

Radioactive Demonstrations of Fluidized Bed Steam Reforming (FBSR) with Actual Hanford Low Activity Wastes: Verifying FBSR as a Supplementary Treatment - #12317

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ABSTRACT

The U.S. Department of Energy's Office of River Protection 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 cleanup mission is to construct and operate the Waste Treatment and Immobilization Plant (WTP). The WTP will separate the tank waste into high-level waste (HLW) 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 cleanup mission in the time frame required by the Hanford Federal Facility Agreement and Consent Order, also known as the Tri-Party Agreement (TPA). 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. Fluidized Bed Steam Reforming (FBSR) is one of the supplementary treatments being considered. FBSR offers a moderate temperature (700-750°C) continuous method by which LAW and other secondary wastes can be processed irrespective of whether they contain organics, nitrates/nitrites, sulfates/sulfides, chlorides, fluorides, and/or radio-nuclides like I-129 and Tc-99. Radioactive testing of Savannah River LAW (Tank 50) shimmed to resemble Hanford LAW and actual Hanford LAW (SX-105 and AN-103) have produced a ceramic (mineral) waste form which is the same as the non-radioactive waste simulants tested at the engineering scale. The radioactive testing demonstrated that the FBSR process can retain the volatile radioactive components that cannot be contained at vitrification temperatures. The radioactive and non-radioactive mineral waste forms that were produced by co-processing waste with kaolin clay in an FBSR process are shown to be as durable as LAW glass.

INTRODUCTION

The Hanford Site in southeast Washington State has 56 million gallons of radioactive and chemically hazardous wastes stored in 177 underground tanks [1]. The U.S. Department of Energy (DOE), Office of River Protection (ORP), through its contractors, is constructing the WTP to convert the radioactive and hazardous wastes into stable glass waste forms for disposal. Within the WTP, the pretreatment facility will receive the retrieved waste from the tank farms and separate it into two treated process streams. The pretreated HLW mixture will be sent to the HLW Vitrification Facility, and the pretreated LAW stream will be sent to the LAW Vitrification Facility. The two WTP vitrification facilities will convert these process streams into glass, which is poured directly into stainless steel canisters. The immobilized HLW canisters will ultimately be disposed of at an offsite federal repository. The immobilized LAW canisters will be disposed of on the Hanford site in the Integrated Disposal Facility (IDF).

The projected throughput capacity of the WTP LAW Vitrification Facility is insufficient to complete the River Protection Program (RPP) mission in the time frame required by the Hanford Federal Facility Agreement and Consent Order, also known as the TPA. Without additional LAW treatment capacity, the mission would extend an additional 40 years beyond December 31, 2047, the Tri-Party Agreement milestone date for completing all tank waste treatment. The life-cycle cost of tank waste cleanup is

strongly influenced by the WTP operating duration. A significant life-cycle cost savings incentive exists to complete tank waste treatment processing at the earliest practical date.

Supplemental Treatment is, therefore, required both to meet the Tri-Party Agreement treatment requirements as well as to cost effectively complete the tank waste treatment mission. The Supplemental Treatment Project will design, construct and operate the processes and facilities required to treat and immobilize into a solidified waste form that portion of the retrieved LAW that is not sent to the WTP's LAW Vitrification facility. Four immobilization technologies are under consideration as part of the Supplemental Treatment Program including: (1) second WTP LAW vitrification, (2) bulk vitrification, (3) cementitious solidification (cast stone), and (4) FBSR.

A Supplemental Treatment down select process will be performed and provide a recommendation to ORP of which of the four immobilization technologies to pursue. Following approval of that decision by ORP, the Supplemental Treatment Program will commence a Conceptual Design project to develop a Critical Decision package for the selected immobilization technology in accordance with DOE Order 413.3. Data from the FBSR Waste Form Qualification (WFQ) test program will be needed to support the go / no-go evaluation of waste form performance and the determination of whether the FBSR technology should be included in the subsequent immobilization technology down select process. Radioactive testing of the FBSR process and mineral product were needed for the WFQ of FBSR. The radioactive testing results to date are documented in this manuscript and more details are given elsewhere. [2,3,4,5,6,7,8] In the program described in this manuscript verification testing was performed by researchers at Pacific Northwest National Laboratory (PNNL).

Fluidized bed steam reforming offers a moderate temperature (700-750°C) continuous method by which LAW wastes and/or other supplementary wastes like WTP Secondary Waste (WTP-SW) can be processed. The FBSR technology can process these wastes into a crystalline ceramic (mineral) waste form that is granular. The granular mineralized waste forms that have been produced by co-processing waste with kaolin clay in an FBSR process with simulated wastes have been shown to be as durable as LAW glass (Table I).

Monolithing of the granular FBSR product is being investigated due to regulatory concerns, i.e. to prevent dispersion during transport or burial/storage. Monolithing is not necessary to meet durability performance requirements because the mineral product degrades by the breaking of atomic bonds in the mineral structure in the same fashion that atomic bonds are broken in vitreous waste forms. Thus the long term performance of both glass and mineral waste forms are controlled by a rate drop that is affinity controlled. Considerable durability testing has already been performed by Savannah River National Laboratory (SRNL) and Pacific Northwest National Laboratory (PNNL) on the non-radioactive granular and monolith FBSR forms: see Table I and Reference 9.

MINERALIZATION OF LAW

Principal contaminants of concern contained in the LAW stream that are expected to impact disposal are Tc-99, I-129, U, Cr, and nitrate/nitrite.[14] During the FBSR process the nitrate and nitrites will be converted to N₂ which will exit the process as off-gas. Any organics will be pyrolyzed into CO₂ and steam. The mineral waste form will sequester the radionuclides and an iron oxide (Fe₂O₃-FeO-Fe₃O₄) added as a denitration catalyst will sequester the Cr as FeCr₂O₄ spinel. The spinels can also accommodate Ni, Pb, Mn and other transition metals.

The Na-Al-Si (NAS) based minerals are primarily composed of nepheline (ideally NaAlSiO₄) and the sodalite family of minerals (ideally Na₈[AlSiO₄]₆(Cl)₂) and nosean (ideally Na₈[AlSiO₄]₆SO₄) which will

Table I. References for 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	Particle Size Distrib.	Monolith & Monolith Testing (PCT; TCLP; ANSI16.1; ASTM C1308; EPA1315)
Non-Radioactive Testing											
HRI/TTT	12/01	6"	LAW Env. C	Ref. 10	Ref. 10, 11	Ref. 12,13 (and PUF testing)	Ref. 14	Bed	Removed By Hand	Gaussian	No
	Ref. 11	6"	LAW Env. C	Ref.15,16,17		None	"Tie-back" Strategy	Fines	Removed by 525 °C Roasting	Gaussian	No
SAIC/STAR	7/03 Ref. 18,19	6"	SBW	Ref. 15,16,17			None	Bed		Gaussian	Yes (20% LAW, 32 % SBW and 45% Startup Bed Ref 20,21)
SAIC/STAR	8/04 Ref.22	6"	LAW (68 Tank Blend)	Ref. 15,16,17		Ref. 17,23,24	Data from Ref. 17,23,24 "Tie-back" Strategy	Bed and Fines Separate		Gaussian	
SAIC/STAR	7/04 9/04 Ref.25	6"	SBW	Ref. 15,16,17		Ref. 17,23	None			Gaussian	
HRI/TTT	12/06 26	15"	SBW	Ref. 27		None	None	Bed and Fines Together		Gaussian	No
HRI/TTT	2008 Ref.28	15"	LAW (68 Tank Blend)	Ref. 29 and 30	Ref. 30	Ref. 4	"Tie-back" Strategy		Not removed	Bi-Modal	Yes Ref. 5,6,7, 29,30, 31
		15"	WTP-SW (recycle)	Ref. 29 and 30	Ref. 30	None	None				
Radioactive Testing (This manuscript and additional references that contain more detail)											
SRNL/BSR	2010 2011	2.75"	WTP-SW (recycle)	Ref. 2,3,5,6	Ref. 2,3,5,6	None	None	Bed	Not removed	Gaussian	Ref. 2,3,5,6
SRNL/BSR	2010 2011	2.75"	LAW (68 Tank Blend), SX-105, AN-103	Ref. 2,5,7,8	Ref. 2,5,7,8	PNNL	"Tie-back" Strategy	Bed	Not removed	Gaussian	Ref. 2, 4,5,7,8

PCT – Product Consistency Test method (ASTM C1285-08); TCLP – Toxicity Characteristic Leaching Procedure; SPFT – Single Pass Flow-Through test (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. – Hanford low activity waste envelope A, B, and C; SBW – Idaho Sodium Bearing Waste; FY1 1 – Joint program between SRNL, PNNL, ORNL; N/A – not applicable

sequester the halides (including I-129), the sulfates/sulfides, and oxyanions such as ReO_4^- , TcO_4^- (ideally $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{ReO}_4)_2$). The rhenium sodalite has been made phase pure (Table II) and the phase pure pertechnetate sodalite is being made in the Shielded Cell at the SRNL. The sodalite and nosean minerals have unique aluminosilicate cages that bond the halides and oxyanions atomically into the cage structure.

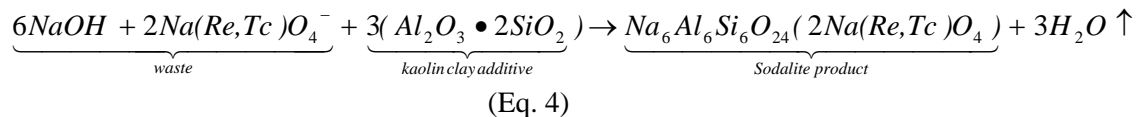
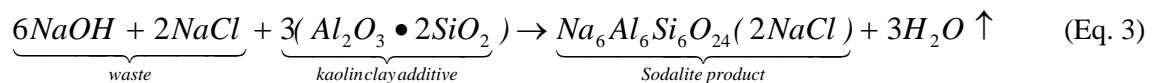
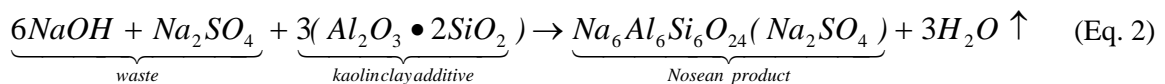
The sodalites are classified [32] as “clathrasils” which are structures with large polyhedral cavities that the “windows” in the cavity are too small atomically to allow the encaged polyatomic ions and/or molecules pass once the structure is formed. They differ from zeolites in that the zeolites have tunnels or larger polyhedral cavities interconnected by windows large enough to allow ready diffusion of the guest species through the crystal.[32] With regard to the substitution of all Si tetrahedra to form the cavities or all Al tetrahedra to form the cavities or a mixture of Si and Al tetrahedra to form the cavities they are all treated as solid solutions with the same cavity structures.[32]

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 II). These cage-structured sodalites were minor phases in HLW supercalcine waste forms (1973-1985) and were found to retain Cs, Sr, and Mo into the cage-like structure. In addition, sodalite structures are known to retain B and Ge in the cage like structures (Table II).

The mineral waste form is produced by co-processing waste with kaolin clay. The cations in the LAW waste; Na, Cs-137, Tc-99, etc, and other species such as Cl, F, I-129, and SO_4 are immediately available to react with the added clay as the clay dehydrates at the DMR temperatures and the aluminum atoms in the clay become charge imbalanced and hence the clay becomes amorphous (loses its crystalline structure) and very reactive at the FBSR temperatures. Stable crystalline clays are known to become reactive amorphous clays when they lose their hydroxyl groups above 550°C . The cations and other species in the waste react with the reactive amorphous meta-kaolin (the term used for dehydrated amorphous clay) to form new stable crystalline mineral structures allowing formation and structural templating at the nano-scale at moderate temperatures as shown by the following reactions:



and for simplicity the remaining reactions are only written for NaOH and not the combined NaOH and sodium nitrates/nitrites:



In addition, nepheline, once formed by reaction of the waste and clay can further react with the waste to form sodalite(s) as shown in the reaction below for rhenium:

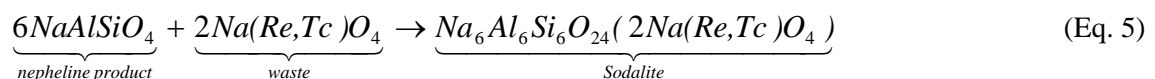


Table II. Substitution of Cations and Oxy-anions in Feldspathoid Mineral Structures

Feldspathoid Minerals		
	Sodalite Family	
Nepheline – Kalsilite Structures ^a	Sodalite Structures ^b	Sulfate Sodalite Nosean Structures
$\text{Na}_x\text{Al}_y\text{Si}_z\text{O}_4$ [41] where $x=1-1.33$, y and $z = 0.55-1.1$	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaCl})_2$ [41]	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{Na}_2\text{SO}_4)$ [34,41]
KAlSiO_4 [41]	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaFl})_2$ [41]	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{Na}_2\text{MoO}_4)$ [33,41]
$\text{K}_{0.25}\text{Na}_{0.75}\text{AlSiO}_4$ [41]	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaI})_2$ [34]	$[\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}][(\text{Ca},\text{Na})\text{SO}_4]_{1-2}$ [35]
$(\text{Na}_2\text{O})_{0.33}\text{NaAlSiO}_4$ [36]	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_2$ [34]	$[(\text{Ca},\text{Na})_6\text{Al}_6\text{Si}_6\text{O}_{24}][(\text{Ca},\text{Na})\text{S},\text{SO}_4,\text{Cl}]_x$ [PDF ^c #17-749]
CsAlSiO_4 [41]	$[\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}](\text{NaReO}_4)_2$ [37]	
RbAlSiO_4 [41]	$[\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}](\text{NaTcO}_4)_2$ [SRNL prepared Jan 2012]	
$(\text{Ca}_{0.5},\text{Sr}_{0.5})\text{AlSiO}_4$ [41]	$[\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}](\text{NaMnO}_4)_2$ [40]	
$(\text{Sr},\text{Ba})\text{Al}_2\text{O}_4$ [41]	$(\text{NaAlSiO}_4)_6(\text{NaBO}_4)_2$ [38,39]	
KFeSiO_4 [41]	$\text{Mn}_4[\text{Be}_3\text{Si}_3\text{O}_{12}]\text{S}$ [34]	
$(\text{Na},\text{Ca}_{0.5})\text{YSiO}_4$ [40]	$\text{Fe}_4[\text{Be}_3\text{Si}_3\text{O}_{12}]\text{S}$ [34]	
$(\text{Na},\text{K})\text{LaSiO}_4$ [40]	$\text{Zn}_4[\text{Be}_3\text{Si}_3\text{O}_{12}]\text{S}$ [34]	
$(\text{Na},\text{K},\text{Ca}_{0.5})\text{NdSiO}_4$ [40]		

a Iron, Ti^{3+} , Mn, Mg, Ba, Li, Rb, Sr, Zr, Ga, Cu, V, and Yb all substitute in trace amounts in nepheline.[41]

b 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 [40]

c Powder Diffraction File

RADIOACTIVE TESTING AND “TIE-BACK” TO NON-RADIOACTIVE TESTING

Bench-scale, pilot-scale, and engineering-scale tests using kaolin clay have all formed the mineral assemblages discussed above with a variety of legacy US DOE waste simulants. A summary of these tests is given in Table I along with a synopsis of the types of durability tests performed and whether or not monolithic waste forms were fabricated and also tested.

A Bench-scale Steam Reformer (BSR) was available at the SRNL to treat actual radioactive wastes to confirm the findings of the non-radioactive FBSR pilot-scale tests performed in 2001, 2004, and the engineering-scale tests performed in 2008 (see references given in Table I). Using this “tie-back” strategy, i.e. demonstrating the similarity of the radioactive mineral products and their durability to the non-radioactive tests allows one to determine the suitability of the waste form for disposal at Hanford based on a 2003 Risk Assessment (RA) of Supplemental Treatment Waste Forms. Detailed discussions of the preliminary RA results are included in Mann et.al. [14]

Radioactive testing at SRNL commenced in 2010 with five planned radioactive demonstrations which were designated as Modules A through E (Table III). Module A commenced in early 2010 with a demonstration of Hanford’s WTP-SW where Savannah River Site (SRS) secondary waste from the HLW Defense Waste Processing Facility (DWPF) was shimmed with a mixture of I-125, I-129, and Tc-99 to chemically resemble the anticipated WTP-SW. Re was also added to determine whether Re was indeed a good non-radioactive simulant for Tc-99. Test results are given elsewhere. [3,6]

Table III. Radioactive Bench-Scale Reformer Tests Being Performed at SRNL

BSR Module	Waste ID	Source of Radioactive Waste	Amount of Radioactive Product Produced (g)
A [3,6]	SRS WTP-SW	Chemical shim of SRS secondary waste sample from DWPF to resemble Hanford WTP- Secondary Waste	96
B [7]	SRS-LAW	Chemical shim of SRS LAW (Tank 50) to resemble Hanford LAW based upon Rassat's Hanford 68 tank blend	640
C [8]	Hanford LAW Sample #1 (medium S, Cl, F, and P)	Hanford Tank 241-SX-105 (medium anions - SO_4^{-2} , Cl^- , F^- , and PO_4^{-3})	317
D [8]	Hanford LAW Sample #2 (low S, Cl, F, and P)	Hanford Tank 241-AN-103 (low anions - SO_4^{-2} , Cl^- , F^- , and PO_4^{-3})	224
E	Hanford LAW Sample #3 (high Cr and high S)	Hanford Tank 241-AZ-101/102 composite (high SO_4^{-2} , high Cr)	TBD

Radioactive Module B testing, the first LAW study, used SRS LAW from Tank 50 chemically trimmed to resemble Hanford's blended 68 tank average LAW known as the Rassat simulant.[42] The Rassat simulant represents about 85% of the LAW chemistry in the single shell tanks. This provides a tie-back to the 2008 engineering-scale FBSR tests at HRI by TTT which used the same simulant [28] and the 2004 pilot-scale FBSR tests at SAIC-STAR.[22]

Thus, the availability of data from the SRS LAW test, and comparisons to the 2004 SAIC/STAR facility pilot-scale and the 2008 HRI engineering-scale facility test results outlined in Table I will provide an important correlation using actual radionuclides to these previous tests that used surrogates. Building correlations between work with radioactive samples and simulants is critical to being able to conduct future relevant simulant tests, which are more cost effective and environmentally sensitive than tests with radioactive wastes. Specifically the following "tie-back" correlations can be derived since all the BSR, pilot-scale, and engineering-scale tests ran the Rassat simulant and the radioactive SRS LAW was shimmed to be chemically like the Rassat simulant.

Approximately six hundred forty (640) grams of radioactive product were made for extensive testing and comparative "tie-backs" to the data collected from non-radioactive pilot-scale tests performed in 2004 and 2008 with the Rassat simulant at HRI by TTT and at the SAIC-STAR facility in Idaho Falls by a team of Idaho National Laboratory, TTT and SRNL. The BSR Module B testing was shimmed with excess Resource Conservation and Recovery Act (RCRA) elements as was the HRI/TTT testing. The BSR was additionally shimmed with Tc-99, Re, I-125, and I-129. The Tank 50 waste had enough Cs that an additional shim was not necessary. In addition, 300 mg Tc-99 per kg of product was shimmed into the last 100 mL of feed processed in the BSR to facilitate the X-ray Absorption Spectroscopy (XAS) studies being performed at the National Synchrotron Light Source (NSLS) located at Brookhaven National Laboratory. The samples were simultaneously shimmed with Re to determine how good a surrogate Re is for Tc in the sodalite mineral structures. Discussion of the XAS studies is documented elsewhere.[5]

Module C testing was performed on actual waste from Hanford Tank SX-105 which contained moderate concentrations of anions such as Cl and SO_4 . No shims of excess RCRA components or radionuclides were added. Three hundred seventeen (317) grams of radioactive product were made for testing. In

addition, 200 mg Tc-99 per kg of product was shimmed into the last 100 mL of feed processed in the BSR to facilitate the XAS studies being performed at the Stanford Synchrotron Radiation Lightsource (SSRL) located at Stanford Linear Accelerator Center National Accelerator Laboratory. The samples were simultaneously shimmed with Re to determine the effectiveness of Re as a surrogate for Tc in the sodalite mineral structures. For Module C, samples were studied that were in the acceptable REDOX range for Re to be in the VII state in a sodalite structure and samples were studied that were known to be outside the REDOX range for Re to be in the VII state, i.e. it would likely be in the +4 state. Discussion of the XAS studies is documented elsewhere.[5]

Module D testing was performed on actual waste from Hanford Tank AN-103 which is a low anion, high sodium tank waste. Two hundred twenty four (224) grams of radioactive product were made for subsequent testing. For all radioactive tests a simulant was prepared and initial testing was performed on the simulants to determine the operational parameters for the BSR. Module E testing, a high Cr and high anion-containing waste which is a mixture of Hanford Tanks AZ-101 and AZ-102, is currently on programmatic hold.

RESULTS AND DISCUSSION

Mass balance

Determining the disposition of key contaminants within a treatment process is a critical consideration for any technology selection process. Previous FBSR engineering-scale tests with LAW simulants indicated that >99.99% of the nonradioactive surrogates for Tc-99 and Cs-137 and >94% of the I-129 surrogate were captured in the mineral product and not released to the off-gas treatment system. For the radioactive BSR tests, mass balance data have been obtained for Tc-99, I-129, I-125, Cs-137 and rhenium. This includes analyzing the granular product, liquid condensate, off-gas filters, and rinse solutions from the post-test cleanout of the BSR apparatus.

Although mass balance does not relate directly to waste form performance, confirming the fate of Tc, Re and I from the actual waste tests is important to confirm prior data from tests with simulants. Reproducible mass balance results add confidence that the key contaminants of concern can be accurately accounted for within the limits of measurement accuracy and detection limits. Mass balance targets for previous demonstrations were to close within +/-10% for major constituents and +/- 30% for minor constituents.[28] In the BSR testing, Tc, Re, I were all present at levels considered minor constituents. The mass balances for Modules A, B, C, and D consisted of identifying key input and output streams and then analyzing these streams for key species.

Mass balance results from Modules A, B, C and D are given in Table IV and will be used to inform the down select process. Module A findings are summarized below and given in reference 6. The data is summarized in Table IV for reference to the other modules since Cs-137 was very high in this feed and the feed had been shimmed with Re, Tc-99, I-129, I-127, and I-125. The significant findings to date of the mass balance from the SRS LAW (Module B) Rassat 68 tank blend, the Hanford (Module C), and the Hanford LAW #2 sample (Module D) are given below: Good mass balance closure on Tc-99, Re, Cs-137, and I-129,-125,-127 in all BSR tests (radioactive and non-Radioactive)

- Module A Radioactive - SRS DWPF Secondary Waste shimmed to match WTP-SW
 - 102% total recovery of Re in the product streams
 - 109% total recovery of Tc-99 in the product streams
 - 98% recovery of I-129, ~93% recovery of I-125, and 151% recovery of I-127 (I-125 is considered to have the highest analytic sensitivity)
- Module B Radioactive - SRS Low Activity Waste shimmed to match Hanford LAW
 - 98% total recovery of Re in the product streams

Table IV. Mass Balance Closure for Radioactive Testing of Modules A, B, C and D

Method	Specie	RAD A (DWPF Melter Recycle WTP Formulation)		RAD B (Tank 50 Rassat Formulation)		RAD C (SX-105)		Rad D (AN-103)	
		Total Recovery (%)	% in Solids ^a	Total Recovery (%)	% in Solids ^b	Total Recovery (%)	% in Solids ^c	Total Recovery (%)	% in Solids ^d
Radio-metric	Cs-137	94	99.32	124	99.0	Indeterminate		Indeterminate	
	I-125	93	98.23	84	95.12	Not Shimmed		Not Shimmed	
	I-129	98	98.04	69	94.50	74.6-88.7	98.33-98.59	100.26	99.58
	Tc-99	109	99.82	87	87.90	80.24	99.74	86.15	99.70
ICP-MS	Tc-99	Not Measured		Below Detection		82.51	99.70	82.85	100
	Re	102	99.49	98	97.90	70.73	99.53	87.69	99.59
	I-127	151	94.0	94	94.94	Not Shimmed		Not Shimmed	
ICP-AES	Al	100	99.94	110	100	105.35	99.99	98.35	100
	Cl	129	100	83	94.10	77.73	98.62	Indeterminate	
	Cr	181	99.94	120	99.90	107.75	100	Indeterminate	
	Na	151	99.72	104	99.50	103.82	99.95	101.70	99.97
	Si	110	99.91	110	100	108.52	99.98	105.00	99.98
IC	SO ₄	Indeterminate		113	95.80	100.33	99.02	Indeterminate	

a solids include bed and fines; fines in condensate and crossbar ranged from Below Detection or zero to 0.04% of the solids

b. solids include bed and fines; fines in condensate and crossbar ranged from Below Detection or zero to 0.5% of the solids

c solids include bed and fines; fines in condensate were zero as a quartz wool plug had been added; crossbar solids ranged from 0- 2.79% except for I-129 which was 12.2% and Cl which was 4.98%

d solids include bed and fines; fines in condensate were zero as a quartz wool plug had been added; crossbar solids ranged from 0- 2.83% except for I-129 which was 30.54%

- 87% total recovery of Tc-99 in the product streams
- 69% total recovery of I-129 in the product streams and 84% recovery of I-125
- Module C - Hanford LAW #1 - medium anion waste (SX-105)
 - 71% total recovery of Re in the product streams
 - 80-83% total recovery of Tc-99 in the product streams
 - 75-89% recovery of I-129; this is the difference of two very small concentrations (input and output) as no excess I-129, I-125 or I-127 was shimmed in this waste
- Module D - Hanford LAW #2 - low anion waste (AN-103)
 - 88% total recovery of Re in the product streams
 - 83-86% total recovery of Tc-99 in the product streams
 - 100% recovery of I-129; this is the difference of two very small concentrations (input and output) as no excess I-129, I-125 or I-127 was shimmed in this waste

Mineralogy

The mineralogy observed for the BSR non-radioactive and radioactive samples for Module B (Rassat simulant) are the same as those of the 2008 ESTD bed products made with the Rassat simulant (Figure 1). The phases were primarily, nepheline, sodalite and nosean. The phases observed agree with the predicted mineralogy from the process control model (MINCALC™) used to target the ESTD and BSR campaigns. Figure 1 shows more nosean (stronger Bragg reflections) than sodalite (weaker Bragg reflections).

For Module C, the mineralogy of the non-radioactive product from the BSR matched the mineralogy of the radioactive product from the BSR (Figure 2a). The phases observed agree with the predicted mineralogy from MINCALC™ of ~80-90 wt% nepheline (stronger Bragg reflections) with ~20-10 wt% sodalite and nosean (weaker Bragg reflections). In this case, the nosean is present in smaller concentrations than sodalite as there is more SO₄ in the feed than halides. For Module D, the mineralogy of the non-radioactive product from the BSR matched the mineralogy of the radioactive product from the BSR (Figure 2b).

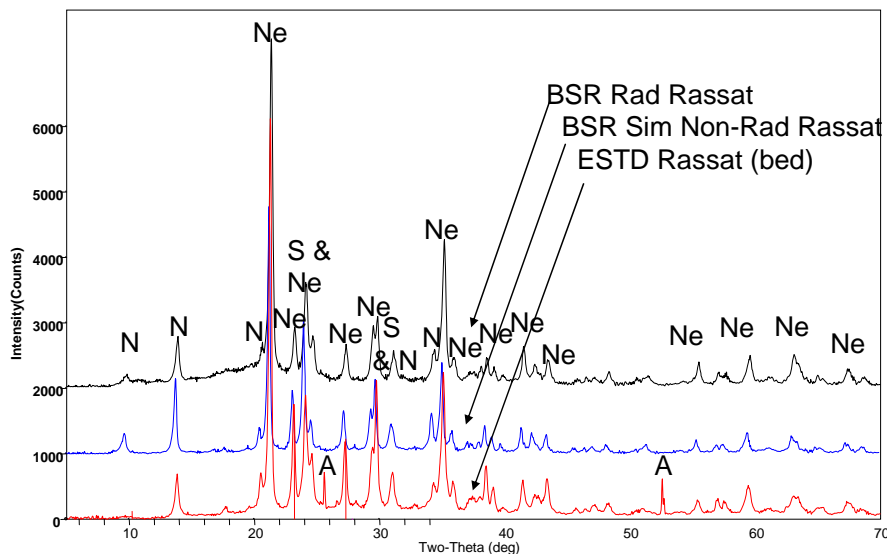


Figure 1. Overlay of X-ray Spectra for BSR Module B (radioactive and non-radioactive) compared to ESTD engineering-scale DMR products (PIB. N is nosean, Ne is nepheline, S is sodalite, and A is Al₂O₃).

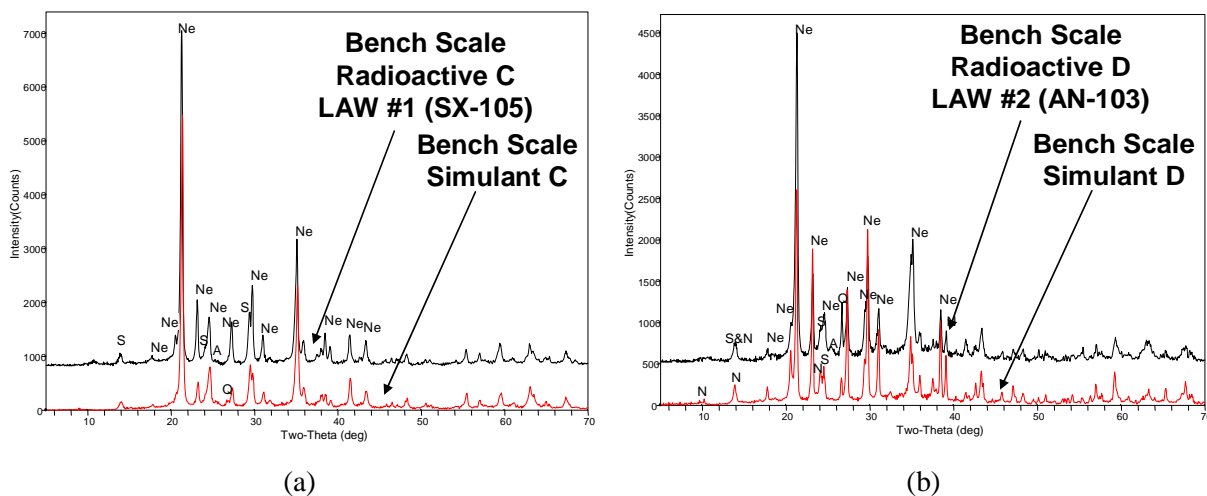


Figure 2a. Overlay of X-ray Spectra for Module C (SX-105) for the BSR bench-scale non-radioactive and radioactive DMR products. Ne is nepheline, S is sodalite, A is Al₂O₃, and Q is quartz Impurities from the clay, b. Overlay of X-ray Spectra for Module D (AN-103) for the BSR bench-scale non-radioactive and radioactive DMR products.

Waste form durability (Product Consistency Test; ASTM C1285)

In mineral waste forms, as in glass, the molecular structure controls dissolution (contaminant release) by establishing the distribution of ion exchange sites, hydrolysis sites, and the access of water to those

sites.[43] For example, in 1998 experiments were performed at Lawrence Livermore National Laboratory (LLNL) by Bourcier on the mineral albite ($\text{NaAlSi}_3\text{O}_8$) and on albite glass.[44] During SPFT testing the albite mineral dissolution was determined to be two orders of magnitude less than the albite glass dissolution. The author states, “the same mechanisms are operating with both glasses and minerals but at different rates.” Thus the long term performance of both glass and mineral waste forms are controlled by a rate drop that is affinity controlled. Therefore, the discussion regarding monolith durability is considered supplementary and not discussed in this paper since monolith selection is based on the scenario that the monolith will not compromise the mineral product durability.

Short term PCT tests were performed by SRNL and Pacific Northwest National Laboratory (PNNL) to compare the relative stability of the LAW BSR products (radioactive and non-radioactive) to the durability of the 2001 and 2004 LAW pilot scale tests on simulants and 2008 LAW engineering scale tests on simulants. Long term PCT tests were performed (e.g. 1,3,6,12 month) to confirm that the performance of the mineral (ceramic) waste form is affinity controlled like vitreous waste forms, i.e. the long term dissolution rate drop is affinity controlled.

The short-term PCT data is in agreement with the data generated in 2001 on AN-107, the 2004 SAIC-STAR facility samples with the Rassat simulant. The correlations shown in Figure 3 were generated with the 7 available PCT responses from the 2001 and 2004 testing of both the bed and the fines. The HRI/TTT 2008 engineering-scale studies are overlain for comparison for the LAW samples (P1B Product Receipt, PR, and High Temperature Filter, HTF, fines) which appear as “x” marks on the graphs. The HRI/TTT 2008 engineering-scale studies for the WTP-SW are overlain (PR and HTF) as open diamonds. The BSR data for non-radioactive and radioactive Modules B and C are overlain with “doughnut” shaped circles around them for emphasis.

As with the 2001 and 2004 data, the pH increases (becomes more caustic) as the surface area of the material is decreased (see Figure 3a). For glass waste forms, pH usually increases with increasing surface area. This is indicative that a buffering mechanism is occurring. Based on the trend of alkali (Na) release being co-linear with Al release (Figure 3b) it was hypothesized that this was an aluminosilicate buffering mechanism. [16,17]

The Na release is colinear with the Al release in the BSR and 2008 engineering scale data as well as in the historical 2001 and 2004 data as seen in Figure 3b. All the other cations appear to be released as a function of the solution pH (Figure 3c, d and e) and this includes Si, S, and Re. This is also in agreement with the historical data.

The Re release plot for the BSR (radioactive and simulant Modules B and C), the 2008 engineering scale, and the historic data appear in Figure 3e. Due to the low concentrations of rhenium, it is a difficult element to measure. It is noteworthy that the Re release from the Module B simulant PCT tracks closely to the Re measured at SRNL for the Module B radioactive Re. These Re concentrations as measured by SRNL are biased low compared to the Re release measured by PNNL for simulant Module B PCT's which were performed independently. However, the simulant Module B Re release, as measured by PNNL, tracks with the radioactive Tc-99 measured by SRNL. Likewise, for Module C, the SRNL analyses for Re in the simulated and radioactive campaigns track each other and track the Tc-99 measured by SRNL. This demonstrates that Re is a good surrogate for Tc-99 during leaching experimentation and that the current radioactive and simulant BSR campaign products match the historic and engineering scale data: the “tie-back” strategy is proven.

The Re releases in the circle on Figure 3e are older data which is also biased low for Re. This is because SRNL changed the dissolution method to measure the Re in the PCT solids being tested during the 2008-2009 timeframe. The older data were measured with a high temperature fusion preparation which may

have volatilized some of the Re. Since that time, SRNL has performed a low temperature dissolution method on the solids which has improved the retention of Re. It should be noted that all the release rates in Figure 3 are below 2 g/m^2 .

Long term PCT tests are performed in the same manner as the short term tests but Method B allows for longer time intervals, in this case, 1 month, 3 month, and 6 month tests. PCT-B tests are useful for generating concentrated solutions to study chemical affinity effects on the dissolution rate. Method B tests at high temperatures and high glass/solution mass ratios can be used to promote the formation of alteration phases to (1) identify the kinetically favored alteration phases (2) determine their propensity to sequester radionuclides, and (3) evaluate the effect of their formation on the continued waste form dissolution rate.

Table V tracks the PCT release rates of analytes as a function of time for the Modular B simulant granular product. The 7-day results are shown with release results from samples leached for one, three, and six months. Release rate of each of the analytes are similar and do not indicate a significant degradation of the granular waste form with time. X-ray diffraction (XRD) was performed and none of the granular phases had degraded and no secondary reaction products had formed.[5] Additional long term tests extended past six months are in progress.

Table V. Time Dependent PCT Results for BSR Module B Simulant Granular Product

Analyte	Normalized g/m^2			
	7 days	1 Month	3 Months	6 Months
Al	2.34E-03	2.22E-03	2.19E-03	2.30E-03
S	4.34E-02	4.74E-02	5.04E-02	5.36E-02
Cs	1.09E-02	NM	9.84E-03	8.05E-03
Re	8.83E-03	8.65E-03	9.23E-03	9.86E-03
Na	1.14E-02	1.22E-02	1.45E-02	1.66E-02
Si	9.86E-04	8.24E-04	5.52E-04	3.32E-04
I	9.82E-04	2.18E-03	2.19E-03	2.34E-03

* Not measured

Waste form durability (Toxicity Characteristic Leach Test)

The TCLP is being used to assess the release of RCRA metals from the granular BSR product. For the purposes of this evaluation, emphasis is on the TCLP results for the granular product even though TCLP testing will eventually be conducted on both the granular and monolithic products. The main purpose of this procedure is to determine whether the FBSR waste form will meet the requirements of the RCRA Land Disposal Restrictions (LDR) since Hanford tank wastes contain hazardous constituents and are listed wastes. The initial focus of the TCLP analyses is on inorganic contaminants, because steam reforming effectively destroys organic materials. TCLP data for the granular products are considered inputs to the down select process, primarily from Modules B and C (SRS LAW and 1st Hanford LAW).

Samples of the aggregate granular Module B simulant were submitted to GEL Laboratories for TCLP analysis and also analyzed by PNNL. The data are tabulated elsewhere [5]

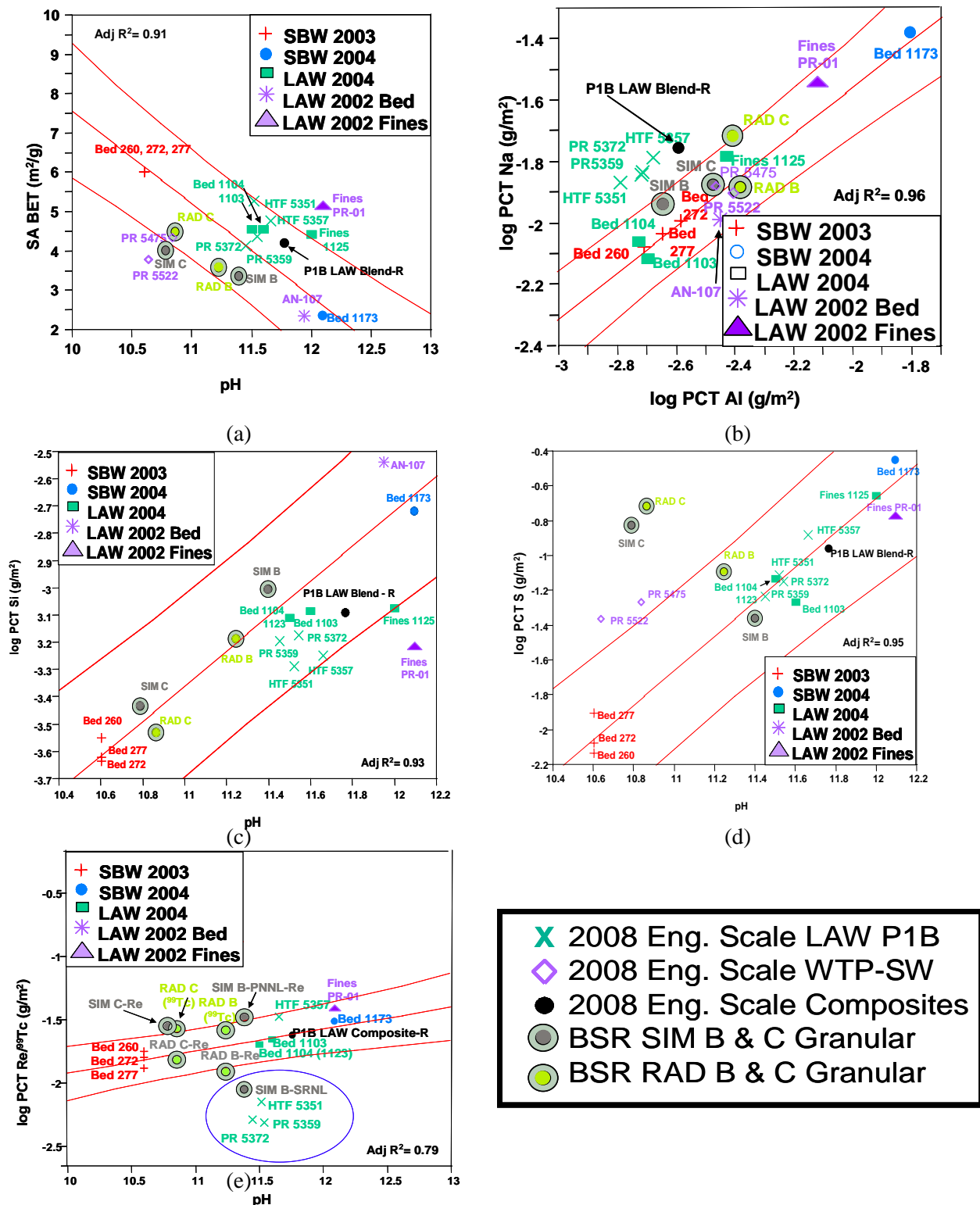


Figure 3. Comparison of the PCT response from the BSR products (radioactive and non-radioactive) to previous pilot and engineering-scale products tested.

CONCLUSIONS

The FBSR process is a good technology for Hanford Supplementary Treatment. The mass balance data indicates that Tc-99, Re, Cs, and I (all isotopes) report to the mineral product and not to the off-gas. The Tc-99 and Re show similar behavior in partitioning between product and off-gas so for mass balance Re is an acceptable simulant for Tc-99. The Tc-99, Re, SO₄ and Cr behavior have been found to correlate to the oxygen fugacity in the FBSR/BSR process, i.e. the REDUction/OXidation (REDOX) equilibrium.

The mineralogy testing indicates that the phases observed agree with the predicted mineralogy from MINCALC™ of ~ 90 wt% nepheline (stronger Bragg reflections) with ~10 wt% sodalite and nosean (weaker Bragg reflections). The mineralogy of all the radioactive campaigns and simulant products from the BSR and ESTD presented here and the simulants tested in 2001 and 2004 pilot scale studies with Hanford simulants all have the same mineralogy.

The conclusions from the short-term and long-term durability testing using ASTM C1285 are as follows:

- ASTM C1285 testing is below 2 g/m² for the constituents of concern (COC)
 - Use of BET surface area to account for the surface roughness of the mineral granules demonstrates that the FBSR product is 2 orders of magnitude lower than the 2 g/m² benchmark
 - Use of the geometric surface area, which ignores the surface roughness of the mineral granules compared to glass, gives an equivalent leach rate to vitreous waste forms
- Long term testing (1, 3, and 6 month) at 90°C by ASTM C1285 has not shown any significant change in the mineral assemblages as analyzed by XRD
- PNNL and SRNL data from ASTM C1285 agree

The conclusions from the TCLP testing are as follows:

- TCLP data are acceptable when RCRA metals are not shimmed in excess and REDOX is controlled
- PNNL and SRNL data from EPA TCLP agree

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