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Radioactive Demonstrations of Fluidized Bed Steam Reforming (FBSR) as a Supplementary Treatment for Hanford's Low Activity Waste (LAW) and Secondary Wastes (SW) - #11593

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ABSTRACT

The U.S. Department of Energy's Office of River Protection (ORP) is responsible for the retrieval, treatment, immobilization, and disposal of Hanford's tank waste. Currently there are approximately 56 million gallons of highly radioactive mixed wastes awaiting treatment. A key aspect of the River Protection Project (RPP) cleanup mission is to construct and operate the Waste Treatment and Immobilization Plant (WTP). The WTP will separate the tank waste into high-level and low-activity waste (LAW) fractions, both of which will subsequently be vitrified.

The projected throughput capacity of the WTP LAW Vitrification Facility is insufficient to complete the RPP mission in the time frame required by the Hanford Federal Facility Agreement and Consent Order, also known as the Tri-Party Agreement (TPA), i.e. December 31, 2047. Therefore, Supplemental Treatment is required both to meet the TPA treatment requirements as well as to more cost effectively complete the tank waste treatment mission. The Supplemental Treatment chosen will immobilize that portion of the retrieved LAW that is not sent to the WTP's LAW Vitrification facility into a solidified waste form. The solidified waste will then be disposed on the Hanford site in the Integrated Disposal Facility (IDF). In addition, the WTP LAW vitrification facility off-gas condensate known as WTP Secondary Waste (WTP-SW) will be generated and enriched in volatile components such as Cs-137, I-129, Tc-99, Cl, F, and SO₄ that volatilize at the vitrification temperature of 1150°C in the absence of a continuous cold cap. The current waste disposal path for the WTP-SW is to recycle it to the supplemental LAW treatment to avoid a large steady state accumulation in the pretreatment-vitrification loop.

Fluidized Bed Steam Reforming (FBSR) offers a moderate temperature (700-750°C) continuous method by which LAW and/or WTP-SW wastes can be processed irrespective of whether they contain organics, nitrates, sulfates/sulfides, chlorides, fluorides, volatile radionuclides or other aqueous components. The FBSR technology can process these wastes into a crystalline ceramic (mineral) waste form. The mineral waste form that is produced by co-processing waste with kaolin clay in an FBSR process has been shown to be as durable as LAW glass. Monolithing of the granular FBSR product is being investigated to prevent dispersion during transport or burial/storage but is not necessary for performance.

A Benchscale Steam Reformer (BSR) was designed and constructed at the Savannah River National Laboratory (SRNL) to treat actual radioactive wastes to confirm the findings of the non-radioactive FBSR pilot scale tests and to qualify the waste form for applications at Hanford. Radioactive testing commenced in 2010 with a demonstration of Hanford's WTP-SW where Savannah River Site (SRS) High Level Waste (HLW) secondary waste from the Defense Waste Processing Facility (DWPF) was shimmed with a mixture of I-125/129 and Tc-99 to chemically resemble WTP-SW. Ninety six grams of radioactive product were made for testing. The second campaign commenced using SRS LAW chemically trimmed to look like Hanford's LAW. Six hundred grams of radioactive product were made for extensive testing and comparison to the non-radioactive pilot scale tests. The same mineral phases were found in the radioactive and non-radioactive testing.

INTRODUCTION

The WTP LAW vitrification facility is insufficient to complete the RPP mission in the time frame required by the TPA as the LAW will be generated at over twice the rate that the currently designed LAW vitrification facility can process the waste. Either a second LAW vitrification facility or another supplemental LAW treatment technology is needed to meet schedule and tank closure deadlines. In addition, the LAW melter off-gas condensate known as WTP Secondary Waste (WTP-SW) will be generated from the WTP vitrification facility and there is no current waste disposal path for the WTP-SW. The WTP-SW is enriched in components such as Cs-137, I-129, Tc-99, Cl, F, and SO₄ that volatilize at the vitrification temperature of 1150°C in the absence of a continuous cold cap.

Fluidized Bed Steam Reforming (FBSR) offers a moderate temperature (700-750°C) continuous method by which LAW and/or WTP-SW wastes can be processed. The FBSR technology can process these wastes into a crystalline ceramic (mineral) waste form that is granular. The granular mineralized waste form that is produced by co-processing waste with kaolin clay in an FBSR process has been shown to be as durable as LAW glass. Monolithing of the granular FBSR product can be used to prevent dispersion during transport or burial/storage but is not necessary for performance. Considerable durability testing by SRNL and PNNL: see Table 1 and reference 1 for a summary of the work already performed and currently in progress including a demonstration of preliminary acceptance in the Hanford Integrated Disposal Facility (IDF).

Performance Assessment Comparisons: “As Durable as Glass”

The NAS waste form is primarily composed of nepheline (ideally NaAlSiO₄) and the sodalite family of minerals (ideally Na₈[AlSiO₄]₆(Cl)₂ which includes nosean (ideally Na₈[AlSiO₄]₆SO₄). Semi-volatile oxyanions such as ReO₄⁻, TcO₄⁻, are expected to replace sulfate in the larger cage structured nosean and halides such as I⁻ and F⁻ are expected to replace chlorine in the nosean-sodalite mineral structures – immobilizing them. The release of semi-volatile radionuclides Tc-99 and I-129 from granular NAS waste forms was hypothesized during preliminary performance testing to be limited by nosean solubility as the Re releases during durability testing tracked the sulfate releases. [7,8,9] The predicted performance of the NAS waste form was found to be equivalent or better than the glass waste form in the initial supplemental LAW treatment technology risk assessment in the granular form [9]. The granular product can be macro-encapsulated to meet transportation and disposal requirements but this is not necessary for performance.

Mineral Waste Forms: “Historical Perspective Vs Commercialization”

Crystalline (ceramic/mineral) waste forms made by moderate temperature (700-750°C) thermal treatment have not been as intensely investigated as those formed at high temperatures (1000-1500°C) by pressing and sintering (SYNROC, supercalcine ceramics, tailored ceramics, and Pu ceramics) [2]. However, crystalline waste forms made from clay have been studied almost continuously since 1953 [2,3]. Often the high temperatures used for sintering created sodalite-cancrinite mineral assemblages. In 1981, Roy [4] proposed low temperature hydrothermally processed low solubility phase assemblages consisting of the micas, apatite, pollucite, sodalite-cancrinite, and nepheline, many of which could be made from reaction of various clays (kaolin, bentonite, illite) with waste.

Table 1. Sources of FBSR Granular/Monolith Product Durability Testing.

Pilot Scale Facility	Date	FBSR Diam.	Acidic and Basic Wastes	Granular PCT Testing	TCLP Granular Form	Granular SPFT Testing	Preliminary Performance Assessment	Product Tested	Coal	PSD	Monolith	Monolith PCT Testing	Monolith SPFT Testing	Monolith ANSI 16.1/ASTM C1308/EPA 1315 Testing	TCLP of Monolithic Form
NON-RADIOACTIVE TESTING															
HRI/TTT	12/01	6"	LAW Env. C	Ref. 5	Ref 5, 6	Ref 7,8 (also PUF testing)	Ref. 9	Bed	Removed By Hand	Gaussian	NO	N/A	N/A	N/A	N/A
	Ref 6 below	6"	LAW Env. C	Ref 10,11,12	Ref 10,11,12	None	None	Fines	Removed by 525 °C Roasting	Gaussian	NO	N/A	N/A	N/A	N/A
SAIC/STAR	7/03 Ref 13	6"	SBW	Ref 10,11,12	Ref 10,11,12	None	None	Bed	Removed by 525 °C Roasting	Gaussian	Yes (Samples were combined; 20% LAW, 32 % SBW and 45% Startup Bed	Ref 14,15	NO	NO	NO
SAIC/STAR	8/04 Ref. 16	6"	LAW Env. A	Ref 10,11,12	Ref 10,11,12	Ref 12,17,18	Data from Ref 12,17,18 being used	Bed and Fines Separate	Removed by 525 °C Roasting	Gaussian			NO	NO	NO
SAIC/STAR	7/04 and 11/04 Ref. 19	6"	SBW	Ref 10,11,12	Ref 10,11,12	Ref 12,17	None	Bed and Fines Separate	Removed by 525 °C Roasting	Gaussian			NO	NO	NO
HRI/TTT	12/06	15"	SBW	Ref 20	Ref 20	None	None	Bed and Fines Separate	Removed by 525 °C Roasting	Gaussian	NO	N/A	N/A	N/A	N/A
HRI/TTT	2008 Ref. 21	15"	LAW Env. A	Ref 22	Ref 22	FY11	FY11	Bed and Fines Together	Not removed	Bi-Modal	YES	Ref. 23	FY11	FY11	FY11
		15"	WTP-SW (melter recycle)	Ref 22	Ref 22	None	None	Bed and Fines Together	Not removed	Bi-Modal	YES		FY11	FY11	FY11
RADIOACTIVE TESTING															
SRNL/BSR	2010	2.75"	WTP-SW (melter recycle)	This study	FY11	FY11	FY11	Fines	Not removed	Gaussian	FY11	FY11	None	FY11	FY11
SRNL/BSR	2010	2.75"	LAW Env. A	This study	FY11	FY11	FY11	Fines	Not removed	Gaussian	FY11	FY11	None	FY11	FY11

FBSR – Fluidized Bed Steam Reformer; PCT – product consistency test method (ASTM C1285-08); TCLP – toxic characterization leachate procedure; SPFT – single pass flow-through test method (ASTM C1662); ANSI16.1/ASTM C1308/EPA 1315 – monolith emersion tests all similar with different leachate replenishment intervals; HRI/TTT – Hazen Research Inc/THOR Treatment Technologies; SAIC/STAR – Science Applications International Corporation/Science and Technology Applications Research; LAW Env. – low activity waste envelope A, B, and C; SBW – sodium bearing waste; PSD - particle size distribution; FY11 – Joint program between SRNL, PNNL, ORNL; N/A – not applicable.

Clay based crystalline (ceramic/mineral) waste forms were not pursued in the late 1970's and early 1980's because there was no continuous commercial technology available that could process the waste/clay mixtures in a hydrothermal environment [2]. A commercial facility to continuously process radioactive wastes at moderate temperatures in a hydrothermal steam environment was built by Studsvik in Erwin, Tennessee in 1999 [24,25]. The Erwin facility uses a steam reforming technology designated as the THERMAL ORGANIC REDUCTION (THORSM) process to pyrolyze Cs-137 and Co-60 organic resins from commercial nuclear facilities. The Erwin facility has the capability to process a wide variety of solid and liquid streams including: ion exchange resins, charcoal, graphite, sludge, oils, solvents, and cleaning solutions at radiation levels of up to 400R/hr.

If kaolin clay is added to an alkali-rich waste during FBSR processing a "mineralized" waste form is produced that is composed of various Na-Al-Si (NAS) feldspathoid minerals discussed above, i.e. sodalites are the potential host minerals for the halides; nosean which has a larger cage structure is the host mineral for sulfate or sulfide species, Re and Tc-99; and nepheline sequesters the remaining alkali by nano-scale reaction of the clay and waste. Bench scale, pilot scale, and engineering scale tests have all formed this mineral assemblage with a variety of legacy United States Department of Energy (US DOE) waste simulants. Illite type clay was tested at the bench scale and shown to form dehydroxylated micas (potential host for future used nuclear fuel recycling wastes including lanthanides, Cs, Sr, Ba, Rb, Tl, etc.) by similar nanoscale reaction of clay and waste [26].

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

An FBSR facility is being designed and constructed at the Idaho National Laboratory (INL) for treatment of their Sodium Bearing Waste (SBW) for potential disposal in the Waste Isolation Pilot Plant (WIPP) [13,16] in the US. Another facility is being considered for use at the Savannah River Site (SRS) to convert a salt supernate waste (Tank 48) containing nitrates, nitrites, and insoluble cesium tetraphenyl borate (CsTPB), to carbonate or silicate minerals which are compatible with subsequent vitrification in the DWPF [27,28]. Pilot-scale testing has also included a variety of DOE wastes producing aluminosilicate waste forms for INL's SBW and Hanford's Low Activity Waste (LAW) [6,19] and LAW melter recycle (referred to throughout this paper as Waste Treatment Plant Secondary Waste, WTP SW).

MINERALOGY

The fluidizing steam used in FBSR processing creates a hydrothermal environment which promotes mineral formation. Clays become amorphous at the nano-scale at the FBSR processing temperature because clays lose their hydroxyl groups between 550-750°C which destabilizes the Al atoms in their structure. Once the Al cation is destabilized the clay becomes amorphous and species in the waste "activate" the unstable Al cation to form new mineral structures. The hydrothermal environment created by the steam and the nano-scale reactivity of the clay catalyze mineralization allowing formation and templating at moderate temperatures. Kaolin clay has been found to template the feldspathoids and the illite clays have been found to template the dehydroxylated micas as radionuclide hosts [26]. Additional iron bearing co-reactants can be added during processing to stabilize any multivalent hazardous species present in a waste in durable spinel phases, i.e. Cr, Ni, Pb iron oxide minerals.

The Na-Al-Si (NAS) mineral waste forms are comprised of nepheline (hexagonal $\text{Na}_x\text{Al}_y\text{Si}_z\text{O}_4$ where x, y, and z nominally each are a value of 1) and other feldspathoid mineral phases which have large cages that trap anion constituents such as Na_2SO_4 (nosean), NaF, NaI, NaCl (sodalite nominally $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{Cl}_2)$) Na_2MoO_4 , NaTcO_4 , NaReO_4 . The feldspathoid mineral nepheline has a ring type structure. A second nepheline phase that has been found is a sodium rich cubic derivative, $(\text{Na}_2\text{O})_{0.33}\text{NaAlSiO}_4$,^f with large twelve-fold oxygen cage like voids [29]. Nepheline also accommodates Cs, Sr, Ti, and Ca (Table 2).

The NAS cage structures are typical of sodalite and/or nosean phases where the cavities in the cage structure bond oxyanions and/or radionuclides to the alumino-silicate tetrahedra and to sodium in the mineral structure. The sodalite minerals are known to accommodate Be in place of Al and S_2 in the cage structure along with Fe, Mn, and Zn (Table 2). These cage-structured sodalites were minor phases in High Level Waste (HLW) supercalcine waste forms¹ and were found to retain Cs, Sr, and Mo into the cage-like structure as indicated in Table 2. In addition, sodalite structures are known to retain B [39,30] and Ge [31] in the cage like structures. Waste stabilization at Argonne National Laboratory-West (ANL-W) currently uses a glass-bonded sodalite ceramic waste form (CWF) for containment of I from electrorefiner wastes from the EBR II fast breeder reactor [32,33].

Table 2. Substitutional Cations and Oxy-anions in Feldspathoid Mineral Structures

Nepheline – Kalsilite Structures*	Sodalite Structures**	Nosean Structures
$\text{Na}_x\text{Al}_y\text{Si}_z\text{O}_4$ [40] where $x=1-1.33$, y and z = 0.55-1.1	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaCl})_2$ [40]	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{Na}_2\text{SO}_4)$ [35,40]
KAlSiO_4 [40]	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaF})_2$ [40]	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{Na}_2\text{MoO}_4)$ [34,40]
$\text{K}_{0.25}\text{Na}_{0.75}\text{AlSiO}_4$ [40]	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaI})_2$ [35]	$[\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}][(\text{Ca},\text{Na})\text{SO}_4]_{1-2}$ [36]
$(\text{Na}_2\text{O})_{0.33}\text{NaAlSiO}_4$ [29]	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_2$ [35]	$[(\text{Ca},\text{Na})_6\text{Al}_6\text{Si}_6\text{O}_{24}][(\text{Ca},\text{Na})\text{S},\text{SO}_4,\text{Cl}]_x$ [PDF ^f #17-749]
CsAlSiO_4 [40]	$[\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}](\text{NaReO}_4)_2$ [37]	
RbAlSiO_4 [40]	$[\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}](\text{NaMnO}_4)_2$ [39]	
$(\text{Ca}_{0.5},\text{Sr}_{0.5})\text{AlSiO}_4$ [40]	$(\text{NaAlSiO}_4)_6(\text{NaBO}_4)_2$ [30,38]	
$(\text{Sr},\text{Ba})\text{Al}_2\text{O}_4$ [40]	$\text{Mn}_4[\text{Be}_3\text{Si}_3\text{O}_{12}]\text{S}$ [35]	
KFeSiO_4 [40]	$\text{Fe}_4[\text{Be}_3\text{Si}_3\text{O}_{12}]\text{S}$ [35]	
$(\text{Na},\text{Ca}_{0.5})\text{YSiO}_4$ [39]	$\text{Zn}_4[\text{Be}_3\text{Si}_3\text{O}_{12}]\text{S}$ [35]	
$(\text{Na},\text{K})\text{LaSiO}_4$ [39]		
$(\text{Na},\text{K},\text{Ca}_{0.5})\text{NdSiO}_4$ [39]		

* Iron, Ti^{3+} , Mn, Mg, Ba, Li, Rb, Sr, Zr, Ga, Cu, V, and Yb all substitute in trace amounts in nepheline.[40]

** Higher valent anionic groups such as AsO_4^{3-} and CrO_4^{2-} form Na_2XO_4 groups in the cage structure where X= Cr, Se, W, P, V, and As [39]

^f Powder Diffraction File

^f Powder Diffraction File (PDF) #39-0101

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

ENGINEERING SCALE TESTING OF HANFORD NON-RADIOACTIVE LAW and WTP-SW

Pilot scale testing has proved successful with non-radioactive simulants of LAW and WTP-SW. The pilot scale testing and product characterization were performed using rhenium as a surrogate for technetium. Granular FBSR products made with simulated Hanford Wastes were tested in 2001-2, 2004 and 2008. The 2001-2 testing was performed by THOR[®] Treatment Technologies (TTT) in a 6" diameter pilot scale single reformer with AN-107 simulated waste (Table 1) at Hazen Research Inc. (HRI) in Golden, Colorado. In 2004 a Hanford non-radioactive LAW simulant that represents a 68 tank blend of Hanford wastes was processed in a 6" diameter single reformer at Science Applications International Corporation (SAIC) Science and Technology Applications Research (STAR) in Idaho Falls, Idaho.

The 68 tank blend is known as the Rassat [41] simulant and represents a blend of all the Hanford wastes that could be retrieved by water dissolution from 68 Hanford single-shell tanks that are considered to contain predominantly saltcake waste. The compositions of the all-saltcake-tank blend and the more limited composite of samples were found to be comparable, indicating that the Rassat simulant is likely representative of retrieved Hanford saltcake wastes.

The Rassat simulant was also tested at HRI in a 15" diameter Engineering Scale Technology Demonstration (ESTD) dual reformer at HRI in 2008 (Table 1). The target concentration for the LAW was increased by a factor of 10 for Sb, As, Ag, Cd, and Tl; 100 for Ba and Re (Tc surrogate); 1,000 for I; and 1,000,000 for Cs based on discussions with the DOE field office and the environmental regulators and an evaluation of the Hanford Tank Waste Envelopes A, B, and C.[42] It was determined through the evaluation of the actual tank waste metals concentrations that some metal levels were not sufficient to achieve reliable detection in the off-gas sampling.[21] Therefore, the identified metals concentrations were increased in the Rassat simulant processed by TTT at HRI to ensure detection and enable calculation of system removal efficiencies, product retention efficiencies, and mass balance closure without regard to potential results of those determinations or impacts on product durability response such as TCLP.[21]

A WTP-SW simulant based on melter off-gas analyses from Vitreous State Laboratory (VSL) was also tested at HRI in the 15" diameter ESTD dual reformer at HRI in 2008 (Table 1). The target concentrations for the RCRA metals and Cs were not increased as they were in the Rassat simulant.

Characterization of the 2008 ESTD simulant testing is reported in reference 22 and summarized in Table 1. Prior to the reference 22 studies the FBSR bed products and fines had been studied independently to determine the leaching mechanisms and appropriate leach tests to perform. In reference 22 the FBSR bed products were studied separately and together: it was shown that the mineral phases observed in the high temperature filter (HTF) fines are the same as the mineral phases in the FBSR bed products and have comparable durability. The combined FBSR bed products and fines from the two ESTD campaigns were monolithed in a geopolymer formulation (GEO-7) made from fly-ash, sodium silicate, and NaOH which was chosen from a downselect of different matrices including cements (Portland and 3 high alumina types), Ceramicrete, hydroceramics, and various geopolymers made from kaolin clays. [14,15,23] The durability of the monolithed FBSR waste forms were compared to the granular product responses.[23]

The 2008 ESTD simulant tests [21], including characterization, monolithing, and durability testing [21,22,23] formed the basis for performing the comparative radioactive tests reported on in this study, and referred to as BSR Modules A and B (Table 3).

Table 3. Radioactive Bench-Scale Reformer (BSR) Tests Being Performed at SRNL

BSR Module	Test ID	Source of Radioactive Waste	Amount of Radioactive Product Made (g)
A	SRS WTP-SW	Shim of SRS melter recycle to resemble Hanford WTP- Secondary Waste	96
B	SRS-LAW	Shim of SRS LAW (Tank 50) to resemble Hanford LAW based upon Hanford 68 tank blend	600

EXPERIMENTAL

Non - Radioactive and Radioactive Bench Scale Testing of SRS Wastes

In contrast to most waste form development programs where benchscale research precedes pilot scale testing, the FBSR process has been run at the pilot and engineering scale (Table 1) with simulants but not at the bench scale with either simulants or radioactive wastes. SRNL has successfully operated a Bench scale Steam Reformer (BSR) in the SRNL Shielded Cells (SC).[43,44] The BSR is a unique SRNL design and this radioactive capability does not exist elsewhere. SRNL also has unique expertise, analytical chemistry skills, and equipment for monolithing the granular FBSR product and measuring durability of waste forms. SRNL currently has two BSR's – one for non-radioactive testing and one for radioactive testing.

Testing with the non-radioactive BSR always precedes radioactive testing as the run parameters must be determined so that the product chemistry and the gas reactions in the BSR match those of the ESTD pilot scale operations. In order to ensure this, the non-radioactive BSR product mineralogy is checked after each campaign to be the same as the ESTD mineralogy, the reduction/oxidation (redox) is measured after each campaign to be in the range of 0.2-0.5 $Fe^{+2}/\Sigma Fe$, and the loss-on-ignition (LOI) at 525°C is measured as an indication of the amount of residual coal^f in the product. The LOI is usually in the range of 0-2 percent.

The WTP-SW (Module A SIM) simulant was made with Re as a surrogate for Tc-99 and non-radioactive isotopes of I and Cs. This simulant was tested in the non-radioactive BSR in order to provide (1) optimization of processing parameters for radioactive testing, (2) granular samples for testing the durability response of the BSR product in comparison with the TTT pilot scale product, and (3) granular products to monolith and compare (durability and compressive strength) to the monolithic waste forms prepared from the ESTD pilot.

Likewise, the Rassat simulant (Module B SIM) that was tested in the ESTD TTT pilot at HRI was tested in the non-radioactive BSR in order to provide (1) optimization of processing parameters for radioactive testing, (2) granular samples for testing the durability response of the BSR product in comparison with the TTT pilot scale product, and (3) granular products to monolith and compare (durability and compressive strength) to the monolithic waste forms prepared from the ESTD pilot.

^f coal is used in the FBSR as the source of auto-catalytic heating and this is described in several papers and patents available at www.thortt.com.

Radioactive Bench Scale Testing of Hanford Wastes

A radioactive DWPF melter recycle was evaporated and shimmed to represent WTP-SW (Module A RAD). Ninety six grams of Module A radioactive product were made in the radioactive BSR (Table 3). Subsequently, a radioactive Tank 50 (Module B RAD) sample of SRS salt supernates was shimmed to represent Hanford Rassat LAW. Six hundred grams of Module B radioactive product were made in radioactive BSR (Table 3) for all the extensive “tie-back” testing to the non-radioactive pilot scale tests in 2003-4 and 2008. These radioactive products are undergoing durability testing in both the granular and the monolithic form to provide needed tie backs to durability testing of the non-radioactive Rassat simulant made in the BSR and ESTD for both the granular product and the monolithic waste form. [1,10, 11,12,14,15,17,18,22,23 and Table 1]

Since SRS HLW melter off-gas condensate from DWPF was shimmed to represent the WTP-SW secondary waste and SRS Tank 50 salt supernate was shimmed to represent the Rassat simulant, a comparison of the non-radioactive target compositions and the analyzed shimmed radioactive wastes is given in Table 4. Note that the radioactive wastes were spiked with Re as well as Tc-99 to determine if Re is a good simulant for Tc-99 in these minerals as the oxyanion.[§] In addition, the Re and Tc-99 are being examined by Synchrotron Accelerator testing at the Brookhaven National Laboratory (BNL) to determine the local bonding of the Re, the Tc-99 and I-125/I-129/I-133 in the mineral waste form, i.e. to determine definitively that the Re, Tc-99 and I reside in the sodalite/nosean cage structures. The DWPF recycle and the Tank 50 sample had sufficient Cs-137 that they did not require additional shimming. I-125 and I-129 were added to both radioactive samples in order to detect these elements radiometrically during leach testing. I-133 was added to both in order to perform Synchrotron radiation studies.

Table 4 indicated that there is good agreement between the composition of the shimmed DWPF waste and the target WTP-SW waste. All shim species added are given in italics and shaded in Table 4. There is good agreement between the composition of the shimmed Tank 50 salt supernates and the Rassat simulants except that the Tank 50 composition was ~4X higher in aluminum than the Rassat simulant. In terms of the FBSR minerals formed this will be compensated for by the mineral stoichiometry (variable x and y in Table 2) and the choice of clay which can be chosen to have variable Si:Al ratios.

RCRA metals such as Cr were added to the evaporated SRS melter recycle to match the WTP-SW target but additional RCRA metals were not added to the Tank 50 waste. Recall that the 2008 Rassat simulant that was made into FBSR product at the engineering scale at HRI was doped with 10X the Sb, As, Ag, Cd, and Tl; 100X the Ba and Re (Tc surrogate); 1,000X for I; and 1,000,000X for Cs. These levels were chosen to achieve reliable detection in the off-gas sampling as discussed above without regard to potential results of those determinations or impacts on product durability response such as TCLP. The BSR campaigns, both non-radioactive and radioactive, were shimmed with these excesses of the RCRA metals. Precipitates formed when the solubility of the RCRA species were exceeded in the Tank 50 sample. The precipitates were sampled and identified by X-ray Diffraction as enriched in sodium antimony (+5) hydroxide, lead phosphate and lead carbonate, and barium nitrate. Since the precipitates were primarily RCRA species which had exceeded their solubility, they were filtered out causing the analyzed compositions shown in Table 4 to be lower than the RCRA species added initially.

A process control strategy for the FBSR mineralizing process was developed by SRNL in 2004 and is based on composition control in the Na-Al-Si (NAS) oxide system. The process control strategy is known as MINCALC–Version 3 and has been used to control the SAIC-STAR campaigns, the ESTD campaigns and the BSR campaigns. MINCALC controls the FBSR product in the region of nepheline/sodalite

[§] similar oxyanion size in the VII oxidation state, i.e. 1.702 (TcO₄⁻) and 1.719 (ReO₄⁻)

formation and can be used to calculate the theoretical weight percent of each of the mineral phases (see Table 5). Note that all campaigns are run with excess clay and hence excess Al_2O_3 and SiO_2 appear in the mineral species predictions. Analysis by X-ray Diffraction (XRD) as shown in Figure 1 confirms that the WTP-SW products from the non-radioactive ESTD, Module A SIM and Module A RAD BSR products are indeed higher in sodalite concentration (~39-45 wt% predicted in shaded regions of Table 5) and lower in nepheline (27.42-32.58 wt%) while the Module B SIM and Module B RAD mineralization is predicted to have only ~1.25-1.7 wt% sodalite but is dominated by nosean (11.33-14.20 wt%) and nepheline (63.75-65.01 wt%). Thus the MINCALC predictions and mineral analyses are confirmatory.

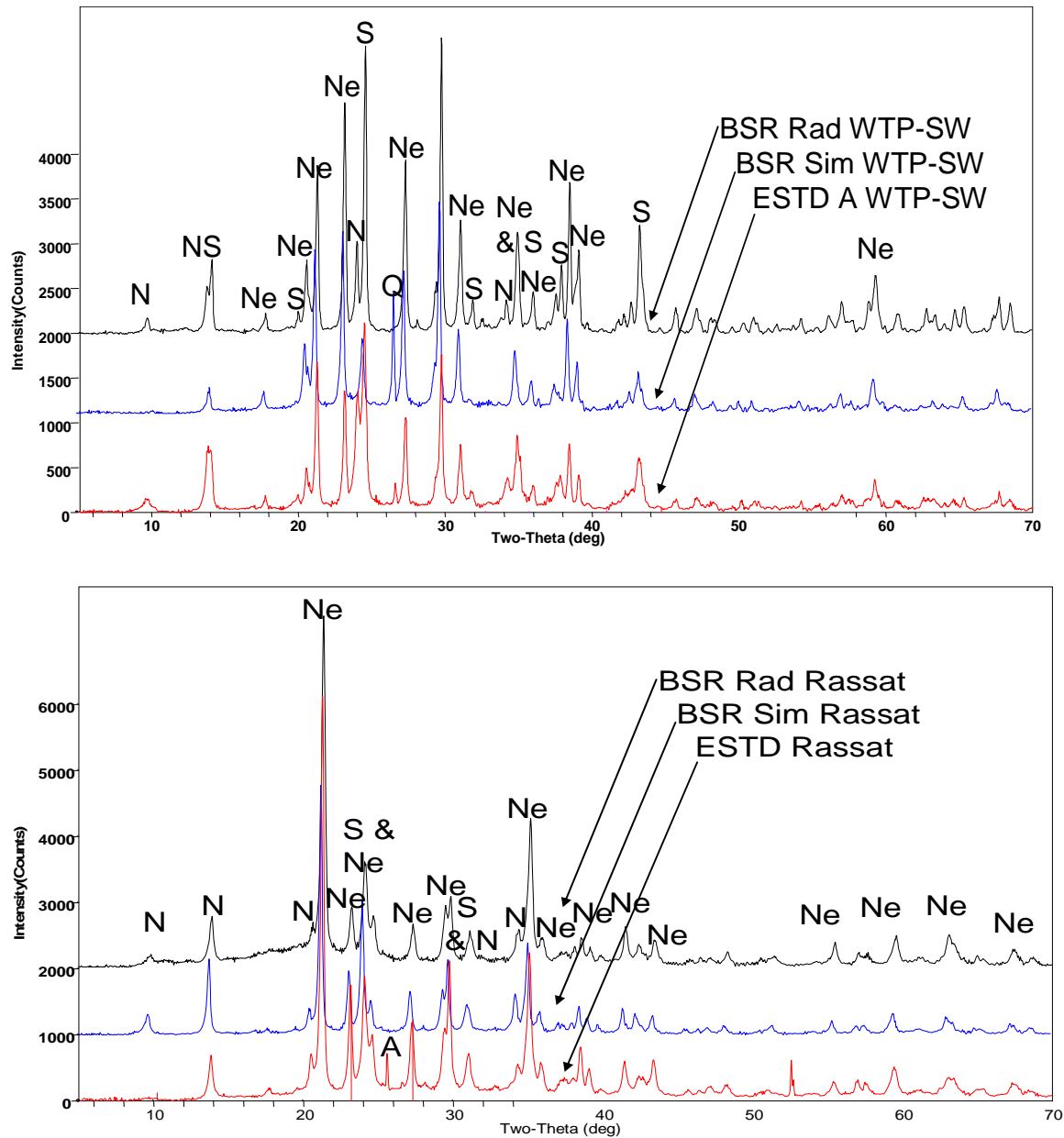


Figure 1. Comparison of mineral phases formed in non-rad 2008 ESTD testing of WTP-SW (top) and LAW (Bottom) to non-radioactive BSR testing and radioactive BSR testing. In all cases the same mineral phases were observed. In WTP-SW more sodalite formed and less nosean while in Rassat testing more nosean and nepheline formed in agreement with Table 5.

Waste Form Durability Testing

For each of the Module A SIM, Module A RAD, Module B SIM, and Module B RAD, the granular products and monoliths made with the granular products are being tested using both short term and long term Product Consistency Tests (ASTM C1285), Single Pass Flow Through Tests (SPFT; ASTM C1662), Pressure Unsaturated Tests (PUF), and monolith immersion tests to determine a forward diffusion rate (ANSI 16.1 or the ASTM variant ASTM C1308) as indicated in Table 1. The EPA toxic characteristic leaching procedure (TCLP) will also be performed and all the results correlated to the non-radioactive pilot scale testing already completed. The testing and waste form qualification is a joint effort between PNNL, ORNL, and SRNL. Preliminary leaching data for Cs and Al in ASTM C1285 testing is given in Figure 2.

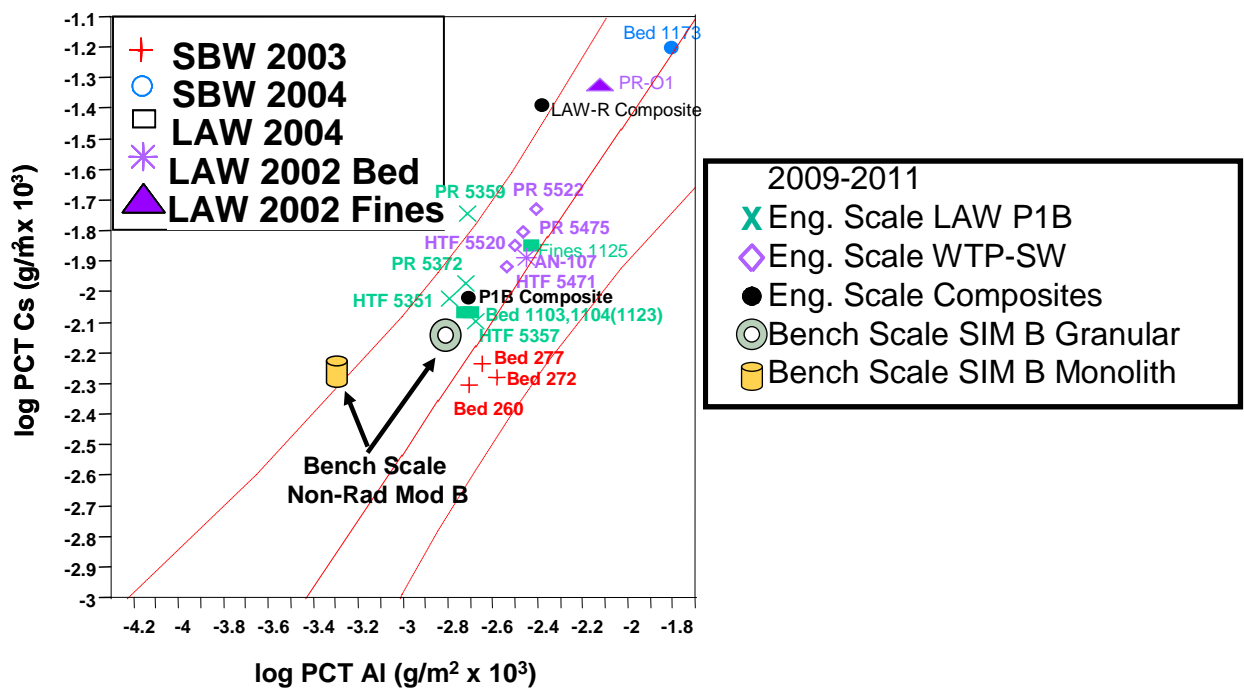


Figure 2. Release rates of Cs and Al developed during 2002-2004 durability testing of pilot scale FBSR product. Data from the 2009-2011 testing of Module B SIM is overlain for comparison.

Table 4. Composition of LAW and WTP-SW Non-Radioactive and Shimmed Radioactive Wastes Tested

		Non-Radioactive Recipe	Non-Radioactive Recipe (Module B SIM)	Analyzed Radioactive (Module B RAD)	Non-Radioactive Recipe (Module A SIM)	Analyzed Radioactive (Module A RAD)
Chemical Name	Element	^b LAW Env. A Rassat simulant 2004 (mol/L)	^{a,b} LAW Env. A Rassat simulant 2008 (mol/L)	Shimmed Tank 50 SRS LAW (mol/L)	Shimmed DWPF Melter Recycle WTP-SW (mol/L)	
Aluminum	Al	0.0637	0.0637	0.2567	0.548	0.4596
Silver	Ag	---	0.00161	<1.74E-05	0.00086	<8.20E-06
Arsenic	As	---	0.00137	6.94E-04	0.00010	8.09E-05 (calc)
Boron	B	---	---	0.0058	0.132	0.16
Barium	Ba	---	0.00751	1.08E-05	0.00002	1.2E-05
Calcium	Ca	---	---	--	---	0.00332
Cadmium	Cd	---	0.0042	4.72E-06	0.00087	6.01E-05
Chromium	Cr	0.0104	0.0104	0.0089	0.00606	0.0067
	Cs-133	5.1E-07	0.013	4.64E-06	0.01469	7.52E-07
	Cs-137	--	--	7.64E-08	--	---
Iron	Fe	---	--	<1.02E-05	---	0.0001
Mercury	Hg	---	---	6.26E-05	---	---
Potassium	K	0.0124	0.0124	0.0140	0.010	0.0135
Lanthanum	La	---	---	<7.2E-06	---	4.5E-06
Lithium	Li	---	---	<2.49E-04	---	0.0036
Magnesium	Mg	---	---	<1.03E-05	---	0.0010
Manganese	Mn	---	---	<2.00E-05	---	0.0004
Sodium	Na	5.0014	5.0161	5.3649	2.668	2.5490
Nickel	Ni	---	0.0106	<3.27E-05	0.00458	9.37E-05
Phosphorus	P	0.0492	0.0492	0.0510	0.007	0.0096
Lead	Pb	---	0.00606	0.0056	0.00131	<9.27E-05
Rhenium	Re	0.0003953	0.0017	0.0016	0.00113	0.00115 (calc)
Antimony	Sb	---	0.00434	0.0002	0.00160	<2.66E-05
Selenium	Se	---	0.00123	1.04E-06	0.00247	---
Silicon	Si	---	---	0.0005	0.018	0.0726

Table 4. Composition of LAW and WTP-SW Non-Radioactive and Shimmed Radioactive Wastes Tested (Continued)

		Non-Radioactive Recipe	Non-Radioactive Recipe (Module B SIM)	Analyzed Radioactive (Module B RAD)	Non-Radioactive Recipe (Module A SIM)	Analyzed Radioactive (Module A RAD)
Chemical Name	Element	^b LAW Env. A Rassat simulant 2004 (mol/L)	^{a,b} LAW Env. A Rassat simulant 2008 (mol/L)	Shimmed Tank 50 SRS LAW (mol/L)	Shimmed DWPF Melter Recycle WTP-SW (mol/L)	
Strontium	Sr	---	---	<9.13E-07	---	1.35E-05
Technetium	Tc	---	---	6.69E-06	---	8.30E-05
Thorium	Th	---	---	<3.99E-05	---	<1.81E-05
Titanium	Ti	---	---	<1.55E-05	---	2.46E-05
Uranium	U	---	---	<3.15E-04	---	0.0005
Zinc	Zn	---	---	0.0001	0.00729	0.0076
Chloride	Cl	0.0438	0.0438	0.0582	0.106	0.094
Fluoride	F	0.0316	0.0316	0.0195	0.219	0.180
Iodide	I-129			2.04E-04		5.25E-05
Iodide	I-125			2.99E-12		5.32E-12
Iodide	I-127	0.000134	0.013	0.0078	0.001	4.22E-05
Sulfate	SO ₄	0.09	0.09	0.1133	0.005	0.0066
Oxalate	C ₂ O ₄	0.0118	0.0118	0.0101	---	---
Acetate	CH ₃ COO	0.132	0.132	N/A	N/A	N/A
Carbonate	CO ₃	0.475	0.475	0.340	0.200	---
Formate	COOH	---	---	0.0056	---	---
Hydroxide	OH	0.739	0.74	0.853	1.564	---
Nitrate	NO ₃	2.31	2.58487	3.8008	1.991	2.060
Nitrite	NO ₂	0.424	0.424	0.0312	0.036	0.003

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

^bLAW simulant used to produce the FBSR samples were based on Rasat et al. (2003)

Table 5. Mineral Speciation Predicted from MINCALC™-Version 3

Mineral Component	Chemical Component	NON-RADIOACTIVE			RADIOACTIVE	
		^b LAW Env. A Rassat simulat Wt%	^{a,b} LAW Env. A Rassat simulat (MOD B SIM) Wt%	WTP-SW (MOD A SIM) Wt%	WTP-SW (MOD A RAD) Wt%	LAW Rassat Tank 50 (MOD B RAD) Wt%
Na Nepheline	Na ₂ Al ₂ Si ₂ O ₈	67.58	63.75	27.42	32.58	65.01
K Nepheline	K _{0.5} Na _{1.5} Al ₂ Si ₂ O ₈ or K ₂ Na ₆ Al ₃ Si ₃ O ₃₂	2.43	2.38	4.94	5.51	2.5
Cl Sodalite	Na ₈ Al ₆ Si ₆ O ₂₄ (Cl ₂)	2.83	2.69	12.96	11.88	3.56
F Sodalite	Na ₈ Al ₆ Si ₆ O ₂₄ (F ₂)	1.97	1.87	25.88	21.84	1.15
I Sodalite	Na ₈ Al ₆ Si ₆ O ₂₄ (I ₂)	1.31	1.25	6.01	5.51	1.65
Nosean	Na ₈ Al ₆ Si ₆ O ₂₄ (SO ₄)	11.93	11.33	1.25	1.70	14.20
Re Sodalite	Na ₈ Al ₆ Si ₆ O ₂₄ (ReO ₄) ₂	0.04	0.15	0.20	0.20	0.14
Tc Sodalite	Na ₈ Al ₆ Si ₆ O ₂₄ (TcO ₄) ₂	---	---	---	0.0133	0.0005
Free Silica	SiO ₂	5.32	7.30	8.00	8.67	4.38
Free Alumina	Al ₂ O ₃	3.49	5.15	8.39	7.02	3.94
SUM		96.89	95.85	95.06	94.93	96.52

CONCLUSIONS

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

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REFERENCES

- 1 Jantzen, C.M., "Mineralization of Radioactive Wastes by Fluidized Bed Steam Reforming (FBSR): Comparisons to Vitreous Waste Forms and Pertinent Durability Testing," SRNL, Aiken, SC(2008).
- 2 Lutze, W. and Ewing, R.C., "Radioactive Waste Forms for the Future," Elsevier Science Publishers, Amsterdam, The Netherlands, 778pp (1988).
- 3 Hatch, L.P., "Ultimate Disposal of Radioactive Wastes," *Am. Scientist*, 41, 410-421 (1953).
- 4 Roy, R., "Hydroxylated Ceramic Waste Forms and the Absurdity of Leach Tests," *Proc. Int. Sem. On Chem. and Process Eng. for High-Level Liquid Waste Solidification*, Vol. 2, Julich, JUL-Conf-42, eds. R. Odoj and E. Merz, 576-602 (1981).
- 5 Jantzen, C.M., "Characterization and Performance of Fluidized Bed Steam Reforming (FBSR) Product as a Final Waste Form," *Ceramic Transactions*, Vol. 155, 319-29, J. D. Vienna, and D.R. Spearing (Eds) (2004).
- 6 Jantzen, C.M., "Engineering Study of the Hanford Low Activity Waste (LAW) Steam Reforming Process," Savannah River Technology Center, Aiken, SC, WSRC-TR-2002-00317, (2002).
- 7 McGrail, B.P., Schaefer, H.T., Marting, P.F., Bacon, D.H., Rodriguez, E.A., McReady, D.E., Primak, A.N., Orr, R.D., "Initial Evaluation of Steam-Reformed Low Activity Waste for Direct Land Disposal," Pacific Northwest National Laboratory, Hanford, WA(2003).
- 8 McGrail, B.P., Pierce, E.M., Schaefer, H.T., Rodriguez, E.A., Steele, J.L., Owen, A.T., Wellman, D.M., "Laboratory Testing of Bulk Vitrified and Steam-Reformed Low-Activity Forms to Support a Preliminary Assessment for an Integrated Disposal Facility," PNNL, Hanford, WA, PNNL-14414, (2003).
- 9 Mann, F.M., Puigh, R.J., Khaleel, R., Finfrock, S., McGrail, B.P., Bacon, D.H., Serne, R.J., "Risk Assessment Supporting the Decision on the Initial Selection of Supplemental ILAW Technologies," PNNL, Hanford, WA, RPP-17675, (2003).
- 10 Pareizs, J.M., Jantzen, C.M., Lorier, T.H., "Durability Testing of Fluidized Bed Steam Reformer (FBSR) Waste Forms for High Sodium Wastes at Hanford and Idaho," SRNL, Aiken, SC, WSRC-TR-2005-00102, (2005).
- 11 Jantzen, C.M., Pareizs, J.M., Lorier, T.H., Marra, J.C., "Durability Testing of Fluidized Bed Steam Reforming (FBSR) Products," 121-37 in *Ceramic Transactions*, V. 176, p.121-137, C. C. Herman, S.L. Marra, D.R. Spearing, L. Vance, and J.D. Vienna (Eds) (2006).
- 12 Jantzen, C.M., Lorier, T.H., Marra, J.C., Pareizs, J.M., "Durability Testing of Fluidized Bed Steam Reforming (FBSR) Waste Forms," WM'06, Tucson, AZ, (2006)
- 13 Marshall, D.W., Soelberg, N.R., Shaber, K.M., "THORsm Bench-Scale Steam Reforming Demonstration," Idaho National Laboratory, Idaho Falls, ID, INEEL/EXT.03-00437, (2003).
- 14 Jantzen, C.M., "Fluidized Bed Steam Reformer (FBSR) Product: Monolith Formation and Characterization," Savannah River National Laboratory, Aiken, SC, WSRC-STI-2006-00033, (2006).
- 15 Jantzen, C.M., "Fluidized Bed Steam Reformer (FBSR) Monolith Formation," WM'07, Tucson, AZ, (2007).
- 16 Olson, A.L., Soelberg, N.R., Marshall, D.W., Anderson, G.L., "Fluidized Bed Steam Reforming of Hanford LAW Using THORsm Mineralizing Technology," INL, Idaho Falls, ID, INEEL/EXT-04-02492, (2004).
- 17 Lorier, T.H., Pareizs, J.M., Jantzen, C.M., "Single Pass Flow through (SPFT) Testing of Fluidized Bed Steam Reforming (FBSR) Waste Forms," SRNL, Aiken, SC, WSRC-TR-2005-00124, (2005).
- 18 Jantzen, C.M., Lorier, T.H., Pareizs, J.M., Marra, J.C., "Fluidized Bed Steam Reformed (FBSR) Mineral Waste Forms: Characterization and Durability Testing," pp. 379-86 in *Scientific Basis for Nuclear Waste Management XXX*. Edited by D. S. Dunn, C. Poinssot, B. Begg. (2007).
- 19 Olson, A.L., Soelberg, N.R., Marshall, D.W., Anderson, G.L., "Fluidized Bed Steam Reforming of INEEL SBW Using THORsm Mineralizing Technology," INL, Idaho Falls, ID, INEEL/EXT-04-02564, (2004).
- 20 Crawford, C.L., Jantzen, C.M., "Durability Testing of Fluidized Bed Steam Reformer (FBSR) Waste Forms for Sodium Bearing Waste (SBW) at INLSRNL, Aiken, SC, WSRC-STI-2007-00319, (2007).
- 21 THOR® Treatment Technologies, Project Number 29387, "Report for Treating Hanford LAW and WTP SW Simulants: Pilot Plant Mineralizing Flowsheet," Document Number RT-21-002, Rev. 1, April 2009.
- 22 Jantzen, C.M., Crawford, C.L., "Mineralization of Radioactive Wastes by Fluidized Bed Steam Reforming (FBSR): Radionuclide Incorporation, Monolith Formation, and Durability Testing," WM'10, Phoenix, AZ, (2010)
- 23 Crawford, C.L. and Jantzen, C.M., "Evaluation of THORTM Mineralized Waste Forms (Granular and Monolith) for the DOE Advanced Remediation Technologies (ART) Phase 2 Project", SRNL-STI-2009-00505, Rev.0 (in review).

- 24 J.B. MASON, T.W. OLIVER, M.P. CARSON, G.M. HILL, WM 99 Conference (1999)
- 25 J.B. MASON, J. McKIBBEN, K. RYAN, D. SCHMOKER, WM03 (2003).
- 26 Jantzen, C.M., Williams, M.R., Bibler, N.E., Crawford, C.L. and Jurgensen, A.R., "Fluidized Bed Steam Reformed (FBSR) Mineral Waste Forms: Application to Cs-137/Sr-90 Wastes for the Global Nuclear Energy Partnership (GNEP)," WSRC-MS-2008-00013 (2008).
- 27 Soelberg, N.R., Marshall, D.M., Bates, S.O., Siemer, D.D., "SRS Tank 48H Steam Reforming Proof-of-Concept Test Report," Idaho National Laboratory, Idaho Falls, ID, INEEL/EXT-03-01118, Rev 1, (2004).
- 28 Jantzen, C.M., "Disposition of Tank 48H Organics by Fluidized Bed Steam Reforming (FBSR)," WSRC-TR-2003-00352, Savannah River Natl. Laboratory, (2003).
- 29 Klingenberg, R. and Felsche, J., "Interstitial Cristobalite-type Compounds (Na₂O)_{0.33}Na[AlSiO₄]," J. Solid State Chemistry, 61, 40-46 (1986).
- 30 Buhl, J.Ch, Englehardt, G. and Felsche, J., "Synthesis, X-ray Diffraction, and MAS n.m.r. Characteristics of Tetrahydroxoborate Sodalite," Zeolites, 9, 40-44 (1989).
- 31 Fleet, M.E., "Structures of Sodium Alumino-Germanate Sodalites," Acta Cryst.C45, 843-847 (1989).
- 32 Sinkler, W., O'Holleran, T.P., Frank, S.M., Richmann, M.K. and Johnson, S.G., "Characterization of a Glass-Bonded Ceramic Waste Form Loaded with U and Pu," Sci.Basis Nucl. Waste Mgt., XXIII, Mat. Res. Soc.: Pittsburgh, PA, 423-429 (2000).
- 33 Moschetti, T.L., Sinkler, W., DiSanto, T. Novy, M.H., Warren, A.R., Cummings, D., Johnson, S.G., Goff, K.M., Bateman, K.J., Frank, S.M., "Characterization of a Ceramic Waste Form Encapsulating Radioactive Electrorefiner Salt," ibid, 577-582 (2000).
- 34 Brookins, D.G., Geochemical Aspects of Radioactive Waste Disposal; Springer-Verlag: NY, 347pp (1984).
- 35 Deer, W.A., Howie, R.A., and Zussman, J., "Rock-Forming Minerals, V. 4," John Wiley & Sons, Inc., NY, 435pp (1963).
- 36 Dana, E.S. "A Textbook of Mineralogy," John Wiley & Sons, Inc., New York, 851pp (1932).
- 37 Mattigod, S.V., McGrail, B.P., McCready, D.E., Wang, L, Parker, K.E. and Young, J.S. "Synthesis and Structure of Perrhenate Sodalite," J. Microporous & Mesoporous Materials, 91 (1-3), 139-144 (2006).
- 38 Tobbens, D.M. and Buhl, J.C. "Superstructure of Sodiumborate Sodalite," Berline Neutron Scattering Center (BENSC) Experimental Report E9, Helmholtz Zentrum fur Materialiene und Energie (formally the Hahn-Meitner Institute), Berlin, Germany (2000).
- 39 Barrer, R.M. "Hydrothermal Chemistry of Zeolites," Academic Press, New York, 360pp (1982): see references by St. J. Thugutt, Z. Anorg. Chem, 2, 65 (1892) and E. Flint, W. Clarke, E.S. Newman, L. Shartsis, D. Bishop and L.S. Wells, J. Res. Natl. Bur. Stds, 36, 63 (1945).
- 40 Deer, W.A. Howie, R.A., Wise, W.S. and Zussman, J., "Rock-Forming Minerals, Vol. 4B, Framework Silicates: Silica Minerals, Feldspathoids and the Zeolites," The Geological Society, London, UK, 982pp (2004).
- 41 Rassat, S.D., Mahoney, L.A., Russell, R.L., Bryan, S.A., Sell, R.L., *Cold Dissolved Saltcake Waste Simulant Development, Preparation, and Analysis*, Pacific Northwest National Laboratory, Hanford, WA, PNNL-14194 Revision 1, (2003).
- 42 Flowsheet Basis and Assumptions Requirements Document, 24590-WTP-RPT-PT-02-005, Rev.3, June 30, 2005
- 43 Burket, P.R., Daniel, W.E., Nash, C.A., Jantzen, C.M., and Williams, M.R., "Bench-Scale Steam Reforming of Actual Tank 48 Waste" US DOE Report SRNL-STI-2008-00105 (September 2008).
- 44 Burket, P.R., Daniel, W.E., Jantzen, C.M., Nash, C.A., Crawford, C.L., Williams, M.R., and Barnes, A.B., "Steam Reforming Technology Demonstration for the Destruction of Organics on Actual DOE Savannah River Site Tank 48H Waste," Paper #9138 WM09.