**Steam Reforming Technology Demonstration for
Conversion of DOE Sodium-Bearing Tank Wastes at Idaho National Laboratory
into a Leach-Resistant Alkali Aluminosilicate Waste Form - 8282**

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ABSTRACT

The patented THOR® fluidized-bed steam reforming (FBSR) technology was selected by the U.S. Department of Energy (DOE) for treatment of sodium-bearing waste (SBW) in the Integrated Waste Treatment Unit (IWTU), currently under construction at the Idaho National Laboratory (INL) Site.[1] SBW is an acidic waste created primarily from cleanup of the fuel reprocessing equipment at the Idaho Nuclear Technology and Engineering Center (INTEC) at the INL. The SBW contains high concentrations of nitric acid, and alkali and aluminum nitrates, along with many other inorganic compounds, including substantial levels of radionuclides. As part of the implementation of the THOR® process at INTEC, an engineering-scale technology demonstration (ESTD) was conducted using a specially designed pilot plant located at Hazen Research, Inc. in Golden Colorado. This ESTD confirmed the efficacy of the THOR® FBSR process to convert the SBW into a granular carbonate-based waste form suitable for disposal at the Waste Isolation Pilot Plant (WIPP).

DOE authorized, as a risk reduction measure, the performance of an additional ESTD to demonstrate the production of an insoluble mineralized product, in the event that an alternate disposition path is required. The additional ESTD was conducted at the Hazen Research facility using the THOR® process and the same SBW simulant employed previously. An alkali aluminosilicate mineral product was produced that exhibited excellent leach resistance and chemical durability. The demonstration established general system operating parameters for a full-scale facility; provided process off-gas data that confirmed operation within regulatory limits; determined that the mineralized product exhibits superior leach resistance and durability, compared to Environmental Assessment (EA) and Low-activity Reference Material (LRM) glasses, as indicated by the Product Consistency Test (PCT); ascertained that Cs and Re (a surrogate for Tc) were non-volatile and were retained in the mineral product; and showed that heavy metals were converted into mineral forms that were not leachable, as determined by the Toxicity Characteristic Leaching Procedure (TCLP) test.

INTRODUCTION

In March of 2005, the DOE announced that CH2M-WG Idaho, LLC (CWI) had been selected to lead the $2.9 billion environmental cleanup of the INL Site. CWI is comprised of Denver-based CH2M HILL and the Boise-based Washington Division of URS Corporation (formerly Washington Group International [WG]). The cleanup project, named the Idaho Cleanup Project (ICP), is a seven-year undertaking to perform the cleanup of key facilities and waste materials at the 890-square-mile site. As the ICP

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[1] Certain information addressed within this paper pertains to Contract No. DE-AC07-05ID14516 between CH2M-WG Idaho, LLC and the U.S. Department of Energy. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

contractor, CWI is responsible for treatment and disposal of radioactive waste; retrieval, disposal, and other remediation related to buried waste; safe management of spent nuclear fuel; disposition of nuclear materials; disposition of reactor and non-reactor nuclear facilities; and other environmental remediation activities. Included in the scope of work for the ICP is the treatment of approximately one million gallons of SBW stored in three underground tanks at the INTEC facility.

The DOE issued the Record of Decision (ROD) selecting steam reforming as the treatment process for SBW in December 2005 [1]. In the ROD, the DOE stated that the preferred disposal path for the SBW would be as remote-handled transuranic (RH-TRU) waste at the Waste Isolation Pilot Plant (WIPP), but that "Until such time as the regulatory approvals are obtained and a determination that the waste is TRU is made, the Department will manage the waste to allow disposal at WIPP or at a geologic repository for spent nuclear fuel (SNF) and HLW."

To meet the requirement to provide dual disposal paths for the SBW, CWI proposed to treat the SBW using the patented THOR® steam reforming waste treatment technology. The THOR® technology can produce a carbonate-based, reduced-volume, final waste form suitable for disposal as RH-TRU at WIPP, and, with minor flowsheet modifications, a leach-resistant alkali aluminosilicate waste form that could be qualified for ultimate disposal in a geologic repository. CWI selected THOR Treatment Technologies, LLC (TTT), a joint venture of WG and Studsvik, Inc. to demonstrate a process and design a treatment plant for processing the SBW. The THOR® plant now being constructed will produce the carbonate-based waste form suitable for disposal as RH-TRU, based on demonstration work discussed in a paper presented at WM2007 [2].

The discussion below provides a summary of the ESTD pilot plant work that has been completed to demonstrate the production of the leach-resistant alkali aluminosilicate waste form in the event that qualification for disposal in a geologic repository is required.

THOR® MINERALIZING PROCESS OVERVIEW

The SBW at INL consists of radioactive aqueous solutions with high concentrations of nitric acid, nitrates, alkalis, and a wide variety of other inorganic compounds. The THOR® mineralizing steam reforming process destroys nitrates, nitrites, and organic materials present in the SBW and produces a dry, leach-resistant alkali aluminosilicate mineral product containing the radionuclides, alkali metals, sulfates, halides, and non-volatile heavy metals present in the SBW [3, 4, 5, 6]. The process converts nitrates and nitrites directly to nitrogen gas. Any organic material is converted to carbon dioxide and water vapor in the steam reformers by a combination of steam reforming and oxidizing reactions. The THOR® mineralizing process flow diagram for treatment of SBW is provided in Figure 1.

The SBW feed, slurried with aluminosilicate clay, is introduced into the first steam reformer, the Denitration and Mineralization Reformer (DMR). The bed particles in the steam reformer are fluidized by introduction of near ambient pressure superheated steam. In the DMR, liquids are evaporated; the vast majority of organics, nitrates and nitrites are destroyed; and the reactive chemicals in the waste feed are converted into a granular mineralized waste product. The second reformer, the Carbon Reduction Reformer (CRR), serves to further reduce any NOx gases from the first reformer and oxidize residual organics to carbon dioxide and water vapor. The gases (mainly carbon dioxide, nitrogen, and water vapor) from the process are filtered through high-efficiency sintered metal filters, HEPA filters, and a mercury adsorber. They are then vented to the atmosphere through a monitored stack. The THOR® final waste product, an alkali aluminosilicate, exhibits leach resistant characteristics equal to or better than EA and LRM glass, as indicated by PCT and TCLP analyses [7, 8, 9, 10].
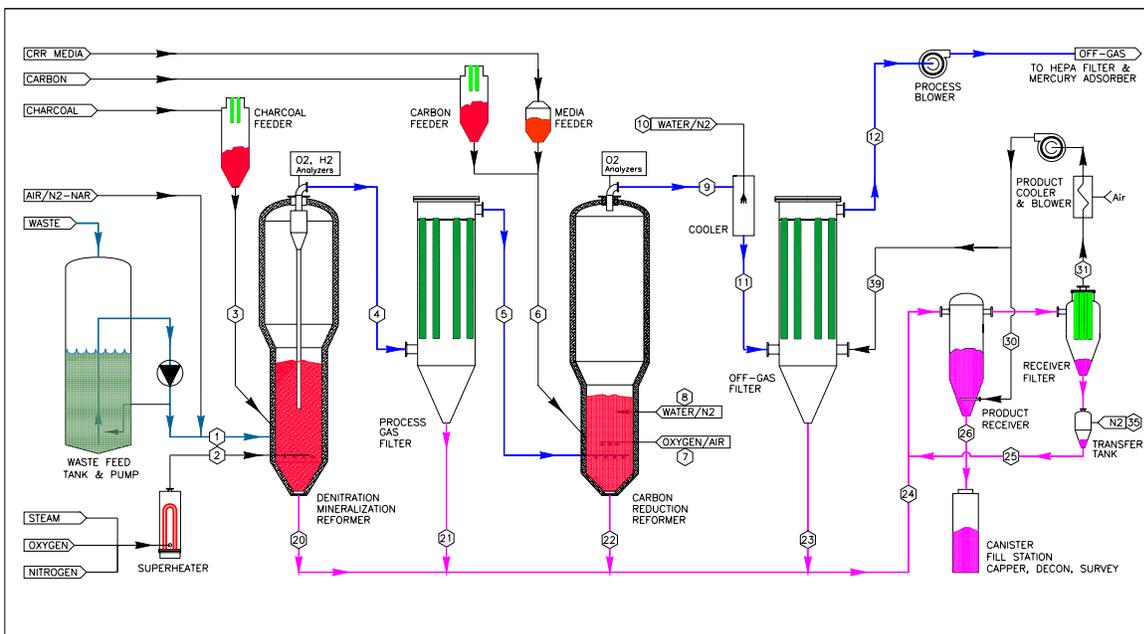
Fig. 1. IWTU process flow diagram for the treatment of SBW.

PROCESS CHEMISTRY

The DMR waste feed, slurried with a Kaolin (aluminosilicate) clay, is atomized into a fluidized mineral bed at 998°K to 1023°K (725°C to 750 ^{o}C). The bed is fluidized with superheated steam, which reacts with metered quantities of granular carbon and oxygen to create a chemically reducing environment. The feed droplets coat the bed particles and quickly react. Water is evaporated, organics are volatized and reformed, nitrates and nitrites are converted to nitrogen gas, and non-volatile constituents are incorporated into leach-resistant mineral species.

Granular carbon, along with a sub-stoichiometric quantity of oxygen, is added directly to the DMR bed. A portion of the carbon oxidizes to produce necessary process energy. The carbon also reacts with the fluidizing steam and water in the feed to produce H_2 and CO via the water gas reaction:
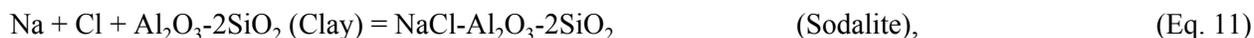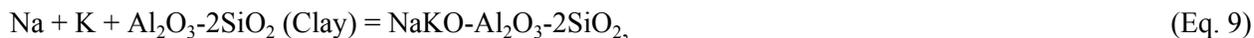
$$C + H_2O \rightarrow CO + H_2. \tag{Eq. 1}$$

The CO reacts further via the water gas shift reaction to produce additional H_2:

$$CO + H_2O \rightarrow CO_2 + H_2. \tag{Eq. 2}$$

The reducing environment in the bed results in the near complete destruction of nitrates and nitrites, with only trace levels remaining in the solid product. These species are converted directly to nitrogen gas, with very low levels of gaseous NOx produced. Some of the possible reactions whereby nitrites and nitrates are converted to nitrogen gas are:

$$NO_3 + 2C \rightarrow NO + 2CO_2, \tag{Eq. 3}$$

$$2NO_2 + 3C \rightarrow N_2 + 2CO + CO_2, \tag{Eq. 4}$$

$$2NO + 2C \rightarrow N_2 + 2CO, \tag{Eq. 5}$$

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O, \tag{Eq. 6}$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2. \tag{Eq. 7}$$

The non-volatile constituents in the waste feed are converted into highly leach resistant mineral forms by reaction with the aluminosilicate clay additive. The mineral species formed are principally alkali aluminosilicates, also referred to as feldspathoid mineral species. These contain unique cage-like structures that retain anions and radionuclides ionically bonded to the aluminosilicate structure and to sodium. These minerals also incorporate other ions elsewhere in their molecular structures. Examples of these minerals are nepheline, nosean, and sodalite, as shown below [11, 12].

$Na + Al_2O3\text{-}2SiO_2$ (clay) = $Na_2O\text{-}Al_2O_3\text{-}2SiO_2$ (Nepheline),   (Eq. 8)

$Na + K + Al_2O_3\text{-}2SiO_2$ (Clay) = $NaKO\text{-}Al_2O_3\text{-}2SiO_2$,   (Eq. 9)

$Na + SO_4 + Al_2O_3\text{-}2SiO_2$ (Clay) = $Na_2SO_4\text{-}Al_2O_3\text{-}2SiO_2$ (Nosean),   (Eq. 10)

$Na + Cl + Al_2O_3\text{-}2SiO_2$ (Clay) = $NaCl\text{-}Al_2O_3\text{-}2SiO_2$ (Sodalite),   (Eq. 11)

$Na + F + Al_2O_3\text{-}2SiO_2$ (Clay) = $NaF\text{-} Al_2O_3\text{-}2SiO_2$.   (Eq. 12)

The granular mineral products are removed from the DMR either at the bottom or as fines elutriated with the process gas stream at the top of the unit.

Any organics in the DMR feed are initially volatized and steam reformed into carbon monoxide, carbon dioxide, hydrogen, and a small quantity of light hydrocarbons, such as methane. Example reactions are:

$C_2H_6 + 2H_2O \rightarrow 2CO + 5H_2$,   (Eq. 13)

$CO + H_2O \rightarrow CO_2 + H_2$,   (Eq. 14)

$C_3H_8 + 2H_2 \rightarrow 3CH_4$.   (Eq. 15)

The process gases exiting the DMR consist mostly of N_2 (from process reactions and instrument purges), H_2O, CO_2, CO, and 0.5% to 4% H_2 (wet basis). There are also low levels of NOx, acid gases, and short-chained organics.

The light hydrocarbons, carbon monoxide, and hydrogen gases generated in the DMR are further steam reformed in the lower portion of the CRR and then oxidized to carbon dioxide and water vapor by the addition of oxygen in the upper portion of the CRR fluidized bed:

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$,   (Eq. 16)

$2CO + O_2 \rightarrow 2CO_2$,   (Eq. 17)

$2H_2 + O_2 \rightarrow 2H_2O$.   (Eq. 18)

If mercury is present in the waste feed, it is not incorporated into the solid product, but is volatized and converted to elemental mercury in the reformers. The off-gas from the process is treated in a mercury adsorber using a sulfur impregnated Granular Activated Carbon (GAC) bed. The GAC media captures and retains the mercury as HgS.

PILOT PLANT EQUIPMENT

The ESTD pilot plant is one-tenth the scale of the IWTU production facility, in terms of process flow rates and cross sectional areas of the reformers. It incorporates all of the process unit operations of the production-scale facility into an integrated system. See Figure 2 for a simplified process flow diagram of the pilot plant. An overview description of the major equipment items is provided below.
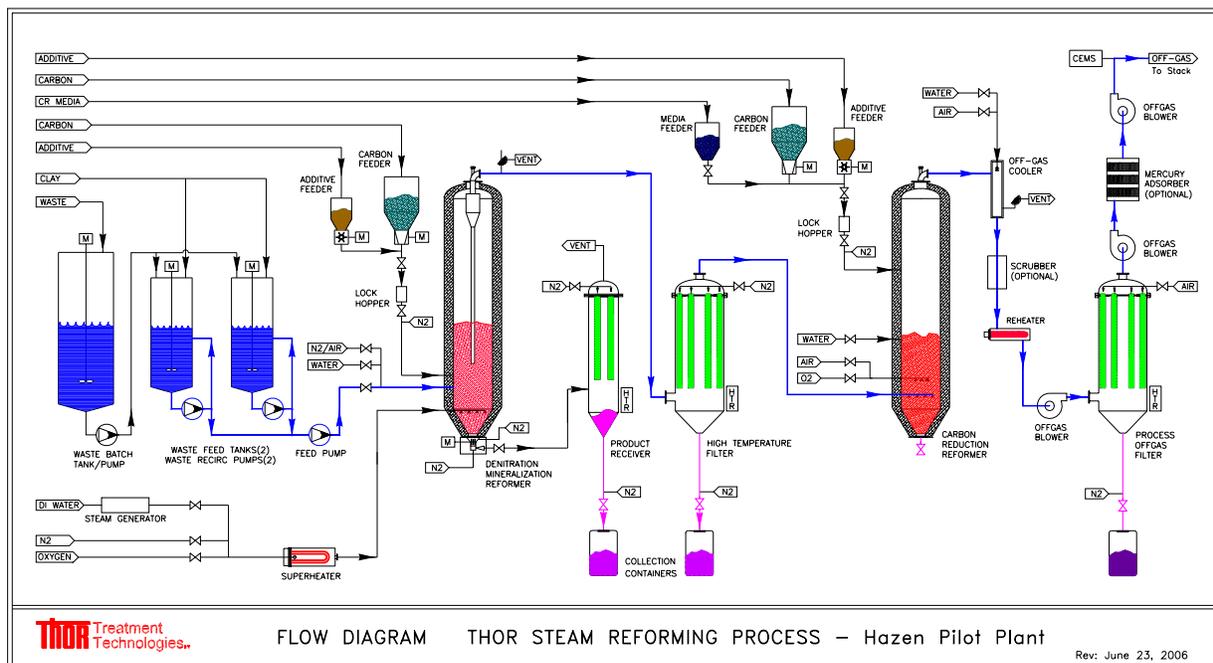

Fig. 2. ESTD process flow diagram.

Liquid Simulant Preparation and Feed System

The SBW simulant feed is made-up using reagent chemicals in the 6000 liter Waste Hold-up Tank. It is transferred in batches to one of two 1800 liter Waste Feed Tanks. If applicable for a specific test, a heavy metal and radionuclide simulant, and an undissolved solids simulant, each representative of those constituents present in the actual SBW, are added to the Waste Feed Tanks. The Kaolin clay is also added to the simulant in the feed tanks, forming the slurry feed for the DMR. This slurry feed is metered into the DMR via a positive displacement feed pump and the flow rate is monitored by a coriolis-type mass flow meter. The simulant is injected into the DMR through a specially designed nozzle that atomizes the feed.

A principal organic hazardous constituent (POHC) is injected into the DMR feed line between the Waste Feed Tanks and the atomizing nozzles during selected tests to determine the Destruction and Removal Efficiency (DRE) of the POHC in the process. The POHC used for this process was benzene, conservatively chosen to represent the organics present in the actual SBW.

Denitration and Mineralization Reformer

The DMR is a 38-cm (15-inch) inside diameter, refractory lined steel vessel. It has a conical bottom equipped with a product removal auger. Just below the auger is a nitrogen jet used to transfer product material to the Product Receiver (PR). The bed media is fluidized with superheated steam via a distributor located near the bottom of the vessel. A mixture of oxygen and nitrogen is metered into the DMR bed via

three injectors located above the superheated steam fluidizing gas distributor. The feed slurry is fed horizontally into the DMR through one of the two feed nozzles located above the fluidizing gas distributor. Bed temperatures are monitored via several thermocouples inserted into the vessel above, below, and in the active bed region. Process pressures and differential pressures are monitored via nitrogen purged pressure taps located throughout the vessel. A cyclone gas/solid separator is installed above the DMR. The cyclone allows the process gases to flow from the DMR to the High Temperature Filter (HTF) and returns larger solids to the active bed via a downcomer pipe. Granular carbon is fed to the DMR via a calibrated feeder and nitrogen impulsed "shot pot" that forces the carbon into the active bed region.

High Temperature Filter and Product Receiver

The process gas from the DMR flows to the HTF. The HTF is a cylindrical metal vessel, 61 cm (24 inches) in diameter, with a conical bottom. It captures any DMR product fines carried over in the process gas stream. The HTF is equipped with candlestick filters that are automatically back-pulsed with nitrogen during operation to remove excess filter cake, based on the differential pressure across the filters. The solid fines that accumulate in the HTF are drained from the bottom of the vessel into ~19-liter (5-gallon) collection containers.

Product solids are removed from the bottom of the DMR by the auger and are pneumatically transferred to the PR via a nitrogen jet. The PR vessel is a cylindrical vessel, 30.5 cm (12 inches) in diameter, with a conical bottom. The PR is fitted with four candlestick filters similar to those used in the HTF. The off-gas from the PR is vented to the freeboard region of the DMR. Product solids are removed from the bottom of the PR in the same manner as for the HTF.

Carbon Reduction Reformer

The process gases flow from the HTF to the fluidizing gas inlet distributors of the CRR located near the bottom of the vessel. The CRR is a 42-cm (17-inch) inside diameter, refractory lined vessel. It has a conical bottom equipped with a valve through which bed material can be removed, although material is typically removed only at the end of an operating period, since solid product does not accumulate in the CRR bed. Oxygen diluted with nitrogen is injected into the CRR above the process gas inlet distributors. The bed region between the inlet distributors and this oxygen injection level operates in a reducing mode to enhance overall process NOx destruction, while the bed region above operates in an oxidizing mode to convert residual CO, H_2, and short chained hydrocarbons to CO_2 and water. Higher in the CRR, additional oxygen is injected to control the process outlet gas oxygen concentration, which in turns keeps the process off-gas carbon monoxide concentration low. The CRR semi-permanent bed media is composed of granular alumina. Granular carbon is fed to the CRR via a calibrated feeder and nitrogen impulsed "shot pot" similar to those used for the DMR. This carbon serves as the energy source for the CRR. The 1123°K to 1323°K (850°C to 1050°C) operating temperature of the CRR bed is automatically controlled by the lower oxygen injection rate, while the oxygen concentration in the exiting process gas is automatically controlled by the upper oxygen injection rate. As with the DMR, bed temperatures are monitored via several thermocouples inserted into the vessel above, below, and in the active bed region, and process pressures and differential pressures are monitored via nitrogen purged pressure taps located throughout the vessel.

Off-gas Cooler and Reheater

The process gas from the CRR passes through the Off-gas Cooler (OGC) in a down flow direction. The OGC is a 61-cm (24-inch) diameter vessel with an atomizing water spray nozzle at the top. The water spray quickly cools the hot process gases to 443°K to 463°K (170°C to 190°C). The off-gas from the OGC flows to the Reheater, which maintains the gas stream at ~423°K (~150°C) to prevent condensation.

Process Baghouse Filter

The off-gas from the Reheater enters the Process Baghouse Filter (PBF) near the bottom of the vessel. The PBF is a vertical, rectangular vessel fitted with filter bags rated for $523^{\circ}K$ ($250^{\circ}C$). The purpose of the PBF is to remove any fine particulates that remain in the off-gas stream. These would typically be very fine alumina or carbon from the CRR bed. The filter bags are automatically back-pulsed with air during operation to remove accumulated fines, based on the differential pressure across the bags. The small quantity of fines that accumulate over time in the PBF are drained into ~19-liter (5 gallon) collection containers, much like is done with the PR and HTF.

Mercury Adsorber and Off-gas Blowers

Just prior to discharge, the off-gas passes through the Mercury Adsorber. This unit consists of two sulfur-impregnated granular activated carbon (GAC) beds in series designed to remove mercury from the off-gas stream. The unit can be bypassed for process start-up or during tests that do not involve mercury.

The system is equipped with three off-gas blowers, one upstream of the PBF, one downstream of the PBF and the third downstream of the Mercury Adsorber. These blowers maintain system gas flows and pressures.

Process and System Off-gas Measurements

Process and system off-gas streams are continuously monitored at three locations. The first measurement point is just downstream of the HTF. Here the Continuous Process Monitoring System (CPMS) monitors the filtered DMR process gas stream for H_2, O_2, CO, CO_2, total hydrocarbons (THC), NO, NO_2, and total NOx. The H_2 concentration is a key parameter for operational control of the DMR. It is used to control the carbon concentration in the DMR bed and hence the reducing environment in the DMR, which in turn is essential to NOx emission control. The second measurement point is just downstream of the CRR, where the O_2 concentration in the process gas leaving the CRR is monitored. This is important to ensure that there is adequate O_2 in this stream so that CO levels are low in the final off-gas. No other gas species are monitored at this point. The final measurement point is at the stack where the Continuous Emissions Monitoring System (CEMS) monitors for O_2, CO, CO_2, THC, NO, NO_2, total NOx, and SO_2.

In addition to the continuous monitoring, manual samples are obtained from ports in the stack. An independent subcontractor obtains these samples in accordance with formal U.S. Environmental Protection Agency (EPA) methods. Analytes of interest include volatile metals (e.g., Hg), low volatility metals (e.g., Cr), semi-volatile metals (e.g., Pb), radionuclide surrogates (Cs, Ce [for Pu], and Re [for Tc]), $HCl + Cl_2$, particulate matter, dioxins/furans, PCBs, volatile organic compounds (VOCs), semi-volatile organic compound (SVOCs), and total organics. Another independent subcontractor analyzes the manual samples obtained in accordance with EPA methods.

Process Data Acquisition and Control System

Process electronic data are obtained and process control is provided by the Data Acquisition and Control System (DACS). The DACS uses programmable automation controllers for control and data acquisition. The system architecture is a combination of LabVIEW software, FieldPoint[2] controllers, and interface modules.[3] LabVIEW software is utilized to monitor and control process operation from human-machine

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[2] LabVIEW and FieldPoint are products of National Instruments, Inc.

[3] Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government, any agency thereof, or any company affiliated with the Idaho Cleanup Project.

interfaces running on personal computers in the control room. Twenty-three process parameters are automatically controlled by the DACS. These include the DMR and CRR temperatures, the DMR fluidizing gas flowrate, the DMR liquid feed rate, the carbon feed rates to the DMR and CRR, and the HTF and PBF filter blowback timers.

THE TEST PROGRAM

The ESTD program consisted of two operational phases: (1) scoping tests and (2) production tests. The scoping tests were designed to verify system operability, confirm basic mineralizing process chemistry, and verify acceptable ranges for process operating parameters. The production tests were designed to demonstrate long-term operability of the integrated process; confirm overall process chemistry and mass balances; establish key operating parameters for a production-scale facility; generate a granular solid product that incorporates the alkali metals, halides, sulfur, radionuclide surrogates, and hazardous metal components for leachability analysis; and gather off-gas emissions data.

The simulant feed for the pilot plant tests was based on the actual composition of the SBW at the INL [13]. Worst-case concentrations of the SBW constituents were used for the simulant recipe. These were usually the highest concentrations observed from actual analyses, except in the case of certain metals that were thought to have positive catalytic (e.g., NOx reduction) effects. In these cases, the lowest observed concentrations were used. Minor waste constituents present in concentrations less than 0.01 $\underline{M}$ were generally not included to reduce the complexity of the make-up. Certain environmentally important constituents such as Hg, Pb, Cr, and the radioactive surrogates Cs, Ce (for Pu), and Re (for Te-99) were exceptions. The target constituent composition for the simulant feed used in the production runs is shown in Table I. For certain test runs, the heavy metals and the full range of radioactive surrogates were not used to minimize industrial hygiene concerns and because their presence was not essential to the objectives of the tests being conducted. For the radioactive surrogates, Ce and Cs were added at the concentrations noted in Table I; Re was used only in production runs P-2 through P-5B at a target concentration of 0.12 g/L.

Table I. Target Simulant Feed Compositions for the Production Tests

Component	Reagent	Production Test Runs	
		Concentration (moles/l)	Concentration (ppm)
Acid	HNO_3 (See Nitrate)	2.83	
Aluminum	$Al(NO_3)_3 \cdot 9H_2O$	0.719	14,697
Boron	H_3BO_3	0.0217	178
Calcium	$Ca(NO_3)_2 \cdot 4H_2O$	0.0731	2,219
Cerium	$Ce(NO_3)_3 \cdot 6H_2O$	0.00483	513
Cesium	$CsNO_3$	0.00353	355
Chromium	$Cr(NO_3)_3 \cdot 9H_2O$	0.00569	224
Iron	$Fe(NO_3)_3 \cdot 9H_2O$	0.0217	918
Lead	$Pb(NO_3)_2$	0.00134	210
Magnesium	$Mg(NO_3)_2 \cdot 6H_2O$	0.0257	473
Manganese	$Mn(NO_3)_2$ (50 wt% sol'n, ρ=1.54)	0.0152	633
Mercury	$Hg(NO_3)_2 \cdot 2H_2O$	0.00713	1,083
Nickel	$Ni(NO_3)_2 \cdot 6H_2O$	0.00255	113
Potassium	KNO_3	0.225	6,664

Table I. continued).

Component	Reagent	Production Test Runs	
		Concentration (moles/l)	Concentration (ppm)
Sodium	NaNO$_3$	2.20	38,317
Zinc	Zn(NO$_3$)$_2$·6H$_2$O	0.008	396
Chloride	NaCl	0.0334	897
Fluoride	HF (28.9 M sol'n)	0.0506	728
Nitrate	HNO$_3$ (69 wt% sol'n, ρ=1.41)	7.53	353,705
Phosphate	Na$_3$PO$_4$·12H$_2$O	0.005	360
Sulfate	Na$_2$SO$_4$	0.107	7,787

Approximately one-third of the SBW waste at INL contains undissolved solids at an average concentration of 80 g/L. A surrogate for these solids was prepared and added to the simulant feed for certain of the test runs. The target concentrations for major constituents of the undissolved solids surrogate were 2.2 wt % Al, 2.6 wt % Fe, 24.3 wt % Si, 13.1 wt % Zr, and 27.2 wt % PO$_4$.

Results of the Scoping Tests

The scoping tests were conducted during the period November 27, 2006, to December 12, 2006. During these tests, 1,578 gallons of SBW simulant were processed into 8,008 pounds of granular solid product during 173 hours of "feed-on" operation. A summary of process conditions for these tests is shown in Table II. No heavy metals, radioactive surrogates, or POHC were used in the simulant feed during the scoping test runs. Undissolved solids were used only in S-7A and S-7B. Two different mineralizing clay concentrations were used, 339 g/L for Tests S-1 through S-3B, and 228 g/L for Tests S-4 through S-7B.

Table II. Scoping Test Process Conditions

Test No.	Feed	Feed Rate, liters/min (gal/min)	DMR Temp. ºK (ºC)	Approx. Clay conc. (g/L)	CRR Temp. ºK (ºC)
S-1	SBW Simulant	0.76 (0.20)	998 (725)	339	1223 (950)
S-2	SBW Simulant	0.57 (0.15)	1023 (750)	339	1223 (950)
S-3A	SBW Simulant	0.57 (0.15)	973 (700)	339	1223 (950)
S-3B	SBW Simulant	0.57 (0.15)	973 (700)	339	1223 (950)
S-4	SBW Simulant	0.57 (0.15)	973 (700)	228	1223 (950)
S-5	SBW Simulant	0.57 (0.15)	1023 (750)	228	1223 (950)
S-6	SBW Simulant	0.57 (0.15)	998 (725)	228	1223 (950)
S-7A	SBW Simulant	0.57 (0.15)	998 (725)	228	1223 (950)
S-7B	SBW Simulant	0.57 (0.15)	998 (725)	228	1223 (950)

The results from the scoping tests included:

- Demonstration of sustainable integrated system operation using a mineralizing flowsheet
- Confirmation of the selected carbon as the DMR reductant/energy source based on NOx destruction, heating value, and maintenance of a stable product bed
- Confirmation of the selected carbon as the CRR energy source based on heating value, low sulfur and ash content, and low attrition in the bed media
- Confirmation of alumina as the start-up bed media in the DMR and the semi-permanent bed media in the CRR based on density, low attrition, and non-agglomerating characteristics
- Establishment of ranges for simulant feed rate and atomizing gas flow rates based on DMR performance characteristics
- Establishment of ranges for DMR fluidizing gas composition and velocities based on performance of the active bed in the DMR
- Confirmation of DMR and CRR operating temperature ranges based on performance characteristics
- Establishment of acceptable "high" and "low" clay addition concentrations to produce a mineralized product.

Results of the Production Tests

The production tests were conducted from December 12, 2006, to December 20, 2006. During these tests, 1,436 gallons of SBW simulant were processed into 6,093 pounds of granular, solid product during 175 hours of "feed-on" operation. A summary of test process conditions is given in Table III. Heavy metals were added to the simulant for all the tests except P-5B. Cs and Ce were used as radioactive surrogates in all the tests, while Re was used in tests P-2 through P-5A. Undissolved solids were added only for test P-1. Four different mineralizing clay concentrations were used to investigate product quality (e.g., leachability and chemical durability) as a function of the quantity of clay used per liter of simulant feed.

Table III. Production Test Process Conditions

Test No.	Feed	Feed Rate, liters/min (gal/min)	DMR Temp. °K (°C)	Approx. Clay conc. (g/L)	CRR Temp. °K (°C)
P-1	SBW Simulant	0.57 (0.15)	1008 (735)	228	1223 (950)
P-2	SBW Simulant	0.57 (0.15)	1008 (735)	228	1223 (950)
P-3	SBW Simulant	0.57 (0.15)	1008 (735)	276	1223 (950)
P-4	SBW Simulant	0.57 (0.15)	1008 (735)	339	1223 (950)
P-5A	SBW Simulant	0.38 (0.10)	1008 (735)	200	1223 (950)
P-5B	SBW Simulant	0.38 (0.10)	1008 (735)	200	1223 (950)

Most of the process operating parameters for the production tests were established and maintained at the optimum conditions, as demonstrated during the scoping runs. These were based on quality of product produced, DMR particle size control, stability of DMR operations, and process and off-gas compositions, as indicated by the CPMS and CEMS.

Solid product samples were obtained from the various product streams during all of the tests. Solid product was removed from the DMR, either via the PR or directly from the active bed as process samples. DMR product fines material was removed from the HTF. A micrograph of DMR solids produced during the production tests is shown in Figure 3. The light colored particles in the figure are product material and the dark irregular shaped particles are carbon reductant. The average elemental compositions of the HTF and DMR product solids produced during the production tests are shown in Table IV. All compositions are normalized to a carbon-free basis.

Fig. 3. Micrograph of DMR solids produced during production tests.

Table IV. Average Composition of DMR and HTF Solids Produced during the Production Tests

Component and Units	Average Composition for DMR Bed Solids	Average Composition for HTF Solids
Al, %	21.090	12.282
B, %	0.017	0.058
Ca, %	2.638	4.614
Fe, %	2.396	1.059
Mg, %	0.244	0.262
Mn, %	0.227	0.224
Na, %	8.034	8.454
K, %	2.121	2.246
Si, %	14.291	13.223
Ce, %	0.078	0.074
Cs, %	0.014	0.067
Cr, %	0.028	0.024
Pb, %	0.024	0.038
Ni, %	0.051	0.022

Table IV. (continued).

Component and Units	Average Composition for DMR Bed Solids	Average Composition for HTF Solids
Zn, %	0.106	0.058
Hg, ppm	0.408	0.996
Re, mg/kg	20.313	120.313
Zr, %	0.072	0.231
Cl, %	0.047	0.372
F,%	0.020	0.190
Ti, %	0.538	0.638
NO_3, %	< 0.005	0.008
PO_4, %	3.946	3.287
SO_4, %	0.184	1.078
CO_3,%	0.559	2.393

The overall macroscopic mass balance for the process closed to within 1.1%. The target for process mass balance closure for the major components (Al, Ca, Fe, K, Na, S, Si, NO_3, and H_2O) was ±10% and ±30% for the minor components. This standard was met for all components except for Na (-11.2%), S (-52.9%), Cs (+40.2%) and Ni (+35.3%). It is believed that the small under-recovery of Na was due to the inability to completely dissolve the mineral structures in the analytical process. The under-recovery of S was likely due to an analytical method inadequacy. This and prior mineralizing tests have showed S to be very difficult to detect in the mineralized product matrix. The over-recovery of Cs was likely due to analytical method issues associated with the simulant feed. The over-recovery of Ni was likely due to the slight erosion of high Ni alloys in the process.

To evaluate hazardous metal leachability, DMR and HTF product samples from each of the four clay loadings were subjected to the TCLP [14]. The INL SBW waste is "listed" under the EPA Resource Conservation and Recovery Act (RCRA) and would have to meet the Universal Treatment Standard (UTS) limits if disposed of at the Yucca Mountain Repository. For this evaluation, samples were measured for the retention of the RCRA metals. The data show that all sample results were less than both the laboratory reporting limit and the UTS limits [15]. This indicates that the RCRA metals present in the SBW simulant are retained in the mineralized product and that the product is highly leach resistant.

To evaluate chemical durability of the solid product material, DMR and HTF samples from each of the four clay loadings were subjected to PCT measurements [16]. Qualified personnel at SRNL performed these tests, with carbon being removed from the material prior to sizing and washing [17]. The DMR samples were sieved to the same size fraction used to express glass waste form performance. Other test parameters matched the nominal test conditions (PCT-A) for testing glass waste form performance. Table V shows the data from the PCT analyses. These results indicate that the mineralized SBW simulant, at increasing clay addition ratios, performed on a level similar to, or better than, EA or LRM glass waste forms with respect to sodium release. The sodium release rate is at least one order of magnitude less than the response for LRM glass. The PCT results, in conjunction with the mass balance, indicate that the FBSR mineral product captures and retains constituents of interest (Cs, Re, anions) and exhibits chemical durability superior to that of the EA and LRM glasses.

Table V. Normalized PCT Releases for SBW Mineralized Products and Reference Materials

Sample Material	pH	NL_{Na} (g/m^2)	NL_{Cs} (g/m^2)	NL_{Re} (g/m^2)	NL_{Si} (g/m^2)	NL_{S} (g/m^2)	NL_{Al} (g/m^2)
200 g-clay/L SBW Lite							
DMR 4726	12.52	0.094	0.013	0.074	0.0015	0.266	0.048
HTF 4728	12.66	0.080	0.025	0.962	0.0002	0.257	0.024
228 g-clay/L SBW Lite							
DMR 4504	12.28	0.144	0.061	0.147	0.0030	0.330	0.015
HTF 4508	12.75	0.103	0.022	0.454	0.0002	0.286	0.029
276 g-clay/L SBW Lite							
DMR 4531	12.10	0.057	0.037	0.118	0.0013	0.198	0.009
HTF 4546	12.38	0.064	0.035	0.248	0.0002	0.221	0.026
339 g-clay/L SBW Lite							
DMR 4637	12.06	0.027	0.029	0.121	0.0008	0.070	0.006
HTF 4649	12.14	0.036	0.024	0.394	0.0001	0.129	0.010
EA Reference	11.85	6.67	—	—	1.960	—	—
LRM Reference	10.90	0.540	—	—	0.160	—	—

Gaseous grab samples were obtained from the stack during the production tests using formal EPA methods. Analysis of off-gas data collected from the CEMS and the EPA protocol manual samples during the production tests indicates that a production-scale process would meet all applicable environmental discharge limits. These include Maximum Achievable Control Technology (MACT) limits for metals, HCl/Cl$_2$, particulate matter, dioxins/furans, VOCs, SVOCs, THC, and CO, as well as the site discharge limits for NOx and SOx. A summary of the emissions data from the production runs is shown in Table VI. The results for Hg do not appear to meet MACT for all samples; however, this was due to contamination of the off-gas piping from a previous test. This is supported by the component mass balance, which showed a 12.4% over-recovery of Hg and by the fact that actual Hg numbers were lower during the production tests when Hg was added to the simulant than during the scoping tests when Hg was not added. The calculated DRE for the POHC (benzene) was 99.989%, minutely less than the target value of 99.99%.

Table VI. Emissions Summary for the Production Tests [15]

Pollutant	Concentration Corrected to 7% O_2	Percent of MACT Limit	Results and Comments
Radioactive Surrogates (Cs, Ce [for Pu], Re [for Tc])	0.9 micrograms/dscm for each	NA	• Removal efficiency >99.997% • No HEPA filters in test system
Low Volatility Metals (As, Be, Cr)	12.5 micrograms/dscm average	~54%	• Meets MACT • No HEPA filters in test system • No As or Be in simulant
Semi-volatile Metals (Cd, Pb)	1.4 microgram/dscm average	~14%	• Meets MACT • Pb Removal Efficiency >99.999% • No Cd in simulant
Volatile Metals (Hg)	6.5 – 12.1 micrograms/dscm	80 – 150%	• Hg removal efficiency ~99.996% • Hg contamination from prior tests negatively impacted results
HCl/Cl_2	0.6 ppm average	~3%	• Meets MACT
Particulate Matter	3.0 ppm average mg/dscm	~88%	• Meets MACT • No HEPA filters in test system
Dioxins/Furans	0.07 nanograms/dscm	~61%	• Meets MACT
PCBs	5 – 10 nanograms/dscm	NA	• Most PCB congeners not detected • Dioxin-like coplanar PCBs not detected
VOCs (POHC was Benzene)	Mostly non-detectable	—	• Benzene destruction efficiency >99.989% vs 99.99% goal
SVOCs	Mostly non-detectable	NA	• One SVOC detected
NOx	Typically <1700 ppm	NA	• One run was ~2,900 ppm • NOx destruction 93 - 96%
THC	<0.3 ppm	<3%	• Meets MACT
CO	10 – 30 ppm	10 – 30%	• Meets MACT
SOx	<40 ppm	NA	• One run was ~200 ppm

CONCLUSION

This pilot plant test demonstrates the capability of the integrated THOR® FBSR process to convert a representative SBW simulant containing RCRA metals, radionuclide surrogates, undissolved solids, and organic contaminants, into a mineralized alkali aluminosilicate product in a safe, efficient, and sustainable manner. The mineralized product exhibits leach resistance and chemical durability equal to or superior to EA and LRM glass, as indicated by TCLP and PCT analyses.

Results indicate that gaseous emissions from a full-scale production facility would be within regulatory limits. Process operating parameters that would apply to a full-scale facility for the processing of SBW using a mineralizing FBSR flowsheet have been identified.

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