated three supplemental treatment technology options (bulk vitrification [BV], fluidized bed steam reformation [FBSR], and cementation or cast stone [CS]) for the immobilization of low-activity tank waste during a preliminary risk assessment (RA). Detailed discussions of the preliminary RA results are included in Mann et al. [1]. Upon completion of the 2003 RA, a decision was made to pursue a pilot-scale test and demonstration facility for BV treatment of selected Hanford low-activity waste (LAW). The BV test and demonstration facility began operation late in 2005, and will provide data to support a final decision on tank waste treatment. In a similar decision made in January 2004, DOE identified the need for additional experimental data, with regard to the steam reforming technology, to make an informed decision with regard
to the selection of a treatment technology and to support the Hanford Federal Facility Agreement and Consent Order milestone (M-62-11) associated with a final decision on the balance of tank waste that is beyond the capacity of the WTP.

The THermal Organic Reduction (THORSM) Treatment Technologies (TTT) Fluidized-Bed Steam Reformation (FBSR) process operates by introducing high sodium nitrate content tank wastes into a moderate temperature (650 – 800°C) fluidized bed. The tank waste is reacted with carbon and iron-based reductants to convert nitrates and nitrites directly to nitrogen gas. Radionuclides, alkali metals, sulfate, chloride, fluoride, and non-volatile heavy metals in the waste stream are reacted with clay (kaolinite) or other inorganic materials to produce a polycrystalline mineral product. Several demonstrations have been conducted to evaluate the ability for the fluidized bed steam reforming (FBSR) technology to treat simulated Hanford LAW and Idaho National Engineering and Environmental Laboratory (INEEL) sodium-bearing waste (SBW). For additional details on and a discussion of the results from these demonstrations see Jantzen [2], Olson et al. [3], Soelberg et al. [4], or visit the THORSM–TTT website (www.thortt.com). In general, these demonstrations have shown that different solid mineral phases are produced as a result of the steam reforming process and the type of co-reactant (e.g., aluminosilicate clay) mixed with LAW or SBW to produce the FBSR product.

A critical component of determining the viability of the FBSR product for the immobilization of LAW or SBW will be to provide quantitative estimates of the release of key contaminants of concern, such as Tc-99, from the engineered portion of the subsurface disposal facility. To provide credible estimates information on the long-term dissolution rate of the FBSR product under conditions that closely mimic the open-flow and transport environment expected in a subsurface disposal system are needed. One of the test methods used to obtain this type of long-term information is the pressurized unsaturated flow (PUF) test method. In addition to other laboratory test methods [e.g., single-pass flow-through, product consistency test, etc.], the information obtained from conducting PUF tests is a critical component for quantifying the long-term durability of and radionuclide release from the FBSR product or any other waste form after disposal. The results from PUF test provide information on the (1) alteration phase or phases that form as a result of accelerated weathering, (2) evolution in the solution chemistry that occurs as a result of the FBSR product-water interaction, and (3) FBSR product-water reaction under hydraulically unsaturated conditions similar to those expected in a disposal-system environment.

Discussed in this paper are the results from an on-going PUF test conducted with the Fluidized Bed Steam Reformer (FBSR) LAW 1123 sample. This sample was produced at the INEELs pilot scale FBSR system located at the Science Applications International Corporation’s (SAIC) Science and Technology Applications Research (STAR) Center, in Idaho Falls, ID.

Experimental Details

Compositional and X-ray Diffraction Analysis

A sample of FBSR LAW 1123 bed material was received from Savannah River National Laboratory (SRNL). The FBSR LAW 1123 sample composition is shown in Table 1. For a detailed discussion of the compositional analyses see Pareizs et al. [5]. In general, the major compositional difference between the SCT02-98 material used by Jantzen [2] and McGrail et al. [6] and the FBSR LAW 1123 product is the higher Fe content (~20x) for the SCT02-98 material. The higher Fe content resulted in the formation of magnetic particles, probably metallic iron in
the SCT02-98 sample which was manufactured in a fluidized bed pilot plant at Hazen Research (Golden, Colorado) during the early stages of development. Unlike the SCT02-98 sample, the FBSR LAW 1123 bed product used in this study was made by mixing Hanford LAW Envelope C simulant with OptiKasT clay and run for 55 hours at the STAR facility in a pilot-scale steam reformer by a team of personnel from STAR Center, INEEL, and THORSM-TTT. During the fabrication process coal was used as a reductant and facilitated the conversion of nitrates to nitrogen gas. An excess of coal is often used during the processing and becomes part of the bed product. The excess coal can be removed with a second oxidizing reformer, but the STAR facility was not equipped with a second oxidizing reformer at the time this material was made. Therefore, excess coal was removed by heating the material to 525°C overnight in an oxidizing atmosphere, prior to testing. The heating process removed 5.57 wt% of unreacted coal from the FBSR LAW 1123 bed product.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>^aFBSR SCT02-98</th>
<th>^bFBSR LAW 1123</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>32.133</td>
<td>32.404</td>
</tr>
<tr>
<td>CaO</td>
<td>0.7819</td>
<td>2.309</td>
</tr>
<tr>
<td>CdO</td>
<td>ND</td>
<td>0.001</td>
</tr>
<tr>
<td>Cl</td>
<td>0.2159</td>
<td>0.130</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.0461</td>
<td>0.117</td>
</tr>
<tr>
<td>CuO</td>
<td>ND</td>
<td>0.013</td>
</tr>
<tr>
<td>F</td>
<td>0.0056</td>
<td>0.100</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.0056</td>
<td>0.272</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.7100</td>
<td>0.301</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>ND</td>
<td>0.003</td>
</tr>
<tr>
<td>MgO</td>
<td>0.1366</td>
<td>0.066</td>
</tr>
<tr>
<td>MnO</td>
<td>0.0743</td>
<td>0.039</td>
</tr>
<tr>
<td>Na₂O</td>
<td>16.870</td>
<td>20.166</td>
</tr>
<tr>
<td>NiO</td>
<td>0.0398</td>
<td>0.013</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.2499</td>
<td>0.458</td>
</tr>
<tr>
<td>PbO</td>
<td>0.0182</td>
<td>0.108</td>
</tr>
<tr>
<td>ReO₂</td>
<td>0.0005</td>
<td>0.005</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.8107</td>
<td>0.624</td>
</tr>
<tr>
<td>SiO₂</td>
<td>29.336</td>
<td>35.620</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.6228</td>
<td>1.184</td>
</tr>
</tbody>
</table>

| Total | 100.0 | 93.932 |

^aND – Not Determined
^b-100 +200 sample used in McGrail et al. [6]. This sample also had minor amounts of Ag₂O, Cs₂O, Li₂O, MoO₂, V₂O₅, ZnO, and ZrO₂.
Approximately 5.57 wt% unreacted coal was removed from the sample prior to testing by heating the material to 525°C in an oxidizing atmosphere.
Powder X-ray diffraction was used to identify crystalline phases contained in the FBSR LAW 1123 bed products. Reflections were consistent with the hexagonal form of nepheline [NaAlSiO₄, PDF# 35-0424] and a sodium aluminum silicate [NaAlSiO₄, PDF# 52-1342] similar to low carnegieite (NaAlSiO₄) [7] were identified as the major crystalline phases in both size fractions. Minor shifts in peaks corresponding to the NaAlSiO₄ phase were observed, indicating a minor amount of chemical or structural difference compared to the phase represented in PDF# 52-1342. Lesser amounts of nosean, [Al₆Si₆O₂₄(SO₄), PDF# 74-1736] and quartz were also identified in both size fractions by their characteristic reflections at 13.83 and 26.64° 2θ, respectively. The only difference observed between the two size fractions by XRD were the presence of two reflections in the <100 and >200 mesh fraction at 29.00 and 44.53° 2θ. These reflections could not be assigned to any known crystalline phase in the PDF data base.

**Material Preparation and Surface Area**

The as received material was sieved into the 450 to 149 µm (<40 to >100 mesh) and 149 to 75 µm (-100 +200 mesh) size fraction with standard ASTM sieves [8]. The sieved material was then washed in 18MΩ ultra pure de-ionized water (DIW), washed again with 18MΩ DIW in an ultrasonic bath, rinsed with ethanol, and dried in a 90°C (±2°C) oven. Each sample before testing was stored at room temperature (~23°C) in a desiccator that contained CaSO₄.

The specific surface area for the <100 to >200 mesh size fraction was determined to be 4.15 ±0.01 m²/g with N₂-adsorption BET [9] measurements [Micromeritics ASAP 2010 surface area analyzer [10]]. This measurement is comparable to the value reported by Lourier et al. [11] for the FBSR LAW 1123 product and approximately two-times higher than the value for the SCT02-098 FBSR product reported by McGrail et al. [6]. For comparison, the geometric surface area for the <100 to >200 mesh size fraction was estimated to be 0.02 m²/g, with the geometric equation McGrail et al. [12,13], Equation (1),

$$S_{GEO} = \frac{3}{\rho r} \tag{1}$$

where $S_{GEO}$ = surface area (m² g⁻¹), $r$ = is the average radius of the particle (m), and $\rho$ = is the particle density (g cm⁻³). The particle density, measured with an Accupyc 1330 He pycnometer, was determined to be 2.663 ±0.005 g cm⁻³. This measured value is comparable to the value of 2.764 ±0.004 g cm⁻³ reported by McGrail et al. [6]. Equation (1) assumes the grains are spherical and the sizes are normally distributed; surface pits, cracks, and other forms of surface roughness do not affect the surface area.

It is important to note that surface area has been recognized as an important factor in quantifying mineral dissolution rates. The proper handling of surface area is one of, if not the most problematic variable, and has been the subject of numerous studies [14]. A large degree of uncertainty is associated with measurements of bulk BET surface area, and the contribution of actual reactive surface area is not always known. For glasses, it has been shown that the geometric surface area best represents the overall glass surface area [13] but no such case currently exists for the FBSR product. As previously discussed, two methods were used to determine the surface area of the FBSR product, calculated geometric [13] and N₂-adsorption BET [9]. A comparison of these values illustrates the calculated geometric surface area is 216 times less than the measured value via N₂-adsorption BET. As previously discussed in McGrail et al. [6], the FBSR product contains a large amount of microporosity that increases the reactive
surface area (Figure 1). A similar observation was also reported by Lorier et al. [11] for the FBSR LAW 1123 bed material. As shown in Figure 1, microporosity is a feature not typically observed in glasses and results in glasses having a surface roughness factor much smaller than the FBSR product, see Table 2. Although use of the BET surface area may overestimate the true reactive surface area, the obvious microporosity indicates that use of the geometric surface area will underestimate the true dissolution rate. Therefore, the dissolution rates reported here have been normalized to the BET surface area. The true reactive surface area is probably less than the BET value, but also probably significantly higher than the geometric value. Additional work will be required to better constrain the reactive surface area of the FBSR product.

Another factor that complicates the surface area estimates is the fact that the FBSR product is composed of several different mineral phases, each of which can have very different surface area measurements and therefore surface roughness factors. This also complicates the evaluation of the results because we can not assign a specific values to any of the know phases that are present.

**Pressurized Unsaturated Flow (PUF) test method**

The PUF apparatus allows for accelerated weathering experiments to be conducted under hydraulically unsaturated conditions, thereby mimicking the open-flow and transport properties of the disposal system environment while allowing the corroding waste form to achieve a final reaction state. The PUF apparatus provides the capability to vary the volumetric water content

![Image of Scanning Electron Microscope image of FBSR 1123 Product.](image_url)

**Table 2.** Comparison Between the Particle Density, BET and Geometric Surface Area, and Surface Roughness Factor of FBSR 1123 and Various Glasses.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Particle Density (g/m³)</th>
<th>Geo. Surf. Area (m²/g)</th>
<th>BET Surf. Area (m²/g)</th>
<th>Surf. Rough.</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁴FBSR LAW 1123</td>
<td>n.a.</td>
<td>0.0212</td>
<td>4.427</td>
<td>208.8</td>
</tr>
<tr>
<td>⁵FBSR LAW 1123</td>
<td>2.663 ±0.005 × 10⁶</td>
<td>0.0200</td>
<td>4.148 ±0.01</td>
<td>216.4</td>
</tr>
<tr>
<td>¹SCT02-98</td>
<td>2.764 ±0.004 × 10⁶</td>
<td>0.0193</td>
<td>2.37 ±0.5</td>
<td>122.8</td>
</tr>
</tbody>
</table>

⁴Geo. Surf. - Calculated geometric surface area determine with Equation (1).
⁵BET Surf. - Braunauer-Emmet-Teller surface area.
¹Surf. Rough. - Surface roughness is the ratio of the BET to the geometric surface area.
⁴Lorier et al. [11], ¹This study, ¹McGrail et al. [6,15], ¹N₂-adsorption BET results.
n.a. – not available.
from saturation to 20% or less, minimize the flow rate to increase liquid residence time, and 
operate at a maximum temperature of 99°C. The PUF column operates under a hydraulically 
unsaturated condition by creating a steady-state vertical water flow, while maintaining uniform 
water content throughout the column; by using gravity to assist in drainage; and by maintaining a 
constant pressure throughout the column. Constant pressure is maintained with a porous Ti plate 
and gas pressure.

This system and test procedure have been described previously by McGrail et al. [16-18] and 
Pierce et al. [19,20], and only a general description will be provided here. The PUF system has a 
7.62-cm long and 1.91-cm diameter column fabricated from a chemically inert material, 
polyetheretherketone (PEEK), so that dissolution reactions are not influenced by interaction with 
the column material (Figure 2). A porous Ti plate with a nominal pore size of 0.2-µm is sealed 
in the bottom of the column to ensure an adequate pressure differential for the conductance of 
fluid while operating under unsaturated conditions [21]. Titanium is chosen because it is highly 
resistant to corrosion and has excellent wetting properties. Once the porous Ti plate is water 
saturated, water but not air is allowed to flow through the 0.2-µm pores, as long as the applied 
pressure differential does not exceed the air entry relief pressure, referred to as the bubble 
pressure, of the Ti plate. If the pressure differential is exceeded, air will escape through the plate 
and compromise the ability to maintain unsaturated flow conditions in the column. The 
computer control system runs LabVIEW™ (National Instruments Corporation) software for 
logging test data from several thermocouples, pressure sensors, inline sensors for effluent pH and 
conductivity, and from an electronic strain gauge that measures column mass to accurately track 
water mass balance and saturation level. The column also includes a PUF port, which is an 
electronically actuated valve that periodically vents the column gases. The purpose of column 
venting is to prevent reduction in the partial pressure of important gases, especially O₂ and CO₂, 
which may be consumed in a variety of chemical reactions.

The PUF column was packed with 14.79 g of crushed <40 to >100 mesh (from 450 to 149 
µm particles) and cleaned FBSR LAW 1123 bed product, which resulted in a fill volume of 5.35 
cm³ and void volume of 15.56 cm³. Finally the bottom 0.81 cm³ of column volume was packed 
with crushed sapphire to provide a filter bed between the FBSR LAW 1123 bed product and the 
Ti porous plate. Previous experiments by McGrail et al. [6] illustrated that colloids produced 
from the FBSR SCT-098 product periodically plugged the porous plate. Therefore, to minimize 
the entrapment of colloidal particles in the porous plate, a filter bed was placed at the base of the 
column. The reader should note that in comparison to the mineral phases contained in the FBSR 
LAW 1123 product, sapphire, a high temperature Al₂O₃ mineral phase, is relatively corrosion 
resistant. In other words, sapphire will have a much slower corrosion rate and is considered to 
be relatively un-reactive; therefore, it is not expected to impact the results of this experiment. 
The surface area was determined by multiplying the calculated geometric surface area, 0.0078 
m² g⁻¹, by the surface roughness factor, SRF = 216 (see Table 2), for the FBSR LAW 1123 bed 
product. The mass difference between the packed and empty column was used to calculate the 
initial porosity of approximately 0.72 ±0.03 (unitless). After packing, the column was then 
vacuum saturated with 18MΩ DIW at ambient temperature. A temperature controller was then 
programmed to heat the column to 90°C (±1°C) in approximately 1 hr (1°C/min). The column 
initially was allowed to desaturate by gravity drainage during heating and was also vented 
periodically to maintain an internal pressure less than the bubble pressure of the porous plate. 
After reaching 90°C (±1°C), the influent valve was opened, and influent was set to a flow rate of

112
2 mL d^{-1}. The influent reservoir containing 18 MΩ DIW was maintained at ambient temperature and periodically refilled during the test. Column venting was set to occur once an hour, so the partial pressure of O₂ and CO₂ could remain relatively constant. Effluent samples were collected into tared vials from which samples were extracted and acidified for elemental analysis with inductively coupled plasma-optical emission spectroscopy (ICP-OES) and -mass spectrometry (ICP-MS).

Figure 2. Top: schematic of the second generation pressurized unsaturated flow (PUF) apparatus, which had the ability to conduct two simultaneous tests. Bottom left: the third generation PUF apparatus, which has the ability to conduct four simultaneous tests. Bottom right: the PUF box (grey box), insulation wrapped column (center of the box), strain gauge (center of the box above the column), pressure/PUF port Teflon line (top left of the column), influent solution Teflon line (top right of the column), effluent solution Teflon line (bottom of the column), thermocouples (type J [blue connector] and type T [black connector] shown inside the box with black/red wire), pH probe (outside the box shown in white), and collection vial (outside the box connected to the pH probe). The third generation PUF apparatus was used to conduct the FBSR LAW 1123 experiment discussed in this report.
PUF dissolution rate and experimental error

The results of chemical analyses on collected effluent samples are used to calculate a normalized release rate according to McGrail et al. [22]

\[
    r_i = \frac{4\varepsilon q(c_{i,L} - c_{i,b})}{bS(1 - \varepsilon)\rho \pi d^2 L f_i}
\]

where \( r_i \) is the normalized dissolution (release) rate of the \( i \)th element (g m\(^{-2}\) d\(^{-1}\)), \( c_{i,L} \) is the effluent concentration of the \( i \)th element (g m\(^{-3}\)), \( c_{i,b} \) is the background concentration of the \( i \)th element (g m\(^{-3}\)), \( d \) is the column diameter (m), \( L \) is the column length (m), \( q \) is the volumetric flow rate (m\(^3\) d\(^{-1}\)), \( S \) is the specific surface area of the glass sample (m\(^2\) g\(^{-1}\)), \( \varepsilon \) is the porosity (unitless), \( \rho \) is the glass density (g m\(^{-3}\)), \( f_i \) is the mass fraction of the \( i \)th element (unitless), and \( \theta \) is the volumetric water content (unitless). The volumetric water content is calculated based on the mass of a volume of water in a fixed column volume, accounting for changes in the solution density resulting from temperature changes. The background concentration for most elements is typically below the estimated quantification limit (EQL) for the respective analysis. The EQL is defined as the lowest calibration standard that can be determined reproducibly during an analytical run within 10% of the certified value multiplied by the sample dilution factor. In cases where the analyte is below the EQL, the background concentration of the element is set at the value of the EQL. An estimate of the 2\( \sigma \) experimental uncertainty for the FBSR LAW 1123 bed product dissolution rates were determined with error propagation. For additional details on the error propagation equation for PUF experiments see Pierce et al. [19].

Results and Discussion

Computer Monitored Test Metrics

Results from the computer-monitored test metrics are shown in Figure 3. As can be seen from the figure, the volumetric water content (\( \theta \)) varied as a function of time and became steady after 220 days of testing. The observed periodic increase in the \( \theta \), as shown in Figure 3, is the result of the effluent line becoming plugged with colloidal reaction products (illustrated by vertical lines). Attempts to collect and analyze this material were unsuccessful, but a more detailed analysis of the porous plate at the end of this experiment should provided additional information about the composition of the colloidal material. Previous experiments with SCT02-98 material by McGrail et al. [6] also observed plugging of the porous plate. The results of SEM-EDS analysis of the porous plate from these early PUF experiments suggested that a Pb mineral phase was precipitating on the surface of the porous plate. Similarly to the volumetric water content, the effluent solution pH and electrical conductivity decreased as the testing time increased (Figure 3).
Solution Chemistry

Results from the analyses of effluent samples are provided in Figure 4. Release of elements from the column illustrates a general trend of decreasing concentration with increasing reaction time. The normalized concentrations of Na, P, Re, and S are as much as $1 \times 10^2$ times greater than Al and $1 \times 10^4$ times greater than Si (Figure 4). It is important to note that majority of the solution samples analyzed for the concentration of Ca, Cr, Fe, K, Mg, Mn, Pb, and Ti were below the EQL. The results for these elements were not included in Figure 4.
The normalized concentration ($NC_i$) was calculated from the element concentrations in the effluent solutions with Equation (3)

$$NC_i = \left(\frac{c_{i,L} - c_{i,b}}{f_i}\right)$$  \hspace{1cm} (3)

where $c_i$ is the effluent and background solution concentration of element $i$ (mg/L) and $f_i$ is the mass fraction of element $i$ in the glass (unitless). The results shown in Figure 4 suggest that under these conditions Na-, P, Re-, and S-bearing solid/mineral phase(s) are more soluble than Al-, Ca-, Cr-, Fe-, Si, and Ti-bearing solid/mineral phase(s). Although all the solutions exiting the PUF column were visibly clear, it is possible that colloids smaller than the 0.2-µm average pore diameter of the porous plate may be exiting the PUF column. Therefore, everything <0.2-µm was analyzed as being in solution. Movement and transport of colloids is to be expected because transport within a PUF column is typically advection-dominated. Similar to previous PUF experiments, this experiment was also advection-dominated, evident by an average Peclet ($P_e$) number of 25.2.

A comparison of the dissolution rates for the major components in FBSR LAW 1123 product is shown in Figure 5. Similar to the concentration data, the rate of element release from the FBSR product decreases as the reaction time increases, although periodic excursions in the reaction rate occasionally occur. Figure 5 illustrates that the release of S and Re are with in the experimental error of one another during the first 80 days of testing. The behavior of Re is extremely important from a performance assessment perspective because it is commonly considered a chemical analogue for the long-lived radionuclide technetium (Tc-99) [23,24].

A similar trend was observed by McGrail et al. [6,25] and they suggested that Re and S are being retained as anions (ReO$_4^-$ and SO$_4^{2-}$) in the structure of a sodalite group mineral such as sodalite or nosean. Sodalite group minerals and other framework aluminosilicates, such as cancrinite, with the general formula, $Na_8[AlSiO_4]_6X_2\cdot nH_2O$, $X = B(OH)_4^-$, Br$, Cl$, CO$_3^{2-}$, I$, \Gamma$,
NO$_3^-$, NO$_2^-$, OH$,^-$, ReO$_4^{2-}$, SCN$,^-$, SO$_4^{2-}$, etc., $n = 0$ to 4, have been synthesized in a large variety of compositions [26-30]. The cage-like structure of these minerals can trap and immobilize up to 9 mol% oxyanions. Recently, Mattigod et al. [31] prepared a perrhenate sodalite and determined the structural refinement. Perrhenate substituted sodalite was not positively identified in the XRD pattern of the bulk material, probably because the relative small amount of Re (0.005 mass%) contained in the FBSR LAW 1123 product make this phase impossible to identify with this technique.

Also shown in Figure 5 is the Tc-99 release rate data from a PUF experiment conducted with the low-activity waste glass, LAWAN102 [19]. A comparison of the steady-state release rate for Tc-99 [(1.0 ±0.3) × 10$^{-2}$ g m$^{-2}$ d$^{-1}$] from LAWAN102 glass to Re [(8.9 ±1.4) × 10$^{-4}$ g m$^{-2}$ d$^{-1}$] from the FBSR product measured to-date suggest LAWAN102 is dissolving approximately 11 times faster. Although these results may suggest the LAW 1123 FBSR product performs comparably to LAW glass, the uncertainty in the reactive surface area for the FBSR product complicates the interpretation of a direct comparison between the Tc-99 release rate from glass and the rate of Re release (a chemical analogue for Tc-99) from the FBSR product.

In summary, these results suggest the FBSR bed product may be a viable option for the accelerated clean-up of LAW at DOE sites. However, additional testing is needed to reach a scientifically defensible conclusion regarding the performance of the actual FBSR under the open-flow and transport environment expected in a subsurface disposal facility.

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References