

Mineralization of Radioactive Wastes by Fluidized Bed Steam Reforming (FBSR): Radionuclide Incorporation, Monolith Formation, and Durability Testing - #10467

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ABSTRACT

Mineral waste forms are typically formed at high temperatures (1100-1500°C) by an array of batch processes, e.g. calcining, hot pressing, cold pressing, sintering, etc. Fluidized Bed Steam Reforming (FBSR) offers a low temperature (700-750°C) continuous method by which to process wastes that are high in organics, nitrates, sulfates/sulfides, or other aqueous components. The granular waste form that is produced is more durable than glass. Monolithing of the granular product can be used to prevent dispersion during transport or burial/storage. A variety of monoliths have been shown to be feasible without compromising the durability of the minerals which host the radionuclides. In the sodium aluminosilicate mineral structures, the contaminants such as Tc-99 are bound in cage shaped structures (sodalite, nosean) or ring (nepheline) structures. The minerals are formed by destabilization of the clay additive at the moderate processing temperature: the clay becomes amorphous at the nanoscale and reactive. The alkali or alkaline earth cations in the waste react with the unstable clay cations and rearrange to a crystalline (mineral) lowest free energy configuration forming mineral species such as NaAlSiO₄. In mineral waste forms, as in glass, the molecular structure controls contaminant release by establishing the distribution of ion exchange sites, hydrolysis sites, and the access of water to those sites. The durability testing (Product Consistency Test; ASTM C1285) of the FBSR mineral waste form has shown that the FBSR product is more durable than glass and that an Al-buffering mechanism controls the release of alkali (Na, K, and Cs) elements and the solution pH controls the release of the other constituents like Re (simulant for Tc-99), S, and Si. This mechanism is known to occur in nature during weathering of aluminosilicate mineral analogs. Additional testing using the Single Pass Flow Through test indicates that the FBSR mineral product is more durable than a glass made from the same waste by ~ 2 orders of magnitude.

INTRODUCTION

Mineral Waste Forms: Historical Perspective

Crystalline (ceramic/mineral) waste forms made by moderate temperature (700-750°C) thermal treatment have not been as intensely investigated as those formed at high temperatures (1000-1500°C) by Hot Isostatic Pressing such as SYNROC or by pressing and sintering (SYNROC, supercalcine ceramics, tailored ceramics, and Pu ceramics) [1]. However, crystalline waste forms made from clay have been studied almost continuously since 1953 [1,2]. In much of the clay based waste form research [3,4,5] the clays were used to sorb radionuclides and then sintered or pressed into waste forms in the absence of hydrothermal reactivity [4,5,6,7]. Often the high temperatures used for sintering created sodalite-cancrinite mineral assemblages as minor

constituents. In 1981, Roy [3] proposed low temperature hydrothermally processed low solubility phase assemblages consisting of the micas, apatite, pollucite, sodalite-cancrinite, and nepheline, many of which could be made from reaction of various clays (kaolin, bentonite, illite) with waste.

Clay based crystalline (ceramic/mineral) waste forms were not pursued in the late 1970's and early 1980's because there was no continuous commercial technology available that could process the waste/clay mixtures in a hydrothermal environment [1]. A commercial facility to continuously process radioactive wastes at moderate temperatures in a hydrothermal steam environment was built by Studsvik in Erwin, Tennessee in 1999 [8,9]. The Erwin facility uses a steam reforming technology designated as the Thermal Organic Reduction (THORsm) process to pyrolyze Cs-137 and Co-60 organic resins from commercial nuclear facilities. The Erwin facility has the capability to process a wide variety of solid and liquid streams including: ion exchange resins, charcoal, graphite, sludge, oils, solvents, and cleaning solutions at radiation levels of up to 400R/hr.

If kaolin clay is added to an alkali-rich waste during processing a "mineralized" waste form is produced that is composed of various Na-Al-Si feldspathoid minerals, i.e. sodalites are the host minerals for the halides and Tc-99; nosean is the host mineral for sulfate or sulfide species; and nepheline sequesters the remaining alkali by nano-scale reaction of the clay and waste. Bench scale, pilot scale, and engineering scale tests have all formed this mineral assemblage with a variety of legacy United States Department of Energy waste simulants. Illite type clay was tested at the bench scale and shown to form dehydroxylated micas (host for future Global Nuclear Energy Partnership, wastes including lanthanides, Cs, Sr, Ba, Rb, Tl, etc.) by similar nanoscale reaction of clay and waste [10].

Commercialization of Mineralizing FBSR

The commercialization of the FBSR technology at the Erwin, Tennessee facility has created interest in this technology for the immobilization of a wide variety of radioactive wastes in the United States. Of special relevance is the capability of the FBSR technology to destroy organics while converting alkali/alkaline earth/rare earth salts to aluminosilicate minerals that are suitable for direct geological disposal and/or to carbonate or silicate species for subsequent vitrification or disposal.

An FBSR facility is being designed and constructed at the Idaho National Laboratory for treatment of their Sodium Bearing Waste (SBW) for potential disposal in the Waste Isolation Pilot Plant (WIPP) [11,12] in the US. Another facility is being considered for use at the Savannah River Site to convert a salt supernate waste (Tank 48) containing nitrates, nitrites, and organic cesium tetraphenyl borate, to carbonate or silicate minerals which are compatible with subsequent vitrification [13]. Pilot-scale testing has also included a variety of tank wastes producing aluminosilicate waste forms for Idaho's SBW and Hanford's Low Activity Waste (LAW) [14,15] and LAW melter recycle (referred to throughout this paper as Waste Treatment Plant Secondary Waste, WTP SW).

The reforming process is effective in pyrolyzing organics and separating sulfur and halogens from organic waste materials at moderate temperatures (650°C for carbonate mineralization and

700-750°C for aluminosilicate mineralization). In the FBSR, the organic compounds are pyrolyzed to CO₂ while nitrate/nitrite species are converted to N₂ through reactions with superheated steam, which is the fluidizing media.[14,16,17] The process is not combustion and is Clean Air Act compliant. The FBSR technology has also been shown to be Hazardous Waste Combustor Maximum Achievable Control Technology compliant for Hg, Cl, CO, total hydrocarbons, and heavy metals [9,18]. A significant benefit of the FBSR process is that liquid secondary wastes from process gas treatment are not produced. All water is released as water vapor.

Durability of the Mineralized FBSR Product

The FBSR mineral waste form is granular in nature. As a granular product it has been shown to be more durable than glass during testing with ASTM C-1285-02 known as the Product Consistency Test, testing with the Single Pass Flow Through Test, and during subsequent performance assessment modeling [19,20,21,22,23,24,25,26]. This is partially due to the high aluminosilicate content of the mineral product which provides a natural aluminosilicate buffering mechanism [20,21,22] that inhibits leaching and is known to occur in nature during weathering of aluminosilicate mineral analogs [27] and in alumina rich vitreous waste forms [28].

Durability testing of the granular FBSR mineral waste form indicates that it is more durable than vitreous waste forms. Thus, monolithing of the granular product is not necessary if the product is containerized. Monolithing may be desirable in certain scenarios in which (1) containment of any fine fraction is necessary, (2) waste form compressive strength requirements exist, and/or (3) stabilization is required for shallow land burial and inadvertent intruder scenarios. Granular and monolith durability will be discussed in this study.

MINERALOGY

The fluidizing steam used in FBSR processing creates the hydrothermal reactivity needed for mineral formation. Clays become amorphous at the nano-scale because clays lose their hydroxyl groups between 550-750°C which destabilizes the octahedral Al atoms in their structure. Once the Al cation is destabilized the clay becomes amorphous and species in the waste “activate” the unstable Al cation to form new mineral structures. The steam and nano-scale reactivity of the clay catalyze mineralization allowing formation and templating at moderate temperatures. Kaolin clay has been found to template the feldspathoids and the illite clays have been found to template the dehydroxylated micas as radionuclide hosts [10]. Additional iron bearing co-reactants can be added during processing to stabilize any multivalent hazardous species present in a waste in durable spinel phases, i.e. Cr, Ni, Pb iron oxide minerals.

The Na-Al-Si mineral waste forms are comprised of nepheline (hexagonal Na_xAl_ySi_zO₄ where x, y, and z nominally each are a value of 1) and other feldspathoid mineral phases which have large cages that trap anion constituents such as Na₂SO₄ (nosean), NaF, NaI, NaCl (sodalite nominally Na₈[Al₆Si₆O₂₄](Cl₂) or Na₆Al₆Si₆O₂₄](2NaCl), Na₂MoO₄, NaTcO₄, NaReO₄. The feldspathoid mineral nepheline and its metastable form known as carnegite, have ring type structures.

Carnegieite is a metastable form of nepheline that usually forms due to rapid cooling. Carnegieite has a similar structure to nepheline but readily transforms to nepheline upon heating. A nepheline phase found in the LAW waste form product is a unique sodium rich cubic derivative, $(\text{Na}_2\text{O})_{0.33}\text{NaAlSiO}_4$,^f with large twelve-fold oxygen cage like voids [29]. While carnegieite and nepheline nominally have Na:Al:Si ratios of 1:1:1, a variety of defect structures with different ratios exist. Nepheline also accommodates Cs, Sr, and Ca.

The feldspathoid cage structures are typical of sodalite and/or nosean phases where the cavities in the cage structure retain anions and/or radionuclides which are ionically bonded to the aluminosilicate tetrahedra and to sodium in the mineral structure. The cage structured feldspathoid system of minerals has the basic structural framework formula $\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}]$. The square brackets in the formula delineate the Al:Si ratio of the aluminosilicate mineral structure which is nominally 1:1 but can exhibit different Al:Si ratios while retaining the cage structure.

Sodalite minerals are known to accommodate Be in place of Al and S_2 in the cage structure along with Fe, Mn, and Zn, e.g. helvite ($\text{Mn}_4[\text{Be}_3\text{Si}_3\text{O}_{12}]\text{S}$), danalite ($\text{Fe}_4[\text{Be}_3\text{Si}_3\text{O}_{12}]\text{S}$), and genthelvite ($\text{Zn}_4[\text{Be}_3\text{Si}_3\text{O}_{12}]\text{S}$) [30]. These cage-structured sodalites were minor phases in High Level Waste (HLW) supercalcine waste forms¹ [31] and were found to retain Cs, Sr, and Mo into the cage-like structure, e.g., Mo as $\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{NaMoO}_4)_2$ [31]. In addition, sodalite structures are known to retain B [32], Ge [33], I [30,33], and Br [30,33] in the cage like structures. Indeed, waste stabilization at Argonne National Laboratory-West currently uses a glass-bonded sodalite ceramic waste form for disposal of electrorefiner wastes for sodium-bonded metallic spent nuclear fuel from the EBR II fast breeder reactor [34,35].

When an iron oxide additive is co-reacted during FBSR processing iron chromium spinel minerals form. The spinels sequester Mg^{2+} , Zn^{2+} , Ni^{2+} , Cr^{3+} , Al^{3+} , and occasionally substitution of Ti^{4+} [36]. The reducing atmosphere of the FBSR process converts any Cr^{6+} in a waste to Cr^{3+} which can then become stabilized in $(\text{Mg,Fe})(\text{Fe,Al,Cr})_2\text{O}_4$ spinels which have been used to stabilize Cr-rich industrial wastes [37] and shown to retain the Cr^{3+} during Toxic Characteristic Leaching Procedure testing at levels that were orders of magnitude below the EPA regulatory Universal Treatment Standard limits [38].

EXPERIMENTAL

Pilot Scale Testing

The granular products tested and monolithed were made in the THOR[®] pilot scale dual reformer at Hazen Research Inc. in Golden, Colorado. This data is compared to previous data generated with a single reformer flowsheet at SAIC Technology Applications Research (STAR) facility in Idaho Falls, Idaho in 2003-4 and at Hazen Research Inc. in 2001 [20,21,22,23].

Hanford Low Activity Waste (LAW) and WTP SW from the planned Hanford LAW melter, e.g. off-gas recycle streams rich in halides and sulfates and Tc-99, were investigated in this study.

^f Powder Diffraction File #39-0101

¹ Supercalcines were the high temperature silicate based “mineral” assemblages proposed for HLW waste stabilization in the United States (1973-1985).

FBSR is being considered for WTP SW after some evaporation instead of evaporation alone. The wastes and clay mixtures reported in this study are given in Table 1. The waste compositions (simulants) are given in Table 2 on a dry feed basis.

Table 1. Formation Conditions of the FBSR Products Tested

Simulant	Formation Temperature (°C)	clay:simulant (g/L)	Test ID
LAW	725	675	P-1A
LAW	725	640	P-1B
WTP SW	680	307	P-2A
WTP SW	700	307	P-2B

Table 2. Composition Ranges of Wastes Mineralized

Oxides and Anions	Oxide/Anion Basis After Organic and Nitrate Removal (wt%)	Organic Content Before Thermal Treatment (wt%)	Nitrate Content Before Thermal Treatment (wt%)	Waste Solution pH
HANFORD TANK WASTES (Composition Envelope “A” AW-101* HRI Pilot 2008)				
Na ₂ O + K ₂ O	86.53	0.97	50.28	14
Al ₂ O ₃	1.81			
SO ₄	7.11			
Cl	1.42			
F	0.74			
Cr ₂ O ₃	0.44			
HANFORD PROJECTED MELTER OFF-GAS RECYCLE WASTES WTP SW (HRI Pilot 2008)				
Na ₂ O + K ₂ O + Cs ₂ O	60.19	0	91.45	>14
Al ₂ O ₃	20.33			
SO ₄	0			
Cl	4.51			
F	6.69			
Cr ₂ O ₃	0.34			

* RCRA metals (Sb, As, Ag, Cd, Ba, and Tl) and radionuclide surrogates (Re, I, Cs) were doped in at 10-1000X

Monolith Formation

Monoliths, representative of final waste forms, were generated from five binder types at a 2-inch cube scale with LAW granular product. Monoliths using both LAW and WTP SW granular products were prepared from three of the best performing binder types into 3-inch diameter by 6-inch tall and 6-inch by 12-inch tall cylinders. The five binders were the following:

- Ordinary Portland Cement, a binder of primarily calcium silicate with some calcium aluminate, and calcium aluminoferrite
- High alumina cements, composed mainly of calcium aluminates rather than calcium silicates (creates lower pH pore water than Ordinary Portland Cement)
- Geopolymers, which are amorphous to semi-crystalline, three-dimensional inorganic silico-aluminate polymers formed by mixing clay with sodium silicate and/or NaOH
- Geopolymers, which are amorphous to semi-crystalline, three-dimensional inorganic silico-aluminate polymers formed by mixing fly ash with sodium silicate and/or NaOH
- Ceramicrete (ceramic cement), which is composed of $MgKPO_4 \cdot 6H_2O$ and made by mixing magnesium oxide, monopotassium phosphate, and Class F fly ash

Chemical and Mineralogical Analyses of Granular and Monolithic Products

Elemental and anion compositions of the steam reforming materials were measured and the coal component considered inert. For elemental analysis, solid samples were digested with a lithium tetraborate fusion at 1000°C followed by a hydrochloric acid uptake. The resulting solutions were analyzed by Inductively Coupled Plasma Emission Spectroscopy for Al, Ca, Cd, Cr, Cs, Cu, Fe, I, K, La, Mg, Mn, Na, Ni, P, Pb, S, Si, and Ti and Inductively Coupled Plasma Mass Spectroscopy for Cs, Re, and I. Anion content was determined from a sodium peroxide/sodium hydroxide fusion at 600°C followed by a water uptake. The resulting solutions were analyzed by Ion Chromatography for NO_3^- , F^- , and Cl^- . The REDOX (iron (II) to total iron ratio) was determined on bed samples where the carbon was removed manually and on the fines including the carbon component as the carbon was too fine to separate manually. The mineralogical speciation of the samples was examined by X-ray Diffraction.

Waste Form Durability Testing

The chemical durability of the pilot scale LAW and WTP SW products from the PR and HTF vessels were determined using ASTM procedure C 1285. Prior to sizing and washing, carbon was removed from the PR and HTF products by roasting in air at 525°C. This ensured that the carbon did not contribute to the measured surface area and that the durability of the PR and HTF products was being measured since the carbon is inert during durability testing. Subsequently, composites of LAW PR and HTF samples and the WTP SW (PR and HTF) were mixed at a ratio of ~20:80 and 30:70, respectively. The composites contained coal during the durability testing and the contribution of the coal fraction to the mass was removed mathematically (1.7 LAW and 11.1 wt% WTP SW). Both methods, e.g. removing the coal by roasting and mathematically adjusting for the coal contribution assume the coal is inert and does not contribute to the durability of the product.

The monolith samples were fabricated with the composite PR and HTF products containing coal. Monoliths also contained up to 20 wt% moisture as determined from drying at 250°C in air overnight. Durability testing of the monoliths was performed with the coal in the product and both the coal and moisture contributions were mathematically accounted for in the reported normalized release rates.

The PR, HTF and composite samples were sized between -100 and +200 mesh (74 μm to 149 μm), the same size fraction used to test glass waste form performance. 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 procedure.

For all samples, ASTM Type I water was used as the leachant, a constant leachant to sample ratio of 10 cm^3/g or 0.01 L/g was used, the test temperature was 90°C, and the test duration was seven days. The test temperature, duration, and SA/V ratio are the nominal test conditions used for testing glass waste form performance.

The PCT test response is given as the normalized release of a given element “i” normalized to its concentration in the waste form, e.g. NL_i . This is the standard units in which the LAW glass specification is given, and necessitates the use of a surface area of the sample releasing species “i” and the volume of the leachant being used which is expressed as the SA/V ratio.

In order to calculate NL_i , the surface area of the material being tested must either be calculated (ASTM C 1285) or measured. In this study, the waste form SA was measured by the Brunauer, Emmett, and Teller method recommended by McGrail [23] due to the high surface roughness and high internal porosity of the FBSR product compared to vitrified waste form products.

The Hanford LAW and INL SBW wastes are listed wastes under the EPA Resource Conservation and Recovery Act. When treated, the waste form must retain the hazardous components at the Universal Treatment Standard limits [38]. The samples were evaluated for retention of the hazardous metals by the EPA Toxicity Characteristic Leaching Procedure, Method 1311 and this is reported elsewhere. [39]

RESULTS AND ANALYSES

Characterization of the Granular Mineralized FBSR Products

The mineral assemblages formed from Hanford LAW and WTP SW simulated wastes when mixed with varying amounts of kaolin clay and processed via FBSR create the feldspathoid mineral assemblages (nepheline, nosean, sodalite) all of which are known to have extensive solid solutions (see for example Fig. 1). The phases formed are primarily nepheline (Na and/or K rich nepheline, Si rich nepheline) which has a large solid solution field along the $\text{SiO}_2\text{-Na}_2\text{O}\bullet\text{Al}_2\text{O}_3$ pseudobinary shown in Fig. 1. The FBSR produces a granular product but also produces fines. The fines have a shorter residence time in the fluidized bed and often form low-carnegieite which has the same chemical composition as nepheline but is less ordered atomically.

The mineral assemblages that were determined by XRD analysis are given in Table 3. The phases identified in the LAW and WTP SW FBSR product are the same as those identified in previous studies at Hazen Research Inc. and at the STAR facility with LAW wastes and INL SBW wastes. These phase assemblages are given in Table 3 for reference.

The REDuction/OXidation of species such as sulfur and rhenium (surrogate for Tc-99) are important because an $\text{Fe}^{+2}/\Sigma\text{Fe}\leq 0.3$ ratio keeps the oxygen fugacity in the DMR between $-\log$

f_{O_2} -19.4 atm. and -21atm. (see EMF series predictions in reference 40). At these oxygen fugacities $\geq 95\%$ of the sulfur is present as SO_4 and can be sequestered in the nosean phase and $\geq 95\%$ of the rhenium is present as Re^{+7} and can be sequestered in the known perhenate sodalite structure [41]), $NaReO_4$ (or $NaTcO_4$). Oxygen fugacities more reducing than $-\log f_{O_2} \sim -20.6$ atm. allow some percentage of the sulfur to exist as sulfides and some percentage of the rhenium to exist as ReO_2 . For the FBSR products examined in this study, the percentages of reduced sulfur and rhenium are given in Table 4.

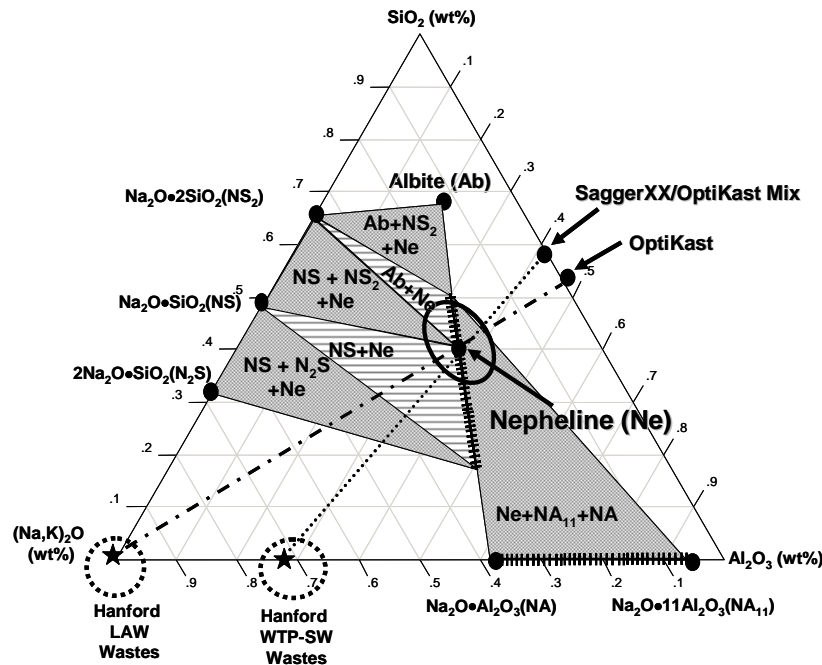


Fig. 1. Ternary phase diagram illustrating the phase compatibility fields for FBSR processing of Hanford high sodium wastes (LAW) and melter recycle (designated WTP SW). The solid circle represents the area in which the feldspathoid minerals form. The shaded triangles indicate what other minerals may potentially appear and hatch marks indicate solid solution phases.

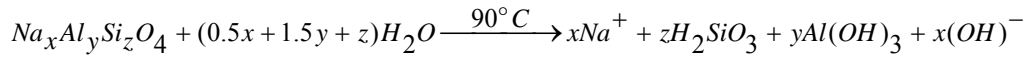
In general, the HTF appears to be more reduced than the bed material but this may be fortuitous as the presence of the coal co-reactant, which cannot be removed from the fines but can manually be removed from the Product Receipt (PR) vessel samples, impacts the analytic results. In addition, the amount of Fe^{+2} used to measure the REDOX in the HTF samples is at the detection limit. Therefore, the REDOX data for the HTF samples may not be as accurate as the REDOX data for the PR samples.

The FBSR bed products (PR vessel) the measured REDOX predicts that 94-95% of the rhenium is in the +7 oxidation state and likely in the sodalite phases observed in Table 3 and 86-89% of the sulfur is in the +4 oxidation state and likely in the nosean phase observed in Table 3. Since these same mineral phases are observed in some of the HTF samples it is likely the HTF samples are more reduced compared to the PR samples as the HTF samples are exposed to an H_2 environment longer than the PR product.

Durability of the Granular Mineralized FBSR Products

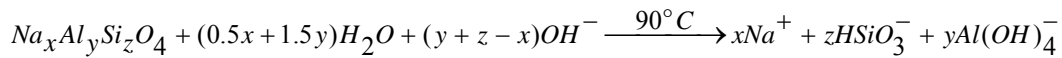
The Product Consistency Test final leachate pH values from this study and the historic FBSR durability data from 2002-2004 indicated that the final PCT solution pH is an inverse function of the sample SA_{BET} (m^2/g), e.g. the pH is lower for samples with a larger surface area (m^2/g). [39] In addition, the pH appears to have some dependency on the stoichiometry of the mineral phases present in the samples as the aluminosilicate buffering mechanism [20, 21] indicates that the mineralogy, especially the Al:Si ratio of the mineral species appears to play a role in the FBSR mineral dissolution mechanisms.

The inverse correlation of pH and surface area is unusual as normally in low Al containing alkali borosilicate glasses the leachate pH increases as more alkali and hydroxide are released to solution from the higher surface of exposed glass. Normally the release of alkali and hydroxide occurs during the early stages of dissolution by ion exchange. For the stoichiometric and non-stoichiometric nephelines and carnegieites (Table 3) found in the historic and current FBSR products and in the the appropriate ion exchange reaction at the start of a Product Consistency Test when the ASTM Type I water pH is ~ 5.5 would be:



The ion-exchange reaction shown in the above equation liberates hydroxide which drives the PCT leachates basic as a function of reaction time. Stoichiometric nepheline (where $x = y = z = 1$) liberates one mole of OH^- for every mole of nepheline. The defect nephelines and carnegieites liberate between 0.9 to 1.53 moles of OH^- . Note that the Si-deficient and sodium rich nephelines liberate the most hydroxide per mole, e.g. 1.45-1.53 moles of OH^- , respectively. A similar mechanism is observed for the leaching of other sodium aluminates such as beta alumina ($NaAl_{11}O_{17}$) formed during FBSR processing.

As the Product Consistency Test continues the solution changes from a pH of 5.5 to >10 and passes through different aqueous stability fields, e.g. $HSiO_3^-$, SiO_3^- and $Al(OH)_4^-$. As the pH increases during Product Consistency Test testing, the equation below becomes dominant for the sodium aluminosilicates. Different nepheline/carnegieite Na:Al:Si ratios and the sodium aluminates complex different amounts of hydroxide as $Al(OH)_4^-$:



Therefore, the leachate pH is particularly dependent on the concentrations of aluminosilicates and aluminates present in the sample being tested and the amount of $Al(OH)_4^-$ formed in the leachate, i.e., the amount of OH^- complexed as $Al(OH)_4^-$. This is shown graphically in Fig. 2 by showing the strong dependence of the Product Consistency Test normalized releases for the alkalis (Na and Cs) versus the normalized releases for alumina.

Table 3. Mineral Phases Analyzed in FBSR Products

	Low-Carnegieite Nominally NaAlSiO ₄	Nepheline Nominally NaAlSiO ₄ or K _{0.25} Na _{0.75} AlSiO ₄	Nosean Na ₆ [Al ₆ Si ₆ O ₂₄](Na ₂ SO ₄) and/or Sodalite Na ₆ [Al ₆ Si ₆ O ₂₄](2NaX where X=Cl,F,I)	Other Minor Components
HANFORD ENVELOPE "C" LAW WASTES (2002) Fe⁺²/ΣFe of Bed = 0.15				
SCT02-098-FM		X	Y	Al ₂ O ₃ , Fe ₂ O ₃ , Fe ₃ O ₄
Fines PR-01	X	X	Y	Al ₂ O ₃ , Fe ₂ O ₃ , Fe ₃ O ₄
HANFORD ENVELOPE "A" LAW WASTES (2004) Fe⁺²/ΣFe of Bed = 0.28-0.81				
Bed 1103	X	X	Y	TiO ₂
Bed 1104	X	X	Y	TiO ₂
Fines 1125	X	Y		TiO ₂
INL SBW WASTES (2003-4) Fe⁺²/ΣFe of Bed = 0.51-0.61				
Bed 260	Y	X	TR	Al ₂ O ₃ and TiO ₂
Bed 272	Y	X	TR	TiO ₂
Bed 277	Y	X	TR	TiO ₂
Bed 1173		X	TR	Al ₂ O ₃ , SiO ₂ , NaAl ₁₁ O ₁₇ and (Ca,Na)SiO ₃
HANFORD ENVELOPE "A" LAW WASTES (2008) Fe⁺²/ΣFe of Bed = 0.41-0.90				
PR Bed Product 5274 (P1A)	Y	Y		Al ₂ O ₃
PR Bed Product 5316 (P1A)	Y	Y		Pyrophyllite*
HTF Fines 5280 (P1A)	Y	Y		NaAl ₁₁ O ₁₇ , TiO ₂
HTF Fines 5297 (P1A)	Y	Y	Y	SiO ₂
PR Bed Product 5359 (P1B)	Y	Y		Pyrophyllite*
PR Bed Product 5372 (P1B)	Y	Y		Pyrophyllite*
HTF Fines 5351 (P1B)	Y	Y		SiO ₂
HTF Fines 5357 (P1B)	Y	Y		TiO ₂
Composite (P1A)	Y	Y		SiO ₂ and TiO ₂
Composite (P1B)	Y	Y		SiO ₂ and TiO ₂
HANFORD MELTER OFF-GAS RECYCLE (WTP SW) WASTES (2008) Fe⁺²/ΣFe = 0.41-0.90				
PR 5475 (P2A)	Y	Y	Y	Pyrophyllite*
HTF Fines 5471 (P2A)	Y	Y		SiO ₂
PR 5522 (P2B)	Y	Y	Y	Pyrophyllite*, TiO ₂
HTF Fines 5520 (P2B)	Y	Y		SiO ₂ and TiO ₂
Composite (P2B)	Y	Y	Y	SiO ₂

X = MAJOR CONSTITUENT; Y = MINOR CONSTITUENT, TR = TRACE CONSTITUENT

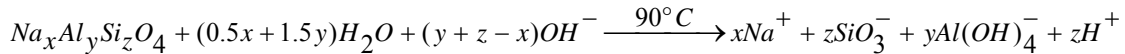
* Al_{1.333}Si_{2.667}O_{6.667}(OH)_{1.333}

Table 4. REDUction/OXidation (REDOX) of Iron, Rhenium (Tc-99), and Sulfur.

Sample	Vessel	Waste	Fe ⁺² /ΣFe	Re ⁺⁷	S ⁺⁴
5280	HTF	LAW	0.734	2.5%	1%
5297	HTF	LAW	0.868		
5351	HTF	LAW	0.898		
5357	HTF	LAW	0.898		
5471	HTF	WTP SW	0.869		
5520	HTF	WTP SW	0.902		
5274	PR	LAW	0.410	94%	86%
5316	PR	LAW	0.581		
5359	PR	LAW	0.508		
5372	PR	LAW	0.500		
5475	PR	WTP SW	0.410	95%	89%
5522	PR	WTP SW	0.463		

* PR = product receipt vessel
HTF = high temperature filter.

Since the initial reactions produce hydroxide while the reaction above complexes hydroxide as the aqueous $Al(OH)_4^-$, the pH of the leachate continues to change depending on the relative rates of these two competing processes and the values of the atomic ratios of Na:Al:Si, e.g. x, y, and z in the equations above. When the pH reaches 11.7, the stable silica species is SiO_3^- . Once in the pH domain of this silicate stability field the leachate reaction at 90°C becomes:



which creates free H^+ . The amount of the H^+ released by these reactions will depend on the amount of each of these phases present and the values of the atomic ratios of Na:Al:Si, e.g. x, y, and z. The more alumina present in a sample, the more aluminosilicate buffering effects the leachate pH and the radionuclide/contaminant releases. For stoichiometric nepheline ($x = y = z = 1$) one mole of H^+ is created. Therefore, the leaching of the FBSR samples from previous studies (2002-2004) and those examined in this study are highly governed by aluminosilicate buffering.

In the current study as well as in previous studies of FBSR durability (2002-2004) S is released to the PCT leachate as a strong function of the leachate final pH as controlled by the aluminosilicate buffering reactions discussed above (Fig. 3). A similar trend was observed in the current and previous studies for Si release to solution as a function of pH. However, in previous studies Re release was determined to be a strong function of solution pH but an even stronger correlation existed between the Re release during durability testing and the initial sample REDOX in this study (Fig. 4) indicating that Re^{+7} in sodalites are more stable than Re present in more reducing oxidation states, e.g. ReO_2 , ReS_2 , $ReSO_4$.

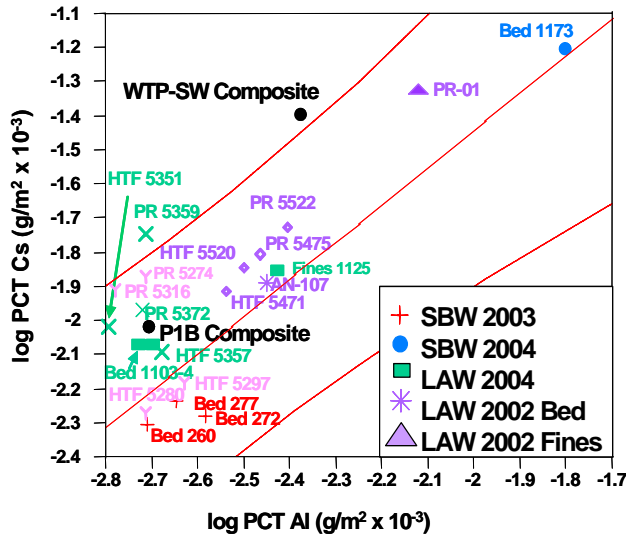


Fig. 2. Linearity of alkali and alumina released to solution. Correlation developed from historic FBSR durability data (2002-2004) shown in the legend and the current data for LAW high clay is indicated by the letter Y, for LAW lower clay is indicated by the letter X, and for WTP SW indicated by a diamond.

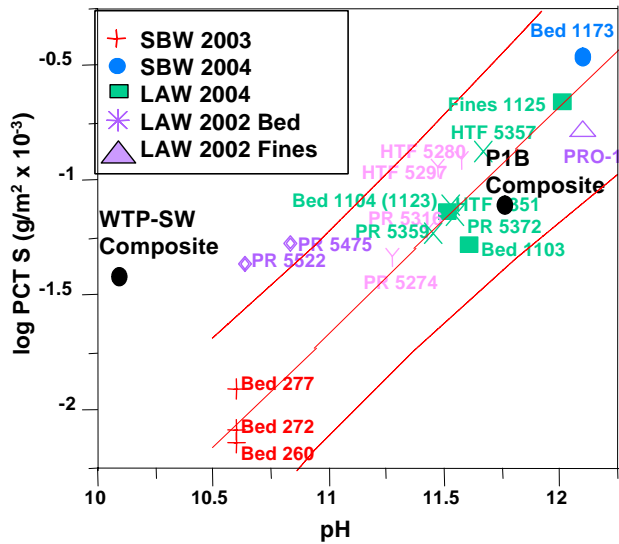


Fig. 3. Relation of sulfur release to solution as a function of pH. Correlation developed from historic FBSR durability data (2002-2004) shown in the legend and the current data for LAW high clay is indicated by the letter Y, for LAW lower clay is indicated by the letter X, and for WTP SW indicated by a diamond.

CHARACTERIZATION AND PERFORMANCE OF THE MONOLITHED MINERALIZED FBSR PRODUCTS

Monolith Formulation and Strength Testing

Seventeen different monolith matrices were made at the 2" x 2" scale with FBSR loadings between 63-85 wt%. These included 3 high alumina cement matrices (FON, S41, and S71) at 2 different waste loadings, one Ordinary Portland Cement at 2 different waste loadings, 6 geopolymers (GEO-1 through GEO-6) made from kaolin clay and sodium silicate, 1 geopolymer (GEO-7) made from fly ash and NaOH, and a Ceramicrete (CER) formulation at 2 different waste loadings. Three formulations were selected from these seventeen based on a combination of optimized durability and compressive strength. These three formulations were scaled up to 3" x 6" and 6" x 12" monoliths which were subjected to additional testing. This study summarizes the results from the seventeen 2" x 2" monolith matrices tested.

All of the monoliths except one high alumina cement (S41-2) and one geopolymer (GEO-4) met the 500 psi compressive strength criteria for wasteforms for shallow land burial. The Ordinary Portland Cement had the highest compressive strength followed by a geopolymer made with clay and sodium silicate (GEO-1) and a geopolymer made with fly ash and NaOH (GEO-7).

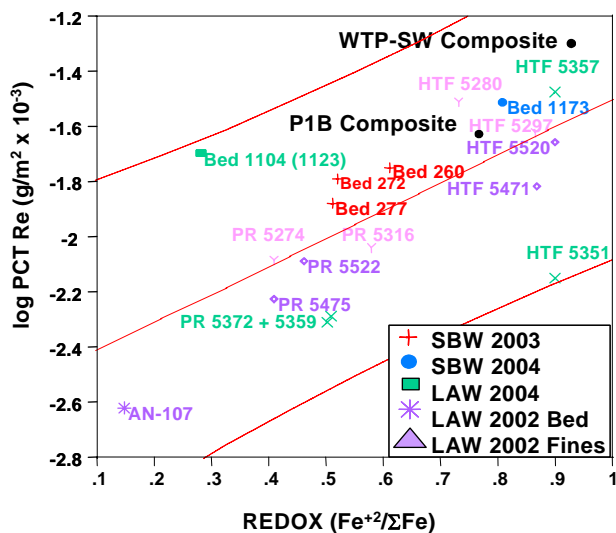


Fig. 4. Relation of rhenium release to sample REDOX state.

Durability of the FBSR Monolithic Waste Form to Glass

In order to compare the relative durability of the FBSR monoliths made with LAW waste to glass made with LAW waste, the Low-Activity Reference glass and the FBSR monoliths were tested using the same leaching protocol, ASTM C-1285. The measured BET surface area data is used to calculate the normalized release of Na⁺ for both the Low-Activity Reference glass and the FBSR monoliths as done in previous studies. [20,21,22] The FBSR granular and monolith products are ~1 order of magnitude more durable than glass if the BET surface area is used during calculation of the normalized release data. If geometric surface areas are used, which does not account for the high surface roughness of the FBSR products, the durability of the two waste forms is about equivalent. This is true for the release of Re (surrogate for Tc-99) in the FBSR waste forms versus the glass waste form as well.

CONCLUSIONS

Fluidized Bed Steam Reforming is a robust technology for the immobilization of a wide variety of radioactive wastes. Due to the moderate processing temperatures, halides, sulfates, and technetium are retained in mineral phases of the feldspathoid family (nepheline, sodalite, nosean, carnegieite, etc). The feldspathoid minerals bind the contaminants such as Tc-99 in cage (sodalite, nosean) or ring (nepheline) structures to surrounding aluminosilicate tetrahedra in the feldspathoid structures. The granular FBSR waste form that is produced is more durable than glass. Monolithing of the granular product has been shown to be feasible. Applications have been tested at the pilot scale for the high sodium, sulfate, halide, organic and nitrate wastes at the Hanford site, the Idaho National Laboratory, and the Savannah River Site.

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SRNL QA procedures adherent to NQA-1 were used throughout this study and the previous studies that were used for comparison.

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