ICP/CON-06-01162
PREPRINT

Steam Reforming Application For Treatment Of DOE Sodium Bearing Tank Wastes At Idaho National Laboratory For Idaho Cleanup Project

Waste Management 2006 Conference

J.B. Mason, K. Wolf, K. Ryan,
S. Roesener, M. Cowen, D. Schmoker,
P. Bacala, B. Landman

March 2006

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may not be made before publication, this preprint should not be cited or reproduced without permission of the author. This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, or any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use, or the results of such use, of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights. The views expressed in this paper are not necessarily those of the United States Government or the sponsoring agency.

The Idaho Cleanup Project
is operated for the
U.S. Department of Energy
by CH2M ◆ WG Idaho, LLC

Idaho
Cleanup
Project

Steam Reforming Application for Treatment of DOE Sodium Bearing Tank Wastes at Idaho National Laboratory for Idaho Cleanup Project

J.B. Mason, K. Wolf, K. Ryan, S. Roesener,
M. Cowen, D. Schmoker, and P. Bacala
THOR Treatment Technologies, LLC
106 Newberry St. SW, Aiken, SC 29801

B. Landman
CH2M WG Idaho, LLC
P. O. Box 1625, Idaho Falls, ID 83415

"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."

ABSTRACT

The patented THOR® steam reforming waste treatment technology has been selected as the technology of choice for treatment of Sodium Bearing Waste (SBW) at the Idaho National Laboratory (INL) for the Idaho Cleanup Project (ICP).

SBW is an acidic tank waste at the Idaho Nuclear Technology and Engineering Center (INTEC) at INL. It consists primarily of waste from decontamination activities and laboratory wastes. SBW contains high concentrations of nitric acid, alkali and aluminum nitrates, with minor amounts of many inorganic compounds including radionuclides, mainly cesium and strontium. The THOR® steam reforming process will convert the SBW tank waste feed into a dry, solid, granular product.

The THOR® technology was selected to treat SBW, in part, because it can provide flexible disposal options to accommodate the final disposition path selected for SBW. THOR® can produce a final end-product that will meet anticipated requirements for disposal as Remote-Handled TRU (RH-TRU) waste; and, with modifications, THOR® can also produce a final end-product that could be qualified for disposal as High Level Waste (HLW).

SBW treatment will be take place within the Integrated Waste Treatment Unit (IWTU), a new facility that will be located at the INTEC. This paper provides an overview of the THOR® process chemistry and process equipment being designed for the IWTU.

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 ICP, is a seven-year undertaking to perform the cleanup of 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

© 2006 THOR Treatment Technologies, LLC. All rights reserved.

other environmental remediation activities. Included in the Scope of Work (SOW) 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 RH-TRU, 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."[1]

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; 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 design and build a THOR® steam reforming waste treatment system for SBW (Figure 1 provides a drawing of the IWTU facility). The THOR® system being designed will produce a waste form suitable for disposal as RH-TRU. The remainder of this paper provides an overview of the THOR® system design for that preferred disposal path. If the DOE calls for disposal of the SBW as HLW, the THOR® system design would undergo several modifications to accommodate a HLW disposal path.

Fig.1. Integrated Waste Treatment Unit Housing the THOR® Steam Reforming Unit

---

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

© 2006 THOR Treatment Technologies, LLC. All rights reserved.

THOR® PROCESS OVERVIEW

SBW at INL consists of radioactive aqueous solutions with high concentrations of nitric acid, nitrates, alkali metals, aluminum, and a wide variety of other inorganic oxides. The THOR® steam reforming process destroys nitric acid, nitrates and organic materials present in the SBW, and produces a dry, solid product. The steam reforming process has been proven to efficiently handle, process, and immobilize the radionuclides, sodium, potassium, sulfate, chlorides, fluorides, and non-volatile heavy metals into a solid matrix [2, 3, 4, 5, 6, 7, 8, 9, 10]. In addition, the process converts nitric acid, nitrates, and nitrites directly to nitrogen gas in the steam reformers. Any organic material in the SBW 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 2.

The SBW tank-waste 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 first steam reformer, liquids are evaporated; the vast majority of organics, nitric acid, nitrates, and nitrites are destroyed; and the reactive chemicals in the waste feed are converted to a 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 (if present) to carbon dioxide and water vapor. The gases (mainly carbon dioxide 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 end-product, an alkali carbonate and aluminate solid, will meet requirements for shipment in the RH-72B shipping container. It is expected that the THOR® end-product will meet anticipated requirements for disposal as RH-TRU.

PROCESS CHEMISTRY

Nitrate Reduction to Nitrogen Gas

The steam reforming process technology has unparalleled performance for nitrate, nitrite and nitric acid reduction with the following demonstrated results:

- Residual nitrate and nitrite content in the reformed solid waste product is < 10 ppm
- Direct conversion of ~ 95% of nitrates, nitrites and nitric acid in waste feed to nitrogen gas
- Total NOx in off-gas from the reformers is < 500 ppm.

Several specific features and reactions have been incorporated into the steam reforming process to achieve the referenced results:

- Fluidized bed material has high surface area and high heat transfer capability
- High energy generation in the DMR evaporates and superheats the water in the typical waste feed
- Strongly reducing conditions are provided by the carbonaceous and metal-based reactants in the DMR and in the CRR

© 2006 THOR Treatment Technologies, LLC. All rights reserved.

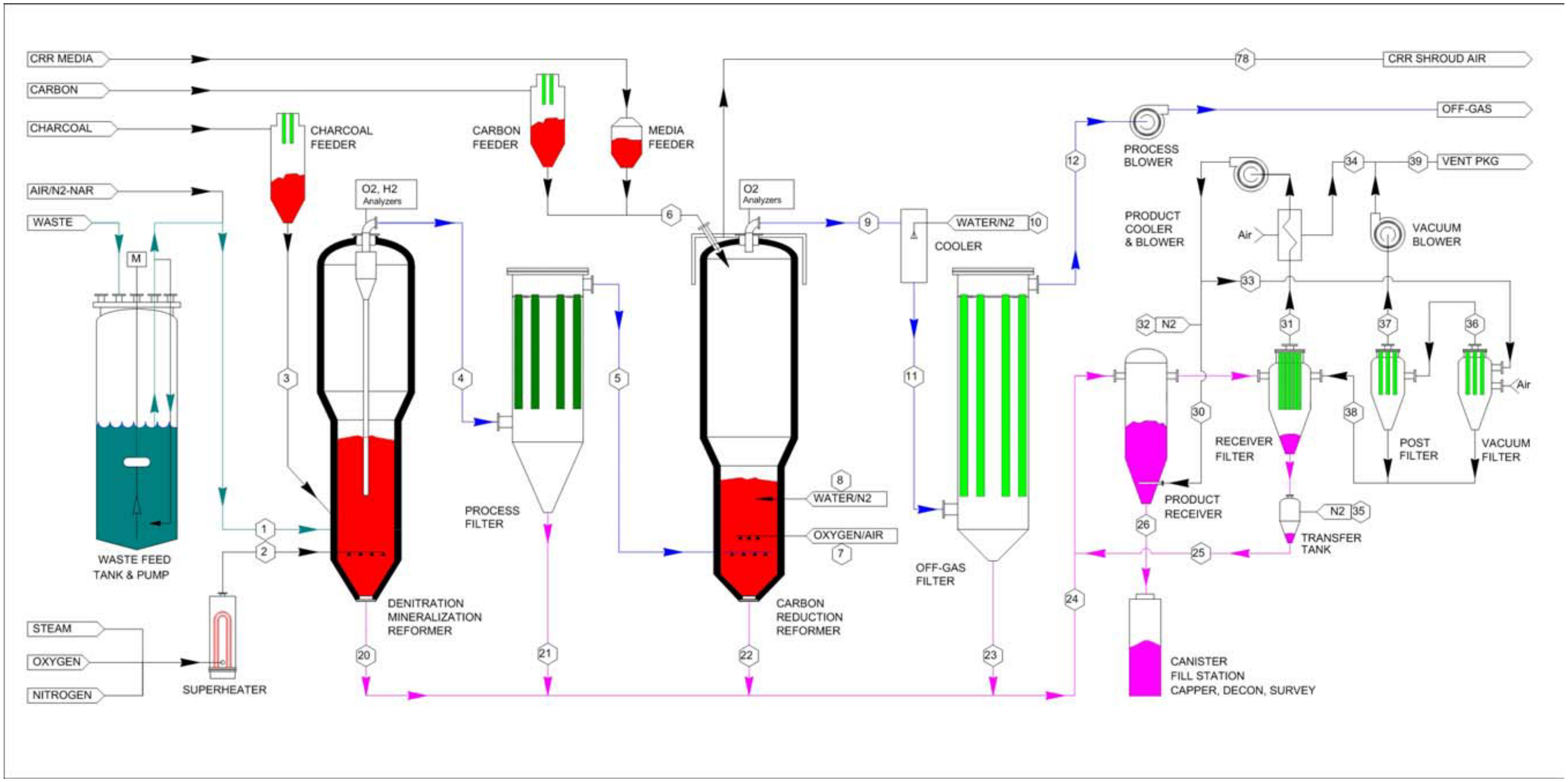

Fig. 2. THOR® Process Flow Diagram

- Near ambient pressure superheated steam generates carbon monoxide and hydrogen inside the bed from the reaction of steam with the carbon reductant(s).

The incoming waste feed to the DMR is atomized into small droplets that coat the fluidized mineral particles and are 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 oxide particles in the fluidized bed. The presence of excess carbon and metal oxides from the SBW results in the unparalleled performance for effective reduction of NOx with only trace levels of residual nitrates in the solid reformed product. Several of the possible reaction mechanisms whereby nitrites and nitrates are converted to nitrogen gas are shown below.

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

$NO_3 + 1C \rightarrow NO_2 + CO$

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

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

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

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

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

$H_2O + C \rightarrow H_2 + CO$

$2NO_3 + 6Fe \rightarrow N_2 + 6\ FeO$

$FeO + C \rightarrow Fe + CO$

Destruction of RCRA and TSCA Organics

Although SBW does not have significant amounts of organics (actual amounts are below detection limits), the steam reforming process will destroy any organics in the waste. This destruction occurs through non-incineration thermal treatment. The organics are initially volatized and steam reformed into carbon dioxide, carbon monoxide, hydrogen, and a small quantity of light hydrocarbons (generally less than 1,000 ppm with methane being the main constituent). These reduction reactions occur in the DMR.

The light hydrocarbons and the carbon monoxide and hydrogen gases generated from the steam reformation of carbon and organic materials 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.

The following typical reactions occur in the DMR:

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

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

$CO + H_2O \rightarrow CO_2 + H_2$

The following typical reactions occur in the CRR:

$CO + H_2O \rightarrow CO_2 + H_2$

© 2006 THOR Treatment Technologies, LLC. All rights reserved.

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

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

Alkali Metal Conversion to Mineral Form

The steam reforming process has the unique capability to convert alkali metals, Na and K, into solid minerals in the fluid bed. The presence of alkali metals in fluid beds has historically proven to be a serious operational problem as sodium and potassium form a variety of low melting point salts with common materials. These low melting point salts can combine to form eutectic mixtures that generally melt at much lower temperatures than the pure compounds. The presence of eutectic compounds in a fluid bed can result in the formation of bulk agglomerations as the melted salts tend to bind the fluidized media particles into larger and larger pieces.

The formation of bulk agglomerations can be addressed in one of two ways. First, the DMR can be operated at a lower temperature to prevent melting of salts in the bed. Second, the addition of selected inorganic co-reactants to a fluid bed can prevent the formation of low melting point eutectic compounds and allow operation of the DMR at temperatures up to 1,023°K (750°C). Certain inorganic co-reactants preferentially substitute for the typical low melting anions of the Na and K salts. The co-reactants are added in proportions needed to generate the desired higher melting point compound, and/or water-insoluble compounds. The co-reactants selected are determined from the chemical make-up of the waste feed to the process. Possible co-reactants include Ca, Mg, Al, Al-Si and P compounds that combine with alkali metals to form synthetic naturally occurring minerals listed below (Note: Only the main elemental constituents are shown for simplicity):

Nepheline, Na-Al-Si, or NAS

Nosean, Na-Al-Si-SO_4

Fairchildite, K-Ca-CO_3

Dawsonite, Na-Al-CO_3

Eitelite, Na-Mg-CO_3

Parantisite, Na-Ti-Si

Maricite, Na-Fe-PO_4

Buchwaldite, Na-Ca-PO_4

Bradleyite, Na-Mg-PO_4-CO_3

Na-PO_4, Na_2CO_3, Na-Al, Mg-PO_4, Na-Mg-PO_4, Ca-Si, Na-(Ca,Fe,Mg)-Si and other similar mineral variations into the hundreds.

For the ICP SBW processing effort, the bed will be operated at lower bed temperatures, and there is a possibility that minor levels of mineralizing co-reactants may be added to combine with certain SBW constituents. The alkali metals present in the SBW will form mainly carbonates and aluminates and the inorganic constituents will form metal oxides and spinels with the iron in the SBW. The carbonates are made from the adsorption of carbon dioxide (from the steam reforming reactions in the DMR), and aluminates are formed with the alkali metals and aluminum, respectively, from the SBW. The combined SBW inorganic minerals are largely

© 2006 THOR Treatment Technologies, LLC. All rights reserved.

carbonates and will have melting points in the 1,023°K to 1,123°K (750°C to 850°C) range. Therefore, in order to reliably convert SBW constituents into carbonates, the DMR will be operated at no higher than 953°K (680 °C) to prevent the carbonates and other salts from partially melting or becoming sticky in the DMR.

Immobilization of Hazardous Metals

The strong reducing environment in the DMR converts certain hazardous metals to non-hazardous valence states (e.g., Cr^{VI} to Cr^{III}).

If mercury is present in the waste feed, it will not be bound-up in the solid product, but will be volatized and converted to elemental mercury in the reformers. The off-gas from the DMR and the CRR process units will be treated in a mercury adsorber using a Granular Activated Carbon (GAC) bed prior to venting to the atmosphere to remove mercury from the process off-gas.

PROCESS EQUIPMENT DESCRIPTION

Denitration and Mineralization Reformer (DMR)

The DMR is operated at near ambient pressure and will maintain an average bed temperature of approximately 893°K (620°C) when producing a carbonate-rich product. Superheated steam, enriched with oxygen, is injected into the bottom of the DMR. The low-pressure steam fluidizes the granular carbonate product particle bed materials in the vessel by means of pipe distributors located above the bottom head of the vessel. These distributors may be removed for cleaning or replacement, if required, without entry into the vessel.

The waste is fed into the DMR through injection ports just above the fluid gas (oxygen enriched steam) distributor. The waste feed is atomized into the vessel, and the water in the waste feed is instantly evaporated and superheated to the bed temperature by the large mass of hot, fluidized product solids. The resulting dried waste solids quickly heat to reaction temperatures. Any organics in the feed are volatized and pyrolyzed upon contact with the hot bed solids. A cyclone gas/solid separation device is installed in the top of the DMR. This device allows the process gases to flow from the DMR to the CRR, and sends larger solids back to the fluidized bed portion of the vessel. The DMR is operated under reducing conditions throughout most of the bed and the entire freeboard zone. Granular carbon is fed to the DMR to provide the nitrate reducing process conditions and to provide the energy required to maintain the DMR at the desired operating temperatures. One nozzle is provided for addition of solid carbon and additives. Accumulated product granules are removed from the bottom of the DMR and are pneumatically transferred to the product receivers where solids are packaged into RH-72B canisters. The DMR is constructed of qualified high-temperature alloy metals.

SBW Process Filter

The process gas from the DMR flows to the process filter, which captures any carbonate-rich DMR product fines carried over in the process gas. The carbonate fines could cause agglomeration in the CRR as the melting point of the carbonate-rich SBW mineral product have a melting point range of 1,023°K to 1,123°K (750°C to 850°C). The filter will operate at 323°K to 373°K (50°C to100°C) below the DMR temperature, and is constructed of qualified high-

© 2006 THOR Treatment Technologies, LLC. All rights reserved.

temperature alloy metals. The process filter elements are a sintered metal type that will efficiently remove particles from the DMR process gases. The filtered solids will be pneumatically transferred to the product receivers where the fines are combined with the granular solids removed from the bottom of the DMR.

Carbon Reduction Reformer

The process gases from the DMR flow through the process gas filter to the fluid gas inlet distributors of the CRR located near the bottom of the CRR vessel. Auto-thermal gas (oxygen) is fed into the CRR directly above the process gas inlet distributors. The CRR operates under reducing and oxidizing conditions. A unique aspect of the CRR is that the bottom of the fluidized bed media produces a strongly reducing environment where residual NOx from the DMR is further converted to nitrogen gas by the presence of the reducing gases in the process gas stream used to fluidize the bottom of the CRR and addition of carbon to the CRR bed. Oxygen is injected into the upper portion of the bed to produce an oxidizing region where the organic materials are destroyed, and the hydrogen and carbon monoxide produced in the DMR are converted to carbon dioxide and water with very high efficiency. Because the CRR has no open-flame combustion, the temperatures throughout the fluidized bed are uniform and only minimal levels of thermal NOx are generated. The DMR and CRR reformers serve to essentially eliminate NOx emissions from the process with ~ 95% efficiency.

The CRR bed media comprises an alumina/clay granular media that forms a semi-permanent fluidized bed. Because essentially no solids are input with the DMR process gases, the only increase in bed solids is from planned additions of media and carbon from the additive feeder system. The media is added only to make-up for bed media particle attrition and carryover (elutriation) of bed media particles to the off-gas treatment system. It is expected that no CRR bed material will be drained during normal operation for the duration of the SBW treatment campaign. A solids drain is provided on the bottom of the CRR to provide remote drain capability in the event maintenance must be performed on the fluidizing or oxygen gas distributor located in the bottom of the CRR.

Under normal operating conditions, the CRR temperature is 1,273°K (1,000°C) and operates under vacuum at the top of the bed. Off-gas from the CRR enters the off-gas treatment system where a water spray cooler quickly cools the hot off-gas to 423°K to 473°K (150°C to 200°C). All of the water is evaporated and is carried with the cooled off-gas as water vapor to the Off-Gas System.

OFF-GAS SYSTEM

Process Vent High Efficiency Particulate Absolute (HEPA) Filters

The process off-gas HEPA Filters are designed to filter process gases from the SBW treatment. Filtered gases then flow to the mercury adsorber.

Mercury Adsorber

The Mercury Adsorber is a dual bed GAC unit designed to remove elemental mercury present in the off-gas. Dual beds are provided so that the GAC media can be replaced for new media when the first bed becomes depleted. The spent carbon bed will be disposed of in accordance with

© 2006 THOR Treatment Technologies, LLC. All rights reserved.

regulations, and a new charge of carbon will be loaded as required to maintain removal efficiency. The off-gas from the mercury adsorber will be monitored, as required by the anticipated air permit.

Continuous Emissions Monitor System (CEMS)

Off gas samples will be taken, the gas sample stream will be analyzed in the CEMS, and the sample will be discharged to the stack. The CEMS unit will continuously monitor for carbon monoxide or total hydrocarbon, except during calibration and routine maintenance work. The off-gas from the THOR® steam reforming process is expected to meet MACT standards.

Building Ventilation System

The process cells and building ventilation flows are filtered by the Building HEPA Filters. To change filter elements, one of the banks of filters is isolated and the filter elements changed out. The discharge from the Ventilation Blowers is vented to the atmosphere through the monitored stack. The discharge air from the Ventilation Blowers is mixed with the process gases and then discharged to the stack where the gases are monitored with a Radiation Monitor.

SBW Product Receivers/Coolers

The Product Receivers/Coolers receive granular and fine particulate solids from the SBW treatment systems. The Product Receiver/Cooler Blower recirculates nitrogen into the receivers to cool the product. The temperature of the product is monitored. Product accumulates in the bottom of the Product Receiver/Cooler. The accumulated solids may be sampled and then transferred by gravity to the RH-72B canister.

The vented nitrogen from the Product Receivers/Coolers flows to the Product Receiver Vent Filter, Vacuum Filter and the Post-Filter. The three product system filters are provided with sintered metal filter media designed to remove > 99.9 % of all solids greater than 2.0 micron in the vent stream.

Canister Fill Station

The Canister Fill Station consists of three parallel trains of equipment to fill, cap, and decontaminate canisters for storage of the processed waste. Each of the three parallel trains consists of the following: a removable shield plug to receive canisters into the cell, a canister fill station transfer cart to move the canisters through the filling and capping process, a canister sealing chute to prevent leakage to the outside of the canister, a canister capping station to close/seal the canister, and a canister swipe and decontamination system to clean any product contamination off the canister. All operations are remote and in-cell.

Canister Transfer and Storage

Filled and surveyed canisters are transferred from the fill station cells to concrete storage vaults by means of a heavily shielded, rail mounted, transfer bell and carrier crane. Each vault holds 16 canisters. Once the storage vault is loaded with 16 canisters, the concrete lid is lowered into position, and the loaded and closed storage vault is transferred to an interim storage building.

© 2006 THOR Treatment Technologies, LLC. All rights reserved.

When the canisters are to be shipped, the storage vault is returned to the process building and the transfer bell transfers each canister into an awaiting RH-72B cask. The loaded cask is closed, surveyed and released from the IWTU for shipment.

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.

© 2006 THOR Treatment Technologies, LLC. All rights reserved.