

# ENGINEERING STUDY OF THE HANFORD LOW ACTIVITY WASTE (LAW) STEAM REFORMING PROCESS (U)

JULY 12, 2002

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***Completeness of Testing***

***This report describes the results of work and testing specified by Roger Roosa. The work and any associated testing followed established quality assurance requirements and was conducted as authorized. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Also reported are any unusual or anomalous occurrences that are different from starting hypotheses. The test results and this report have been reviewed and verified.***

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## LIST OF ACRONYMS

ANL-W	Argonne National Laboratory-West
CWF	Ceramic Waste Form
EA	Environmental Assessment
EPA	Environmental Protection Agency
FBSR	Fluidized Bed Steam Reformer
HIP	Hot Isostatic Pressing
HLW	High Level Waste
LAW	Low Activity Waste
LLW	Low Level Waste
IC	Ion Chromotography
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
MACT	Maximum Achievable Control Technology
NAS	Sodium Aluminosilicate
PCT	Product Consistency Test (ASTM C-1285)
REDOX	REDuction/OXidation
SEM	Scanning Electron Microscopy
SRTC	Savannah River Technology Center
SYNROC	SYNthetic ROCK
TCLP	Toxic Characteristic Leaching Procedure
THOR	THERmal Organic Reduction
UTS	Universal Treatment Standards
VOC	Volatile Organic Compound
VSL	Vitreous State Laboratory
XRD	X-Ray Diffraction



## ABSTRACT

The fluidized bed steam reforming (FBSR) technology should be further evaluated as a final waste form for Hanford LAW wastes. This technology produces stable mineralized phases which are more durable than a high sodium vitrified waste form. The mineral phases are the same as many of the phases produced in higher temperature waste forms such as supercalcline, glass-bonded ceramics, and SYNthetic ROCK (SYNROC) yet the phases are produced at moderate steam reformer operating temperatures. The mineral phases bind the radionuclide and hazardous species in cage structured mineral phases. The radionuclides and hazardous species are ionically bonded to silica and alumina tetrahedra in the structure as well as to Na ions.

Specific attributes of the fluidized bed steam reforming (FBSR) process and the final waste form produced are summarized below:

- robust technology capable of accommodating wide ranges of feeds and additives including high concentrations of sulfate
- ability to retain sulfate will lead to increased waste loadings and accelerated stabilization of Hanford's LAW vs. LAW vitrification
- continuous throughput technology (not a batch operation) allowing for accelerated solidification of Hanford's LAW wastes
- mineral waste species exhibit a superior durability to LAW glass in both ASTM C1285 and EPA TCLP testing
- durability is incongruent and the radionuclides (Cs and Re as simulants for Cs<sup>137</sup> and Tc<sup>99</sup>) are released at a rate lower than that of Na (Na release is <2 g/m<sup>2</sup>)
- medium temperature process low enough not to vaporize radionuclides but high enough to destroy volatile organic compounds (VOC's) in the presence of catalysts
- process generates minimal acid off-gases as the anions (SO<sub>4</sub><sup>=</sup>, F<sup>-</sup> and Cl<sup>-</sup>) remain in the waste form
- waste form mineral phases are cage like structures that trap radionuclides and anions
- waste form mineral phases are known to have survived millions of years in natural surface or near surface environments
- waste form mineral phases alter to zeolites that have the same cage-like structures and will likely still retain the radionuclides and anions

## 1.0 SUMMARY OF TESTING

### 1.1 OBJECTIVES

The goals of this study are the following:

- description of the feasibility and flexibility of the fluidized bed steam reformer process (FBSR)
- description of the mineral phases that comprise the FBSR ceramic waste form (CWF) in terms of
  - atomic bonding of radionuclides and anions such as  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{F}^-$  in cage-structured aluminosilicate mineral phases
  - similarities to mineral phases in HLW high temperature ceramic waste forms
  - similarities to mineral phases in LAW hydroceramic waste forms
  - occurrence of mineral phases in nature and long term geologic stability
- comparison of the attributes of the FBSR ceramic waste form over high temperature ceramic and hydroceramic waste forms
- comparison of the attributes of the FBSR ceramic waste form over vitrified waste forms for Low Activity Waste (LAW)
- demonstrate the durability of the FBSR waste form using ASTM C1285-97 (also known as the Product Consistency Test-A)
  - incongruent leaching vs. congruent leaching
- durability testing of FBSR waste form using the Environmental Protection Agency (EPA) Toxic Characteristic Leaching Procedure (TCLP)

### 1.2 CONDUCT OF TESTING

Scoping FBSR tests were performed at Hazen Research, Inc. in Golden, Colorado between December 6, 2001 and December 20, 2001 using the Studsvik THOR<sup>sm</sup> process. The FBSR waste forms were made with 150 gallons of Hanford AN-107 LAW simulant (a portion of the 3200 gallon batch shown in Table I) obtained from the Vitreous State Laboratory (VSL). The radionuclide  $\text{Tc}^{99}$  was simulated with Re while  $\text{Cs}^{137}$  was simulated with stable cesium ( $\text{Cs}^{133}$ ). The results of all of the final waste form testing performed at Hazen Research, Inc. under reducing FBSR conditions will be summarized in this report (Scoping Tests 1 and 2 and Production Run 2). Additional testing performed at Hazen Research, Inc. under oxidizing FBSR conditions will be discussed comparatively since there was only one set of tests run under these conditions.

The waste form durability and chemical analyses specific to Scoping Test 02 when the FBSR was operated under reducing conditions will be discussed in detail. Coal was used to assist in denitration of the waste at temperatures between 715-735°C. Kaolin clay, small amounts of excess  $\text{SiO}_2$ , and iron oxide were the only waste form additives. The clay was not calcined

before processing. The waste loading achieved with Scoping Test 02 was ~27 wt% since 73 wt% additives were used. This corresponds to an Na<sub>2</sub>O loading of 19.82 wt%.

Table I Composition of As-Made Simulant Plus Re Spike

Slurry Analyte	Raw Chemical	Amount Required, lbs/Batch
Al	Al(NO <sub>3</sub> ) <sub>3</sub> •9H <sub>2</sub> O	3,235.95
Ca	Ca(NO <sub>3</sub> ) <sub>2</sub> •4H <sub>2</sub> O	67.22
Cr	Na <sub>2</sub> CrO <sub>4</sub> •4H <sub>2</sub> O	27.4
Cs	CsNO <sub>3</sub>	0.42
Fe	Fe(NO <sub>3</sub> ) <sub>3</sub> •9H <sub>2</sub> O	400.95
K	KOH	54.70
La	La <sub>2</sub> O <sub>3</sub>	0.82
Na	NaOH, 50% sol.d=1.53	5,656.39
Ni	NiO	12.38
Pb	PbO	8.47
Re	NaReO <sub>4</sub> (spike added by Hazen)*	0.0233
Cl	NaCl	61.42
F	NaF	148.47
PO <sub>4</sub>	Na <sub>3</sub> PO <sub>4</sub> •12H <sub>2</sub> O	292.13
SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	313.69
NO <sub>2</sub>	NaNO <sub>2</sub>	1,845.05
NO <sub>3</sub>	NaNO <sub>3</sub>	4,157.71
CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	2,546.64
TOC	Na <sub>2</sub> EDTA.2H <sub>2</sub> O	222.88
	Na <sub>3</sub> HEDTA.2H <sub>2</sub> O	662.16
	Sodium Acetate	261.03
	Sodium Formate	327.72
	Sodium Oxalate	165.12
	Sodium Gluconate	162.67
	Glycolic Acid	640.98
	Nitrilotriacetic Acid	186.22
	Citric Acid	542.23
	Iminodiacetic Acid	175.30
	Water	14,590.44
	Slurry Volume, gal	3,200

\*spike was 5 grams of NaReO<sub>4</sub> in 150 gallons of slurry which is equivalent to 0.0233 lbs of NaReO<sub>4</sub> in 3200 gallons of slurry

Durability testing of the FBSR sample SCT02-098-FM from Scoping Test 02 was performed at SRTC. Durability testing was performed using ASTM C1285-97 (PCT-A test protocol) by the test developer. The PCT-A test was run for 7 days at 90°C in stainless steel vessels. Triplicate samples were tested along with two standard glasses; the ARM-1 standard and the Environmental Assessment (EA) glass<sup>1</sup> standard used to assess the durability of HLW vitrified waste forms.

Sample SCT02-098-FM was dissolved using a lithium borate fusion and a second dissolution performed via a Na<sub>2</sub>O<sub>2</sub> fusion (ASTM C1463). Each dissolution type was analyzed twice, once with no dilution and once with a 10X dilution. All four replicate analyses were averaged. A glass standard, Batch 1 glass, was analyzed simultaneously for quality assurance. The sample was analyzed for anions (phosphorous and sulfur) and cations by both Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) (ASTM C1463). In addition, the sample was dissolved in a Na<sub>2</sub>O<sub>2</sub> dissolution with a water uptake and analyzed for additional anions by Ion Chromatography (IC) (ASTM D4327). The PCT leachates were analyzed for cations by both Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) (ASTM C1109) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). Anion analysis of the PCT leachates is still in progress.

Dissolution of sample SCT02-098-FM was also performed by H<sub>2</sub>SO<sub>4</sub>/HF in the presence of NH<sub>4</sub>VO<sub>3</sub> followed by colorimetric determination of Fe<sup>2+</sup> and total Fe ( $\Sigma$ Fe) in order to determine the reduction/oxidation (redox) equilibria of the sample in terms of the Fe<sup>2+</sup>/ $\Sigma$ Fe ratio.<sup>2</sup> A standard glass, the EA glass,<sup>1</sup> with a known and reproducible redox, was used during the analysis for quality assurance.

X-Ray Diffraction (XRD) analyses were performed at Hazen Research, Inc. in Golden Colorado and confirmed at SRTC for sample SCT02-098-FM. XRD was performed at SRTC both before and after durability testing. Scanning Electron Microscopy (SEM) of the phases and the distribution of the anions and radionuclide simulants among the phases is still in progress.

Testing of the FBSR final waste form using the EPA TCLP protocol was performed by Evergreen Analytical, an EPA certified laboratory, under subcontract to Hazen Research, Inc. The results of the testing of samples from the FBSR process fabricated under both reducing and oxidizing conditions are summarized in this report.

### 1.3 RESULTS AND PERFORMANCE AGAINST OBJECTIVES

The PCT-A testing of the FBSR SCT02-098-FM demonstrated that the normalized sodium release was <2 g/m<sup>2</sup> while the release of the simulated radionuclides Re and Cs were an order of magnitude lower. TCLP testing indicates that all hazardous constituent releases for Cr, Ni, and Pb are lower than the EPA Universal Treatment Standard (UTS) limits for listed wastes. Retention of SO<sub>4</sub><sup>=</sup> in the waste form was verified to be ~100%.

## **1.4 QUALITY REQUIREMENTS**

All test procedures used at SRTC are compliant with RW-0333P quality assurance.

## **1.5 ISSUES**

The durability testing performed in this report (ASTM C1285-97 and TCLP) indicates that FBSR LAW waste forms are more durable than LAW vitrified waste forms even without optimizing the formulations. The mineral phases composing the FBSR LAW waste form are known to have survived millions of years in natural environments. Their alteration products are primarily other cage structured mineral phases such as hydrated zeolite phases which will continue to atomically bond and retain the anions and radionuclides.

## **2.0 PROCESSING FEASIBILITY AND FLEXIBILITY OF THE FLUIDIZED BED STEAM REFORMER PROCESS (FBSR)**

The FBSR process has been shown to simultaneously denitrate and convert high sodium Hanford LAW wastes to solid mineral phases containing the sodium, anions such as  $\text{SO}_4^-$ , and radionuclides. The Hanford LAW surrogate comprised a basic, sodium/aluminum nitrate solution that also contained a significant amount of sulfate, chloride, fluoride and organic compounds as well as certain heavy metals and radionuclide surrogates (Table I). The mineral phases were optimized as a final waste form and as a product that could be used to recycle off-gas blowdown solutions enriched in  $\text{SiO}_2$ , sulfates, chlorides, and fluorides<sup>3</sup> from LAW vitrification to the vitrification process as an alternative to evaporation. This study concentrates on the use of FBSR technology to produce mineral phases as a final waste form. The particular mineral phases that formed depend on the additives co-fired in the steam reformer with the LAW waste. For example  $\text{Na}_2\text{SiO}_3$  could be formed for off-gas condensate recycle to a vitrification facility if only  $\text{SiO}_2$  were added. For final waste form mineralization a combination of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  had to be added in the form of kaolin clay.

### **2.1 FBSR FINAL WASTE FORM DEMONSTRATIONS**

Hazen Research, Inc. performed denitration and final waste form mineralization demonstrations under both oxidizing and reducing conditions (see Table II). A solid sodium-alumina-silicate product, predominately  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-2\text{SiO}_2$ , was produced in the FBSR by the addition of a kaolin clay co-reactant with the Hanford LAW surrogate. The Na-Al-Si (NAS) product was produced during the scoping tests SCT-01 and SCT-02 and during the two production runs PR-01 and PR-02.

Table II Fluidized Bed Steam Reformer (FBSR) Demonstration Program

<b>Product</b>	<b>Operating Mode</b>	<b>Scoping Test No.</b>	<b>Production Run No.</b>
Na <sub>2</sub> O-Al <sub>2</sub> O <sub>3</sub> -2SiO <sub>2</sub>	Reducing	SCT-01 (18.6 hrs) SCT-02 (4.8 hrs)	PR-02 (21.7 hrs)
Na <sub>2</sub> O-Al <sub>2</sub> O <sub>3</sub> -2SiO <sub>2</sub>	Oxidizing	None	PR-01 (23.3 hrs)

The first four days of SCT-01 testing were short test series utilized to optimize the direct conversion of nitrates and nitrites to nitrogen gas in the FBSR. The type of carbon reductant and catalyst used was varied to provide high NO<sub>x</sub> conversions. The final SCT-01 test run demonstrated the Reformer's ability to reliably and continuously maintain NO<sub>x</sub> levels in the FBSR off-gas at less than 500ppm.

The initial SCT-01 scoping test experienced localized build-up of hollow, tubular shaped agglomerations (approximately 19mm to 32mm (0.75" to 1.25") OD by 50mm to 100mm (2" to 4")L) around the simulant feed injection nozzle and the mast tip to the injection nozzle. These problems were remediated by providing improved gas velocities and mechanically moving the mast further away from the injector.

The SCT-02 test run was terminated when a short duration carbon reductant injection/transfer line plug occurred. The unplugging efforts allowed excess oxygen to enter the bed and cause poor fluidization and an excess of oxygen in one area of the bed. The non-uniform fluidization caused an agglomeration of the waste form to occur and the SCT-02 test was terminated after only 4.8 hours. The carbon transfer line pluggage is considered anomalous by Studsvik because the 6 inch bed diameter FBSR demonstration unit contains a less than optimal solids addition transfer system compared to the full scale unit at Erwin, TN. A larger FBSR such as the one at Erwin, TN uses a transfer system with a higher purge gas flow and an in-bed downcomer that eliminates additive transfer line plugging events that occasionally occurred throughout the demonstration tests.

The PR-02 demonstration run successfully produced an NAS product without the presence of agglomeration or significant operational problems. The PR-02 run was terminated when the planned simulant waste feed volume was processed as planned.

The PR-01 demonstration run successfully produced an NAS product without the presence of agglomeration or significant operational problems. The PR-01 run was terminated when the planned processing time had elapsed.

### 2.1.1 OFF-GAS PERFORMANCE

The LAW simulant tested contained various organic compounds, plus  $\text{Cs}^{133}$  as a substitute for  $\text{Cs}^{137}$ , and Re as a substitute for  $\text{Tc}^{99}$ . Organic destruction was demonstrated at the 650-750°C steam reformer operating temperature in the presence of various reductants. The reductants also successfully converted the  $\text{NO}_3^-$  and  $\text{NO}_2^-$  in the feed, present primarily as  $\text{NaNO}_3$ ,  $\text{AlNO}_3$ , and  $\text{NaNO}_2$ , into  $\text{N}_2$  gas while the carbon containing reductants were converted to  $\text{CO}_2$  and  $\text{H}_2$  gas. Volatile organic compounds (VOC's) are destroyed during operation of the FBSR. Organic destruction efficiencies of 99.7% were achieved when the FBSR was run under reducing conditions and 99.9% was achieved when the FBSR was run under oxidizing conditions. Therefore, the gaseous emissions from the FBSR are not hazardous under the Maximum Achievable Control Technology (MACT) requirements of the Clean Air Act as  $\text{NO}_x$  and CO gases would be. Optimization of the processing conditions to maximize  $\text{CO}_2$  (favored under oxidizing conditions) and  $\text{N}_2$  (favored under reducing conditions) will be necessary to comply with MACT regulations. Because of the presence of a secondary thermal converter there are no flammability concerns due to the presence of small quantities of  $\text{H}_2$ .

Combinations of  $\text{SO}_4^{=}$ ,  $\text{Cl}^-$  and  $\text{F}^-$  in steam creates mixed acid off-gases which are removed by the scrubber system of the FBSR off-gas. Hazen Research, Inc. indicates that <20 ppm  $\text{SO}_x$  is in the off-gas upstream of the scrubber and <2.5 ppm  $\text{SO}_x$  downstream of the scrubber. Very low concentrations of acid gases, e.g. Cl, F,  $\text{SO}_x$  and  $\text{NO}_x$ , were formed in the scrubber solution as shown in Table III when compared to the quantities of these species in the input in the waste feed. These low concentrations are indicative of the low quantities of acid gases released by the reforming process. The vast majority of the acid gas species are incorporated into the solid sodium product phases with less than 4% to 8% of the acid gases volatilized to the off-gas system. The fact that there is so little  $\text{SO}_4$  in the scrubber solution (Table III) is a direct indication that the  $\text{SO}_4$  in the LAW surrogate was not volatilized in the FBSR and was not in the off-gas. Analyses of the solid samples indicated that >91% of the  $\text{SO}_4^{=}$ , >93% of the  $\text{Cl}^-$ , and >92% of the  $\text{F}^-$  was retained in the solid product). In addition, the scrubber solutions can be recycled to the FBSR since they are so dilute.

Table III Off-gas Scrubber Solution Composition

Components	Scrubber Solution Composition	Percent Component in Scrubber Solution versus Input in Waste Feed
Ca	3 ppm	1.7% (suspect hard water)
Cl	20 ppm	3.4%
CO <sub>3</sub>	6,680 ppm	NA, absorbed CO <sub>2</sub>
Cr	0.04 ppm	<0.05%
F	<40 ppm	4.0%
Na	12 ppm	<0.02%
SO <sub>4</sub>	146 ppm	4.5%
NO <sub>2</sub>	<6 ppm	NA
NO <sub>3</sub>	<6 ppm	NA
Others	<Detectable	NA
pH	8.9	
Conductivity	8,190 umhos/cm	

During the Hazen demonstration, Cs and Re volatility were also monitored and retention of these simulated radionuclides in the mineral phases was calculated to be high, 99.9% and 99.995%, respectively. This calculation is based on the scrubber solution analyses which indicate that <0.10% of the total Cs and < 0.003% of the total Re were found in the scrubber solutions (the remaining percentages are assumed to be in the final waste form). This is supported by additional operating experience at the Studsvik Erwin facility which has demonstrated Cs and Co retention in the solid products of ~99.94%. Capture of the Cs and Re in the waste form is a combination of the low processing temperatures, the use of a ceramic filter to remove fine micron size particles, and the ability of the sodium-alumino-silicate (NAS) mineral phases to accommodate these species into their structures.

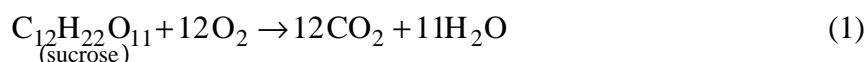
### 2.1.2 REDOX CONTROL

Redox control is achieved in the FBSR process by use of charcoal or sugar. These reductants and proprietary catalysts are the control for converting the nitrates in the feed to N<sub>2</sub> and the organics to CO<sub>2</sub> and H<sub>2</sub>. The use of these reductants also appears to be controlling the redox of the Cr, Re and possibly the SO<sub>4</sub><sup>=</sup>, thus preventing these species from volatilizing and enhancing the retention of these species in the FBSR waste form. More work is needed on the measurement of the redox of the final mineral phases and a chemical analysis of the final

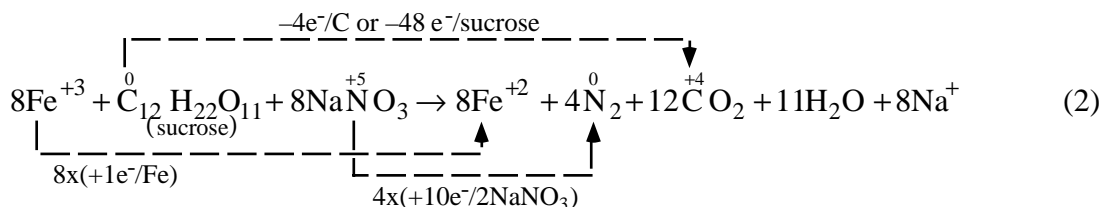


mineral phases is needed in order to determine the relation between the redox and the waste form retention of these species.

From the batch makeup sheets reviewed it became clear that an assumption had been made that 1 mole of sucrose carbon reduces 1 mole of  $\text{NO}_2$  and that one mole of sucrose carbon reduces 1.5 mole of  $\text{NO}_3$ . While the amount of carbon added in each of the demonstration tests appears to have been sufficient, the reducing power of a carbon containing additive and the oxidizing power of nitrates in the feed are not the exact ratios used during the demonstration but are molar quantities related to the number of electrons exchanged between the oxidizing and reducing species (see Equations 1-2)<sup>4</sup> as follows:



or stated in different terms, the following reaction can be postulated:



which is 1.25 electron transfer equivalents in sucrose per 1 mole of  $\text{NO}_3$ . Some work is needed on the optimization of the form of the carbon added and its reducing power.

### 2.1.3 AGGLOMERATION

Agglomeration due to the usage of a 6" FBSR demonstration unit was discussed in Section 2.1 and was related to both non-uniform temperature and/or fluidization flow velocities, e.g. agglomeration was observed when cooler temperatures in the bottom of the bed allowed moisture to accumulate. Methods to ensure uniform bed temperatures and uniform fluidization flow velocities are well understood and occurred during feed pluggages as discussed in Section 2.1. However, bed temperatures and fluidization flow velocities need to be optimized for final waste form processing.

### 3.0 THE MINERAL PHASES THAT COMPRISE THE FBSR CERAMIC WASTE FORM (CWF)

Ceramic waste forms have long been known to exhibit equivalent and often superior durability compared to vitreous waste forms for HLW stabilization. Ceramic waste forms have been intensely investigated<sup>5</sup> for stabilization of HLW wastes but were eventually abandoned due to the following considerations:

- high processing temperatures (1100°C to 1400°C) which caused vaporization of radionuclides such as Tc<sup>99</sup> and Cs<sup>137</sup>
- presence of a leachable glassy intergranular phase which sometimes adversely impacted durability<sup>20</sup>
- tendency to undergo radiation damage at the radiation doses experienced with HLW in the form of metamictization (transformation to an amorphous rather than a crystalline structure)
- complex processing (isostatic pressing followed by sintering and/or hot isostatic pressing, HIPing)
- batch processing (poor attainment due to batch nature of producing small pucks or samples)

The FBSR process as applied to LAW waste stabilization does not share any of these concerns since the process runs at ~700°C, it is a continuous process (not batch), and LAW waste does not have a high enough radionuclide dose to cause metamictization. At the low processing temperatures of the FBSR process an intergranular glassy phase is probably not produced although this needs to be examined in more detail.

#### 3.1 ATOMIC BONDING OF RADIONUCLIDES AND ANIONS IN CAGE-STRUCTURED SODIUM ALUMINOSILICATE (NAS) MINERAL PHASES

The sodium aluminosilicate (NAS) mineral phase assemblage(s) are anhydrous feldspathoid phases such as sodalite which are unique because they have cage-like structures formed of aluminosilicate tetrahedra (Figure 1) similar to hydrous Zeolite-A. The remaining feldspathoid minerals, such as nepheline, have a silica “stuffed derivative” ring type structure. The 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. 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 are used to delineate the alumina:silica ratio of the aluminosilicate cage structure which is 1:1.

Zeolite-A,  $\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}] \cdot 27\text{H}_2\text{O}$ , is a phase related structurally to the feldspathoids sodalite and nosean<sup>13</sup> because the alumina:silica ratio of the aluminosilicate cage structure is

the same as that found in the sodalites (Figure 1). Zeolite-A is a double unit cell of sodalite without the NaCl, Na<sub>2</sub>SO<sub>4</sub>, NaOH, or Na<sub>2</sub>CO<sub>3</sub> groups inside the cage (Table IV). Zeolite-A has adherent waters of hydration that are not present in the feldspathoid minerals. However, Zeolite-A can transform into sodalite at temperatures as low as 85°C and this transformation has been well studied.<sup>6</sup>

The nomenclature of the feldspathoid series of mineral species is governed by the species that occupy the cavities in the aluminosilicate framework and whether or not the resulting crystals have cubic or hexagonal crystal structures. Sodalite has the formula Na<sub>8</sub>[Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>](Cl<sub>2</sub>). The cage is occupied by two sodium and two chlorine ions in natural sodalites.<sup>7</sup> The formula can also be written as Na<sub>6</sub>[Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>]•(2NaCl) to indicate that two NaCl are ionically bonded in the cavities of the cage structure while the remaining Na:Si:Al have a 1:1:1 stoichiometry.<sup>7</sup> When the 2NaCl are replaced by Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, 2NaNO<sub>3</sub>, and/or 2NaOH, the mineral and/or chemical names are as given in Table IV.

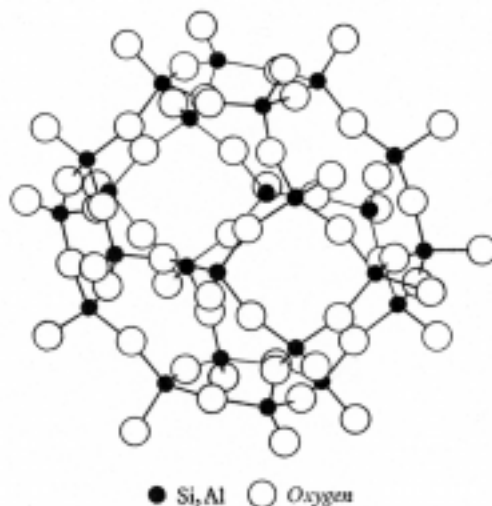


Figure 1. Part of the aluminosilicate framework in the structure of the feldspathoid sodalite.<sup>7</sup>

One of the feldspathoid cage structured minerals found in the FBSR waste form is nosean (see Table V), (Na<sub>6</sub>[Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>](Na<sub>2</sub>SO<sub>4</sub>)). Nosean has Na<sub>2</sub>SO<sub>4</sub> atomistically bonded in the sodalite cage like structure. Since the Cl<sup>-</sup>, SO<sub>4</sub><sup>=</sup>, and/or S<sub>2</sub> are atomistically bonded inside the sodalite cage structure, these species do not readily leach out of the respective FBSR waste form mineral phases. It should also be noted that the minerals hauyne and lazurite which are all cage structured minerals in the sodalite family (Table IV) can accommodate either SO<sub>4</sub> or S<sub>2</sub> depending on the redox of the sulfur during the steam reforming process. Regardless of the FBSR redox the feldspathoid minerals can accommodate sulfur as either sulfate or sulfide. Sodalite minerals are known to accommodate Be in place of Al and S<sub>2</sub> in the cage structure along with Fe, Mn, and Zn, e.g. helvite (Mn<sub>4</sub>[Be<sub>3</sub>Si<sub>3</sub>O<sub>12</sub>]S), danalite

(Fe<sub>4</sub>[Be<sub>3</sub>Si<sub>3</sub>O<sub>12</sub>]S), and genthelvite (Zn<sub>4</sub>[Be<sub>3</sub>Si<sub>3</sub>O<sub>12</sub>]S).<sup>7</sup> These cage-structured sodalites are also found to retain Mo, Cs, and Sr (see discussion in Section 3.2), B,<sup>8</sup> Ge,<sup>9</sup> I,<sup>9,7</sup> and Br.<sup>9,7</sup>

A second feldspathoid mineral found in the FBSR waste form is nepheline (NaAlSiO<sub>4</sub>).<sup>10</sup> Nepheline is a hexagonal structured feldspathoid mineral (see Table V). The ring structured aluminosilicate framework of nepheline forms cavities within the framework. There are eight large (nine-fold oxygen) coordination sites and six smaller (8-fold oxygen) coordination sites.<sup>7</sup> The larger sites nine-fold sites can hold large cations such as Cs, K, and Ca while the smaller sites accommodate the Na. The K analogue is known as leucite (KAlSi<sub>2</sub>O<sub>6</sub>). In nature, the nepheline structure is known to accommodate Fe, Ti and Mg as well.

The remaining aluminosilicate mineral found in the FBSR waste form is a sodium rich cubic structured nepheline derivative (Na<sub>2</sub>O)<sub>0.33</sub>Na[AlSiO<sub>4</sub>] (PDF#39-0101). This nepheline derivative structure has large (twelve-fold oxygen) cage like voids in the structure.<sup>11</sup> This cage structured nepheline is not known to occur in nature but the large cage like voids should be capable of retaining large radionuclides, especially monovalent radionuclides such as Cs.

Other minor phases such as corundum (Al<sub>2</sub>O<sub>3</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>) that are identified in the FBSR waste form (see Table V) come from the bed media used and the catalyst added.

Table IV Structurally Related Zeolite and Feldspathoid (Sodalite and Cancrinite) Group Mineral Phases

Substitution In Cage Structure	Chemical Formula	Common or Mineral Name	Density (g/cm <sup>3</sup> )	Crystal Type	Ref.
<b>Precursor</b>					
NONE	Na <sub>12</sub> [Al <sub>12</sub> Si <sub>12</sub> O <sub>48</sub> ] • 27H <sub>2</sub> O	Zeolite-A	1.99 <sup>‡</sup>	Cubic	12
<b>Sodalite Group (Anhydrous)</b>					
2NaCl	Na <sub>6</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ](2NaCl)	Sodalite	2.31 <sup>*</sup>	Cubic <sup>*</sup>	7
2NaOH	Na <sub>6</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ](2NaOH)•1.5H <sub>2</sub> O	Basic Sodalite or Hydroxysodalite	2.215 <sup>**</sup>	Cubic <sup>**</sup>	13
2NaNO <sub>3</sub>	Na <sub>6</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ](2NaNO <sub>3</sub> )	Nitrated Sodalite	2.342	Cubic	PDF#50-0248
Na <sub>2</sub> SO <sub>4</sub>	Na <sub>6</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ](Na <sub>2</sub> SO <sub>4</sub> )	Nosean	2.21 <sup>tt</sup>	Cubic <sup>tt</sup>	14
1-2(Ca,Na)SO <sub>4</sub>	(Na) <sub>6</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ]((Ca,Na)(S,SO <sub>4</sub> ) <sub>1-2</sub> ) <sup>t</sup>	Hauyne	2.4 <sup>t</sup>	Cubic <sup>t</sup>	7
x(Ca,Na)(S,SO <sub>4</sub> ,Cl)	(Ca,Na) <sub>6</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ]((Ca,Na)S,SO <sub>4</sub> ,Cl) <sub>x</sub> <sup>t</sup>	Lazurite	2.43	Cubic	PDF #17-749
<b>Cancrinite Group (Anhydrous)</b>					
2NaNO <sub>3</sub>	Na <sub>6</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ](2NaNO <sub>3</sub> )•4H <sub>2</sub> O	Nitrated Cancrinite	2.51	Hexagonal	PDF #38-513
(Na,Ca,K) <sub>2</sub> CO <sub>3</sub>	(Na,Ca,K) <sub>6</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ]((Na,Ca,K) <sub>2</sub> CO <sub>3</sub> ) <sub>1-6</sub> •2.1H <sub>2</sub> O	Cancrinite	2.60	Hexagonal	PDF #25-776
2(Na, K)Cl	(Na,Ca,K) <sub>6</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ](2(Na,K)Cl) <sub>2-3</sub>	Microsommitte	2.34	Hexagonal	PDF #20-743
2(Na, K)Cl	(Na,Ca,K) <sub>6</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ]((Na,K) <sub>2</sub> SO <sub>4</sub> ,Cl) <sub>3</sub>	Davyne	2.46	Hexagonal	PDF #20-379
Na <sub>2</sub> CO <sub>3</sub>	Na <sub>6</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ](Na <sub>2</sub> CO <sub>3</sub> )	Natrodavyne	Not given	Hexagonal	PDF #15-794

t PDF #20-1087 \* PDF # 20-495 ‡ PDF #11-0590 and #38-241  
tt PDF #17-538 \*\* PDF #11-401

Table V Mineral Phases Reported by Hazen Research, Inc. for FBSR Final Waste Form

Mineral Phases Formed in FBSR at ~700°C under reducing conditions – Scoping Tests 01	Mineral Phases Formed in FBSR at ~700°C under reducing conditions – Scoping Tests 02	Mineral Phases Formed in FBSR at ~700°C under reducing conditions Production Test 02	Mineral Phases Formed in FBSR at ~700°C under oxidizing conditions Production Test 01
NaAlSiO <sub>4</sub> (Nepheline)	NaAlSiO <sub>4</sub> (Nepheline)	NaAlSiO <sub>4</sub> (Nepheline)	NaAlSiO <sub>4</sub> (Nepheline)
(Na <sub>2</sub> O) <sub>0.33</sub> NaAlSiO <sub>4</sub> (Cubic Nepheline)			(Na <sub>2</sub> O) <sub>0.33</sub> NaAlSiO <sub>4</sub> (Cubic Nepheline)
Na <sub>8</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> (SO <sub>4</sub> ) (Nosean)	Na <sub>8</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> (SO <sub>4</sub> ) (Nosean)	Na <sub>8</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> (SO <sub>4</sub> ) (Nosean)	Na <sub>8</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> (SO <sub>4</sub> ) (Nosean)
Al <sub>2</sub> O <sub>3</sub> (Corundum)	Al <sub>2</sub> O <sub>3</sub> (Corundum)	Al <sub>2</sub> O <sub>3</sub> (Corundum)	Al <sub>2</sub> O <sub>3</sub> (Corundum)
Fe <sub>2</sub> O <sub>3</sub> (Hematite)	Fe <sub>2</sub> O <sub>3</sub> (Hematite)	Fe <sub>2</sub> O <sub>3</sub> (Hematite)	

### 3.2 SIMILARITIES TO MINERAL PHASES IN HLW HIGH TEMPERATURE CERAMIC WASTE FORMS

The FBSR technology uses alkali aluminosilicate (NAS) host phases to accommodate the waste species as did the supercalcine high temperature ceramics investigated for HLW waste disposal >25 years ago (see Table VI). Similar silicate mineral phases are also formed in the glass-bonded sodalite ceramic waste form (CWF) developed at Argonne National Laboratory –West (ANL-W) for disposal of electrorefiner wastes from a treatment process for sodium-bonded metallic spent nuclear fuel from the EBR II fast breeder reactor (see Table VI).

Supercalcines were the high temperature silicate based “natural mineral” assemblages proposed for HLW waste stabilization in the United States (1973-1985). Subsequently, a titania based SYNthetic ROCK (SYNROC) of “natural mineral” assemblages was developed in Australia.<sup>15</sup> Supercalcine waste forms are aluminosilicate based crystalline assemblages of mutually compatible, refractory, and leach-resistant solid solution phases proposed for the incorporation of HLW ions.<sup>16</sup>

The supercalcine aluminosilicate and oxide phases that held the radioactive constituents in their atomic structures were dubbed “radiophases” which were formed by spray calcining nitrated waste into a powder, mixing the denitrated powdered calcined waste with additives, pellitizing under pressure, and sintering or hot isostatically pressing at high temperatures (1100-1300°C). In one case, the additives were mixed with the simulated HLW prior to calcination.<sup>17</sup> An assemblage of silicate mineral phases such as apatite (host for lanthanides), pollucite (host for Cs), and other oxide host phases for Sr, Ba, U, Zr, etc. were formed<sup>16,18</sup> If the waste contained considerable Na and Si, then phases such as nepheline formed while wastes enriched in Al formed high temperature phases such as Al<sub>2</sub>O<sub>3</sub> and magnetoplumbite aluminate species.<sup>19,20</sup> The feldspathoid, sodalite, was a minor mineral phase in supercalcines but was found to incorporate Cs and Sr and Mo into the cage-like structure, e.g. Mo as (NaAlSiO<sub>4</sub>)<sub>6</sub>(NaMoO<sub>4</sub>)<sub>2</sub>.<sup>21</sup>

Table VI Similarity of Mineral Phases in FBSR Waste Forms to Other HLW and LAW Waste Forms

Mineral Phases Formed in FBSR at ~700°C under reducing conditions	Mineral Phases Formed in High Temperature HLW Ceramic Waste Forms	Mineral Phases in INEEL Glass Bonded Sodalite Waste Forms	Mineral Phases in LAW Hydroceramic Waste Forms
Nosean (Sodalite Family)	(NaAlSiO <sub>4</sub> ) <sub>6</sub> (NaMoO <sub>4</sub> ) <sub>2</sub>	Sodalite	Sodalite + Zeoite-A
Nepheline	Nepheline	Nepheline	
Cubic Nepheline			
Corundum	Corundum		
Hematite			

About 3 years ago, ANL-W developed a glass bonded ceramic waste form (CWF) for management of electrorefiner salt wastes containing Pu, U, Cs, Na, K, Li, Ba, and Cl, where the alkali, alkaline earths and rare earth species are all present as chlorides.<sup>22,23</sup> The electrorefiner salt is admixed with Zeolite-A at 500°C. The salt-loaded zeolite is then mixed with a borosilicate glass frit (in a weight ratio of 3:1) and hot isostatically pressed to obtain a consolidated, durable waste form at 850°C and 100 MPa. The four mineral phases formed are (Pu,U)O<sub>2-x</sub>, sodalite (see Table III), NaCl, and nepheline in a borosilicate glass matrix.

In summary, the FBSR technology produces waste form mineral species that have been well studied for stabilization of HLW waste. The basis for the FBSR waste form is thus well scientifically founded and documented.

### **3.3 SIMILARITIES TO MINERAL PHASES IN LAW HYDROCERAMIC WASTE FORMS**

The formation of aluminosilicate product phase(s) by the FBSR process are also similar to the hydrous phases in LAW hydroceramic waste forms (see Table VI). Recently, these low temperature hydroceramics have been investigated under EMSP funding for INEEL sodium bearing waste (SBW) and SRS salt supernate processing.<sup>24,25,26</sup> The hydroceramic process forms zeolitic and feldspathoid phases from high sodium nitrate solutions. The nitrated waste solutions are calcined at 650-750°C with sucrose to denitrate and dewater the solutions. The calcine is then admixed with metakaolin (clay) and water to a thick paste and warm pressed at ~200°C in a pressure vessel in the presence of steam. While these denitration and hydrothermal processes are performed sequentially during hydroceramic waste form processing, these steps occur simultaneously during FBSR processing. In addition, the higher temperature of the FBSR process causes dehydration of the zeolite phases into the anhydrous feldspathoids.

The resulting hydroceramic waste form is a zeolite and/or mixed zeolite and feldspathoid “cage structured” mineral assemblage capable of hosting various anions and radionuclides (see Section 3.2 and 3.1). The hydroceramic waste forms have been durability tested and perform well against the HLW Environmental Assessment (EA) glass.<sup>25,26</sup> Zeolite phases are thermodynamically favored to form in high caustic environments in the presence of Si and Al, even at ambient temperatures. In tank zeolite formation was discovered in the SRS M-Area tanks<sup>27</sup> and during caustic (NaOH) dissolution of aluminosilicate filters at boiling temperatures in air.<sup>28</sup> This suggests that feldspathoids in the presence of aqueous solutions will hydrate into their zeolite analogs while still retaining the radionuclides and anions of concern.

### **3.4 OCCURRENCE OF MINERAL PHASES IN NATURE AND LONG TERM GEOLOGIC STABILITY**

The sodalite group of minerals occurs in undersaturated (with respect to silica) plutonic, volcanic, and metasomatized carbonate rocks. Common associations are cancrinite (a mineral similar to sodalite in structure-see Table IV), melanite (a garnet), and nepheline ( $\text{NaAlSiO}_4$ ). Concentrations of up to 2.87 wt% Mo have been reported in natural sodalites.<sup>29</sup>

Mechanisms for the alteration of sodalite group minerals have not been examined in detail, but many hydrothermal alteration products have been identified. Sodalite altering to other zeolites has been reported most frequently. Thomsonite, natrolite, and gismondine have been the zeolites identified.<sup>7</sup> Sodalite altering to cancrinite has been reported.<sup>7</sup> Nosean and hauyne transformation to cancrinite have also been reported at elevated temperature and pressure, e.g.  $\sim 480^\circ\text{C}$  in the pressure range of 1000-2000 bars  $\text{pH}_2\text{O}$ .<sup>30</sup> However, these severe conditions are not anticipated in a LAW disposal environment.

Nepheline is the characteristic mineral of alkaline rich rocks. Nepheline is the most common feldspathoid. Nepheline can be formed as a primary phase of magmatic crystallization, as a product of metasomatism (reaction with hot water solution in the earth known as nephelinization), and/or as a result of reaction of high silica (acid) and low silica (basic) magmas with calcium rich sediments.<sup>31</sup> Nephelines have survived in nature for 879-1144 million years where the ages of the natural formations have been determined by K-Ar dating.<sup>31</sup>

In aqueous environments under ambient pressures, the most common alteration products formed as alteration “rinds” have been called “hydro-nepheline.” Hydro-nepheline has the composition  $\text{NaAlSiO}_4 \cdot 0.5\text{H}_2\text{O}$ .<sup>32</sup> Nepheline has also been reported to alter to sodalite<sup>30</sup> and to other zeolites. Under hydrothermal conditions ( $295^\circ\text{C}$  and 1.6 Kbar pressure) nepheline converted to a mixture of muscovite (a mica) and analcite (a zeolite) after 135 days. However, these severe conditions are not anticipated in an LAW disposal environment.

## **4.0 ATTRIBUTES OF THE FBSR WASTE FORM OVER HLW CERAMIC AND LAW HYDROCERAMIC WASTE FORMS**

The FBSR process forms geologically stable mineral phases analogous to those formed in several different HLW ceramic waste forms (see Table VI). However, the FBSR process retains volatile radionuclides and hazardous species that could not be retained in the HLW high temperature ceramic processes because the FBSR operates at temperatures of  $\sim 700^\circ\text{C}$ . The FBSR waste form process is continuous rather than a batch process such as cold isostatic pressing coupled with high temperature sintering or hot isostatically pressing (HIPing). In addition, the application to LAW type wastes minimizes concerns about the radiation stability of the mineral phases.



The FBSR waste process also forms geologically stable mineral phases analogous to those formed in hydro-ceramic waste forms for LAW wastes (see Table VI). However, the FBSR process is superior to the hydro-ceramic processes in that the denitration and hydrothermal reactions occur simultaneously in the steam reformer instead of each step being a different unit operation. In addition, the FBSR waste form process is continuous rather than the batch process needed to hydrothermally warm press individual products in stainless steel Parr vessels at 200°C in the presence of steam, a process similar to HIPing at low temperatures.

## **5.0 ATTRIBUTES OF THE FBSR CERAMIC WASTE FORM OVER LAW VITRIFIED WASTE FORMS**

The FBSR waste process forms geologically stable mineral phases analogous to those formed in several different HLW ceramic waste forms (see Table VI). Sodalite is known only to dissolve in strong acid like concentrated HCl.<sup>7</sup> The geologic stability of these mineral phases in nature indicates that they will be more durable than LAW glass in natural environments. In addition, the FBSR stable mineral phases convert to zeolites which retain the cage-like structures that contain the radionuclides, hazardous, and anionic species of concern.

In addition, the FBSR mineral phases can accommodate the high Na concentrations of the LAW wastes as well as the high anion content, especially the high  $\text{SO}_4^-$  of the Hanford LAW wastes. The continuous nature of the process at higher  $\text{SO}_4^-$  loadings will allow accelerated remediation of the Hanford LAW wastes in a waste form that appears to be superior to glass.

The preliminary testing of the FBSR waste form indicates that it meets all regulatory limits (see Section 7.0), for listed waste at the UTS limits while vitrification does not perform as well consistently. This regulatory driver will allow the LAW FBSR product to be delisted while delisting of a vitrified waste form may be problematic. Delisting the waste for burial is an estimated cost savings of \$5958 per cubic foot of waste disposed.<sup>f</sup>

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<sup>f</sup> Disposal of listed mixed waste at the SRS is \$6000/ft<sup>3</sup> while disposal as radioactive (low level) waste once the waste is delisted costs only \$42/ft<sup>3</sup> (Site Training Radiological Worker Training Study Guide, Rev. 11, Westinghouse Savannah River Company (1997).

## 6.0 CHARACTERIZATION AND DURABILITY OF THE FBSR WASTE FORM AT SRTC

### 6.1 IDENTIFICATION OF FBSR MINERAL PHASES

The phases identified by Hazen Research in the FBSR Sample from Scoping Test 02 (Sample SCT02-098-FM) are given in Table VII. The phases identified for the same sample at SRTC are given for comparison in Table VII. Analysis at SRTC indicated the presence of a minor second iron oxide phase, magnetite ( $\text{Fe}_3\text{O}_4$ ) in addition to the hematite ( $\text{Fe}_2\text{O}_3$ ). Nepheline (the hexagonal type) is the major component with subordinate amounts of nosean and corundum. The cubic structured nepheline was not observed in this sample but was observed in the production run of a similar material. Since the FBSR Scoping Test samples were not optimized, the relative amounts of the two types of nepheline and sodalite (nosean) will vary with optimization of waste additives, e.g. types of clay or other aluminosilicates, and processing parameters.

Table VII Phases Identified by X-Ray Diffraction in FBSR Sample SCT02-098-FM

Mineral Phases Identified by Hazen Research, Inc.	Mineral Phases Identified by SRTC before PCT-A Testing	Mineral Phases Identified by SRTC after PCT-A Testing
$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4)$ (Nosean)	$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4)$ (Nosean)	$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4)$ (Nosean)
$\text{NaAlSiO}_4$ (Nepheline)	$\text{NaAlSiO}_4$ (Nepheline)	$\text{NaAlSiO}_4$ (Nepheline)
$\text{Al}_2\text{O}_3$ (Corundum)	$\text{Al}_2\text{O}_3$ (Corundum)	$\text{Al}_2\text{O}_3$ (Corundum)
$\text{Fe}_2\text{O}_3$ (Hematite)	$\text{Fe}_2\text{O}_3$ (Hematite)	$\text{Fe}_2\text{O}_3$ (Hematite)
	$\text{Fe}_3\text{O}_4$ (Magnetite)	$\text{Fe}_3\text{O}_4$ (Magnetite)

### 6.2 CHEMICAL AND REDOX ANALYSIS

A complete chemical analysis of FBSR Scoping Test 02 Sample SCT02-098-FM was performed using the methods outlined in Section 1.2. The average of the replicate analyses is given in Table VIII. The replicate redox analyses are given in Table IX. The average redox of the two replicate analyses in Table IX were used to calculate the relative proportions of FeO and  $\text{Fe}_2\text{O}_3$  in the steam reformer waste form as given in Table VIII. The values of  $\text{Fe}^{+2}/\Sigma\text{Fe}$  in Table IX and the speciation of this ratio as FeO and  $\text{Fe}_2\text{O}_3$  in Table VIII indicates that the steam reformer product is not overly reducing, e.g. elemental Fe cannot exist, despite the fact that the reformer ran under reducing conditions in the presence of coal as a reductant.

The Cs values in Table VIII appear to be >100% of the amount added in the feed while the Re is about 66% of that added in the feed. Additional tests are being performed to see if this is analytic sensitivity at these low concentrations or sampling variability of the product. Based on the analysis provided in Table VIII, a waste loading of 27 wt% was calculated by assuming that all of the SiO<sub>2</sub>, all of the Al<sub>2</sub>O<sub>3</sub> and all of the Fe<sub>2</sub>O<sub>3</sub> and FeO are waste form additives.

Table VIII. Chemical Analysis of FBSR Sample SCT02-098-FM

<b>Analytic Method</b>	<b>Oxide</b>	<b>Wt%</b>
ICP-ES	Al <sub>2</sub> O <sub>3</sub>	31.7436
ICP-ES	B <sub>2</sub> O <sub>3</sub>	0.2576
ICP-ES	CaO	0.7332
ICP-ES	Cr <sub>2</sub> O <sub>3</sub>	0.0716
ICP-MS	Cs <sub>2</sub> O	0.0029
ICP-ES/Redox	Fe <sub>2</sub> O <sub>3</sub>	5.4471
ICP-ES/Redox	FeO	0.8749
ICP-ES	K <sub>2</sub> O	0.6975
ICP-ES	La <sub>2</sub> O <sub>3</sub>	0.0117
ICP-ES	Na <sub>2</sub> O	19.8156
ICP-ES	NiO	0.0814
ICP-ES	P <sub>2</sub> O <sub>5</sub>	0.2176
ICP-ES	PbO	0.0248
ICP-MS	PbO	0.0175
ICP-MS	ReO <sub>2</sub>	0.0005
ICP-ES	SiO <sub>2</sub>	34.8706
ICP-ES	SO <sub>4</sub>	1.1175
IC	NO <sub>2</sub>	<0.0005
IC	NO <sub>3</sub>	<0.0005
	SUM	95.9681

Table IX. Replicate Redox Analyses of FBSR Sample SCT02-098-FM

<b>Analysis</b>	<b>EA Standard</b>	<b>AN107-A</b>	<b>AN107-B</b>
Fe <sup>+2</sup>	0.088	0.058	0.056
ΣFetotal)	0.458	0.377	0.376
Fe <sup>+2</sup> /ΣFe	0.192	0.154	0.149

### 6.3 PRODUCT CONSISTENCY TESTING

The PCT-A was performed in triplicate on sample SCT02-098-FM in conjunction with glass durability standards, e.g. the ARM-1 and EA glasses. Stainless steel vessels (304L) were used as specified in the PCT-A leaching protocol. The PCT response was calculated as indicated in Equation 3.

$$NL_i = \frac{c_i(\text{sample})}{(f_i) \bullet (SA/V)} \quad (3)$$

where  $NL_i$  = normalized release (g<sub>waste form</sub>/ m<sup>2</sup>)  
 $c_i$  (sample) = concentration of element "i" in the solution (g<sub>i</sub>/L)  
 $f_i$  = fraction of element "i" in the unleached waste form (unitless)  
 $SA$  = surface area of the final waste form in m<sup>2</sup>  
 $V$  = leachate volume in m<sup>3</sup>/L

The logarithm of the  $NL_i$  was taken for each replicate and then averaged per ASTM C1285-02 (PCT-A protocol).

The PCT responses measured in this study for Sample SCT02-098-FM and the standard glasses tested are summarized in Table X. It is evident that the leach testing was in control as the response for the EA glass is within the allowable standard deviations of the reference response shown in Table X.

The leaching of Sample SCT02-098-FM demonstrates that the normalized Na release is 1.74 g/m<sup>2</sup> within the 2 g/m<sup>2</sup> Hanford specification. In addition, it is obvious that the AN-107 FBSR waste form leaches incongruently instead of congruently\* as most vitrified waste forms. Incongruent dissolution of a waste form means that some of the dissolving species are released preferentially to others. Incongruent dissolution is diffusion-controlled and can be either surface reaction-limited under conditions of near saturation or mass transport-controlled. Mass transport is considered to include diffusion control either within the solid or

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\* Congruent dissolution of a waste form means that the dissolving species are released 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. In a system open to mass transport (for congruent or incongruent leaching), the release of a radionuclide from a waste package is a function of the rate of release from the waste form and the rate of transport away from the waste form surface. In the case where the dissolution rate is faster than the transport rate, a solubility limiting secondary phase will precipitate and set a "solubility limit" for the radionuclide. If the transport rate is faster than the dissolution rate, then saturation with a secondary phase will not occur and the release of the radionuclide from the waste package is a function of the dissolution rate of the waste form, e.g. "surface reaction limits."

across diffusion barriers and subsequent mass transport within the fluid phase. 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 ceramic waste form.<sup>20</sup>

Incongruent dissolution is only detrimental to a waste form if a radionuclide species is released preferentially to a matrix element. In the FBSR final waste form the radionuclide release (Cs and Re) is retarded preferentially to the matrix element, Na, release (Table X).

Therefore, the release of Cs and Re an order of magnitude lower than the release of Na indicates that the Cs and Re are likely bonded differently or in different phases than the Na. Hence, Cs and Re leach at a different, slower, incongruent rate similar to the release of Si and Al (Table X), rather than to Na. This is noteworthy because the Hanford specification for Na release for vitrified waste forms is an indicator for the congruent release of Tc<sup>99</sup> since Na and B and Tc<sup>99</sup> are all released at similar stoichiometric rates (congruently) from vitrified waste forms.<sup>33,34,35,36,37,38,39,40,41,42,43,44</sup> The incongruent release of Cs and Re is not attributed to the use of stainless steel vessels as numerous studies have shown that neither Cs nor Tc<sup>99</sup> have an affinity for stainless steel vessels.<sup>39,33</sup>

Table X PCT Performance of Sample SCT02-098-FM and the Glass Standards Tested Compared to the Durability Response of Known Standards and Other Glasses

Sample	pH	NL(B) g/m <sup>2</sup>	NL(Na) g/m <sup>2</sup>	NL(Cs) g/m <sup>2</sup>	NL(Re) g/m <sup>2</sup>	NL(Si) g/m <sup>2</sup>	NL(Al) g/m <sup>2</sup>
EA	11.64	7.76	6.05			2.21	0.09
ARM-1	10.47	0.29	0.27			0.15	0.09
AN-107	11.95	1.27	1.74	0.16	0.29	0.35	0.46
EA REF	11.85	8.37	6.67			1.96	
LAW REF	10.90	0.55	0.54			0.16	0.14
AN-102 RAD	10.60	0.29	0.35			0.12	

The solids remaining after PCT testing were analyzed by X-ray Diffraction and all of the same phases were present as before PCT testing (see Table VII and Figure 2).

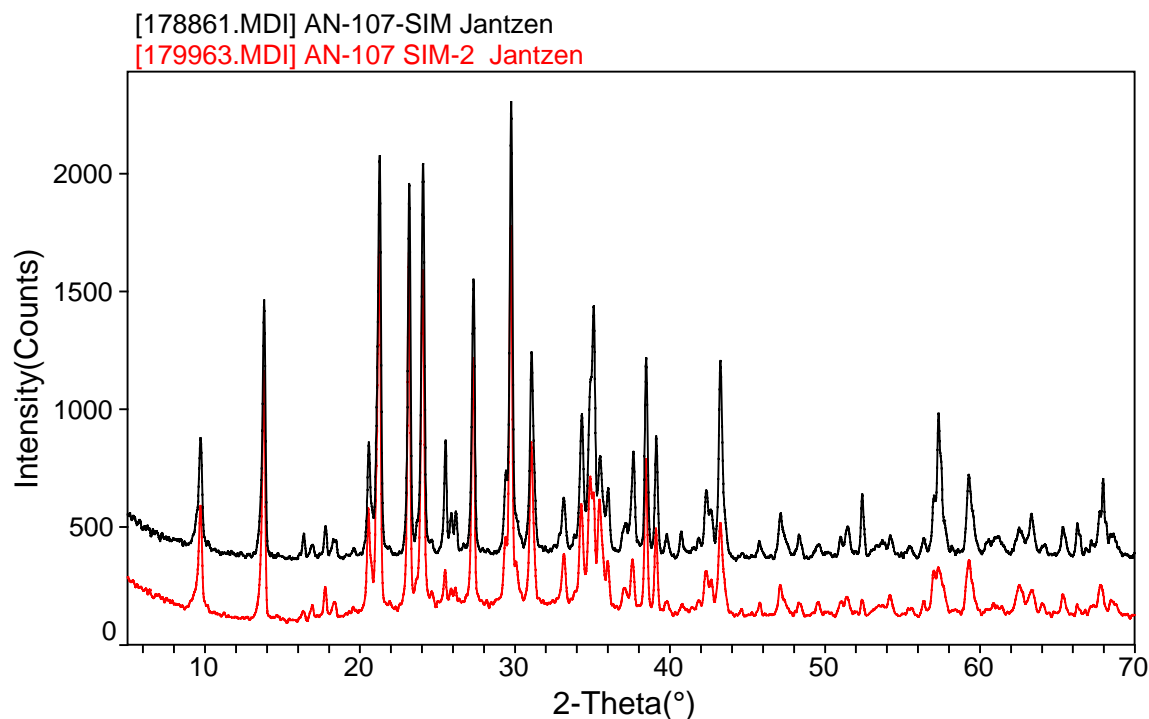


Figure 2. Comparison of X-Ray Diffraction Spectra Before and After PCT Leaching.

## 7.0 REGULATORY TESTING OF FBSR WASTE FORM

The mineral phases formed during the FBSR process were subject to the EPA TCLP leaching protocol. All of the mineral phases, regardless of particle size, appear to have met the characteristically hazardous TCLP limits given in Table XI Column A below for the inorganic species. However, the U.S. Environmental Protection Agency (EPA) revised the Resource Conservation and Recovery Act (RCRA) Phase IV Land Disposal Restrictions (LDR's) on May 26, 1998 which requires characteristically hazardous wastes (raw waste that fails TCLP at the values in Table IV Column A) to be treated to meet the LDR Universal Treatment Standards (UTS) prior to land disposal (TCLP values in Table IV Column B). Since 1994, listed wastes, such as the Hanford LAW which is listed by process history, must be treated to the Universal Treatment Standard (UTS) limits (Table IV Column B). The data provided by Hazen Research to determine if the Cr and Pb met the more stringent UTS limits in Column B of Table XI indicated that all samples passed TCLP at the UTS limits.

Delisting the final LAW waste form may also be accomplished by delisting the final waste form at the point of generation so that the UTS are not applicable. The EPA calculates delisting levels and risk levels for a given waste form using their DRAS code (EPACMTP

model) for calculation of major pathways for human exposure to a given waste. If the allowable concentrations in the TCLP leachate of the waste, as calculated by DRAS, are higher than the Toxicity Characteristic (TC) level for the TC constituents in Table IV, then the delisting level for the TC constituents can be capped at the TC regulatory limits given in Table IV Column A. The UTS levels may or may not apply to a delisted waste. This is still highly debated even within the EPA. However, a waste form that meets the EPA UTS treatment standard limits should be easily delisted.

Table XI. TCLP Characteristically Hazardous and Universal Treatment Standard (UTS) Limits

	<b>A</b>	<b>B</b>
	<b>Characteristic TCLP Limits 40CFR268.40 (ppm)</b>	<b>UTS TCLP Limits (ppm) Federal Register, V.63, No. 100 p.28748-9 May 28, 1998</b>
<b>As</b>	5.0	5.0
<b>Ba</b>	100.0	21
<b>Cd</b>	1.0	0.11
<b>Cr</b>	5.0	0.60
<b>Pb</b>	5.0	0.75
<b>Hg</b>	0.2	0.025
<b>Se</b>	1.0	5.7 (1.0)*
<b>Ag</b>	5.0	0.14
<b>Zn</b>	---	4.3
<b>Ni</b>	---	11
<b>Sb</b>	---	1.15
<b>Be</b>	---	1.22
<b>Tl</b>	---	0.20
<b>V</b>	---	1.6

\* 1.0 or still hazardous

The results of Hazen Research, Inc. TCLP testing is provided in Table XII for produced under reducing FBSR (Scoping Test 01 and Production Test 02) and oxidizing FBSR conditions (Production Test 01) since no TCLP testing had been performed on sample SCT02-098-FM from Scoping Test 02.

Table XII. TCLP Testing of FBSR Scoping Samples for Run 1 of the same Composition as Scoping Samples for

<b>Element of Concern</b>	<b>Ranges of TCLP Releases for FBSR Under Reducing Conditions</b>	<b>TCLP Releases for FBSR Under Reducing Conditions</b>	<b>Final UTS TCLP Limits Federal Register, V.63, No. 100 p.28748-9 May 28, 1998</b>
<b>As</b>	Not in simulant	Not in simulant	5.0
<b>Ba</b>	Not in simulant	Not in simulant	21
<b>Cd</b>	Not in simulant	Not in simulant	0.11
<b>Cr</b>	0.015-0.060	0.001-0.018	0.60
<b>Pb</b>	0.005-0.023	0.002-0.067	0.75
<b>Hg</b>	Not in simulant	Not in simulant	0.025
<b>Se</b>	Not in simulant	Not in simulant	5.7 (1.0)*
<b>Ag</b>	Not in simulant	Not in simulant	0.14
<b>Zn</b>	Not in simulant	Not in simulant	4.3
<b>Ni</b>	0.001-3.11	0.66-2.80	11
<b>Sb</b>	Not in simulant	Not in simulant	1.15
<b>Be</b>	Not in simulant	Not in simulant	1.22
<b>Tl</b>	Not in simulant	Not in simulant	0.20
<b>V</b>	Not in simulant	Not in simulant	1.6

\* 1.0 or still hazardous



## 8.0 CONCLUSIONS

The following can be concluded about the use of Fluidized Bed Steam Reforming (FBSR) as a final waste form for Hanford's LAW waste:

- FBSR is a robust technology capable of accommodating wide ranges of feeds and additives including high concentrations of sulfate
- FBSR's ability to retain sulfate will lead to increased waste loadings and accelerated stabilization of Hanford's LAW vs. LAW vitrification
- FBSR is a continuous throughput technology (not a batch operation) allowing for accelerated solidification of Hanford's LAW wastes
- FBSR's mineral waste species exhibit a superior durability to LAW glass in both ASTM C1285 and EPA TCLP testing
- FBSR's durability is incongruent and the radionuclides (Cs and Re as simulants for Cs<sup>137</sup> and Tc<sup>99</sup>) are released at a rate lower than that of Na (Na release is <2 g/m<sup>2</sup>)
- FBSR is a medium temperature process low enough not to vaporize radionuclides but high enough to destroy volatile organic compounds (VOC's) in the presence of a reductant and a catalyst
- FBSR is efficient at volatilizing VOC's
- FBSR off-gases are MACT compliant, N<sub>2</sub> and CO<sub>2</sub> are produced instead of NO<sub>x</sub> and CO due to redox control and steam reformer operating parameters
- FBSR does not generate acid off-gases as the anions (SO<sub>4</sub><sup>=</sup>, F<sup>-</sup> and Cl<sup>-</sup>) stay in the waste form
- FBSR waste form mineral phases are cage like structures that trap radionuclides and anions
- FBSR waste form mineral phases are known to have survived millions of years in natural surface or near surface environments
- FBSR waste form mineral phases alter to zeolites that have the same cage-like structures and will likely still retain the radionuclides and anions
- FBSR waste forms are regulatory compliant at the Universal Treatment Standard (UTS) making delisting of the final waste form more assured (at an estimated cost savings of \$5952/ft<sup>3</sup> for disposal)<sup>f</sup>

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<sup>f</sup> Disposal of listed mixed waste at the SRS is \$6000/ft<sup>3</sup> while disposal as radioactive (low level) waste once the waste is delisted costs only \$42/ft<sup>3</sup> (Site Training Radiological Worker Training Study Guide, Rev. 11, Westinghouse Savannah River Company (1997).

## **9.0 RECOMMENDATIONS**

On the basis of this feasibility review and durability testing, the fluidized bed steam reforming (FBSR) technology should be further evaluated as a final waste form for Hanford LAW wastes. This technology combines the best processing attributes of previously studied supercalcine, glass-bonded ceramics, and hydroceramic waste forms and is thus scientifically founded. The cage like feldspathoid mineral phases are potentially better radiophases than the previous aluminosilicates studied and they are not prone to H<sub>2</sub> generation from radiolytic decomposition of H<sub>2</sub>O containing waste forms such as hydroceramics.

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## APPENDIX A. QUALIFICATIONS OF AUTHOR (C. M. JANTZEN)

### **Educational Background:**

B.S.	Geology 1967 Queens College of the City University of New York
M.S.	Geochemistry 1970 Queens College of the City University of New York
1969-70	Department of Geochemistry, The Pennsylvania State University
Ph.D.	Materials Science & Engineering (glass chemistry) 1978 State University of New York at Stony Brook

### **Professional Background:**

1977-1979	University of Aberdeen, Department of Chemistry, Postdoctoral Research Fellow. Responsible for development of cementitious waste forms for stabilization of US and UK high level nuclear wastes.
1979-1981	Rockwell International Science Center, Member of the Technical Staff. Responsible for development of ceramic waste forms for high level nuclear wastes. Included supercalcine ceramics, high Al containing ceramics, and Synroc C and D ceramics.
1981-1982	Bechtel Group, Senior Engineer. Responsible for materials selection decisions for the Defense Waste Processing Facility (DWPF) and design review of high level waste processes for the Japanese.
1982-present	Savannah River Technology Center (Westinghouse Savannah River Co. and E.I. duPont deNemours & Co.), Sr. Advisory Scientist. Responsible for glass chemistry and formulation for stabilization of high level, hazardous and mixed wastes at various DOE/DOD sites and in the commercial sector. Research in glass physical property measurements, glass decomposition mechanisms, glass leaching and dissolution mechanisms. Development of statistical process/product control by which the DWPF and the Transportable Vitrification System (TVS) currently operate.
1989-present	Clemson University, Department of Ceramic Engineering. Adjunct Professor
1988-present	South Carolina State Registered Geologist



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**Professional Society Activities:**

- 1970-present Member of American Ceramic Society (ACerS; Nuclear, Glass, and Basic Science Divisions; Contributing Editor Phase Diagrams for Ceramists from 1982-1994; Associate Editor, Journal of the American Ceramic Society from 1982-present)
- 1996-1997 President American Ceramic Society
- 1991-1997 Executive Committee (VP, Treas. Pres. Elect)/Board of Trustees, ACerS
- 1982-present National Institute of Ceramic Engineers
- 1979-present Materials Research Society (1989-91 Executive Committee; 1991-93 Council)
- 1967-present Mineralogic Society of America

**National/International Committees:**

- 1997-2000 National Research Council of the National Academy of Sciences Commission on Physical Science, Mathematics and Astronomy
- 1987-present ASTM committee C14 on Glass and Glass Standards
- 1987-present ASTM committee C26 on Nuclear Fuel Cycle (developer of PCT)
- 1992-1996 ASTM committee D34 on Waste Management (1992-1994-chaired subcommittee on mixed waste standards)

**Honors/Awards:**

- 1975 NATO Grant to examine phase transformations of high temperature oxides and glasses by small angle neutron scattering at Kernforschungsanlage (KFA), Jülich, W. Germany
- 1981 Winner of American Ceramic Society Nuclear Division Best Paper Award
- 1990 Fellow, ACerS
- 1992 George Westinghouse Corporate "Gold" Signature Awards of Excellence  
1994  
1996 (highest corporate award achievable at national level)

1993	ASTM Committee C26 Achievement Award
1997	Citizens for Nuclear Technology Awareness (CNTA) Distinguished Scientist
1999	Celebrating Women in Engineering” Nationwide Awardee, American Society Mech. Engineers (ASME) Section at City University of New York, NY
1998	Queens College Alumni Star Awardee, Queens College, NY,NY
2000	State University of New York at Stony Brook, Distinguished Alumna
2000	Alfred University Scholes Lecture Award in Industrial Ceramic Engineering

**Publications/Patents:**

~200 external publications; 7 U.S. patents

**Selected Publications in Ceramic and Cement Waste Form Development & Durability**

Jantzen, C.M., Clarke, D.R., Morgan, P.E.D. and Harker, A.B., "**Leaching of Polyphase Nuclear Waste Ceramics: Microstructural and Phase Characterization,**" J. Am. Ceram. Soc., 65[6], 292-300 (1982).

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Jantzen, C.M. **"Evaluation of Experimental Factors That Influence the Application and Discrimination Capability of the Product Consistency Test,"** U.S. DOE Report WSRC-TR-90-526, 54p (1990).

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Jantzen, C.M. and Brown, K.G., **“Statistical Process Control of Glass Manufactured for the Disposal of Nuclear and Other Wastes,”** Am. Ceramic Society Bulletin, 72, 55-59 (May, 1993).

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