

## Fluidized Bed Steam Reformer (FBSR) Monolith Formation

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### ABSTRACT

Fluidized Bed Steam Reforming (FBSR) is being considered as an alternative technology for the immobilization of a wide variety of aqueous high sodium containing radioactive wastes at various DOE facilities in the United States. The addition of clay, charcoal, and a catalyst as co-reactants converts aqueous Low Activity Wastes (LAW) to a granular or “mineralized” waste form while converting organic components to CO<sub>2</sub> and steam, and nitrate/nitrite components, if any, to N<sub>2</sub>. The waste form produced is a multiphase mineral assemblage of Na-Al-Si (NAS) feldspathoid minerals with cage-like structures that atomically bond radionuclides like Tc-99 and anions such as SO<sub>4</sub>, I, F, and Cl. The granular product has been shown to be as durable as LAW glass. Shallow land burial requires that the mineralized waste form be able to sustain the weight of soil overburden and potential intrusion by future generations. The strength requirement necessitates binding the granular product into a monolith. FBSR mineral products were formulated into a variety of monoliths including various cements, Ceramicrete, and hydroceramics. All but one of the nine monoliths tested met the <2g/m<sup>2</sup> durability specification for Na and Re (simulant for Tc-99) when tested using the Product Consistency Test (PCT; ASTM C1285). Of the nine monoliths tested the cements produced with 80-87 wt% FBSR product, the Ceramicrete, and the hydroceramic produced with 83.3 wt% FBSR product, met the compressive strength and durability requirements for an LAW waste form.

### INTRODUCTION

The most important requirement for Hanford’s low activity waste (LAW) form for shallow land disposal is the chemical durability of the product. A secondary, but still essential specification, is the compressive strength of the material with regards to the strength of the material under shallow land disposal conditions, e.g. the weight of soil overburden and potential intrusion by future generations, because the term “near-surface disposal” indicates disposal in the uppermost portion, or approximately the top 30 meters, of the earth's surface.<sup>§</sup>

The FBSR mineral waste form for LAW is granular in nature. As a granular product it has been shown to be as durable as Hanford’s LAW glass during testing with ASTM C-1285-02 known as the Product Consistency Test (PCT) [1,2,3,4] and testing with the Single Pass Flow Through

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<sup>§</sup> Waste that would decay to acceptable levels within 100 years is defined as Class A or B waste, and institutional controls are believed to be effective at limiting inadvertent intruder risk from these classes of waste. Waste that would decay to acceptable levels for an inadvertent intruder within 500 years was defined as Class C waste. Class C waste was envisioned to be segregated from other classes of waste and to be disposed of deeper than Class A and B wastes, and to be disposed of with an intruder barrier that would prevent contact for 500 years.

(SPFT) Test [4,5,6]. Hanford Envelope A and Envelope C FBSR products made with simulants both performed well during PCT and SPFT testing and during subsequent performance assessment modeling [5,7]. This is partially due to the high aluminosilicate content of the mineral product which provides a natural aluminosilicate buffering mechanism [2,3,4] that inhibits leaching and is known to occur in nature during weathering of aluminosilicate mineral analogs [8].

In order for the Na-Al-Si (NAS) granular mineral product to meet the compressive strength requirements for a Hanford waste form, the granular product needs to be made into a monolith. Additionally, the Hanford intruder scenario for disposal in the Immobilized Low Activity Waste (ILAW) trench is mitigated as there is reduced intruder exposure when a waste form is in a monolithic form.

During the feasibility testing of a monolith binder described in this study, four parameters were monitored:

- FBSR loading (which was not optimized for each waste form tested)
- waste form density
- compressive strength
- durability
  - binding agent should not compromise the durability of the NAS product
  - binding agent should not create an unfavorable pH environment

It is the goal of the present study to survey cementitious waste forms based on Ordinary Portland Cement (OPC), Ceramicrete, and hydroceramics as binders by correlating FBSR loading, density and compressive strength and then determine if these binders affect the product performance in terms of the durability response. This will be done by making a one-to-one comparison of the PCT response measured on granular NAS mineral products (mixed bed and fines products) with the PCT response of the monolithed NAS product in the different binders.

## **MONOLITH OPTIMIZATION CRITERIA**

### **Durability**

The Product Consistency Test (PCT) was developed between 1987 and 1994 when it became an ASTM standard for HLW borosilicate glass [9]. In 1997 and 2002 the scope was broadened to include hazardous waste glasses, mixed waste glasses, and glass ceramics [10]. Based on extensive testing of glasses and glass-ceramics, including a seven-laboratory round robin, and confirmatory testing with radioactive samples, the PCT has been shown to be reproducible, to distinguish between waste forms of different durability and homogeneity, to yield reliable results rapidly, and to be amenable to being performed in shielded cell facilities with radioactive samples. Additional PCT testing of ceramic waste forms has occurred since 2002 and application of this test to ceramic waste forms is currently being considered by ASTM.

The use of the PCT test protocol for vitrified waste at Hanford was applied for testing the consistency of both the HLW vitrified waste and the immobilized LAW vitrified waste forms [11]. At Hanford the PCT is used to determine the waste form leaching and durability in

conjunction with ANSI/ANS-16.1 [12] and the PCT is used for determining waste form stability [11,10]. The Hanford contract [13] and the ILAW Product Compliance Plan specifies the following:

“The normalized mass loss of sodium, silicon, and boron shall be measured using a seven day product consistency test run at 90°C as defined in ASTM C1285-97. The test shall be conducted with a glass to water ratio of 1 gram of glass (-100 +200 mesh) per 10 milliliters of water. The normalized mass loss shall be less than 2.0 grams/m<sup>2</sup>.”

Lithium, sodium, and boron releases are normally monitored for a homogeneous vitreous waste form since they have been shown [14,15,16,17,18,19,20,21,22] to represent the maximum radionuclide release from glass, e.g. the most soluble radionuclide, Tc-99, present at  $\sim 4.1 \times 10^{-4}$  weight % in the waste form, has been shown to be released at the same maximum normalized concentration as boron, lithium, and sodium. While relating maximum Tc-99 release to Na, Li, B release for a material that leaches congruently<sup>‡</sup> is an acceptable practice once the congruent relationship among these elements has been established, this has to be done for each phase present in a glass-ceramic or mineral waste form because each phase leaches at a different rate, e.g. the multiphase waste form leaches incongruently.<sup>†</sup> Alternatively, the radionuclide release or a surrogate release must be measured, e.g. substitution of Re for Tc-99.

In addition, the Hanford contract [13] requires durability testing by the Vapor Hydration Test (VHT). Because the VHT test interpretation for waste forms other than glass has not been investigated and the results of this test are used solely for engineering calculations of contaminant release [11], the PCT durability test was used in this study as the screening test for the FBSR monoliths.

### **Compressive Strength**

In the 1983 (Revision 0) of 10 CFR 61.56(b)(1), regarding the stability of a waste form for shallow land burial, a minimum compressive strength criterion for waste buried at a depth of 45 feet was established, e.g. 50 psi after curing for minimum of 28 days. Later, the burial depth was increased to 55 feet and the minimum compressive strength criterion was increased to 60 psi after curing for 28 days. In the early 1990's the compressive strength criterion was re-evaluated. Because OPC mortars (cement, lime, silica sand and water) are capable of achieving compressive strengths of 5000-6000 psi, the minimum compressive strength for a waste form for shallow land burial was increased to 500 psi after curing for 28 days. The rationale was that low-level radioactive waste material constituents are not capable of providing the physical and chemical functions of silica sand in a cement mortar and so a reasonable compressive strength was 1/10<sup>th</sup> that of a cement made with silica sand [23]. Based on this criteria the Hanford contract [13] for LAW specifies the following:

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<sup>‡</sup> Congruent dissolution of a waste form, like glass, is the dissolving of species in their stoichiometric amounts. For congruent dissolution, the rate of release of a radionuclide from the waste form is proportional to both the dissolution rate of the waste form and the relative abundance of the radionuclide in the waste form.

<sup>†</sup> Incongruent dissolution of a waste form means that some of the dissolving species are released preferentially compared to others. Preferential phase dissolution, ion-exchange reactions, grain-boundary dissolution, and dissolution-reaction product formation (surface crystallization and recrystallization) are among the more likely mechanism of incongruent dissolution, which will prevail, in a complex polyphase waste form.

“The mean compressive strength of the waste form shall be determined by testing representative non-radioactive samples. The compressive strength shall be at least 3.45E6 Pa (500 psi) when tested in accordance with ASTM C39/C39M-99 or an equivalent testing method”

Because OPC mortars achieve ~75% of their 28 day strength in 7 days of curing [24], samples cured for only 7 days were compression tested in this study with the assumption that any monolith passing the compression test after curing for 7 days would pass the compression test after a total of 28 days of curing under the same conditions.

## **Waste Loading**

For disposal of FBSR wastes at Hanford in Richland, WA there is an additional specification that governs the waste loading. The waste loading for Hanford LAW are specified in terms of the amount of Na<sub>2</sub>O from the waste that can be accommodated in a vitrified waste form. The most stringent of these criteria is for Envelope A waste. The specification (Section 2.2.2.2 of the Product Requirements) [13] states:

“Waste Loading: The loading of waste sodium from Envelope A in the ILAW glass shall be greater than 14 weight percent based on Na<sub>2</sub>O. The loading of waste sodium from Envelope B in the ILAW glass shall be greater than 3.0 weight percent based on Na<sub>2</sub>O. The loading of waste sodium from Envelope C in the ILAW glass shall be greater than 10 weight percent based on Na<sub>2</sub>O.”

Because the FBSR product made with the Hanford LAW Envelope A waste in 2003-2004 [2,3] contained 20.87 wt% Na<sub>2</sub>O, all of which came from the waste, any monoliths developed should not dilute the product concentration to less than 14 wt% Na<sub>2</sub>O. Therefore, the FBSR LAW Envelope A waste loading must be  $\geq 67$  wt%, the Envelope B FBSR waste loading must be  $\geq 14$  wt%, and the Envelope C FBSR waste loading must be  $\geq 47$  wt%.

## **EXPERIMENTAL**

### **Initial Waste Characterization**

Between 2003 and 2004 the durability of FBSR mineral waste forms produced during three different pilot scale demonstrations at the Science Applications International Corporation (SAIC) Science and Technology Applications Research (STAR) facility in Idaho Falls, ID were evaluated [2,3]. The NAS mineral waste forms produced (Table 1) included granular bed material after steady state operations were achieved and the finer mineral material from the high temperature filter hereafter referred to as the filter fines. Bed material from a 2003 and a 2004 STAR pilot scale campaign [25, 26] with Idaho National Laboratory (INL) Sodium Bearing Waste (SBW) and bed and filter fines from a third pilot scale demonstration [27] with a Hanford LAW Envelope A waste simulant had previously been characterized and durability tested at SRNL by the ASTM C1285 procedure [2,3]. The type of simulated wastes tested and the duration of each test are given in Table 1.

Table 1 Pilot Scale FBSR Samples Tested in 2003-2004 at the SAIC STAR Facility

Demonstration	Sample ID	Total Operating Time (TOT)	Bed Turnover	Description
July 2003 SBW [25]	Bed 260	82 hrs	Unknown †	Dynamic bed product
	Bed 272	82 hrs	Unknown †	Dynamic bed product
	Bed 277	82 hrs	Unknown †	Dynamic bed product
August 2004 LAW [27]	Bed 1103	55 hrs and 30 min	97.4%	Dynamic bed product
	Bed 1104	55 hrs and 30 min	99.7%	Final bed product
	Fines 1125	55 hrs and 30 min	100%	Final filter fines
October 2004 SBW [26]	Bed 1173	100 hours	92%	Final bed product

† Unknown due to several defluidizing events

Portions of the SBW and LAW bed and filter fines products were available from the pilot scale campaigns (final and intermediate bed product materials) for monolith formation and testing. All of the bed products (some of which contained Al<sub>2</sub>O<sub>3</sub> startup bed) and fines were combined and mixed. The charcoal was roasted out of the FBSR products before durability testing by heating the samples to 525°C overnight [28]. The charcoal is ~78 wt% carbon, 7.5 wt% H<sub>2</sub>O, 1 wt% N<sub>2</sub>, 3 wt% O<sub>2</sub>, and 2 wt% H<sub>2</sub> compounds all of which are volatile when ashed. There is a residual ash of ~8.5 wt% which is primarily SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO. The charcoal had been removed by ashing in the durability testing of the granular FBSR products [2,3] in order to eliminate charcoal content as a variable during testing since the charcoal will be engineered out of the FBSR product. This also facilitates comparison to the results presented in References 2 and 3, which are also reported on a charcoal free basis. References 2 and 3 document that the ashing does not change the phase chemistry of the FBSR product.

Solid samples of the composite granular FBSR product were digested with a lithium tetraborate fusion at 1000°C followed by a hydrochloric acid uptake [29,30]. The resulting solutions were analyzed by Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) for Ag, Al, Ca, Cd, Cr, Cs, Cu, Fe, K, La, Mg, Mn, Na, Ni, P, Pb, S, Si, and Ti and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) for Cs and Re. Anion content was determined from a sodium peroxide/sodium hydroxide fusion at 600°C followed by a water uptake [31]. The resulting solutions were analyzed by Ion Chromatography (IC) for NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, and Cl<sup>-</sup>.

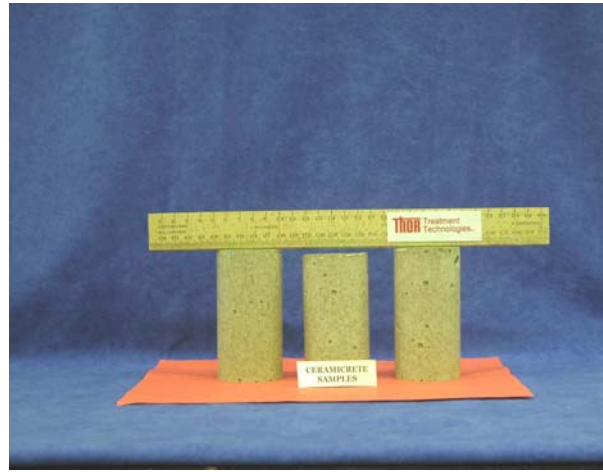
### Cement Monoliths

Cement monoliths were fabricated from Type II Portland Cement. It should be noted that Type I and Type II OPC are very similar [24] and either could have been used for the formulations.

Cement monoliths with 80-87wt% FBSR loading on a dry basis were fabricated. Formulations A to C were 84, 87, and 80% FBSR loaded with no pozzolanic additives. Formulations D and E were 80-81% FBSR loaded with precipitated silica (representing a chemically pure pozzolanic material such as fly ash) to see if the overall durability of the cement monoliths would improve with excess silica was present to react with the CaOH formed by the hydration of OPC. Fly ash was not chosen as a pozzolanic additive as it contains large concentrations of impurities that may have complicated the durability testing of the cement monoliths. All cement monoliths were set in Teflon<sup>®</sup> molds that had 2" x 2" chambers. Teflon<sup>®</sup> was chosen so that a mold release would not have to be used. All cement monoliths were set for 7 days in air at ambient temperature before compression testing (Fig. 1a).



(a)



(b)



(c)

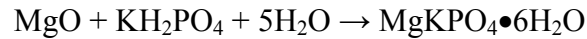


(d)

Fig. 1. Monoliths of (a) cement set for 7 days, (b) Ceramicrete set for 14 days, and (c) hydroceramics set for 7 days at 40°C, (d) hydroceramics set for 7 days at 90°C.

## Ceramicrete Monoliths

Ceramicrete is a blend of MgO and monopotassium phosphate (KH<sub>2</sub>PO<sub>4</sub>). The blend is mixed with a stoichiometric amount of water according to the formulation:



The reaction product on the right hand side of the equation is Ceramicrete, a rapid setting phosphate ceramic [32]. Ceramicrete monoliths were made at Argonne National Laboratory (ANL) at an FBSR loading of 35.7 wt%. The monoliths were cured at ambient temperature for two weeks, unmolded, the ends polished, and then shipped to SRNL for durability testing. The open porosity of the samples (see Fig. 1b) was evaluated by ANL using a water immersion method. It was negligible in all cases. In order to evaluate the volume change after solidification, ANL measured the packed powder density and determined that at 33.3 wt.% loading a volume reduction of ~25% had been achieved.

## Hydroceramic Monoliths

Hydroceramics are made by the solidification of denitrated high sodium waste with NaOH and metakaolin clay [33], e.g. kaolin clay that has been heat treated at  $\geq 700^\circ\text{C}$  to render it amorphous. The samples which are mixed to a “bread dough” consistency, extruded into a mold, and cured in steam. Reference 33 recommends a cure at  $40^\circ\text{C}$  in a 100% humidity chamber overnight and cured for an additional 24 hours at  $90^\circ$  in a steam saturated atmosphere. The curing ensures that the NaOH and metakaolin react to form zeolite mineral phases which are the hydroceramic analogs of the FBSR feldspathoid minerals.

In this study the 50%, 60% and 80 FBSR product loadings on a dry basis were tested. The first three waste loadings were set in the Teflon<sup>®</sup> molds and cured in a humidity chamber overnight at  $40^\circ\text{C}$ . The samples were then unmolded and cured at  $40^\circ\text{C}$  in steam for an additional 24 hours before compression testing (Fig. 1c). These samples produced insufficient strength in 7 days. A second set of hydroceramic blocks were made and set in steel molds so they could be cured at higher temperatures, e.g.  $70^\circ\text{C}$ . These samples produced insufficient strength in 6 days. The change to steel molds was necessitated because the hydroceramics were sticking to the Teflon<sup>®</sup> molds. A third set of hydroceramic blocks were made in duplicate and cured overnight at  $90^\circ\text{C}$  in steel molds at 100% humidity and cured for an additional 7 days at  $90^\circ\text{C}$  in the unmolded state at 100% relative humidity before compression testing (Fig. 1d).

Due to time constraints, the 1<sup>st</sup> set of hydroceramics was used for durability testing even though these monoliths did not meet the final compressive strength requirement. This was done under the assumption that the binder effects from the clay and NaOH added to form the hydroceramics would be the same or worse for a monolith incompletely reacted than one completely reacted.

## Monolith Characterization

Since the FBSR product and the binders were well mixed before each was cured and all of the sample was used to make each monolith, subsamples of each monolith were considered to be

representative of the entire block. The broken pieces were analyzed by the same dissolution and ICP-ES and ICP-MS methods outlined above. Weight loss to determine the water content was determined after heating 700°C for 8 hours.

### Compressive Strength Testing

The 2" x 2" square blocks of concrete and hydroceramics were compression tested using ASTM C 109-02 and the Ceramicrete cylinders were compression tested using ASTM C39-04A. All compression testing was performed at SRS. Comparative compression testing with ASTM C39 was available for the Ceramicrete monoliths from ANL.

### Durability Testing

The chemical durability of the steam reformer pilot scale products was determined using ASTM procedure C 1285-02 [34]. The monolithed samples were ground and sized between -100 and +200 mesh (74 μm to 149 μm), the same size fraction used to express glass waste form performance and used to test the granular FBSR bed and fines products. To remove the electrostatic fines, the sized material was washed six times with 100% ethanol. Water was not used for washing for fear of removing any water soluble phases prior to leaching as cautioned by the ASTM C1285-02 procedure. For all samples, ASTM Type I water [35] was used as the leachant, a constant leachant to sample ratio of 10 cm<sup>3</sup>/g or 0.01 L/g was used, the test temperature was 90°C, and the test duration was seven days. The test temperature and 7 day test duration are the nominal test conditions used for glass waste form performance, e.g. PCT-A.

The Product Consistency Test (PCT) results can be expressed as a normalized concentration (NC<sub>i</sub>) which have units of g<sub>waste form</sub>/L<sub>leachant</sub>, or as a normalized release (NL<sub>i</sub>) in g<sub>waste form</sub>/m<sup>2</sup>, or as a normalized rate (NR<sub>i</sub>) in g<sub>waste form</sub>/m<sup>2</sup>·day where “i” is the chemical element of interest. Normalized releases, NL<sub>i</sub> and NR<sub>i</sub>, are normalized by the amount of element “i” in the sample, and by the surface area (SA) of the sample releasing species “i” and the volume (V) of the leachant being used. Normalized concentrations, NC<sub>i</sub>, are only normalized to the amount of element “i” in the sample and not by the SA/V ratio. The calculations are given in Eq. 1.

$$NL_i = \frac{c_i(\text{sample})}{f_i \cdot (SA/V)} \quad \text{or} \quad NC_i = \frac{c_i(\text{sample})}{f_i} \quad (\text{Eq. 1})$$

where  $NL_i$  is the normalized release (g<sub>waste form</sub>/m<sup>2</sup>)  
 $NC_i$  is the normalized concentration (g<sub>waste form</sub>/L<sub>leachant</sub>)  
 $c_i(\text{sample})$  is the concentration of element  $i$  in the leachate solution (g/L)  
 $f_i$  is the fraction of element  $i$  in the unleached waste form (unitless).

In order to calculate NL<sub>i</sub>, the units used in the Hanford specification for LAW glass durability, the surface area of the material being tested must either be calculated (ASTM C 1285, Appendix XI) or measured. In this study the surface area was measured by the BET method [36] recommended by McGrail [5]. All open pores, inclusions, irregularities, etc. penetrable by the inert gas (nitrogen for this work) are accounted for in the surface area. This surface area may be different from the surface area penetrable by water during a leaching test [37] but is the best



measurement available. The SA/V ratio is simply calculated by dividing the measured BET surface area by the leachant volume.

## RESULTS

### Composite FBSR Waste Characterization

The analyses of the granular composite INL STAR campaign products (SBW and LAW) used for the formation of monoliths were analyzed using the methods outlined above. The results are reported in Reference 38. Excess  $\text{Al}_2\text{O}_3$  in the analysis indicates that there is a significant contribution of startup bed  $\text{Al}_2\text{O}_3$  in the composite. This is confirmed by the X-ray Diffraction (XRD) spectra which indicated that  $\text{Al}_2\text{O}_3$  was a major component of the composite along with bed and fines products containing nepheline ( $\text{Na}_{6.8}\text{Al}_{6.3}\text{Si}_{9.7}\text{O}_{32}$ ), sodalite ( $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$ ), nosean ( $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$ ) which were the main phases found in the 2004 SBW and LAW campaigns. The XRD spectra of the composite also indicated some partially reacted  $\text{NaAl}_{5.9}\text{O}_{9.4}$  and  $\text{SiO}_2$  from the 2003 SWB bed products was present.

Based on the analyzed compositions of the individual waste streams mixed to make the composite (reported in Reference 2 and 38) an algorithm was written and regressed with a non-linear modeling routine in JMP software. The algorithm fit the following equation to the final composite composition analyzed in this study and reported in [38]:

$$a_1 \bullet \text{Al}_2\text{O}_3 + a_2 \bullet \text{SBW03} + a_3 \bullet \text{SBW04} + a_4 \bullet \text{LAW04}$$

The non-linear fit indicated that the composite was composed of ~45% startup bed, 17% SBW 2003, 15% SBW 2004, and 20% LAW 2004. The fit gives an adjusted  $R^2$  of 99.8% and a root mean square error (RMSE) of 0.7496. The contribution of the LAW 2004 material to the composite may be underestimated in the algorithm fit since  $\text{SO}_3$  is very high in the composite and the LAW products (bed and fines) are the largest contributors to the  $\text{SO}_3$  content.

### Monolith Compressive Strength

Four of the five cement monoliths tested in this study had compressive strengths >500 psi after 7 days (Fig. 2a). A 5% substitution of precipitated  $\text{SiO}_2$  for OPC as a pozzolanic additive improved the cement monolith compressive strength up to 2710 psi (formulation D) while a 17.5% substitution decreased the compressive strength (formulation E) at ~80% FBSR loadings (formulation C with no  $\text{SiO}_2$ ). Lowering the FBSR loading to 80 wt% (formulation C) from 84 and 87 wt% (formulations A and B) also improved the compressive strength (Fig. 2a).

The Ceramicrete monolith compressive strengths were measured at SRNL and ANL. The SRNL compressive strength measurements were higher than those of ANL but the SRNL measurements were made after an additional ~1 month of curing. ANL's compressive strength value is plotted in Fig. 2a. The densest and highest waste loaded hydroceramic cured at 90°C for 1 week had superior compressive strength (>1500 psi) compared to all the other hydroceramics cured at 90°C. The 90°C cured sample compressive strengths are plotted in Fig. 2a.

All of the monoliths except one cement (Cement E) and one hydroceramic (Hydroceramic A) had >500 psi strength after either 7 (cement and hydroceramics) or 14 (Ceramicrete) day cures. Of the samples that had achieved 60-87 wt% FBSR product loadings (Fig. 2a) only the 50% loaded hydroceramic sample did not achieve the >500 psi strength requirement.

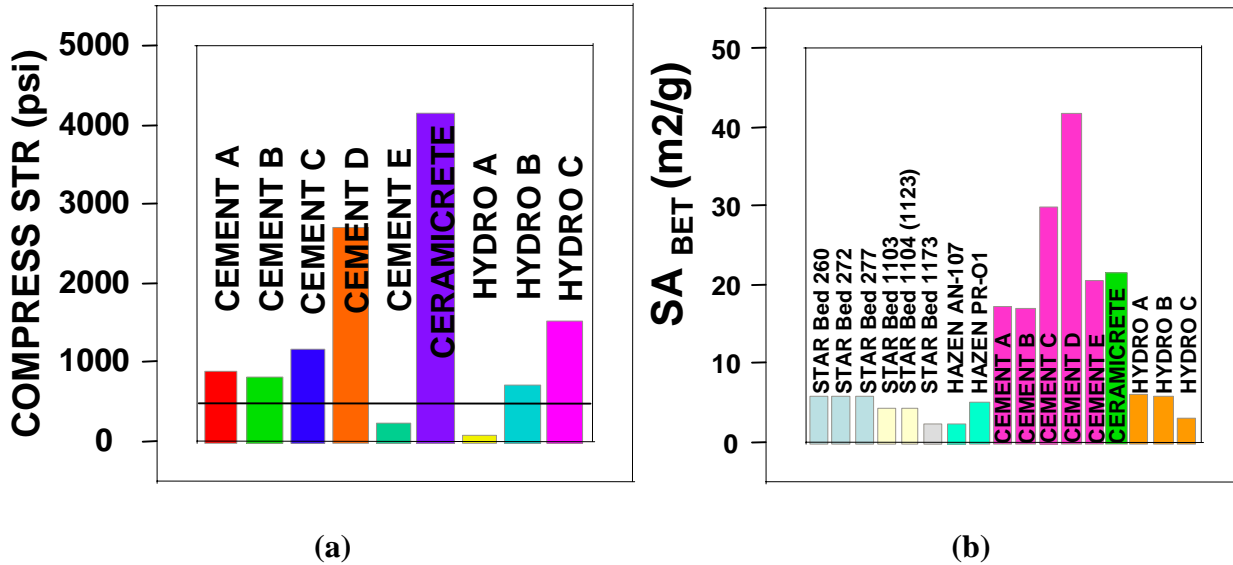


Fig. 2. Comparative FBSR compressive strengths and BET surface areas.

### Monolith Characterization and Durability

Durability testing via the Product Consistency Test requires that the fraction of each element in the monolithic solid be known (see  $f_i$  term in Eq. 1). The wt% of each element in the monoliths was analyzed including the amount of water. A mass balance was performed on the analyses. The samples were then converted to an anhydrous basis to determine the  $f_i$  on a dry weight basis as the water content of the monoliths does not participate in the leaching (Table 2).

The monoliths were analyzed by X-ray Diffraction (XRD) to ensure that the monolithing agents had not decomposed the FBSR mineral phases [38]. The mineralogic phases remained unaltered and in some cases new phases from the binder hydration appeared. For example, the hydrated  $MgKPO_4 \cdot 6H_2O$  phase of Ceramicrete was observed during XRD analysis of this monolith.

The surface area of all of the samples was measured by the BET method using  $N_2$ . From Fig. 2b it can be seen that the cement and Ceramicrete monoliths have much higher BET surface areas than the hydroceramics. This is likely due to the fact that when cement hydrates needle like crystallites of calcium silicate hydrate (CSH) form that are initially hydrous and crystallize giving an interlocking structure that gives concrete its strength. These CSH phases create additional surface area. A comparison of the BET surface areas of the bed products in the granular samples and the monolithed samples is given in Fig. 2b.



The monoliths were durability tested in triplicate along with glass standards and blanks that are required by the PCT procedure to ensure test control. The standard releases agreed with previous round robin testing of these glasses. The data for the standards and blanks are reported elsewhere [38]. The average triplicate leach responses for the nine monoliths tested are tabulated in Table 3.

The PCT leachate analyses for Re (surrogate for Tc-99) from Table 3 are shown graphically in Fig. 3. This figure indicates that Re (surrogate for Tc-99 which is the major radionuclide of concern at Hanford for shallow land burial) leaches at  $<0.42 \text{ g/m}^2$  for all but one monolith which leaches at  $<0.75 \text{ g/m}^2$ . These releases are  $\ll 2 \text{ g/m}^2$  ( $2000 \times 10^{-3}$  in the units shown on the figure) specification for Na release for LAW glass where the Na release specification is tied to the Tc-99 release by the congruent nature of the leaching in a vitrified waste form.

An aluminosilicate buffering mechanism was observed during leaching of the granular FBSR products [2,3], these trends were not observed when the same bed products were embedded in the monolithing binders tested in this study. In addition, Re, S, and Si in the granular FBSR products were a strong function of solution pH. These trends are not observed in the monolith leach results. This is likely due to interactions of the binder phases (calcium silicates in cement, magnesium phosphates in Ceramicrete, and zeolites and NaOH in hydroceramics) with the leachate which complicates the interpretation of the leachate analyses.

Table 3. Average of Triplicate PCT Results\* Compared to LAW Standards (Units in  $10^{-3} \text{ g/m}^2$ )

Monolith Tested	Al ( $\text{g/m}^2 \times 10^{-3}$ )	Cs ( $\text{g/m}^2 \times 10^{-3}$ )	Na ( $\text{g/m}^2 \times 10^{-3}$ )	Re ( $\text{g/m}^2 \times 10^{-3}$ )	S ( $\text{g/m}^2 \times 10^{-3}$ )	Si ( $\text{g/m}^2 \times 10^{-3}$ )
Cement A	5.82	119	146	420	2.76	1.62
Cement B	5.68	136	163	382	4.48	1.03
Cement C	3.71	93.4	97.6	212	2.09	0.95
Cement D	296	7,040	7,250	19,900	123	49.8
Cement E	1.78	30.5	70.5	206	3.11	0.974
Ceramicrete	0.247	76.6	85.7	185	6.55	0.772
Hydroceramic A	13.7	8.80	198	297	34.2	2.29
Hydroceramic B	10.1	9.41	161	132	29.6	3.74
Hydroceramic C	6.49	44.9	224	329	46.1	13.6
Hanford Specification for Glass	2,000	2,000	2,000	2,000	2,000	2,000
LRM Glass [39]	142	---	550	---	---	169

\* The presence of alumina startup bed does not affect these numbers as the release of an element to the leachate is normalized by the amount of the element measured in the product, e.g. the data from Table 2.

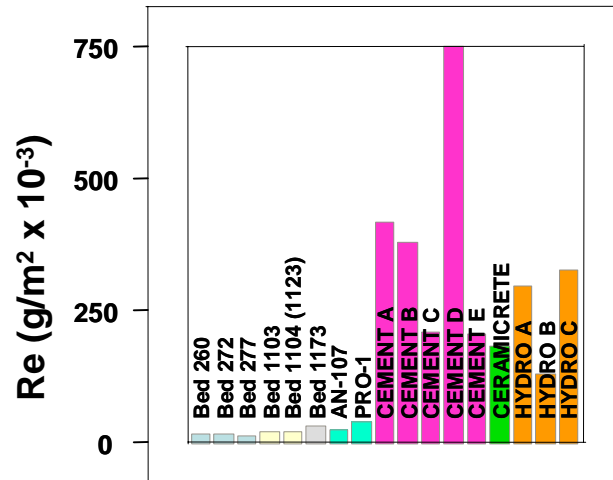


Fig. 3. PCT triplicate leachate analyses for Re (surrogate for Tc-99) in g/m<sup>2</sup>.

## CONCLUSIONS

It is feasible to stabilize granular FBSR product in a variety of compatible binders. Three cement formulations and one hydroceramic formulation met all of the monolith development criteria including the waste loading criteria for Hanford LAW Envelope A, the compressive strength criteria for shallow land burial, and the durability criteria based on Na and Re release during PCT (ASTM C1285) analysis.

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Ceramicrete FBSR. Cast Stone. CH2M Hill, Inc. Fluidized Bed Steam Reforming Waste Form. Prepared by Advanced Remediation Technologies (ART) Project Hanford off-gas recycle simulant spiked with Re, and RCRA metals Processed through Hazen Engineering Scale Technology Demonstration (ESTD) Facility FBSR granular product encapsulated in GEO7 geopolymer matrix at SRNL 2-inch x 4-inch cylinders provide to PNNL for characterization. Fluidized Bed Steam Reformer product characterization Demonstrate compliance with waste acceptance criteria Engineering-scale process demonstrations. Ceramicrete, DuraLith. Mechanisms of radionuclide retention to support waste form selection. Fluidized Bed Steam Reforming (FBSR) is being considered as an alternative technology for the immobilization of a wide variety of aqueous high sodium containing radioactive wastes at various DOE facilities in the United States. The strength requirement necessitates binding the granular product into a monolith. FBSR mineral products were formulated into a variety of monoliths including various cements, Ceramicrete, and hydro-ceramics. All but one of the nine monoliths tested met the. Do you want to read the rest of this article? Request full-text.