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STABILIZATION OF SAVANNAH RIVER NATIONAL LABORATORY (SRNL) AQUEOUS WASTES BY FLUIDIZED BED STEAM REFORMING (FBSR)

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November 2004

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SRNL
SAVANNAH RIVER NATIONAL LABORATORY

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EXECUTIVE SUMMARY

The Savannah River National Laboratory (SRNL) is a multidisciplinary laboratory operated by Westinghouse Savannah River Company (WSRC) in Aiken, South Carolina. Research and development programs have been conducted at SRNL for ~50 years generating non-radioactive (hazardous and non-hazardous) and radioactive aqueous wastes. Typically the aqueous effluents from the R&D activities are disposed of from each laboratory module via the High Activity Drains (HAD) or the Low Activity Drains (LAD) depending on whether they are radioactive or not. The aqueous effluents are collected in holding tanks, analyzed and shipped to either H-Area (HAD waste) or the F/H Area Effluent Treatment Facility (ETF) (LAD waste) for volume reduction. Because collection, analysis, and transport of LAD and HAD waste is cumbersome and since future treatment of this waste may be curtailed as the F/H-Area evaporators and waste tanks are decommissioned, SRNL laboratory operations requested several proof of principle demonstrations of alternate technologies that would define an alternative disposal path for the aqueous wastes.

Proof of principle for the disposal of SRNL HAD waste using a technology known as Fluidized Bed Steam Reforming (FBSR) is the focus of the current study. The FBSR technology can be performed either as a batch process, e.g. in each laboratory module in small furnaces with an 8" by 8" footprint, or in a semi-continuous Bench Scale Reformer (BSR). The proof of principle experiments described in this study cover the use of the FBSR technology at any scale (pilot or full scale). The proof of principle experiments described in this study used a non-radioactive HAD simulant.

The FBSR process produces a granular mineral waste form. The mineral waste form can be sodium carbonate based, sodium silicate based, or sodium aluminosilicate (NAS) based. The aqueous HAD waste is anion rich and cation poor. Therefore additives that provide the cations Na^+ , Ca^{+2} , Al^{+3} , and Si^{+4} were needed to form the mineral phases. The sodium aluminosilicate (NAS) minerals have cage-like structures that stabilize the Cl, F, I, other anions and radio-nuclides in the aqueous laboratory waste and the NAS phases are the preferred mineral host because of these retention qualities.

The FBSR technology was shown to be a suitable technology for disposal of SRNL HAD waste via any number of disposal paths. The FBSR technology is suitable for HAD waste disposal whether the technology is carried out in individual laboratory modules or in a centralized facility within SRNL. The latter, which provides for semi-continuous processing would be a more efficient method of HAD waste disposal.

The FBSR process yields 90-93% volume reductions as demonstrated in this study. There is ~3925 L of HAD waste generated in SRNL on a yearly basis. Therefore, FBSR of the HAD waste would create ~575 kgs of solid waste per year. These solids will likely have to be collected and recycled back to a waste or feed tank for subsequent vitrification in the Defense Waste Processing Facility (DWPF) because of the high doses of radioactivity associated with the large volume reductions or disposed of directly into a DWPF canister for burial at the federal Yucca Mtn. Repository. Recycle to DWPF would require a determination of the compatibility of

the minerals produced with the DWPF process. Previous studies on SRS salt supernates have indicated that the carbonates and silicates are compatible with recycle to DWPF. Disposal at Yucca Mtn. would require qualification of the FBSR NAS mineral waste form as an alternative to vitrification. This study concentrated on producing the NAS FBSR mineral phases because these phases have the best anion and radionuclide retention, can be substituted for DWPF frit, and are the most flexible in terms of disposal paths.

FBSR formulations that can be solidified into a monolith for direct disposal in the SRS burial ground were also investigated in this study. By co-addition of both sodium and calcium silicates, calcium aluminoferrite, and calcium aluminate, the FBSR product can be made naturally cementitious. The addition of the extra co-additives causes a volume increase and therefore a dilution of the radioactivity that may allow the monoliths to meet the SRS burial ground Waste Acceptance Criteria (WAC).

Formation of the NAS granular minerals was successful including retention of the anions and hazardous species. Formation of the naturally monolithic FBSR product was successful. Formation of the granular sodium silicate mineral was not successful in that it did not incorporate the Cl in the simulated HAD waste.

Based on the results and conclusions presented in this study, the following recommendations are made:

- Investigations of one or more successful formulations from this study should be verified with radioactive HAD wastes on the batch scale and the semi-continuous BSR scale.
- The hazardous constituent spike used in this study should be analyzed so that the sulfate retention of the FBSR products produced in this study can be better quantified.
- Additional testing such as the Toxic Characteristic Leaching Procedure (TCLP), compressive strength, and Scanning Electron Microscopy (SEM) analyses on the naturally cementitious monoliths should be completed to evaluate the suitability of this form for land disposal.
- Alternative sources of calcium silicates should be investigated to make monolithic waste forms that are naturally cementitious to see if the monolith properties can be improved, e.g. compressive strength
- Fabrication of sodium carbonate FBSR products which may be more compatible with recycle to a waste or feed tank for subsequent vitrification in DWPF should be evaluated
- The use of sodium hydroxide and clay should be more fully investigated because only one test was performed with this combination of co-reactants and this combination of co-additives appeared more promising than the use of other NAS additives.
- Investigate the SRS burial ground Waste Acceptance Criteria (WAC) criteria for FBSR monolith disposal

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LIST OF ACRONYMS

BSR	Benchscale Steam Reformer
CAA	Clean Air Act
CNAS	Calcium Sodium Alumino Silicate
DTA	Differential Thermal Analysis
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
EPA	Environmental Protection Agency
ETF	Effluent Treatment Facility
FBSR	Fluidized Bed Steam Reforming
HAD	High Activity Drain
HLC	High Level Caves
HLW	High Level Waste
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
LAD	Low Activity Drain
LLRW	Low Level Radioactive Waste
MACT	Maximum Achievable Concentration Technology
ML	Mobile Laboratory
NAS	Sodium Alumino-Silicate
OPC	Ordinary Portland Cement
RCRA	Resource Conservation and Recovery Act
SEM	Scanning Electron Microscopy
SRS	Savannah River Site
SRNL	Savannah River National Laboratory
TCLP	Toxic Characteristic Leaching Procedure
THOR	Thermal Organic Reduction
WAC	Waste Acceptance Criteria
WIPP	Waste Isolation Pilot Plant
WSRC	Westinghouse Savannah River Co.
XRD	X-ray Diffraction

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1.0 INTRODUCTION

The Savannah River National Laboratory (SRNL) is a multidisciplinary laboratory operated by Westinghouse Savannah River Company (WSRC) in Aiken, South Carolina. Research and development programs have been conducted at SRNL for ~50 years generating non-radioactive (hazardous and non-hazardous) and radioactive waste materials. This study addresses only the liquid wastes generated from the laboratories area. These include [1]:

- Low-activity aqueous wastes which may or may not be hazardous due to mercury or organic content. These include process water and waste from non-radioactive chemical experiments. These wastes are typically disposed of in laboratory modules via Low-Activity Drains (LAD).
- High-activity aqueous waste from chemical experiments in the laboratories and in the Shielded Cells. This waste may or may not be hazardous due to mercury and/or organic content. These wastes are typically disposed of in laboratory modules via High-Activity Drains (HAD).

Typically the LAD and HAD aqueous effluents from the technical area are collected in 5,900 gallon and 3,670 gallon holding tanks fitted with agitators, in 776-A. When a tank is nearly full, a well-mixed sample is taken and sent for routine analyses. If the waste meet acceptable limits [1] the HAD waste can be shipped to an H-Area evaporator for volume reduction. The transfer is by steam jet in 776-A to a tanker trailer that holds approximately 4,000 gallons. For LAD aqueous wastes the tanker is not shielded. For HAD aqueous wastes the tanker trailer is shielded. The HAD wastes are shipped to H-Canyon and LAD wastes to the F/H Effluent Treatment Facility (ETF).

Because collection, analysis, and transport of LAD and HAD waste to H-Area is cumbersome and since future treatment of this waste may be curtailed as the F/H-Area evaporators and waste tanks are decommissioned, research and development efforts have been initiated within SRNL to determine a disposal path for these wastes that is not dependent on H-Area evaporators and ETF. The development of an alternative waste disposal technology for SRNL LAD and HAD waste

will enable SRNL research and development activities to be independent of other radioactive facilities on the Savannah River Site (SRS).

The first phase of the investigation was to determine the feasibility of four different alternative disposal methods for HAD waste: Solidification/Stabilization, Local Treatment at Point of Contact, FBSR, and Hybrid Microwave Technology. The objective of the first phase was to perform proof of principal scoping tests for each of the selected technologies. This report presents the results for the FBSR feasibility tests on a non-radioactive HAD simulant.

2.0 BACKGROUND: FLUIDIZED BED STEAM REFORMING (FBSR)

Studsvik built and tested a commercial Low-Level Radioactive Waste (LLRW) FBSR Processing Facility in Erwin, TN, in 1999. In January 2000, commercial operation commenced [2]. The Erwin Facility has the capability to safely and efficiently receive and process a wide variety of solid and liquid LLRW streams including: ion exchange resins, charcoal, graphite, sludge, oils, solvents, and cleaning solutions with contact radiation levels of up to 100 R/hr. The licensed and heavily shielded SPF can receive and process liquid and solid LLRWs with high water and/or organic content. The solid product produced is volume reduced during processing, drummed, and sent to Barnwell for final disposal.

The Erwin facility employs the Thermal Organic Reduction (THORsm) process, developed by Studsvik, which utilizes pyrolysis*/steam reforming technology. THORsm reliably and safely processes a wide variety of LLRW's in a unique, moderate temperature (~700°C), dual-stage, pyrolysis/reforming, fluidized bed treatment system. The reforming process has demonstrated effectiveness in volatilizing/combusting organics and separating sulfur and halogens from inorganic waste materials. Of special relevance is the capability of the THORsm technology to convert nitrates to nitrogen and sodium salts to sodium compounds that are suitable for direct disposal and/or subsequent vitrification.

In the THORsm FBSR process, a granular/particle bed material is fluidized with low pressure superheated steam. Pyrolysis is not combustion as no oxygen is present; therefore the FBSR technology is Environmental Protection Agency (EPA) Clean Air Act Maximum Achievable Concentration Technology (CAA/MACT) compliant.

THORsm performed 11 >10 pilot scale demonstrations on high Na containing Hanford salt simulants. The liquid waste was mixed in a batch/feed tank with selected co-reactants, including the additives necessary to make the final product into any of the following product phases (Table 2-1):

- Na₂CO₃ (no additives needed)
- Na₂SiO₃ (SiO₂ added)
- Na aluminosilicates (kaolin clay added)

* Pyrolysis chemically decomposes organic materials by heat in the absence of oxygen, e.g. C_xH_y + Heat → CH₄ + C.

Table 2-1. THORsm Pilot Scale Demonstrations with Hanford High Sodium Wastes

Number of Pilot Demonstrations	Additive	Mineral Product	Product Application
5	Clay	Sodium aluminosilicates such as nepheline (NaAlSiO_4), sodalite ($\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}](2\text{NaCl})$), and nosean ($\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{Na}_2\text{SO}_4)$) that can stabilize problematic anions such as Cl, F, and SO_4	FBSR product may be acceptable as a final mineral waste form for land disposal, Yucca Mountain, Waste Isolation Pilot Plant (WIPP), etc. In small quantities the FBSR product would likely be compatible with subsequent vitrification as a frit substitute.
3	Sand or Silica	Sodium silicate	FBSR product may be acceptable as a final mineral waste form for disposal at WIPP. FBSR product may be used as a partial frit replacement in HLW melter.
3	CO_2	Sodium carbonate	FBSR product may be acceptable as a final mineral waste form for disposal at WIPP. FBSR product may be used as a partial frit replacement in HLW melter.

Several chemical and physical reactions take place in the steam reformer:

- Evaporation of all liquid
- Denitration of the nitrates and nitrites (>99%) in the waste feed into nitrogen gas by the reductants added
- Conversion of organics into CO_2
- Reduction and stabilization of hazardous metals, e.g. Cr^{+6} is reduced to a non-hazardous valence state, e.g. Cr^{+3}

The FBSR technology has been demonstrated to be effective at remediation of the following:

- Hanford Low Activity Waste into either carbonates or silicates that can subsequently be vitrified [3]
- Hanford Low Activity Waste and SRS salt supernate into a final waste form (aluminosilicate mineral) for land disposal [3, 4, 5]

- INEEL Sodium Bearing Waste into a carbonate form acceptable to WIPP as a final waste form [6]
- SRS T48 HLW supernate with tetraphenyl borate into either carbonates or silicates that are compatible with subsequent vitrification in DWPF [7, 8]
- SRS Low-Curie and High-Curies salt supernates [9] into carbonate, silicate, and NAS mineral forms for burial at WIPP or Yucca Mtn.

This latter study demonstrated that the FBSR reactions can be duplicated in Al_2O_3 crucibles in small laboratory scale furnaces that fit into most SRS laboratory module hoods. All demonstrations to date have been performed with high pH (~14) SRS salt supernate simulants including high OH and high NO_3 simulants.

3.0 POTENTIAL APPLICATIONS OF FLUIDIZED BED STEAM REFORMING TO SRNL AQUEOUS WASTES

In order for the FBSR technology to be applicable to SRNL laboratory wastes a demonstration on an acidic laboratory waste simulant was needed. The FBSR Technology would allow SRNL's Laboratory waste to be remediated in any of the following ways (see also Figure 3-1):

- LAD waste could be sent to Erwin for processing into a solid carbonate, silicate, or aluminosilicate mineral form that could be disposed of in WIPP if found to be classified as TRU waste after concentration
- LAD waste could be sent to Erwin for processing into a solid aluminosilicate mineral form that could be disposed of in Barnwell or the SRS burial ground if found to be classified as non-TRU waste after concentration
- HAD waste, if volume reduced, could be processed in a semi-continuous BSR facility operated within SRNL, e.g. processed into a solid carbonate or silicate form that could be disposed of in a DWPF waste tank for subsequent vitrification
- HAD waste, if volume reduced, could be processed on a laboratory module scale in small furnaces, e.g. processed into a solid carbonate or silicate form that could be collected in the SRNL High Level Caves (HLC) and shipped to a DWPF waste or feed tank for subsequent vitrification or disposal directly into a HLW canister for shipment to Yucca Mtn.
- HAD waste, if volume increased, could be processed on a laboratory module scale or in a BSR operated in one wing of the building and solidified into a monolith for on site burial depending on the SRS burial ground Waste Acceptance Criteria (WAC)

Moreover, FBSR is being looked at for remediation of other "orphan" wastes at SRS and there is a possibility that an FBSR facility may be built at SRS for stabilization of these wastes.

The experiments discussed in this report focus on SRNL HAD waste disposal by the FBSR technology on a batch laboratory module scale, e.g. in small furnaces, and in a semi-continuous Bench Scale Reformer (BSR). FBSR formulations that are silicate based are investigated for recycle to a DWPF processing tank for subsequent vitrification. FBSR formulations that are sodium aluminosilicate (NAS) based are investigated for recycle to a DWPF processing tank for subsequent vitrification or direct disposal in WIPP or Yucca Mtn. FBSR formulations that can be solidified into a monolith for direct disposal in the SRS burial ground are also investigated. This proof of principle will cover the use of FBSR technology at any scale (pilot or full scale) in the future.

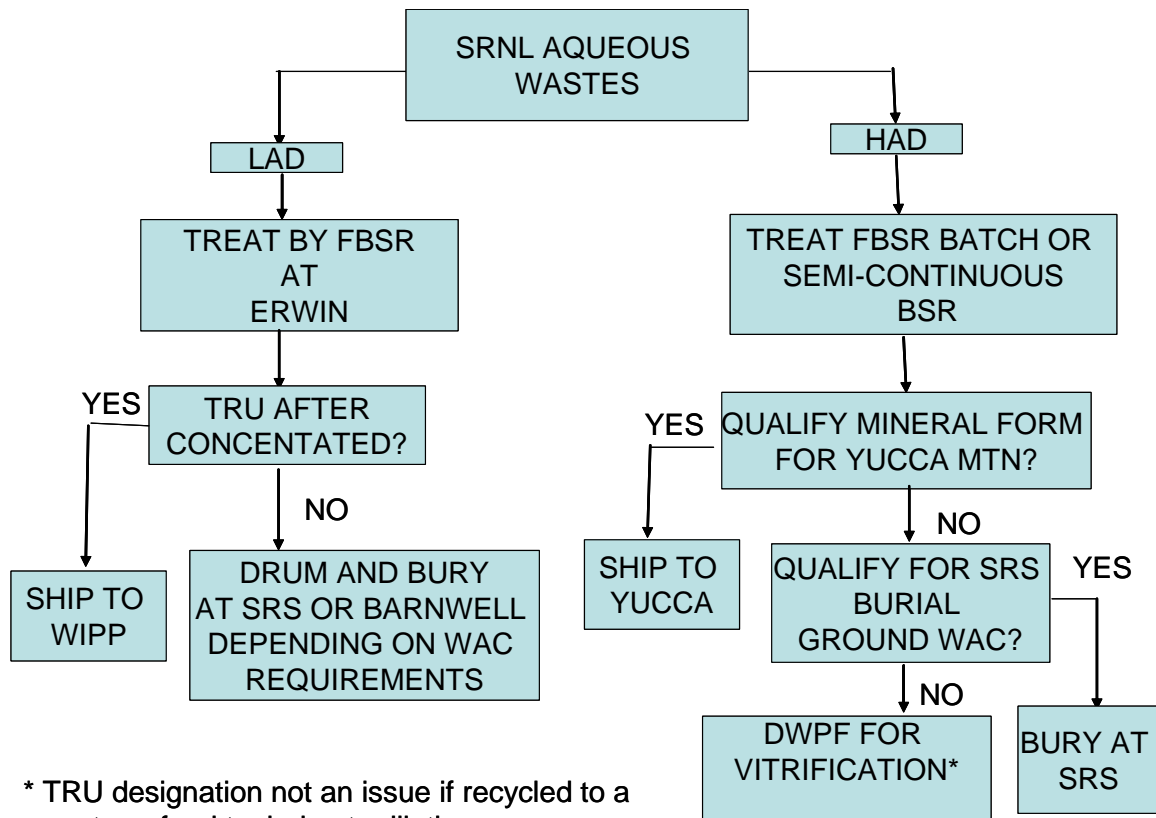


Figure 3-1. FBSR Options Matrix for Laboratory Waste Disposal.

4.0 EXPERIMENTAL

4.1 Preparation of the High Activity Drain Simulant

A simulated (non-radioactive) High Activity Drain (HAD) waste was prepared by the SRNL Mobile Lab. The simulated waste was a mixture of the following types of sludge and glass dissolutions typical of 773-A B-wing aqueous wastes before neutralization and disposal in the HAD:

- 8 L of mixed acid sample digestion (HF/HNO₃/HCl/H₃BO₃ acids)
- 8 L of aqua regia (HCl/HNO₃ acids)
- 8 L of sodium peroxide/sodium hydroxide fusion (Na₂O₂/NaOH/HCl)

The chemical composition of the simulant is given in Table 4-1.

Table 4-1. Composition of Simulated High Activity Drain Waste

Analyte	Concentration (mg/L)	Analyte	Concentration (mg/L)
Ag [†]	0.131	Na [†]	2750
Al [†]	45.2	Ni [†]	3.44
As [†]	<0.120	P [†]	0.376
B [†]	541	Pb [†]	<0.020
Ba [†]	0.454	S [†]	1.65
Ca [†]	17.6	Se [†]	<0.120
Cd [†]	<0.010	Si [†]	150
Cr [†]	0.478	Sr [†]	0.125
Cu [†]	1.43	Ti [†]	1.95
Fe [†]	106	Zn [†]	1.59
K [†]	14.9	Zr [†]	2.67
Li [†]	166	F ^{-‡}	1460
Mg [†]	10.4	Cl ^{-‡}	6500
Mn [†]	16.4	NO ₃ ^{-‡}	21300

[†] From ICP-ES

[‡] From IC

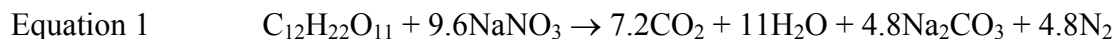
Because SRNL HAD waste is EPA Resource Conservation and Recovery Act (RCRA) characteristically hazardous, 15 mL of a RCRA metals spike solution (see Table 4-2 for solution composition) was added per L of the simulated HAD waste.

Table 4-2. Elemental Composition of RCRA Metals Solution

Metal	Concentration in RCRA Metals Solution (mg/L)	Concentration in Solution with 15 mL Metals Solution per 1 L HAD Waste Simulant (mg/L)
Antimony	75.0	1.15
Arsenic	326.2	5
Beryllium	79.6	1.22
Cadmium	7.2	0.11
Lead	48.9	0.75
Selenium	65.2	1
Thallium	13.0	0.2
Vanadium	104.4	1.6
Zinc	280.5	4.3

4.2 Steam Reformer Product Fabrication in Crucibles

Three processes were used for fabricating the steam reforming product in crucibles. In the one step process, lab waste is mixed with a solid co-reactant such as clay or silica and sucrose. The sucrose assists in the denitration allowing it to occur at lower temperatures than it would in the absence of sucrose. The sucrose also drives the nitrates and nitrites to N₂ instead of NO_x as indicated in Equation 1 and Equation 2. The amount of sucrose added to all the experiments was 2X the stoichiometric amount indicated by Equation 1 and Equation 2.



The aqueous waste, co-reactant, and sucrose are dried to a peanut butter-like consistency at 50°C to avoid splatter, and heated to 725°C for 24 hours, all in a 100 mL Al₂O₃ open crucible in a small muffle furnace with an 8" by 8" footprint. The drying step can be conducted in a separate drying oven to accommodate ~1000 mL of HAD waste at a time. Alternatively, larger crucibles and a larger oven can be used depending on the volume of wastes to be remediated. The one step process reproduces the evaporation, denitration, organic destruction, and anhydrous mineralization that occur during the FBSR process. While the 1 step process does not allow for the hydrothermal reactions to occur that would occur in a continuous or semi-continuous FBSR, it does produce the mineral phases of interest. This is the simplest small scale static FBSR process that can effectively be carried out in a single laboratory module hood. The one step process is, therefore, the preferred process if the waste remediation is to occur on a laboratory-by-laboratory module basis.

The 2 step process is the same as the one step process, but after heating at 725°C the product from the crucible is wetted and is placed in a Parr pressure vessel (sealed) for 24 hours at 90°C. The two step process reproduces the evaporation, denitration, organic destruction, and hydrothermal mineralization that occur during the FBSR process.

The three step process adds an additional heating to the two step process - 24 hours at 725°C in an open crucible to drive off waters of hydration from the mineralization that occurred during hydrothermal processing in the Parr pressure vessels. Table 4-4 is a summary of the steam reformer product samples prepared for this study. Included in the table are target products, number of steps, simulant amount, and reagents, including sucrose.

The SRNL aqueous laboratory waste is anion rich and cation poor (Table 4-1). Therefore additives that provided the cations Na^+ , Ca^{+2} , Al^{+3} , and Si^{+4} were needed to form the feldspathoid minerals (Table 4-3). These minerals have cage-like structures that stabilize the Cl, F, I, other anions and radio-nuclides in the aqueous laboratory waste. Two different sources of Na^+ were used during experimentation, commercially available Zeolite-A ($\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]\bullet 27\text{H}_2\text{O}$) and NaOH plus kaolin clay (Table 4-4). Once source of Ca^{+2} was used during experimentation, Ordinary Portland Cement (OPC).

Recent experimentation [9] has demonstrated that the formation of the sodium aluminosilicate feldspathoid minerals is well described by the known ternary phase diagram for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system (Figure 4-1 [10]). The successful Hanford AN-107 mineral waste form made by THORSM [2, 3, 4] is shown on the ternary phase diagram as the light rectangle and represents the target sodium aluminosilicate (NAS) mineral phase for the SRNL laboratory waste stabilization. The laboratory waste composition from Table 4-1 is converted to a calcine basis (composition once evaporated and denitrated) and shown by the star on $\text{SiO}_2-\text{Al}_2\text{O}_3$ binary side of the ternary diagram. The dark triangle represents the composition of the Zeolite-A additive. The dark rectangle represents the composition of the clay and NaOH mixture added.

Lab experiments # 1, 2, 3, 6, 7, and 8 were all formulated to make the target NAS mineral phases similar to the AN-107 in granular form (Figure 4-1). These mineral forms may be able to be disposed of in the SRS burial ground and/or recycled to the DWPF feed tank for subsequent vitrification due to the small quantity of NAS that will be formed (see Section 5.3). Laboratory 4 was formulated to make Na_2SiO_3 which would also be acceptable to DWPF as a frit substitute but probably not acceptable as a waste form for burial. The NAS and Na_2SiO_3 starting additives and target compositions are all shown on Figure 4-1.

The chemistry for the calcium sodium aluminosilicates (CNAS) in quaternary composition space are not as easily diagramed but have the advantage that they are naturally cementitious after mineralization at 725°C. Therefore, they can be set into blocks or cylinders for direct disposal. Lab experiments #5, 9 and 10 were attempted in order to make a naturally monolithic waste form for direct disposal (Table 4-4).

Table 4-3. Feldspathoid Minerals Commonly Found in FBSR

Substitution In Cage Structure	Chemical Formula	Common or Mineral Name	Density (g/cm ³)	Crystal Type	Ref.
Precursor					
NONE	Na ₁₂ [Al ₁₂ Si ₁₂ O ₄₈]•27H ₂ O	Zeolite-A	1.99 [‡]	Cubic	11, 13
Nephelines and Stuffed Cristobalites					
UNKNOWN	(K,Na)AlSiO ₄	Nepheline	2.63	Hexagonal	PDF#35-424
UNKNOWN	NaAlSiO ₄	Carnegeite	2.401	Cubic	PDF #11-221
UNKNOWN	(Na ₂ O)≤0.33NaAlSiO ₄	Na rich Nepheline	2.64	Cubic	PDF #39-101
UNKNOWN	Na _{1.45} Al _{1.45} Si _{0.55} O ₄	Stuffed Cristobalite	2.62	Cubic	PDF #49-2
UNKNOWN	Na _{1.95} Al _{1.95} Si _{0.05} O ₄	Stuffed Cristobalite	2.72	Tetragonal	PDF # 49-3
UNKNOWN	Na _{1.75} Al _{1.75} Si _{0.25} O ₄	Stuffed Cristobalite	2.72	Orthorhombic	PDF # 49-4
UNKNOWN	Na _{1.65} Al _{1.65} Si _{0.35} O ₄	Stuffed Cristobalite	2.69	Tetragonal	PDF # 49-5
UNKNOWN	Na _{1.55} Al _{1.55} Si _{0.45} O ₄	Stuffed Cristobalite	2.674	Orthorhombic	PDF # 49-6
UNKNOWN	Na _{1.15} Al _{1.15} Si _{0.85} O ₄	Stuffed Cristobalite	2.578	Orthorhombic	PDF # 49-7
UNKNOWN	Na ₃ MgAlSi ₂ O ₈	Stuffed Cristobalite	Not given	Orthorhombic	PDF # 49-8
Sodalite Group					
2NaCl	Na ₆ [Al ₆ Si ₆ O ₂₄](2NaCl)	Sodalite	2.31 [*]	Cubic [*]	12
2NaOH	Na ₆ [Al ₆ Si ₆ O ₂₄](2NaOH)•1.5H ₂ O	Basic Sodalite or Hydroxysodalite	2.215 ^{**}	Cubic ^{**}	13
2NaNO ₃	Na ₆ [Al ₆ Si ₆ O ₂₄](2NaNO ₃)	Nitrated Sodalite	2.342	Cubic	PDF#50-0248
Na ₂ SO ₄	Na ₆ [Al ₆ Si ₆ O ₂₄](Na ₂ SO ₄)	Nosean	2.21 ^{tt}	Cubic ^{tt}	14
xNaOH + y H ₂ O	Na ₆ [Al ₆ Si ₆ O ₂₄](xNaOH)•yH ₂ O	Basic Nosean			13
1-2(Ca,Na)SO ₄	(Na) ₆ [Al ₆ Si ₆ O ₂₄][(Ca,Na)SO ₄] ₁₋₂ ^t	Hauyne	2.4 ^t	Cubic ^t	14
x(Ca,Na)(S,SO ₄ ,Cl)	(Ca,Na) ₆ [Al ₆ Si ₆ O ₂₄][(Ca,Na)S,SO ₄ ,Cl] _x ^t	Lazurite	2.43	Cubic	PDF #17-749
Cancrinite Group					
2NaNO ₃	Na ₆ [Al ₆ Si ₆ O ₂₄](2NaNO ₃)•4H ₂ O	Nitrated Cancrinite	2.51	Hexagonal	PDF #38-513
(Na,Ca,K) ₂ CO ₃	(Na,Ca,K) ₆ [Al ₆ Si ₆ O ₂₄][(Na,Ca,K) ₂ CO ₃] _{1.6} •2.1H ₂ O	Cancrinite	2.60	Hexagonal	PDF #25-776
2(Na, K)Cl	(Na,Ca,K) ₆ [Al ₆ Si ₆ O ₂₄](2(Na,K)Cl) _{2.3}	Microsommite	2.34	Hexagonal	PDF #20-743
2(Na, K)Cl	(Na,Ca,K) ₆ [Al ₆ Si ₆ O ₂₄][(Na,K) ₂ SO ₄ ,Cl] ₃	Davyne	2.46	Hexagonal	PDF #20-379
Na ₂ CO ₃	Na ₆ [Al ₆ Si ₆ O ₂₄](Na ₂ CO ₃)	Natrodavyne	Not given	Hexagonal	PDF #15-794

t PDF #20-1087

tt PDF #17-538

* PDF # 20-495

** PDF #11-401

‡ PDF #11-0590 and #38-241

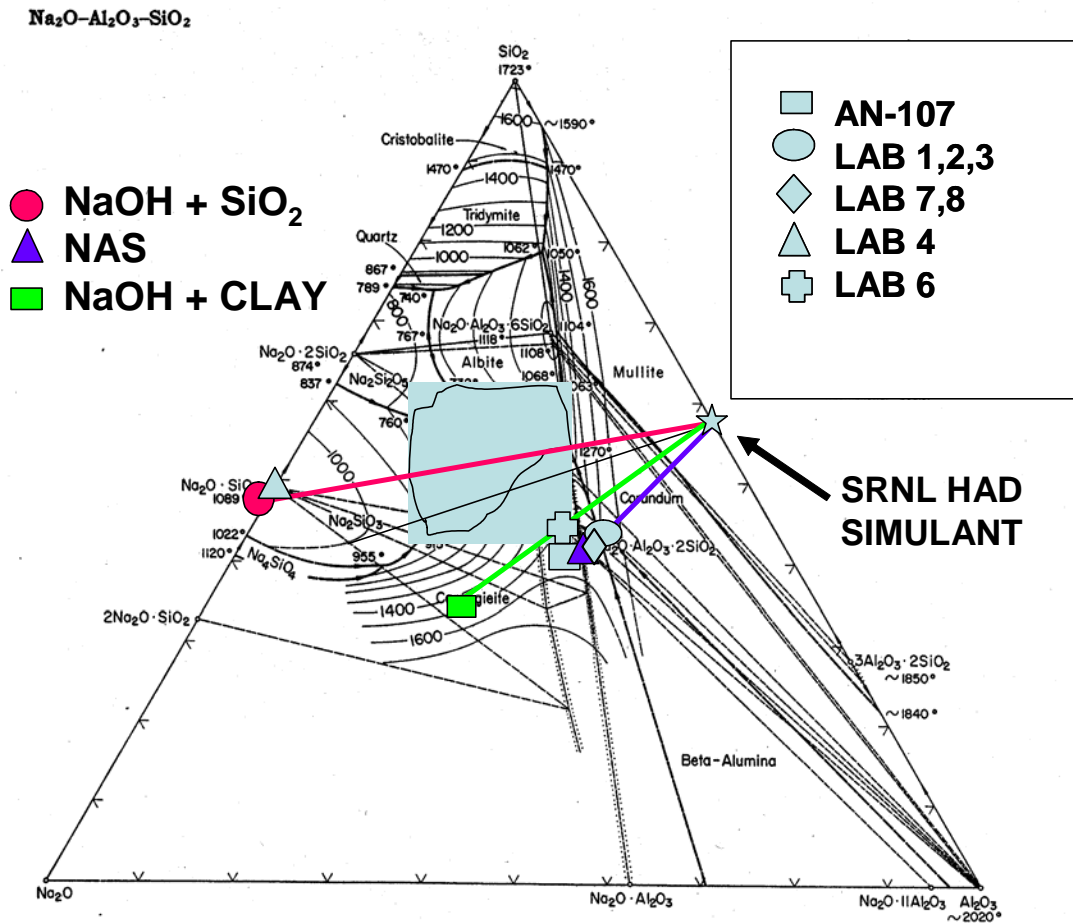


FIG. 501.—System Na₂O-Al₂O₃-SiO₂; composite.

E. F. Osborn and Arnulf Muan, revised and redrawn "Phase Equilibrium Diagrams of Oxide Systems," Plate 4, published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.

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Figure 4-1. Ternary phase diagram for the Na₂O-SiO₂-Al₂O₃ system

Table 4-4. Summary of Steam Reformer Product Samples

Sample ID	LAB-1	LAB-2	LAB-3	LAB-4	LAB-5	LAB-6	LAB-7	LAB-8	LAB-9	LAB-10
Desired Steam Reformer Product Form †	Granular NAS	Granular NAS	Granular NAS	Granular Na ₂ SiO ₃	Monolithic CNAS	Granular NAS	Granular NAS	Granular NAS	Monolithic CNAS	Monolithic CNAS
Steps	1	2	3	1	1	1	1	1	1	1
Simulant with RCRA metals (mL)	47	47	47	85.7	35.7	35.7	47	47	71.43	71.43
50% NaOH (mL)	None	None	None	8.57	3.57	3.57	None	None	None	None
Sucrose Stoichiometry	2X	2X	2X	2X	2X	2X	2X	2X	2X	2X
Sucrose (g)	1.15	1.15	1.15	2.1	0.87	0.87	1.15	1.15	1.75	1.75
Reagent(s)	Zeolite A	Zeolite A	Zeolite A	NaOH + SiO ₂	NaOH + OPC	NaOH+ Clay	Zeolite A	Zeolite A	Zeolite A + OPC	Zeolite A + OPC
Grams Solid Reagent	9.37	9.37	9.37	4	7.5	7.5	13.399	13.822	95 + 100	95 + 50
Additive Loading (wt%)	93	93	93	95	95	95	95	98	97.5	96.5

† NAS = sodium aluminosilicate; CNAS = calcium sodium aluminosilicate; OPC = ordinary Portland cement;

4.3 Steam Reformer Product Fabrication in the SRNL Benchscale Steam Reformer

The bench-top steam reformer (BSR) is a two-stage unit used to produce the same mineralized products and gases as a fluidized bed steam reformer (FBSR). A schematic of the unit is shown in figure 4-2.

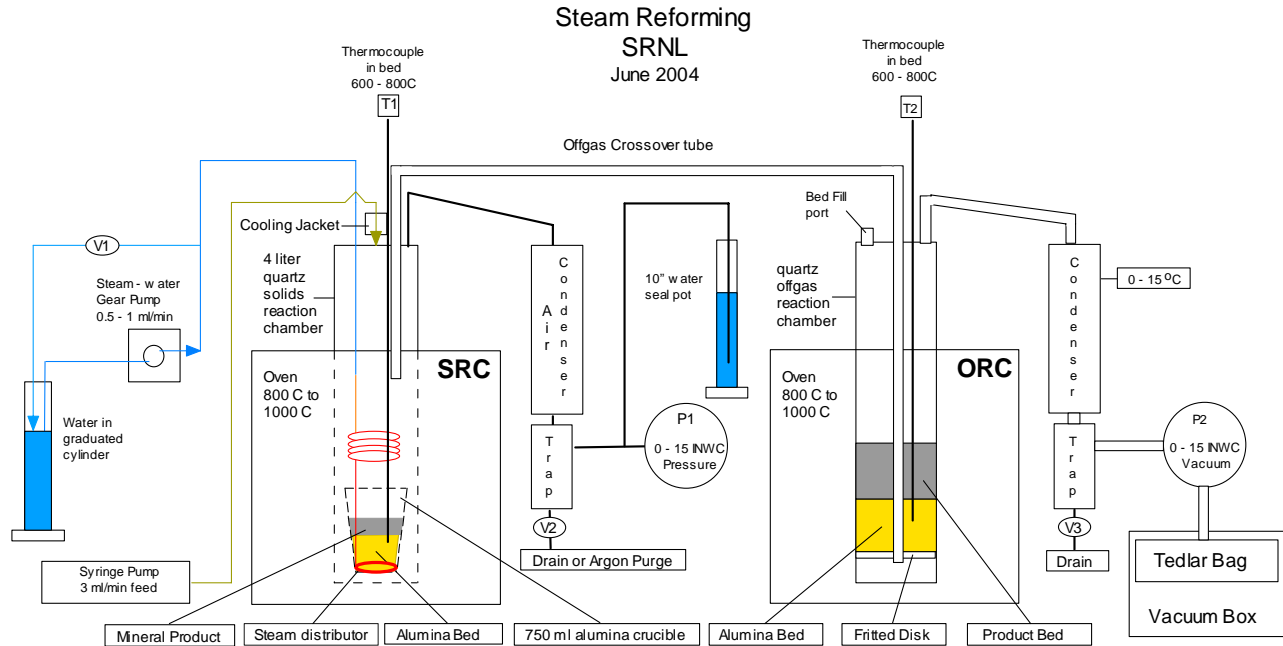


Figure 4-2. Schematic of the SRNL Benchscale Steam Reformer

The solids reaction chamber (SRC) holds a crucible into which a steam distributor, submerged in an alumina bed, is used to produce the superheated steam needed for the reactions. The premixed feed slurry is dripped into the crucible where the reactions take place.

Gases and steam leaving the crucible travel through an insulated crossover tube and into the Off-gas Reaction Chamber (ORC) of the unit where the gases then go through more heated alumina before reacting with ground up product that comes from a previous run. The resulting steam is condensed and collected in a trap and the non-condensable gases are dried through desiccant before being collected in a Tedlar bag.

Two additional Steam Reformer products, LAB-7PB and LAB-10PB, were produced in SRNL's Benchscale Steam Reformer (BSR). The BSR was run at 725°C for 4 hours with the same co-reactants and sucrose concentrations as indicated in Table 4-4. Lab waste #7, a granular NAS waste form, and Lab waste #10, a monolithic waste form, were both tested in the BSR. It was especially important to run one of the monolithic waste form tests in the BSR with real steam to ensure that the OPC used as a source for calcium and silica did not react in the continuous steam environment.

5.0 RESULTS

5.1 Granular FBSR Products

5.1.1 Zeolite A Additives

The SRNL aqueous wastes only contain about 1.5 wt% total solids after evaporation and denitration. Therefore, the additives had to contain the necessary cations (Na^+ and Ca^{+2}) to complex the anion rich waste. The additive loadings were high but gave large volume reductions (Section 5.3). Laboratory experiments LAB 1, LAB 2, and LAB 3 had a 93% additive loading while LAB 7 and LAB 8 had 95% and 98% additive loadings, respectively.

LAB 1 and LAB 2 made the desired Cl host phase sodalite from the HCl in the HAD waste. The X-ray Diffraction (XRD) analysis of LAB 1 and LAB 2 indicated that there was excess NaCl present in the product that did not get bound up in the preferred sodalite mineral host phase (Table 5-1) when tested in the crucibles by the one step and two step process. This may indicate that the additive loading is not sufficiently high enough, e.g. does not provide enough cations, to complex all the anions in the HAD waste or that the one and two step processes are insufficient at immobilization. LAB 3, the three step process, at 93% additive loading made the desired phases without any excess NaCl (Table 5-1). This may be due to excess volatilization of the residual NaCl in the third step as shown in Table 5-2.

LAB 7 and LAB 8 made the desired sodalite and nepheline host phases when experiments using Zeolite A as the primary source of Na^+ were performed at 95 and 98% additive loadings using only the one step process (Table 5-1). These experiments also retained more Cl than the LAB 2 and LAB 3 samples (Table 5-2) indicating that the higher additive loadings are necessary to retain all the anions in the HAD waste.

Experiment LAB 7, at a 95% Zeolite A additive loading was also fabricated in the BSR. The product sample from the BSR had residual NaCl in the pattern suggesting that a 98% additive loading is more reasonable to tie up all of the HAD anions in the cage like sodalite and nepheline phases. This sample retained more Cl than any of the crucible experiments (sample LAB 7PB in Table 5-2).

5.1.2 NaOH and Kaolin Clay Additives

Lab 6 was made from NaOH and OptiKasT kaolin clay (Table 4-4). It had a ~95% additive loading and also produced the desired Cl rich sodalite and nepheline phases without any excess NaCl being observed in the XRD of the product (Table 5-1). This indicates that slightly higher concentrations of HAD waste may be solidified in the FBSR NAS phases if reacted with clay and NaOH instead of Zeolite-A so that the waste is incorporated during reaction of the NaOH and the clay.

5.1.3 NaOH and Silica Additives

The attempt to make Na_2SiO_3 with the HAD simulant was not successful (LAB 4). While a different sodium silicate product was made ($\text{Na}_2\text{Si}_2\text{O}_5$), the major phase produced was NaCl with minor NaF and SiO_2 as other products. This phase assemblage indicates that the Cl in the HAD waste sequestered the Na from the NaOH to form NaCl and NaF and the SiO_2 remained unreacted.

5.2 Monolithic FBSR Products

5.2.1 Zeolite A and Ca-Silicate Additives

Experiments LAB 9 and LAB 10 attempted to make monolithic, naturally cementitious, waste forms from the SRNL aqueous HAD waste. In these tests both the Zeolite-A used in the granular tests and Portland cement were used as a source of cations and silica. In both of these tests the Zeolite-A additive was present at 95 wt%. In LAB 9 an amount of Portland cement equal to the Zeolite-A was added to the HAD simulant before treatment. In LAB 10 the amount of Portland cement was $\frac{1}{2}$ the amount of the Zeolite-A added. LAB 9 and LAB 10 made the desired sodalite, nepheline, and calcium silicate (larnite) phases and contained some extra Portland cement phases (calcium aluminates and calcium aluminoferrites) which were expected (Table 5-1).

The LAB 10 formulation was also treated in the BSR to determine if the steam would affect the Portland cement. This was by far the most successful monolithic test performed in that the product phases were sodalite, nepheline, zeolite-A and larnite (Table 5-1). Moreover, the OPC did not react in the steam and a free flowing powder was produced.

After the samples were heat treated and ground they were set with water at a water to cement (W/C) ratio of ~ 0.6 [15] and left to cure for a month. All of the samples, LAB 9 (crucible), LAB 10 (crucible and BSR) all set into cylindrical waste forms (see Figure 5-1). The LAB 10 crucible sample did not set well but the LAB 10 BSR sample and the LAB 9 crucible samples set very well into cylinders that could be used for direct disposal.

5.2.2 NaOH and Ca-Silicate Additives

LAB 5 was made with NaOH and Portland cement using the cement and the NaOH as a source of cations but only using the cement as a source of silica and alumina. This experiment was not very successful in that excess NaCl from the HAD waste was the major phase observed (Table 5-1) along with other Portland cement phases such as calcium aluminoferrite (brownmillerite) and portlandite.

After this sample was heat treated and ground it was set with water at a water to cement (W/C) ratio of 0.6 [15] and left to cure for a month. Even though the Cl was still present as NaCl according to the XRD analyses, this sample set well into a cylindrical disc (see Figure 5-1 for a photo). This sample was set into a disc instead of a cylinder as a smaller amount of waste product had been made than LAB 9 and LAB 10.



Figure 5-1. Photo of Monolithic FBSR Products (Lab 10, Lab 9, and Lab 5)

5.3 Chemical Analyses

Results of chemical analyses of the lab waste products are given in Table 5-2 (anions) and Table 5-3 (cations). All analyses were performed in duplicate since the FBSR product can be variable on a localized scale. For the aluminosilicate waste forms, sodium, aluminum and silicon were converted to oxides and normalized for comparison to the targeted composition. This comparison is given in Table 5-4. The comparison confirms that waste form compositions achieved were the compositions desired. Table 5-3 (cations) also indicates that the RCRA elements were retained in the waste form.

The anion analyses given in Table 5-2 show that:

- Nearly all the nitrate was destroyed. Additional sucrose or coal could be added to get higher destruction if necessary.
- Nearly all the chloride was retained (i.e., not volatilized) during sample fabrication.
- Fluoride was volatilized during sample preparation
- Sulfate content was much higher than expected based on analyzed simulated HAD waste composition. This is likely due to sulfate that was present in the RCRA spike which was not analyzed. The results do show that sulfate had not volatilized during processing; however, this cannot be quantified without analysis of the RCRA spike.

5.4 Volume Reductions/Increases

Most of the LAB waste experiments afforded large volume reductions relative to the volume of the original HAD waste (see Table 5-5). For the granular products that can be recycled to a DWPF feed tank or a waste tank, the volume reductions range from 90-93%. Therefore, a tanker truck of 4000 gallons of HAD waste would only make 280 gallons of solid granular waste product. However, there is only ~3925 L (1037 gallons) of HAD waste generated in SRNL on a yearly basis. Therefore, FBSR of a years worth of HAD waste would create ~104 gallons of granular waste or ~575 kgs of solid waste per year assuming an FBSR product density of 1.46 kg/L. However, this waste would be highly radioactive.

For the monolithic FBSR products that may be acceptable for on site burial, one produced a volume decrease of 93% (LAB 5) but the phases produced were poorly cementitious. LAB 9 and LAB 10 which were cementitious produced volume increases of 48% and 9% respectively compared to the original HAD waste volume.

Table 5-1. Summary of Steam Reformer Product Sample Results

Sample ID	Temp (°C)	Time at Temp	Parr Vessel Treat	Major Phase Desired	Major Phases Identified by X-Ray Diffraction	Minor Phases Identified by X-Ray Diffraction
Open Crucible Tests						
LAB-1	725	24	NO	Sodalite/Nepheline	Sodalite [Na ₈ (AlSiO ₄) ₆ Cl ₂] Nepheline [NaAlSiO ₄]	NaCl
LAB-2	725	24	YES	Sodalite/Nepheline	Sodalite [Na ₈ (AlSiO ₄) ₆ Cl ₂] Nepheline [Na _{6.65} Al _{6.24} Si _{9.76} O ₃₂]	NaCl
LAB-3	725	24	YES	Sodalite/Nepheline	Sodalite [Na ₈ (AlSiO ₄) ₆ Cl ₂] Nepheline [NaAlSiO ₄]	None
LAB-4	725	24	NO	Na ₂ SiO ₃	NaCl	Na ₂ Si ₂ O ₅ , NaF, Quartz [SiO ₂]
LAB-5	725	24	NO	Sodalite/Nepheline and Ca-Silicates	NaCl, CaO, Larnite [Ca ₂ SiO ₄],	Brownmillerite [Ca ₂ Fe _{1.52} Al _{0.48} O ₅]Portlandite [Ca(OH) ₂], Perovskite [CaTiO ₃]
LAB-6	725	24	NO	Sodalite/Nepheline	Sodalite [Na ₈ (AlSiO ₄) ₆ Cl ₂] Nepheline [Na ₃ K(Al _{0.44} Si _{0.56}) ₈ O ₁₆]	Anatase [TiO ₂] Quartz [SiO ₂]
LAB-7	725	24	NO	Sodalite/Nepheline	Sodalite [Na ₈ (AlSiO ₄) ₆ Cl ₂] Nepheline [NaAlSiO ₄]	None
LAB-8	725	24	NO	Sodalite/Nepheline	Sodalite [Na ₈ (AlSiO ₄) ₆ Cl ₂] Nepheline [NaAlSiO ₄]	None
LAB-9	725	24	NO	Sodalite/Nepheline and Ca-Silicates	Sodalite [Na ₈ (AlSiO ₄) ₆ Cl ₂] Nepheline [NaAlSiO ₄] Larnite [Ca ₂ SiO ₄]	Brownmillerite [Ca ₂ Al _{1.38} Fe _{0.62} O ₅]
LAB-10	725	48	NO	Sodalite/Nepheline and Ca-Silicates	Nepheline [Na _{6.65} Al _{6.24} Si _{9.76} O ₃₂] Larnite [Ca ₂ SiO ₄]	Calcium Aluminate [4CaO•3(Al ₂ O ₃)]
Benchscale Steam Reformer						
LAB-7PB	725	24	NO	Sodalite/Nepheline	Sodalite [Na ₈ (AlSiO ₄) ₆ Cl ₂] Nepheline [NaAlSiO ₄]	NaCl
LAB-10PB	725	48	NO	Sodalite/Nepheline and Ca-Silicates	Sodalite [Na ₄ Al ₃ Si ₃ O ₁₂ C] Nepheline [Na ₃ K(Al _{0.44} Si _{0.56}) ₈ O ₁₆] Zeolite 4A [Na ₉₂ Al ₉₂ Si ₁₀₀ O ₃₈₄], Larnite [Ca ₂ SiO ₄]	None

Table 5-2. Anion Concentrations (wt%) of SRNL HAD Waste Samples After Solidification

Sample ID	Mobile Lab ID	F	Cl	NO ₂	NO ₃	PO ₄	SO ₄
Lab-1 (A)	04-1167	<0.100	5.69	<0.100	0.088	<0.010	0.039
Lab-1 (B)	04-1167	<0.100	4.96	<0.100	0.064	<0.010	0.034
Lab-2 (A)	04-1168	<0.100	4.86	<0.100	0.082	<0.010	0.038
Lab-2 (B)	04-1168	<0.100	4.88	<0.100	0.082	<0.010	0.038
Lab-3 (A)	04-1169	<0.100	3.84	<0.100	0.079	<0.010	0.040
Lab-3 (B)	04-1169	<0.100	3.45	<0.100	0.062	<0.010	0.039
Lab-4 (A)	04-1170	1.74	15.3	<0.100	0.036	<0.010	<0.010
Lab-4 (B)	04-1170	1.74	15.3	<0.100	0.037	<0.010	<0.010
Lab-5 (A)	04-1171	0.694	5.97	<0.100	0.039	<0.010	1.80
Lab-5 (B)	04-1171	0.733	6.04	<0.100	0.040	<0.010	1.78
Lab-6 (A)	04-1172	<0.100	6.37	<0.100	0.342	<0.010	0.072
Lab-6 (B)	04-1172	<0.100	6.50	<0.100	0.368	<0.010	0.070
Lab-7 (A)	04-1173	<0.100	4.89	<0.100	0.076	<0.010	0.045
Lab-7 (B)	04-1173	<0.100	4.88	<0.100	0.076	<0.010	0.045
Lab-7 PB (A)	04-1174	<0.100	6.67	<0.100	0.087	<0.010	0.043
Lab-7 PB (B)	04-1174	<0.100	6.38	<0.100	0.076	<0.010	0.043
Lab-8 (A)	04-1175	<0.100	4.52	<0.100	0.088	<0.010	0.046
Lab-8 (B)	04-1175	<0.100	4.43	<0.100	0.085	<0.010	0.043
Lab-9 (A)	04-1176	<0.100	0.720	<0.100	0.043	<0.010	1.08
Lab-9 (B)	04-1176	<0.100	0.699	<0.100	0.041	<0.010	0.658
Lab-10 (A)	04-1177	<0.100	0.924	<0.100	0.040	<0.010	0.937
Lab-10 (B)	04-1177	<0.100	0.975	<0.100	0.051	<0.010	0.980
Lab-10 PB (A)	04-1178	<0.100	0.937	<0.100	0.044	<0.010	0.834
Lab-10 PB (B)	04-1178	<0.100	0.927	<0.100	0.042	<0.010	0.830

Table 5-3. Cation Concentrations (wt%) of SRNL HAD Waste Samples After Solidification

Sample ID	Mobile Lab ID	Ag	Al	As	Ba	Be	Ca	Cd	Cr	K	Na	Ni	Pb	S	Se	Si	Ti	V	Zn
Lab-1 (A)	04-1167	<0.010	17.3	<0.010	0.007	<0.001	0.062	<0.010	0.026	0.094	15.8	0.018	<0.010	<0.100	<0.010	17.6	0.012	0.006	0.008
Lab-1 (B)	04-1167	<0.010	16.6	<0.010	0.007	<0.001	0.057	<0.010	0.015	0.080	15.8	0.011	<0.010	<0.100	<0.010	17.3	0.008	0.006	0.008
Lab-2 (A)	04-1168	<0.010	12.7	<0.010	0.007	<0.001	0.045	<0.010	0.013	0.064	11.6	0.010	<0.010	<0.100	<0.010	13.3	0.006	0.006	0.011
Lab-2 (B)	04-1168	<0.010	13.0	<0.010	0.007	<0.001	0.047	<0.010	0.012	0.062	11.7	0.011	<0.010	<0.100	<0.010	13.3	0.006	0.006	0.007
Lab-3 (A)	04-1169	<0.010	17.3	<0.010	0.007	<0.001	0.060	<0.010	0.015	0.086	15.8	0.011	<0.010	<0.100	<0.010	17.8	0.008	0.006	0.006
Lab-3 (B)	04-1169	<0.010	16.7	<0.010	0.007	<0.001	0.061	<0.010	0.016	0.088	15.2	0.013	<0.010	<0.100	<0.010	17.7	0.008	0.006	0.007
Lab-4 (A)	04-1170	<0.010	0.188	<0.010	0.006	<0.001	0.012	<0.010	0.014	<0.010	31.9	0.015	<0.010	<0.100	<0.010	16.1	0.003	0.006	0.012
Lab-4 (B)	04-1170	<0.010	0.183	<0.010	0.006	<0.001	0.014	<0.010	0.015	<0.010	31.3	0.013	<0.010	<0.100	<0.010	16.0	0.004	0.006	0.010
Lab-5 (A)	04-1171	<0.010	1.74	<0.010	0.023	<0.001	28.9	<0.010	0.016	0.219	13.4	0.013	<0.010	0.592	<0.010	5.78	0.090	0.024	0.019
Lab-5 (B)	04-1171	<0.010	1.76	<0.010	0.023	<0.001	28.9	<0.010	0.015	0.215	14.4	0.013	<0.010	0.605	<0.010	5.86	0.095	0.024	0.027
Lab-6 (A)	04-1172	<0.010	15.8	<0.010	0.010	<0.001	0.049	<0.010	0.021	0.097	17.5	0.013	<0.010	<0.100	<0.010	16.0	0.681	0.017	0.007
Lab-6 (B)	04-1172	<0.010	16.0	<0.010	0.010	<0.001	0.059	<0.010	0.022	0.094	17.7	0.012	<0.010	<0.100	<0.010	16.2	0.711	0.017	0.009
Lab-7 (A)	04-1173	<0.010	17.2	<0.010	0.007	<0.001	0.069	<0.010	0.017	0.103	16.1	0.011	<0.010	<0.100	<0.010	17.7	0.008	0.006	0.009
Lab-7 (B)	04-1173	<0.010	17.4	<0.010	0.006	<0.001	0.064	<0.010	0.014	0.093	17.3	0.011	<0.010	<0.100	<0.010	17.8	0.008	0.005	0.006
Lab-7 PB (A)	04-1174	<0.010	18.9	<0.010	0.006	<0.001	0.059	<0.010	0.018	0.091	17.0	0.013	<0.010	<0.100	<0.010	16.8	0.007	0.006	0.010
Lab-7 PB (B)	04-1174	<0.010	17.7	<0.010	0.006	<0.001	0.061	<0.010	0.014	0.090	16.2	0.010	<0.010	<0.100	<0.010	16.7	0.007	0.005	0.010
Lab-8 (A)	04-1175	<0.010	16.9	<0.010	0.007	<0.001	0.177	<0.010	0.014	0.088	15.2	0.009	<0.010	<0.100	<0.010	17.4	0.009	0.005	0.006
Lab-8 (B)	04-1175	<0.010	17.2	<0.010	0.007	<0.001	0.060	<0.010	0.013	0.091	15.4	0.009	<0.010	<0.100	<0.010	18.0	0.007	0.006	0.005
Lab-9 (A)	04-1176	<0.010	9.56	<0.010	0.020	<0.001	22.5	<0.010	0.018	0.225	7.71	0.012	<0.010	0.554	<0.010	13.5	0.076	0.020	0.014
Lab-9 (B)	04-1176	<0.010	9.52	<0.010	0.020	<0.001	23.8	<0.010	0.020	0.223	7.52	0.011	<0.010	0.500	<0.010	13.5	0.077	0.020	0.015
Lab-10 (A)	04-1177	<0.010	11.2	<0.010	0.016	<0.001	15.8	<0.010	0.017	0.242	8.94	0.009	<0.010	0.310	<0.010	16.4	0.055	0.015	0.011
Lab-10 (B)	04-1177	<0.010	11.0	<0.010	0.016	<0.001	15.2	<0.010	0.017	0.254	9.21	0.010	<0.010	0.312	<0.010	16.3	0.054	0.015	0.013
Lab-10 PB (A)	04-1178	<0.010	13.1	<0.010	0.016	<0.001	13.6	<0.010	0.015	0.167	9.93	0.027	<0.010	0.283	<0.010	14.7	0.052	0.015	0.011
Lab-10 PB (B)	04-1178	<0.010	13.5	<0.010	0.016	<0.001	14.0	<0.010	0.015	0.171	10.1	0.047	<0.010	0.285	<0.010	14.5	0.058	0.014	0.012

Table 5-4. Comparison Between Targeted and Measured Sodium, Aluminum, and Silicon Oxides in Lab Waste Samples

		Normalized Oxide Wt%		
		Na ₂ O	Al ₂ O ₃	SiO ₂
Lab-1 (Crucible)	Target	23.3	35.1	41.5
	Measured	23.5	35.3	41.2
Lab-2 (Crucible)	Target	23.3	35.1	41.5
	Measured	22.9	35.5	41.6
Lab-3 (Crucible)	Target	23.3	35.1	41.5
	Measured	23.0	35.3	41.7
Lab-4 (Crucible)	Target	57.2	0.1	42.7
	Measured	55.1	0.5	44.4
Lab-6 (Crucible)	Target	24.0	34.1	42.0
	Measured	26.9	34.1	39.0
Lab-7 (Crucible)	Target	22.9	35.4	41.7
	Measured	24.2	35.1	40.8
Lab-7PB (BSR)	Target	22.9	35.4	41.7
	Measured	24.1	37.3	38.6
Lab-8 (Crucible)	Target	22.9	35.4	41.8
	Measured	22.7	35.5	41.7

Table 5-5. Volume Reductions/Increases for FBSR HAD Products

Sample ID	Type of SR Additive	Type of SR Product	Bulk Density Prod (Kg/L)	Volume Reduction (%)	Volume Increase
LAB WASTE 1, 2, 3	Zeolite-A	Granular	1.46*	93	N/A
LAB WASTE 4	NaOH+SiO ₂	Granular	1.46*	92	N/A
LAB WASTE 5	NaOH+OPC	Monolithic	1.65**	93	N/A
LAB WASTE 6	NaOH+Clay	Granular	1.46*	92	N/A
LAB WASTE 7	Zeolite-A	Granular	1.46*	90	N/A
LAB WASTE 8	Zeolite-A	Granular	1.46*	90	N/A
LAB WASTE 9	Zeolite-A + OPC	Monolithic	1.34**	N/A	148
LAB WASTE 10	Zeolite-A + OPC	Monolithic	1.35***	N/A	109

*value reported for granular FBSR bed product [6]; **value calculated from measured dimensions and weight.

6.0 CONCLUSIONS

The FBSR technology was shown to be a suitable technology for disposal of SRNL HAD waste via any number of disposal paths. The FBSR technology is suitable for HAD waste disposal whether the technology is carried out in individual laboratory modules or in a centralized facility within SRNL. The latter, which provides for semi-continuous processing would be a more efficient method of HAD waste disposal.

The simplest batch laboratory crucible process is performed in a small muffle furnace with an 8" by 8" footprint. The one step process was shown to adequately make granular FBSR product when 95-98 wt% Zeolite-A was added to SRNL aqueous laboratory waste (Tests LAB 7 and LAB 8) although the hydrothermal reactions that catalyze the FBSR product formation were not duplicated. Experiment LAB 7 was shown to be successful in the BSR at 95% additive loading and would probably perform better at the 98 wt% additive loading of the LAB 8 formulation. These FBSR products make the desired sodalite and nepheline mineral host phases that sequester Cl, F, and SO₄ from the HAD waste. The one step open crucible process was also shown to be successful when ~95% of other additives (combined NaOH 50% solution and kaolin clay) were added to SRNL aqueous waste (LAB 6). These granular wastes reduce the HAD volume by 90-93 wt% so that it can be recycled to a DWPF process or waste tank.

Formation of Na₂SiO₃ from NaOH 50% solution and silica was not successful (Test LAB 4). Formation of a naturally cementitious FBSR product from HAD waste and Portland cement was also not successful (LAB-5) in that the desired mineral phases were not achieved. LAB-5 did however set when mixed with water although the material was still somewhat friable.

The FBSR process yields 90-93% volume reductions as demonstrated in this study. There is ~3925 L of HAD waste generated in SRNL on a yearly basis. Therefore, FBSR of the HAD waste would create ~575 kgs of solid waste per year. These solids will likely have to be collected and recycled back to a waste or feed tank for subsequent vitrification in the Defense Waste Processing Facility (DWPF) because of the high doses of radioactivity associated with the large volume reductions or disposed of directly into a DWPF canister for burial at the federal Yucca Mtn. Repository. Recycle to DWPF would require a determination of the compatibility of the minerals produced with the DWPF process. Previous studies on SRS salt supernates have indicated that the carbonates and silicates are compatible with recycle to DWPF. Disposal at Yucca Mtn. would require qualification of the FBSR NAS mineral waste form as an alternative to vitrification. This study concentrated on producing the NAS FBSR mineral phases because these phases have the best anion and radionuclide retention, can be substituted for DWPF frit, and are the most flexible in terms of disposal paths.

The monolithic tests where both Zeolite-A and Portland cement were added before the FBSR roasting stage were successful and the resulting free flowing powder could be set with water for direct disposal in the SRS burial ground depending on the WAC and permitting issues. The monolithic tests produced volume increases of 9-48% which dilutes the radioactivity of the HAD waste monolith closer to acceptable WAC limits.

7.0 RECOMMENDATIONS/PATH FORWARD

Based on the results and conclusions presented in this study, the following recommendations are made:

- Investigations of one or more successful formulations from this study should be verified with radioactive HAD wastes on both the batch scale and the semi-continuous BSR scale.
- The hazardous constituent spike used in this study should be analyzed so that the sulfate retention of the FBSR products produced in this study can be better quantified.
- Additional testing such as the Toxic Characteristic Leaching Procedure (TCLP), compressive strength, and Scanning Electron Microscopy (SEM) analyses on the naturally cementitious monoliths should be completed to evaluate the suitability of this form for land disposal.
- Alternative sources of calcium silicates should be investigated to make monolithic waste forms that are naturally cementitious to see if the monolith properties can be improved, e.g. compressive strength.
- Fabrication of sodium carbonate FBSR products which may be more compatible with recycle to a waste or feed tank for subsequent vitrification in DWPF should be evaluated.
- The use of sodium hydroxide and clay should be more fully investigated because only one test was performed with this combination of co-reactants and this combination of co-additives appeared more promising than the use of other NAS additives.
- Investigate the SRS burial ground Waste Acceptance Criteria (WAC) criteria for FBSR monolith disposal.

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