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Durability Testing of Fluidized Bed Steam Reforming (FBSR) Products (U)

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DURABILITY TESTING OF FLUIDIZED BED STEAM REFORMING (FBSR) PRODUCTS

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ABSTRACT

Fluidized Bed Steam Reforming (FBSR) is being considered as a potential technology for the immobilization of a wide variety of radioactive wastes but especially aqueous high sodium wastes at the Hanford site, at the Idaho National Laboratory (INL), and at the Savannah River Site (SRS). The FBSR technology converts organic compounds to CO_2 and H_2O, converts nitrate/nitrite species to N_2, and produces a solid residue through reactions with superheated steam, the fluidizing media. If clay is added during processing a "mineralized" granular waste form can be produced. The mineral components of the waste form are primarily Na-Al-Si (NAS) feldspathoid minerals with cage-like and ring structures and iron bearing spinel minerals. The cage and ring structured minerals atomically bond radionuclides like Tc^{99} and Cs^{137} and anions such as SO_4, I, F, and Cl. The spinel minerals appear to stabilize Resource Conservation and Recovery Act (RCRA) hazardous species such as Cr and Ni. Durability testing of the FBSR products was performed using ASTM C1285 (Product Consistency Test) and the Environmental Protection Agency (EPA) Toxic Characteristic Leaching Procedure (TCLP). The FBSR mineral products (bed and fines) evaluated in this study were found to be two orders of magnitude more durable than the Hanford Low Activity Waste (LAW) glass requirement of 2 g/m^2 release of Na^+. The PCT responses for the FBSR samples tested were consistent with results from previous FBSR Hanford LAW product testing. Differences in the response can be explained by the minerals formed and their effects on PCT leachate chemistry.

INTRODUCTION

Fluidized Bed Steam Reforming (FBSR) is being considered as a potential technology for the immobilization of a wide variety of radioactive wastes. Studsvik built and tested a commercial Low-Level Radioactive Waste (LLRW) FBSR Processing Facility in Erwin, TN, which began commercial operations in July 1999.[1] In January 2000, high throughput operations at Erwin commenced.[2] The Erwin facility employs the THermal Organic Reduction ($THOR^{sm}$) process, developed by Studsvik, which utilizes pyrolysis[*]/steam reforming technology. $THOR^{sm}$ reliably and safely processes a wide variety of LLRWs in a unique, moderate temperature (~700°C), dual-stage, pyrolysis/reforming, fluidized bed treatment system. The reforming process has demonstrated effectiveness in pyrolizing organics and separating sulfur and halogens from inorganic waste materials. Of special relevance is the capability of the $THOR^{sm}$ technology to convert nitrates to nitrogen and sodium salts to sodium compounds that are suitable for direct disposal and/or subsequent vitrification. If clay is added during processing a "mineralized" granular waste form can be produced.

Applications of the FBSR technology to produce a granular waste form from Hanford high sodium wastes commenced in 2001 when Studsvik demonstrated the technology at Hazen Research in Golden, Colorado.[2,3] Since the FBSR technology is applicable to aqueous high

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[*] Pyrolysis chemically decomposes organic materials by heat in the absence of oxygen, e.g. $C_xH_y + \text{Heat} \rightarrow CH_4 + C$.

sodium organic containing wastes at Hanford, Idaho National Laboratory (INL), and the Savannah River Site (SRS), additional pilot scale tests of this technology were performed during 2003 and 2004 at the Science Applications International Corporation (SAIC) Science and Technology Applications Research (STAR) facility in Idaho Falls, Idaho. The pilot scale tests were performed on both Hanford and INL wastes at the STAR facility by a team of scientists from STAR, INL, and THOR^{sm} Treatment Technologies (TTT). The durability of the mineral waste forms produced at the STAR facility during three pilot scale FBSR demonstrations was evaluated by the Savannah River National Laboratory (SRNL). Measurement of the STAR waste form product durability and a comparison to previous durability testing[4,5] of the Hazen waste form product is the focus of the present study.

The wastes processed at STAR and durability tested in this study were the acidic (pH~2) INL Sodium Bearing Waste (SBW)[6,7] and the Hanford basic (pH~14) Low Activity Waste (LAW) Envelope A.[8] The SBW wastes tested were representative of wastes stored in Tank WM-180 at the Idaho Nuclear Technology and Engineering Center (INTEC). They were ~2M Na^+, and ~1.9M Al^{+3} with a $NaReO_4$ spike (5.4×10^{-4}M) to simulate $NaTcO_4$, Cs, Cl and I. The LAW Envelope A waste had total organic carbon ~3.5 g/L, ~5M Na^+, a $NaReO_4$ spike (5.2×10^{-4}M) to simulate $NaTcO_4$, Cs, Cl, F, and I.[9] The SBW and LAW waste forms tested in this study included the granular mineral material produced in the fluidized bed after steady state operations were achieved (Table I) and the fines mineral material from the filter.

The durability of the bed and fines products from the STAR LAW Envelope A demonstration produced in this study were compared to the durability of the bed (SCT-02) and fines (PR-01) products from a Hanford Envelope C waste (AN-107) demonstration performed by Studsvik, Inc., at Hazen Research in Golden, Colorado.[4] The Hanford Envelope C waste tested in 2001-2002 had total organic carbon ~3.45 g/L, ~7.3M Na^+, a $NaReO_4$ spike (3.22×10^{-5}M) to simulate $NaTcO_4$, Cs, Cl, and F but no I. It should be noted that the Studsvik pilot scale runs were much shorter than the STAR campaigns (Table I).

Table I. Pilot Scale FBSR Samples Tested in 2003-2004

Demonstration	Sample ID	Total Operating Time (TOT)	Bed Turnover (%)	Description
July 2003 SBW[6]	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[8]	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[7]	Bed 1173	100 hours	92	Final bed product
December 2001[2,3]	AN-107 (SCT-02)	4.8	Unknown	Dynamic bed product
	PR-01	23.3	Unknown	Dynamic filter fines

† unknown due to two defluidizing events that required a new starting bed

MINERALOGY

The Na-Al-Si (NAS) mineral waste forms are comprised of nepheline (hexagonal $Na_xAl_ySi_zO_4$ where x, y, and z nominally each are a value of 1),[10] and other feldspathoid mineral phases which have large cages that trap anion constituents such as Na_2SO_4 (nosean), NaI, NaCl (sodalite nominally $Na_8[Al_6Si_6O_{24}](Cl_2)$ or $Na_6Al_6Si_6O_{24}](2NaCl)$,[11] NaF, Na_2MoO_4, $NaTcO_4$, $NaReO_4$. The feldspathoid mineral nepheline and its metastable form known as carnegeite, have a silica "stuffed derivative" ring type structures. Carnegieite is a metastable form of nepheline that usually forms due to rapid quenching. Carnegieite has a similar structure to nepheline but readily transforms to nepheline upon heating at longer reaction times. A nepheline phase found in the Studsvik LAW waste form product is a unique sodium rich cubic derivative, $(Na_2O)_{0.33}NaAlSiO_4$,[f] with large twelve-fold oxygen cage like voids[12]. While carnegieite and nepheline nominally have Na:Al:Si ratios of 1:1:1, a variety of defect structures with different ratios exist.

The NAS 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 $Na_6[Al_6Si_6O_{24}]$. The square brackets in the formula are used to 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 ($Mn_4[Be_3Si_3O_{12}]S$), danalite ($Fe_4[Be_3Si_3O_{12}]S$), and genthelvite ($Zn_4[Be_3Si_3O_{12}]S$).[11] These cage-structured sodalites were minor phases in High Level Waste (HLW) supercalcine waste forms[†13] and were found to retain Cs, Sr, and Mo into the cage-like structure, e.g., Mo as $Na_6[Al_6Si_6O_{24}](NaMoO_4)_2$ [13]. In addition, sodalite structures are known to retain B[14], Ge[15], I[11,15], and Br[11,15] in the cage like structures. Indeed, waste stabilization at Argonne National Laboratory-West (ANL-W) currently uses a glass-bonded sodalite ceramic waste form (CWF) for disposal of electrorefiner wastes for sodium-bonded metallic spent nuclear fuel from the EBR II fast breeder reactor [16,17].

When an iron oxide co-reactant is added during FBSR processing an AB_2O_4 spinel mineral known as magnetite forms.[3] In magnetite the A lattice site is Fe^{2+} while the B lattice site is Fe^{3+}. However, substitutions of Mg^{2+}, Zn^{2+} Ni^{2+}, and Mn^{2+} in the A site are common and substitutions of Cr^{3+}, small amounts of Al^{3+}, and occasionally substitution of Ti^{4+} in the B site are common[18]. The conversion of Cr^{6+} to Cr^{3+} at the elevated temperature and reducing atmosphere of the FBSR process will convert any Cr^{6+} in a waste to Cr^{3+} which can then becomes stabilized in $(Mg,Fe)(Fe,Al,Cr)_2O_4$ spinel. Stabilization of Cr^{3+} has recently been investigated for the stabilization of Cr-rich industrial wastes in glass ceramics.[19] The stabilization of large concentrations of Cr^{3+} in the spinel glass ceramics demonstrated that Cr Toxic Characteristic Leaching Procedure (TCLP) responses were orders of magnitude below the EPA regulatory Universal Treatment Standard (UTS)[20] limits.

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[f] PDF#39-0101

[†] Supercalcines were the high temperature silicate based "natural mineral" assemblages proposed for HLW waste stabilization in the United States (1973-1985).

EXPERIMENTAL

Chemical Composition

Elemental and anion compositions of the steam reforming materials were measured. The carbon was removed by heating the samples to 525°C overnight. This temperature was chosen because it is high enough to oxidize (remove) the carbon in the presence of air, but not high enough to change the composition or the phase assemblages. This is the temperature specified in a United States Geological Survey (USGS) procedure[21] for carbon removal in preparation for the analysis of coal combustion by-products. Samples before and after this heating were examined by X-ray Diffraction (XRD) to verify that the phase assemblages had not changed. The compositions are reported on a carbon free basis.

For elements, solid samples were digested with a lithium tetraborate fusion at 1000°C followed by a hydrochloric acid uptake[22,23]. The resulting solutions were analyzed by Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) 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 (ICP-MS) for Cs, La, Re, and I. Anion content was determined from a sodium peroxide/sodium hydroxide fusion at 600°C followed by a water uptake[24]. The resulting solutions were analyzed by Ion Chromatography (IC) for NO_3^-, F^-, and Cl^-.

The REDOX (iron(II) to total iron ratio) was determined[25] on samples where the carbon was removed by hand. Heating samples to remove the carbon likely would have oxidized the sample and changed the ratio.

Waste Form Surface Area (SA) Measurements

The Product Consistency Test (PCT) results can be expressed as a normalized concentration (NC_i) which have units of $g_{\text{waste form}}/L_{\text{leachant}}$, or as a normalized release (NL_i) in $g_{\text{waste form}}/m^2$, or as a normalized rate (NR_i) in $g_{\text{waste form}}/\ m^2\cdot$day where “i” is the chemical element of interest. Expression of the PCT test response as NL_i, the standard units in which the LAW glass specification is given, necessitates the use of the surface area (SA) of the sample releasing species “i” and the volume (V) of the leachant being used which is expressed as the SA/V ratio. An examples of the calculation is given below:

$$NL_i = \frac{c_i(sample)}{f_i \cdot (SA/V)} \tag{1}$$

where NL_i is the normalized release ($g_{\text{waste form}}/m^2$)
$c_i\ (sample)$ is the concentration of element i in the leachate solution (g_i/L)
f_i is the fraction of element i in the unleached waste form ($g_i/g_{\text{waste form}}$)
SA/V is the surface area of the final waste form divided by the leachate volume (m^2/L)

In order to calculate NL_i, the surface area of the material being tested must either be calculated (ASTM C 1285, Appendix XI[26]) or measured. In this study, the waste form SA was measured by the Brunauer, Emmett, and Teller[27] (BET) method recommended by McGrail[5] due to the high surface roughness and high internal porosity of the FBSR product compared to vitrified waste form products. Additional information about the relative surface area roughness factors of FBSR and vitrified waste form see Reference 28.

Product Consistency Test (ASTM C1285-02)

The chemical durability of the FBSR pilot scale products was determined using ASTM procedure C 1285-02[26]. Prior to sizing and washing, carbon was removed from the material. The bed product 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 C1285-02 procedure. The filter fines material was neither washed nor sieved, as all this material was smaller than 200 mesh or 74 µm and exhibited a Gaussian distribution.

For all samples, ASTM Type I water[29] 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.

Toxicity Characteristic Leaching Procedure (TCLP)

The Hanford LAW and INL SBW wastes are listed wastes under the EPA Resource Conservation and Recovery Act (RCRA). When treated, the waste form must retain the hazardous components at the UTS limits[20]. Two samples made with LAW and INL SBW simulants representing the final steady state FBSR bed and filter fines from the 2004 LAW campaign (Bed #1104 and Filter Fines #1125) and the SBW campaign (Bed 1173) were evaluated for retention of the hazardous metals by the EPA Toxicity Characteristic Leaching Procedure, Method 1311 (TCLP)[30]. Greater than 100 g samples of as-received material (i.e., carbon was not removed from these samples) were then submitted to Acura Analytical Laboratory of Norcross, GA, an EPA-certified laboratory.

RESULTS AND DISCUSION

Chemical Composition

The measured cation and anion compositions of the STAR FBSR bed products and fines are given in Table II. The elemental results are given on a carbon-free basis. The results in Table II are those used to normalize the PCT releases (the f_i term) in Equation 1 for the amount of constituent "i" in the sample.

The elemental analyses in Table II can be converted to an oxide and/or a mineral basis for mass balance purposes[28] since the FBSR waste plus co-reactants are all converted to oxides, halides (chlorides, fluorides, iodides) and sulfate minerals during processing. During conversion the measured REDOX ratios given in Table II are used to speciate elemental Fe as FeO and Fe_2O_3. By use of an electromotive force (EMF) series developed for SRNL by Schreiber[31] the amount of Cr present as Cr^{n+} (n is chromium in a mixed oxidation state of +3, +4, +5) vs. Cr^{6+} can also be determined. The measured REDOX given in Table II when coupled with the EMF series developed by Schreiber[31] indicates that 86% of the Cr in the STAR SBW 2003 FBSR product was Cr^{n+} , 78% of the Cr in the STAR LAW 2004 FBSR product was Cr^{n+}, and ~91% of the Cr in the STAR 2004 SBW FBSR product was Cr^{n+}. For comparison about 62% of the Cr in the Hazen 2002 FBSR product was Cr^{n+} based on previously measured REDOX ratio.[4]

The mineral mass balances show that the 2003 and 2004 SBW FBSR products had Al_2O_3 from the Al_2O_3 starting bed. This prediction is consistent with the bed turnovers given in Table I and with the identification of excess Al_2O_3 in samples Bed 260 and Bed 1173 by X-ray Diffraction (Table III). For the 2003 SBW samples (Beds 260, 272, and 277), a silicon deficient sodium aluminosilicate was identified by XRD ($Na_{1.45}Al_{1.45}Si_{0.55}O_4$). This accounts for the absence, by XRD analysis, of Al_2O_3 in Bed 272 and Bed 277 (Table III).

Surface Area to Volume Ratio

Table IV gives the results of surface area to volume ratios calculated from BET surface area measurements. The results given in Table IV are on a carbon-free basis. This was done because (1) carbon content has an impact on BET surface area and (2) carbon is not part of the actual mineral product, e.g. it is inert in terms of the PCT response, (3) carbon will be not be part of the waste form product in a full scale production facility because it will be removed by a second oxidizing reformer (the pilot scale facility was not equipped with tandem reformers and this had to be simulated). Thus, a surface area to volume ratio that included carbon may underestimate PCT release and not be representative of the full scale process. Therefore, SA/V results on carbon-free samples were used in calculating PCT release rates in this study.

Because glass has virtually no significant void surface area, i.e. no microporosity, and FBSR product has significant voids and surface area, McGrail et al.[5] determined that the measured BET surface area should be used during the calculation of release rates for the FBSR product and the calculated geometric surface area should be used during the calculation of release rates for glass. In this study the BET surface area is used for the FBSR products and compared to glass dissolution using the BET surface area measured for glass (Table IV).

Product Consistency Test Results

Three sets of samples from the INL FBSR campaigns were evaluated by the Product Consistency Test. The samples were (1) simulated SBW campaign products from July 2003, (2) LAW campaign products from August 2004, and (3) SBW campaign products from October 2004. Leachate concentrations were calculated from Equation 1 as normalized releases using the measured SA_{BET} (m^2/g). These results are presented in Table V.

Leachate Aluminosilicate Buffering

The PCT final leachate pH values from Table V and the surface areas from Table IV indicate that the final PCT solution pH is an inverse function of the sample SA_{BET} (m^2/g) (Figure 1), e.g. the pH is lower for samples with a larger SA_{BET} (m^2/g). In addition, the pH appears to be dependent on the mineral phases present in the samples (Table III). For example, the STAR 2004 LAW fines have a measured SA_{BET} (m^2/g) that is about the same as the SA_{BET} (m^2/g) measured for the 2004 LAW bed material, e.g. the sample microporosity is similar, but the solution pH values of the bed and the fines are very different. This indicates that the mineralogy, especially the Al:Si ratio of the mineral species formed may play a role in the FBSR mineral dissolution mechanism.

The inverse correlation of pH and SA 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 III) found in the STAR SBW 2003 and 2004 FBSR products and in the Hazen AN-107 campaigns the appropriate ion exchange reaction at the start of a PCT test when the ASTM Type I water pH is ~5.5 would be:

$$Na_xAl_ySi_zO_4 + (0.5x + 1.5y + z)H_2O \xrightarrow{90^\circ C} xNa^+ + zH_2SiO_3 + yAl(OH)_3 + x(OH)^- \qquad (2)$$

Table II. Elemental and Anion Content of Steam Reformer Bed and Fines

Species (Wt%)	**2003 SBW FBSR Products**			**2004 LAW FBSR Products**			**2004 SBW FBSR Product**	**2002 LAW FBSR Products**		
	Bed 260	**Bed 272**	**Bed 277**	**Bed 1103**	**Bed 1104**	**Fines 1125**	**Bed 1173**	**Bed AN-107[4]**	**Bed AN-107[4]**	**Fines PR-01**
Al	22.4	19.5	20.1	17.40	17.15	18.35	20.3	16.8	20.6	17.1
Ca	0.452	0.553	0.549	1.27	1.65	1.27	2.71	0.524	0.406	3.17
Cd	NM	NM	NM	<0.001	<0.001	<0.001	<0.01	NM	NM	NM
Cr	NM	NM	NM	0.09	0.08	0.07	0.068	0.049	0.019	0.030
Cs	NM	NM	NM	1.42×10^{-4}	1.13×10^{-4}	1.72×10^{-3}	3.07×10^{-2}	2.7×10^{-3}	4.4×10^{-4}	1.30×10^{-3}
Cu	NM	NM	NM	0.02	0.01	0.01	0.011	NM	NM	0.020
Fe	1.70	1.05	1.01	0.18	0.19	0.17	0.707	4.49	5.14	1.07
I	NM	NM	NM	$<2 \times 10^{-5}$	$<2 \times 10^{-5}$	$<2 \times 10^{-5}$	NM	NM	NM	NM
K	2.16	2.99	3.05	0.27	0.25	0.26	3.29	0.579	0.564	1.24
La	NM	NM	NM	3.00×10^{-3}	2.38×10^{-3}	3.60×10^{-3}	5.71×10^{-3}	NM	NM	8.28×10^{-3}
Mg	0.108	0.129	0.125	0.03	0.04	0.04	0.242	NM	NM	0.260
Mn	NM	NM	NM	0.03	0.03	0.03	0.275	NM	NM	0.170
Na	11.2	12.7	12.4	15.26	14.96	16.50	12.3	14.7	12.5	17.3
Ni	NM	NM	NM	0.01	0.01	0.01	0.040	0.064	0.028	0.050
P	0.733	0.997	0.914	0.21	0.20	0.20	0.375	0.095	0.108	.220
Pb	NM	NM	NM	<0.1	<0.1	<0.01	<0.01	0.023	0.019	<0.1
Re	1.36×10^{-2}	2.02×10^{-2}	2.34×10^{-2}	5.63×10^{-3}	4.10×10^{-3}	3.95×10^{-3}	4.75×10^{-3}	4.0×10^{-4}	5.1×10^{-4}	1.55×10^{-3}
S	0.135	0.212	0.149	0.29	0.25	0.38	0.041	0.12	0.293	0.26
Si	15.2	17.1	17.1	16.70	16.65	20.10	17.6	16.3	14.1	16.6
Ti	0.735	0.621	0.569	0.74	0.71	0.76	0.713	NM	NM	0.710
F^-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	NM	NM	NM
Cl^-	<0.1	<0.1	<0.1	0.18	0.13	0.10	0.092	NM	NM	<0.1
NO_3^-	0.258	0.325	0.309	<0.01	<0.01	<0.01	<0.1	NM	0.32	0.09
$Fe^{2+}/\Sigma Fe$	0.61	0.52	0.51	NM	0.28	NM	0.81	0.15	0.15	NM

NM = Not measured.

Table III. Mineral Phases Identified in the Pilot Scale Products Tested

	$NaAlSiO_4$ Carnegieite (PDF #11-0220)	$(K_{0.25}Na_{0.75})AlSiO_4$ K-substituted Nepheline (PDF#74-0387)	$Na_{0.89}Al_{0.9}Si_{1.1}O_4$ Si rich Nepheline (PDF#79-0993)	$NaAlSiO_4$ Nepheline (PDF#35-0424)	$Na_{1.53}Al_{0.92}Si_{0.92}O_4$ Na-rich Nepheline (PDF # 39-0101)	$Na_{1.45}Al_{1.45}Si_{0.55}O_4$ Si deficient Carnegieite (PDF#49-0002)	$Na_6[Al_6Si_6O_{24}](Na_2SO_4)$ Nosean (PDF#73-1734, 17-0535)	$Na_6[Al_6Si_6O_{24}](2NaCl)$ Sodalite (PDF #82-0517) Un-named Sodalite (PDF#42-0215)	Al_2O_3 (from Starting Bed) Corundum (PDF #74-1081, 42-1468, 10-0173)	TiO_2 (clay impurity) Anatase (PDF #21-1272)	SiO_2 (clay impurity) Quartz (PDF#85-1053)	$NaAl_{11}O_{17}$ Beta-Alumina (PDF# 76-0923)	$Na_{5.27}Ca_3(SiO6O18)$ Combeite (PDF# 78-1650)	Fe_3O_4 (PDF#79-0416, #19-0629) Fe_2O_3 (PDF#33-0664)
July 2003 SBW CAMPAIGNS														
Bed 260		X				Y		TR	Y	TR				
Bed 272		X				Y		TR		TR				
Bed 277		X				Y		TR		TR				
August 2004 LAW CAMPAIGNS														
Bed 1103	X		X				Y			TR				
Bed 1104	X		X				Y			TR				
Fines 1125	X		TR							TR				
October 2004 SBW CAMPAIGNS														
Bed 1173		X						TR	Y		TR	TR	Y	
AN-107 2002 LAW CAMPAIGNS														
SCT02-098-FM				X	Y		Y		TR					Y
Fines PR-01	X			X			Y		Y					Y

X = Major constituent; Y = Minor constituent, TR = trace constituent

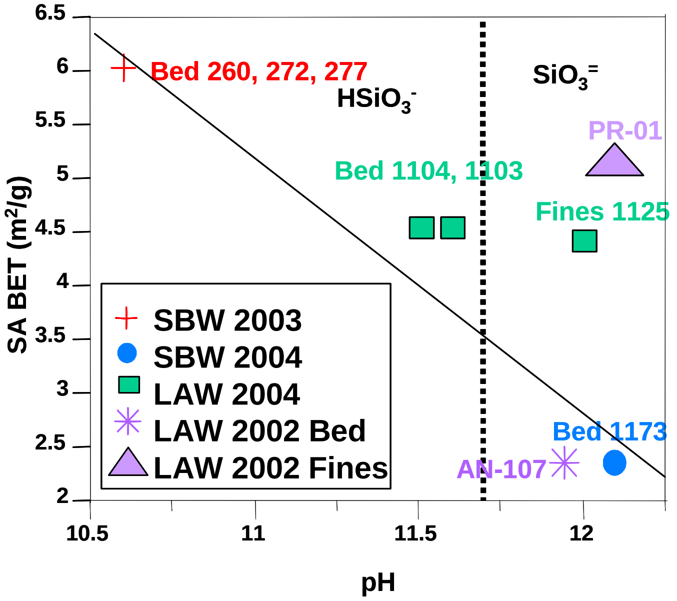

Figure 1. Relationship between surface area (SA$_{BET}$) and PCT final leachate pH.

Table IV. Density, BET Surface Area (SA$_{BET}$) and Calculated Surface Area to Volume (SA$_{BET}$/V) Ratio of FBSR Products and Glass

Sample	Particle Density by Pycnometry (g/m^3)	Measured SA$_{BET}$ (m^2/g)	Calculated SA$_{BET}$/V (m^2/L)
July 2003 SBW CAMPAIGNS			
Bed 260	3.30 x 10^{-6}	6.03 [†]	603
Bed 272	3.13 x 10^{-6}	6.03 [†]	603
Bed 277	2.73 x 10^{-6}	6.03 [†]	603
August 2004 LAW CAMPAIGNS			
Bed 1103 [‡]	2.53 x 10^{-6}	4.53	453
Bed 1104	2.53 x 10^{-6}	4.53	453
Fines 1125	2.46 x 10^{-6}	4.41	441
October 2004 SBW CAMPAIGNS			
Bed 1173	2.76 x 10^{-6}	2.36	236
Hazen LAW CAMPAIGNS			
Bed SCT-02	2.66 x 10^{-6}	2.37	237
PR-01 Fines	2.50 x 10^{-6}	5.15	515
Low Activity Reference Material (LRM)			
LRM Glass	NM	0.04	4

NM – Not Measured; [‡] Density and SA$_{BET}$ not measured on sample Bed 1103, assumed to be the same as Bed 1104.

Table V. Measured PCT pH Values and Calculated Normalized Elemental Releases

	pH	NL_{Na} (g/m^2)	NL_{Cs} (g/m^2)	NL_{Re} (g/m^2)	NL_{Si} (g/m^2)	NL_{S} (g/m^2)	NL_{Al} (g/m^2)
July 2003 SBW CAMPAIGNS							
Bed 260	10.6	8.39×10^{-3}	4.97×10^{-3}	17.8×10^{-3}	0.283×10^{-3}	7.32×10^{-3}	1.95×10^{-3}
Bed 272	10.6	10.2×10^{-3}	5.24×10^{-3}	16.2×10^{-3}	0.232×10^{-3}	8.45×10^{-3}	2.60×10^{-3}
Bed 277	10.6	9.27×10^{-3}	5.84×10^{-3}	13.2×10^{-3}	0.240×10^{-3}	12.5×10^{-3}	2.25×10^{-3}
August 2004 LAW CAMPAIGNS							
Bed 1103	11.6	7.62×10^{-3}	8.50×10^{-3}	21.7×10^{-3}	0.817×10^{-3}	53.4×10^{-3}	2.00×10^{-3}
Bed 1104	11.5	8.63×10^{-3}	8.48×10^{-3}	19.9×10^{-3}	0.773×10^{-3}	72.9×10^{-3}	1.86×10^{-3}
Fines 1125	12.0	16.4×10^{-3}	14.0×10^{-3}	Not Meas	0.839×10^{-3}	219×10^{-3}	3.70×10^{-3}
October 2004 SBW CAMPAIGNS							
Bed 1173	12.1	41.8×10^{-3}	63.2×10^{-3}	30.8×10^{-3}	1.91×10^{-3}	353×10^{-3}	15.9×10^{-3}
Hazen 2002 LAW (AN-107) CAMPAIGNS							
Bed AN-107*	11.95	10.3×10^{-3}	1.3×10^{-3}	2.4×10^{-3}	2.9×10^{-3}	Not Meas	3.57×10^{-3}
Fines PR-01	12.1	28.7×10^{-3}	47.5×10^{-3}	39.1×10^{-3}	0.61×10^{-3}	168×10^{-3}	7.61×10^{-3}

* Calculated from the data in Reference 4 and the BET surface area measured by McGrail[5] on the same crushed and washed bed product.

The ion-exchange reaction shown in Equation 2 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 carnegeites liberates 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 the beta alumina ($NaAl_{11}O_{17}$; Table III) formed in the STAR 2004 SBW (most likely as an incomplete reaction product since unreacted SiO_2 was also found in this sample). The beta alumina liberates hydroxide by ion exchange in the presence of the SiO_2 via a similar reaction to that in Equation 2:

$$NaAl_{11}O_{17} + SiO_2 + 18H_2O \xrightarrow{90^\circ C} Na^+ + H_2SiO_3 + 11Al(OH)_3 + OH^- \qquad (3)$$

which can be generalized like the reaction in Equation 2 to the following:

$$Na_xAl_yO_{17} + zSiO_2 + (0.5x + 1.5y + z)H_2O \xrightarrow{90^\circ C} xNa^+ + zH_2SiO_3 + yAl(OH)_3 + x(OH)^- \qquad (4)$$

As the PCT 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 PCT testing, Equation 5 becomes dominant for the sodium aluminosilicates (including the beta alumina plus SiO_2). Per Equation 5 different nepheline/carnegieite Na:Al:Si ratios complex different amounts of hydroxide as $Al(OH)_4^-$:

$$Na_xAl_ySi_zO_4 + (0.5x + 1.5y)H_2O + (y + z - x)OH^- \xrightarrow{90^\circ C} xNa^+ + zHSiO_3^- + yAl(OH)_4^- \qquad (5)$$

Therefore, the leachate pH is particularly dependent on the amount of alumina 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 can be confirmed graphically (Figure 2) by showing the strong dependence of the PCT normalized releases for the alkalis (Na and Cs) versus the normalized releases for alumina from Table V.

Since reactions 2 and 4 continue to produce hydroxide while reaction 5 continues to complex hydroxide as the aqueous $Al(OH)_4^-$ species, the pH 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. When the pH reaches 11.7, the stable silica species is $SiO_3^=$. At this point reaction 6 becomes dominant at 90°C:

$$Na_xAl_ySi_zO_4 + (0.5x + 1.5y)H_2O + (y + z - x)OH^- \xrightarrow{90^\circ C} xNa^+ + zSiO_3^- + yAl(OH)_4^- + zH^+ \quad (6)$$

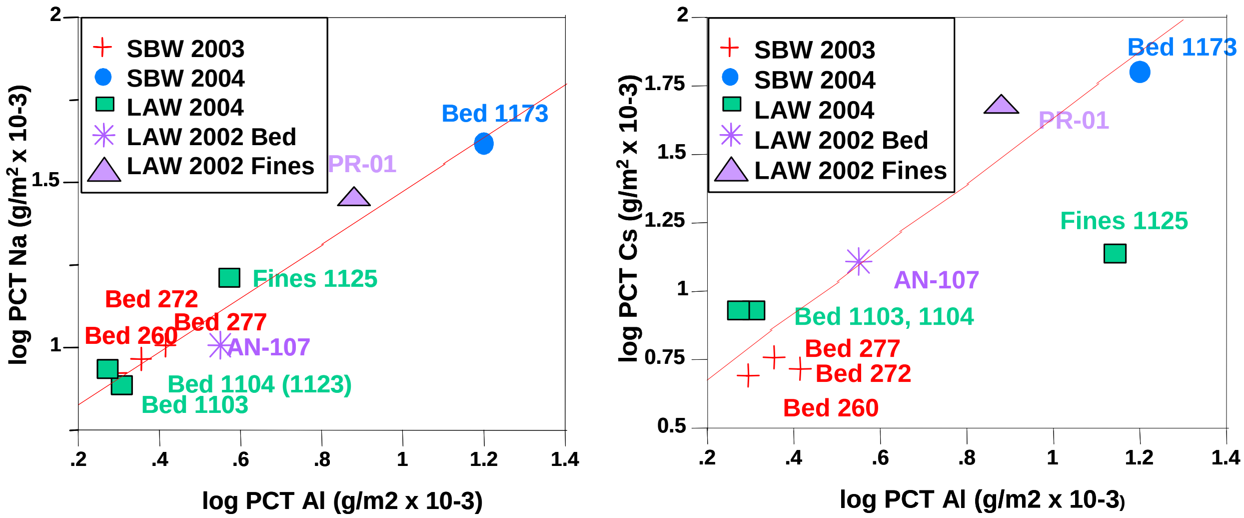

Figure 2. Linearity of alkali and alumina released to solution. Alkali dissolution generates free OH^- in solution while alumina in solution complexes OH^- from solution.

Equation 6 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. In particular, Equation 6 when applied to the sample with beta alumina and unreacted SiO_2 is very dependent on the relative amounts of each of these phases present. The H^+ released serves to further buffer the solution pH in addition to the pH consumed by the aqueous complex $Al(OH)_4^-$. Thus the more alumina present in a sample, the more aluminosilicate buffering effects the leachate pH. For stoichiometric nepheline ($x=y=z=1$) one mole of H^+ is created. For some of the defect nepheline/carnegieite phases anywhere from 0.55 to 1.1 moles of free H^+ can be generated to further buffer the leachate pH.

Therefore, the leaching of the STAR 2003 SBW samples are highly governed by aluminosilicate buffering and H^+ buffering since more Al rich mineral phases were found in this FBSR product relative to all the others (Table III). The STAR 2003 SBW samples have a PCT pH of ~10.6 (Table V and Figure 1). The 2003 SBW bed product was highest in Al_2O_3 content of any of the campaigns tested at the STAR facility even after the bed materials were corrected for the presence of unreacted Al_2O_3 bed material (see Table II).

The leaching of the STAR 2004 LAW bed samples (1103 and 1104) are also governed by aluminosilicate buffering as they contain both stoichiometric carnegieite and an Si-rich nepheline (Table III). Note that the STAR 2004 LAW fines leachate pH is ~12 (FBSR product 1125). This pH is higher (Table V and Figure 1) than the bed LAW 1103 and 1104 bed products because they are less well buffered. This is confirmed by the fact that the fines contain less (only a ”trace”) of the Si-rich nepheline instead of it being a major phase as it is in the bed samples (Table III). For comparison the leaching of the Hazen 2002 AN-107 sample is governed solely by the aluminosilicate buffering of stoichiometric and Na-rich nepheline (Table III). The Hazen 2002 fines (PR-01) are governed by the stoichiometric nepheline and carnegieite aluminosilicate reactions (Equations 2, 5 and 6).

The leaching of the STAR 2004 SBW bed sample (1173) is affected by the unreacted beta alumina, unreacted SiO_2, and SiO_2 in the form of a different sodium calcium silicate (combeite; see Table III). The presence of unreacted silicates and aluminates indicates that complete reaction was not achieved in the bed for some reason. This bed material had the highest pH of all the samples tested indicating that very little leachate buffering was occurring.

Durability of Species as a Function of Leachate pH

Figure 3 shows that the Re, S, and Si released to the PCT leachate are a strong function of the leachate final pH as controlled by the aluminosilicate buffering reactions discussed above. The Re-pH correlation has an R^2=0.83, the S-pH correlation has an R^2=0.96, and the Si-pH correlation has an R^2=0.94. The poorer correlation of Re with pH is likely due to the difficulties in measuring this element which was only present at concentrations of 0.0044 to 0.028 wt% ReO_2 in the final FBSR bed product (Table II) and at lower concentrations in the leachate. Because the Re, S, and Si release are each strongly correlated to pH, the releases are highly correlated to each other.

Comparison of FBSR Product to Glass

In order to compare the relative durability of the Low-Activity Reference glass (LRM) to the steam reformer product a bar graph was constructed showing the logarithm of the PCT release in g/m^2 of Na^+ for the STAR (2003-2004) and Hazen (2002) FBSR bed and fines products and the published values for Na^+ release from LRM glass (Figure 4). The data for the LRM glass is compared two different ways. According to McGrail et al.[5], the geometric surface area is intended to be used in tests where glass has been ground and sieved to a specific mesh size. If the geometric surface area is used for the LRM glass, then the FBSR bed products are ~1.5 orders of magnitude more durable than glass and the fines are ~1 order of magnitude more durable than glass. If the glass BET surface area is used then the FBSR products (bed and fines) are still 1-1.5 orders of magnitude more durable than glass. The 2 g/m^2 release of Na^+ for LAW glass required by the Hanford PCT specification is shown in Figure 4 as a reference line (bolded at the top of the graph). Since the 2 g/m^2 release of Na^+ requirement is based on the geometric surface area of the glass it was normalized to the measured glass BET surface area. The Na^+ release limit is set for glass because the Na^+ release is equal to the Tc^{99} release due to the congruent leaching of these species from a glass. For FBSR products, which undergo incongruent leaching, e.g. the Tc^{99} or Re surrogate and Na^{+} are not released at equivalent rates, the specification should apply to the Re release which is lower than the Na^{+} release. The FBSR bed products are ~2 orders of magnitude lower than the Hanford glass release specification.

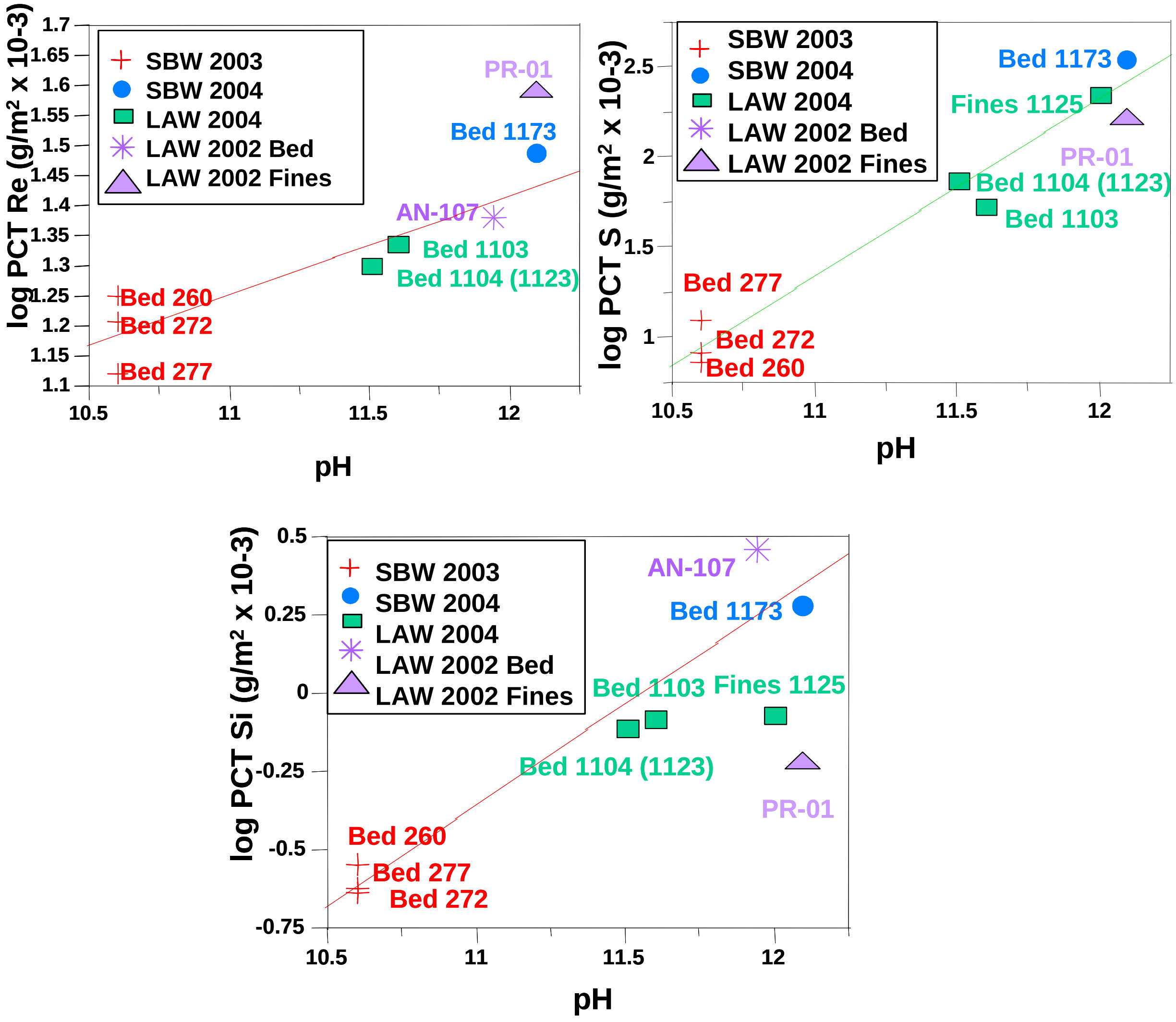

Figure 3. Leachate Re, S, and Si concentrations as a function of the pH of the final leachate.

Toxicity Characteristic Leaching Procedure (TCLP)

TCLP results for LAW Bed 1104 and LAW Fines 1125 from the STAR LAW campaigns and SBW Bed 1173 from the STAR SBW campaigns are presented in Table VI. Note that the samples submitted for TCLP were not sized or sieved and contained the coal from the original bed product. The samples met the criteria for the EPA RCRA Universal Treatment Standards for all of the constituents in the simulants except for Cr. Of the three samples submitted, SBW Bed 1173 had the lowest Cr release but still did not meet the UTS standards.

The TCLP response for Cr from the 2004 testing is inconsistent with the TCLP performance of the Hazen AN-107 FBSR campaign products (values shown in Table VI for comparison). When the mineral phases present in the 2004 testing are compared to the mineral phases present in the Hazen 2002 testing (Table III) it can be shown that the 2004 samples did not form the Cr-host mineral magnetite. Without this host phase to stabilize the Cr^{3+} in an insoluble form it is likely oxidized during the TCLP test even though the REDOX analyses in Table II (coupled with the EMF series developed by Schreiber[31]) indicates that 78% of the Cr in the STAR LAW 2004 FBSR product was Cr^{n+} (where n = +3, +4 or +5), and ~91% of the Cr in the STAR 2004 SBW FBSR product was Cr^{n+}.

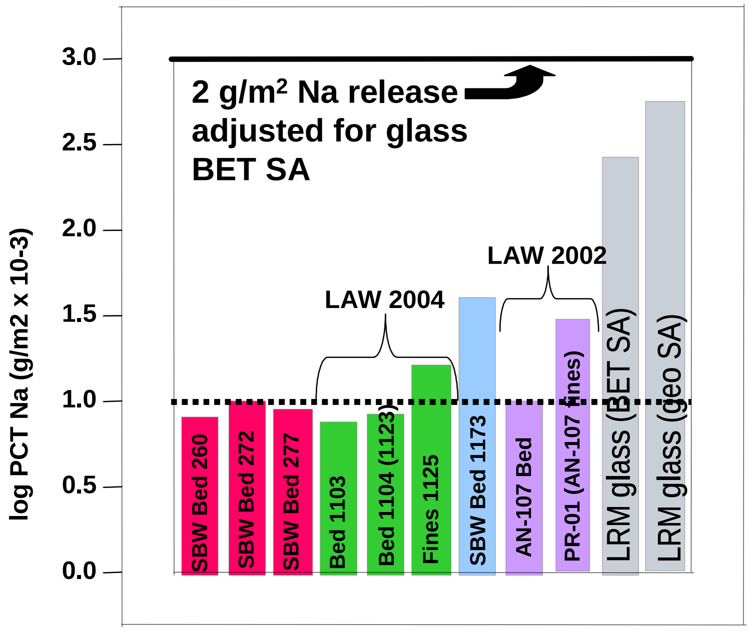

Figure 4. Comparison of FBSR bed products and fines durability for Na^+ compared to the Low-Activity Reference Material (ARM glass) standard.

Table VI. Toxic Characteristic Leaching Procedure (TCLP) Results

	August 2004 LAW		October 2004 SBW	2002 Hazen LAW	Universal Treatment Standard ‡ (mg/L)
Element	Bed 1104 (mg/L)	Fines 1125 (mg/L)	Bed 1173 (mg/L)	AN-107 (mg/L)	
As	NM	NM	NM	NM	5
Ba	0.069 [a]	0.17 [a]	<0.034	NM	21
Cd	NM	NM	NM	NM	0.11
Cr	9.2	8.4	0.82 [a]	0.015–0.06	0.60
Pb	0.046 [a]	<0.0310	<0.031	0.002–0.067	0.75
Se	NM	NM	NM	NM	5.7
Ag	NM	NM	NM	NM	0.14
Hg	NM	NM	<0.001	NM	0.025

‡ 40 CFR 268.48 –"Universal Treatment Standards"; [a] Result is above method detection limit, but below reporting limit; NM – These elements were not measured because they were not in the simulated waste.

CONCLUSIONS

- The FBSR products (bed and fines) are ~1.5 orders of magnitude more durable than glass, well below the 2 g/m^2 release of Na$^+$ for glass required by the Hanford LAW glass specification
  - two orders of magnitude is consistent with the findings of McGrail[5] during Single Pass Flow Through (SPFT) testing and Pressurized Unsaturated Flow (PUF) testing[32]
- The PCT response for the SBW and LAW samples can be explained by the mineralogy and an aluminosilicate buffering mechanism that controls the leachate pH
  - Cs and Na release are co-linear with Al release
  - S, Re, and Si release are strong linear functions of leachate pH
- Residual carbon in the FBSR samples should be removed prior to leach testing as it has a significant effect on the measured surface area and the bulk density of the FBSR products
- Resource Conservation and Recovery Act (RCRA) Toxic Characteristic Leaching Procedure (TCLP) results for the 2003-2004 pilot scale tests indicated that the bed products and fines failed TCLP for chromium release at the Universal Treatment Standard (UTS) limits but passed for the remaining constituents of concern
  - testing in 2002 had demonstrated that the LAW FBSR products did pass the RCRA TCLP at the UTS limits for chromium release
  - the samples that passed TCLP testing for Cr at the UTS limits contained the iron mineral host phase magnetite spinel which sequesters chromium as Cr^{+3} into its insoluble structure
  - formation of the spinel host phase for Cr is controlled by adding an iron co-reactant to the FBSR during processing

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