Steam Reforming Technology Demonstration Program for Treatment of DOE Sodium Bearing Tank Wastes at Idaho National Laboratory

K. Ryan, B. Mason, K. Wolf
THOR Treatment Technologies, LLC
106 Newberry St. SW, Aiken, SC 29801 USA

A. Olson
CH2M WG Idaho, LLC
P. O. Box 1625, Idaho Falls, ID 83415 USA

ABSTRACT[1]

The patented THOR® steam reforming waste treatment technology has been selected by the Department of Energy (DOE) for treatment of Sodium Bearing Waste (SBW) at the Idaho National Laboratory (INL). 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 test demonstration (ESTD) was conducted using a specially designed pilot plant located at Hazen Research, Inc. in Golden Colorado.

The purpose of the ESTD was to confirm and optimize operation of the THOR® dual fluidized bed steam reforming (FBSR) process for treating the SBW. The performance of the integrated FBSR thermal and off-gas systems was demonstrated while treating waste simulants representative of the actual SBW. Simulants were utilized that consisted of highly acidic nitrate solutions, with both dissolved and undissolved solids (UDS). The SBW simulant solutions were converted into a dry, granular solid, consisting of carbonate and aluminate product compounds. The successful performance of the integrated FBSR system was verified and demonstrated.

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 Boise-based Washington Group International. The cleanup project, named the Idaho Cleanup Project or 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 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.

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 RH-TRU at the Waste Isolation Pilot Plant (WIPP), but that "Until such time as the

---

[1] "Certain information addressed within this Article 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."

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."[2]

In order to meet the requirement to provide dual disposal paths for the SBW, CWI proposed to treat the SBW with the patented THOR® steam reforming waste treatment technology. The THOR® technology can produce a final waste product that is suitable for disposal as RH-TRU at WIPP; and with modifications, it can produce a different waste form that could be qualified for ultimate disposal in a HLW geologic repository. CWI selected THOR Treatment Technologies, LLC (TTT), an affiliate of Washington Group International, to demonstrate a process and design a treatment plant for processing the SBW. The THOR® plant being designed will produce a waste form suitable for disposal as RH-TRU.

This paper provides a summary of the ESTD pilot plant work that has been completed in support of the design and ultimately the operation of the IWTU facility for processing of the SBW.

THOR® 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® steam reforming process destroys nitrates, nitrites, and organic materials present in the SBW and produces a dry, granular solid product containing the radionuclides, alkali metals, sulfates, halides, and non-volatile heavy metals present in the SBW [2, 3, 4, 5, 6, 7, 8, 9, 10, and 11]. 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® process flow diagram for treatment of SBW is provided in Figure 1.

The SBW feed 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 to a granular solid 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 carbonate and aluminate solid, will meet requirements for shipment in the RH-72B shipping container. It is expected that the product will meet anticipated requirements for disposal as RH-TRU.

PROCESS CHEMISTRY

The DMR waste feed is atomized into a fluidized mineral bed at $873^{o}K$ to $943^{o}K$ ($600^{o}C$ to $670\ ^{o}C$). This bed is fluidized with superheated steam and a small amount of oxygen. The feed droplets coat the bed particles and are instantly dried. The large active surface of dried nitrates readily reacts with hot carbon reductant particles, carbon monoxide and hydrogen gases, and the reduced metal and metal oxide particles in the fluidized bed. This reducing environment 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 NOx produced.

---

[2] DOE/EIS-0287, Record of Decision for the Idaho High-Level Waste and Facilities Disposition Final Environmental Impact statement, December 2005, p.1.

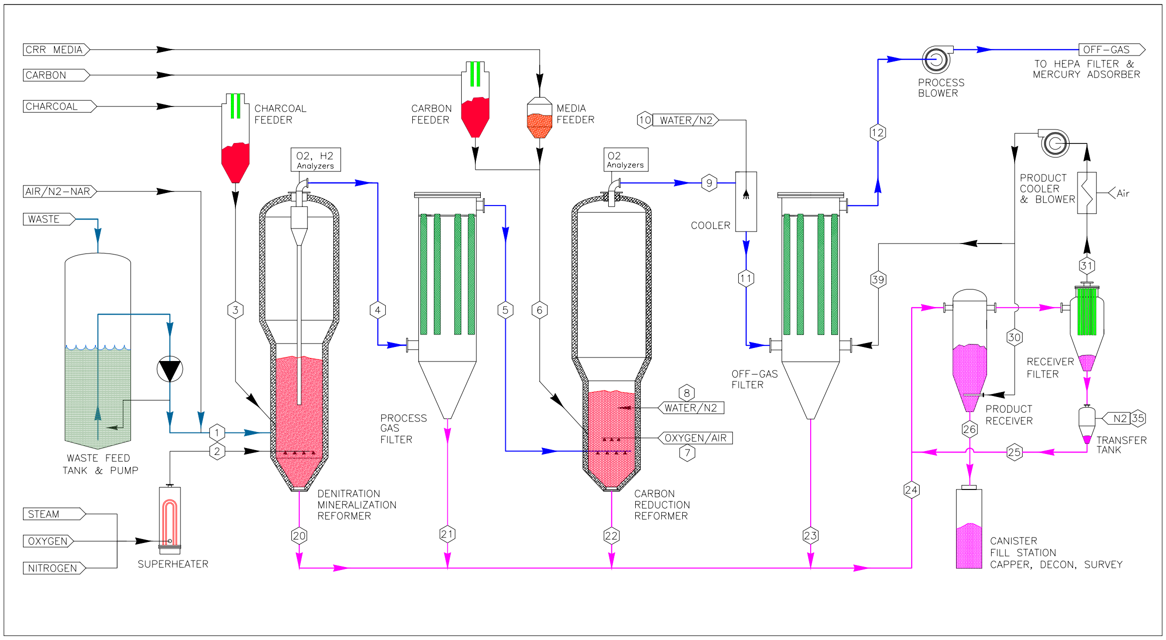

Fig. 1. IWTU Process flow diagram for the treatment of SBW

Several of the possible reaction mechanisms whereby nitrites and nitrates are converted to nitrogen gas are shown below.

$$NO_3 + 2C \rightarrow NO + 2CO$$

$$2NO_3 + 4C \rightarrow N_2 + 2CO + 2CO_2$$

$$2NO + 2C \rightarrow N_2 + 2CO$$

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

$$NO_3 + C \rightarrow NO_2 + CO$$

$$2NO_2 + 3C \rightarrow N_2 + 2CO + CO_2$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

Granular carbon is added directly to the DMR bed. A portion of this carbon oxidizes to produce necessary process energy. It also serves as the reductant which facilitates the above reactions. Carbon reacts with the fluidizing steam and water in the feed to produce H_2 and CO via the water gas reaction:

$$C + H_2O \rightarrow CO + H_2$$

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

$$CO + H_2O \rightarrow CO_2 + H_2$$

The bulk of the granular solid product produced in the DMR consists of carbonate compounds. For example, in a reducing environment, sodium nitrate in the feed reacts with carbon to produce a sodium carbonate product, as well as nitrogen gas and carbon monoxide:

$$2\ NaNO_3 + 4C \rightarrow Na_2CO_3 + N_2 + 3CO$$

The granular solid 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 dioxide, carbon monoxide, hydrogen, and a small quantity of light hydrocarbons, with methane being the main constituent:

$C_xH_y + xH_2O \rightarrow xCO + (x+y/2)\ H_2$

$C_xH_y + 2(x-y/s)H_2 \rightarrow xCH_4$

$CO + H_2O \rightarrow CO_2 + H_2$

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

The light hydrocarbons and the 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 addition of oxygen to the fluidizing gases in the upper portion of the CRR:

$CO + H_2O \rightarrow CO_2 + H_2$

$2CO + O_2 \rightarrow 2\ CO_2$

$2H_2 + O_2 \rightarrow 2\ H_2O$

If mercury is present in the waste feed, it is not bound-up in 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 (cinnabar).

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.

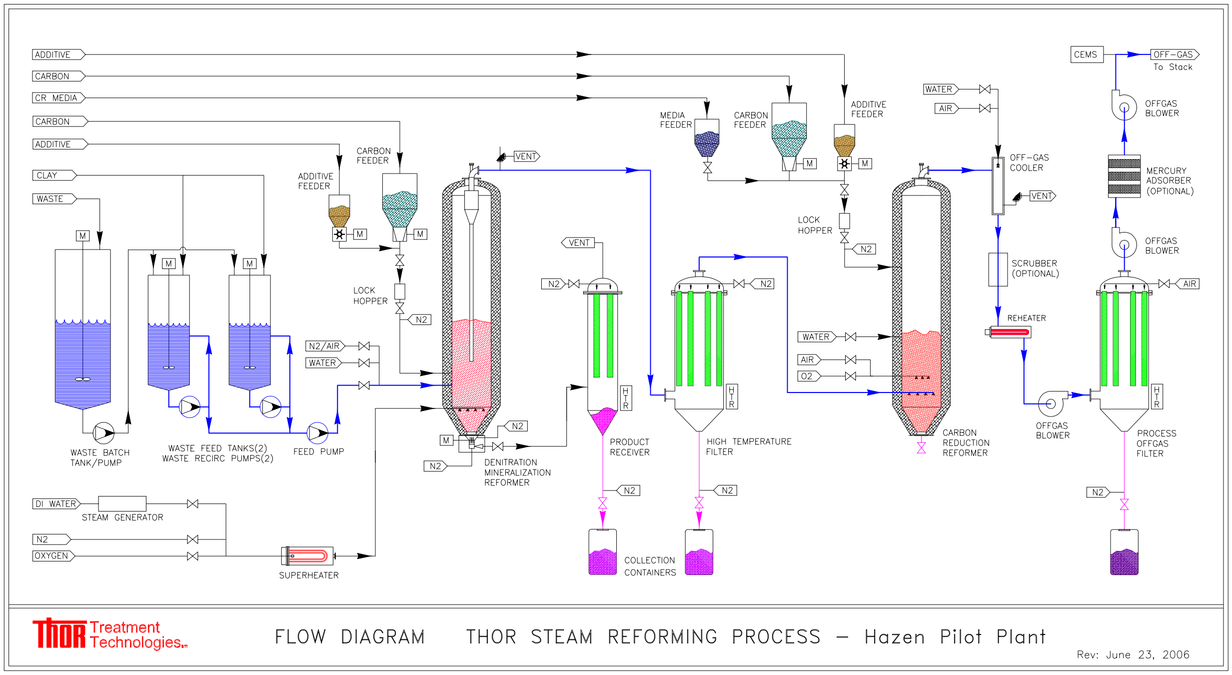

Fig. 2. ESTD Process flow diagram

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 simulant and an undissolved solids simulant, each representative of those constituents present in the actual SBW, are added to the Waste Feed Tanks. The SBW simulant is metered into the DMR via a peristaltic feed pump and the flow rate is monitored by a coriolis-type mass flow meter. The simulant is injected into the DMR by one of two specially designed atomizing feed nozzles.

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 Destructive Removal Efficiency (DRE) of the POHC in the process. The POHC used for this process was monochlorobenzene, conservatively chosen to represent the organics present in the actual SBW.

Denitration and Mineralization Reformer (DMR)

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 oxygen enriched superheated steam via a distributor located near the bottom of the vessel. SBW surrogate is fed horizontally into the DMR through one of the two feed nozzles located several inches 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 vibratory feeder and nitrogen impulsed “shot pot” that forces the carbon into the active bed region.

High Temperature Filter (HTF) and Product Receiver (PR)

The process gas from the DMR flows to the HTF. The HTF is a cylindrical stainless steel vessel, 61 cm (24 inches) in diameter, with a conical bottom. It captures any carbonate-rich DMR product fines carried over in the process gas stream. The carbonate fines could cause agglomeration in the CRR, as they have a melting point range of 1023^{o}K to 1123^{o}K (750°C to 850°C), well below the 1123^{o}K to 1323^{o}K (850^{o}C to 1050^{o}C) operating temperature range of the CRR. The HTF is equipped with candlestick filters, made of either of sintered metal or silicon carbide. The filters 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 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 stainless steel vessel, 30.5 cm (12 inches) in diameter, with a conical bottom. The PR is fitted with four sintered metal 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 (CRR)

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 several inches 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’s semi-permanent bed media is composed of granular alumina. Granular carbon is fed to the CRR via a calibrated vibratory feeder and nitrogen impulsed “shot pot” similar to those used for the DMR. This carbon serves as the energy source for the CRR and consists of low-sulfur petroleum coke. The 1123^{o}K to 1323^{o}K (850^{o}C to 1050^{o}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 (OGC) and Reheater

The process gas from the CRR passes through the OGC in a down flow direction. The OGC is a 61 cm (24 inch) diameter, 244cm (96 inch) long stainless steel vessel with an atomizing water sprayer at the top. The water spray quickly cools the hot process gases to 443^{o}K to 463^{o}K (170^{o}C to 190^{o}C). The off-gas from the OGC flows to the Reheater, a 25 kW electric heater, which maintains the gas stream at ~423^{o}K (~150^{o}C) to prevent condensation.

Process Baghouse Filter (PBF)

The off-gas from the Reheater enters the PBF near the bottom of the vessel. The PBF is a vertical, rectangular vessel fitted with Teflon-coated fiberglass felt filter bags rated for 523^{o}K (250^{o}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 three 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 Measurement

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. These samples are pulled by an independent subcontractor in accordance with formal EPA methods. Analytes of interest included volatile metals (e.g., Hg), low volatility metals (e.g., As and Cr), semi-volatile metals (e.g., Pb), radionuclide surrogates (Cs and Ce [for Pu]), HCl + Cl_2, particulate matter, dioxins/furans, PCBs, volatile organic compounds (VOCs), semi-volatile organic compound (SVOCs), and total organics. The manual gas samples obtained were analyzed by another independent subcontractor in accordance with EPA methods.

Process Data Acquisition and Control System (DACS)

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

Following construction of the pilot plant, basic checkout and functional tests were performed to verify safety and operability of the process equipment. When these tests were completed, a readiness review was conducted to verify the integrated pilot plant was ready for operation.

The pilot plant testing program consisted of three operational phases: (1) Scoping Tests, (2) Carbonate Phase 1 Production Tests (CP1), and (3) Carbonate Phase 2 Production Tests (CP2). The scoping tests were designed to demonstrate basic system operability and verify acceptable ranges for process operating parameters. The production tests were designed to demonstrate long-term operability of the integrated process, confirm process chemistry and mass balances, establish key operating parameters for the production-scale facility, obtain data to confirm IWTU design parameters, obtain product data to verify the final waste form is chemically compatible with disposal at WIPP, and gather off-gas emissions data to support the environmental permitting process.

The simulant feed for the pilot plant tests was based on the actual composition of the SBW at the INL [12]. 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 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 and Ce were exceptions. The target compositions for the simulant feeds used in the production runs are shown in Table I. For certain test runs, the heavy metals and 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.

---

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

Table I. Target Simulant Feed Compositions for the Production Tests

Component	**Reagent**	**CP-1**		**CP-2**	
		Concentration (moles/l)	**Concentration (ppm)**	**Concentration (moles/l)**	**Concentration (ppm)**
Cations in Solution					
Acid	HNO_3 (See Nitrate)	2.88		2.88	
Aluminum	$Al(NO_3)_3{\cdot}9H_2O$	0.719	14900	0.719	14900
Arsenic	$H_3AsO_4{\cdot}0.5H_2O$	0.000492	28.4	0	0
Boron	H_3BO_3	0.0217	180	0.0217	180
Calcium	$Ca(NO_3)_2{\cdot}4H_2O$	0.0731	2250	0.0731	2250
Cerium	$Ce(NO_3)_3{\cdot}6H_2O$	0.0483	5210	0.00483	521
Cesium	$CsNO_3$	0.0353	3610	0.00353	361
Chromium	$Cr(NO_3)_3{\cdot}9H_2O$	0.00569	228	0.00569	228
Iron	$Fe(NO_3)_3{\cdot}9H_2O$	0.0217	932	0.0217	932
Lead	$Pb(NO_3)_2$	0.00134	214	0.00134	214
Magnesium	$Mg(NO_3)_2{\cdot}6H_2O$	0.0257	480	0.0257	480
Manganese	$Mn(NO_3)_2$ (50 wt% sol'n, ρ=1.54)	0.0152	642	0.0152	642
Mercury	$Hg(NO_3)_2{\cdot}2H_2O$	0.00713	1100	0.00713	1100
Nickel	$Ni(NO_3)_2{\cdot}6H_2O$	0.00255	115	0.00255	115
Potassium	KNO_3	0.225	6670	0.225	6670
Sodium	$NaNO_3$	2.20	38900	2.20	38900
Zinc	$Zn(NO_3)_2{\cdot}6H_2O$	0.00498	250	0.008	402
Anions in Solution					
Chloride	$NaCl$	0.0334	912	0.0334	912
Fluoride	HF (28.9 M sol'n)	0.0506	740	0.0506	740
Nitrate	HNO_3 (69 wt% sol'n, ρ=1.41)	7.59	362,000	7.59	362,000
Phosphate	$Na_3PO_4{\cdot}12H_2O$	0.0138	1000	0.005	362
Sulfate	Na_2SO_4	0.107	8070	0.107	8070

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 28, 2005 to January 13, 2006. A summary of process conditions for these tests is shown in Table II. No heavy metals, radioactive surrogates or undissolved solids were used in the simulant feed during the scoping test runs.

Table II. Scoping Test Process Conditions

Test No.	Feed	Feed Rate, liters/min (gal/min)	DMR Carbon Reductant	DMR Temp. °K (°C)	CRR Bed Media	CRR Carbon	CRR Temp. °K (°C)
S-1	Water	0.38 (0.1)	Wood-based carbon	923 (650)	Alumina	Coke	1123 (850)
S-2	SBW Simulant	0.76 (0.2)	Wood-based carbon	873 (600)	Alumina	Coke	1323 (1050)
S-3	SBW Simulant	0.95 (0.25)	Wood-based carbon	913 (640)	Alumina	Coke	1323 (1050)
S-4	SBW Simulant	0.76 (0.2)	Coal	893 (620)	Alumina	Coke	1323 (1050)
S-5	SBW Simulant	0.76 (0.2)	Coal	923 (650)	Alumina	Coke	1123 (850)
S-6	SBW Simulant	0.76 (0.2)	Coal	873 (600)	Alumina	Coke	1123 (850)
S-7	SBW Simulant	0.76 (0.2)	Coal	943 (670)	Alumina	Coke	1123 (850)
S-8	SBW Simulant	1.13 (0.3)	Coal	943 (670)	Alumina	Coke	1223 (950)

The results from the scoping tests included:

- Demonstration of sustainable integrated system operation.
- Demonstration that an off-gas scrubber system was not required based on very low stack emissions of SO_2, HCl, and Cl_2.
- Demonstration that H_2 and O_2 react to mutually exclude the component with the lower concentration and that there is no potential for formation of flammable mixtures in the process from stream reforming reactions.
- Selection of coal as the DMR reductant/energy source based on NOx destruction, heating value, and maintenance of a stable product bed.
- Selection of petroleum coke 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.
- Selection of DMR and CRR operating temperature ranges based on numerous performance characteristics.

Results of the Production Tests

During the two phases of production tests, a total of ~29,900 liters (~40,400 kg) of simulant feed were processed into ~7,300 kg of granular solid product. The CP1 tests were conducted January 16 through February 10, 2006, and processed ~20,600 liters (~27,700 kg) of simulant feed into ~5,200 kg of product in 334 hours of "feed-on" operations. The CP2 tests were conducted May 30 to June 9, 2006, and processed ~9,300 liters (~12,700 kg) of simulant feed into ~2,100 kg product in 164 hours of "feed-on" operation. Summaries of test process conditions for CP1 and CP2 are shown in Tables III and IV, respectively.

Table III. CP1 Production Test Process Conditions

Test No.	**Feed**	**Feed Rate, liters/min (gal/min)**	**DMR Bed Media**	**DMR Carbon Reductant**	**DMR Temp, ^{o}K (^{o}C)**	**CRR Bed Media**	**CRR Carbon**	**CRR Temp, ^{o}K (^{o}C)**
P-1	SBW	0.95 (0.25)	Product	Coal	913 (640)	Alumina	Coke	1223 (950)
P-2A	SBW + 80 g/l UDS	0.95 (0.25)	Product	Coal	913 (640)	Alumina	Coke	1223 (950)
P-3B	SBW + 80 g/l UDS + Heavy Metals	0.95 (0.25)	Product	Coal	913 (640)	Alumina	Coke	1223 (950)
P-4A-1	SBW + 80 g/l UDS + Heavy Metals + POHC	0.95 (0.25)	Product	Coal	943 (670)	Alumina	Coke	1123 (850)
P-4A-2	SBW + 80 g/l UDS + Heavy Metals + POHC	0.95 (0.25)	Product	Coal	873 (600)	Alumina	Coke	1123 (850)
P-4A-3	SBW + 80 g/l UDS + Heavy Metals + POHC	0.95 (0.25)	Product	Coal	873 (600)	Alumina	Coke	1323 (1050)
P-4A-4	SBW + 80 g/l UDS + Heavy Metals + POHC	0.95 (0.25)	Product	Coal	943 (670)	Alumina	Coke	1323 (1050)
P-4A-5	SBW + 80 g/l UDS + Heavy Metals + POHC	1.32 (0.35)	Product	Coal	943 (670)	Alumina	Coke	1323 (1050)
P-4A-6	SBW + 80 g/l UDS + Heavy Metals + POHC	1.32 (0.35)	Product	Coal	873 (600)	Alumina	Coke	1123 (850)
P-5	SBW + 120 g/l UDS + Heavy Metals	0.95 (0.25)	Product	Coal	913 (640)	Alumina	Coke	1223 (950)
P-6	10% SBW + 120 g/l UDS + Heavy Metals	0.95 (0.25)	Product	Coal	873 (600)	Alumina	Coke	1223 (950)

Table IV. CP2 Production Test Process Conditions

Test No.	**Feed**	**Feed Rate, liters/min (gal/min)**	**DMR Bed Media**	**DMR Carbon Reductant**	**DMR Temp. ^{o}K (^{o}C)**	**CRR Bed Media**	**CRR Carbon**	**CRR Temp. ^{o}K (^{o}C)**
Preheat	None	0	Alumina	Coal	Heat up from ambient to 913 (640)	Alumina	Coke	Heat up from ambient to 1223 (950)
CP2-1	SBW	0.95 (0.25)	Carbonate Product &	Coal	913 (640)	Alumina	Coke	1223 (950)

			Alumina					
CP2-1	SBW	0.95 (0.25)	Carbonate Product & Alumina	Coal	913 (640)	Alumina	Coke	1223 (950)
CP2-1/ CP2-2	SBW	0.95 (0.25)	Carbonate Product	Coal	913 (640)	Alumina	Coke	1223 (950)
CP2-2	SBW	0.95 (0.25)	Carbonate Product	Coal	913 (640)	Alumina	Coke	1223 (950)
CP2-2	SBW	0.95 (0.25)	Carbonate Product	Coal	913 (640)	Alumina	Coke	1223 (950)
CP2-2	SBW	0.95 (0.25)	Carbonate Product	Coal	913 (640)	Alumina	Coke	1223 (950)
CP2-2	SBW	0.95 (0.25)	Carbonate Product	Coal	913 (640)	Alumina	Coke	1223 (950)
CP2-3	SBW	0.95 (0.25)	Carbonate Product	Coal	913 (640)	Alumina	Coke	1223 (950)
CP2-4	SBW	0.95 (0.25)	Carbonate Product	Coal	913 (640)	Alumina	Coke	1223 (950)

The test conditions for CP1 were designed to be representative of the feed and process conditions that would be encountered in the IWTU production facility during actual SBW processing operations and to demonstrate practical operating ranges for the major process parameters (e.g., process feed rate and reformer temperatures). The test conditions for CP2 were limited to the "best" process operating conditions, as demonstrated during CP1, and were intended to further investigate issues identified during CP1. These included particle size control in the DMR bed, optimization of DMR bed product production vs. HTF fines generation, and optimization of CRR operation.

For both test phases, gaseous grab samples were obtained from the stack using formal EPA methods and solid product samples were obtained from the various product streams. Most of the solid product was removed from the DMR, either via the PR or directly from the active bed as process samples. The balance of the DMR product material was removed from the HTF. The average elemental compositions of the HTF and DMR product solids produced during the core CP1 tests (P-4A-1 through P-4A-6) and during CP2 following 95% conversion of the start-up bed to product bed, are shown in Table V. All compositions are normalized to a carbon-free basis. A micrograph of DMR solids produced during CP2 is shown in Figure 3. The spherical particles in the figure are product material and the irregular shaped particles are carbon reductant.

Solid product samples from CP1 were analyzed to determine their potential acceptability for disposal at WIPP. The analyses were performed to determine the presence or absence of certain chemical or physical characteristics that would preclude WIPP disposal of IWTU product material. The characteristics analyzed for were explosivity, pyrophoricity, ignitability, reactivity, and detectable liquids. The product samples were negative for these characteristics.

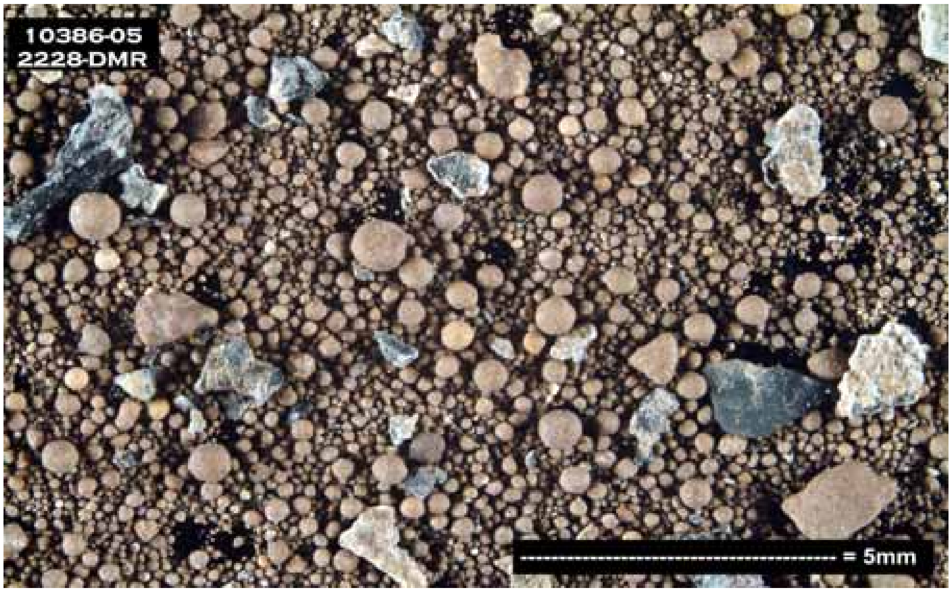

Fig. 3. Micrograph of DMR solids produced during CP2.

Table V. Average Composition of DMR and HTF Solids Produced during the CP1 and CP2 Tests

Component	Average Composition for CP1, wt%		Average Composition for CP2, wt%	
	DMR Bed Solids P-4A-1 through P-4A-6	HTF Solids P-4A-1 through P-4A-6	DMR Bed Solids	HTF Solids
Al	10.8	7.94	12.6	11.8
Ca	1.39	1.53	3.81	3.19
Fe	1.78	1.38	1.61	1.18
Heavy Metals (As, Cr, Hg, Pb)	0.297	0.217	0.210	0.269
K	3.42	3.96	5.50	5.33
Minor	4.84	6.87	1.85	1.83
Na	20.7	20.20	25.7	27.9
Si	8.65	10.8	4.10	1.50
CO_3	11.38	8.62	24.5	23.7
Halides	0.867	1.45	1.57	2.12
NO_3	0.015	0.077	0.010	0.035
O_2	24.3	23.6	20.6	17.3
PO_4	5.67	7.73	0.28	0.32
SO_4	5.21	4.83	7.02	7.79

The target for process mass balance closure for the major elements (Al, Na, C, and Si) was +/-10% and +/- 30% for the balance of the elements. This standard was met for all components except for Ca and

Ce during CP1. This was likely due to the variability of Ca concentration in the coal and Ce analytical inaccuracies. The mass balance standard was met for all the elements during CP2.
Analysis of off-gas data collected from the CEMS and the EPA protocol grab samples during CP1 and CP2 indicates the production-scale process will meet all applicable environmental discharge limits. These include Maximum Achievable Control Technology (MACT) limits for metals, HCl/Cl_2, particulate matter, dioxins/furans, VOC’s, SVOC’s, THC, and CO, as well as the site discharge limits for NOx and SOx. A summary of the emissions data from CP1 and CP1 is shown in Table VI.

Table VI. Emissions Summary for CP1 and CP2

Pollutant	Concentration Corrected to 7% O_2	Percent of MACT Limit	Results and Comments
Radioactive Surrogates (Cs, Ce [for Pu])	Non-detectable	NA	• Removal efficiency >99.999% • No HEPA filters in test system
Low Volatility Metals (As, Be, Cr)	2 – 3 micrograms/dscm	~10%	• Meets MACT • Removal efficiency >99.998% • No Be in simulant
Semi-volatile Metals (Cd, Pb)	<1 microgram/dscm	<10%	• Meets MACT • Pb Removal Efficiency >99.999% • No Cd in simulant
Volatile Metals (Hg)	2 – 6 micrograms/dscm	25 – 75%	• Meets MACT • Hg removal efficiency ~99.999%
HCl/Cl2	0.6 – 8 ppm	3 –33%	• Meets MACT
Particulate Matter	0.3 – 2 mg/dscm	10 – 60%	• Meets MACT • No HEPA filters in test system
Dioxins/furans	0.01 to 0.02 nanograms/dscm	<10%	• Meets MACT
PCBs	5 – 10 nanograms/dscm	NA	• Most PCB congeners not detected • Dioxin-like coplanar PCBs not detected
VOCs (POHC was MCB)	Mostly non-detectable	<5%	• Meets MACT • No MCB detected • Removal efficiency ~99.9997% using detection limit values vs 99.99% per MACT
SVOCs	Mostly non-detectable	NA	• Two SVOCs detected, each only once near the detection limit
NOx	Typically <1000 ppm	NA	• One run was ~2,600 ppm • NOx destruction averaged ~98%
THC	<0.3 ppm	<3%	• Meets MACT
CO	10 – 60 ppm	10 – 60%	• Meets MACT
SOx	<60 ppm	NA	• One run was ~200 ppm

CONCLUSION

The ESTD demonstrated the capability of the integrated THOR® steam reforming process to convert SBW simulant in a variety of formulations, including heavy metals, undissolved solids, and organic contaminants, into a granular solid product in a safe, efficient, and sustainable manner. Gaseous emissions from the process were found to be within regulatory limits and the solid products generated displayed none of the characteristics that would preclude disposal at WIPP. System parameters critical to the design and operation of the full-scale IWTU facility were either developed or confirmed and a number of lessons-learned necessary to enhance the design of the major IWTU unit operations were developed and implemented in the detailed design of the IWTU facility.

REFERENCES

1. DOE/EIS-0287, Record of Decision for the Idaho High-Level Waste and Facilities Disposition Final Environmental Impact statement, December 2005.
2. C. M. JANTZEN, "Engineering Study of the Hanford Low Activity Waste (LAW) Steam Reforming Process (U)," WSRC, TR, 2002, 00317, Rev. 0, Savannah River Technology Center, July 12, 2002.
3. D. W. Marshall, N. R. Soelberg, K. M. Shaber, "THOR® Bench, Scale Steam Reforming Demonstration," INEEL/EXT, 03, 00437, Idaho National Engineering and Environmental Laboratory, May 2003. (Phase 1 Report)
4. C. M. Jantzen, "Disposition of Tank 48-H Organics by Fluidized Bed Steam Reforming (FBSR) (U)," WSRC, TR, 2003, 00352, Rev. 0, Savannah River Technology Center, September 18, 2003.
5. B. P. Mcgrail, et al., "Initial Suitability Evaluation of Steam, Reformed Low Activity Waste for Direct Land Disposal," PNWD, 3288, WTP, RPT, 097, Rev. 0, Battelle, Pacific Northwest Division, January 2003.
6. B. P. Mcgrail, "Laboratory Testing of Bulk Vitrified and Steam, Reformed Low, Activity Forms to Support a Preliminary Assessment for an Integrated Disposal Facility," PNNL, 14414, Pacific Northwest National Laboratory, September 2003.
7. F. M. Mann, "Risk Assessment Supporting the Decision on the Initial Selection of Supplemental ILAW Technologies," RPP, 17675, Rev. 0, CH2MHILL Hanford Group, Inc., September 29, 2003.
8. C. M. Jantzen, "Characterization and Performance of Fluidized Bed Steam Reforming (FBSR) Product as a Final Waste Form (U)," WSRC, MS, 2003, 00595, Revision 0, Savannah River National Laboratory.
9. N. R. Soelberg, D. W. Marshall, S. O. Bates, D. D. Taylor, "Phase 2 THOR® Steam Reforming Tests for Sodium, Bearing Waste Treatment," INEEL/EXT, 04, 01493, Idaho National Engineering and Environmental Laboratory, January 30, 2004.
10. B. P. Mcgrail, D. H. Bacon, R. J. Serne, K. M. Krupka, R. J. Puigh, R. Khaleel, and S. Finfrock, "Risk Assessment Supporting the Decision on the Initial Selection of Supplemental ILAW Technologies", F. M. Mann, CH2M Hill Hanford Group, Inc., Pacific Northwest National Laboratory and Fluor Federal Services, Inc., RPP, 17675, Rev. 0, September 2003.
11. "Pilot Plant Report for Treating Sodium-Bearing Waste Surrogates—Carbonate Flowsheet", Idaho Cleanup Project, Integrated Waste Treatment Unit, Project Number 28276, Document

Number RT-ESTD-PMR-001, Revision 0, Idaho Cleanup Project, THOR Treatment Technologies and Washington Group International, October 2006.

12. “Feed Compositions for the Sodium-Bearing Waste Treatment Process,” INEEL/EXT-2000-01378, Revision 4, June 2004.