

Radioactive Demonstration of Mineralized Waste Forms Made from Hanford Low Activity Waste (Tank SX-105 and AN-103) by Fluidized Bed Steam Reformation (FBSR) – 14317

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ABSTRACT

One of the immobilization technologies under consideration as a Supplemental Treatment for Hanford's Low Activity Waste (LAW) is Fluidized Bed Steam Reforming (FBSR). The FBSR technology forms a mineral waste form at moderate processing temperatures thus retaining and atomically bonding the halides, sulfates, and technetium in the mineral phases (nepheline, sodalite, nosean, carnegieite). Additions of kaolin clay are used instead of glass formers and the minerals formed by the FBSR technology offers (1) atomic bonding of the radionuclides and constituents of concern (COC) comparable to glass, (2) short and long term durability comparable to glass, (3) disposal volumes comparable to glass, and (4) higher Na₂O and SO₄ waste loadings than glass. The higher FBSR Na₂O and SO₄ waste loadings contribute to the low disposal volumes but also provide for more rapid processing of the LAW. Recent FBSR processing and testing of Hanford radioactive LAW (Tank SX-105 and AN-103) waste is reported and compared to previous radioactive and non-radioactive LAW processing and testing.

INTRODUCTION

The United States (U.S.) DOE ORP is responsible for the retrieval, treatment, immobilization, and disposal of Hanford's tank waste. A key aspect of the River Protection Project (RPP) cleanup mission is to construct and operate the Hanford Tank Waste Treatment and Immobilization Plant (WTP). 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. Supplemental Treatment is likely to be 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.

Four immobilization technologies are under consideration as part of the Supplemental Treatment Program including:

- second WTP LAW vitrification
- bulk vitrification
- cementitious solidification (caststone)
- fluidized bed steam reforming (FBSR).

The DOE has made substantial past investments in evaluating each of the proposed vitrification processes (WTP LAW and bulk vitrification) and cementitious (Caststone) solidification processes at Hanford. Additionally, numerous other sites within the DOE complex have examined the performance of cementitious solidification of LAW for a number of years. DOE had made some, but not sufficient, investments in the FBSR process to produce a mineralized waste form for Hanford LAW immobilization. This study is, therefore, focused on collecting the essential data

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required to objectively evaluate the FBSR waste form as a LAW immobilization alternative to the other technologies.

BACKGROUND

Fluidized Bed Steam Reforming (FBSR) offers a moderate temperature (700-750°C) continuous method by which LAW feeds can be processed irrespective of whether they contain organics, nitrates, sulfates/sulfides, chlorides, fluorides, volatile radionuclides or other aqueous components, thus minimizing pretreatment requirements. The FBSR technology can process these wastes into a crystalline ceramic (mineral) waste form. The mineral waste form is produced by co-processing waste with kaolin clay in an fluidized bed steam reformer in the presence of steam. The mineral product, which is granular, has been shown to be comparable in durability to LAW glass, i.e. leaches Tc-99, Re and Na at $<2\text{g/m}^2$ during American Standards and Testing Materials (ASTM) C1285 (Product Consistency Test) durability testing, Single-Pass Flow Through Testing (SPFT or ASTM 1662), and Pressure Unsaturated Flow (PUF) testing. Considerable durability testing has been performed by SRNL and the Pacific Northwest National Laboratory (PNNL) including tests to demonstrate the waste form will meet preliminary waste acceptance criteria for the Hanford IDF. The granular waste forms also pass the Environmental Protection Agency (EPA) Toxic Characteristic Leach Procedure (TCLP) test for all RCRA components at the Universal Treatment Standards (UTS) limits. The pertinent references for all of the durability testing on the FBSR granular product from 2002 to present are summarized in Table 1.

Monolithing of the granular FBSR product can prevent dispersion during transport and/or during burial/storage. To be accepted for near-surface disposal at Hanford, a waste form is required to meet an acceptance criterion for compressive strength of 500 psi. This requirement is derived from an NRC Branch Technical Position on Low Level Waste (LLW) forms which specifies 500 psi is needed to preclude subsidence in the waste disposal site. A monolithic waste form of 500 psi would also reduce the potential impact to human health from potential future intruder scenarios at the waste site. While a monolith is desirable for control of dispersion, burial site subsidence, and intruder prevention there are other means by which this requirement can be met for a granular waste form, e.g. waste stabilization in High Integrity Containers (HIC's). Both monoliths and HIC's will be compared in terms of IDF disposal volumes and the relative Na_2O oxide waste loading criteria for Hanford LAW.

While monolithing of the granular FBSR product is not necessary for waste form durability, monolithing was investigated in a number of studies (Table 1). Monolithing was investigated in geopolymers made from both fly ash and clay, various cements (Ordinary Portland Cement (OPC) and three high alumina cements), Ceramicrete, and hydroceramics.[13,14,22,23,25,26,29] The durability of the monolithed FBSR waste forms were then compared to the granular product durability responses.[23] The FBSR bed products and fines 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.[22] Monolith studies from 2008 to the present were performed on bed and fines products co-mingled at the relative ratios that they were produced. Monolithing in an inorganic geopolymer binder, which is amorphous, macro-encapsulates all the granules. The pertinent references for all of the testing on the monolithic products are summarized in Table 1.

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Wastes intended for disposal in Hanford's IDF must meet requirements of DOE Order 435.1 and permit requirements established by Washington State Ecology. Initial draft waste acceptance criteria for a secondary waste form are based on the draft IDF waste acceptance criteria [1] and criteria related to free liquids, compliance with land disposal restrictions, compressive strength, and leachability.

For disposal of FBSR wastes at Hanford there is an additional specification that governs the waste loading for glass. Waste loading for Hanford Immobilized Low Activity Wastes (ILAW) are specified in terms of the amount of Na_2O from the waste that can be accommodated in the waste form. The most stringent of these criteria is for Envelope A waste which is the most common waste type at Hanford. The specification (Section 2.2.2.2 of the Product Requirements) [2] states:

“Waste Loading: The loading of waste sodium from Envelope A in the ILAW glass shall be greater than 14 weight percent based on Na_2O . The loading of waste sodium from Envelope B in the ILAW glass shall be greater than 3.0 weight percent based on Na_2O . The loading of waste sodium from Envelope C in the ILAW glass shall be greater than 10 weight percent based on Na_2O .”

If the FBSR granular product needs to be monolithed versus disposal in a HIC it should not dilute the product Na_2O concentration to less than ~14 wt% Na_2O so that the Na_2O content will be comparable to ILAW Envelope A glass. Therefore, the FBSR loading in a monolith should be ≥ 67 wt% to be comparable to ILAW glass

Table 1. Previous References for FBSR Granular/Monolith Product Durability Testing

Pilot Scale Facility	Date	FBSR Diam.	Acidic and Basic Wastes	Gran. PCT Testing	TCLP of Gran. Form	Gran. SPFT Testing	Preliminary Risk Assessment	Product Tested	Coal	Particle Size Distribution (PSD)	Monolith	Mono. PCT Testing	Mono. SPFT Testing	Mono. ANSI/ANS 16.1/ ASTM C1308 Testing	TCLP of Mono. Form	
Non-Radioactive Testing																
HRI/TTT	12/01 Ref 3	6"	LAW Env. C	Ref. 4	Ref 3,4	Ref 5, 6 and PUF testing 7)	Ref. 8	Bed	Removed By Hand	Gaussian	No	N/A				
		6"	LAW Env. C	Ref 9,10,11		None	"Tie-back" Strategy 28	Fines	Removed by 525°C Roasting		Yes (Samples were combined; 20% LAW, 32 % SBW and 45% Startup Bed	Ref 13,14	N/A			
SAIC/STAR	7/03 Ref 12	6"	SBW			None	None	Bed								
SAIC/STAR	8/04 Ref. 15	6"	LAW Rassat			Ref 11,16, 17 and PUF 18	Data from Ref 11,16,17 "Tie-back" Strategy 28	Bed and Fines Separate								
SAIC/STAR	7/04 and 11/04 Ref. 19	6"	SBW			Ref 11,16	None									
HRI/TTT	12/06	15"	SBW	Ref 20		None	None				No	N/A				
HRI/TTT	2008 Ref. 21		LAW Rassat	Ref 22, 23,24, 25,26	Ref 23,22, 25,26	27	"Tie-back" Strategy 28	Bed and Fines Together	Not removed		Bi-Modal	Yes	Ref 23	^P NNL	28	
			WTP-SW			None	None					None	Ref 29,30	23,22, 25,26		
Radioactive Testing																
SRNL/BSR	2010-2013	2.75"	LAW Rassat	28, 26,31		27,32 and PUF 33	"Tie-back" Strategy 28	Bed and Fines Together	Not removed	Gaussian	Yes	28	32	28		
			WTP-SW	29,26,31		None	None					29	None	29	29	

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PCT – product consistency test method (ASTM C1285-08); SPFT – single pass flow-through test method (ASTM C1662); ANSI/ANS16.1/ASTM C1308/EPA 1315 – monolith emersion tests all similar with different leachate replenishment intervals; Pressure Unsaturated Flow Test (PUF); -LAW Env. – low activity waste envelope A, B, and C; PSD - particle size distribution; FY11 – Joint program between SRNL, PNNL, ORNL; SRNL Test Results are complete and documented [28,34]PNNL Test Results are complete and documented and a downselect document has been prepared [26]; N/A – not applicable

For a cementitious grout waste forms at Hanford, there is a PA requirement on nitrate/nitrite leaching that limits the grout waste loading. [35] There are also LDR limits for concentrations of hazardous organics from grout waste forms as well.[35 and 40 CFR 268] Nitrate/nitrite and solvents/organics get destroyed in the FBSR process and so this criteria is always met. Table 2 was developed to summarize the likely requirements that an FBSR granular product in a HIC and/or stabilized in a monolith binder would likely need to meet for the Hanford IDF.

Table 2. Summary of Requirements for an FBSR LAW Waste Form

Test Criteria	Requirement for FBSR Product (Granular or Monolithic)
Compressive Strength after 28 day cure (psi) for monolith	≥500
Crystalline Phases	Phase Identification
PCT Re or Tc (g/m ²) for granular and monolith*	< 2.0
ANSI/ANS 16.1 or ASTM C1308 (Leaching Index, LI after 90 days leaching) of a monolith	Tc-99 and/or Re ≥ 9 Na ≥ 6
Na ₂ O waste loading for Envelope A wastes	≥14 wt%
Na ₂ O waste loading for Envelope B wastes	≥3 wt%
Na ₂ O waste loading for Envelope C wastes	≥10 wt%
Toxicity Characteristic Leaching Procedure (TCLP)	< Universal Treatment Standards (UTS)
Nitrate/nitrite leaching requirement for grout PA	Not Applicable (nitrate/nitrite destroyed in processing)
Solvent/organic leaching requirement for LDR	Not Applicable (solvents/organics destroyed in processing)

*in vitreous waste forms Na leaches congruently with Tc-99 and Re; in mineral waste forms Na leaches incongruently with Tc-99 and Re and the radionuclide release must be measured instead of the Na

“TIE BACK” STRATEGY

Two identical Benchscale Steam Reformers (BSR) were designed and constructed at SRNL, one to treat simulants and the other to treat actual radioactive wastes. The results from the non-radioactive BSR were used to determine the parameters needed to operate the radioactive BSR in order to confirm the findings of non-radioactive FBSR pilot scale and engineering scale tests and to qualify an FBSR LAW waste form for applications at Hanford.

Radioactive testing of LAW with the BSR commenced using Savannah River Site (SRS) Tank 50 LAW chemically trimmed to look like Hanford’s blended LAW known as the Rassat simulant (68 tank blend) as this simulant composition had been tested in the non-radioactive BSR, the non-radioactive pilot scale FBSR at the Science Applications International Corporation-Science and Technology Applications Research (SAIC-STAR) facility in Idaho Falls, ID and in the THOR™ Treatment Technology (TTT) Engineering Scale Technology Demonstration (ESTD) at Hazen Research Inc. (HRI) in Denver, CO. This provided a “tie back” between radioactive BSR testing and non-radioactive BSR, the 2002 TTT/HRI pilot scale, the 2004 INL SAIC-STAR pilot scale, and the TTT/HRI 2008 engineering scale testing and the Risk Assessment (RA) performed the pilot scale FBSR product 2002.[7,8] See Table 3 for a comparison of all the scale FBSR’s and the wastes processed

Several hundred grams each of non-radioactive and radioactive BSR product were made for extensive testing and comparison. The importance of the BSR radioactive modules SX-105 (Module C), AN-103 (Module D), and the planned AZ-101/AZ-102 (Module E) BSR tests are how well they compare to the radioactive BSR Rassat simulant (Module B) made with radioactive SRS LAW and provide the tie back to the remaining pilot scale (2002 and 2004) and engineering scale (2008) tests.

Table 3. Comparison of Pilot-scale, Engineering-scale, and Bench-scale FBSR's

Facility/ Reformer	Column Diameter	Externally or Internally Heated?	Dual or Single Reformer Flowsheet?	Reductant of Choice	Iron Oxide Catalyst (IOC)?	Waste
TTT 2001-2002 (non-radioactive)	6"	External and with Coal	Single	BB charcoal	Yes	AN-107
SAIC-STAR 2003-2004 (non-radioactive)	6"	External and with Coal	Single	BB charcoal	No	SBW
						Rassat
TTT ESTD 2006-2008 (non-radioactive)	15"	Internal	Dual	Bestac coal	Yes	WTP-SW
						Rassat
SRNL BSR (non-radioactive and radioactive)	2.75"	External and with Coal	Dual	Bestac coal	Some tests	WTP-SW
						Rassat
						SX-105
						AN-103
						AZ-101/ AZ-102 (Simulant Only)

EXPERIMENTAL

The SRNL BSR duplicated the 15" TTT engineering scale dual reformer flowsheet operated by TTT at HRI.[36] The SRNL BSR's, both the non-radioactive and radioactive units, had dual reformers but the second reformer known as the Carbon Reduction Reformer (CRR) was not used as none of the wastes tested contained organics. Testing was performed with and without a iron oxide catalyst (IOC) as noted in Table 3.¹ The same coal was used in the BSR as in the TTT/HRI engineering scale testing (Table 3). The BSR tested radioactive and non-radioactive LAW compositions from Hanford Tank SX-105 and Tank AN-103 and preparations were made to process a blend of AZ-101/AZ-102 before funding issues precluded processing of the last tank waste blend. These test results were compared to the test results from the Hanford Rassat (68 tank blend).[28]

The radioactive Hanford wastes received at SRNL were analyzed so that a surrogate recipe could be developed. During Module B radioactive testing, Re had been determined to be a good surrogate for Tc-99 in the off-gas mass balance, product retention, and in durability testing. [28]

¹ The IOC is used as a processing additive to improve nitrate/nitrite destruction and to provide a reduced iron mineral host (spinel) for chromium in the +3 state so that Cr is not leached out of the FBSR product

Thus, SX-105 and AN-103 non-radioactive and radioactive wastes were shimmed with Re as a surrogate for Tc-99 in order to provide additional supporting data that Re was indeed a good surrogate for Tc-99. The radioactive tank samples already contained Tc-99 and no additional Tc-99 was shimmed into the wastes except for one sample made especially for Tc speciation by X-ray Absorption Spectroscopy (XAS).[18] The tank waste simulant recipes' were made to perform tests in the SRNL non-radioactive BSR to determine the parameters for the radioactive BSR campaigns.

Due to funding constraints, the AZ-101/AZ-102 testing (Module E) only consisted of analyzing the radioactive waste when received after shimming it with Re in preparation for the radioactive BSR campaigns, developing a recipe for a simulant, shimming the simulant with Re, performing non-radioactive BSR campaigns, analyzing the FBSR products and off-gas, and performing durability testing on the product. Therefore, the data collected primarily from SX-105 and AN-103 BSR campaigns and testing will be discussed preferentially to the data collected on AZ-101/AZ0102.

The data collected on the radioactive and non-radioactive SX-105 and AN-103 coupled with the non-radioactive FBSR AZ-101/AZ-102 [34] are compared to the Module B Rassat 68 tank blend testing [28] and all of the other non-radioactive testing performed in pilot and engineering scale FBSR's with the Rassat simulant to provide the "tie-back" between simulant and radioactive testing and between bench-scale, pilot-scale, and engineering scale testing.

MINCALC™, a process control strategy developed by SRNL for FBSR processing, was used to control the LAW FBSR BSR product in the region of the desired phases (nepheline and sodalite) (region in Figure 1 where the blue rectangle for the pilot scale AN-107 tests lies). MINCALC™ converts the molar compositions' of the measured waste (simulant or radioactive) to element weight percent on a wet basis and then to oxide weight percent on a dry calcine basis. The Al_2O_3 and SiO_2 from the clay additive and the $(\text{Na,K,Cs})_2\text{O}$ and Al_2O_3 contributions from the waste are weighted by waste loading and (100-waste loading), respectively, until the tie-line between the clay composition on the SiO_2 - Al_2O_3 binary and the waste composition on $(\text{Na,K,Cs})_2\text{O}$ - Al_2O_3 binary pass through the AN-107 region of Figure 1 where it is known that acceptable FBSR product is made.[4,5,6,7]

The Hanford radioactive waste compositions are shown along the Na_2O - Al_2O_3 base of the triangle in Figure 1. It is obvious from the positions of the AN-103 and SX-105 points on the base of the triangle that AN-103 (Module D) had much more Al_2O_3 in it than SX-105 (Module C). This composition difference is accounted for by the MINCALC™ process control in Excel® by choosing a clay or a mixture of clays along the Al_2O_3 - SiO_2 side of the triangle that forces the waste-clay mixture through the AN-107 box where it has been determined that the desired NAS minerals are made. [4,5,6,7] Note that the AN-103 was processed with the $\text{Al}(\text{OH})_3$ solids that had precipitated.

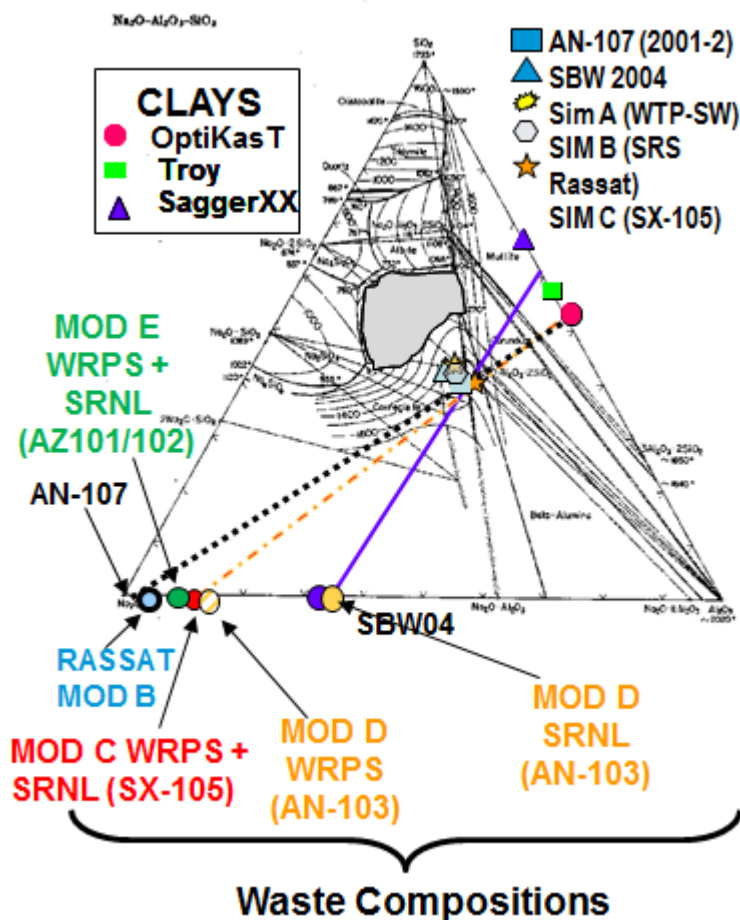


Figure 1. $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (NAS) MINCALC™ Process Control Phase Diagram

Note: The composition of the SX-105 (Module C) radioactive waste as analyzed by WRPS and SRNL is shown along the base of the MINCALC™ triangle ($\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ binary) along with the analyses of AN-103 (Module D) analyzed by WRPS (filtered) and SRNL (unfiltered), and AZ101/AZ102 (Module E) analyzed by WRPS and SRNL. The unfiltered SRNL analyses were used for the AN-103 (Module D) radioactive BSR campaigns. The Rassat simulant (Module B) is shown along the base of the triangle for comparison along the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ binary. The position of the potential clay additives are shown on the $\text{Al}_2\text{O}_3-\text{SiO}_2$ binary.

The granular products and the off-gas were analyzed to determine the partitioning of the radionuclides and constituents of concern (COC) to the granular product and off-gas (see reference 34 for details of the analyses). Extensive testing and characterization of the granular product material from Modules C (SX-105) and Module D (AN-103) were made including the following (ASTM and EPA) tests:

- ASTM C1285 (Product Consistency Test) testing of granular waste forms
 - Comparison of granular BSR radioactive SX-105 product to Rassat 68 tank blend ESTD and pilot scale granular non-radioactive and radioactive waste forms (short and long term testing)

- Comparison of granular radioactive to granular non-radioactive waste forms made from the SX-105 simulants using the SRNL BSR
- EPA Manual SW-846 Method 1311, TCLP
 - Comparison of granular BSR radioactive SX-105 and AN-103 to ESTD and pilot scale granular and monolithic non-radioactive waste forms made from the Rassat simulant
 - Comparison of granular radioactive to granular non-radioactive waste forms made from the SX-105 and AN-103 simulants made using the SRNL BSR
 - Comparison of the granular non-radioactive waste forms made from SX-105, AN-103 and AZ-1-1/AZ-102 to each other and to the Rassat 68 tank blend as a function of REDuction/Oxidation (REDOX)

Additional experimental details can be found in Reference 34.

RESULTS AND DISCUSSION

The analysis of the FBSR solids is given in Table 4. Note that the Al content of the radioactive SX-105 is 18.4 wt% which is equivalent to 34.8 wt% Al_2O_3 in the FBSR product and the Na content of the SX-105 and AN-103 are 15.8 and 15.7 wt% respectively which is equivalent to 21.16 wt% Na_2O in the FBSR product. All of the Na_2O comes from the LAW as the clay does not contain any Na_2O : FBSR products far exceed the 14, 10, and 3 wt% Na_2O waste loading criteria for LAW glass. The chemical analyses given in Table 4 also demonstrates that all nitrates and nitrites are destroyed during FBSR processing.

Mass balance for the radioactive SX-105 and AN-103 campaigns is given in Table 5. The findings for the radioactive and non-radioactive SX-105 and AN103 FBSR campaigns are summarized below:

- The mass balances of Tc-99, Re, Cs-137/Cs-133, and I-129/I-125/I-127 were determined in the BSR systems (non-radioactive and radioactive).
 - Good mass balance closure was achieved on Tc-99, Re, Cs, I and chloride in the Module C (SX-105) and Module D (AN-103) campaigns.
 - Module C- Hanford LAW Tank SX-105
 - 71-98% recovery of Re in the product streams for radioactive and simulant campaigns, respectively
 - 80-83% recovery of Tc-99 for once through processing which is ~2.5X greater retention than LAW glass for once through processing
 - ~75% recovery of I-127 (non-radioactive) and I-129 (radioactive)
 - 78-100% recovery of chloride, radioactive and non-radioactive, respectively
 - ~100% recovery of Cs in the simulant campaigns, issues with cross contamination in the radioactive campaigns (see Table 5)
 - Module D – Hanford LAW Tank AN-103
 - 90-95% recovery of Re in simulant runs, 88% recovery in radioactive campaign
 - 83-86% recovery of Tc-99 for once through processing which is ~2.6X greater retention than LAW glass for once through processing
 - 100% recovery of I-127 (non-radioactive) in two simulant campaign and 100% recovery of I-129 (radioactive) in the radioactive campaign
 - 86% recovery of Cl in the simulant campaigns
 - 87% recovery of Cs in the simulant campaigns, issues with cross contamination in the radioactive campaigns (see Table 5)
- The data indicates Tc-99, Re, Cs, and I (all isotopes) report preferentially to the mineral product

- Tc-99 and Re show similar behavior in partitioning between the product and off-gas: for mass balance Re is an acceptable simulant for Tc-99

The chemical analyses given in Table 4, the REDOX ratio as measured analytically by the $Fe^{2+}/\text{Sum Fe}$, the coal content measured by Loss-on-Ignition (LOI) at 525°C, and mineralogy measured by X-ray

Table 4. Granular Product Analyses for Simulant and Radioactive SX-105 and AN-103 Samples

Species	Module C – Tank		Module D - Tank AN-103	
	Radioactiv Wt%	Simulant Wt%	Radioactiv Wt%	Simulant Wt%
Al	1.86E+01	1.77E+01	1.84E+01	1.67E+01
As	NA	NA	<1.08E-03	NA
B	1.42E-02	5.93E-03	1.15E-02	5.19E-03
Ba	4.93E-03	4.84E-03	1.18E-02	9.97E-03
Ca	4.05E-02	1.00E-01	6.14E-02	1.16E-01
Cd	<1.01E-03	<5.57E-0	6.89E-04	<1.06E-04
Ce	5.80E-03	<3.28E-0	6.27E-04	6.32E-03
Co	<9.35E-04	<6.72E-0	1.22E-03	<4.42E-04
Cr	1.38E-01	1.20E-01	1.35E-02	1.13E-02
Cs	high blank	6.84E-04	1.58E-04	1.35E-02
Cu	6.60E-03	3.72E-03	7.30E-03	<4.92E-03
Fe*	1.38E+00	1.35E+00	1.76E+00	1.48E+00
K	1.88E-01	1.57E-01	5.71E-01	5.27E-01
La	3.29E-03	3.02E-03	4.05E-03	3.88E-03
Li	5.61E-03	4.37E-03	5.51E-03	2.95E-03
Mg	1.55E-02	1.95E-02	5.48E-02	5.45E-02
Mn	1.04E-03	8.33E-04	1.40E-03	1.14E-03
Mo	<4.92E-03	<1.35E-0	<4.86E-03	3.64E-03
Na	1.58E+01	1.52E+01	1.57E+01	1.57E+01
Ni	<7.31E-03	2.40E-03	<3.59E-03	2.09E-03
P	3.88E-01	3.16E-01	6.04E-02	4.55E-02
Pb	1.35E-03	<3.05E-0	2.64E-03	5.59E-03
Re	2.69E-02	4.70E-02	3.47E-02	4.69E-02
S	2.66E-01	2.92E-01	1.41E-01	1.22E-01
Sb	6.27E-03	NA	<8.25E-02	NA
Se	<2.16E-03	NA	<2.17E-03	NA
Si	1.89E+01	1.85E+01	1.75E+01	1.77E+01
Sn	<3.37E-03	<1.56E-0	<4.42E-03	<8.08E-04
Sr	2.93E-03	3.11E-03	7.68E-03	6.74E-03
Th	1.55E-03	NA	1.40E-03	NA
Ti	7.69E-01	7.33E-01	7.91E-01	8.15E-01
U	2.90E-04	NA	6.28E-04	NA
Zn	5.33E-03	2.65E-03	5.59E-03	2.21E-03
Zr	3.04E-03	<2.49E-0	5.70E-03	4.43E-03

Species	Module C – Tank		Module D - Tank AN-103	
	Radioactive	Simulant	Radioactive	Simulant
Cs-137	1.66E-08	NA	3.04E-08	NA
Tc-99	3.99E-04	NA	2.23E-04	NA
I-129	3.01E-05	NA	4.68E-05	NA

NA – Not Analyzed, *Fe – Iron constituent was not added to simulant feed but is present in the simulant granular product from both the added Fe(NO₃)₃·9H₂O and the added clay

Table 4. Granular Product Analyses for Simulant and Radioactive SX-105 and AN-103 (Continued)

Species	Module C – Tank SX-105		Module D - Tank AN-103	
	Radioactive	Simulant	Radioactive	Simulant
	Wt%	Wt%	Wt%	Wt%
Cl ⁻	2.31E-01	2.06E-01	2.12E-01	2.27E-01
Br ⁻	NA	NA	NA	<9.46E-02
F ⁻	<5.02E-02	<2.13E-01	<4.69E-02	<9.46E-02
HCO ₂ ⁻	NA	NA	NA	<9.46E-02
I ⁻	NA	3.17E-02	NA	7.90E-02
	Wt%	Wt%	Wt%	Wt%
NO ₃ ⁻	<5.02E-02	<2.13E-01	<4.69E-02	<9.46E-02
NO ₂ ⁻	<5.02E-02	<2.13E-01	<4.69E-02	<9.46E-02
C ₂ O ₄ ²⁻	7.37E-02	<2.13E-01	<4.69E-02	<9.46E-02
PO ₄ ³⁻	9.64E-01	9.27E-01	1.81E-01	<4.73E-01
SO ₄ ²⁻	6.43E-01	6.71E-01	2.56E-01	<9.46E-02
	g/cc	g/cc	g/cc	g/cc
Density	2.60	2.49	NM	NM

NA – Not Analyzed, NM – Not Measured

Table 5. Mass Balance of Radioisotopes and Re for BSR Radioactive Testing

Method	Radio-isotope	RAD B (SRS LAW) [28]		RAD C (Hanford SX-105) [34]		RAD D (Hanford AN-103) [34]	
		Total %	Product %	Total %	Product %	Total %	Product %
Radiometric	Cs-137	124	99	Indeterminate			
	I-125*	84	95	Not shimmed			

	I-129	75-87	95	75-89	86-88	100	69
	Tc-99	87	88	80	98	86	98
ICP-MS	Tc-99	Analysis not Performed		83	98	83	98
	Re	98	98	71	98	88	98

*Signal for I-125 is stronger and more accurate than for I-129

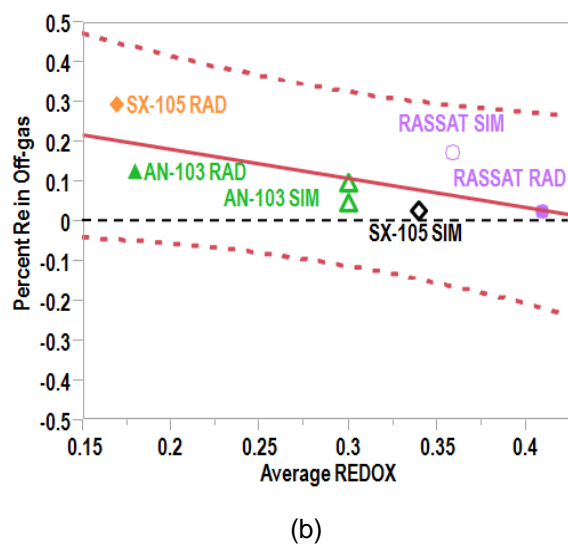
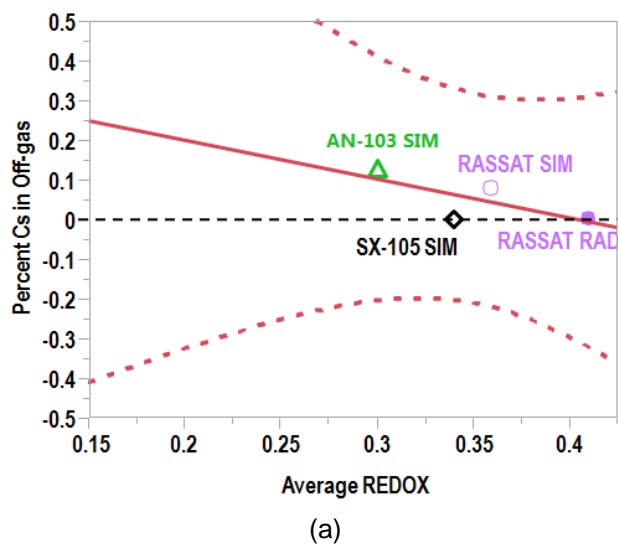
Diffraction (XRD) were measured on a Turbula® mixed composite of “on-spec” granular product for SX-105 and AN-103. The goals of all the radioactive and non-radioactive BSR testing was to match the chemistry, REDOX, LOI and mineralogy to those of the engineering scale ESTD tests performed by TTT/HRI. There was an effort to keep the residual coal content, where coal is used for autothermal heating of the FBSR and denitration, below 2 wt%. Thus products having the correct REDOX, LOI and mineralogy were deemed “on-spec” and any other products (more oxidized or more reduced) were deemed “off-spec” and not used for subsequent durability testing. It should be noted that both “on-spec” and “off-spec” granular products had the same mineral phases and chemistry, and hence these factors were not a discriminating characteristic. The actual LOI, REDOX and calculated oxidation state speciation of rhenium and sulfur from Reference 37 are summarized in Table 6.

Table 6. LOI, REDOX and Speciation of Rhenium and Sulfur

Waste	Sample	LOI (%)	Fe ⁺² /ΣFe	Re ⁺⁷ (%)	SO ₄ (%)
Module C (Tank SX-105)	Simulant	1.32	0.34	98	99
	Radioactive	3.50	0.17	100	100
	Radioactive Tc-99 Spike	3.35	0.39	97	98
Module D (Tank AN-103)	Simulant	1.62	0.30	99	100
	Radioactive	6.22	0.18	100	100
Module E (Tank AZ101/AZ102)	Simulant with IOC	0.70	0.13	100	100
	Simulant without IOC	1.15	0.06	100	100

Since the various BSR radioactive campaigns had slightly different REDOX conditions from each other (Table 6) the mass balance values were plotted against REDOX to see if the processing REDOX had any impact on the releases of multi-valent species to the off-gas. As can be seen in Figure 2, no trends of multi-valent species releases to the off-gas were noted as a function of REDOX.[26] The plots shown in Figure 2 for Cs, Re, Tc-99, and I release have correlations with R² < 0.5 which means there is no discernable trend. The dashed line at 0 release of each component in Figure 2 to the off-gas indicates that the apparent trends are likely due to analytic error as the percentage releases are all <0.5%.

The mineralogy and qualitative amounts observed for the BSR non-radioactive and radioactive samples for SX-105 and AN-103 are the same as those of Module B (Rassat 68 tank blend) non-radioactive and radioactive and the same as those observed in the engineering scale ESTD simulated bed products. The phases were primarily, two types of nepheline (one of hexagonal symmetry and one of orthorhombic symmetry), and cubic nosean with minor cubic sodalite. The sodalite and nosean peaks do not appear in every x-ray diffractogram. This is because there is a large region of solid solution between sodalite ($\text{Na}_8(\text{AlSiO}_4)_6\text{Cl}_2$) and nosean ($\text{Na}_8(\text{AlSiO}_4)_6\text{SO}_4$) [38,39] because the two species are isostructural. Therefore, when fitting XRD patterns to the “best matching” set of Bragg reflections, sometimes the nosean and sodalite are identified separately and sometimes as one or the other of the two species depending on the relative concentration of each present. The orthorhombic nepheline is designated as nepheline (O) but may be low-carnegieite which has the same composition as nepheline and is orthorhombic. More details can be found in Reference 34. The FBSR minerals were found to retain Re in the cage structure (~100%) of the granular mineral products and varying percentages of Tc-99 depending on the REDOX conditions.[18] Coupling the results of this study with previous radioactive BSR studies demonstrates that when anions such as Cl, F, and I are present or oxyanions such as TcO_4^- or ReO_4^- , more sodalite forms. If more SO_4^{2-} is present the sodalite structured phase nosean forms. If anions, SO_4^{2-} , Re and Tc are low, then less sodalite/nosean forms and more nepheline forms. Cs and K can be accommodated in either nepheline or sodalite where they substitute for Na.



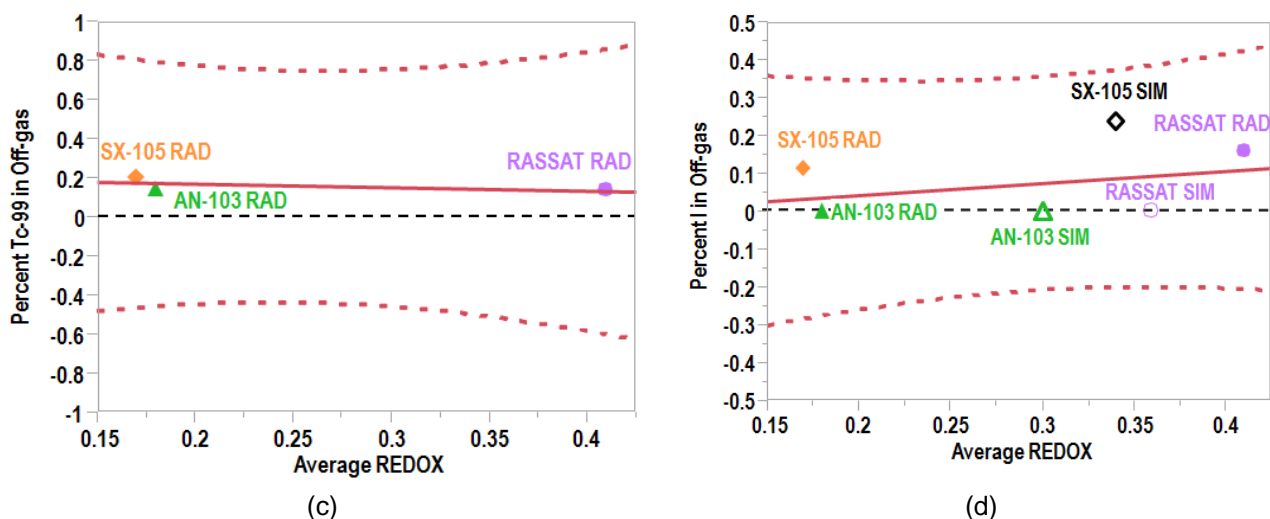


Figure 2. Lack of Correlation of REDOX and Multi-valent Species Release to BSR Off-gas.

The 7-day PCT was conducted on the BSR Module C simulant and radioactive SX-105 BSR products and long term PCT tests are performed in the same manner as the short term tests. The long term tests, the PCT Method B, allows for longer time intervals, in this case, 1 month, 3 month, 6 month, and/or 12 month tests. PCT-B tests are useful for generating concentrated solutions to study chemical affinity effects on the dissolution rate. PCT 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. The results of the short term and long term testing are summarized below:

- Short term ASTM C1285 (Product Consistency Test-A) testing is below 2 g/m² LAW glass leach rate limit for the COC by 2 orders of magnitude or 100-200X
 - 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 LAW glass leach rate limit
 - Use of the geometric surface area, which ignores the surface roughness of the mineral granules and assumes the granules are hard spheres which is incorrect, gives an equivalent leach rate to LAW vitreous waste forms
 - All the durability results from SX-105 (Module C non-radioactive and radioactive) are in agreement with the data from the SRS LAW BSR testing (non-radioactive and radioactive) and the ESTD testing in 2008 and pilot scale testing from 2001 and 2004
 - Re is a good surrogate for Tc-99 during leaching experimentation proving that the current radioactive and simulant BSR campaign products using Re and Tc-99 match the historic and engineering scale data that used Re only
 - An aluminum buffering mechanism appears to control the leachate pH and all other element releases are released as function of solution pH for all radioactive and non-radioactive LAW wastes tested

- The dependence of the leach rate on pH in PCT testing is supported by the pH dependency reached during SPFT and PUF testing of the Rassat FBSR ESTD and BSR products in other studies performed at PNNL. [27,32,33]
- Long term testing (1, 3, 6 month and/or 1 year) at 90°C by ASTM C1285 of Module C (SX-105) non-radioactive and radioactive has not shown any significant change in the mineral assemblages as analyzed by X-Ray Diffraction (XRD);34
 - Silica concentrations in solution decrease with time indicating solution supersaturation: reaction products would have formed when the solution saturates or supersaturates if they were going to form.[34]
 - Re is a good surrogate for Tc-99 during long term leaching experimentation proving that the current radioactive and simulant BSR campaign products using Re and Tc-99 match the historic and engineering scale data that used Re only.
- No dissolution trends were observed with the REDOX of the FBSR products [26]
 - When the Tc-99 is not in the sodalite cage structure (more reduced FBSR products) it is found associated with sulfide which forms from sulfate under reduced conditions and it forms the highly insoluble TcS_2 mineral phase [18,26]

The TCLP data for the simulants were tested in South Carolina at EPA certified laboratories. Because the Tank SX-105 and AN-103 samples were listed waste the FBSR products were sent to PNNL who subcontracted with EPA certified laboratories in Washington state. These data are reported in references 26 and 34. The TCLP data are acceptable when REDOX is $>0.30 Fe^{2+}/\text{Sum Fe}$ or at lower REDOX if the IOC is present and provides a spinel host for Cr^{+3} . An IOC algorithm was derived [34] to quantify how much IOC is needed to stabilize chromium in an iron chrome spinel if REDOX is $<0.30 Fe^{2+}/\text{Sum Fe}$.

DISPOAL VOLUMES

The disposal volumes for FBSR products in HIC's and/or as monoliths were compared to the disposal volumes for LAW glass and for the baseline Caststone for a 5M sodium LAW. The results are shown graphically in Figure 3 and the details of the calculations can be found in reference 26. Figure 3 demonstrates that the FBSR waste forms (HIC's or monoliths) are comparable in lowering waste disposal volume to glass waste forms compared to Caststone. The HIC offers the largest Na_2O waste loading of any of the FBSR options with Na_2O waste loadings in the range of $> 20 wt\%$. High Na_2O waste loadings translate into more rapid processing of LAW. Other monolith options shown in Figure 3 have lower Na_2O waste loadings due to dilution by the monolithic binder but still provide for a disposal volume decrease. These binders include geopolymers (GEO), two high Al_2O_3 containing cements, and Ordinary Portland Cement (OPC).

CONCLUSIONS

The FBSR waste form can accommodate $>20 wt\%$ Na_2O waste loading which is higher than LAW glass. This allows for faster waste processing and minimal disposal volumes. The FBSR process can successfully process any precipitates such as $Al(OH)_3$ that were present in the AN-103 tank waste without any preprocessing. Excess Al is easily accommodated for by adjustment of the composition of the clay additive in the FBSR MINCALC™ process control. Due to the moderate processing temperatures, FBSR retains Cs-137, Re, Tc-99 and I-129 in the FBSR product. The mineral durability is comparable to glass waste forms in both short term ASTM C1285 testing (PCT-A) and long term testing (PCT-B) at all scales of processing. No

reaction products are formed in over a year of durability testing with the SX-105 and Rassat simulant products. The FBSR product passes TCLP at the UTS limits required for listed wastes.

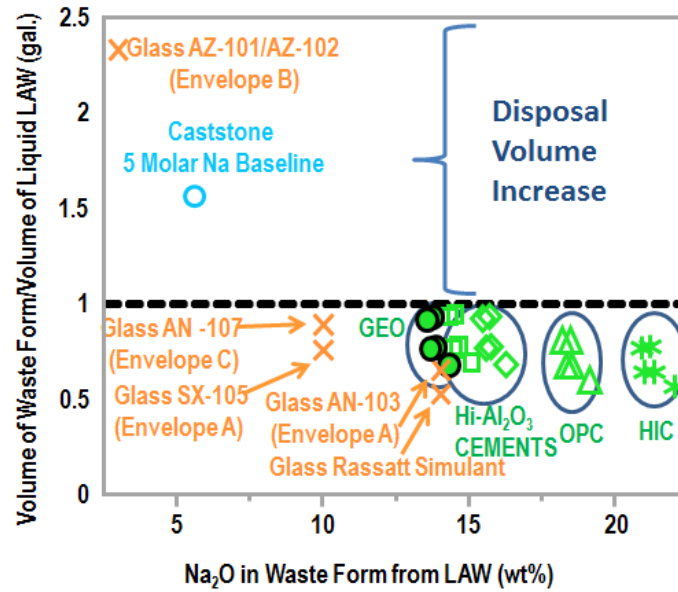


Figure 3. Volumes of waste form produced per volume of liquid LAW. All waste forms below the dashed line at 1.0 create a disposal volume reduction while those above the 1.0 create a disposal volume increase. FBSR waste forms are comparable to glass waste forms.

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