Fluidized Bed Steam Reforming (FBSR) of High Level Waste (HLW) Organic and Nitrate Destruction Prior to Vitrification: Crucible Scale to Engineering Scale Demonstrations and Non-Radioactive to Radioactive Demonstrations - 9406

C.M. Jantzen, M.R. Williams, P.R. Burket, C.L. Crawford, and W.E. Daniel
Savannah River National Laboratory
Aiken, SC 29808
carol.jantzen@srnl.doe.gov

ABSTRACT

Over a decade ago, an in-tank precipitation process to remove Cs-137 from radioactive high level waste (HLW) supernates was demonstrated at the Savannah River Site (SRS). The full scale demonstration with actual HLW was performed in SRS Tank 48 (T48). Sodium tetraphenylborate (NaTPB) was added to enable Cs-137 extraction as CsTPB. The CsTPB, an organic, and its decomposition products proved to be problematic for subsequent processing of the Cs-137 precipitate in the SRS HLW vitrification facility for ultimate disposal in a HLW repository. Fluidized Bed Steam Reforming (FBSR) is being considered as a technology for destroying the organics and nitrates in the T48 waste to render it compatible with subsequent HLW vitrification. During FBSR processing the T48 waste is converted into organic-free and nitrate-free carbonate-based minerals which are water soluble. The soluble nature of the carbonate-based minerals allows them to be dissolved and pumped to the vitrification facility or returned to the tank farm for future vitrification. The initial use of the FBSR process for T48 waste was demonstrated with simulated waste in 2003 at the Savannah River National Laboratory (SRNL) using a specially designed sealed crucible test that reproduces the FBSR pyrolysis reactions, i.e. carbonate formation, organic and nitrate destruction. This was followed by pilot scale testing of simulants at the Science Applications International Corporation (SAIC) Science & Technology Application Research (STAR) Center in Idaho Falls, ID by Idaho National Laboratory (INL) and SRNL in 2003-4 and then engineering scale demonstrations by THOR® Treatment Technologies (TTT) and SRS/SRNL at the Hazen Research, Inc. (HRI) test facility in Golden, CO in 2006 and 2008. Radioactive sealed crucible testing with real T48 waste was performed at SRNL in 2008, and radioactive Benchscale Steam Reformer (BSR) testing was performed in the SRNL Shielded Cell Facility (SCF) in 2008.

INTRODUCTION

An In Tank Processing (ITP) technology was developed at the Savannah River Site (SRS) to remove Cs-137 from high level waste (HLW) supernates. During the ITP process monosodium titanate (MST) and sodium tetraphenylborate (NaTPB) were added to the salt supernate to adsorb Sr-90/Pu-238 and precipitate Cs-137 and K as CsTPB and KTPB, respectively. This process was demonstrated at the SRS in 1983 [1]. The demonstration facility consisted of Tank 48, a 4.9 million liter, carbon steel, underground HLW tank that had been retrofitted with chemical addition and process monitoring equipment. The actual demonstration was performed on a 1.89 million liter batch of radioactive salt supernate that was chemically treated and filtered. This produced 1.7 million liters of decontaminated supernate, which was disposed of in saltstone, and

200,605 liters of 2.5 wt% Cs rich precipitate. The precipitate was washed to reduce the sodium concentrations and concentrate the TPB. The washed precipitate was stored in T48 for ultimate disposal in borosilicate glass in the Defense Waste Processing Facility (DWPF).

The 1983 ITP process demonstration was considered a success and construction of a permanent ITP facility was started in 1985. In order to make the ITP waste compatible with the high temperature DWPF vitrification process, the benzene emitted from the ITP had to be destroyed. The ITP precipitate conditioning started with washing in the Late Wash Facility to remove non-radioactive salts and reduce nitrite concentration. This washing was to be followed by decomposition of the TPB to benzene and separation of the benzene from the aqueous waste in the DWPF Salt Cell. The benzene was to be burned in the SRS Consolidated Incinerator Facility (CIF) while the cesium, titanium, and boron rich residues were vitrified in the DWPF [2].

The permanent ITP facility initiated radioactive operation in September 1995. The first feed was 492,050 liters of salt solution and 141,180 liters of NaTPB, mixed with the heel of precipitate in T48 that remained from the 1983 demonstration. During processing, benzene evolved in T48 at higher rates than anticipated from decomposition of the NaTPB. Although the operational safety limit for benzene emission was never approached, the DOE initiated a stop work order and in 1998 abandoned the ITP project. New technologies for Cs-137 removal have been researched and are about to be implemented. Since 1996, radioactive sludge vitrification in the DWPF has proceeded without the ITP alkali boron contribution.

Currently T48 has about 946,250 liters of slurry which contains KTPB and CsTPB. T48 needs to be returned to service in order to free up tank space in the high level waste (HLW) system. The TPB organics in the T48 slurry need to be converted to a form suitable for processing in the DWPF or returned to the tank farm for future vitrification.

The FBSR is a technology that is capable of destroying the alkali TPB, benzene, and other organic byproducts, as well as the nitrates, and converting them to $(Na, K, Cs)_2CO_3$, CO_2 gas, N_2 gas, and H_2O vapor [3,4] at moderate temperatures (~650°C). Other components in the waste are converted to oxides, silicates, phosphates, and iron titanates. The FBSR can be electrically heated (units of $\leq$15.2 cm) or operated in an auto-thermal mode (units > 15.2 cm). In the auto-thermal mode the energy needs are supplied by the interaction of superheated steam with waste organics and carbon additives. Auto-thermal steam reforming is the preferred mode of operation for engineering or production scale units.

The FBSR technology converts organic compounds to CO_2 and H_2O, converts nitrate/nitrite species to N_2, and produces mineralized waste forms through reactions with superheated steam, which is the fluidizing gas. The reforming process pyrolyzes and oxidizes organics. Therefore the FBSR technology at the Studsvik Processing Facility (SPF) in Erwin, TN, which pyrolyzes organic resins from commercial nuclear reactors. These resins contain Cs-137 and Co-60. The SPF and the FBSR process has been determined to be Clean Air Act (CAA) compliant by Region IV of the Environmental Protection Agency (EPA). In addition, pilot scale testing by INL at the SAIC STAR facility has demonstrated that the FBSR process is CAA Hazardous Waste Combustor (HWC) Maximum Achievable Control Technology (MACT) compliant for Hg, Cl, CO, total hydrocarbons [3] and other heavy metal constituents [5].

The following crucible scale (SRNL), pilot scale (INL and SRNL), and engineering scale (TTT and SRNL) evaluations are summarized in this report based on T48 simulants:

- destruction of TPB and other organic byproducts at >99% efficiency with the FBSR process operating between 650-725°C in crucible scale, pilot scale, and engineering scale
- destruction of nitrates at >99% efficiency with addition of sugar or coal as a reductant
- destruction of antifoam with the FBSR process operating between 650-725°C
- formation of Na_2CO_3 FBSR product which is compatible with mixing the FBSR product into a DWPF feed tank for subsequent vitrification or return to the tank farm
- formation of a Na_2SiO_3 or Na_4SiO_4 FBSR product which is compatible with mixing the FBSR product into a DWPF feed tank or as an addition to the Slurry Mix Evaporator (SME) in place of frit
- assessment of the melting temperature of the Na_2CO_3 and Na_2SiO_3 FBSR products to evaluate impacts (if any) on melt rate
- assessment of a feed forward process control strategy, e.g. predicting the product composition from the feed composition
- evaluation of the compatibility of the FBSR product with the Waste Acceptance Criteria (WAC) for vitrification at the Savannah River Site

The following crucible and bench scale evaluations are summarized in this report based on an actual T48 radioactive sample:

- destruction of TPB and other organic byproducts at >99% efficiency with the FBSR process operating at 650°C for the crucible scale (SRNL) experiments and between 645-676°C for the benchscale steam reformer (BSR) experiments at SRNL
- destruction of nitrates at >99% efficiency with addition of sugar or coal as a reductant for radioactive crucible and BSR experiments
- destruction of antifoam with the FBSR process operating between 645-676°C for radioactive crucible and BSR experiments
- formation of Na_2CO_3 FBSR product which is compatible with mixing the FBSR product into a DWPF feed tank for subsequent vitrification or return to the tank farm
- assessment of a feed forward process control strategy, e.g. predicting the product composition from the feed composition

These evaluations demonstrate that FBSR is a viable organic and nitrate destruction methodology prior to vitrification of T48 waste or prior to the return of the dissolved carbonate product to the Tank Farm for future vitrification.

BACKGROUND

Studsvik built and started test operation of the SPF, a Low-Level Radioactive Waste (LLRW) FBSR Processing Facility in Erwin, TN, in 1999 [6]. Commercial operation commenced in January 2000.[3] The SPF has the capability to process a wide variety of solid and liquid LLRW streams including: ion exchange resins, charcoal, graphite, sludge, oils, solvents, and cleaning solutions at radiation levels of up to 400R/hr. The licensed and heavily shielded SPF can also receive and process liquid and solid LLRWs with high water and/or organic content. The reforming process has demonstrated effectiveness in destroying organics and separating sulfur and halogens from inorganic waste materials. Of special relevance is the capability of the THOR® technology to convert nitrates to N_2 and sodium salts to sodium compounds that are suitable for disposal and/or subsequent vitrification.

In late 2001, Studsvik demonstrated the capability of producing sodium aluminosilicate (Na-Al-Si or NAS) waste forms for Hanford's sodium-bearing low activity waste (LAW) [4]. Other demonstrations performed by TTT showed that LAW waste could be transformed into carbonate, aluminate, or silicate feed material for the LAW Hanford melter. Addition of aluminosilicate clay during pyrolysis produces a $NaAlSiO_4$ (nepheline)-sodalite mineral product that sequesters halides, sulfates and rhenium (a Tc-99 surrogate). The nepheline-sodalite minerals have been shown to perform well as a final waste form [4,7,8,9,10,11].

In November 2002, TTT was contracted to demonstrate the FBSR technology to produce a carbonate waste solid for INL's acidic and radioactive Sodium-Bearing Waste (SBW) [12]. This demonstration successfully converted the SBW to a Na_2CO_3 product that met the Waste Isolation Pilot Plant (WIPP) Waste Acceptance Criteria (WAC) for transuranic (TRU) waste. During the demonstration, mercury was quantitatively stripped from the product but cesium, rhenium (Tc-99 surrogate), and the heavy metals were retained in the solid product. Nitrates were not detected in the product and NO_x destruction exceeded 98% [12]. The off-gas was mostly (76%) H_2O (wet, N_2-free basis). CO levels averaged 1.3%, while the measured CH_4 levels averaged 0.1%. A significant benefit of the FBSR process is that it produces zero-liquid releases. All water is released via the stack as water vapor.

In 2003, SRS/SRNL initiated testing of the FBSR technology for the remediation of T48 wastes. This paper summarizes all of the non-radioactive and radioactive demonstrations for converting T48 waste to organic free solid carbonates. It also summarizes tests conducted in crucibles which are considered a "static" environment and tests conducted in fluidized beds which are considered "dynamic" environments. The crucibles and some of the smaller pilot scale demonstrations were conducted in externally heated environments while other demonstrations were performed in larger engineering pilot scale facilities that were auto-thermally heated.

EXPERIMENTAL

Choice of Reductant for Static vs Dynamic Testing

FBSR's are nominally operated at temperatures between 540°C and 750°C. An FBSR can be electrically heated externally if the diameter of the reaction chamber is small enough. For larger diameter FBSR units, heat must be generated in an auto-thermal mode. Sugar was used as a reductant in pilot scale testing in a small diameter externally heated FBSR at the SAIC STAR facility in Idaho Falls, ID and bench scale testing in externally heated crucibles (radioactive and non-radioactive) at the SRNL. Coal was used as a reductant in radioactive pilot scale tests by TTT in a larger diameter, auto-thermally heated FBSR at HRI and the radioactive demonstration and in the SRNL BSR, which was both externally heated and auto-thermally heated. The auto-thermal heating is facilitated by bleeding in small quantities of oxygen to partially oxidize the coal and to react with the H_2 being produced by the pyrolysis reactions to create more steam which is an exothermic reaction.

Coal and sugar have the same reducing capacity, each exchanges four electrons per carbon during oxidation from C to CO_2 gas. Coal is more efficient as a source of heat for auto-thermally heated units than sugar. This may be due to the fact that each mole of sugar also creates 11 moles of H_2O which converts to steam and would consume energy if used in an auto-thermally heated environment. However, the creation of the 11 moles of steam in the sealed crucible environment is desirable as the only other source of steam inside the crucible is the water in the aqueous portion of the waste since the sealed crucible is a static environment and there is no fluidizing steam.

The carbon in sugar is 100% pure carbon, while coal is only ~85% carbon or volatile organics and 15% moisture and inorganic ash from residual plant matter (this parameter varies from batch to batch). Sugar is, therefore, a more reliable and consistent reductant than coal in situations where external heating is used. The parameter that one needs to control is the oxygen fugacity, log f_{O_2}, of the pyrolysis reactions and not the type of reductant. A reduced oxygen fugacity ensures the destruction of the organics in the waste via pyrolysis and the reduction of the nitrates and nitrites in the waste. The log f_{O_2} can be determined by measuring the $Fe^{+2}/\Sigma Fe$ ratio of the solid product sample with the experimentally determined Electromotive Force Series (EMF) determined by Schreiber [13] for FBSR matrices (see Fig. 1). The $Fe^{+2}/\Sigma Fe$ ratio is also known as the REDuction/OXidation (REDOX) ratio of the product. A comparison of the measured REDOX for each of the demonstrations discussed below will demonstrate that similar REDOX ratios, and thus similar log f_{O_2} (atm.), were achieved in the various static and dynamic tests.

T48 Simulant Crucible Tests by SRNL [14]

A simulant of the Tank 48 solution was prepared according to Table I. This slurry had approximately 13.7 wt% solids. Antifoam (IIT Corp. B52) was added at 100 ppm antifoam for every 1 wt% solids [15]. Five wt% $Fe(NO_3)_3 \bullet 9H_2O$ was added as a REDOX indicator to ensure that the $Fe^{+2}/\Sigma Fe$ ratio of the solid product sample could be measured from which the oxygen fugacity, log f_{O_2}, of the pyrolysis reactions inside the sealed crucibles could be determined so that it could be proven that pyrolysis occurred instead of combustion [14].

The Tank 48 simulant was batched into stainless steel beakers. The slurry was carbonated with dry ice to convert the NaOH to Na_2CO_3 until a pH of ~9.5 was reached. This pretreatment from pH 13.3 to 9.5 also minimized foaming of the slurry. This ensured that once the carbonated material was put into a sealed crucible that a CO_2 atmosphere would be maintained. This served to duplicate the CO_2 rich atmosphere in the FBSR.

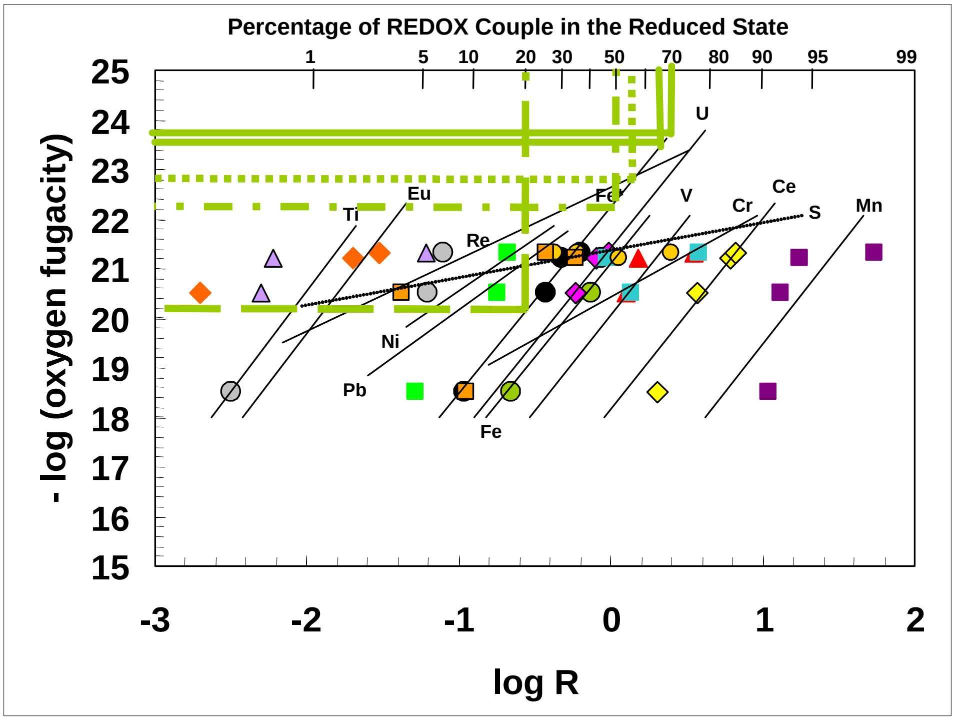

Fig. 1. Electromotive Force (EMF) series developed by Schreiber for FBSR Reactions [13]. Log R is log ($X^{red}/X^{oxidized}$) so measuring the ($Fe^{red}/Fe^{oxidized}$) in the FBSR product (vertical lines) fixes the log (oxygen fugacity) as indicated by the horizontal lines. The solid vertical and horizontal lines are the nonradioactive crucibles and the HRI engineering scale demonstration. The small dotted line is the maximum reduction achieved in the SAIC STAR facility. The long dashed line indicates the minimum reduction achieved in the SAIC STAR facility and the reduction achieved in the radioactive crucible study at SRNL. The dash-dot line indicates the minimum reduction achieved in the SRNL BSR.

Table I. Tank 48 Simulant Recipe

Species	M/L
NaTPB	0.0728
NaOH	1.8425
$NaNO_2$	0.4709
$NaNO_3$	0.2753
Na_2CO_3	0.1295
$NaAlO_2$	0.1118
Na_2SO_4	0.0071
Na_3PO_4	0.0077
NaCl	0.0088
NaF	0.0059
KNO_3	0.0779

Sucrose was the reductant of choice for the crucible scale tests, which were static and externally heated. A test matrix was developed that varied three different levels of reductant based on the following stoichiometric equations:

$$C_{12}H_{22}O_{11} + 9.6NaNO_3 \rightarrow 7.2CO_2 + 11H_2O + 4.8Na_2CO_3 + 4.8N_2 \qquad \text{(Eq. 1)}$$

$$C_{12}H_{22}O_{11} + 16NaNO_2 \rightarrow 4CO_2 + 11H_2O + 8Na_2CO_3 + 8N_2 \qquad \text{(Eq. 2)}$$

Where the stoichiometric ratio of [C]:[N] for nitrate species is 12/9.6=1.25 (Equation 1) and 12/16=0.75 for nitrite species (Equation 2). Similar equations can be written when coal, or a different source of carbon, is used as the reductant.

Three levels of sucrose (none, ½X stoichiometric, and 1X stoichiometric) and three different reaction times (1/2 hour, 3 hours, and 48 hours) were tested. High purity (99.999%) Al_2O_3 crucibles were used to simulate Al_2O_3 bed material and to determine if the FBSR product would adhering to the simulated bed media. Temperatures of 650ºC and 725ºC were tested to see which temperatures and which levels of reductant optimized the water gas shift reaction (WGSR). The lower melting Na_2CO_3 and Na_2SiO_3 FBSR products were targeted for initial study [14]. Only the carbonate tests are discussed in this manuscript since the solid carbonate form was chosen for subsequent pilot and engineering scale study. Since the simulant feed was pre-carbonated, no other additions were needed to optimize the Na_2CO_3 product.

The carbonated slurries were dried to a "peanut butter" consistency to ensure that some H_2O remained in the sample to create steam for the WGSR. Alumina crucibles were sealed with nepheline ($NaAlSiO_4$) gel that softens and seals at a temperature lower than the test temperature. This prevents air inleakage during reaction, but allows other gases to escape by slow diffusion through the gel seal. The sealed samples were placed in a calibrated furnace at the test temperature designated in Table II. This generated a combined atmosphere of steam, CO from decomposition of the sucrose and CO_2; thus duplicating the FBSR gas mixtures. The furnace was purged with 99.99% Ar to ensure that no O_2 mixed with any H_2 or CO that escaped through the crucible seal.

T48 Simulant Pilot Scale Tests by INL and SRNL [16]

The SAIC STAR pilot scale facility used a single reformer flowsheet with an externally heated 15.2 cm (6") unit. The STAR pilot scale demonstration was performed with the same simulant given in Table I. The reductant of choice was sugar, which reacted with the oxygen liberated from the denitration reactions. The amount of sugar added was determined from Equations 1 and 2. Stoichiometric ratios of 1-2X sugar were tested. Feeds were pre-carbonated by bubbling CO_2 or by adding oxalic acid. In some of the higher (2X) sugar tests, oxygen was added to the steam to mitigate higher total hydrocarbon (THC) releases but this was found to be unnecessary. Five wt% $Fe(NO_3)_3 \bullet 9H_2O$ was added as a REDOX indicator to ensure that the $Fe^{+2}/\Sigma Fe$ ratio of the solid product sample could be measured. The silica bed media complexed with the T48 waste and created pluggages. However, an alumina bed media was shown to work well with the T48 waste. Temperatures ranged from 625-650°C during successful operation. Testing above 700°C was shown to cause the carbonate product to melt.

Table II. Simulated T48 Steam Reformer Analytic Results

Test #	Temp (°C)	Sugar Stoichiometry	Coal	Residence Time (hrs)	Major Phases Identified by XRD	Minor Phases Identified by XRD	NaTPB, 3PB, 2PB (ug/g)	NO$_x$ (%) Destruction	TOC (%) Dextruction
Feed									
T48-0	60	0	N/A	N/A	$Na_3H(CO_3)_2(H_2O)_2$, $Na(NO_3)$, $NaNO_2$, $Na_2CO_3\bullet H_2O$	Na_2SiO_3, $KAl(SO_4)_2(H_2O)_{12}$	95,100,<5	0	0
Non-Radioactive Crucible Tests (2003) [14]									
T48-1	725	0	N/A	½	$Na_2CO_3\bullet H_2O$, Na_2CO_3	$Ca_8Al_2Fe_2O_{12}CO_3(OH)_2\bullet 22H_2O$	<5,<5,<5*	30.1	>99.5
T48-2	725	0	N/A	3	$Na_2CO_3\bullet H_2O$, Na_2CO_3	$Ca_8Al_2Fe_2O_{12}CO_3(OH)_2\bullet 22H_2O$	<5,<5,<5*	4.3	>99.5
T48-2B	650	0	N/A	3	$Na_2CO_3\bullet H_2O$, Na_2CO_3	$NaNO_{3,}$ $Ca_8Al_2Fe_2O_{12}CO_3(OH)_2\bullet 22H_2O$	<5,<5,<5*	24.5	>99.5
T48-3	725	½	N/A	3	$Na_2CO_3\bullet H_2O$, Na_2CO_3	$Ca_8Al_2Fe_2O_{12}CO_3(OH)_2\bullet 22H_2O$	<5,<5,<5*	99.5	>99.5
T48-4	725	1	N/A	½	$Na_2CO_3\bullet H_2O$, Na_2CO_3	NONE	<5,<5,<5*	98.1	>99.5
T48-5	725	1	N/A	3	$Na_2CO_3\bullet H_2O$, Na_2CO_3	$Ca_8Al_2Fe_2O_{12}CO_3(OH)_2\bullet 22H_2O$	<5,<5,<5*	97.5	>99.5
T48-5B	650	1	N/A	3	$Na_2CO_3\bullet H_2O$, Na_2CO_3	NONE	<5,<5,<5*	99.1	>99.5
T48-13	650	1	N/A	48	$Na_2CO_3\bullet H_2O$, Na_2CO_3	NONE	<5,<5,<5*	99.0	>99.5
SAIC STAR Non-Radioactive Pilot Scale Tests (2004) [12]									
Tests 8-9	625-650	2	N/A	N/A	Na_2CO_3 calculated	NONE	<10,<10,<10*	99.6-99.99	99.83-99.89
TTT-HRI Non-Radioactive Engineering Scale Tests (2006) [17]									
PROD-1 to 4	640-675	N/A	1-1.5	N/A	$Na_2CO_3\bullet H_2O$, Na_2CO_3, $Na_3H(CO_3)_2\bullet 2H_2O$	$NaAlSiO_4 + NaAlSiO_4\bullet H_2O +$ $Na_2Al_{22}O_{34} + SiO_2$	<50, <100,<100*	>99.2->99.4	>99.9
Radioactive Crucible Tests [2008; 18]									
RAD 1-4	650	1	N/A	3-8	Na_2CO_3	$Na_{1.95}Al_{1.95}Si_{0.05}O_4$, $Na_{14.88}Al_{15.26}Si_{32.74}O_{96}$	<10,<10,<10*	100	Not Meas.
Radioactive Benchscale Steam Reformer (BSR) Tests (2008) [19]									
BSR	645-676	N/A	1-1.5	N/A	$Na_2CO_3\bullet H_2O$, Na_2CO_3, $Na_3H(CO_3)_2\bullet 2H_2O$	$Na_8(AlSiO_4)_6(OH)_2\bullet 2H_2O$, $Na_2Al_2SiO_6$	<5,<5,<5*	>99.6->99.8	Not Meas.

* corresponds to >99.8% destruction

T48 Simulant Engineering Scale Tests by TTT and SRS/SRNL [17]

An FBSR engineering-scale test demonstration (ESTD) unit was built and operated at the Hazen Research Inc. (HRI) in Golden, Colorado. The ESTD was an ~1/2-scale unit for the T48 process. It included all unit operations present in the full-scale unit, excluding the product packaging equipment. The ESTD used a dual reformer flowsheet: a Denitration and Mineralization Reformer (DMR) which operated at temperatures low enough that the carbonates would not melt, i.e. 640-675°C, and a Carbon Reduction Reformer (CRR) which operated at ~950°C to destroy any residual hydrogen, organics, or organic byproducts that may have carried over from the DMR.

The engineering scale testing of the THOR® steam reforming process was conducted in a two-phase demonstration program. Phase 1 was a series of optimization tests to develop operating conditions and evaluate potential alternate reductants for use in the reformers. Phase 2 consisted of a series of tests to demonstrate operation of the pilot plant for extended periods while demonstrating destruction of TPB ions, nitrates, biphenyls, diphenyl mercury, benzene, and other species. These tests were performed during September-October 2006. The production test series consisted of a matrix of variable operating conditions that included feed composition, feed rate, temperature, and bed media (alumina and sodium carbonate product). Coal was the reductant of choice in the DMR and propylene glycol in the CRR. During these tests, 12,528 liters of T48 simulant were processed into 2347 kg of granular solid product during 126.2 hr of "feed-on" operation. The composition of the simulant was similar to that in Table I and is given in Reference 17.

T48 Radioactive Crucible Scale Tests by SRNL [18]

Crucible scale testing with actual radioactive T48 material was performed at SRNL in 2008. The radioactive crucible scale testing was performed to duplicate the test results that had been performed with the T48 simulant in 2003. [14] The comparison of the results using radioactive T48 feed to those reported with simulants provided proof that the radioactive tank waste behaves in a similar manner to the simulant. Demonstration of similar behavior for the actual radioactive T48 slurry to the simulant was considered important as a preparatory step for the more complex BSR testing with radioactive waste.

The testing protocol used in 2003 [14] and outlined above was repeated, i.e. sealed high purity alumina crucibles containing a pre-carbonated and partially evaporated ("peanut butter consistency") T48 sample. Sealing of the crucibles was accomplished by using the same 'nepheline gel' sealant. A 1X stoichiometric amount of sugar was used (see Equations 1 and 2) and Table II. The sealed crucibles were heat-treated at 650ºC under constant argon flow to inert the system. Ferric nitrate was added as a REDOX indicator. Solid product dissolution in water was used to measure soluble cations and anions, and to investigate insoluble fractions of the product solids. Radioanalytical measurements were performed on the T48 feed material and on the dissolved products.

T48 Radioactive Benchscale Steam Reformer (BSR) Tests by SRNL [19]

The radioactive BSR tests are described in another paper in these conference proceedings [19]. The BSR was assembled in the SRNL Shielded Cell Facility (SCF) mockup shop on a 3' x 4' stainless steel pan. Bolts were welded to the pan and the equipment was strapped to the pan using heavy duty wire ties. All the connections were made and the system was leak checked prior to placement into the cell. A special lifting yoke was fabricated and the BSR was lowered into the cell as a single unit using a crane. The estimated total weight of the BSR was 220 pounds and the weight distribution was designed to be fairly even. All control units and mass spectrometers for recording the off-gas measurements were located outside the radioactive cells with the connections being made via KAPL (Knoll's Atomic Power Laboratory) plugs. Condenser/bubbler/dry ice condenser units were necessary for pretreatment of the off-gas to prevent filter pluggages or damage to the mass spectrometers.

The Benchscale steam reformer was designed and constructed at SRNL and uses the same dual reformer flowsheet as the engineering scale FBSR at HRI. The same coal reductant was used in the BSR demonstration as in the engineering scale demonstration at HRI. The BSR was operated so that equivalent flows to those used during the 2006 engineering scale demonstration were maintained during the radioactive runs. The BSR feed rate was the primary parameter for scaling this process to the engineering scale process. Ferric nitrate was added as a REDOX indicator.

In the ESTD FBSR, oxygen was bled in to partially oxidize coal to provide the process heat. In the BSR, the heat was added by chemical reaction with oxygen and by an electric furnace to control the temperature to 670°C at the control thermocouple point. Zirconia beads were used as the bed media to allow steam to enter the reformers through distributor plates located beneath the beads. The bed was not truly fluidized so a stalagmite grew as feeding continued. The first four inches of the stalagmite formed in a region where the temperature was between 676°C and 645°C, which is within the temperature range for making good product. Samples were taken from this region and analyzed separately from the upper samples, which often contained unreacted coal.

Analyses for All Simulant and Radioactive Demonstrations

Solid samples from all the demonstrations were analyzed at SRNL. The analyses included X-ray diffraction (XRD) to determine if the desired FBSR products were achieved. Samples were measured by High Pressure Liquid Chromatography (HPLC) to determine if the TPB was adequately destroyed by the FBSR reactions. Analyses were also conducted to determine if any secondary TPB reaction products were present, e.g., 3PB and 2PB. Total Carbon (TC), Total Inorganic Carbon (TIC), and Total Organic Carbon (TOC) were also analyzed. All samples were analyzed for $Fe^{+2}/\Sigma Fe$ analysis by the Baumann method [20].

Samples were measured by Ion Chromatography (IC) for NO_2^-, NO_3^-, and SO_4^{-2} to determine the fate of these anions and the percent nitrate destruction. Differential Thermal Analysis (DTA) was only performed on the non-radioactive crucible scale products to determine the melting temperature. For the radioactive crucible and BSR tests the carbonate product was dissolved in water to determine the soluble and insoluble carbonate species present and the radionuclide content. For the BSR tests, the off-gas was measured by on-line GC-mass spectrometer.

DISCUSSION

Choice of Reductant for Static vs Dynamic Testing

The use of sugar for the non-radioactive static crucible tests, the nonradioactive pilot scale tests, and the nonradioactive engineering scale tests (whether static or dynamic, whether externally heated or auto-thermally heated, whether coal or sugar was used as a reductant) all produced log f_{O_2} fugacities of -20.2 to -22.2 atmospheres (Table III) indicating very reducing conditions. For comparison air has a log f_{O_2} of 0.21 atmospheres. The radioactive crucible studies and the radioactive BSR tests produced log f_{O_2} fugacities of -20.2 to ≥ -22.2 atmospheres (Table III)

Table III. Comparison of REDOX ratios of Crucible Studies with a Sugar Reductant and the HRI Pilot Scale Tests with Coal Reductant

Demonstration	Conditions	$Fe^{+2}/\Sigma Fe$ Measured	log f_{O_2}
Non-radioactive Crucibles [14]	No sugar; 650-725°C; 0.5-3 hours	0.70	-23.8
Non-radioactive Crucibles [14]	1X sugar; 650-725°C; 0.5-3 hours	0.65	-23.6
Non-radioactive SAIC-STAR pilot Scale [16]	2X sugar plus O_2; 650°C	0.2-0.54	-20.2 to -22.2
HRI pilot DMR and High Temperature Filter (HTF) [17]	Coal; 640°C; 48 hours	0.63-0.66	-23.6 to -24.0
Radioactive Crucibles in SRNL SCF [18]	1X sugar; 650°C; 3-8 hours	0.21	-20.2
Radioactive BSR in SRNL SCF [19]	Coal; 645-676°C	0.5-1.0	≥ -22.2

T48 Simulant Crucible Tests by SRNL [14]

A sample (T48-0) was tested as a baseline. The T48-0 sample was carbonated, antifoam and $Fe(NO_3)_3 \bullet 9H_2O$ were added, and the sample was dried at 60°C. This sample was analyzed for TPB, anions, TC, TIC, TOC and REDOX as a baseline case (see Table II). These analyses demonstrated that there was 95,100 ug/g of TPB (Table II) present in the samples after the carbonation and drying steps. The presence of the TPB was also confirmed by the measurement of TOC, which showed 19,500 mg/L of organic carbon. Either the TPB or the antifoam (an organic) may have reacted with the $Fe(NO_3)_3 \bullet 9H_2O$ because a Fe^{+3} dried solution should have had a REDOX measurement of ~0 and the measurement was 0.44. This indicated that a considerable amount of Fe^{+2} was present or that the organics interfered with the REDOX measurement. Anion analysis of the T48-0 base case indicated <100 ug/g of NO_2^- and 163,000 ug/g or 16.3 wt% of NO_3^-. This number was used with the measured NO_3^- data [14] to calculate the NO_3^- destruction values given in Table II.

The crucibles were tested at two different temperatures, 650°C and 725°C (Table II). Tetra-phenylborate (TPB) was completely destroyed in all the samples tested, i.e., the TPB, 2PB and 3PB were all <5 ug/g indicating that the thermal treatment destroyed all the TPB and its derivatives. This was confirmed by the TOC analyses of <100 ug/g. These initial tests indicated that FBSR is a viable technology for destruction of the organics in T48 (Table II).

For all of the FBSR samples in which the desired product was Na_2CO_3 (samples T48-1 through T48-5B and T48-13), analyses by XRD indicated that a mixture of $Na_2CO_3 \bullet H_2O$ (thermonatrite) and Na_2CO_3 (natrite) was formed regardless of temperature and residence time in the furnace (Table II). When a reductant was not used, the nitrate was not completely destroyed (Table II). Tests T48-5B or T48-13 appeared optimal for making the Na_2CO_3 FBSR product and destroying all the organics and nitrates at ~650°C with 1X stoichiometric sugar and 3-48 hour residence time: no minor phases were identified as incomplete reactants (Table II). No adherence of the carbonate phases on the Al_2O_3 crucibles was noted. Therefore, if the FBSR startup bed is Al_2O_3 there should not be any particle agglomeration with the Al_2O_3 [14].

The FBSR product sample T48-5B (primarily Na_2CO_3 made at 650°C) was measured by DTA to determine the melting temperature. The melt temperature was 980°C. This melt temperature is compatible with melting of the carbonate phases directly in a melter. However, this could cause large volumes of CO_2 to be released. However, the SRS DWPF melter uses a preprocessing strategy in the Sludge Receipt and Adjustment Tank (SRAT) that destroys carbonate by addition of mixed formic and nitric acids that simultaneously controls the melter REDOX equilibria [21,22].

T48 Simulant Pilot Scale Tests by INL and SRNL [16]

A program was initiated in 2003 between SRNL and INL to demonstrate "proof-of-concept" for using FBSR to pretreat the T48 waste for vitrification [16]. The objectives of the tests included 1) >99 % destruction of TPB, nitrates, and nitrites, 2) acceptable bed performance (no agglomeration), 3) acceptable bed product that could become feed to the DWPF melter, and 4) use of sugar as a reductant for nitrate destruction because of its compatibility with DWPF processing.

The demonstration was performed in the 15.24 cm (6") diameter FBSR at the SAIC STAR facility. The pilot scale unit was externally heated and temperatures of 625°C, 650°C, and 750°C were tested. The 750°C campaign was unsuccessful due to bed agglomeration (partial melting of the carbonate products). At temperatures of 625-650°C all the test objectives were met [16] and no bed agglomeration was experienced. During the last two campaigns (Tests 8 and 9) sugar was used at 2X the stoichiometric ratio and oxygen was added to the fluidizing steam. This created REDOX values that were somewhat more oxidizing than noted in the non-radioactive crucible studies with only 1X the stoichiometric amount of sugar (see Table III) but were still at log f_{O_2} fugacity of -20.2 to -22.2 atmospheres. The results from the SAIC STAR pilot scale and the SRNL crucible studies on the same non-radioactive simulant were identical in terms of the product phases produced, nitrate destruction (99.6-99.9%), TPB destruction (>99.8%), and TOC destruction (99.83-99.89%) as shown in Table II.

T48 Simulant Engineering Scale Tests by TTT and SRS/SRNL [17]

Engineering "scale proof-of-concept" steam reforming tests to evaluate the performance of Tank 48 waste in a 15" diameter auto-thermally heated FBSR at HRI tested various reductants including sugar. The use of sugar as a reductant did not supply the energy needs to sustain the auto-thermal operation of the unit and coal was used during the final production run campaigns.

The objectives of the engineering scale demonstrations were the same as those of the 2003 SAIC STAR demonstration. All the test objectives were met at operating temperatures of 640-670°C without significant bed agglomeration [17]. The measured product REDOX values were almost identical to those of the non-radioactive crucible studies, which used sugar, (see Table III) at log f_{O_2} fugacities of -23.6 to -24.0 atmospheres.

The results from the HRI engineering scale demonstration, the SAIC STAR pilot scale, and the SRNL crucible studies on the similar non-radioactive simulants were identical in terms of the product phases produced, nitrate destruction (>99.2 to >99.4%), TPB destruction (>99.8%), and TOC destruction (>99.99%) as shown in Table II.

T48 Radioactive Crucible Scale Tests by SRNL [18]

All aspects of the non-radioactive crucible scale testing with simulated T48 waste were demonstrated to be repeatable with the actual radioactive feed. The TPB destruction was shown to be > 99% and the final solid product was a mixture of various sodium carbonate crystalline minerals (Table II). Less than 10 wt% of the final solid products were insoluble components comprised of Fe/Ni/Cr/Mn containing sludge components and Ti from monosodium titanate present in T48 waste. REDOX measurements on the radioactive solid products indicate a reducing atmosphere with extremely low oxygen fugacity (Table III). This is evidence that the sealed crucible tests performed in the presence of sugar under constant argon purge were successful in duplicating the pyrolysis reactions occurring during pilot and engineering scale testing. Soluble anion measurements confirmed that using sugar as reductant at 1X stochiometry was successful in destroying nitrate/nitrite (Table II). Radioanalytical measurements indicated that ~ 92% of the starting Cs-137 was retained in the solid product, which was within the uncertainty of the analysis and calculations performed.

T48 Radioactive Benchscale Steam Reformer (BSR) Tests by SRNL [19]

The objectives of the radioactive BSR demonstrations were the same as those of the SAIC STAR pilot scale demonstration and the HRI ESTD FBSR demonstrations except that actual radioactive feed was used in the SRNL SCF. All the test objectives were met at operating temperatures between 645-676°C. Three runs with radioactive T48 material were performed in the BSR. The TPB was destroyed to > 99% for all radioactive BSR tests (Table II). The feed nitrate/nitrite was destroyed to >99% for all radioactive BSR tests the same as the ESTD FBSR and the desired soluble carbonates were formed (Table II). Insoluble solids analyzed by XRD did not detect insoluble carbonate species. However, they still could have been present at levels below 2 wt%, the sensitivity of the XRD methodology. Insoluble solids XRD characterization indicated that various Fe/Ni/Cr/Mn phases were present. These crystalline phases are associated with the insoluble sludge components of Tank 48H slurry and impurities in the coal ash. Greater than 90% of the radioactivity was captured in the product for all three runs in the BSR. The $Fe^{+2}/\Sigma Fe$ REDOX measurements ranged from 0.58 to 1 for the three radioactive benchscale tests. REDOX measurements > 0.5 showed a reducing atmosphere (log f_{O_2} of -22.2 or lower atmospheres) was maintained in the DMR indicating that pyrolysis was occurring.(see Table III).

Carbonate Transport and Melter Compatibility

DTA experiments performed in 2003 [14] indicate that dry FBSR carbonate product melts at a sufficiently low temperature that it is compatible with direct melting. However, it is easier to transport the sodium carbonate, which is soluble, as a slurry to either the melter feed tank for immediate vitrification or to the tank farm for future vitrification in the DWPF melter. In either case, the product will be decarbonated via the existing DWPF acid addition strategy for carbonate destruction in the SRAT. This will eliminate any potential for CO_2 off-gas surges or foaming in the DWPF melter. Initial calculations have indicated that the components in the organic free FBSR product, including the residual coal, are compatible with processing in the DWPF melter which operates nominally at an $Fe^{+2}/\Sigma Fe=0.2$ ratio. [21,22]

CONCLUSIONS

The objectives of non-radioactive and radioactive testing (crucible, pilot scale, engineering scale and BSR) were fulfilled as documented by the following:

- complete destruction of TPB in all samples processed at temperatures between 625-676°C,
- >99% destruction of nitrate
- >99% destruction of TOC and TPB including TPB byproducts, benzene, phenyl, biphenyl, phenol, and antifoam
- production of Na_2CO_3 or one of its hydrates for all tests in which Na_2CO_3 was the desired product phase,
- compatibility of Na_2CO_3 with the HLW melt processes,
- reproduction of the pyrolysis reactions in the sealed crucible studies, i.e. feed conversion to carbonate minerals, destruction of the organics and nitrates
    - sealed crucible studies achieved the same oxygen fugacity as the HRI engineering scale demonstration
- reproduction of the pyrolysis reactions with the BSR, i.e. feed conversion to carbonate minerals, destruction of the organics and nitrates, and the oxygen fugacity of the HRI engineering scale demonstrations.
- replication of radioactive T48 waste results using simulated wastes.

REFERENCES

1. D.D. WALKER, M.J. BARNES, C.L. CRAWFORD, R.F. SWINGLE, R.A. PETERSON, M.S. HAY, and S.D. FINK “Decomposition of Tetraphenylborate in Tank 48H,” U.S. DOE Report WSRC-TR-96-0113, Rev. 0, Westinghouse Savannah River Co., Aiken, SC (May 1996).
2. C.M. JANTZEN, “Glass Compositions and Frit Formulations Developed for DWPF,” U.S. DOE Report DPST-88-952, E.I. duPont deNemours & Co., Savannah River Laboratory, Aiken, SC (November 15, 1988).
3. J.B. MASON, J. McKIBBEN, K.RYAN, and D. SCHMOKER, “Steam Reforming Technology for Denitration and Immobilization of DOE Tank Wastes,” Waste Management 03 (2003).
4. C.M. JANTZEN, “Engineering Study of the Hanford Low Activity Waste (LAW) Steam Reforming Process,” U.S. DOE Report WSRC-TR-2002-00317, Westinghouse Savannah River Co., Aiken, SC (2002).
5. N.R. SOLEBERG, D.W. MARSHALL, S.O. BATES, and D.D. TAYLOR, “Phase 2 THOR® Steam Reforming Tests for Sodium Bearing Waste Treatment,” U.S. DOE Report INEEL/EXT-04-01493, Rev. 1 (2004)
6. J.B. MASON, T.W. OLIVER, M.P. CARSON, and G.M. HILL, “Studsvik Processing Facility Pyrolysis/Steam Reforming Technology for Volume and Weight Reduction and Stabilization of LLRW and Mixed Wastes,” Waste Management 99 (1999).
7. B.P.McGRAIL, H.T. SCHAEF, P.F. MARTIN, D.H. BACON, E.A. RODRIQUEZ, D.E. McCREADY, A.N. PRIMAK, and R.D. ORR, “Initial Evaluation of Steam-Reformed Low Activity Waste for Direct Land Disposal,” U.S. DOE Report PNWD-3288, Battelle Pacific Northwest, Richland, WA (2003).
8. C.M. JANTZEN, “Characterization and Performance of Fluidized Bed Steam Reforming (FBSR) Product as a Final Waste Form,” Ceramic Transactions 155, 319-329 (2004).
9. J.M. PAREIZS, C.M. JANTZEN, and T.H. LORIER, “Durability Testing of Fluidized Bed Steam Reformer (FBSR) Waste Forms for High Sodium Wastes at Hanford and Idaho,” U.S. DOE Report WSRC-TR-2005-00102 (July 2005).
10. T.H. LORIER, J.M. PAREIZS, and C.M. JANTZEN, “Single-Pass Flow Through (SPFT) Testing of Fluidized Bed Steam Reforming (FBSR) Waste Forms,” U.S. DOE Report WSRC-TR-2005-00124 (2005).
11. C.M. JANTZEN, J.M. PAREIZS, T.H. LORIER, and J.C. MARRA, “Durability Testing of Fluidized Bed Steam Reforming (FBSR) Products,” Ceramic Transactions, 176, 121-137 (2006).
12. D.W. MARSHALL, N.R. SOELBERG, K.M. SHABER, “THOR® Bench-Scale Steam Reforming Demonstration,” U.S. DOE Report INEEL/EXT.03-00437, Idaho National Engineering & Environmental Laboratory, Idaho Falls, ID (2003).
13. H.D. SCHREIBER, "REDOX State of Model Fluidized Bed Steam Reforming Systems Final Report Subcontract AC59529T,” VMI Research Laboratories, VMI, Lexington, VA 24450 (December 2007).
14. C.M. JANTZEN.“Disposition of Tank 48 Organics by Fluidized Bed Steam Reforming (FBSR),” U.S. DOE Report WSRC-TR-2003-00352, Rev.1, Westinghouse Savannah River Co., Aiken, SC (2004).
15. M.A. BAICH, D.P. LAMBERT, P.R. MONSON, “Laboratory Scale Antifoam Studies for the STTPB Process,” U.S. DOE Report WSRC-TR-2000-00261, Westinghouse Savannah River Co., Aiken, SC (2000).
16. N.R.SOELBERG, D.W. MARSHALL, S.O. BATES, and D. SIEMER, “SRS Tank 48 Waste Steam-Reforming Proof-of-Concept Results,” U.S. DOE Report INEEL/EXT-03-01118, Rev. 1 (May 2004).
17. Thor® Treatment Technologies, “Pilot Plant Report for Treating T48H Simulants Carbonate Flowsheet,” Document Number 28927-WEC-RPT-00001 : Rev.2 (May 2007).
18. C.L. CRAWFORD, “Crucible Testing of Tank 48H Radioactive Waste Sample Using Fluidized Bed Steam Reforming (FBSR) for Organic Destruction,” U.S. DOE Report WSRC-STI-2008-00337 (2008).
19. P.R. BURKET, W.E. DANIEL, C.M. JANTZEN, C.A. NASH, C.L. CRAWFORD, M.R. WILLIAMS, and A.B. BARNES, “Steam Reforming Technology Demonstration for the Destruction of Organics on Actual DOE Savannah River Site Tank 48H Waste,” this proceedings paper #9138.
20. E.W. BAUMANN, "Colorimetric Determination of Iron(II) and Iron(III) in Glass," Analyst, 117, 913-916 (1992).
21. C.M. JANTZEN, J.R. ZAMECNIK, D.C. KOOPMAN, C.C. HERMAN, and J.B. PICKETT, “Electron Equivalents Model for Controlling REDuction/OXidation (REDOX) Equilibrium During High Level Waste (HLW) Vitrification,” U.S. DOE Report WSRC-TR-2003-00126, Rev.0 (May 9, 2003).
22. C.M. JANTZEN and M.E. STONE, “Role of Manganese Reduction/Oxidation (REDOX) on Foaming and Melt Rate in High Level Waste (HLW) Melters,” US DOE Report WSRC-STI-2006-00066 (2007).