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**2009 Pilot Scale Fluidized Bed Steam Reforming Testing Using the THOR®  
(Thermal Organic Reduction) Process: Analytical Results for Tank 48H  
Organic Destruction - 10408**

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**ABSTRACT**

The Savannah River Site (SRS) must empty the contents of Tank 48H, a 1.3 million gallon Type IIIA HLW storage tank, to return this tank to service. The tank contains organic compounds, mainly potassium tetrphenylborate that cannot be processed downstream until the organic components are destroyed. The THOR® Treatment Technologies (TTT) Fluidized Bed Steam Reforming (FBSR) technology, herein after referred to as steam reforming, has been demonstrated to be a viable process to remove greater than 99.9% of the organics from Tank 48H during various bench scale and pilot scale tests. These demonstrations were supported by Savannah River Remediation (SRR) and the Department of Energy (DOE) has concurred with the SRR recommendation to proceed with the deployment of the FBSR technology to treat the contents of Tank 48H. The Savannah River National Laboratory (SRNL) developed and proved the concept with non-radioactive simulants for SRR beginning in 2003. By 2008, several pilot scale campaigns had been completed and extensive crucible testing and bench scale testing were performed in the SRNL Shielded Cells using Tank 48H radioactive sample.

SRNL developed a Tank 48H non-radioactive simulant complete with organic compounds, salt, and metals characteristic of those measured in a sample of the radioactive contents of Tank 48H. FBSR Pilot Scaled Testing with the Tank 48H simulant has demonstrated the ability to remove greater than 98% of the nitrites and greater than 99.5% of the nitrates from the Tank 48H simulant, and to form a solid product that is primarily alkali carbonate. The alkali carbonate is soluble and, thus, amenable to pumping as a liquid to downstream facilities for processing. The FBSR technology was demonstrated in October of 2006 in the Engineering Scale Test Demonstration (ESTD) pilot scale steam reformer at the Hazen Research Inc. (HRI) facility in Golden, CO. Additional ESTD tests were completed in 2008 and in 2009 that further demonstrated the TTT steam reforming process ability to destroy organics in the Tank 48 simulant and produce a soluble carbonate waste form. The ESTD was operated at varying feed rates and Denitration and Mineralization Reformer (DMR) temperatures, and at a constant Carbon Reduction Reformer (CRR) temperature of 950°C. The process produced a dissolvable carbonate product suitable for processing downstream. ESTD testing was performed in 2009 at the Hazen facility to demonstrate the long term operability of an integrated FBSR processing system with carbonate product and carbonate slurry handling capability. The final testing demonstrated the integrated TTT FBSR capability to process the Tank 48 simulant from a slurry feed into a greater than 99.9% organic free and primarily dissolved carbonate FBSR product slurry.

This paper will discuss the SRNL analytical results of samples analyzed from the 2008 and 2009 THOR® steam reforming ESTD performed with Tank 48H simulant at HRI in Golden, Colorado. The final analytical results will be compared to prior analytical results from samples in terms of organic, nitrite, and nitrate destruction.

## INTRODUCTION

Currently, Tank 48 has about 250,000 gallons of slurry which contain potassium and cesium tetraphenylborate (KTPB and CsTPB) [1, 2]. Tank 48 needs to be returned to service in order to free up tank space in the HLW system. The phenylborate organics in the Tank 48 slurry need to be removed or destroyed before this waste can be processed in the DWPF melter or returned to the tank farm for future vitrification.

The FBSR technology is capable of destroying the alkali TPB, benzene, and other organic byproducts, as well as the nitrates present to  $(\text{Na, K, Cs})_2\text{CO}_3$ ,  $\text{CO}_2$  gas,  $\text{N}_2$  gas, and  $\text{H}_2\text{O}$  in the form of steam [3, 4] at moderate temperatures ( $\sim 650^\circ\text{C}$ ). Other components in the waste are converted to oxides, silicates, phosphates, and iron titanates. The FBSR can be electrically heated (pilot scale units of 6" or less) or operated in an auto-thermal mode (pilot scale or engineering scale units  $> 6''$ ). In the auto-thermal mode, the energy needs are supplied by the incoming superheated steam and by the oxidation of organics from the waste and carbon reductants added as co-reactants via the water gas shift reaction (WGSR). For engineering or production scale units, auto-thermal steam reforming is the preferred mode of operation.

The following evaluations are summarized in this report based on a well characterized Tank 48 radioactive and non-radioactive simulant test samples analyzed at the crucible scale (SRNL), pilot scale (INL and SRNL), and engineering scale (TTT and SRNL):

- destruction of phenylborates and other organic byproducts with the steam reforming process operating between  $650\text{-}725^\circ\text{C}$  in crucible scale, pilot scale, and engineering scale at  $>99.9\%$
- destruction of nitrate at  $>99.5\%$  and nitrite at  $>98\%$  with addition of reductant
- destruction of antifoam with the FBSR process operating between  $650\text{-}725^\circ\text{C}$
- formation of  $\text{Na}_2\text{CO}_3$  FBSR product to be compatible with mixing the FBSR product into a DWPF feed tank for subsequent vitrification or return to the tank farm
- formation of a  $\text{Na}_2\text{SiO}_3$  or  $\text{Na}_4\text{SiO}_4$  FBSR product to be 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  $\text{Na}_2\text{CO}_3$  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

These evaluations demonstrate that steam reforming process is a viable organic and nitrate destruction technology.

## **BACKGROUND**

Studsвик has demonstrated the effectiveness of the steam reforming process in destroying organics and separating sulfur and halogens from inorganic waste materials [3,5,6]. Of special relevance is the capability of the THOR<sup>®</sup> steam reforming technology to convert nitrates to N<sub>2</sub> and sodium salts to sodium compounds that are suitable for disposal and/or subsequent vitrification [4,7,8,9,10,11,12].

In 2003, the SRS initiated a study of the steam reforming technology for the remediation of Tank 48 waste. This study summarizes all of the non-radioactive and radioactive demonstrations of converting Tank 48 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 scale facilities that were auto-thermally heated.

## **EXPERIMENTAL**

### **Choice of Reductant for Static vs Dynamic Testing**

The FBSR is nominally operated at temperatures between 540°C to 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. 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 Savannah River National Laboratory (SRNL) used sugar as a reductant. Non-radioactive pilot scale testing by TTT in a larger diameter auto-thermally heated FBSR at HRI and the radioactive demonstration in the SRNL BSR which was both externally heated and auto-thermally heated used coal. The auto-thermal heating is assisted by bleeding in small quantities of oxygen to complex the H<sub>2</sub> being produced by the pyrolysis reactions to create more steam as this reaction is exothermic.

Coal and sugar have the same reducing capacity, each exchanges four electrons per carbon during oxidation from C<sup>0</sup> to CO<sub>2</sub> gas but 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 creates 11 moles of H<sub>2</sub>O which converts to steam and would consume energy if used in an auto-thermally heated environment. 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 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 ~75% carbon and 25% 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 achievable. The parameter to control the reducing FBSR environment 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. 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 the FBSR demonstrations discussed below proved similar  $\log f_{O_2}$ , were achieved in various static and dynamic tests.

#### Tank 48 Simulant Crucible Tests (SRNL, 14)

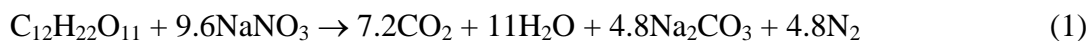
A simulant of the Tank 48 solution was prepared according to Table I. This slurry had approximately 13.7 wt% solids. Antifoam (IIT Corp. B52) was added at 100 ppm antifoam per wt% solids [15]. Five wt%  $Fe(NO_3)_3 \cdot 9H_2O$  was added as a REDOX indicator to ensure that the  $Fe^{+2}/\Sigma Fe$  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, i.e. it could be proven that pyrolysis occurred instead of combustion [14].

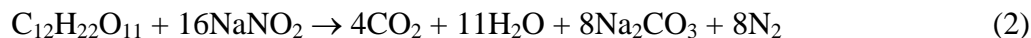
The Tank 48 simulant was batched into stainless steel beakers. The slurry was carbonated with dry ice to convert the NaOH to  $Na_2CO_3$  until a pH of ~9.5 was reached. This pretreatment from pH 13.3 to 9.5 also minimized foaming of the slurry. This ensured that once the carbonated material was put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

**Table I. Tank 48 Simulant Recipe**

Major Chemical Compounds	Concentration (Moles/Liter)
NaTPB	0.0728
NaOH	1.8425
NaNO <sub>2</sub>	0.4709
NaNO <sub>3</sub>	0.2753
Na <sub>2</sub> CO <sub>3</sub>	0.1295
NaAlO <sub>2</sub>	0.1118
Na <sub>2</sub> SO <sub>4</sub>	0.0071
Na <sub>3</sub> PO <sub>4</sub>	0.0077
NaCl	0.0088
NaF	0.0059
KNO <sub>3</sub>	0.0779

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





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). Note that similar equations can be written when coal or a different source of solid carbon is used as the reductant.

Three different levels of  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  (sucrose) (no sucrose,  $\frac{1}{2}$  mass of sucrose, and full mass of sucrose) and three different reaction times (1/2 hour, 3 hours, and 48 hours) were tested. High purity (99.999%)  $\text{Al}_2\text{O}_3$  crucibles were used to simulate  $\text{Al}_2\text{O}_3$  bed material and to determine if the FBSR product was adhering to the simulated bed media. Temperatures of  $650^\circ\text{C}$  and  $725^\circ\text{C}$  were tested to see which levels of reductant optimized the WGSR at which temperatures. The lower melting  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SiO}_3$  FBSR products were targeted for initial study [14]. Only the carbonate tests are discussed in this manuscript since the 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  $\text{Na}_2\text{CO}_3$  product.

The carbonated slurries were dried to “peanut butter” consistency to ensure that some  $\text{H}_2\text{O}$  remained in the sample to create steam for the WGSR. Alumina crucibles were sealed with nepheline ( $\text{NaAlSiO}_4$ ) 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  $\text{CO}_2$  thus duplicating the FBSR gas mixtures. The furnace was purged with 99.99% Argon to ensure that no  $\text{O}_2$  mixed with any  $\text{H}_2$  or CO that escaped through the crucible seal.

### **Tank 48 Simulant Pilot Scale Tests (INL and SRNL, 16)**

The SAIC STAR pilot scale facility uses a single reformer flowsheet. It is an externally heated 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 carbon in the form of sucrose or sugar (100% mass to 200% mass of sucrose) were tested. Feeds were pre-carbonated by bubbling  $\text{CO}_2$  or by adding oxalic acid. In some of the higher (200% mass of sucrose) tests oxygen was added to the steam to mitigate higher total hydrocarbon (THC) releases but this was found to be unnecessary for THC releases. Five wt%  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was added as a REDOX indicator to ensure that the  $\text{Fe}^{+2}/\Sigma\text{Fe}$  ratio of the solid product sample could be measured. Silica bed media complexed with the Tank 48 waste and created pluggages. However, alumina bed media was shown to work well with the Tank 48 waste. Temperatures varied from  $625\text{--}650^\circ\text{C}$  during successful operation. Testing above  $700^\circ\text{C}$  was shown to cause the carbonate product to melt.

### **Tank 48 Simulant Engineering Scale Tests (TTT and SRNL, 17)**

A steam reforming ESTD unit was built and operated at HRI. The ESTD is a nine-tenth-scale unit for the Tank 48 process. It includes all unit operations present in the full-scale unit,

excluding the product packaging equipment. The ESTD uses a dual reformer flowsheet: a DMR which operates at temperatures low enough that the carbonates do not melt, i.e. 640-675°C, and a CRR which operates at ~950°C to destroy any residual organics or organic byproducts that may be carried over past the DMR.

The engineering scale testing of the THOR<sup>®</sup> 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 phenylborate ions, nitrates, biphenyls, diphenyl mercury, benzene, and other species. These tests were completed 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, 3310 gal of Tank 48 simulant were processed into 5174 lb 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.

**Table II Simulated Non-Radioactive and Radioactive T48 Steam Reformer Analytic Results**

Test #	Temp (°C)	Sugar Stoichiometry	Coal Stoichiometry	Residence Time (hrs)	Major Phases Identified by X-Ray Diffraction (XRD)	Minor Phases Identified by XRD	Phenylborates NaTPB, 3PB, 2PB concentration (ug/g)	NO <sub>x</sub> (%) Destruction	Total Organic Carbon (%) Destruction
<b>Feed</b>									
T48-0	60	0	N/A	N/A	Na <sub>3</sub> H(CO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> , Na(NO <sub>3</sub> ), NaNO <sub>2</sub> , Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O	Na <sub>2</sub> SiO <sub>3</sub> , KAl(SO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>12</sub>	95,100,<5	0	0
<b>Non-Radioactive Crucible Tests (2003; 14)</b>									
T48-1	725	0	N/A	½	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub>	Ca <sub>8</sub> Al <sub>2</sub> Fe <sub>2</sub> O <sub>12</sub> CO <sub>3</sub> (OH) <sub>2</sub> •22H <sub>2</sub> O	<5,<5,<5*	30.1	>99.5
T48-5B	650	1	N/A	3	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub>	NONE	<5,<5,<5*	99.1	>99.5
T48-13	650	1	N/A	48	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub>	NONE	<5,<5,<5*	99.0	>99.5
<b>SAIC STAR Non- Radioactive Pilot Scale Tests (2004; 12)</b>									
Tests 8-9	625-650	2	N/A	N/A	Na <sub>2</sub> CO <sub>3</sub> calculated	NONE	<10,<10,<10*	99.6-99.99	99.83-99.89
<b>TTT-HRI Non-Radioactive Engineering Scale Tests (2006; 17)</b>									
PROD-1 to 4	640-675	N/A	1-1.5	N/A	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub> , Na <sub>3</sub> H(CO <sub>3</sub> ) <sub>2</sub> •2H <sub>2</sub> O	NaAlSiO <sub>4</sub> + NaAlSiO <sub>4</sub> •H <sub>2</sub> O + Na <sub>2</sub> Al <sub>22</sub> O <sub>34</sub> + SiO <sub>2</sub>	<50, <100,<100*	>97.7	>99.9
<b>TTT-HRI Non-Radioactive Engineering Scale Tests Phase 1(2008; 23)</b>									
P-1 to -4 T48V-1	617-666	N/A	1-1.5	N/A	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub>	NaAlSiO <sub>4</sub> + NaTi <sub>2</sub> O <sub>4</sub> + SiO <sub>2</sub> + Na <sub>8</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>2</sub> (CO <sub>3</sub> ) <sub>0.5</sub> (OH)•3H <sub>2</sub> O	<10,<10,<10*	>99.3	>99.9
<b>TTT-HRI Non-Radioactive Engineering Scale Tests Phase 3(2009; 24, 25)</b>									
T48-1-1A To T48-1-4	630-650	N/A	1-1.5	N/A	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>3</sub> H(CO <sub>3</sub> ) <sub>2</sub> •2H <sub>2</sub> O	NaAlSiO <sub>4</sub> + TiO <sub>2</sub> + SiO <sub>2</sub> + Na <sub>8</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>2</sub> (CO <sub>3</sub> ) <sub>0.5</sub> (OH)•3H <sub>2</sub> O	<0.7,<8,<8*	>98	>99.9
<b>Radioactive Crucible Tests (2008; 18)</b>									
RAD 1-4	650	1	N/A	3-8	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>1.95</sub> Al <sub>1.95</sub> Si <sub>0.05</sub> O <sub>4</sub> , Na <sub>14.88</sub> Al <sub>15.26</sub> Si <sub>32.74</sub> O <sub>96</sub>	<10,<10,<10*	100	Not Meas.
<b>Radioactive Benchscale Steam Reformer (BSR) Tests (2008; 19)</b>									
BSR	645-676	N/A	1-1.5	N/A	Na <sub>2</sub> CO <sub>3</sub> •H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub> , Na <sub>3</sub> H(CO <sub>3</sub> ) <sub>2</sub> •2H <sub>2</sub> O	Na <sub>8</sub> (AlSiO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub> •2H <sub>2</sub> O, Na <sub>2</sub> Al <sub>2</sub> SiO <sub>6</sub>	<5,<5,<5*	>99.6->99.8	Not Meas.

\* corresponds to &gt;99.8% destruction



### **Tank 48 Radioactive Crucible Scale Tests (SRNL, 18)**

Crucible scale testing with actual radioactive Tank 48 material was performed at SRNL in 2008. The radioactive crucible testing was performed to duplicate the test results that had been performed with the Tank 48 simulant in 2003 [14]. The comparison of the results using radioactive Tank 48 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 Tank 48 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. A 1X stoichiometric amount of sugar was used (see Equations 1 and 2) and Table II. The equivalent coal carbon stoichiometry in Table II is 1-1.5 times that for sucrose or sugar to account for coal ash not contributing to Equations 1 and 2. The sealed crucibles were heat-treated at 650°C 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.

### **Tank 48 Radioactive Benchscale Steam Reformer (BSR) Tests (SRNL, 19)**

The radioactive BSR tests are described in another paper published in the Waste Management 2009 Proceedings [19]. The BSR was assembled in the SRNL Shielded Cell Facility (SCF) mockup shop on a 3' x 4' stainless steel pan. All control units and mass spectrometers for recording the off-gas measurements were located outside the radioactive cells with the connections being made to BSR equipment via KAPL plugs (9 SCF inner wall connection tubes developed at Knolls Atomic Power Laboratory, KAPL). Condenser/bubbler/dry ice condenser units were necessary for pretreatment of the off-gas to prevent filter pluggages or damage to the mass spectrometers from hot gases produced by the BSR.

The BSR 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 is the primary parameter for scaling this process to the engineering scale process. Ferric nitrate was added as a REDOX indicator.

In the ESTD steam reformer, oxygen was bled in to provide the heat necessary by consuming H<sub>2</sub> generated by interactions of organics and carbon with steam. 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. Very large 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 is 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 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 steam reformer products were achieved. Samples were measured by High Pressure Liquid Chromatography (HPLC) to determine if the phenylborates were adequately destroyed by the steam reforming reactions. Analyses were also conducted to determine if any secondary phenylborate reaction products were present, e.g., triphenyl (3PB) and biphenyl (2PB) borates. Total Carbon (TC), Total Inorganic Carbon (TIC), and Total Organic Carbon (TOC) were also measured. All samples were analyzed for  $\text{Fe}^{+2}/\Sigma\text{Fe}$  analysis by the Baumann method [20].

Samples were measured by Ion Chromatography (IC) for  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  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 gas chromatographs.

## 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  $\log f_{\text{O}_2}$  fugacities of -20.2 to -22.2 atmospheres (

Table III) indicating very reducing conditions. For comparison air has a  $\log f_{\text{O}_2}$  of 0.21

atmospheres. The radioactive crucible studies and the radioactive BSR tests produced  $\log f_{\text{O}_2}$

fugacities of -20.2 to  $\geq$  -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	$\text{Fe}^{+2}/\Sigma\text{Fe}$	$\log f_{\text{O}_2}$
Non-radioactive Crucibles [14]	No sugar; 650-725°C; 0.5-3 hours	0.70	-23.8
Non-radioactive Crucibles [14]	Full mass sugar; 650-725°C; 0.5-3 hours	0.65	-23.6
Non-radioactive SAIC-STAR pilot Scale [16]	200% mass sugar plus $\text{O}_2$ ; 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]	Full mass 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
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#### Tank 48 Simulant Crucible Tests (SRNL, 14)

A sample (T48-0) was tested as a baseline. The T48-0 sample was carbonated, antifoam and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were added, and the sample was dried at 60°C. This sample was analyzed for phenylborates, anions, TC, TIC, TOC and REDOX as a baseline case (see Table II). These analyses demonstrated that there was 95,100 ug/g of phenylborates (Table II) present in the feed samples after the carbonation and drying steps. The presence of the phenylborates was also confirmed by the measurement of TOC, which showed 19,500 ug/g of organic carbon. Either the phenylborates or the antifoam (an organic) may have reacted with the  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  because an all  $\text{Fe}^{+3}$  dried solution should have had a REDOX measurement of ~0 and the measurement was 0.44. This indicated that a considerable amount of  $\text{Fe}^{+2}$  was present or that the organics interfered with the REDOX measurement. Anion analysis of the T48-0 base case indicated <100 ug/g of  $\text{NO}_2^-$  and 163,000 ug/g or 16.3 wt% of  $\text{NO}_3^-$ . This number was used with the measured  $\text{NO}_3^-$  data [14] to calculate the  $\text{NO}_3^-$  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 <5ug/g indicating that the thermal treatment destroyed all the phenylborates 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 Tank 48 (Table II).

For all of the FBSR samples in which the desired product was  $\text{Na}_2\text{CO}_3$  (samples T48-1 through T48-5B and T48-13), analysis by XRD indicated that a mixture of  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  (thermonatrite) and  $\text{Na}_2\text{CO}_3$  (natrite) was formed regardless of temperature and residence time in the furnace (Table II). When a reductant was not used, the nitrate was incompletely destroyed (Table II). Tests T48-5B or T48-13 appeared optimal for making the  $\text{Na}_2\text{CO}_3$  FBSR product and destroying all the organics and nitrates at ~650°C with the full mass of carbon stoichiometrically from sugar and 3-48 hour residence time: no minor phases were identified as incomplete reactants (Table II). No adherence of the carbonate phases onto the  $\text{Al}_2\text{O}_3$  crucibles was noted. Therefore, if the FBSR startup bed is  $\text{Al}_2\text{O}_3$ , there should not be any particle agglomeration with the  $\text{Al}_2\text{O}_3$  [14].

The FBSR product sample T48-5B (primarily  $\text{Na}_2\text{CO}_3$  made at 650°C) was measured by Differential Thermal Analysis (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  $\text{CO}_2$  to be released.

#### Tank 48 Simulant Pilot Scale Tests (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 Tank 48 waste for vitrification [16]. The objectives of the tests included 1) >99 % destruction of phenylborates, nitrates, and nitrites, 2) acceptable performance (no agglomeration), 3) acceptable bed product that could become feed to the DWPF melter, and 4) use of sugar or sucrose as a reductant for nitrate destruction because of its compatibility with DWPF processing.

The demonstration was performed in the 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) a 200% mass of carbon as sugar was used and oxygen added to the fluidizing steam. This created REDOX values that were somewhat more oxidizing than noted in the non-radioactive crucible studies with only the full mass of carbon, 100%, as sugar (see Table III) but were still at log  $f_{O_2}$  fugacities of -20.2 to -22.2. 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%), phenylborate destruction (>99.8%), and TOC destruction (99.83-99.89%) as shown in Table II.

### **Tank 48 Simulant Engineering Scale Tests (TTT and SRR/SRNL, 17, 23)**

Engineering scale 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 sucrose or 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, 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->99.4%), TPB destruction (>99.8%), and TOC destruction (>99.99%) as shown in Table II.

The 2008 ESTD Validation Tests [23] at the HRI pilot scale test facility were performed to resolve design issues identified from the 2006 ESTD test [17]. The steam reforming process capability to destroy organics in the Tank 48 waste and to generate sodium carbonate base product was successfully demonstrated in 2006. The limited number of feed and product samples analyzed from 2008 tests was to verify that with the design modifications implemented in 2008, the steam reforming process is still capable of treating Tank 48 organic waste and generating sodium carbonate base product. The 2008 and 2006 HRI sample analytical results both demonstrated that the organics (tetra-, tri-, bi-, and mono-phenylborate), nitrites, and nitrates in the feed are being destroyed greater than 99% and that a primary sodium carbonate product is being formed as shown in Table III.

### **Tank 48 Radioactive Crucible Scale Tests (SRNL, 18)**

All aspects of the non-radioactive crucible scale testing with simulated Tank 48 waste were demonstrated to be repeatable with the actual radioactive feed. The phenylborate destruction was shown to be > 99% and the final solid product is a mixture of various sodium carbonate crystalline minerals (Table II). Less than 10 wt% of the final solid products are insoluble components comprised of Fe/Ni/Cr/Mn containing sludge components and Ti from monosodium titanate present in Tank 48 waste. REDOX measurements on the radioactive solid products indicate a reducing atmosphere with extremely low oxygen fugacity (Table III) evidence that the sealed crucible tests performed in the presence of sugar or sucrose under constant argon purge were successful in duplicating the pyrolysis reactions occurring during pilot and engineering scale testing. Soluble anion measurements confirm that using sugar or sucrose as a reductant at full mass carbon stoichiometry was successful in destroying nitrate/nitrite (Table II).

### **Tank 48 Radioactive Benchscale Steam Reformer (BSR) Tests (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 Tank 48 material were performed in the BSR. The phenylborate 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 steam reformer and the desired soluble carbonates were formed (Table II). Insoluble solids analyzed by X-Ray Diffraction (XRD) did not detect insoluble carbonate species. However, they could still have been present at levels below 2 wt%, the detection limit of the XRD methodology. Insoluble solids XRD characterization indicated that various Fe/Ni/Cr/Mn phases are 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  $\text{Fe}^{+2}/\Sigma\text{Fe}$  REDOX measurements ranged from 0.58 to 1 for the three radioactive BSR tests. REDOX measurements > 0.5 showed a reducing atmosphere ( $\log f_{\text{O}_2}$  of -22.2 or lower atmospheres) was maintained in the DMR as shown in

Table III.

### **Carbonate Transport and Melter Compatibility (TTT and SRS/SRNL, 24, 25)**

Differential Thermal Analysis (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 HLW DWPF melter. In either case the product will be decarbonated via the existing DWPF acid addition strategy for carbonate destruction in the Slurry Receipt Adjustment Tank (SRAT). This will eliminate any potential for CO<sub>2</sub> 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  $\text{Fe}^{+2}/\Sigma\text{Fe}$  ratio of 0.2.[21, 22]

The 2009 ESTD Validation Tests [24, 25] at the HRI Pilot Scale Test facility were performed primarily to demonstrate the capability of the integrated FBSR Product Handling System to convert the liquid Tank 48 simulant into a dissolved carbonate product form transportable through the SRS tank farm for future vitrification in the HLW DWPF. The limited number of feed and product samples analyzed from the tests was to verify that with the implemented product design modifications to slurry FBSR product, the FBSR process is still capable of destroying Tank 48 organic waste and generating sodium carbonate product. The analytical results of the 2009 product streams shown in Table III indicates similar characteristics including carbonate compound formation, organic and nitrate destruction as samples analyzed in 2006 and 2008 by SRNL. The SRNL analysis of Phase 3 samples was performed in accordance with the Tank 48 Treatment Project – Hazen ESTD Validation Testing Task Technical and Quality Assurance Plan Procedures [24].

## CONCLUSIONS

The purposes of non-radioactive and radioactive tests (crucible, pilot scale, engineering scale and bench scale) were fulfilled as documented by the following:

- Phenylborate was completely destroyed in all samples tested at temperatures between 625-676°C,
- >99% destruction of nitrate was achieved
- >99% destruction of organic carbon and phenylborate including phenylborate byproducts, benzene, phenyl, biphenyl, phenol, and antifoam
- $\text{Na}_2\text{CO}_3$  or one of its hydrates was produced for all tests in which  $\text{Na}_2\text{CO}_3$  was the desired product phase,
- $\text{Na}_2\text{CO}_3$  was shown to be compatible with the HLW DWPF process,
- tests with simulated wastes generate the same results as those with actual radioactive Tank 48 wastes

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