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DISPOSITION OF TANK 48H ORGANICS BY FLUIDIZED BED STEAM REFORMING (FBSR) (U)

C. M. Jantzen

Publication Date: September 18, 2003

Approved by:

J.C. Griffin, Research Manager
Waste Processing Technology Section

Savannah River Technology Center
SRTC
We Put Science to Work

Westinghouse Savannah River Company
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Aiken, SC 29808

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DISPOSITION OF TANK 48H ORGANIC SLURRY BY FLUIDIZED BED STEAM REFORMING (FBSR) (U)

C. M. Jantzen

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LIST OF ACRYNOMS

ADS	Analytic Development Section of SRTC
CIF	Consolidated Incinerator Facility
DTA	Differential Thermal Analysis
DWPF	Defense Waste Processing Facility
EMF	Electro Motive Force
FBSR	Fluidized Bed Steam Reforming
HLW	High Level Waste
HPLC	High Pressure Liquid Chromotagraphy
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
INEEL	Idaho National Engineering & Environmental Laboratory
ITP	In Tank Processing
LAW	Low Activity Waste
LLRW	Low Level Radioactive Waste
MACT	Maximum Achievable Concentration Technology
ML	Mobile Laboratory
PHA	Precipitate Hydrolysis Aqueous
REDOX	REDuction/OXidation
SBW	Sodium Bearing Waste
SME	Slurry Mix Evaporator
SPF	Studsvick Processing Facility
SRAT	Sludge Receipt Adjustment Tank
SRS	Savannah River Site
SRTC	Savannah River Technology Center
TC	Total Carbon
THOR	THermal Organic Reduction
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TPB	Tetraphenylborate
TRU	TRansUranic
WAC	Waste Acceptance Criteria
WIPP	Waste Isolation Pilot Plant
WGSR	Water Gas Shift Reaction
WSRC	Westinghouse Savannah River Co.
XRD	X-ray Diffraction

EXECUTIVE SUMMARY

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} as CsTPB, respectively. This process was demonstrated at the SRS in 1983. The demonstration produced 53,000 gallons of 2.5 wt% Cs rich precipitate containing TPB, which was later washed and diluted to 250,000 gallons. This material is currently stored in SRS Tank 48H. The washed precipitate was to ultimately be disposed in borosilicate glass in the Defense Waste Processing Facility (DWPF). Due to safety concerns the ITP process was abandoned in 1998, and new technologies are being researched for Cs^{137} removal.

In order to make space in the SRS Tank farm, the Tank 48H waste must be removed. Therefore, the Tank 48H waste must be processed to reduce or eliminate levels of nitrates, nitrites, and sodium tetraphenyl borate (NaTPB) in order to reduce impacts of these species before it is vitrified at the DWPF. Fluidized Bed Steam Reforming (FBSR) is being considered as a candidate technology for destroying the nitrates and the NaTPB prior to melting. The Idaho National Engineering and Environmental Laboratory (INEEL) was tasked to perform a proof-of-concept steam reforming test to evaluate the technical feasibility for pretreating the Tank 48H waste. The crucible (bench scale) tests conducted at the Savannah River Technology Center (SRTC) were initiated to optimize and augment the parameters subsequently tested at the pilot scale at INEEL.

The purposes of the current study, organic destruction and downstream processing of T48H waste slurry were fulfilled. TPB was destroyed in all 19 samples tested with the simulated FBSR process at operational temperatures 650-725°C. A test temperature of 650°C optimized NO_3 destruction during the formation of an Na_2CO_3 FBSR product. A test temperature of 725°C optimized NO_3 destruction during formation of a sodium silicate FBSR product. Destruction of nitrate at >99% was achieved with addition of sugar as a reductant at 1X stoichiometry and total organic carbon analyses indicated that excess reductant was not present in the FBSR product. The use of sugar at 1X stoichiometry appears to ensure that excess reductant is not contained in the FBSR product that would alter the REDuction/OXidation (REDOX) equilibrium of the DWPF melter, while simultaneously assuring that NO_3 is destroyed adequately. Destruction of anitfoam with the simulated FBSR process was also achieved at operating temperatures between 650-725°C based on measured total organic carbon.

Sealed crucible tests with wet Tank 48H slurries ensured that the Water Gas Shift Reactions (WGSR) that occur in the FBSR process were duplicated in the bench scale tests. Sodium carbonate (Na_2CO_3) was produced in all the bench scale studies in which Na_2CO_3 was the desired FBSR product phase. The Na_2CO_3 product was shown to be compatible with the DWPF melt process as it melts at 980°C, as measured by differential thermal analysis.

For all bench scale tests in which Na_4SiO_4 or Na_2SiO_3 was the desired FBSR product, a sodium silicate with a different stoichiometry (Na_2O:SiO_2) formed. This was determined to be a problem caused by water absorption of the finely particulate SiO_2 additives used and the consumption of SiO_2 by a potassium aluminate zeolite (faugesite) that formed during processing. Optimization of the Na_2O:SiO_2 ratio of the Tank 48 feed is still needed. Formation of a sodium silicate (mixed with Na_2CO_3 or alone) 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 for subsequent vitrification. The mixtures melted at temperatures of 1022°C and 1049°C, respectively, as measured by differential thermal analysis. The melt temperatures of the Na_2CO_3 and Na_2SiO_3 FBSR products (980°C and 1022-1049°C) are low enough to ensure that addition of the FBSR product to the DWPF will not adversely impact melt rate. The impact of excess carbonate on the acid addition strategy in the DWPF Sludge Receipt and Adjustment Tank was not included in this study and still needs to be examined.

The recommended test parameters for the subsequent pilot scale testing of Tank 48H simulant at Idaho National Engineering and Environmental Laboratory (INEEL) were given by the following:

- Al_2O_3 bed media to avoid sticking and particle agglomeration
- 650°C at 1X stoichiometric sugar 3-48 hours residence time to make a Na_2CO_3 product (conditions for tests T48-5B and T48-13)
- 725°C at 1X stoichiometric sugar for 48 hours residence time for the Na_2SiO_3 product (conditions for test T48-14)

The sealed crucible studies and precarbonation of the feed demonstrated that bench scale studies can duplicate the complex reactions, especially the Water Gas Shift Reactions (WGSR) that occur in the FBSR process. This was monitored by adding Fe^{+3} compounds to the starting Tank 48 slurries and measuring the final $Fe^{+2}/\Sigma Fe$ ratio. Using a published correlation between the log of the oxygen fugacity (log f_{O_2}) and the $Fe^{+2}/\Sigma Fe$ ratio the effective log f_{O_2} inside the sealed crucibles could be calculated. Very negative values of the log f_{O_2} indicated that there was virtually no oxygen present in the sealed crucibles. Knowing the log f_{O_2} and the reaction temperatures, the associated $\log p_{H_2O} / p_{H_2}$ and $\log p_{CO_2} / p_{CO}$ atmospheres in the sealed crucibles could be calculated from known correlations. The associated $\log p_{H_2O} / p_{H_2}$ and $\log p_{CO_2} / p_{CO}$ atmospheres were a very positive indication that the WGSR was controlling the atmosphere inside the sealed crucibles and that oxygen was absent.

DISPOSITION OF TANK 48H ORGANIC SLURRY BY FLUIDIZED BED STEAM REFORMING (FBSR) (U)

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1.0 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 and precipitate Cs^{137} as CsTPB respectively. This process was demonstrated at the SRS in 1983 [1]. The demonstration facility consisted of Tank 48H, a 1.3 million gallon, carbon steel, underground HLW tank that had been retrofitted with chemical additional and process monitoring equipment. The actual demonstration was performed on a 500,000 gallon batch of radioactive salt supernate that was chemically treated and filtered. This produced 450,000 gallons of decontaminated filtrate, which was disposed of in saltstone, and 53,000 gallons 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 Tank 48H for ultimate disposal in borosilicate glass in the Defense Waste Processing Facility (DWPF).

The 1983 ITP process 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 130,000 gallons of salt solution and 37,300 gallons of NaTPB to the heel of precipitate in Tank 48H that remained from the 1983 demonstration. During processing, benzene evolved in Tank 48H 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. Alternate technologies for Cs^{137} removal have been selected and demonstrated in laboratory testing. Operation of the Late Wash Facility and the DWPF Salt Cell facilities were abandoned and DWPF radioactive sludge vitrification commenced in 1996 without the ITP alkali boron contribution.

Currently Tank 48H has about 250,000 gallons of slurry which contains potassium and cesium tetraphenylborate (KTPB and CsTPB). Tank 48H needs to be returned to service by August 2005 in order to free up tank space in the high level waste (HLW) system [3]. The TPB organics in the Tank 48H slurry need to be removed or destroyed before this slurry is pumped out and processed downstream.

In 2001, a team evaluated processing options that would return Tank 48H to routine HLW service [4]. The team used a Systems Engineering approach to evaluate 40 alternatives. While most options decomposed the organics with catalysts, oxidants, and/or acids, one thermal treatment was recommended for further investigation, i.e. Fluidized Bed Steam Reforming (FBSR).

The candidate thermal process for the Tank 48H organic destruction, FBSR, is capable of destroying the organic KTPB and CsTPB at moderate temperature and converting it to $(Cs,Na)_2O$ or $(Cs,Na)_2CO_3$ or $(Cs,Na)SiO_3$, CO_2 gas, and H_2O in the form of steam [5,6]. The high nitrate and nitrite content of the Tank 48H slurry will be converted to N_2 during FBSR processing, thereby minimizing NO_x emissions during processing. Any organics are oxidized to CO_2 instead of CO during processing. The FBSR can be electrically heated (pilot scale units) or operated in an auto-thermal mode, whereby the energy needs are supplied by the incoming superheated steam and by the oxidation of organics from the waste and carbon reductants. For production scale units, auto-thermal steam reforming is the preferred mode of operation. Since there is no open flame as in incineration and since the product emissions are CO_2 and N_2 instead of CO and NO_x, the FBSR process is Clean Air Act and Maximum Achievable Concentration Technology (MACT) compliant. The solid oxide or mineral phases produced, e.g. $(Cs,Na)_2O$ or $(Cs,Na)_2CO_3$ or $(Cs,Na)SiO_3$, are considered compatible with subsequent processing of the FBSR remediated Tank 48H feed to borosilicate glass in the Defense Waste Processing Facility (DWPF).

The purposes of the current study were to demonstrate the following objectives with a Tank 48H simulant:

- destruction of TPB with the FBSR process operating between 650-725°C
- destruction of nitrate at >99% with addition of sugar as a reductant
- destruction of anitfoam with the FBSR process operating between 650-725°C
- formation of Na_2CO_3 FBSR product to be compatible with mixing the FBSR product into a DWPF feed tank for subsequent vitrification
- formation of a Na_2SiO_3 or Na_4SiO_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 for subsequent vitrification
- assessment of the melting temperature of the Na_2CO_3 and Na_2SiO_3 FBSR products to ensure that addition of the FBSR product to the DWPF will not adversely impact melt rate
- optimization of the amount of reductant to ensure that excess reductant was not contained in the FBSR product that would alter the REDuction/OXidation (REDOX) equilibrium of the DWPF melter [7]

- optimization of test parameters for subsequent pilot scale testing of Tank 48H simulant at Idaho National Engineering and Environmental Laboratory (INEEL)
- demonstration that bench scale studies in crucibles can duplicate the complex reactions in the FBSR process

2.0 FLUIDIZED BED STEAM REFORMING (FBSR)

2.1 Demonstrations by THOR^{sm}

Studsvik built and tested a commercial Low-Level Radioactive Waste (LLRW) FBSR Processing Facility in Erwin, TN, in 1999 [8]. In January 2000, the throughput rate was increased and commercial operation commenced [5]. The Studsvik Processing Facility (SPF) 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 100R/hr. The licensed and heavily shielded SPF can receive and process liquid and solid LLRWs with high water and/or organic content.

The Erwin facility employs the THermal Organic Reduction (THOR^{sm}) process, developed by Studsvik, which utilizes pyrolysis[*]/steam reforming technology. THOR^{sm} reliably and safely processes a wide variety of LLRWs 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 THOR^{sm} technology to convert nitrates to nitrogen and sodium salts to sodium compounds that are suitable for direct disposal and/or subsequent vitrification.

In February 2002, THOR^{sm} demonstrated the capability of producing sodium aluminosilicate waste forms for Hanford's sodium-bearing low activity waste (LAW) [6]. Non-radioactive simulants of 8.1M Na^+ were successfully tested in a 6-inch pilot scale facility that was located at Hazen Research in Colorado.[†] Other demonstrations performed by Hazen showed that LAW waste could be transformed into Na_2CO_3, $NaAlO_2$, or Na_2SiO_3 feed material for the LAW Hanford melter (Table 1). Addition of no solid co-reactant will yield a sodium carbonate product. Sodium combines with carbon dioxide in the reformer gases to provide a sodium carbonate product. The generation of sodium carbonate in this type of application has been studied since the 1950s in fluid bed denitration systems [5]. Addition of a $Al(OH)_3$ co-reactant will provide an $NaAlO_2$ product, addition of SiO_2 will provide an Na_2SiO_3 product. Addition of kaolin clay will provide an $NaAlSiO_4$ product (Table 1). The latter has been shown to perform well as a final waste form [6, 9]. Testing on Hanford LAW surrogates has shown that over 95% of

---

[*] Pyrolysis chemically decomposes organic materials by heat in the absence of oxygen, e.g. C_xH_y + Heat $\rightarrow CH_4 + C$.

[†] The solution was diluted to 5.2M Na^+ to homogenize the feed before processing due to the observation of precipitated solids in the feed tank

the sulfur compounds, fluorides and chlorides in the waste feed react in the steam reformer with the clay co-reactant and become an integral part of the final $NaAlSiO_4$ waste product's crystalline structure [5].

In November 2002, THOR^{sm} was contracted to demonstrate the FBSR technology to produce a final waste form for Idaho National Engineering and Environmental Laboratory acidic and radioactive Sodium-Bearing Waste (SBW) [10]. This demonstration successfully converted the high sodium waste to an Na_2CO_3 product that met the Waste Isolation Pilot Plant (WIPP) Waste Acceptance Criteria (WAC) for transuranic (TRU) waste. During the demonstration data were collected to determine the nature and characteristics of the product, the operability of the technology, the composition of the off-gases, and the fate of key radionuclides (cesium and technetium) and volatile mercury compounds. The product contained a significant fraction of elemental carbon residues. Mercury was quantitatively stripped from the product but cesium, rhenium (Tc surrogate), and the heavy metals were retained. Nitrates were not detected in the product and NO_x destruction exceeded 98%. The demonstration was considered successful and no bed agglomeration was experienced [10]. The steam reformer off-gas was monitored and it was determined that no O_2 was present. 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. The O_2 and H_2 levels in the off-gas were low enough that they did not pose a significant threat of forming an explosive mixture.

Table 1. THOR^{sm} Pilot Scale Demonstrations Performed at Hazen Research

Number of Pilot Demon-strations	Solid Additive	Mineral Product	Purpose
5	Clay	Sodium aluminosilicates that can stabilize problematic anions such as Cl, F, and SO_4	Stabilization in final mineral waste form
3	Sand	Sodium silicate	Dehydration, denitration, organic destruction of LAW waste for subsequent vitrification and/or dehydration of melter blowdown for recycle to a melter
2	$Al(OH)_3$	Sodium aluminate	Dehydration, denitration, organic destruction of LAW waste for subsequent vitrification and/or dehydration of melter blowdown for recycle to a melter
3	None	Sodium carbonate	Dehydration, denitration, organic destruction of LAW waste for subsequent vitrification and/or dehydration of melter blowdown for recycle to a melter

2.2 Operation and Flowsheet Options

In the THOR^{sm} FBSR process, a granular/particle bed material is fluidized with low pressure superheated steam. The tank waste is mixed in a batch/feed tank with select co-reactants, including the additives necessary to make the final product into any of the applications listed in Table 1. The FBSR feed slurry is injected into the bottom of the fluidized bed just above the fluid gas (steam) distributors. Additional solid co-reactants, such as granular carbon and iron oxide reductants, are co-fed to the fluidized bed. The lower zone of the fluid bed is operated in strongly reducing conditions to facilitate reduction of nitrates and nitrites to nitrogen gas. The upper zone of the fluid bed is operated under oxidizing condition by injection of oxygen into the upper zone of the fluidized bed. The oxidizing zone converts residual carbon reductants and organics into carbon dioxide and water vapor. Several chemical and physical reactions take place in the steam reformer [5]:

- Evaporation of all liquid.
- Conversion of all sodium, potassium, and aluminum in the waste feed into a stable mineralized product (choices are given in Table 1). The mineral product contains any radionuclides and inorganic elements in the waste feed stream in the form of oxides, carbonates, aluminates and/or silicates.
- Denitration of the nitrates and nitrites (>99%) in the waste feed into nitrogen gas by the carbon and metal reductant solids and CO and H_2 gases in the bed.
- Conversion of organics into CO_2 by a two step process. First organics are decomposed into light volatile hydrocarbons such as methane, carbon monoxide, hydrogen, carbon dioxide, and water in the lower zone of the reformer bed. In the upper zone of the reformer bed, oxygen is injected to more fully oxidize the gaseous constituents. The off-gas stream from the reformer consists of water vapor, carbon dioxide, nitrogen, fine particles of solid product, minor carbon particle carryover, and small quantities of acid gases not converted to a mineralized form in the reformer.
- Reduction and stabilization of any hazardous metals. For example hazardous metals such as Cr^{+6} are reduced to a non-hazardous valence state, e.g. Cr^{+3}, and are chemically bound in the solid product. Other hazardous metals, such as lead, have also been determined to be chemically bound in the solid product.[6]

The THOR^{sm} FBSR is typically operated under vacuum at 700°C to 750°C. A typical flowsheet is shown in Figure 1. The >99% conversion of nitrates to nitrogen requires the following [5]:

- fluidized bed material with high surface area and high heat transfer capability
- high energy generation to evaporate and superheat the water in a typical waste feed
- strongly reducing conditions that are provided by the reductants added to the process

- superheated steam that generates carbon monoxide and hydrogen inside the bed from the reaction of steam with the carbon reductant(s)
- co-reactant(s) that convert the alkali metals (Na and K) into higher melting point mineral compounds to prevent formation of low melting point eutectic salts and unwanted bulk agglomerations in the fluid bed.

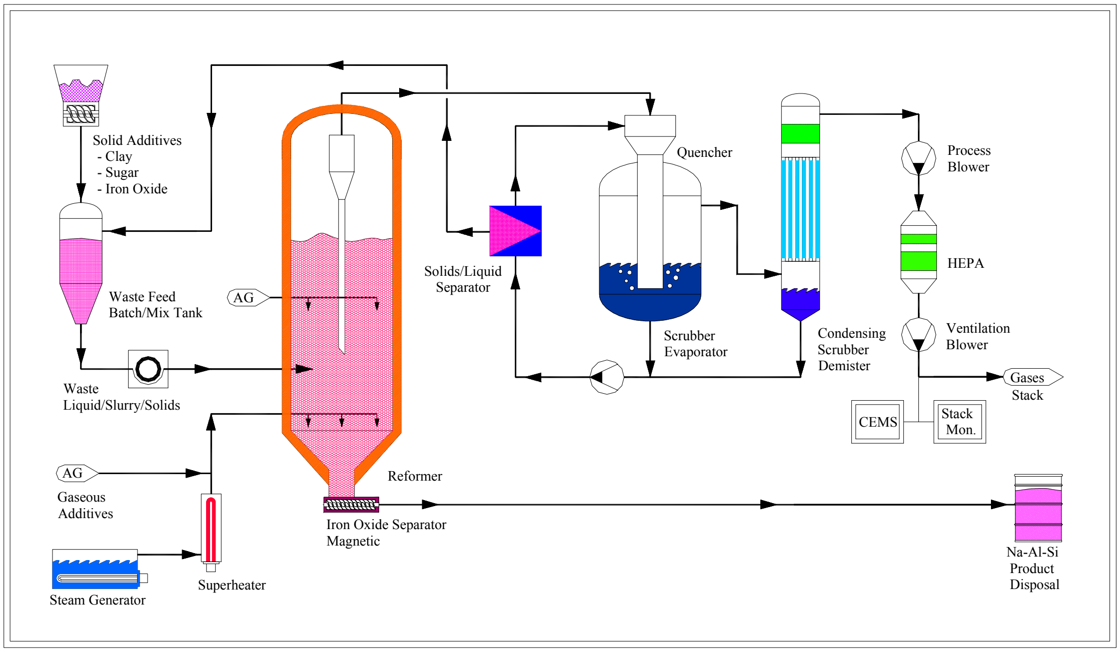


Figure 1 Typical FBSR flowsheet proposed by THOR for DOE Tank wastes [5].

The fluidized bed material can include ceramic media and/or reformed product granules/powders. The incoming waste feed coats the fluidized particles and is instantly dried. The large active surface of dried nitrates readily reacts with the hot carbon reductant particles, carbon monoxide and hydrogen gases, and the reduced metal and metal oxides particles in the fluidized bed. Hydrogen and CO are formed by the water gas reaction (Equation 1) and the steam reforming process (Equation 2). The CO in the gaseous mixture resulting from Equation 1 and Equation 2 can be made to react with more water in the water gas shift reaction (WGSR) given in Equation 3. These reactions are important sources of heat that facilitate the dehydratrion, denitration, and reaction of the waste plus additive mixtures.

Equation 1 $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

Equation 2 $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2\ (g)$

Equation 3 $H_2O\ (g) + CO\ (g) \rightarrow H_2\ (g) + CO_2$

Free hydrogen promotes radical generation and chain reaction propagation in the bed and gaseous particle disengaging freeboard section. Steam also oxidizes all carbon-donating solids, including char. During the INEEL SBW steam reformer demonstrations sugar was used as the reductant along with activated carbon. This facilitated the decomposition of nitrates in the feed and reduced NO_x to elemental nitrogen. Excess sucrose pyrolyzed, at the process temperatures, producing a finely divided carbon char. The activated carbon and the char reacted with the process steam to produce carbon monoxide and hydrogen gas via Equation 3.

Even though carbon monoxide and hydrogen are produced in equimolar quantities by the water-gas shift reaction (Equation 3), a significant portion of the carbon monoxide reacts with other gaseous species. Examples of this are the methanation reaction, and reactions with NO_x to form nitrogen gas. The WGSR (Equation 3) is, however, the most dominant and results in molar hydrogen concentrations that are several times higher than the molar concentration of carbon monoxide [10].

$$\begin{gathered} CO + 3H_2 \rightarrow CH_4 + H_2O \\ CO + NO_2 \rightarrow CO_2 + NO \\ CO + NO \rightarrow CO_2 + ½N_2 \end{gathered}$$

Hydrogen is believed to be more effective in reducing NO_x to elemental nitrogen than CO, although reactions with intermediate sugar pyrolysis products may also contribute significantly to NO_x destruction [10]. Examples of the hydrogen reactions are as follows:

$$\begin{gathered} H_2 + NO_2 \rightarrow H_2O + NO \\ H_2 + NO \rightarrow H_2O + ½N_2 \end{gathered}$$

Enrichment of the fluidizing steam with CO_2 may help convert the product to a carbonate phase; however, this is counter-productive in terms of the water gas shift reaction (Le Chatelier’s Principal). Thus, if high partial pressures of CO_2 are desired, then it is preferable to add more solid carbon [11].

Experience has shown that thermal denitration without the presence of a reductant will result in reduction of residual nitrates in the solid product of only up to 90%, i.e. 90% of the incoming nitrates are thermally volatized leaving approximately 10% of incoming nitrates in the final solid waste product. The typical total NO_x content of other thermal denitration processes, without use of a reductant, will range from 20,000 ppm to over 50,000 ppm total NO_x in the process off-gas [5]. The addition of carbonaceous reductants to nitrate wastes in a thermal denitration process has shown substantial improvements with up to 98% nitrate reduction in the solid product and a corresponding reduction of total NO_x in the process off-gas to 3,000 ppm to 10,000 ppm. A further order of magnitude improvement in nitrate conversion is possible by use of both carbonaceous and metal-based iron oxide reductants in the fluid bed [5].

A significant benefit of the THOR^{sm} steam reforming process is that the facility produces zero-liquid releases. The Erwin facility has been commercially operational at full-scale for three years with no release of liquids [5]. All water is released as water vapor out the monitored ventilation stack. All organics are processed through the reformer.

Trace radioactive particulates remaining in the off-gas stream after the quencher/scrubber/evaporator are removed by HEPA filtration prior to discharge of gases to the atmosphere. Volatile radionuclides processed at Erwin include tritium, carbon^{14} and iodine [5]. If desired, the iodine can be adsorbed by granular activated carbon media downstream of the HEPA filter. It is not normally feasible to remove the carbon^{14}, as it will have been converted to carbon^{14} dioxide and cannot be easily separated from non-radioactive carbon dioxide. Any tritium is converted to water vapor in the process. If mercury is present in the waste feed, a mercury removal capability will need to be designed in the off-gas system as mercury will volatize to the gas phase during thermal treatment [5]. THOR^{sm} anticipates that a commercially available granular activated carbon or gold impregnated media can be placed downstream of the HEPA filter to remove essentially all volatile mercury from the off-gas stream [5].

Table 2. Discharges and Emissions from a Production-Scale THOR^{sm} Steam Reforming Process for Tank Wastes [5]

Material	Discharge/Emission
SOx	<10 ppm in off-gas at stack
NOx:	
• NO_2	<5 ppm in off-gas at stack
• NO	<25 ppm in off-gas at stack
• N_2O, Others	<25 ppm in off-gas at stack
HCl	<10 ppm in off-gas at stack
HF	<2 ppm in off-gas at stack
CO	<25 ppm in off-gas at stack
Radionuclides:	
• Tritium	Tritium is converted to water vapor and is released up the monitored stack. An optional off-gas condenser can be provided to fully condense water and discharge water and tritium to groundwater if required.
• Carbon^{14}	Carbon^{14} is converted to carbon dioxide and is released up the monitored stack.
• Iodine	Iodine will be released up the stack unless adsorption media is placed downstream of the HEPA filter to remove iodine from the off-gas.
• Other	>99.99% retained in the solid product
Mercury	Mercury is removed from the off-gas by means of adsorption media downstream of HEPA filters.
Scrubber Salts	Scrubber salts are recycled to the reformer waste feed. There are no scrubber salt solution or dried salt discharges.
H_2O	Water is evaporated and discharged through the plant stack as water vapor. Process has zero-liquid releases.

3.0 EXPERIMENTAL

A simulant of the Tank 48H solution was prepared according to Table 3. This slurry has approximately 13.7 wt% solids after the TPB decomposes. In order to make a minimum of 30 grams of solid product, a test batch consisted of 218.66 grams of simulant to which 5 wt% Fe_2O_3 was added as $Fe(NO_3)_3 \bullet 9H_2O$ (0.38gms). Antifoam (IIT Corp. B52) was added at 100 ppm antifoam per wt% solids [12] or 0.21 grams per batch. The Fe_2O_3 was added to provide an indicator of the REDuction/OXidation (REDOX) equilibrium that the sample experienced in sealed crucibles inside the oven. Having ~ 5 wt% Fe_2O_3 present enabled the $Fe^{+2}/\Sigma Fe$ ratio of the solid product sample to be measured from which the oxygen fugacity, f_{O_2}, of the reaction atmosphere could be determined. All samples were sent to the Savannah River Technology Center (SRTC) Mobile Laboratory (ML) for $Fe^{+2}/\Sigma Fe$ analysis by the Baumann method [13,14].

Table 3 Tank 48H 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

The T48H simulants were 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 “acidification” from pH 13.3 to 9.5 also minimized foaming of the slurry (Figure 2). 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 control of the atmosphere in the FBSR with CO_2 gas.

The reductant of choice was sucrose. A test matrix (Table 4) was developed that varied three different levels of reductant based on the following stoichiometric equations:

Equation 4 $C_{12}H_{22}O_{11} + 9.6NaNO_3 \rightarrow 7.2CO_2 + 11H_2O + 4.8Na_2CO_3 + 4.8N_2$

Equation 5 $C_{12}H_{22}O_{11} + 16NaNO_2 \rightarrow 4CO_2 + 11H_2O + 8Na_2CO_3 + 8N_2$

Where the stoichiometric ratio of [C]:[N] for nitrate species is 12/9.6=1.25 (Equation 4) and 12/16=0.75 for nitrite species (Equation 5). The desired [C]:[N] ratio is 0.97 which is computed by adding the following two terms together: 1.25 times the moles of NO_3 from all sources plus 0.75 times the moles of NO_2 from all sources for 0.22 L (the size of a sample batch) of the simulant given in Table 3 and the $Fe(NO_3)_3•9H_2O$ added as a REDOX indicator. The final moles of sucrose to add was then calculated as follows:

Sucrose (M) = (Desired stoichiometric factor)*([C]:[N] ratio of 0.22L feed)*(moles NO_3+NO_2 in feed)/12

In the test matrix (Table 4) three different levels of sucrose (none, ½X stoichiometric, and 1X stoichiometric) and three different reaction times (1/2 hour, 3 hours, and 48 hours) were tested. The reaction times in a static crucible that could reproduce the chemistry of an active FBSR environment was a complete unknown. High purity (99.999%) Al_2O_3 crucibles were used to simulate Al_2O_3 bed material and to determine if the FBSR product was adhering to the simulated bed media. Temperatures of 650ºC and 725ºC were tested to see which levels of reductant optimized the WGSR (Equation 3) at which temperatures.

The known melt temperatures of alumina containing FBSR products are high. Nepheline ($NaAlSiO_4$) melts incongruently to carnegieite at 1280°C which then does not melt until 1526°C [15] if pure. The FBSR $NaAlO_2$ has a known melt temperature of 1680°C [16] if pure. The melt temperatures may be 100-200°C lower if other alkali or alkaline earth or iron substitutions are incorporated into the FBSR sodium aluminate containing products. The high melting temperature, refractory nature of these FBSR products was felt to be inappropriate for subsequent processing of the Tank 48H FBSR product in DWPF, e.g. high Al_2O_3 containing FBSR products could impact DWPF's melt rate and attainment rate. Hence, the lower melting Na_2CO_3 and Na_2SiO_3 FBSR products were targeted for study. Since the feed was already carbonated nothing needed to be added to the samples to optimize the Na_2CO_3 product. Precipitated silica was added to the tests where the desired final FBSR product was Na_2SiO_3 or Na_4SiO_4.

The carbonated slurries were dried to peanut butter consistency per procedure ITS-00052, Rev. 0 [17]. This ensures that some H_2O remains in the sample to create steam for the WGSR. Sealed crucible reaction is achieved by sealing Al_2O_3 crucibles with nepheline ($NaAlSiO_4$) gel that melts at a temperature lower than that at which the WGSR occurs. This causes the crucible to seal before the slurry reacts so that air inleakage does not occur during reaction. This is extremely important as air inleakage will alter the reactions as monitored by the measured REDOX ratio, $Fe^{2+}/\Sigma Fe$, and allow oxidizers and reductants to escape rather than reacting with the species in the slurry and additives.

The sealed samples were placed in a calibrated furnace at the test temperature designated in the test matrix. This generated a combined atmosphere of steam, CO from decomposition of the sucrose, and CO_2 from decomposition of the Na_2CO_3 formed during carbonation thus duplicating the CO-steam environment necessary for the WGSR (Equation 3) and CO_2. The furnace was purged with 99.99% Ar to ensure that no O_2

mixed with any H_2 that diffused through the crucible seal thus eliminating any concern of explosive gas mixtures and duplicating the deoxygenated high CO_2 atmosphere of the FBSR process.

Figure 2. Tank 48H simulated slurry during (left) and after (right) carbonation. Note foaming in sample before and during carbonation.

Samples were analyzed by X-ray diffraction (XRD) to determine if the desired FBSR product was achieved. Samples were measured by High Pressure Liquid Chromatography (HPLC) after digestion to determine if the TPB was adequately destroyed by the FBSR reactions. Secondary reaction products such as 3PB and 2PB were also analyzed for. Total carbon (TC), Total Inorganic Carbon (TIC), and Total Organic Carbon (TOC) were also analyzed.

Samples were measured for $Fe^{+2}/\Sigma Fe$ in duplicate to determine the f_{O_2} of the atmosphere inside the Al_2O_3 crucible during reaction. Samples were measured by Ion Chromatography (IC) for NO_2, NO_3, F, Cl and SO_4 to determine the fate of these anions and the percent nitrate destruction. For those samples that the desired FBSR product was a silicate, samples were were dissolved using a $LiBO_2$ fusion and the solution analyzed by Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES) for Na, K, and Si to determine if the correct ratios of silica additive had been achieved during experimentation.

Table 4 Simulated T48H Steam Reformer Optimization Matrix, X-Ray Diffraction Analysis, HPLC Analysis, and Nitrate Destruction

Test #	Temp °C	Time 48 Hour	Time ½ Hour	Time 3 Hour	Sugar None	Sugar ½X	Sugar 1X	Add	Major Phase Desired	Major Phases Identified by X-Ray Diffraction	Minor Phases Identified by X-Ray Diffraction	NaTPB, 3PB, 2PB (ug/g)	100-(Heated/Baseline NO_3 (from Table 5) wt%*100) =% Destroyed
T48-0								0	Na_2CO_3	$Na_3H(CO_3)_2(H_2O)_2$, $Na(NO_3)$, $NaNO_2$, $Na_2CO_3\bullet H_2O$	Na_2SiO_3, $KAl(SO_4)_2(H_2O)_{12}$	95,100 <5,<5	100-((16.3/16.3)*100)= 0%
T48-1	725		X		X			0	Na_2CO_3	$Na_2CO_3\bullet H_2O$, Na_2CO_3	$Al(OH)_3$ (?), $Ca_8Al_2Fe_2O_{12}CO_3(OH)_2\bullet 22H_2O$	<5,<5,<5	100-((11.4/16.3)*100)=30.1%
T48-2	725			X	X			0	Na_2CO_3	$Na_2CO_3\bullet H_2O$, Na_2CO_3	$Al(OH)_3$ (?), $Ca_8Al_2Fe_2O_{12}CO_3(OH)_2\bullet 22H_2O$	<5,<5,<5	100-((15.6/16.3)*100)=4.3%
T48-2B	650			X	X			0	Na_2CO_3	$Na_2CO_3\bullet H_2O$, Na_2CO_3	$Al(OH)_3$ (?),$NaNO_3$, $Ca_8Al_2Fe_2O_{12}CO_3(OH)_2\bullet 22H_2O$	<5,<5,<5	100-((12.3/16.3)*100)=24.5%
T48-3	725			X		X		0	Na_2CO_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	100-((0.09/16.3)*100)=99.5%
T48-4	725		X				X	0	Na_2CO_3	$Na_2CO_3\bullet H_2O$, Na_2CO_3	Ca_2SiO_4 (?), $Al(OH)_3$(?)	<5,<5,<5	100-((0.31/16.3)*100)=98.1%
T48-5	725			X			X	0	Na_2CO_3	$Na_2CO_3\bullet H_2O$, Na_2CO_3	$Ca_8Al_2Fe_2O_{12}CO_3(OH)_2\bullet 22H_2O$ $Al(OH)_3$(?)	<5,<5,<5	100-((0.41/16.3)*100)=97.5%
T48-5B	650			X			X	0	Na_2CO_3	$Na_2CO_3\bullet H_2O$, Na_2CO_3	NONE	<5,<5,<5	100-((0.15/16.3)*100)=99.1%
T48-6	725		X		X			Fine SiO_2	Na_4SiO_4	Na_2CO_3, $Na_2CO_3\bullet H_2O$, $K_{48.2}Al_{48.2}Si_{143.8}O_{384}\bullet 243H_2O$	Na_2SiO_3	<5,<5,<5	100-((10.6/16.3)*100)=35.0%
T48-7	725			X	X			Fine SiO_2	Na_4SiO_4	Na_2CO_3, Na_2SiO_3, $Na_{7.89}(AlSiO_4)_6(NO_3)_{1.92}$	$Na_2CO_3\bullet H_2O$ NaTPB (?)	<5,<5,<5	100-((5.98/16.3)*100)=63.3%
T48-7B	650			X	X			Fine SiO_2	Na_4SiO_4	Na_2CO_3, Na_2SiO_3, $Na_{7.89}(AlSiO_4)_6(NO_3)_{1.92}$	$Na_2CO_3\bullet H_2O$, $K_{48.2}Al_{48.2}Si_{143.8}O_{384}\bullet 243H_2O$	<5,<5,<5	100-((9.55/16.3)*100)=41.4%
T48-8	725			X		X		Fine SiO_2	Na_4SiO_4	Na_2CO_3, $Na_2CO_3\bullet H_2O$, Na_2SiO_3,	$KAlSiO_4$, $K_{48.2}Al_{48.2}Si_{143.8}O_{384}\bullet 243H_2O$	<5,<5,<5	100-((0.78/16.3)*100)=95.2%
T48-9	725		X				X	Fine SiO_2	Na_4SiO_4	Na_2CO_3, $Na_2CO_3\bullet H_2O$, Na_2SiO_3, $K_{48.2}Al_{48.2}Si_{143.8}O_{384}\bullet 243H_2O$	$KAlSiO_4$	<5,<5,<5	100-((1.18/16.3)*100)=92.8%
T48-10	725			X			X	Fine SiO_2	Na_4SiO_4	$Na_2CO_3\bullet H_2O$, Na_2SiO_3, $K_{48.2}Al_{48.2}Si_{143.8}O_{384}\bullet 243H_2O$	NONE	<5,<5,<5	100-((0.22/16.3)*100)=98.7%
T48-10B	650			X			X	Fine SiO_2	Na_4SiO_4	Na_2CO_3, $Na_2CO_3\bullet H_2O$, Na_2SiO_3, $K_{48.2}Al_{48.2}Si_{143.8}O_{384}\bullet 243H_2O$	$KAlSiO_4$	<5,<5,<5	100-((0.96/16.3)*100)=94.1%
T48-11 (see 6)	725	X		X	X			Fine SiO_2	Na_4SiO_4	Na_2SiO_3, $K_{48.2}Al_{48.2}Si_{143.8}O_{384}\bullet 243H_2O$	$Na_2CO_3\bullet H_2O$	<5,<5,<5	100-((0.03/16.3)*100)=99.8%
T48-12 (see10)	725	X		X			X	Fine SiO_2	Na_4SiO_4	$Na_2CO_3\bullet H_2O$ Na_2SiO_3	NONE	<5,<5,<5	100-((0.19/16.3)*100)=98.8%
T48-13 (see 5B)	650	X					X	0	Na_2CO_3	$Na_2CO_3\bullet H_2O$, Na_2CO_3	NONE	<5,<5,<5	100-((0.16/16.3)*100)=99.0%
T48-14	725	X					X	Fine SiO_2	Na_4SiO_4 faujesite	$Na_2CO_3\bullet H_2O$, Na_2SiO_3	$Na(NO_3)$	<5,<5,<5	100-((0.25/16.3)*100)=98.5%
T48-15	725	X					X	Fine SiO_2	Na_2SiO_3 faujesite	$Na_2CO_3\bullet H_2O$, $Na_2Si_2O_5$	Na_2SiO_3, $Na(NO_3)$ $K_{48.2}Al_{48.2}Si_{143.8}O_{384}\bullet 243H_2O$	<5,<5,<5	100-((0.10/16.3)*100)=99.4%

4.0 QUALITY ASSURANCE

All the data reported in this study were developed under the quality assurance given in technical task plan WSRC-RP-2003-00396 [18]. The research program and task plan were developed to address TTR-HLE-TTR-2003-102. The data are recorded in notebook WSRC-NB-2003-00140.

5.0 RESULTS AND DISCUSSION

5.1 Static Vs. Dynamic Tests and Reaction Residence Time

Due to the static nature of the environment inside the crucibles compared to the active environment of a steam reformer, most of the crucible FBSR samples were stratified and thus inhomogeneous (see photos in Appendix A). Reaction times of 48 hours produced the most homogeneous, least stratified, and best-reacted, samples. Samples were ground and mixed to homogenize them before any analyses were performed.

5.2 Baseline Testing

A sample (T48-0) was tested as a baseline. The T48-0 sample was carbonated, anitfoam and $Fe(NO_3)_3{\bullet}9H_2O$ were added, and the sample was dried at 60°C. This sample was analyzed for TPB by HPLC, for anions, for TC, TIC, TOC and REDOX as a baseline case (see Table 4, Table 5 and Table 6). These analyses demonstrated that there was 95,100 ug/g of TPB (Table 4) present in the samples after the carbonation and drying steps. The presence of the TPB was also confirmed by the measurement of TOC in sample T48-0 (Table 6) which showed that 19,500 ug/g of organic carbon that was present in the sample. Either the TPB or the anitfoam (an organic) may have reacted with the $Fe(NO_3)_3{\bullet}9H_2O$ because an all Fe^{+3} dried solution should have had a REDOX measurement of ~0 and T48-0 had a measured $Fe^{+2}/\Sigma Fe$ of 0.44 (Table 6) indicating that a considerable amount of Fe^{+2} was present or that the organics interfered with the REDOX measurement. Anion analysis of the base case indicated <100 ug/g of NO_2 and a NO_3 content of 163,000 ug/g or 16.3 wt% (Table 5). This number was used with the rest of the measured NO_3 data in Table 5 to calculate the NO_3 destruction values given in Table 4.

5.3 Tetraphenylborate Destruction

Samples were tested at two different temperatures, 650°C and 725°C (Table 4). Tetraphenylborate (TPB) was completely destroyed in all the samples tested, e.g. the TPB, 2PB and 3PB were all <5ug/g indicating that the thermal treatment destroyed all the TPB and its derivatives. This was confirmed by the TOC analyses for all the samples thermally treated, <100 ug/g of TOC (Table 6). This indicates that FBSR is a viable technology for destruction of the organics in Tank 48H.

5.4 Carbonate FBSR Products

For all of the FBSR simulated samples in which the desired product was Na_2CO_3 (samples T48-1 through T48-5B and T48-13), analysis by XRD indicated that a mixture of $Na_2CO_3 \bullet H_2O$ and Na_2CO_3 was formed regardless of temperature and residence time in the furnace (Table 4). However, for the T48-13 sample that was heated at 650°C for 48 hours, the XRD analysis indicated no minor constituents. This meant that the minor constituents that had appeared in the same sample reacted for only 3 hours were due to incomplete reaction. Test T48-5B or T48-13 appeared optimal for making the Na_2CO_3 FBSR product at 650°C, 1X stoichiometric sugar and 3-48 hour residence time as no minor phases were identified as incomplete reactants. Only the two primary phases Na_2CO_3 and $Na_2CO_3 \bullet H_2O$ were present in the T48-5 and T48-13 samples.

5.5 Silicate FBSR Products

In the current study Na_4SiO_4 was chosen as the FBSR phase of choice because it melts at ~1120°C and can only coexist with a liquid phase down to temperatures as low as 1040°C. This choice was made to limit any potential liquid phase in the steam reformer that might cause bed agglomeration. Na_2SiO_3 may be acceptable for use as feed in the DWPF as its melting temperature is ~1080°C but it can coexist with a Na_2O-SiO_2 liquid phase that melts as low as 825°C and may cause bed agglomeration. Sodium silicate (Na_2SiO_3) was the silicate FBSR product phase made by THOR^{sm} in their pilot scale studies (Table 1) with Hanford's high Na^+ containing Low Activity Waste (LAW).

For all of the simulated FBSR samples in which the desired product was Na_4SiO_4 with a Na_2O:SiO_2 ratio of 2:1 (T48-6 through T48-12), a potassium aluminosilicate zeolite phase known as faujasite ($K_{48.2}Al_{48.2}Si_{143.8}O_{384} \bullet 243H_2O$) was identified by XRD and a sodium silicate of a 1:1 Na_2O:SiO_2 stoichiometry had formed (Table 4). Excess SiO_2 does not appear on the XRD pattern since the precipitated SiO_2 that was added to the sample is amorphous and will not give an XRD signal. It was apparent that the faujesite was consuming some of the SiO_2 that was meant to form the 2:1 sodium silicate phase.

Subsequent testing (T48-14) was designed to compensate for the silica being consumed by the faujesite. X-ray Diffraction analysis (Table 4) indicated that the major phases in the T48-14 sample after a 48 hour residence time were indeed the faujasite and the 1:1 Na_2O:SiO_2 phase. Another test (T48-15) that was designed to make the sodium silicate with a 1:1 stoichiometry of Na_2O:SiO_2 , gave an XRD pattern for yet another sodium silicate with a Na_2O:SiO_2 stoichiometry of 1:2 ($Na_2Si_2O_5$). This sample also had unreacted Na_2CO_3 present and presumably XRD amorphous SiO_2.

Analysis of all the silicate FBSR products was performed to determine if the correct ratios of Na_2O:SiO_2 had been added during experimentation. These analyses indicated that some of the Na_2O:SiO_2 ratios measured (Table 5) were biased low by ~20%. This may be because the precipitated silica contains absorbed water that was not factored into the batching calculation.

Even at 48 hours residence time (samples T48-12, T48-14, and T48-15) not all of the sodium carbonates present in the silicate FBSR samples converted to sodium silicate. The XRD spectra indicates the presence of carbonate phases and the high concentrations of TIC in Table 6 indicate large quantities of unreacted carbonate. Thus, incomplete reaction of the carbonates and silica is occurring at reaction temperatures of 650-725°C even with finely precipitated silica. Higher temperatures and the presence of excess SiO_2 may be necessary to force the final conversion of the carbonates to silicates under FBSR conditions.

In summary, if a silicate FBSR phase was desired, a silica FBSR phase was the major phase formed with carbonate and faujesite always present. Although the exact Na_2O:SiO_2 ratio of the desired FBSR silicate phase was never achieved due to incomplete reaction and silica deficient starting mixtures, this would not hinder the usage of any sodium silicate FBSR material made from Tank 48H slurry in DWPF. Achieving the desired Na_2O:SiO_2 ratio for silicate based FBSR products needs further optimization.

5.6 Nitrate and Sugar Destruction

In the sample test matrix (Table 4), samples with the designation of B indicate comparison of tests at the two different reaction temperatures. These were designed into the test matrix to test the optimum NO_3 destruction at the various temperatures, e.g. optimize the WGSR. Hence samples T48-2B, 5B, 7B and 10B were tested at 650°C while samples T48-2, 5, 7, and 10 were tested at 725°C.

For two of the pairs of samples tested at the different temperatures, T48-2 and 2B and T48-5 and 5B, the desired FBSR product was Na_2CO_3. Samples T48-2 and T48-2B had no sugar and samples T48-5 and T48-5B had 1X stoichiometric sugar. Comparison of the XRD spectra of the two tests without sugar demonstrates that the FBSR products in absence of sugar includes undecomposed $NaNO_3$ which indicates that nitrate destruction is incomplete when sugar is absent at 650°C and 725°C, e.g. when sugar is absent there is no CO to optimize the WGSR. This is confirmed by the nitrate analyses in Table 5 and the nitrate destruction percentages given in Table 4 which indicate that nitrate was not destroyed at either temperature for samples T48-2 and T48-2B. For the sample pair T48-5 and T48-5B sucrose was present at 1X stoichiometry. These samples had 99.1% and 97.5% NO_3 destruction at the 650°C and 725°C temperatures respectively (Table 4). This indicates that the WGSR may be better optimized at 650°C than at the 725°C. Likewise, the TOC analyses in Table 6 indicate no residual TOC in the form of sucrose in the samples and the XRD spectra did not indicate any residual $NaNO_3$ (Table 4).

For two of the pairs of samples tested at the different temperatures, T48-7 and 7B and T48-10 and 10B, the desired FBSR product was a sodium silicate. Sample T48-7B had no sugar and Sample T48-10B had 1X stoichiometric sugar. Comparison of the XRD spectra of the two tests without did not show any undecomposed $NaNO_3$ but the nitrate analyses shown in Table 5 indicate that considerable NO_3 remains in the samples without sugar. The nitrate destruction percentages given in Table 4 for these samples indicate that nitrate was only partially destroyed at either temperature for samples T48-7 and T48-7B, e.g. 41.4% and 63.3% at the lower and higher temperatures, respectively. For the sample pair T48-10 and T48-10B sucrose was present at 1X stoichiometry. These samples had 98.7% and 94.1% NO_3 destruction at the 650°C and 725°C temperatures respectively (Table 4). This again indicates that the WGSR may be better optimized at 650°C than at the 725°C. Likewise, the TOC analyses in Table 6 indicate no residual TOC in the form of sucrose in the samples and the XRD spectra did not indicate any residual $NaNO_3$ (Table 4).

The small amount of TOC measured in all the samples (Table 6) indicates that at ½ to 1X sugar stoichiometry that most of the sugar and char are consumed during denitration and that the FBSR product should not be overly reducing and thus compatible with DWPF processing of the FBSR product.

5.7 Particle Agglomeration

No adherence of the silicate or carbonate phases onto the Al_2O_3 crucibles was noted in any of the tests. Therefore, if the FBSR bed media used is Al_2O_3 there should be little sticking and particle agglomeration regardless of whether the FBSR product is carbonate or silicate. This also indicates that the Na_2SiO_3 phase that was produced most often as an FBSR product in this study (see the XRD identifications in Table 4) appears to be an acceptable FBSR product phase. This was confirmed by the pilot scale testing completed by THOR^{sm} (Table 1) on the Hanford AN-107 simulant.

5.8 FBSR Product Melt Temperatures

FBSR product samples T48-5B (Na_2CO_3 made at 650°C), T48-10 (mixed Na_2CO_3 and Na_2SiO_3 and faujesite), and T48-11 (Na_2SiO_3 and faujesite) were measured by Differential Thermal Analysis (DTA) to determine their melting temperature. The melt temperatures were 980°C, 1022°C, and 1049°C, respectively. These melt temperatures are all compatible with melting of these phases in the DWPF although the presence of carbonate on pre-melter processing in the Slurry Receipt Adjustment Tank (SRAT) and alteration of the DWPF frit composition to accommodate these species is still necessary.

Table 5. Analysis of Anions and Cations in Tank 48H Simulated FBSR Products

Test #	**ML Lab ID Anions/ Cations**	**NO_2 (ug/g)**	**NO_3 (ug/g)**	**PO_4 (ug/g)**	**SO_4 (ug/g)**	**K_2O (wt%)**	**Na_2O (wt%)**	**SiO_2 (wt%)**	**Alkali /SiO_2**
T48-0	03-0968	<100	163000	2550	3000	N/A	N/A	N/A	N/A
T48-1	03-0914	<100	114000	1740	3750	N/A	N/A	N/A	N/A
T48-2	03-01915	<100	156000	1690	3850	N/A	N/A	N/A	N/A
T48-2B	03-01916	<100	123000	2350	4500	N/A	N/A	N/A	N/A
T48-3	03-01917	<100	947	<100	4380	N/A	N/A	N/A	N/A
T48-4	03-01918	<100	3080	2980	4500	N/A	N/A	N/A	N/A
T48-5	03-01919	<100	4060	1970	4080	N/A	N/A	N/A	N/A
T48-5B	03-01920	<100	1480	2730	4700	N/A	N/A	N/A	N/A
T48-6	03-01921 03-0921	<100	106000	2240	3980	1.46	40.44	24.82	1.69
T48-7	03-01922 03-0922	<100	59800	2010	4180	1.63	42.60	24.82	1.78
T48-7B	03-01923 03-0923	<100	95500	2370	3970	1.59	42.87	23.96	1.86
T48-8	03-01924 03-0924	<100	779	2600	3900	1.66	43.67	23.75	1.91
T48-9	03-01925 03-0925	<100	11800	2920	4040	1.87	42.60	24.17	1.84
T48-10	03-01926 03-0926	<100	2210	3550	4350	1.83	47.72	23.53	2.11
T48-10B	03-01927 03-0927	<100	9640	3120	3990	1.64	44.89	20.86	2.23
T48-11	03-01928 03-0928	<100	332	3880	4660	2.35	45.83	27.38	1.76
T48-12	03-01929 03-0929	<100	1930	1930	4190	2.10	47.05	23.96	2.05
T48-13	03-1020	<100	1640	3380	4410	N/A	N/A	N/A	N/A
T48-14	03-1016 03-1016	<100	2450	3470	4430	1.73	49.07	28.67	1.77
T48-15	03-1017 03-1017	<100	1020	2710	3370	1.66	39.63	47.92	0.86

Table 6. Measured REDOX, Total Carbon, Total Inorganic Carbon, and Total Organic Carbon for Simulated Tank 48H FBSR Products

Test #	ML Lab ID	$Fe^{+2}/\Sigma Fe$	Calc- $\log f_{O_2}$	ADS Lab ID	TC (ug/g)	TIC (ug/g)	TOC (ug/g)
T48-0	03-0968	0.44	-7.36	300197937	61900	42400	19500
T48-1	03-01914	0.70	-9.78	300197938	65300	65300	<100
T48-2	03-01915	0.67	-9.50	300197939	66200	66200	<100
T48-2B	03-01916	0.74	-10.14	300197940	60000	60000	<100
T48-3	03-01917	0.83	-10.96	300197941	80300	80300	<100
T48-4	03-01918	0.73	-10.05	300197942	78300	78300	<100
T48-5	03-01919	0.62	-9.05	300197943	70500	70500	<100
T48-5B	03-01920	0.86	-11.23	300197944	84000	84000	<100
T48-6	03-01921	0.77	-10.41	300197945	35300	35300	<100
T48-7	03-01922	0.90	-11.59	300197946	34900	34900	<100
T48-7B	03-01923	0.85	-11.14	300197947	36200	36200	<100
T48-8	03-01924	0.20	-5.24	300197948	43100	43100	<100
T48-9	03-01925	0.75	-10.23	300197949	46800	46800	<100
T48-10	03-01926	0.80	-10.68	300197950	50900	50900	<100
T48-10B	03-01927	0.78	-10.50	300197951	50800	50800	<100
T48-11	03-01928	0.21	-5.33	300197952	50100	50100	<100
T48-12	03-01929	0.78	-10.50	300197953	42200	42200	<100
T48-13	03-1020	0.37	-6.78	300197954	41200	41200	<100
T48-14	03-1016	0.79	-10.59	300197955	37900	37900	<100
T48-15	03-1017	0.60	-8.87	300197956	19100	19100	<100

5.9 REDOX Measurements and the Water Gas Shift Reaction (WGSR)

Although the FBSR product is not borosilicate glass it is a mixture of oxide species. Therefore, the Electro-Motive Force (EMF) REDOX series developed for DWPF glasses, as illustrated in Figure 3, should approximate the REDOX of the FBSR product, et al.[19]. This ordering of REDOX couples in oxygen fugacity-REDOX ratio space (Figure 3) defines an electrochemical series in terms of the ease of reduction of particular multivalent ions [19]. Using Figure 3, the measured iron REDOX and total iron ratios from Table 6 for the FBSR product can be used to approximate both the oxygen fugacity (availability of oxygen) in the crucible tests and the relative partial pressures of log $\log\ p_{H_2O}/p_{H_2}$ and $\log\ p_{CO_2}/p_{CO}$ at the reaction temperature which are the partial pressures of the two half reactions for the WGSR given in Equation 3.

The ratio of the Fe^{+2} to the total iron is indicated across the top of Schreiber's REDOX series (Figure 3). The relation between the $Fe^{+2}/\Sigma Fe$ and the $\log f_{O_2}$ is quantified from this graphical description at ~ 5 wt% total iron by the following relationship:

Equation 6
$$-\log f_{O_2}(EMF) = -3.42 - 9.08 * \left(\frac{Fe^{+2}}{\Sigma Fe}\right)$$

By substituting the measured $\left(\frac{Fe^{+2}}{\Sigma Fe}\right)$ ratio for all the glasses in "Model Data" into Equation 6, one can then determine the f_{O_2} conditions achieved in the FBSR crucible studies.

The average REDOX ratio for the 15 FBSR reactions at 725ºC are -log f_{O_2} = 9.69 (or log f_{O_2} = -9.69) while the average –log f_{O_2} values for the 4 FBSR reactions at 650ºC are 10.75 (or log f_{O_2} = -10.75). These negative log f_{O_2} values mean that no oxygen was present during the FBSR reactions.

This can also be expressed as $\log\, p_{H_2O} / p_{H_2}$ or $\log\, p_{CO_2} / p_{CO}$ because of the thermodynamic equilibrium

$$2H_2O\uparrow \rightarrow 2H_2\uparrow + O_2\uparrow$$

and

$$2CO_2\uparrow \rightarrow 2CO\uparrow + O_2\uparrow$$

Published correlations [20] between –log f_{O_2}, temperature, and $\log\, p_{H_2O} / p_{H_2}$ allows the $\log\, p_{H_2O} / p_{H_2}$ in the FBSR crucible studies at 725ºC to be estimated as between +5.5-6 while the FBSR crucible studies at 650ºC experienced a $\log\, p_{H_2O} / p_{H_2}$ in the range of ~ +5. These positive values mean that the $\log\, p_{H_2O} / p_{H_2}$ values are high as they should be to promote the WGSR.

Published correlations [20] between –log f_{O_2}, temperature, and $\log\, p_{CO_2} / p_{CO}$ allows the $\log\, p_{CO_2} / p_{CO}$ in the FBSR crucible studies at 725ºC to be estimated at ~ +5.5 while the FBSR crucible studies at 650ºC experienced a $\log\, p_{CO_2} / p_{CO}$ in the range of ~ +4.5-5. These positive values, which match the $\log\, p_{H_2O} / p_{H_2}$ values reported above, mean that the $\log\, p_{CO_2} / p_{CO}$ values are high as they should be to promote the WGSR.

The use of the REDOX measurements and approximations, therefore, confirms that highly deoxygenated conditions were achieved and that the crucible studies simulated the WGSR conditions.

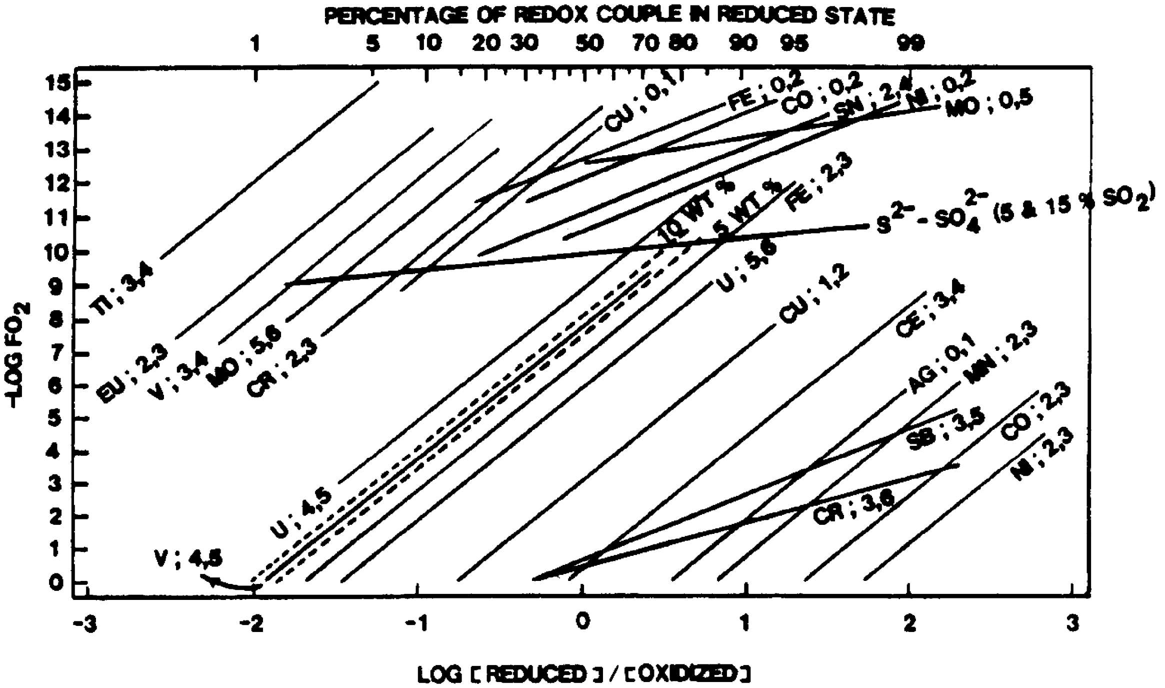


Figure 3. Schreiber's relationship between imposed oxygen fugacity (–log $f(O_2)$) and the REDOX ratio (log([reduced ion]/[oxidized ion])) for multivalent elements doped into SRL-131 melt at 1150°C. The broken lines represent 5 and 10 wt% Fe in SRL-131. This ordering of the REDOX couples in fugacity-REDOX space defines an Electro Motive Force (EMF) series describing the ease of reduction of the ions represented.

5.10 Volumes of FBSR Product For DWPF

The 250,000 gallons of T48H slurry should make ~29,470 gallons of solid FBSR Na_2SiO_3 solid product or ~26,246 gallons of solid FBSR Na_2CO_3 solid product for subsequent treatment in the DWPF. This is an 88 and 90% volume reduction. This calculation assumes a final FBSR product density of 1.46 g/cc which was the number measured for the Na_2CO_3 solid FBSR bed product by INEEL [10].

It is recommended that the solid FBSR products, especially the Na_2CO_3 product be added to the DWPF sludge waste tank so that the product can be decarbonated via the existing DWPF acid addition strategy for carbonate destruction in the SRAT. This should eliminate any potential for CO_2 off-gas surges or foaming in the DWPF melter. It is calculated that 25,500 gallons of steam reforming product (almost all of T48) could be added to the next 500,000 gallon DWPF sludge batch (at 18 wt% solids). This is based on the substitution of ~7 wt% Na_2O from the steam reformer product being substituted for 7 wt% Na_2O in a given DWPF frit. This was the same approach taken when the sodium-borate rich Precipitate Hydrolysis Aqueous (PHA) components were substituted for 7 wt% of the DWPF frit, e.g. instead of adding 72 wt% frit to 28 wt% waste, a mixture of 65 wt% frit plus 7 wt% PHA was added to 28 wt% waste [21]. Additional investigation of the 7 wt% Na_2O substitution to the next sludge batch would need to be further assessed in the DWPF frit development program.

6.0 CONCLUSIONS

The purposes of the current study, organic destruction and downstream processing of T48H waste slurry, were fulfilled as documented by the following:

- TPB was destroyed in all 19 samples tested with the simulated FBSR process at operational temperatures 650-725°C
    - the 650°C operational temperature seemed to optimize the NO_3 destruction
- destruction of nitrate at >99% was achieved with addition of sugar as a reductant at 1X stoichometry and TOC analyses indicated that excess reductant was not present in the FBSR product
- destruction of anitfoam with the simulated FBSR process was also achieved at operating temperatures between 650-725°C based on measured TOC
- for all tests in which Na_2CO_3 was the desired FBSR product phase, Na_2CO_3 was produced
    - the Na_2CO_3 product was shown to be compatible with the DWPF melt process as it melted at 980°C as measured by DTA
- for all tests in which Na_4SiO_4 or Na_2SiO_3 was the desired FBSR product a different sodium silicate formed (Na_2O:SiO_2 ratios were not correct)
    - this was determined to be a problem with water absorption of the SiO_2 additives used and the consumption of SiO_2 by a potassium aluminate zeolite (faugesite) that formed
    - optimization of the Na_2O:SiO_2 ratio of the feeds still need to be optimized
    - formation of a sodium silicate (mixed with Na_2CO_3 or alone) 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 some of the frit for subsequent vitrification because the mixtures melted at temperatures of 1022°C and 1049°C, respectively, as measured by DTA
- the melt temperature of the Na_2CO_3 and Na_2SiO_3 FBSR products (980°C and 1022-1049°C is low enough to ensure that addition of the FBSR product to the DWPF will not adversely impact melt rate
- the use of sugar at 1X stoichometry appears to ensure that excess reductant is not contained in the FBSR product that would alter the REDuction/OXidation (REDOX) equilibrium of the DWPF melter while simultaneously assuring that NO_3 is destroyed adequately
- the recommended test parameters for pilot scale testing of Tank 48H simulant at Idaho National Engineering and Environmental Laboratory (INEEL) were given by samples T48-5B for the Na_2CO_3 product and by T48-14 for the Na_2SiO_3 product

- the sealed crucible studies demonstrated that bench scale studies can duplicate the complex reactions, especially the Water Gas Shift Reactions, and the associated $\log p_{H_2O} / p_{H_2}$ and $\log p_{CO_2} / p_{CO}$ atmospheres in the FBSR process.

7.0 RECOMMENDATIONS

- Re-examine the tests that used less than 1X stoichiometric sugar (to ensure no carbon residue in the FBSR product going to DWPF) at 48 hours residence time

- Optimize the SiO_2 addition strategy to ensure that a Na_2SiO_3 silicate product FBSR product is produced

- Revisit the melting temperature of the silicate FBSR products once they are optimized

- Investigate the compatibility of the Na_2CO_3 and Na_2SiO_3 FBSR products with DWPF acid addition strategy

- Investigate the frit modifications that would be necessary to accommodate either a Na_2CO_3 and Na_2SiO_3 FBSR product in DWPF

APPENDIX A

PHOTOGRAPHIC DOCUMENTATION OF SAMPLE INHOMOGENEITY


T48-1

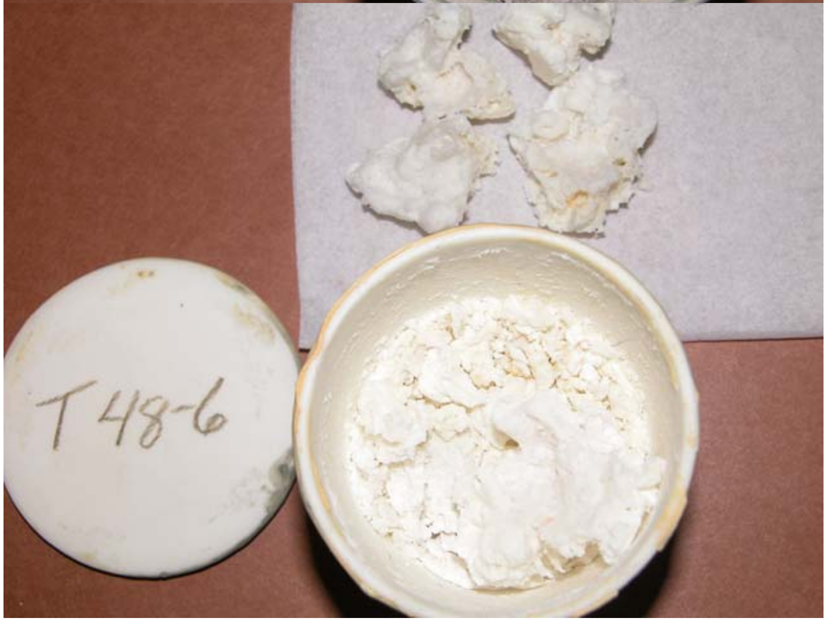

T48-2


T48-
2B


T48-3


T48-4
T48-5


T48-
5B

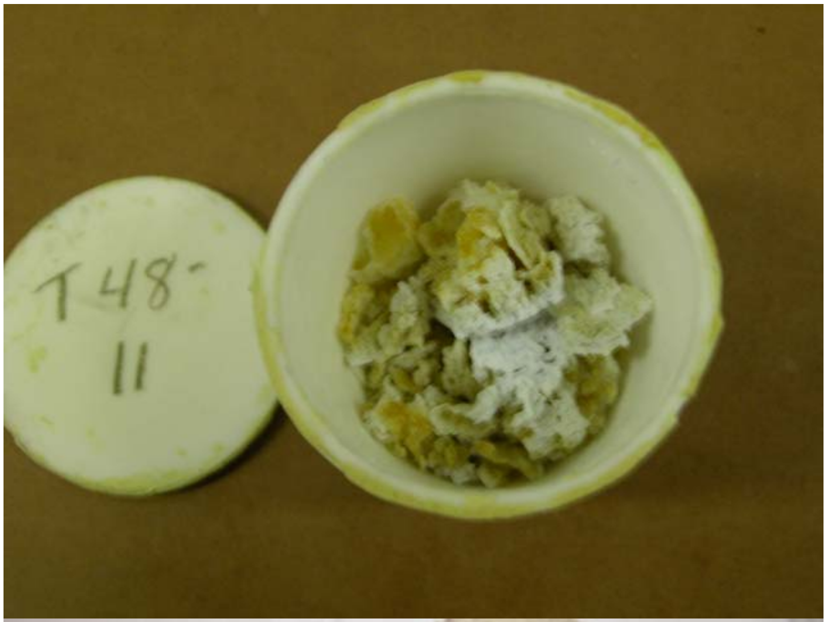

T48-6


T 48-7
T 48-7B


T48-8
T48-9

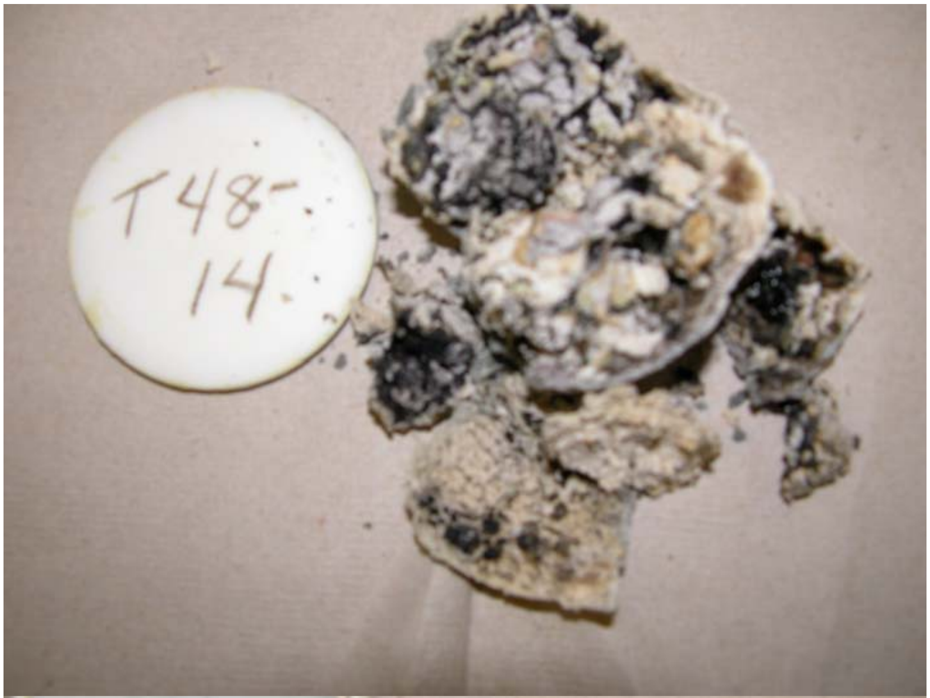

T 48-
10


T48-
10B


T 48"
11


T 48"
12


1 48
13


T48-
14


T48-
15

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