

STEAM REFORMING TECHNOLOGY FOR DENITRATION AND IMMOBILIZATION OF DOE TANK WASTES

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ABSTRACT

THOR Treatment Technologies, LLC (TTT) is a joint venture of Studsvik, Inc. (Studsvik) and Westinghouse Government Environmental Services Company, LLC formed to further develop, market, and deploy Studsvik's patented THORsm non-incineration, steam reforming waste treatment technology. This paper provides an overview and update of the THORsm technology as applied to the denitration and conversion of Department of Energy (DOE) tank wastes to an immobilized mineral waste form. Results of recent fluidized bed demonstration tests using non-radioactive surrogates for Hanford Low Activity Waste (LAW) and Idaho National Engineering and Environmental Laboratory (INEEL) Sodium Bearing Waste (SBW) are discussed. Ongoing work to produce a monolithic waste form and TTT's modular, transportable facility concept are also discussed.

Using the THORsm steam reforming technology to treat nitrate containing tank wastes could significantly benefit the DOE by accelerating waste processing schedules, reducing capital and life cycle costs, reducing processing and programmatic risks, and positioning the DOE to meet or exceed its stakeholder commitments for tank closure. As a specific application, use of the THORsm technology could facilitate processing of over 75% of Hanford tank wastes without the use of vitrification, yielding substantial life cycle cost savings and a final waste form that is superior to borosilicate glass in leach resistance and product durability.

INTRODUCTION

Tank wastes are composed of a wide range of radioactive salt cakes, sludges, and supernatant solutions that contain high concentrations of alkali metals, aluminum, nitrates, nitrites, nitric acid or hydroxides, and sulfates, with significant concentrations of chlorides, fluorides, heavy metals, radionuclides, and organics. The THORsm steam reforming process has been proven to efficiently immobilize the radionuclides, alkali metals, sulfate, chlorides, fluorides, and non-volatile heavy metals into a stable, water insoluble mineral matrix.

In the THORsm process (See Figures 1 and 2), waste feed, superheated steam, and co-reactants are introduced into a dual fluidized bed steam reformer system where liquids are evaporated; organics are destroyed; and reactive chemicals, radionuclides, and non-volatile heavy metals are converted into a mineralized solid waste product. The first bed, the Denitration and Mineralization Reformer (DMR) provides a strongly reducing environment, large surface area, and adequate residence time for the waste to fully and efficiently react. Reductants, typically carbon and an optional iron-based catalyst, are used to convert nitrates and nitrites directly to nitrogen gas. Clay or other inorganic co-reactants are added to the waste feed to convert the radionuclides, alkali metals, sulfate, chloride, fluoride, phosphates, and non-volatile heavy metals into a solid mineral product. Different co-reactants are used to produce different mineral

products. For example, an aluminosilicate clay co-reactant produces a product consisting primarily of water insoluble alkali aluminosilicate minerals. The DMR operates safely at near ambient pressure and moderate temperatures (600–750°C).

The second fluidized bed reformer, called the Carbon Reduction Reformer (CRR), accepts the process gases and entrained fines from the DMR. The CRR operates in an oxidizing mode at 800°C to 1000°C and converts carbon fines and residual organic gases to carbon dioxide and water vapor. The dual reformer process destroys all organics in the waste feed, including RCRA and TSCA constituents. The off-gas from the CRR, mostly nitrogen, water vapor, and carbon dioxide, is cooled, filtered, and monitored prior to released to the atmosphere as a Maximum Achievable Control Technology (MACT) compliant emission stream.

Alkali aluminosilicate minerals are the preferred final waste forms for applications that require waste immobilization without vitrification. For disposal sites that require immobilized monolithic solids, a monolithic alkali aluminosilicate waste form can be produced. For wastes that must be vitrified, the preferred product is a sodium carbonate based granular solid, which can be readily vitrified in joule-heated melters. The sodium carbonate product can be provided as the granular solid or as an aqueous solution/slurry for feed to a vitrification facility. The granular solid alkali aluminosilicate or sodium carbonate waste forms are suitable for direct disposal of transuranic (TRU) wastes at the Waste Isolation Pilot Plant (WIPP).

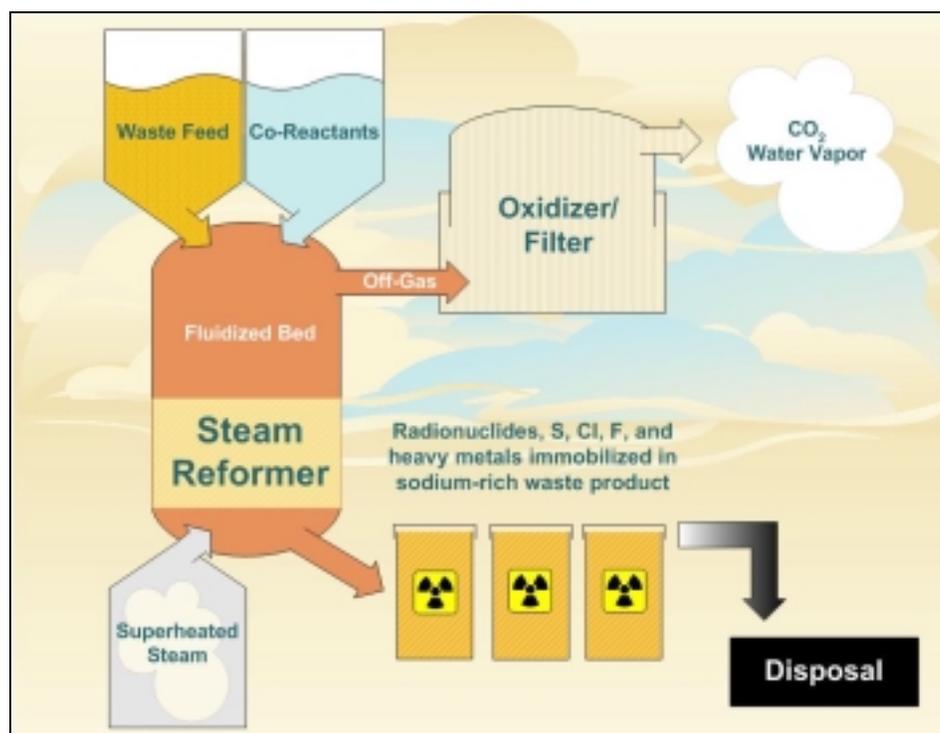


Fig. 1. Simplified Flow Diagram of the THORsm Fluidized Bed Steam Reforming Process.

PROCESS TECHNOLOGY OVERVIEW

The following sections provide a more detailed discussion of process operation and chemistry; reduction of nitrates to nitrogen; conversion of alkali metals to leach resistant mineral forms; immobilization of radionuclides; immobilization of hazardous metals; destruction of organics, including RCRA and TSCA species; neutralization of acid gases; removal of solids carryover from the DMR; and finally, secondary process waste generation, emissions, and discharges. A simplified flow diagram of the steam reforming process is provided in Figure 1. A more detailed process flow diagram is provided in Figure 2.

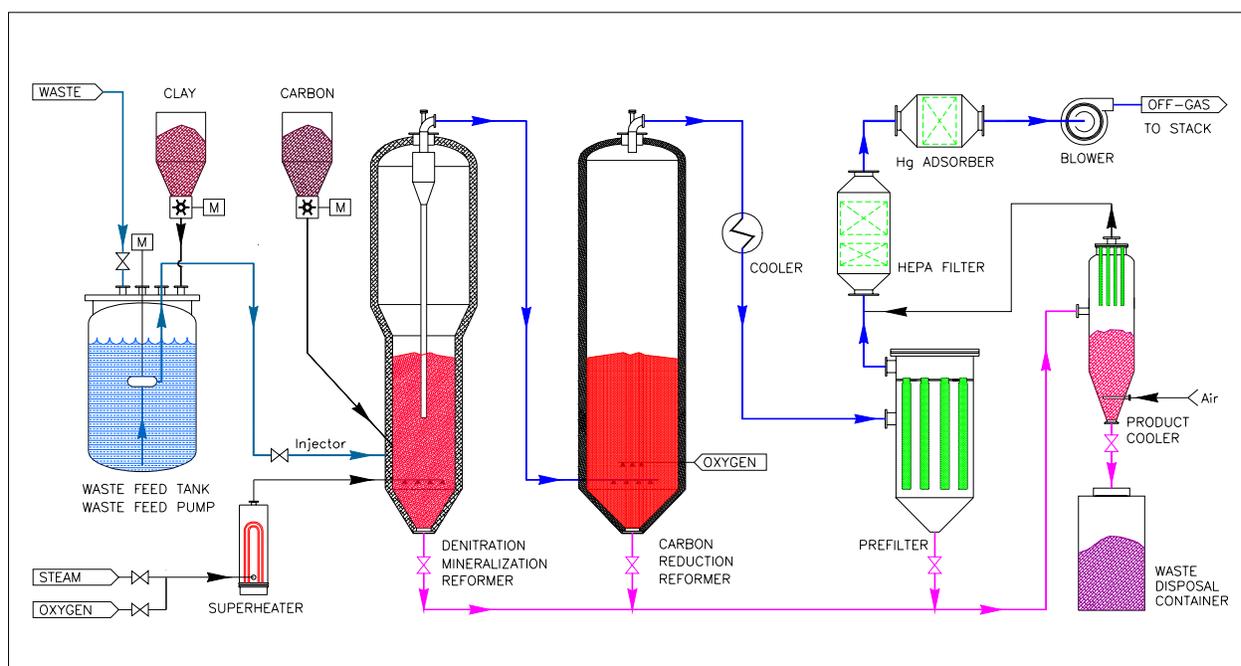


Fig. 2. Process Flow Diagram of the THORSM Fluidized Bed Steam Reforming Process

PROCESS OPERATION AND CHEMISTRY OF THE STEAM REFORMERS

In the DMR, the granular bed material is fluidized with superheated steam at near-ambient pressure. The tank waste is injected directly into the fluidized bed by means of a positive displacement pump. If an immobilized mineral product is desired, a co-reactant such as aluminosilicate clay is slurried with the waste feed prior to injection. The feed mixture is sprayed into the bed via a special atomizing nozzle. Solid reductants, such as granular carbon and an optional iron oxide catalyst, are added directly to the DMR bed. The carbon is oxidized in the bed by the superheated steam and oxygen, creating a strongly reducing environment and providing heat energy to drive the steam reforming reactions. The DMR is operated under these strongly reducing conditions and at temperatures of 600°C to 750°C to facilitate the conversion of nitrates and nitrites to nitrogen gas with minimal production of NO_x. These high-temperature reducing (oxygen deficient) conditions also evaporate all liquids and decompose complex organic compounds into simple organics molecules. These reactions leave behind the non-volatile feed constituents, which are converted into mineralized solids containing >99% of the

radionuclides, non-volatile heavy metals, alkali metals, aluminum, and most other inorganic elements present in the waste feed. Halogens and sulfur/sulfates are also mineralized with >95% incorporated into the mineral matrix. Certain hazardous metals are reduced to a non-hazardous valence state (e.g., Cr (VI) is reduced to Cr (III)) and are chemically bound in the solid product. Mercury, if present in the waste feed, is volatilized in the DMR, but is removed with >99% efficiency by a Granulated Activated Carbon (GAC) bed in the off-gas system.

The process gases from the DMR flow to the CRR, which is operated under oxidizing conditions by injection of oxygen into the middle zone of the fluidized bed. The DMR process gases pass through the CRR oxidizing zone, which converts residual carbon reductant and organic gases, hydrogen, and carbon monoxide into carbon dioxide and water vapor. The DMR process gases also contain trace amounts of Cl, F, and S acid gases, which are converted into non-volatile calcium minerals by reaction with calcium additives in the CRR bed. The CRR reformer operates under slight vacuum at 800°C to 1000°C.

The DMR can be electrically heated (small units) or operated in an auto-thermal mode, whereby all thermal energy needs are supplied by the incoming superheated steam and by the oxidation of organics from the waste and carbon reductants. For production scale units, auto-thermal steam reforming is the preferred mode of operation.

NITRATE REDUCTION TO NITROGEN GAS

Substantial research has been performed over the past 50 years to develop an efficient nitrate destruction process. Studsvik developed the THORsm steam reforming technology to provide unparalleled performance in nitrate destruction, with the following demonstrated results:

- Direct conversion of >96% of nitrates and nitrites in the waste feed to nitrogen gas [1,2,8],
- Nitrate destruction efficiencies in solid products of >99.9% [8], with residual nitrate content in the reformed solid waste product <10 ppm [1,2], and
- Total NO_x in off-gas from the reformers <300 ppm (dry basis) [1,2,8].

This exceptional process performance requires that several specific features and reactions be incorporated into a single step thermal process: 1) fluidized bed material with high surface area and high heat transfer capability, 2) high energy generation to evaporate and superheat the water in the typical aqueous waste feed, 3) a strongly reducing environment that is provided by the carbon and metal-based reductants, 4) superheated steam that generates carbon monoxide and hydrogen inside the bed from the reaction of steam with the carbon reductant(s), and 5) co-reactant(s) that convert the alkali metals (e.g., Na and K) into higher melting point mineral compounds to prevent formation of low melting point eutectic salts and unwanted bulk agglomerations in the fluidized bed.

The fluidized bed particles can consist of ceramic media (e.g., alumina start-up bed) and/or reformed granular product minerals. The incoming waste feed coats or impacts the fluidized particles and is instantly dried. The large active surface of dried nitrates readily reacts with the hot carbon reductant particles, low levels of carbon monoxide and hydrogen gases, and the reduced metal particles in the fluidized bed to form nitrogen gas.

ALKALI METAL CONVERSION TO LEACH-RESISTANT MINERAL FORMS

The THORsm steam reforming process has the unique capability to incorporate alkali metals, as well as most other non-volatile inorganic elements, into stable, leach resistant mineral matrices. The addition of selected inorganic co-reactants to the reducing fluidized bed prevents the formation of low melting point eutectic compounds, which could otherwise cause bed agglomerations. For example, certain co-reactants preferentially react with the low melting point anions of Na and K salts. The preferred co-reactants include aluminosilicate clay and Ca and Al compounds that combine with the alkali metals to form synthetic naturally occurring minerals. The typical minerals formed by the addition of aluminosilicate clay to the waste feed are alkali aluminosilicates, e.g.:

- $\text{Na} + \text{Al}_2\text{O}_3\text{-2SiO}_2 \text{ (Clay)} = \text{NaAlSiO}_4$ (Nepheline)
- $\text{Na} + \text{SO}_4 + \text{Al}_2\text{O}_3\text{-2SiO}_2 \text{ (Clay)} = \text{Na}_6 [\text{Al}_6 \text{Si}_6 \text{O}_{24}] \cdot (\text{Na}_2\text{SO}_4)$ (Nosean)
- $\text{Na} + \text{Cl} + \text{Al}_2\text{O}_3\text{-2SiO}_2 \text{ (Clay)} = \text{Na}_6 [\text{Al}_6 \text{Si}_6 \text{O}_{24}] \cdot (2\text{NaCl})$ (Sodalite)

K may partially substitute for Na in the above mineral structures.

In addition to forming stable minerals that do not melt at typical fluidized bed operating temperatures, these compounds have ring and cage-like structures that capture and chemically bind the non-volatile inorganic constituents of the waste feed into water insoluble, leach-resistant mineral matrices [1,2,4,5,6,7]. Elements that have been shown to bind into the mineral matrices include: Na, K, Al, Ca, Mg, S, Fe, Mn, Zn, Mo, Si, Cl, F, Br, B, Be, Cs, Sr, and Re (as a surrogate for Tc) [1,2,4,7,8].

If a clay co-reactant is not used in the process, the resultant waste product is a carbonate based solid, e.g.:

- $\text{Na} + \text{CO}_2 = \text{Na}_2\text{CO}_3$ (Sodium Carbonate)

Most sodium and potassium compounds, like sodium carbonate, are water-soluble and may require further stabilization (e.g., vitrification) prior to disposal to prevent water leaching of the product. For this reason, the preferred products are the water-insoluble species such as Nepheline, Nosean, and Sodalite. These compounds have demonstrated Toxicity Characteristic Leaching Procedure (TCLP) leaching rates that are substantially lower than the Land Disposal Restriction (LDR) Universal Treatment Standard (UTS) limits for heavy metals [1,8].

IMMOBILIZATION OF RADIONUCLIDES

Years of experience in production scale operations and testing have shown that >99.8% of radionuclide species in the process feed are immobilized in the mineralized waste form. This degree of radionuclide capture has been demonstrated in the Studsvik commercial plant in Erwin,

Tennessee and with non-radioactive surrogates in pilot plant demonstrations for the processing of DOE LAW and SBW.

In the pilot plant demonstrations, non-radioactive Cs and Re (as surrogates for Cs¹³⁷ and Tc⁹⁹, respectively) were added to the waste feed solution to determine the capture efficiency of the corresponding radioactive species. Essentially complete retention (>99%) of the Cs and Re in the product solids was demonstrated [1,2,8]. Additionally, when subjected to the Product Consistency Test (PCT), single pass flow through (SPFT) test, and pressurized unsaturated flow (PUF) test, the alkali aluminosilicate product produced in the first LAW pilot plant demonstration exhibited Cs and Re releases less than those observed for borosilicate glass waste forms [1,4,5].

IMMOBILIZATION OF HAZARDOUS METALS

The strong reducing environment in the DMR converts certain hazardous heavy metals to non-hazardous valence states. For example, Cr(VI) is reduced to Cr(III) and is incorporated into the alkali aluminosilicate product. The other nonvolatile hazardous metals (e.g., Pb) are also chemically bound up in the solid product [8]. The solid product has been shown to pass the TCLP, easily meeting the LDR UTS limits for leachability by a factor of 10 to 100 for all hazardous metal species [1,8].

Mercury is quantitatively volatilized in the DMR and passes through the off-gas system to sulfur impregnated Granular Activated Carbon (GAC) beds downstream of the HEPA filters, where it is absorbed. Mercury removal efficiencies of >99.9% have been demonstrated [8].

DESTRUCTION OF RCRA AND TSCA ORGANICS

The THORsm steam reforming process destroys organics in the wastes, including any Resource Conservation and Recovery Act (RCRA) and Toxic Substance Control Act (TSCA) organic constituents. Specifically, the THORsm non-incineration thermal treatment process destroys RCRA organic waste codes D018 through D043 and F001 through F005 and TSCA-listed PCBs.

The organics are initially volatilized and steam reformed in the DMR into carbon dioxide, carbon monoxide, hydrogen, and a small quantity of light hydrocarbons, such as methane and ethylene [1]. These light hydrocarbons, as well as the carbon monoxide and hydrogen, are oxidized in the CRR to carbon dioxide and water vapor by the addition of oxygen to the middle zone of the CRR bed.

DOE has studied the potential formation of dioxin and furan compounds in a steam reforming process. The results of this work (DOE Contract No. DE-AR21-95MC32091 with ThermoChem, 1995) confirm that dioxins and furans are not generated in the steam reformer and typical off-gas systems. Indeed, any dioxins or furans in the waste feed are destroyed in the reformer systems.

NEUTRALIZATION OF ACID GASES AND REMOVAL OF SOLIDS CARRYOVER

Testing on Hanford LAW and INEEL SBW waste feed surrogates has shown that, on a mass basis, the vast majority of the sulfur compounds, fluorides, and chlorides in the waste feed react in the DMR with the clay co-reactant and become an integral part of the final solid waste product crystalline structure. A small percentage of the S, Cl, and F in the incoming waste feed forms volatile acid gases, which pass out of the DMR [1,2,8] and are largely absorbed on the Ca-rich bed in the CRR, forming such compounds as CaF_2 and CaCl_2 .

A filter removes and collects the fine particulates that carry over from the CRR for packaging with the solid product from the reformers. When a clay mineralizing co-reactant is used, the majority of the solid product comprises granular alkali aluminosilicate minerals removed from the bottom drains of the DMR and CRR.

SECONDARY WASTE GENERATION, EMISSIONS, AND DISCHARGES

A significant benefit of the THORsm steam reforming process is that it produces zero liquid releases. A production scale THORsm steam reforming plant has been operated by Studsvik in Erwin, Tennessee for the processing of low-level radioactive waste for over five years, with no release of liquids. All water is released as water vapor out the monitored ventilation stack. All organics are processed through the reformer process system and are converted to carbon dioxide and water vapor with a Destruction and Removal Efficiency (DRE) exceeding 99.99%.

The emissions of SO_x , HCl, HF, NO_x and other regulated pollutants are estimated in Table I. The emissions data presented in Table I represent actual readings from the Erwin plant's Continuous Emissions Monitoring System (CEMS) and correlations based on CEMS data from bench-scale and pilot-scale demonstration programs [1,2,8].

Table I. Discharges and Emissions from a Production-Scale THORsm Steam Reforming Process for Tank Wastes.

Material	Discharge/Emission
SO _x	<10 ppm in off-gas at stack
NO _x :	
• NO ₂	<100 ppm in off-gas at stack
• NO	<55 ppm in off-gas at stack
• N ₂ O, Others	<25 ppm in off-gas at stack
HCl	<10 ppm in off-gas at stack
HF	<2 ppm in off-gas at stack
CO	<20 ppm in off-gas at stack
Radionuclides:	
• Tritium	Tritium is converted to water vapor and is released up the monitored stack. An optional off-gas condenser can be provided to condense water and discharge water and tritium to groundwater, if required.
• Carbon ¹⁴	Carbon ¹⁴ is converted to carbon dioxide and is released up the monitored stack.
• Iodine	Iodine will be released up the stack unless absorption media is placed downstream of the HEPA filter to remove iodine from the off-gas.
• Other	>99.99% retained in the solid product; balance will be removed on HEPA filters (DF>10 ⁸)
Mercury	Mercury is removed from the off-gas by means of absorption media downstream of HEPA filters. Demonstrated mercury removal is >99.9% [8].
H ₂ O	Water is evaporated and discharged through the plant stack as water vapor. Process has zero-liquid releases.

COMMERCIAL RADIOACTIVE WASTE PROCESSING EXPERIENCE

The Studsvik Processing Facility (SPF) located in Erwin, Tennessee has been in commercial operation processing low-level radioactive waste (LLW) for over five years. The SPF has the capability to safely and efficiently receive and process a wide variety of solid and liquid LLW streams including: ion exchange resins (IER), charcoal, graphite, sludge, oils, solvents, plastics, paper, wood, and cleaning solutions with contact radiation levels of up to 400 R/hr. The licensed and heavily shielded SPF can receive and process liquid and solid LLW with high water and/or organic content at feed rates of over 1000 lb/hr.

The SPF employs the THORsm steam reforming technology. The THORsm technology is suitable for processing hazardous, mixed, and dry active waste (DAW) LLW with appropriate licensing and waste feed modifications. The final reformed residue product comprises a non-dispersible, granular solid suitable for long-term storage or direct burial in a qualified container.

Operations have demonstrated consistent, safe, reliable, operating characteristics with volume reductions up to 15:1 and mass reductions up to 10:1 when processing depleted ion exchange resins, with over 99.8% of all radionuclides in the waste feed incorporated into the final solid product. Over 165,000 cu ft of LLW ion exchange resin, oils, aqueous liquids, granular carbon, and over 10,000 cu ft of LLW paper, clothing, and plastics have been successfully processed for commercial nuclear power plant customers since commencement of commercial operation in July 1999. A description of the SPF is available on the Internet. Search for “Studsvik Processing Facility” or visit the Studsvik website.

DEMONSTRATION PROGRAM EXPERIENCE

Studsvik developed the THORsm steam reforming process over a period of several years, conducting the initial proof-of-concept demonstration for the treatment of nitrate liquid waste in 1997. This demonstration was conducted in concert with the process qualification runs for the SPF commercial plant. Since that time, several additional bench-scale and pilot-scale test programs have been performed to qualify and optimize the steam reforming process. The processing of simulated LAW, SBW, and Savannah River Site (SRS) Tank 48 nitrate tank wastes into carbonate and mineralized waste forms has been demonstrated. Eight separate demonstration programs have been conducted to date for the treatment of hazardous and radioactive nitrate liquid wastes using the THORsm technology. These are summarized in Table II.

ONGOING WORK WITH THE THORSM MINERALIZED WASTE FORM

TTT continues to pursue new ways to make the THORsm technology more useful for the treatment and disposition of DOE tank wastes. One way TTT is doing this is through the production of a monolithic final waste form that is both chemically and physically immobile. The basic steam reformer product is a granular mineral solid, which is chemically immobile in that it is not water soluble or leachable. For some applications, however, a monolithic waste form is favored, such that dispersibility is not an issue. At this writing, tests are in progress to produce monolithic waste forms from the SBW and LAW fluidized bed steam reformer (FBSR) products produced during the 2004 pilot plant work at Science Applications International Corporation's (SAIC) STAR Center, located in Idaho Falls, Idaho. Results from these tests will soon be available.

Table II. Demonstration Tests of the THORsm Technology for the Treatment of Nitrate Containing Liquid Wastes.

<i>Location Timeframe</i>	<i>Purpose/Conditions</i>	<i>Simulant Used</i>	<i>Reformer Equipment</i>	<i>Results</i>
Hazen Research, Golden, CO 1997	Initial proof-of-concept demonstration for the processing of liquid waste in an FBSR. Simulant was processed with sugar and carbon reductants and an iron oxide catalyst. The system was operated at ~725°C.	5.2 M NaNO ₃	6-inch FBSR	The FBSR performed well, producing a solid granular carbonate product. NO _x emissions were <100 ppm (dry basis) for the majority of the run.
SAIC STAR Center, Idaho Falls, ID 08/2000	Scoping study for the processing of SBW. Main simulant processed was a simplified SBW recipe. Sugar and carbon were used as reductants. Operating temperature was 600°C to 640°C.	Simplified SBW	3-inch FBSR	A finely divided carbonate product was produced. NO _x reduction was qualitatively observed, but was significant. The process was found to be viable and additional testing was recommended.
Hazen Research, Golden, CO 11/2001	Demonstration of the processing of LAW. Used carbon and sugar reductants and an iron oxide catalyst. Also used a clay additive for some of the operations. Non-radioactive Cs and Re (as surrogates for Cs-137 and Tc-99) were added to the waste simulant. The system was operated at ~725°C.	Hanford LAW: AN-107	6-inch FBSR	Successfully produced a mineralized alkali aluminosilicate product, predominantly Nosean and Nepheline, using a clay additive. Produced a carbonate product without the clay. The alkali aluminosilicate product passed TCLP. PCT, pressurized unsaturated flow (PUF), and single pass flow through (SPFT) tests showed the product to have durability comparable or superior to LAW borosilicate glass [1,4,5]. Greater than 99% of the radioactive surrogate elements and non-volatile heavy metals were captured in the solid waste products. NO _x destruction was ~99%.

Table II. Demonstration Tests of the THORsm Technology for the Treatment of Nitrate Containing Liquid Wastes (cont.).

<i>Location Timeframe</i>	<i>Purpose/Conditions</i>	<i>Simulant Used</i>	<i>Reformer Equipment</i>	<i>Results</i>
SAIC STAR Center, Idaho Falls, ID 01/2003	Phase 1 demonstration of the processing of SBW. Sugar and carbon reductants were employed in varying ratios. Iron oxide catalyst was also used. Non-radioactive Cs and Re (as surrogates for Cs-137 and Tc-99) were added to the waste simulant. The system operated at 675°C to 725°C.	INEEL SBW	6-inch FBSR	Successfully produced a granular carbonate product in over 100 hours of continuous operation. Greater than 99% of surrogate radioactive elements and non-volatile heavy metals were captured in the solid waste product. Hg was captured in a GAC bed in the off-gas system. NO _x destruction was >98%.
SAIC STAR Center, Idaho Falls, ID 09/2003	Demonstration of the treatment of the SRS Tank 48H waste solution. Key goals were destruction of nitrates, nitrites, benzene, and tetraphenylborate (TPB) to facilitate vitrification in Defense Waste Processing Facility (DWPF). Test conditions were established through experimental laboratory work at Savannah River National Laboratory (SRNL).	SRS Tank 48	6-inch FBSR	Successfully produced sodium carbonate solid waste form suitable for treatment at DWPF. Demonstrated >99% destruction of nitrates, nitrites, benzene, and TPB.
SAIC STAR Center, Idaho Falls, ID 11/2003	Phase 2 demonstration of the processing of SBW. Used different solid carbon and sugar reductants in varying ratios to each other and to the simulant feed rate. Non-radioactive Cs and Re (as surrogates for Cs-137 and Tc-99) were added to the waste simulant. The system was operated at ~675°C without a clay additive and later at ~725°C with the clay. Various types and quantities of iron catalysts were used, including none.	INEEL SBW	6-inch FBSR	Successfully produced a granular carbonate product without the clay additive and an alkali aluminosilicate product with the clay. NO _x destruction averaged ~93% for the carbonate flow sheet and ~74% for the mineralizing flow sheet. NO _x destruction without the iron catalyst was demonstrated. Greater than 99% of radioactive surrogate elements and non-volatile heavy metals were captured in the solid waste product. Hg was captured with >99.9% efficiency in a GAC bed in the off-gas system.

Table II. Demonstration Tests of the THORsm Technology for the Treatment of Nitrate Containing Liquid Wastes (cont.).

<i>Location Timeframe</i>	<i>Purpose/Conditions</i>	<i>Simulant Used</i>	<i>Reformer Equipment</i>	<i>Results</i>
SAIC STAR Center, Idaho Falls, ID 07/2004 and 09-10/2004	Phase 3 demonstration of the processing of SBW into a fully mineralized alkali aluminosilicate product. Carbon and clay additives and addition ratios were specified through experimental laboratory work at Savannah River National Laboratory (SRNL). Non-radioactive Cs and Re (as surrogates for Cs-137 and Tc-99) were added to the waste simulant. Temperature was ~725°C.	INEEL SBW	6-inch FBSR	Successfully produced a granular alkali aluminosilicate product, predominantly Nepheline and Carnegieite. NO _x destruction averaged >90% for the two July runs and >96% for the single September/October run, both without iron catalyst. >99% NO _x destruction was demonstrated for specific carbon reductant conditions. Feed nozzle issues impacted operations during the first runs, but improvements allowed a full 100 hours of “feed-on” operation without significant process issues during the latter run. Greater than 99% of radioactive surrogate elements and non-volatile heavy metals were captured in the solid waste product and Hg was captured with >99.9% efficiency in a GAC bed in the off-gas system for all the runs.
SAIC STAR Center, Idaho Falls, ID 08/2004	Phase 3 demonstration of the processing of LAW into a fully mineralized alkali aluminosilicate product. Carbon and clay additives and addition ratios were specified through experimental work at SRNL. Non-radioactive Cs and Re (as surrogates for Cs-137 and Tc-99) were added to the waste simulant. Temperature was ~725°C.	HANFORD LAW: Envelope A Composite	6-inch FBSR	Successfully produced a granular alkali aluminosilicate product, predominately Nosean, Carnegieite/sodium aluminosilicates, and Nepheline, the desired mineral phases and the same as those produced in the Hazen demonstration in 2001. NO _x destruction stabilized at >96%, without an iron catalyst. Greater than 99% of radioactive surrogate elements and non-volatile heavy metals were captured in the solid waste product. Hg was captured with >99.9% efficiency in a GAC bed in the off-gas system.

DEPARTMENT OF ENERGY DEPLOYMENT INITIATIVES

Over the past three years, the DOE has expressed interest in the THORsm process for denitration and stabilization of high nitrate tank wastes. The success of the above-discussed demonstrations has shown the capability of THORsm to process waste streams at all the DOE sites with significant inventories of these wastes. To facilitate rapid deployment and accelerated processing of the nitrate wastes, TTT would employ a modular, transportable processing system. Process equipment would be integrated into discrete modules at an off-site fabrication facility. The modules would then be joined together and the process equipment would be tested at the fabrication facility. The modules would then be disconnected and shipped as units to the site, where they would be rejoined on a pre-poured concrete slab. Necessary utility and waste line connections would be made and the waste processing system would undergo final testing, readiness review, and would be put into radioactive service.

Figure 3 illustrates the modular system designed for deployment at the SRS site for processing Tank 48H waste. The modular system includes all the process vessels arranged in their modules. A modular steel shield wall would be installed around the modules to provide effective radiation shielding. Both the shield structure and the modular process systems are designed to meet all seismic and spill protection requirements. A separate ventilation module houses the HEPA filters and ventilation blowers. An additives skid provides the clay, carbon, and any other co-reactants added to the reformers. Typical utility services for a full-scale modular system include: low-pressure steam, instrument air, water for direct spray cooling of the CRR off-gas, electricity for the blowers and fluidizing gas superheaters, nitrogen for purges, and oxygen.

Following the completion of its waste processing mission, the modular, transportable facility could be decontaminated and relocated to another area or could be easily decontaminated, decommissioned, and the individual modules sent to an appropriate waste disposal site.

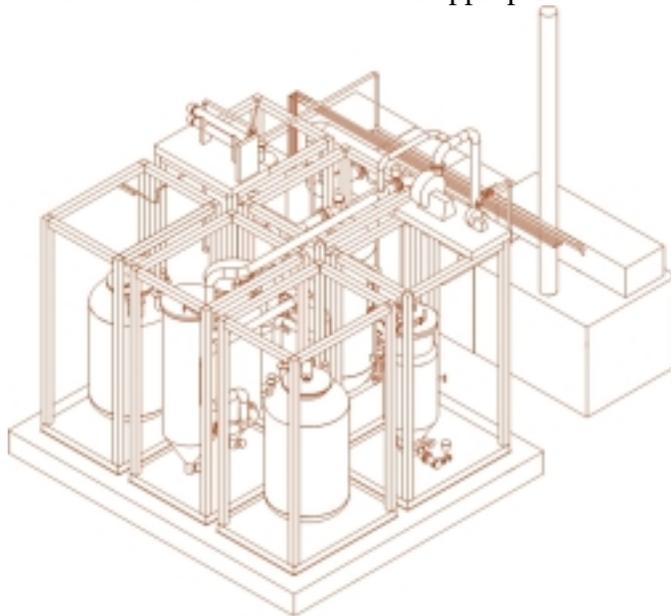


Fig. 3. Modular Steam Reforming System for Savannah River Site Tank 48H Application.

CONCLUSION

In summary, the THORsm process has many salient features:

- Waste feed can include solids, liquids, slurries, and gases.
- A wide variety of liquid waste streams can be processed, e.g., both acidic and basic tank wastes can be processed without neutralization.
- Nitrates, nitrites, and nitric acid are destroyed with >95% efficiency with less than 300 ppm NO_x levels in the facility off-gas.
- S, Cl, F, and P are immobilized in a stable, water insoluble mineral form, with no secondary process waste streams and <10 ppm SO_x, HCl, or HF in off-gas at stack
- Alkali metals, radionuclides, and non-volatile heavy metals are immobilized into a stable, water insoluble, alkali aluminosilicate mineral form.
- Hg is volatilized in the process and captured with 99.9% efficiency in GAC beds in the off-gas system.
- Greater than 99% of radionuclides are incorporated into the solid product. Tritium, carbon¹⁴, and iodine are generally partitioned to the off-gas.
- Alkali aluminosilicate product meets LDR UTS limits for heavy metal leachability (TCLP)
- Final solid product can be alkali aluminosilicate or sodium carbonate in granular or monolithic form.
- Systems operate at near atmospheric pressure or under vacuum.
- Safe passive shutdown can be accomplished in <15 seconds.
- Reformer contains very low inventory of unreacted waste.
- Facility is zero-liquid release, as water vapor is discharged up the stack.
- Wastes with high water content, high organic contents, and high sulfate content are efficiently processed.
- Process can be expeditiously deployed, relocated, and dispositioned as a modular, transportable facility.
- The THORsm process is covered by issued and pending patents, see US Patent No. 6,280,694 and 6,084,147.

REFERENCES

1. 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.
2. D.W. MARSHALL, N.R. SOELBERG, K.M. SHABER, "THORsm Bench-Scale Steam Reforming Demonstration," INEEL/EXT-03-00437, Idaho National Engineering and Environmental Laboratory, May 2003.
3. C. M. JANTZEN, "Disposition of Tank 48H Organics by Fluidized Bed Steam Reforming (FBSR) (U)," WSRC-TR-2003-00352, Rev. 0, Savannah River Technology Center, September 18, 2003.
4. 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, Jan. 2003.
5. 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.
6. 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.
7. 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.
8. 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.