

THORsm Steam Reforming Process For Hazardous and Radioactive Wastes

Technology Report

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1.0 EXECUTIVE SUMMARY

THOR Treatment Technologies, LLC (TTT) is a joint venture formed in June 2002 by Studsvik, Inc. (Studsvik) and Westinghouse Government Environmental Services Company LLC (WGES) to further develop, market, and deploy Studsvik's patented THORsm non-incineration, steam reforming waste treatment technology. This technology report provides an overview of the THORsm steam reforming process as applied to the denitration of nitrate containing tank wastes and conversion of the denitrated tank waste as well as hazardous wastes to an immobilized, mineral final waste form.

Using the THORsm steam reforming technology to treat nitrate containing tank wastes could significantly benefit the Department of Energy (DOE) by reducing capital, operating, and overall life-cycle costs, reducing processing and programmatic risks, and positioning the DOE to meet or exceed its stakeholder commitments for tank closure. Specifically, use of the THORsm technology can facilitate processing of up to 75% of tank wastes without the use of vitrification. This will result in substantial capital, operating cost, and schedule savings over vitrification.

DOE tank wastes comprise a wide range of salt cakes and supernate solutions that contain high concentrations of sodium, aluminum, nitrates, nitrites, nitric acid, hydroxides, and sulfates with substantial concentrations of radionuclides, chlorides, fluorides, phosphates, heavy metals, and most other inorganic elements as well. The THORsm steam reforming process has been proven to efficiently handle, process, and immobilize the radionuclides, sodium, sulfate, chlorides, fluorides, phosphates, and non-volatile heavy metals into a stable, water insoluble mineral matrix.

Other hazardous wastes that can be efficiently processed by the THORsm process include: organic solvents, spent activated carbon, sludges, off-gas scrubber recycle streams, decon solutions, oils, ion exchange media and resins, plastics, sodium hydroxide solutions, and wastes with high concentrations of Cl, F, S, P, and heavy metals, where the final waste must be stabilized to meet heavy metal and radionuclide leach resistance and disposal site performance requirements.

In the THORsm process, waste feed, superheated steam, and co-reactants are introduced into a fluidized bed steam reformer vessel where liquids are evaporated, organics are destroyed, and reactive chemicals in the waste feed are fully converted to a stable mineralized waste product that incorporates almost all of the radionuclides and heavy metals. For the waste to fully and efficiently react, the steam reformer provides a large surface area due to the fluidized bed design. Carbon and iron-based additives (reductants) are used to convert nitric acid, nitrates and nitrites directly to nitrogen gas in the reformer. Clay or other inorganic co-reactants are added to the waste feed or bed to convert the radionuclides, alkali metals (sodium and potassium), sulfate, chloride, fluoride, phosphate, and non-volatile heavy metals into an immobilized mineral product.

The steam reforming process destroys RCRA and TSCA organic constituents. Toxic organics are converted to carbon dioxide and water vapor in the steam reformers by a combination of steam reforming and oxidizing reactions.

Off-gases from the steam reformer vessels may be treated by an optional wet scrubber technology to neutralize minor amounts of corrosive acids gases and by filtration to remove any fine particulates that may be carried out of the reforming vessels with the off-gas. The off-gases are cooled, and HEPA filtered so that the primary emissions released to the atmosphere from the process are carbon dioxide and water vapor. A conceptual representation of the steam reforming process is provided in Figure 1.

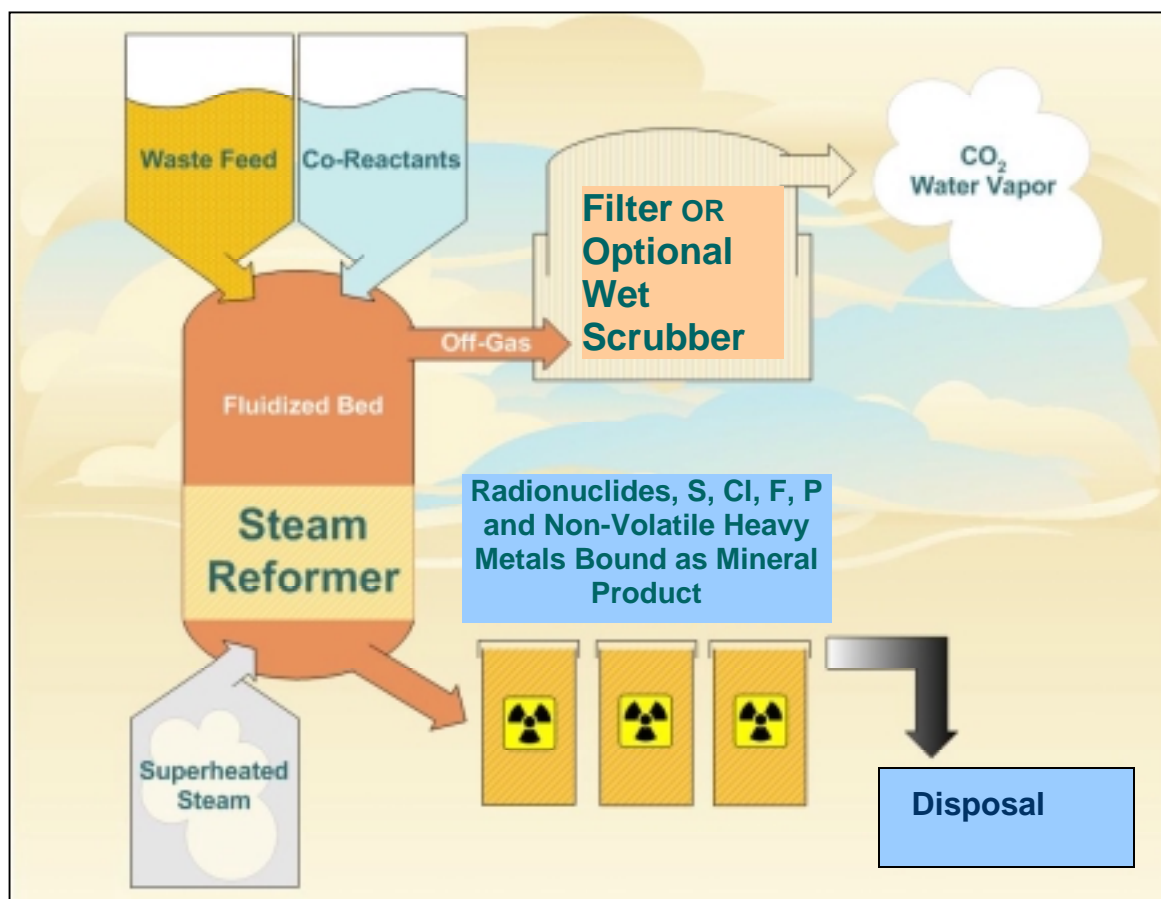


FIGURE 1 THORsm FLUIDIZED BED STEAM REFORMING PROCESS

The THORsm steam reforming process consists of a moderate temperature (650 to 750°C) fluidized bed vessel, operating under a vacuum, where tank wastes are reacted with selected additives and co-reactants to achieve the following;

- Nitrates, nitrites, and nitric acid are directly reduced to nitrogen gas with less than 300 ppm of NO_x present in the process gas from the reformer (>98% conversion to nitrogen);

- Sodium, potassium, and aluminum in the waste feed are converted to a stable, water insoluble mineral product, e.g. mostly sodium-alumina-silicate, $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-2\text{SiO}_2$, (Na-Al-Si) that has a Na_2O loading of greater than 19% by weight;
- Sulfates, chlorides, phosphates, and fluorides in the waste feed are bound within the Na-Al-Si mineral structure so that less than 5% is volatilized to the off-gas;
- Radionuclides in the waste feed are retained (>99.9%) in the solid, mineralized product, with the exception of tritium, carbon¹⁴, and iodine that are largely volatilized;
- The mineralized product will pass the Toxicity Characteristic Leach Procedure (TCLP) test Land Disposal Restriction (LDR) Uniform Treatment Standard (UTS) limits for heavy metals and has less than 10 ppm residual nitrates and nitrites;
- A second stage reformer provides high destruction and removal efficiency (DRE) of organics in the waste feed, e.g. RCRA organics are converted to carbon dioxide and water vapor with DRE of >99.99% and TSCA organics are converted to carbon dioxide and water vapor with DRE of >99.9999%;
- The second stage reformer also adsorbs residual acid gases from the first stage reformer to form mineralized calcium products of Cl, F, and sulfate. Off-gas emission are Maximum Achievable Control Technology (MACT) compliant;
- Sodium carbonate, Na_2CO_3 , or sodium silicate, $\text{Na}_2\text{O}-2\text{SiO}_2$, products can be produced from TRU wastes that can be directly shipped to the Waste Isolation Pilot Project (WIPP);
- Sodium carbonate, Na_2CO_3 , or sodium silicate, $\text{Na}_2\text{O}-2\text{SiO}_2$, products can be produced and then directly vitrified in a joule-heated melter;
- Other mineral products that can be produced include: sodium aluminate, calcium phosphate, calcium chloride, calcium fluoride, and calcium sulfate.

2.0 THORsm STEAM REFORMING TECHNOLOGY DESCRIPTION

2.1 PROCESS TECHNOLOGY OVERVIEW

The patented Thermal Organic Reduction (THORsm) process comprises a two-stage reformer system operating under a vacuum. The first stage consists of a fluid bed steam reformer vessel (Denitration and Mineralization Reformer, DMR) that is fluidized with superheated steam. Waste feed and co-reactants are introduced into the DMR fluidized bed. In the DMR fluidized bed liquids are evaporated; organics are destroyed; nitrates, nitrites, and nitric acid are converted to nitrogen gas; and reactive chemicals are fully converted to a stable solid waste product, such as Na-Al-Si or calcium compounds. The DMR reformer generally operates in a strongly reducing environment to provide high nitrate and mineralization conversions. A flow diagram of the process is provided in Figure 2.

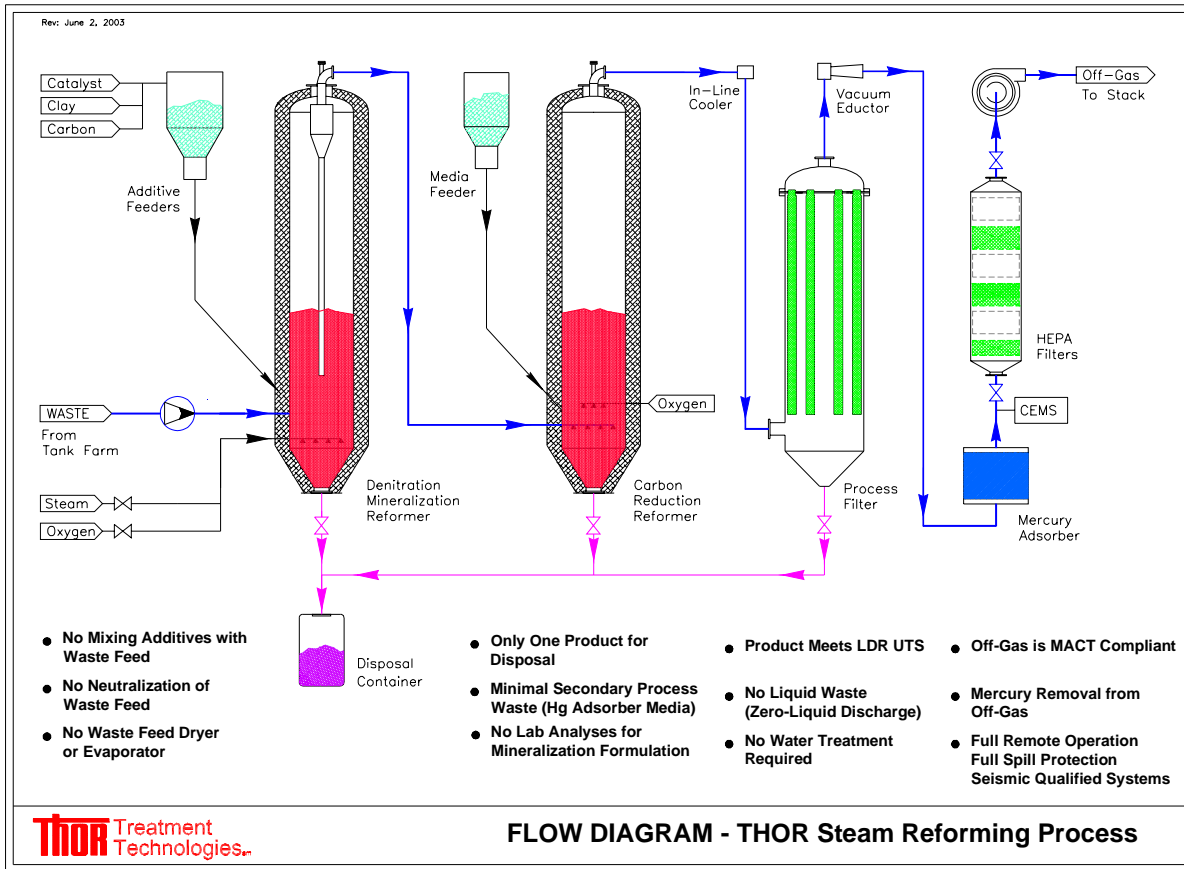


FIGURE 2 FLOW DIAGRAM OF THE THORSM STEAM REFORMING PROCESS

The second stage reformer (Carbon Reduction Reformer, CRR) operates in an oxidizing environment to gasify any carbon fines carried over in the process gases from the first stage DMR reformer. The CRR reformer completes the destruction of organics to carbon dioxide and water vapor and conversion of any trace acid gases to stable calcium compounds.

The off-gases from the CRR reformer are cooled by direct water cooling and any particulates are then filtered out by the process filter (PRF). If mercury is present in the waste, the mercury will volatilize in the reformers and will be removed from the off-gas by the mercury adsorber (granular activated carbon adsorber, GAC). The cooled and filtered off-gases are then HEPA filtered and released up the monitored exhaust stack. The only significant gaseous emissions are carbon dioxide and water vapor. Thus, no secondary process waste is generated and the facility has zero-liquid releases.

The inorganic constituents in the waste, as well as the radionuclides, non-volatile heavy metals, Cl, F, S, and P, will be converted to stable minerals in the reformers. The main mineralized

products produced by the THORsm reforming process are listed below. The minerals are generally not water soluble except for the Na-Si, Na-Al, Na₂CO₃, and CaCl₂, which are partially to fully water soluble. The relative amount of each product compound is dependent upon the type of co-reactants used and the inorganic composition of the waste:

- Sodium-alumina-silicate (Na₂O-Al₂O₃-2SiO₂, Na-Al-Si) with substituted Cl, F, P, sulfate and heavy metals in the crystalline structure
- Sodium silicate (Na₂O-2SiO₂, Na-Si)
- Sodium aluminate (Na₂O-2Al₂O₃, Na-Al)
- Sodium carbonate (Na₂CO₃)
- Sodium calcium silicate (Na-Ca-Si)
- Calcium sulfate (CaSO₄)
- Calcium chloride (CaCl₂)
- Calcium fluoride (CaF₂)
- Calcium phosphate (Ca₃(PO₄)₂)

Na-Al-Si is the preferred final waste product for applications that require waste immobilization without vitrification or grouting. The granular form of all products would be suitable for direct disposal at the Waste Isolation Pilot Plant (WIPP). For wastes that must be vitrified, the preferred product is sodium silicate and sodium calcium silicate or, alternatively, sodium carbonate, which can be readily vitrified in joule-heated melters.

The following sections of this technical overview provide discussions of process chemistry in the steam reformers, reduction of nitrates to nitrogen, conversion of alkali metals to stable mineral form, neutralization of acid gases, destruction of RCRA and TSCA organics, reduction and immobilization of hazardous metals, removal of solids carryover from the reformer, and finally, secondary process waste generation, emissions, and discharges.

2.2 PROCESS CHEMISTRY IN THE MINERALIZATION STEAM REFORMER

In the first stage DMR steam reformer, the granular/particle bed material is fluidized with low pressure superheated steam. The waste feed is injected into the bottom of the fluidized bed just above the fluid gas (steam) distributors. Normally the waste is injected into the DMR with no pH adjustment and without co-reactants or additives. The additional solid additives and co-reactant(s), such as carbon, clay, silica and/or catalysts, are added directly to the fluid bed as granules or powders. The DMR is operated in strongly reducing conditions to facilitate high reduction of nitric acid, nitrates, and nitrites to nitrogen gas.

The following physical and chemical reactions take place in the DMR:

- All liquids are evaporated.
- Sodium, potassium, and aluminum in the waste feed are converted into a stable mineralized product, which contains essentially all the radionuclides and inorganic elements in the waste feed stream (see Figure 4).
- Nitric acid, nitrates, and nitrites in the waste feed are reduced to nitrogen gas by the carbon reductant and metal catalyst solids and the CO and H₂ gases in the bed (see Figure 3).
- Organics are initially converted by pyrolysis into volatile hydrocarbons in the lower zone of the reformer bed. In the upper zone of the DMR bed, steam reforming reactions convert most organics to mainly water vapor, CO, CO₂, and H₂, with small amounts of methane and ethylene and traces of other heavier volatile organics. The process gas stream from the top of the DMR reformer consists of water vapor, carbon dioxide, nitrogen, fine particles of solid product, minor carbon particle carryover, and small quantities of acid gases not converted to a mineralized form in the reformer.
- 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. Other non-volatile heavy metals, such as lead, are also chemically bound in the solid Na-Al-Si product.
- The granular product solids accumulate in the DMR and are periodically drained out the bottom as the final solid product. The fluid bed particles comprise the product solids, except during initial start-up of the plant.

The DMR is operated at 650°C to 750°C and can be electrically heated (small units) or operated in an auto-thermal mode. For auto-thermal operation, the energy needs are supplied by the incoming superheated steam and by the introduction of oxygen with the steam to provide oxidation of the organics and carbon from the waste and reductants. For production scale units, auto-thermal steam reforming is the preferred mode of operation.

In the second stage CRR reformer, the granular bed media is fluidized by the process gases from the cyclone outlet from the top of the DMR. The CRR is operated in an oxidizing mode by the introduction of autothermal gas (oxygen, AG) into the bottom of the CRR fluid bed. In the CRR, the following physical and chemical reactions take place:

- Fine carbon particles that are carried over (elutriated) in the process gases from the DMR are gasified to CO₂ by contact with oxidizing steam.
- Residual volatile organics in the process gases from the DMR are reformed and oxidized into CO₂ and water vapor, as shown in Figure 5. The off-gas stream from the CRR consists almost exclusively of water vapor, carbon dioxide, nitrogen, and fine particles of elutriated product solids.
- Trace acid gases in the process gases from the DMR are adsorbed by reaction with the CRR bed media. The bed media consists of calcium carbonate (crushed limestone/dolomite) and/or calcium silicate particles. The calcium media is an efficient adsorbent of acid gases such as Cl, F, S, and P compounds. The calcium media converts the acid gases to the corresponding calcium salts, which are largely water insoluble.

2.3 NITRATE REDUCTION TO NITROGEN GAS

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

- Residual nitrate content in reformed solid waste product is <10 ppm,
- Direct conversion of >98% of nitric acid, nitrates, and nitrites in waste feed to nitrogen gas, and
- Total NO_x in off-gas is <300 ppm in the DMR process outlet gas.

The above referenced high conversion of nitrates to nitrogen requires that several specific features and reactions be incorporated into the single step THORsm DMR reformer process: 1) fluidized bed media with high surface area and high heat transfer capability, 2) high energy generation to evaporate and superheat the water in the typical liquid or slurry waste feeds, 3) strongly reducing operating condition that is provided by the carbonaceous and metal-based reductants/catalysts, 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 (Na and K) into higher melting point mineral compounds to prevent formation of low melting point eutectic salts and unwanted bulk agglomerations in the fluid bed.

The fluidized bed media in the DMR typically consists of accumulated mineralized product granules. The incoming waste feed coats the fluidized particles and is instantly dried. The thin 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. Figure 3 illustrates several of the many possible reaction mechanisms whereby nitrates and nitrites are converted to nitrogen gas.

Experience has shown that thermal denitration without the presence of a reductant will result in reduction of residual nitrates in the solid product of up to 90%, i.e. 90% of the incoming nitrates are thermally volatilized leaving approximately 10% of incoming nitrates in the final solid waste product. Typical thermal denitration processes that do not use a reductant will have 20,000 ppm to over 50,000 ppm total NO_x in the process off-gas. The addition of carbonaceous reductants to nitrate wastes in a thermal denitration process has shown substantial improvements, with up to 98% nitrate reduction in the solid product and a corresponding reduction of total NO_x in the process off-gas to 5,000 ppm to 10,000 ppm. A further order of magnitude improvement in nitrate conversion is possible by use of carbonaceous and metal-based reductants in the fluid bed. The presence of low-cost metal oxides, e.g. iron oxide particles, in the fluid bed provides unexcelled performance of the THORsm process for effective reduction of NO_x in the off-gas (<300 ppm total NO_x) and only trace levels (<10 ppm) of residual nitrates in the solid reformed product, as summarized above.

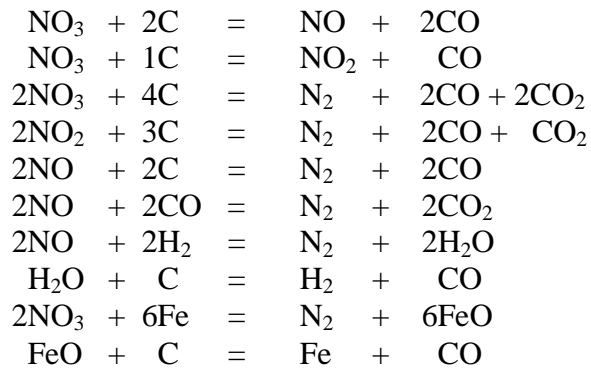


FIGURE 3 STEAM REFORMER CHEMISTRY CONVERTS NITRATES INTO NITROGEN GAS

2.4 ALKALI METAL CONVERSION TO MINERAL FORM

The THORsm steam reforming process has the unique capability to convert alkali metals, Na and K, into stable 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 such as sulfate, chloride, silica, borate, and many other inorganic materials. These low melting point salts 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 usually results in the formation of bulk agglomerations, as the melted salts tend to bind the fluidized media particles into larger and larger pieces.

Studsvik has performed intensive work in developing and proving that the addition of selected inorganic co-reactants to a reducing fluid bed can prevent the formation of low melting point eutectic compounds. Certain inorganic co-reactants preferentially substitute for the typical low melting point anions of the Na and K salts. The preferred co-reactants include alumina-silicates (clays), silica, Ca, Mg, Al, and P compounds that combine with alkali metals to form synthetic naturally occurring minerals as listed below (Note: Only the main elemental constituents are shown for simplicity):

- Nepheline, Na-Al-Si
- Nosean, Na-Al-Si-SO₄
- Fairchildite, K-Ca-CO₃
- Natrofairchildite, Na-Ca-CO₃
- Dawsonite, Na-Al-CO₃
- Eitelite, Na-Mg-CO₃
- Shortite, Na-Ca-CO₃
- Parantisite, Na-Ti-Si
- Maricite, Na-Fe-PO₄
- Buchwaldite, Na-Ca-PO₄
- Bradleyite, Na-Mg-PO₄-CO₃

- Combeite, Na-Ca-Si
- Na-PO₄, Na₂CO₃, Na-Al, Mg-PO₄, Na-Al-PO₄, Na-Mg-PO₄, Ca-Si, Na-(Ca,Fe,Mg)-Si, and
- Other similar mineral variations numbering into the hundreds.

The generation of water-insoluble sodium/potassium/aluminum/calcium products is preferred; however, most sodium and potassium compounds are water-soluble, e.g. sodium carbonate, sodium aluminate, etc. The water-soluble sodium compounds will generally require further stabilization (grouting, solidification, vitrification, etc.) prior to disposal to prevent water dissolution of the buried product into the ground water. Therefore, the generation of water-insoluble alkali metal products is very desirable. For this reason, the preferred products are the water-insoluble species such as Nosean and Nepheline. The Nepheline, Nosean, and related sodium-alumina-silicate compounds form a crystalline, cage-like structure that has the ability to substitute and bind large atoms (such as cesium, technetium, and other radionuclides and heavy metals) within the crystalline structure to produce a highly leach-resistant product. The sodium-alumina-silicate compounds have demonstrated TCLP leaching that is substantially lower than the Land Disposal Restrictions (LDR) Universal Treatment Standard (UTS) limits for heavy metals. The Cl, F, P, and sulfate in wastes are also incorporated into the crystalline structure of the sodium-alumina-silicate compounds. The THORsm process can thereby provide a very high retention and mineralization of acid gases.

In order to generate the alkaline earth mineralized compounds mentioned above, the following co-reactants can be utilized, each co-reactant would be added in the proportions needed to generate the desired higher melting point compound, and/or water-insoluble compounds. Figure 4 provides typical simplified reaction equations for formation of the main mineralized products.

- Addition of lime (CaO) or other Ca compounds such as calcium carbonate, calcium silicate or nitrate could provide conversion of alkaline earths to Ca rich final product, e.g. Natrofairchildite.
- Addition of magnesia (MgO) would produce minerals rich in magnesia, e.g. Eitelite.
- Addition of clays (alumina-silicates such as kaolin, bentonite, etc) to produce a Nepheline, Nosean or other related sodium-alumina-silicates. Clays are considered to be aluminum compounds.
- Addition of only Al compounds including; aluminum nitrate, Al(NO₃)₃, aluminum hydroxide or tri-hydrate Al(OH)₃; aluminum metal particles, etc. will produce a sodium-aluminate product compound. Aluminum nitrate has been used by the DOE INEEL calciner for many years to produce sodium aluminate in an oxidizing fluid bed with no reducing zone. Aluminum hydroxide is used by Studsvik at the Studsvik Processing Facility (SPF) in Erwin, TN to produce sodium aluminate rich products in a reducing environment.
- Addition of phosphate compounds produces bonded ceramic minerals such as Maricite, Buchwaldite, Bradleyite or other PO₄ containing compounds. For waste feeds containing phosphate compounds, such as tri-butyl phosphate, the final solid product would be an inorganic phosphate as listed above. To bond with phosphate in the waste, it is preferred that a clay or calcium additive be used to make a water-insoluble product.

- Addition of silica compounds produces a sodium silicate product.
- Addition of no solid co-reactant will yield a sodium carbonate product. Sodium will combine with carbon dioxide in the DMR gases to provide a sodium carbonate product. The generation of sodium carbonate in this type of application has been known since the 1950s in test fluid bed denitration systems.

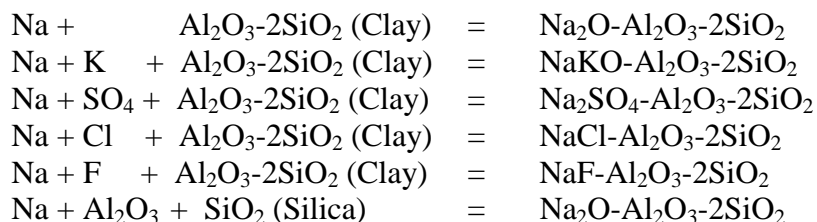


FIGURE 4 STEAM REFORMER CHEMISTRY CONVERTS SODIUM, POTASSIUM, ALUMINUM, SULFATES, CHLORIDES, FLUORIDES, AND RADIONUCLIDES INTO SODIUM-ALUMINA-SILICATES

2.5 DESTRUCTION OF RCRA AND TSCA ORGANICS

The non-incineration THORsm steam reforming process destroys organics in the wastes, including any RCRA and TSCA organic constituents. Specifically, the 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 monoxide, hydrogen, and a small quantity of light hydrocarbons, such as methane and ethylene. 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 oxidized to carbon dioxide and water vapor by addition of oxygen to the fluidizing gases in the CRR .

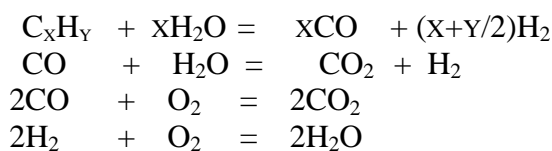


FIGURE 5 AUTO-THERMAL STEAM REFORMER CHEMISTRY CONVERTS HYDROCARBONS INTO CARBON DIOXIDE AND WATER VAPOR

The formation of dioxin and furan compounds has been studied by the U.S. Department of Energy (DOE) for a steam reforming process that has similar organic destruction capability to the THORsm process. The results of the extensive organic destruction demonstration program (DOE Contract No. DE-AR21-95MC32091 with Thermo-Chem, 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 will be destroyed in the reformer systems.

2.6 NEUTRALIZATION OF ACID GASES AND REMOVAL OF SOLIDS CARRYOVER FROM OFF-GAS

Testing on DOE Hanford liquid low activity waste (LAW) surrogates (Envelope C composition) has shown that over 94% of the sulfur compounds, fluorides, and chlorides in the waste feed react in the steam reformer with the co-reactant additives, particularly clay, and become an integral part of the final mineralized sodium-alumina-silicate waste product crystalline structure, as shown in Figure 4. A small amount of the S, Cl, P, and F in the incoming waste feed forms volatile acid gases, which pass through the DMR and are adsorbed in the downstream CRR calcium bed, as shown in Figure 6. If the waste contains very high levels of S, Cl, P, and/or F compounds, an optional wet quencher/scrubber unit can be installed between the outlet of the process filter and the mercury adsorber to remove any residual acid gases.

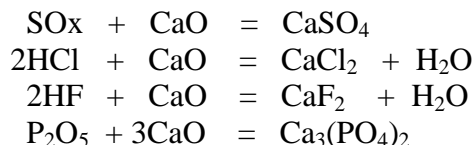


FIGURE 6 CRR REFORMER CALCIUM BED MEDIA ADSORBS AND NEUTRALIZES ACID GASES BY FORMING LOW-VOLUME CALCIUM SALTS

2.7 IMMOBILIZATION OF HAZARDOUS METALS

The strong reducing environment in the DMR converts certain metals, including the hazardous heavy metal Cr, to non-hazardous valence states. For example, Cr(VI) is reduced to Cr(III) and is incorporated into the sodium-alumina-silicate product. In addition, virtually all of the lead and nickel that enters the reformer is chemically bound up in the sodium-alumina-silicate product. The Na-Al-Si product has been shown to pass the TCLP test easily meeting the LDR UTS limits for leachability by a factor of 10 to 100. Mercury has been shown to be volatile in the THORsm process. Mercury will partition to the off-gas as elemental mercury and would be removed by the granular activated carbon adsorber, shown on Figure 2. Cadmium is also retained in the mineral products, but TCLP leach data on cadmium is unavailable at this time. Typical TCLP results for the Na-Al-Si product are: Cr <0.06ppm, Ni <2.8ppm, and Pb <0.07ppm.

Additional work is needed to determine the performance of the THORsm process for immobilizing other heavy metals. Studsvik has had broad experience with processing wastes with Cr, Ni and Pb; however, most commercial Low Level Radioactive Wastes (LLW) do not

contain more than trace quantities of other heavy metals. It is expected that other heavy metals will also be retained in the solid products.

2.8 SECONDARY WASTE GENERATION, EMISSIONS, AND DISCHARGES

A significant benefit of the THORsm steam reforming process is that the facility produces zero-liquid releases and no secondary solid wastes, except the mercury adsorber media. The Erwin facility has been commercially operational at full-scale for four 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 and converted into carbon dioxide and water vapor.

TABLE 1 DISCHARGES AND EMISSIONS FROM A PRODUCTION-SCALE THORsm STEAM REFORMING PROCESS FOR NITRATE WASTES

Material	Discharge/Emission
SO _x	<10 ppm in off-gas at stack, wet basis
NO _x :	
• NO ₂	<20 ppm in off-gas at stack, wet basis
• NO	<300 ppm in off-gas at stack, wet basis
• N ₂ O, Others	<10 ppm in off-gas at stack, wet basis
HCl	<10 ppm in off-gas at stack, wet basis
HF	<10 ppm in off-gas at stack, wet basis
CO	<40 ppm in off-gas at stack, wet basis
Radionuclides:	
• Tritium	Tritium is converted to water vapor and is released up the monitored stack. An optional off-gas condenser can be provided to fully condense water and discharge water and tritium to groundwater if required.
• Carbon ¹⁴	Carbon ¹⁴ is converted to carbon dioxide and is released up the monitored stack.
• Iodine	Iodine will be released up the stack unless adsorption media is placed downstream of the HEPA filter to remove iodine from the off-gas.
• Other	>99.99% retained in the solid product
Mercury	Mercury is removed from the off-gas by means of adsorption media in the off-gas stream
Secondary Process Wastes:	
• Scrubber Liquids	None
• Scrubber Salts	None
• Other	None, except for mercury adsorber media
H ₂ O	Water is evaporated and discharged through the plant stack as water vapor. Process has zero-liquid releases.

The emissions data presented in Table 1 represent actual readings from the Erwin steam reforming facility CEMS and correlations based on CEMS data from previous bench-scale and pilot-scale demonstration programs performed by Studsvik and TTT, including results of nitrate destruction demonstrations.

The only significant gaseous effluents from the THORsm process are carbon dioxide and water vapor. Trace radioactive particulates remaining in the off-gas stream after the process filter are removed by HEPA filtration prior to discharge of gases to the atmosphere. Volatile radionuclides include tritium, carbon¹⁴ and iodine. If desired, the iodine can be adsorbed by granular activated carbon media downstream of the HEPA filter. It is not normally feasible to remove the carbon¹⁴, as it will have been converted to carbon¹⁴ dioxide and cannot be easily separated from non-radioactive carbon dioxide. The tritium will be converted to water vapor in the process. It is often preferable to release the tritium up the monitored stack versus to the groundwater. However, if desired, the water vapor can be condensed and the water in the process off-gas can then be discharged as a liquid effluent.

3.0 PROCESS EQUIPMENT FUNCTIONAL DESCRIPTION

This section provides a functional description of the processing equipment that is required to safely and efficiently process DOE LLW sodium nitrate and nitric acid tank wastes. The process equipment consists of the following major systems, as shown on the flow diagram, Figure 2:

- Waste feed system
- Denitration and mineralization steam reformer (DMR)
- Carbon reduction steam reformer (CRR)
- Process filter
- Product packaging system
- Mercury removal adsorber
- Off-gas HEPA filtration system
- Auxiliary systems and utility services

3.1 WASTE FEED SYSTEM

The waste feed system comprises the following main hardware components:

- Waste feed pump
- Associated instrumentation and controls, piping, valves, etc.

The waste is metered directly into the DMR from a waste supply/holdup tank, tanker truck, or shipping container. During the waste transfer operations, on-line mass and density measurements will be taken of the incoming waste solution/slurry. The required co-reactants and reductants will then be calculated, by a control system algorithm, based on the on-line

measurement readings. The THORsm process does not require that frequent samples be taken and analyzed prior to processing the waste. The addition rate of the co-reactants can be changed while processing to provide the optimal usage of additives while eliminating the need to premix the additives with the waste solution/slurry. It is recommended that sampling be performed for each major waste type to determine the optimum type of co-reactant and additives and to preset the ranges for the additive calculation.

If desired, an interim holdup tank can be installed to provide surge capacity to minimize the frequency of waste transfers from facilities, such as DOE's large underground storage tanks, or to eliminate the need to continuously transfer waste over weekends.

The waste feed pump continuously meters the waste feed solution/slurry into the DMR. Peristaltic pumps have been routinely used for this service, as they require minimal maintenance that involves only hose changeout. Alternatively, a progressive cavity pump could be used on larger systems. A nominal, pumpable slurry composition is 50% water and 50% all other constituents by weight. The number of pumps is dependent on the size of the reformer. A single waste feed pump can efficiently inject waste into a reformer with fluid bed diameter of up to 36". Each pump is provided with the following instrumentation and features:

- Remote pump casing level indication
- Remote pump suction and discharge pressure indication
- Remote flush and drain capability
- Quick-disconnects for hose and pump covers with optional remote washdown and disassembly capability
- Remote isolation valves
- Variable speed drive

3.2 DENITRATION AND MINERALIZATION STEAM REFORMER

The denitration and mineralization steam reformer (DMR) is a fluidized bed contactor unit operated at 600 to 800°C and under a slight vacuum (0 to -20 inch W.C.). For tank waste and most other applications, the fluidized bed material is generally granular product solids that accumulate in the bed during processing. Superheated steam is used to fluidize the product solids bed by means of pipe distributors located above the bottom head of the fluid bed vessel. For auto-thermal operation, oxygen is mixed with the fluidizing steam and input through the same fluid gas distributors. Pipe type fluid gas distributors are preferred for radioactive service as the fluid gas nozzles can be remotely removed, if required, without entry inside the reformer. Figure 7 is a photograph of the top of the 18" steam reformer installed at the Studsvik Processing Facility (SPF). The main LLW processing reformer at the SPF is 45" diameter.

The waste feed mixture is injected by the waste feed pump(s) into the bottom of the fluid bed just above the fluid gas distributors. The water in the waste feed is instantly evaporated and superheated to the bed temperature by the large mass of hot, fluidized product solids. As the water in the waste feed evaporates, the dried waste solids quickly heat to reaction temperatures. Organics in the waste feed are volatilized and pyrolyzed upon contact with the hot bed solids. The volatile organics are subjected to steam reformation in the bed. The nitric acid, nitrates, and nitrites are converted to nitrogen gas when they come into contact with the reducing agents in the bed.

FIGURE 7 STEAM REFORMER: 18" DIAMETER FLUID BED WITH CERAMIC FILTER



The alkali metals, non-volatile heavy metals, radionuclides, S, Cl, F, P, and other inorganic constituents combine with the co-reactant(s), such as clay, to form stable, high melting point, crystalline minerals that become the final solid product. The superheated steam, residual acid gases, fine product particulates and some carbon fines are carried (elutriated) out of the bed by the upward flow of fluidizing and reaction product gases. The accumulated product solids are semi-continuously removed from the bottom of the reformer as a fully immobilized, water-insoluble product, if clay is used as the mineralization additive.

Other additives, such as iron oxide and other base metal or precious metal catalysts, are introduced directly into the bed during operations by means of a downcomer nozzle/pipe inside the fluid bed, as shown on Figure 2. A carbon reductant is semi-continuously added to the reformer bed to provide carbon for the reforming reactions and to provide energy for the reformer reactions.

The main energy requirements in the DMR include: evaporation and superheating the incoming water in the waste feed, heating up the inorganic and organic constituents in the waste feed, and heat of reaction for endothermic reformation reactions of steam with carbon and organics. The main sources of energy for the reformer are: superheat of the incoming steam fluidizing gas, reaction of nitrates with reductants to form nitrogen gas, and oxidation of organics and carbon reductants in the bed. The majority of the energy is provided by oxidation of the organics and carbon reductants in the bed.

This mode of internal-to-the-bed energy production in a steam reformer is termed auto-thermal steam reforming and is the preferred method for heating large-scale fluid beds, especially in radioactive service, as there are no heater components that can fail. Small fluid beds can be heated by means of external electrical heaters. Larger fluid beds can be heated by external or internal electrical or combustion-fired heaters and/or heating tubes. However, the use of electrical or combustion-fired heat input is not recommended on larger fluid beds in highly radioactive service, as the required high temperature of the heating surfaces causes decreased heater life and increased maintenance, which are both very undesirable in a radioactive application.

The DMR vessel has two sections. The lower section contains the fluidized product solids bed. The upper section is a larger diameter freeboard that provides for a reduction in gas velocities and disengagement of solid particles from the rising gases. The majority of particles entrained in the fluidizing gases thereby drop by gravity back into the bed. High efficiency cyclones are installed in the top of the freeboard section to provide efficient removal of the majority of fine particles still entrained in the fluidizing gases. The cyclones have a nominal particle size removal rating of 15-20 microns with a corresponding pressure drop of 15 to 25 inch W.C. The process gases leaving the DMR consist mostly of water vapor, carbon dioxide, hydrogen, carbon monoxide, and nitrogen, with trace levels of volatile organics, and acid gases, along with some solid product and carbon fines carryover.

The steam reformer vessel is made of a high temperature alloy designed and fabricated in accordance with ASME Pressure Vessel Code, Section VIII, Division 2, making it able to withstand pressure surges from any postulated upset or off-normal condition. The steam reformer is provided with the following features and auxiliary systems:

- Several thermocouples are provided to monitor zones in the fluidized bed. The thermocouples are inserted through sealed access thermowells/pipes that allow the thermocouples to be remotely changed out, even during operations.
- Three pressure taps are located in the reformer to provide operating level control data.
- An oxygen controller restricts free oxygen levels to <2% in the reformer outlet process gas stream.
- Fluidizing gas distributors, pipe style, are removable through the side of the vessel without vessel entry.
- Cyclones for solid particle retention. Each cyclone is provided with a flanged access port through the top head of the vessel. In the unlikely event that the cyclones become plugged, the cyclones can be remotely cleaned without entry to the vessel and without removal of the cyclone from the vessel.
- Product outlet valve. The product can be removed by gravity transfer from the bottom of the reformer or alternatively, an eductor jet with isolation valve can be provided on the bottom of the fluid bed vessel to pneumatically transfer the solids for storage or packaging for disposal. When using the pneumatic transfer method, the removed solids are pneumatically transferred, by a recirculating nitrogen gas stream, to a product receiver vessel for product cooling and packaging for disposal. The entire solids content of the reformer can be remotely drained via this eductor valve when needed for remote vessel inspections or feed or additive nozzle change-outs.

- Waste feed injector(s). A triple wall, pipe-in-pipe, atomizing waste feed injector is used to provide plug-free injection of waste feed slurries into the hot fluid bed. Inert gas or air can be used in the injector to keep the nozzle cool and to optimize waste feed atomization. The level of waste feed atomization is the principal means for controlling particle size control in the DMR.

3.3 CARBON REDUCTION REFORMER

The carbon reduction steam reformer (CRR) is a fluid bed contactor that is placed downstream of the DMR. The CRR is fluidized by the hot process steam and gases from the gas outlet of the DMR. Fine solid particles that are elutriated from the DMR also enter the CRR with the process gases. The refractory-lined CRR operates at 800 to 1,100°C in an auto-thermal steam reforming mode to reduce the carbon fines in the elutriated solids from the DMR by converting them to carbon dioxide; remove trace acid gases from the DMR by reaction with the CRR calcium bed particles to produce mineralized calcium compounds; and oxidize residual volatile organics, carbon monoxide and hydrogen from the DMR to carbon dioxide and water vapor.

The CRR bed media is fluidized by the hot process gases (with elutriated fines) from the DMR. Two fluidizing gas distributors are installed in the bottom of the CRR: one lower distributor header to provide uniform fluidization of the CRR bed by use of process gases from the DMR and one upper distributor for uniform distribution of oxygen into the bed. The CRR operates in an oxidizing environment with 2% to 10% by volume excess oxygen in the gas outlet from the CRR vessel. To increase the CRR temperature, additional carbon is added to the DMR. The resultant carbon fines and reformer gases from the DMR will then be oxidized to provide energy in the CRR bed. To decrease the CRR temperature, the carbon injection rate to the DMR can be reduced and/or water can be injected into the CRR bed through the service water (SW) injector.

The CRR fluidized bed media will mainly consist of calcium carbonate media (crushed limestone/dolomite). As the calcium bed adsorbs trace acid gases from the DMR process gases, additional calcium media will be added on an occasional batch-add basis. The media will serve as a semi-permanent bed as the fines elutriated from the DMR will also be elutriated out of the CRR as well. Accumulated bed will be drained out the bottom in the same manner as product solids are removed from the DMR vessel.

The CRR vessel is made of an alloy outer shell with internal refractory lining. The vessel is designed and fabricated in accordance with ASME Pressure Vessel Code, Section VIII, Division 2, making it able to withstand pressure surges from any postulated upset or off-normal condition. The CRR steam reformer is provided with the following features and auxiliary systems:

- Several thermocouples are provided to monitor zones in the fluidized bed. The thermocouples are inserted through sealed access thermowells/pipes that allow the thermocouples to be remotely changed out, even during operations.
- Three pressure taps are located in the reformer to provide operating level control data.
- Product outlet valve. The product can be removed by gravity transfer from the bottom of the reformer or alternatively, an eductor jet with isolation valve can be provided on the

bottom of the fluid bed vessel to pneumatically transfer the solids for storage or packaging for disposal. When using the pneumatic transfer method, the bed solids are removed from the reformer through the jet eductor. The eductor serves as the solids outlet flow control valve. The removed solids are pneumatically transferred, by a recirculating nitrogen gas stream, to a product receiver vessel for product cooling and packaging for disposal. The entire solids content of the reformer can be remotely drained via this eductor valve when needed for remote vessel inspections or feed or additive nozzle change-outs.

3.4 OFF-GAS COOLER

The hot off-gas from the outlet of the CRR is cooled by a direct water spray air-atomizing nozzle inserted into the off-gas duct at the top of the CRR vessel. The cooled off-gas is then filtered by the process filter (PRF). The temperature of the off-gas at the outlet of the gas cooler will be 180 to 250°C. The cooling water and atomizing air are controlled as required to maintain the PRF temperature within the desired operating range. An automatic solenoid isolation valve is installed on the water supply to provide fast water shutoff in the event the automated process shutdowns are initiated.

3.5 PROCESS FILTER

The process filter vessel (PRF) is installed downstream of the CRR. The purpose of the PRF filter is to remove and collect any fine solids elutriated from the CRR. The PRF filter comprises a vertical vessel designed to hold high-temperature rated bag-type filter elements. An automated instrument air gas pulse-back manifold is provided to clean the filter elements with the filter on-line. External electrical heaters maintain the filter elements and vessel above the gas dew point to prevent moisture condensation on the filter media during start-up and shutdown periods.

3.6 VACUUM EDUCTOR

The filtered off-gas from the outlet of the PRF filter will pass through the vacuum eductor. The vacuum eductor provides negative pressure for maintaining the PRF, CRR, and freeboard of the DMR under a negative pressure/vacuum. The eductor is provided with motive compressed air. The eductor motive airflow is controlled as required to maintain the pressure in the freeboard of the DMR at 0 to -40 inch W.C vacuum.

3.7 OFF-GAS HANDLING AND MONITORING SYSTEMS

The off-gas filtration and discharge system provides components to filter and monitor the off-gas from the process system prior to discharge up the plant stack. Effective, commercially available hardware components have been selected and proven in actual radioactive service. The off-gas filtration and monitoring system is comprised of the following major components:

- HEPA filters
- Ventilation blower
- Continuous emissions and radionuclide monitors

The off-gas stream is commingled with the facility ventilation airflow and is then passed through banks of HEPA filters. Redundant HEPA filters are provided so that filter elements can be removed and new elements installed while the process system remains on-line. In the event mercury is present in the waste feed stream, an optional granular activated carbon adsorption unit can be placed on the inlet of the HEPA filters to remove any gas-phase elemental mercury. The ventilation blowers provide airflow throughout the facility and controlled levels of negative pressure in various equipment areas. The combined ventilation airflow and clean, cool process off-gases are discharged through a permitted and licensed discharge stack.

Continuous Emission Monitor Systems (CEMS) monitor the gases in the process. Three sets of CEMS will be provided:

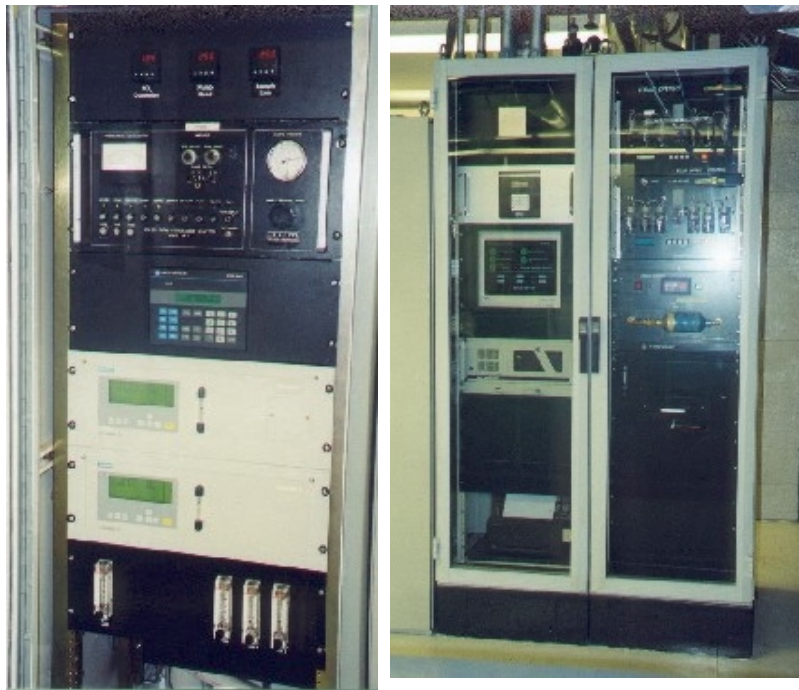
- Gas Outlet of DMR: monitor for O₂ and H₂
- Gas outlet of CRR: monitor for O₂
- Gas outlet of the process filter and vacuum eductor: monitor off-gas for H₂O, O₂, N₂, CO, CO₂, THC, HCl, NO, NO₂, and total NO_x. Total off-gas flow downstream of the eductor shall be continuously monitored and recorded. The off-gas CEMS is operated during start-up and during process qualification to develop process emissions data as a function of system performance. Following start-up and process qualification, the off-gas CEMS is used only as required by the facility air permit.

The DMR CEMS monitors the process gas at the outlet of the steam reformer for the purpose of process control and includes on-line indication of oxygen and hydrogen. The hydrogen monitor is used to control the level of reductants in the DMR fluid bed. The conversion of nitric acid, nitrates and nitrites to nitrogen is proportional to the level of hydrogen generated in the DMR bed by the reformation reactions. If the hydrogen level exceeds the desired levels, the carbon reductant addition rate is decreased. If the hydrogen level decreases below the desired level, the carbon addition rate is increased. The level of hydrogen is simple to control and only minor fluctuations are seen. If oxygen levels in the DMR process outlet gas increases above 2%, the entire THORsm process system will automatically shutdown and the oxygen, steam, and waste feed are isolated to the DMR and a full system nitrogen purge commences.

The CRR CEMS monitors the outlet of the CRR for oxygen for process control purposes. The oxygen monitor actively controls the oxygen input to the CRR reformer bed. The desired level of excess oxygen is set during the process qualification operations and is then automatically controlled during operations. The normal excess oxygen content of the CRR off-gas is 2% to 8% by volume free oxygen.

FIGURE 8 CEMS AND RADIOACTIVE EMISSIONS MONITORING SYSTEMS

The third set of CEMS monitors the process off-gas for documentation of emissions. No process control is required from the off-gas CEMS. The off-gas CEMS analyzes for total hydrocarbon (THC), H₂O, O₂, N₂, CO, CO₂, HCl, SO_x, and NO, NO₂, and total NO_x. These readings are continuously recorded for data analysis and record keeping purposes. Figure 8 shows photographs of the CEMS (left) and the radionuclide monitor (right) systems installed at the SPF.



For radioactive waste processing applications a complete radioactive stack monitoring systems is provided as required by the applicable air permit and radioactive materials handling license.

3.8 PROCESS ADDITIVES - SOLIDS FEEDERS

The THORsm process will utilize several consumables/additives in the process operations. Normally, three additives/co-reactants will be required in the DMR: clay powder, carbon granules and iron oxide particles. One additive will be required in the CRR: calcium carbonate particles. The calcium carbonate particles will also be introduced into the DMR for first time start-up when no mineral product solids are available.

The DMR solids addition system includes two loss-in-weight feeders with air locks, one for clay and one for carbon. The clay and carbon feeders provide continuous addition of the additives/co-reactants to the DMR bed. Additionally, one hopper with remote isolation valves is provided for batch additions of the iron oxide and other catalysts. The outlets of the carbon and clay feeders and catalyst hopper are connected to a common solids transfer line that enters the DMR vessel

near the elevation of the middle of the bed. A small purge of nitrogen keeps the transfer line open into the DMR.

The calcium media feeder for the CRR consists of a hopper provided with a top fill/closure valve and a bottom mounted solids dump valve, identical to the iron oxide hopper for the DMR. The outlet of the calcium media hopper valve ties into the solids transfer line into the CRR. A small purge of air keeps the transfer line open into the CRR.

3.9 PRODUCT PACKAGING SYSTEM

The product packaging system is required for processing radioactive wastes. This section describes the product packaging system for radioactive applications. The product packaging system receives the pneumatically transferred product solids from the eductors on the bottom of the DMR and CRR reformers and process filter vessels. The product packaging system can provide two primary packaging options: (1) non-monolithic final waste form where the granular solids are placed as free-flowing solids in a bulk container for disposal or storage, or (2) monolithic final waste form where the granular product solids are mixed with a cement-like binder and the slurry is placed in a bulk container where the mixture of solids and binder cures to form a monolithic solid with compressive strength exceeding 500 psi. The following equipment is provided as part of the product packaging system:

Granular Solid Packaging System Option

- Product receiver and holdup tank
- Pneumatic transfer blower
- Transfer gas cooler
- Bulk container fillport
- Bulk container lid closure station
- Bulk container transfer cart

Monolithic Solid Packaging System Option

- Product holdup tank
- Binder storage and feeder system
- Bulk container fillport with in-container mixer
- Bulk container lid closure station
- Bulk container transfer cart

Product solids are generally semi-continuously withdrawn from the bottom of the DMR and occasionally withdrawn from the bottom of the CRR and process filter vessels as needed to maintain the solids level in the fluid beds and filter at the desired depths. The individual vessel outlet eductor is used to control the discharge of the product solids from each vessel.

The product solids accumulate in the product receiver vessel, PRR, where the solids are cooled by means of recirculating nitrogen gas. A sintered metal filter assembly is located in the upper section of the PRR vessel to remove product fines from the pneumatic transfer loop. The filter assembly is periodically cleaned by means of remote operation of nitrogen pulse valves. The product receiver/tank is similar to the unit now in radioactive service at the SPF. The PRR vessel is provided with the following features:

- Sintered metal filter assembly
- Nitrogen gas pulse-back valves for remote cleaning of the filter assembly
- Thermocouples (3)
- Pressure transmitters (3)
- Nuclear level monitor

A gas-to-air cooler and gas blower are provided on the outlet of the PRR vessel filter assembly to compress the gas for reuse in the pneumatic gas/product transfer loop and to cool the contents of the PRR vessel. The recycle of cooled and filtered transfer gas minimizes the use of nitrogen gas.

Product solids from the PRR vessel are metered to the bulk container fillport where solids drop by gravity into the bulk container. The fillport is provided with dual elastomeric seals with leak detection purge gas between the seals. A remotely operated scissor lift or equivalent assembly allows lowering and raising of the fillport. Figure 9 is a photograph of the solid product packaging station fillport and container capper assemblies installed at the SPF. The fillport has the following features:

- Dual seal assembly for connection to bulk container
- Dual seal leak detector using purge gas
- Lifting/lowering assembly
- Pneumatic vibrator for fully clearing flexible hose/pipe assembly
- In-container mixer drive adapter – optional, rotates in-container mixer blades for binding solids into monolith inside the container.
- CCTV

For the monolithic solid packaging system option, the granular solids are mixed with a cement binder slurry inside the bulk container. This method of in-container solidification has been used successfully in nuclear power stations for over 20 years with high reliability. Each bulk container (vertical right circular cylinder) is provided with a low-cost, in-container mixer blade system. The fillport connection provides a drive adapter that interfaces with the in-container mixer blades with an external hydraulic drive.

To fill a container and obtain a monolithic solid final waste form, the water for the binder is first metered into the empty container, the mixer blade rotation commences, and binder powder is then added. The product solids are then metered into the cement slurry and mixed to form a homogeneous slurry. When the container is full, the mixing operation continues until the viscosity of the waste and cement increases due to curing. The mixer blade rotation is stopped

and the container is then decoupled from the fillport. The permanent lid is remotely placed and sealed on the container.

The fillport opening for the monolithic packaging option is one 12" diameter or two 4" to 6" diameter sized ports. For the monolithic option, the fillport is provided with a CCTV camera to allow remote visual monitoring of the in-container mixing operation.

For applications that require a monolithic final waste form but do not allow use of an in-container mixer, an in-line mechanical binder mixing system has been

successfully used in the nuclear power stations for mixing wastes with cements and similar binders. In this case, a suitable in-line mixer has proven to be a counter-rotating blender with cam-style, lobed paddles that are self-cleaning. For the in-line mixing method, the cement/water slurry is premixed in a remote mixing tank and the cement/water slurry is metered into the in-line mixer with the metered solid product to form a uniform product/binder mixture that then drops by gravity into the bulk container.

The volume of product in the container is monitored during the container fill operation. The container cart is provided with vibrators for densification of dry bulk solids. The container transfer cart is provided with the following features:

- Remote drive
- Track mounted wheeled cart
- Remote level detectors – radiation based, collimated (2)
- Product densification vibrators

The container closure station involves robotic closure/capping of the bulk container. Closures can include snap-on lids, screw-on lids, welded-on lids, or other options depending on the type of container selected, container materials of construction, and burial waste acceptance criteria (WAC) requirements.

The bulk container fill operation for granular solids involves the following sequence of operations: placement of an empty container on container transfer cart, movement of cart with container under fillport, extension of fillport and connection of fillport to container, filling container with product, disengagement of fillport, capping of container, movement of cart with

**FIGURE 9 SOLID PRODUCT PACKAGING STATION –
FILLPORT AND CONTAINER CAPPER**



full container to survey and external surface decontamination area, and movement of cart and container to container shipment or storage area.

3.10 AUXILIARY EQUIPMENT AND UTILITY SERVICES

The steam reforming process is provided with auxiliary and utility systems and services to support continuous operations. The utility service systems are installed in non-contaminated, indoor and/or outdoor areas. The auxiliary services include:

SCADA control system	Oxygen supply	Service Air
Motor control center	Nitrogen supply	Steam supply
Transformer	Instrument air	Demineralized Water
HVAC Condensers		

The Supervisory Control and Data Acquisition system (SCADA) provides computerized human-machine interface for all aspects of the process. The SCADA provides full remote operation of all systems in radiological and contaminated areas as well as auxiliary and utility services that interface with the thermal process. The SCADA provides multi-layer alarming functions, interlocks, and automated control functions. The SCADA is located in a dedicated control room where operators continuously monitor process and facility operations. Remote CCTV monitors and CEMS and radiological monitor readouts are provided in the control room.

An outdoor transformer with protective switchgear, motor control centers, and uninterruptible power supply (UPS) are provided to safely distribute electrical power and control all electrical equipment. The UPS is designed to provide 20 minutes of continuous SCADA operation of all instruments, controls and valves in the event of a total loss of power to the facility. An optional standby generator can be provided if a secure secondary power source is not available to maintain operation of the ventilation system in the event of a total loss of normal power to the facility. All thermal and process operations can be safely secured in less than one minute in the event of a total loss of power. The motor control center buses are split and electrical loads are arranged to ensure redundant blowers are powered off different buses.

Steam is produced for the process in a propane or natural gas-fired boiler with an operating pressure of <15 psig. The steam is then superheated to approximately 600°C with a 480 volt, three-phase electrical superheater prior to injection into the DMR steam reformer fluid gas distributors. A demineralized water supply system provides make-up water to the steam boiler.

Nitrogen is used in the process as purge gas for instruments to prevent moisture accumulation in the process pressure transmitter sensing lines and to purge and/or cool the waste feed injectors, and waste packaging system seals. Nitrogen is also used to transfer dry solids to prevent potential caking from excess moisture. A liquid nitrogen supply tank and evaporator provide the normal nitrogen needs. The nitrogen system will provide a continuous supply of purge nitrogen in the event of a loss of electrical power to the facility. The nitrogen is used to purge all process equipment during all shutdown operations. This allows full shutdown capability and inerting of

process system in less than one minute, even in the event of a total loss of power to the facility. The nitrogen supply system is located outdoors.

Oxygen is provided by a liquid oxygen tank and evaporator located outdoors. Gaseous oxygen feed is provided to two process inputs: the superheater inlet for the DMR fluidizing gas distributor and to the CRR upper gas distributor. The oxygen system is constructed of qualified and specially cleaned stainless steel components with redundant, automated isolation valves.

If instrument air is not available at the system installation location, two redundant air compressors and a dryer skid provide instrument air. The instrument air is used to power remote actuated valves and to operate power tools during maintenance. The system also provides air to maintenance personnel for breathing and comfort cooling when contact maintenance is required in potentially contaminated areas. The breathing air system provides adsorbers, filters, and controls to assure personnel safety. Compressed service air is required to provide motive air to the process vacuum eductors.

An HVAC system provides temperature control and building ventilation in the accessible areas of the process facility.

3.11 PROCESS CONSUMABLES

The THORsm process utilizes several consumables to efficiently convert nitric acid, nitrates, and nitrites to nitrogen and alkali metals, heavy metals, Cl, F, S, P, and other inorganics to the desired mineral products. Table 2 lists the consumables that are recommended to produce a Na-Al-Si product from a sodium nitrate waste stream.

TABLE 2 PROCESS CONSUMABLES FOR NA-AL-SI PRODUCT

Consumable	Process Function	Quantity
Carbon (granular)	DMR: Nitrate reductant DMR: Iron oxide reductant DMR and CRR: Energy source	Depends on water content of waste
Iron oxide (particles)	DMR: Nitrate reductant catalyst	2% of product solids by weight
Kaolin clay (powder)	DMR: Mineral co-reactant binds Na, K, Al, S, Cl, F, P, non-volatile heavy metals, and radionuclides into water insoluble mineral form (sodium-alumina-silicate)	1 mole clay (Al ₂ O ₃ -2SiO ₂) to 1 mole Na ₂ O
Calcium Carbonate (particles)	CRR: Bed media and trace acid gas adsorption	2% of product solids by weight

4.0 EXPERIENCE SUMMARY

4.1 DEMONSTRATION PROGRAM EXPERIENCE

Studsvik developed the THORsm steam reforming process over a period of several years. Extensive bench-scale and pilot-scale test programs were implemented to qualify and optimize the steam reforming process and to make the technology economical, reliable, and robust. In addition to the multi-year Studsvik test program that developed the THORsm process, now in commercial radioactive operations at the SPF located in Erwin, TN, four additional demonstration programs have been implemented specifically for processing DOE nitrate wastes.

Studsvik performed the initial proof-of-process denitration test program concurrent with the qualification test program performed for the SPF. The test was performed using the Studsvik 6" fluid bed system at the Hazen Research facility located in Golden, CO. The test was performed on 5.2 M NaNO₃ with sugar, carbon, and iron oxide reductants. The fluid bed operated throughout the entire demonstration run with no in-bed agglomerations, with NO_x in the reformer off-gas consistently below 500 ppm. For over half of the test program, the NO_x levels in the reformer off-gas were <100 ppm. A low volume sodium carbonate product was obtained. Figure 10 is a photograph of the pilot-scale fluid bed test facility in Hazen, CO.

A second test program was performed by Lockheed Martin Idaho Technologies Company (LMITCO) using acidic INEEL sodium bearing waste (SBW) surrogate. The demonstration investigated several changes in operating

FIGURE 10 PILOT-SCALE FLUID BED REFORMER DEMONSTRATION SYSTEM ASSEMBLY



parameters and use of additives in a small, 3" diameter, lab-scale fluid bed system installed at SAIC's STAR facility in Idaho Falls, ID. The final process runs demonstrated high conversion of nitrates to nitrogen with <500 ppm NO_x in the reformer off-gas. A sodium carbonate product was produced throughout the test program without agglomeration in the fluid bed.

Studsvik performed a third demonstration under contract with Bechtel National Inc. The bench-scale demonstration of the THORsm process used Hanford LAW (Envelope C) surrogate. The demonstration utilized Studsvik's 6" fluid bed system located at Hazen's facility. The demonstration was performed in November and December 2001. The test results were very positive, with successful operation of the process to generate consistent Na-Al-Si, Na-Si, and sodium carbonate products. The off-gas from the process, over a several day period, confirmed the high nitrate conversion to nitrogen gas with the same results as in the initial Studsvik test.

The mineralized Na-Al-Si product produced during the Bechtel test program has been subjected to numerous analytical tests to determine the leach resistance and projected long-term performance of the mineral product in a radioactive disposal environment. The results of the test program and analytical tests are available in three reports that are summarized below.

The first report was prepared by Studsvik and is titled, "Hanford LAW Waste THORsm Steam Reforming Denitration and Sodium Conversion Demonstration," Final Report, TR-SR01-1. The second report was prepared by Savannah River Technology Center (SRTC) and is titled, "Engineering Study of the Hanford Low Activity Waste (LAW) Steam Reforming Process (U)," by Carol M. Jantzen, dated July 12, 2002. The third report was prepared by Battelle, Pacific Northwest National Laboratory (PNNL) and is titled, "Initial Suitability Evaluation of Steam-Reformed Low Activity Waste for Direct Land Disposal," by B.P. McGrail et.al., dated January 2003. The SRTC report has been publicly released and is available on the THOR Treatment Technologies website, www.THORTT.com.

The Bechtel-Studsvik-Hazen test has shown the following results for the THORsm process Na-Al-Si product, as quoted from the SRTC report:

- "Robust technology capable of accommodating wide ranges of feeds and additives including high concentrations of sulfate" (pg 1)
- "Mineral waste species exhibit a superior durability to LAW glass in both ASTM C1285 and EPA TCLP testing" (pg 1)
- "Medium temperature process low enough not to vaporize radionuclides but high enough to destroy volatile organic compounds (VOCs) in the presence of catalysts: (pg 1)
- "Process generates minimal acid off-gases as the anions (SO₄⁼, F⁻ and Cl⁻) remain in the waste form" (pg 1)
- "Waste form mineral phases are cage like structures that trap radionuclides and anions" (pg 1)
- "Waste form mineral phases are known to have survived millions of years in natural surface and near surface environments" (pg 1)

A summary of the operations for the Bechtel-Studsvik-Hazen test program includes the following:

- The demonstration program proceeded without the presence of agglomerations with continuous, reliable operation.
- NO_x levels in the reformer outlet gases were maintained at <500 ppm total NO_x.
- The vast majority of acid gas components in the waste feed were retained in the mineral crystalline structure, e.g. >91% of the SO₄⁻, >93% of the Cl⁻, and >92% of the F⁻.
- Organic destruction of >99.7% in the DMR reformer. The second stage CRR reformer was not included in the test flowsheet. The THORsm system at Studsvik's SPF includes a reformer followed by a thermal oxidizer that together maintains >99.995% organic destruction and removal efficiency on a continuous basis.
- The vast majority of the radionuclide surrogates were retained in the leach resistance mineral product, e.g. >99.9% of Cs and >99.995% of Re (Tc surrogate)
- The solid Na-Al-Si product contained several heavy metals that exhibited low leachability in the Toxic Characteristics Leach Procedure (TCLP) test, e.g. Cr <0.06 ppm, Pb <0.07 ppm, and Ni <2.80 ppm.

THOR Treatment Technologies (TTT) performed a fourth demonstration of the THORsm steam reforming process under contract with Bechtel BWXT Idaho (BBWI) in January 2003. The demonstration utilized a 6" fluid bed system designed by BBWI and construct by SAIC at the STAR facility in Idaho Falls, ID.

The BBWI-TTT demonstration processed Sodium Bearing Waste (SBW) surrogate, which is a nitric acid based sodium nitrate solution. The SBW surrogate contained several heavy metals, including mercury. The demonstration consisted of a continuous 100 hour run. The process utilized no co-reactant additives, which produced a sodium carbonate product with notable levels of sodium aluminate due to the fairly high concentration of aluminum in the SBW. Scoping tests demonstrated that the THORsm process can efficiently convert concentrated nitric acid into nitrogen gas as well as nitrates and nitrites.

BBWI has prepared a report that discusses the test operations and analytical results. The BBWI report is titled, "THORsm Bench-Scale Steam Reforming Demonstration," by D.W. Marshall, N.R. Soelberg and K.M. Shaber, dated May 2003. The final report is has been issued and will be available on the TTT website, www.THORTT.com.

The BBWI demonstration achieved excellent results as summarized below:

- Nitric acid, nitrates and nitrates were converted to nitrogen in the DMR reformer with >98% efficiency with <300 ppm total NO_x in the reformer outlet gas
- Continuous, reliable operations were achieved throughout the 100 hr demonstration run
- A uniform granular sodium carbonate/sodium aluminate product was produced
- The acid gases anions SO₄⁻ and Cl⁻ were essentially completely retained in the solid products, whereas, the F⁻ mass balance was inconclusive

- The non-radioactive surrogates Cs and Re (surrogate for Tc) were retained in the solid product, e.g. Cs >92% and Re >98% retained in the solid product (limited by mass balance closure)
- No agglomerations were noted in the reformer bed during the 100 hr of operation
- Mercury partitioned to the off-gas as elemental mercury. The solid product retained <0.02% of the mercury in the waste feed. The sulfur impregnated granular activated carbon mercury adsorbent removed ~76% of the mercury from the off-gas stream. Essentially all mercury was converted to the elemental form.

4.2 COMMERCIAL RADIOACTIVE WASTE PROCESSING EXPERIENCE

The Studsvik Processing Facility (SPF) has been in commercial operation processing low-level radioactive waste (LLW) since July 1999. 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, plastic filters, personal protective clothing, 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, see Figure 11. A cut-away view of the SPF is shown on the front cover of this report.



FIGURE 11—STUDSVIK PROCESSING FACILITY – ERWIN, TN

The SPF employs the THORsm process, described in Section 2.0 above. The THORsm steam reforming technology is suitable for processing hazardous, mixed, and dry active (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, robust operating characteristics with volume reductions up to 30:1 and weight reductions up to 20:1 when processing depleted, mixed bed ion exchange resins, with over 99.98% of all radionuclides in the waste feed incorporated into the final solid residue product. Over 100,000 cu ft of LLW ion exchange resin, oils, aqueous liquids, plastics, and granular carbon have been successfully processed since commencement of commercial radioactive operations.

A description of the SPF is available on the internet – search for “Studsvik Processing Facility” or visit the Studsvik and TTT websites.

4.3 INTELLECTUAL PROPERTY

US Patent No. 6,280,694 has been issued to Studsvik, Inc. for the denitration process described in this technology report. The patent covers methods for denitration and immobilization of tank wastes with nitrates using steam in a fluid bed, including the following features:

- Use of steam with reductants (carbonaceous and/or metals, e.g., iron oxide) for converting nitrates to nitrogen in a reducing environment
- Use of a steam agitated (fluidized) bed with nitrate wastes and additives
- Use of oxygen in a steam environment with nitrate waste
- Use of co-reactants in a reducing steam environment (such as phosphate or aluminum compounds, e.g. clay) to immobilize alkali metals (Na and K)

In addition to the above issued patent, Studsvik has pending patent applications in the U.S. and foreign countries that cover minor alternative methods for denitration and immobilization, including use of alternative fluidizing gases with and without oxygen and use of alternative reductants and co-reactants.

5.0 MODULAR SYSTEM DEPLOYMENT

THOR Treatment Technologies (TTT) has developed a unique modular system deployment design that can significantly reduce the capital cost for a turnkey process system. This section discusses the modular approach for deployment of the THORSM steam reforming process. Typical fixed facility construction is still feasible and may be desirable for facilities that will operate for periods of several decades.

5.1 MODULAR SYSTEM SPECIFICATIONS

This section discusses the modular deployment of two different sized steam reforming systems: one over-the-road portable system that can process up to 1.0 gpm of liquid or slurry feed and a larger, high capacity transportable system that can process from 10 to 20 gpm of liquid or slurry feed, depending on the water content of the waste feed. The smaller portable system is designed to use a single 30” diameter DMR reformer and is designated THOR-130. The larger capacity system uses two 72” diameter DMR reformers with each set of reformers and support vessels in a separate process module with a common ventilation and additive module. The combined dual train 72” diameter reformer system is designated THOR-272. Process systems with other capacities and sizes can be designed as required by each application. The facility specifications for the two THORSM systems are provided in Table 10 below. Equipment descriptions are as shown in the flow diagram, Figure 2, and as described in Section 2.0.

TABLE 3 THORSM MODULAR SYSTEM DEPLOYMENT – SYSTEM SPECIFICATIONS

Specification	THOR-130	THOR-272
Nominal Throughput	1.0 gpm	10.0 gpm
DMR Reformer:		
<ul style="list-style-type: none"> • Quantity of Reformers • Inside Diameter • Operating Pressure • Operating Temperature • Bed Material • Operating Environment 	One 30 inch (760 mm) Vacuum: -40 to 0 inch W.C. 725°C Mineralized Product Steam Reforming - Reducing	Two 72 inch (1830 mm) Vacuum: -40 to 0 inch W.C. 725°C Mineralized Product Steam Reforming - Reducing
CRR Reformer:		
<ul style="list-style-type: none"> • Quantity of Reformers • Inside Diameter • Operating Pressure • Operating Temperature • Bed Material • Operating Environment 	One 42 inch (1020 mm) Vacuum: -100 inch W.C. 900 to 1100°C Calcium Granules Steam Reforming -Oxidizing	Two 96 inch (2450 mm) Vacuum: -100 inch W.C. 900 to 1100°C Calcium Granules Steam Reforming -Oxidizing

<p>Process Module:</p> <ul style="list-style-type: none"> • Quantity Modules • Dimensions • Radiation Shielding • Major Equipment each Module: <ul style="list-style-type: none"> ○ Waste Feed Tank ○ DMR Reformer ○ In-Line Cooler ○ Process Filter ○ Vacuum Eductor ○ Product Receiver ○ Product Packaging 	<p>One 16ftW x 24ftL x 40ft Ht up to 10” Carbon Steel</p> <p>One One One One One One One</p>	<p>Two 30ftW x 57ftL x 45ft Ht up to 10” Carbon Steel</p> <p>One One One One One Two Two</p>
<p>Ventilation Module:</p> <ul style="list-style-type: none"> • Quantity Modules • Dimensions • Radiation Shielding • Major Equipment: <ul style="list-style-type: none"> ○ HEPA Filters ○ Vent Blowers ○ CEMS ○ Radiation Monitors ○ Switchgear/MCCs 	<p>One 14ftW x 40ftL x 14ftHt None Required</p> <p>Four, 1x2 HEPA Two, One Redundant One Set One Set One Set</p>	<p>One 22ftW x 57ftL x 26ftHt None Required</p> <p>Sixteen, 1x3 HEPA Four, Two Redundant One Set One Set Two Sets</p>
<p>Additive Addition Module:</p> <ul style="list-style-type: none"> • Quantity Modules • Dimensions • Radiation Shielding • Major Equipment: <ul style="list-style-type: none"> ○ Clay Feeder ○ Carbon Feeder ○ Catalyst Feeder ○ CRR Media Feeder 	<p>One 14ftW x 24ftL x 14ftHt None Required</p> <p>One One One One</p>	<p>One 22ftW x 37ftL x 17ftHt None Required</p> <p>Two Two Two Two</p>
<p>Utility Services:</p> <ul style="list-style-type: none"> • Electrical Power • Nitrogen • Oxygen • Steam • Fire/Service Water • Compressed Air 	<p>480VAC, 375 amp 60 SCFM 100 SCFM 400 lb/hr 0.5 to 1 gpm 200 SCFM</p>	<p>480VAC, 3000 amp 300 SCFM 1000 SCFM 4500 lb/hr 5 to 10 gpm 2000 SCFM</p>
<p>Safety and Containment:</p> <ul style="list-style-type: none"> • Secondary Spill Protection • Seismic Qualified Systems • Seismic Qualified Structure • Seal-Welded Structure 	<p>Yes Yes Yes Yes</p>	<p>Yes Yes Yes Yes</p>

5.2 MODULAR SYSTEM DESIGN AND CONSTRUCTION

Both the THOR-130 and THOR-272 systems are based upon principals of modular design and construction common in the oil field and used for certain applications in the commercial nuclear sector for temporary service equipment used during outages. TTT personnel have designed, constructed and utilized a wide variety of modular equipment in radioactive service over the past twenty years. Modules typically include process vessels and tanks, pumps, blowers, piping, instrumentation and controls, shielding, spill containment, etc. - all integrated into space and cost-efficient structural steel building enclosures.

The unique features of modular design require that the structural steel enclosure support the vessels and equipment during transport and operations. The steel enclosures are generally much stronger than built-in place buildings and support structures. For radioactive applications, the steel structure is fully seal-welded with built-in spill protection liners. The steel enclosure is, therefore, much tighter than most built-in place concrete and “Butler-type” steel buildings. Meeting seismic design specifications is readily achieved, as shipping forces are generally higher than seismic forces.

A principal benefit of modular construction is that the modules can be constructed and tested in a qualified, indoor, module fabrication shop where construction efficiencies and stable labor staff produce quality construction with minimum cost and schedule. Another advantage is that modules can be transported from one operational site to other sites providing tremendous savings over building multiple plants.

A module construction effort comprises the following steps:

- Prepare temporary foundation slab for module construction at module shop
- Place module base frame steel and weld together
- Install module sides and top structural steel beams and weld together
- Install equipment supports and major interior steel, such as fixed shielding
- Install major equipment such as vessel and blowers
- Install outer steel siding and roof plates, continuous steel plate skin panels, on module columns and beams and seal weld in place
- Install minor equipment
- Install piping and cable trays
- Pull power cables and terminate
- Install instruments and terminate wiring
- Checkout electrical, align motors, and hydrotest piping
- Checkout control system terminations and bump motors
- Start-up subsystems
- Perform integrated system operations – operate all systems and utility services as an integrated process system
- Perform acceptance tests and train operators

- Disassemble interconnecting cables and piping between modules and utility skids
- Load-out modules and skids and ship to operations location
- Set equipment on permanent foundation slab at operating location
- Interconnect piping and cables between modules at operating location
- Start-up systems and perform final checkout and operational readiness review
- Start processing waste

The reassembly of modules at the operational location is greatly simplified by the use of quick-disconnect cables, field bus instruments, and break-out pipe spools. Reassembly and checkout of the entire THOR-130 system at the operations location should take no more than 3 weeks. The much larger THOR-272 system would take approximately 6 weeks to interconnect and perform start-up checkouts. For installations that will be permanent, the modules can be welded to fixed embedments in the permanent foundation slab and interconnecting pipe and personnel passages can be welded so as to provide complete spill protection and contamination control.

The complete module assembly for THOR-130 is shown in Figure 12. The modules are close connected and occupy a very small footprint. For radioactive operations, carbon steel shielding provides effective, efficient shielding with minimal space requirements. The major shielding for the process module is provided by the use of exterior concrete slabs or steel plates that are bolted to the exterior of the module structure. This approach minimizes shipping weight and allows use of an optimal amount of shielding, only the amount of shielding that is actually required is put installed. This feature also allows additional shielding to be added, even during operations. The steel structure provides the seismic restraint and load carrying capacity for the shielding. The THOR-130 system is portable and can be easily disassembled for reuse at other operating locations. The seal-welded steel structure and internal stainless steel liners provide full containment and hazardous spill protection. Seal tightness can be tested if desired. Open or enclosed stairs provide personnel access to the maintenance and equipment access areas.

The complete module assembly for THOR-272 is shown in Figure 13. The modules are close connected and occupy a very small footprint for the high throughput capacity of the plant. For radioactive operations, carbon steel plate shielding provides effective, efficient shielding with minimal space requirements where needed on the interior of the process module. The major shielding of the two process modules is provided by the use of exterior concrete slabs or steel plates that are bolted to the exterior of the module structures. For some interior shielded walls, iron oxide granular shot is used. This approach minimizes shipping weight and allows use of an optimal amount of shielding, only the amount of shielding that is actually required is installed. This feature also allows additional or more effective shielding to be added, even during operations. The steel structure provides the seismic restraint and load carrying capacity for the shielding materials. The THOR-272 system is transportable and due to its large size is generally transported to and set-up for permanent use at a single operating locations. The seal-welded steel structure and internal stainless steel liners provide full containment and spill protection. Seal tightness can be tested if desired. Open or enclosed stairs provide personnel access to the maintenance and equipment access areas.

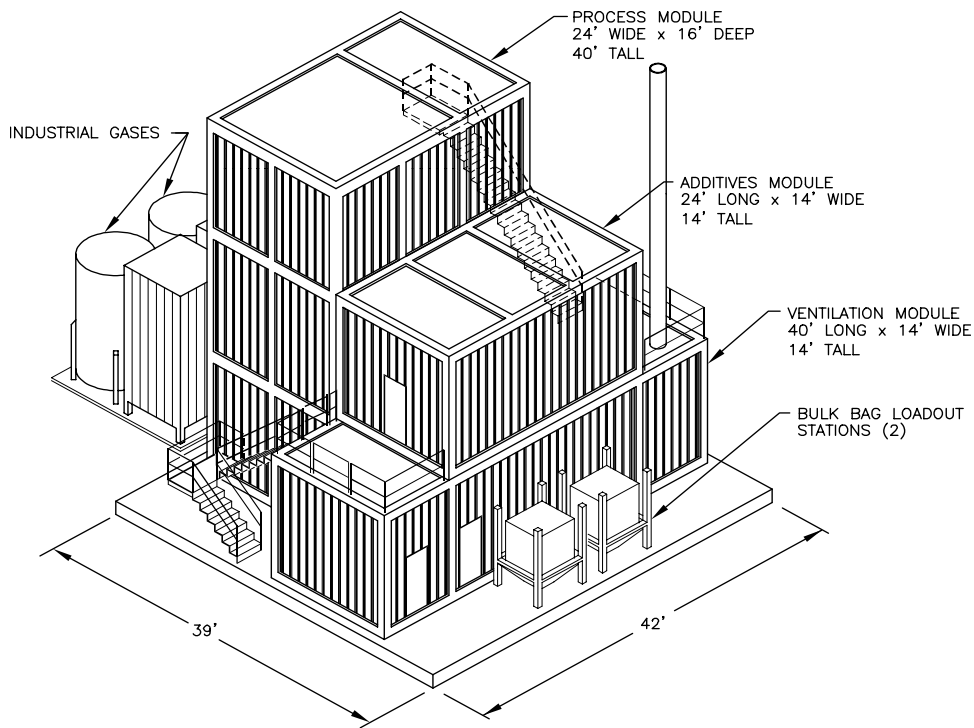


FIGURE 12 THOR-130 MODULAR SYSTEM ASSEMBLY

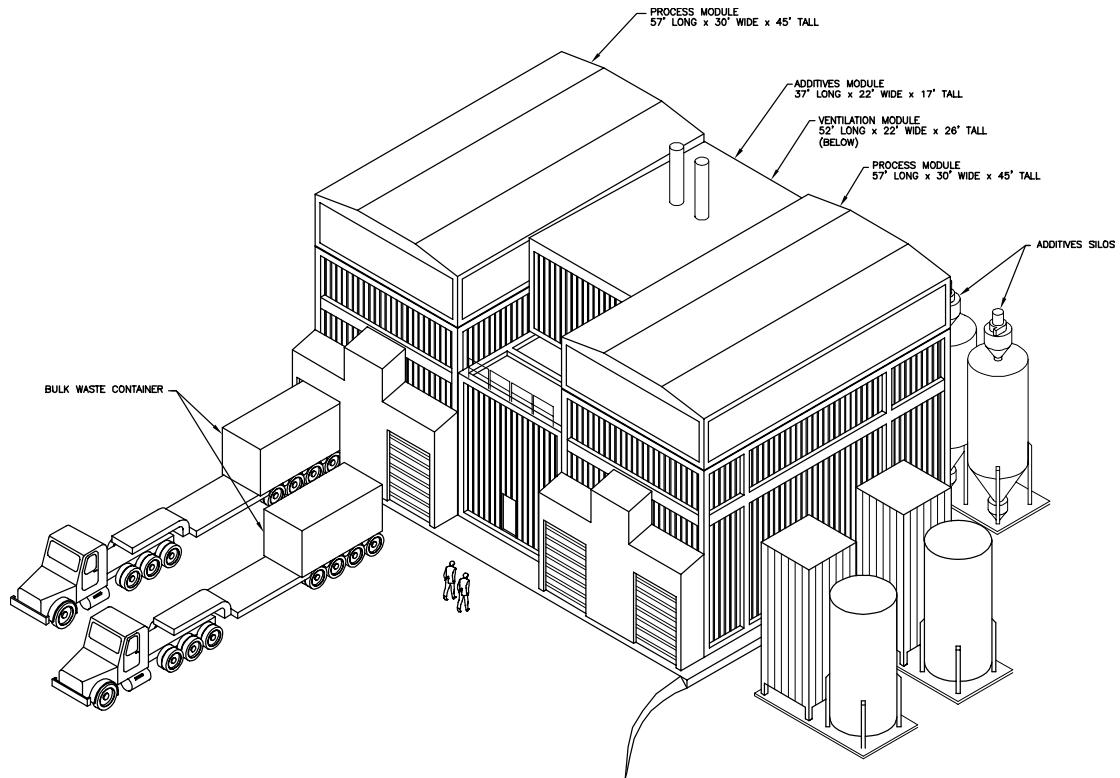


FIGURE 13 THOR-272 MODULAR SYSTEM ASSEMBLY

5.3 MODULAR SYSTEM SHIPMENT

Most modules can be transported over-the-road by using low-boy type heavy haul tractor trailers. This is true of the THOR-130 modules and the THOR-272 modules, except for the larger THOR-272 process module. For the THOR-272 process module, a multi-axle, transport carrier is required. Transport of the THOR-272 process module is usually limited to barge transport with short haul carrier movement from the barge unloading area to the facility production location. Figure 14 shows an illustration of the shipping methods used for the THOR-130 system and Figure 15 shows an illustration of the shipping method used for the THOR-272 system.

The modules use a heavy structural steel frame with load beams that transfer the loads from the process equipment supports to the truck or transporter vehicle frame. For modules that are less than 200 tons, a crane is used to lift the completed module onto the transport trailer. For the heavy THOR-272 process module, hydraulic lifting jacks are used to lift the module off the construction foundation and the multi-axle carrier is then backed under the module and the jacks are lowered to settle the module onto the transporter.

5.4 MODULAR SYSTEM LIFE CYCLE COSTS

The combined modular system design and construction and the simple, robust THORsm process can provide substantial savings for facility cost and operations and maintenance costs. Figure 16 provides a graphical indication of the life cycle costs for typical sizes of THORsm systems. Two graphs are shown in Figure 16, the upper graph is for more concentrated sodium nitrate wastes, such as DOE Hanford LAW tank waste with 3 to 10 M Na content, and the lower graph is for dilute wastes such as DOE Hanford WTP LAW melter scrubber recycle and Savannah River Site DWPF melter scrubber recycle. The life cycle cost graph assumes a 15-year amortization of all facility design, construction, and start-up costs and include all operations and maintenance costs.

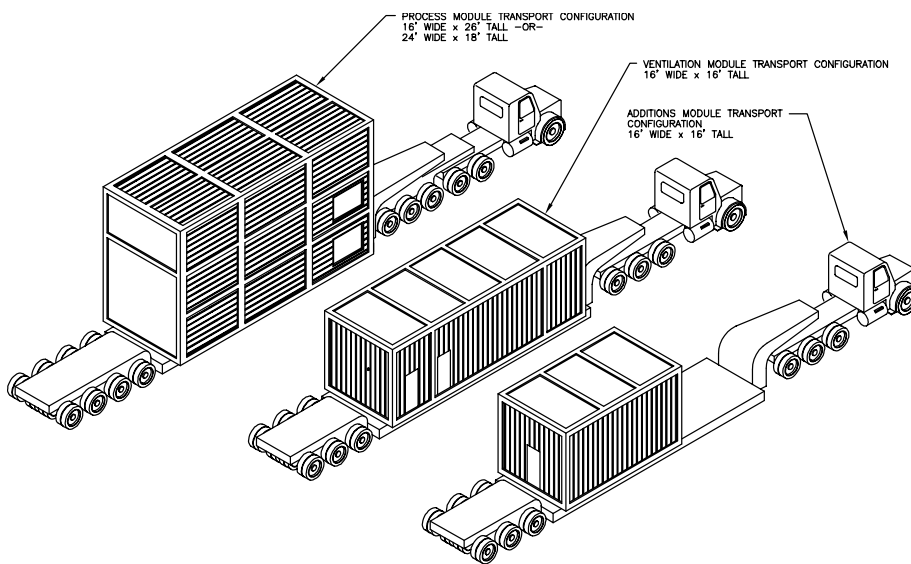


FIGURE 14 THOR-130 SHIPPING ARRANGEMENT

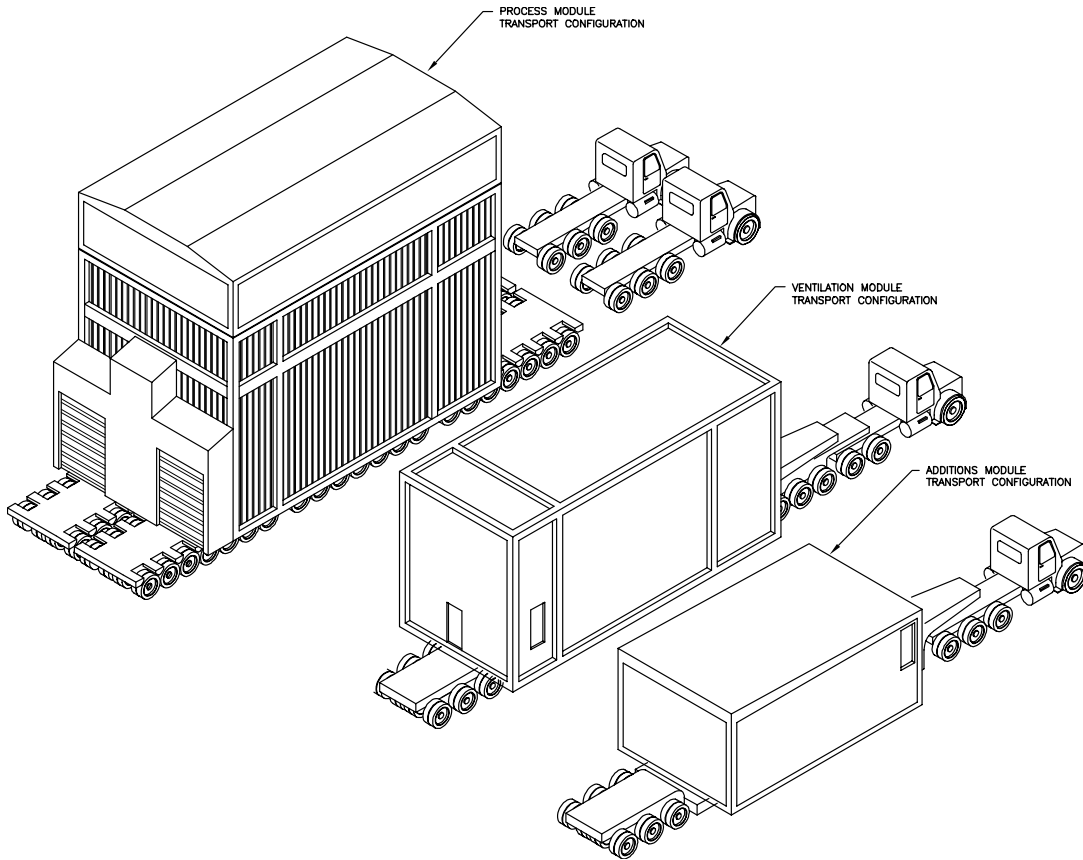


FIGURE 15 THOR-272 SHIPPING ARRANGEMENT

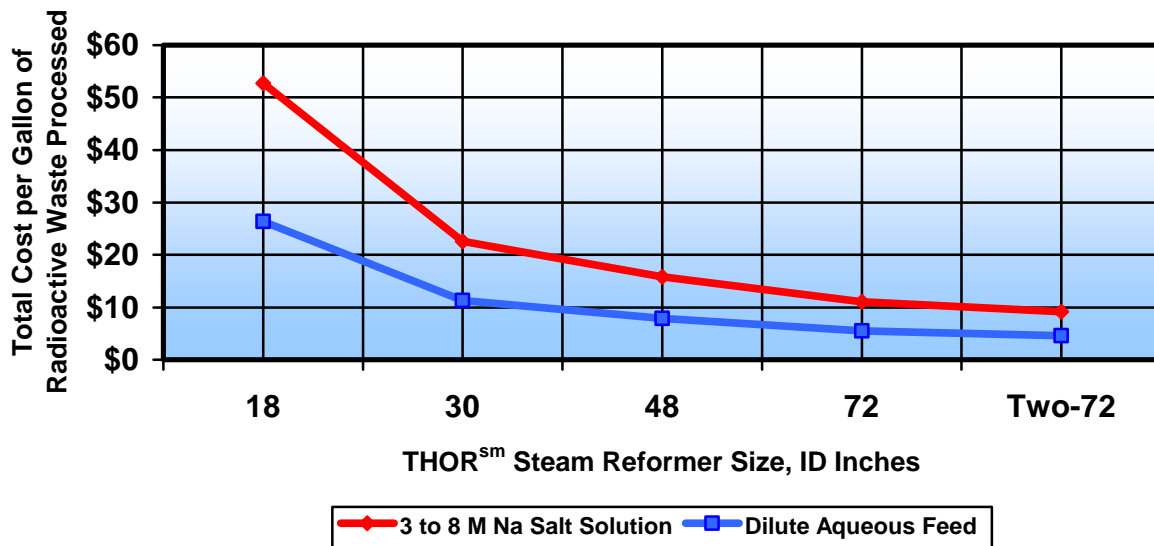


FIGURE 16 THORSM STEAM REFORMING SYSTEM – LIFE CYCLE COSTS

5.5 SUMMARY

In summary, the THORsm process has many salient features as listed below:

- Waste feed can include solids, liquids, slurries, and gases.
- Acidic and basic tank wastes can be processed without neutralization.
- Nitrates, nitrites and nitric acid are destroyed with <10 ppm residual nitrates in solid product, < 300 ppm NO_x in reformer off-gas (wet basis).
- S, Cl, P, and F are immobilized in a stable Na-Al-Si mineral form, with no secondary scrubber solution waste stream and <10 ppm SO_x, HCl, or HF in off-gas at stack.
- Alkali metals, radionuclides, and non-volatile heavy metals are immobilized in stable, water insoluble, Na-Al-Si mineral form.
- Greater than 99.9% of radionuclides are incorporated into the solid product. Tritium, carbon¹⁴, and iodine are generally partitioned to the off-gas.
- Na-Al-Si product meets LDR UTS limits for heavy metal leachability (TCLP test).
- Final solid product can be sodium-alumina-silicate, sodium carbonate, sodium silicate, sodium aluminate, or calcium compound.
- Systems operate under vacuum (0 to -120 inch W.C.).
- Safe shutdown can be accomplished in <1 minute.
- Reformers contain a very low inventory of unreacted waste.
- Vessels can be drained of contents and decontaminated by acid or water washes to allow contact maintenance on most components.
- Facility is zero-liquid release, as water vapor is discharged up the stack.
- Wastes with high water content, high organic contents, high phosphate, and/or high sulfate content are efficiently processed.
- Process simplicity allows efficient modularization of process systems.
- Process has been used in commercial radioactive service for 4 years, processing ion exchange resins with high salt content, as well as oils, plastics, spent carbon, etc., with contact does rates of up to 400 Rad/hr.

6.0 APPENDICES

6.1 COMPARISON OF THORsm WITH OTHER REFORMER TECHNOLOGIES

The THORsm process is the only steam reforming technology that has processed large volumes of radioactive wastes. The THORsm process is the only known thermal process that can produce an immobilized final waste product without the use of grout or vitrification. Nitrates are directly converted to nitrogen gas in a single step with <300 ppm total NO_x in the reformer outlet gases. The Na-Al-Si product effectively retains the S, Cl, P, and F in the final immobilized product, in a single step, without the need for secondary salt solution waste processing or wet scrubber systems. No secondary process wastes are produced, unless the mercury adsorber is required, and the facility has zero-liquid releases. Table 4 compares the THORsm process with other commercially available steam reformer technologies for nitrate containing wastes.

TABLE 4 THORsm OUTPERFORMS OTHER REFORMER TECHNOLOGIES

Feature	THOR sm	Duratek/Synthetica	Thermo-Chem
Fluid Bed Steam Reforming Process	Yes	No	Yes
Volume of LLW Processed	>100,000 cuft	<3,000 cuft	0
Demonstrations – Non-Rad	1997, 2000, 2001, 2003	1995	1995-1997
Waste Feed Surrogates	Hanford LAW-B, DAW, INEEL SBW, Organics	Hanford LAW	DAW, Organics
Product Composition	Na-Al-Si or Na-Al or Na-Si or Na ₂ CO ₃	Na ₂ CO ₃	Ash
Product Water Solubility	Insoluble (Na-Al-Si)	Soluble	Partly Soluble
Pass TCLP – LDR UTS	Yes (Na-Al-Si)	No, unless Grouted	No, unless Grouted
Immobilized	Yes (Na-Al-Si)	No, unless Grouted	No, unless Grouted
Residual Nitrates in Product	<5 ppm	~5,000 ppm	Not Tested
S, Cl, F Retention in Product	>95%	Unknown	Not Reported
Off-Gas from Reformer:			
<ul style="list-style-type: none"> • Nitrate Conversion to N₂ • NO_x in Off-Gas • SO_x, HCl, HF 	<ul style="list-style-type: none"> >98% to N₂ <300ppm <20 ppm 	<ul style="list-style-type: none"> ≤5% to N₂ >20,000 ppm Unknown 	<ul style="list-style-type: none"> Not Reported Not Tested Unknown
Reference/DOE Contract		DE-AC04-76DP00789	DE-AR21-95MC32091

6.2 FULL-SCALE THORsm APPLICATIONS ACROSS THE DOE COMPLEX

The THORsm process is suitable for applications for thermal treatment of a wide variety of LLW including the following waste streams:

Hanford:

- High sulfate LAW
- WTP LAW melter scrubber recycle
- WTP Cs/Sr spent ion exchange resins
- Balance of Mission LAW

Savannah River:

- DWPF effluent
- Out-of-Spec tank waste (Tank 48)
- Saltstone LAW feed
- Spent solvents (F-Canyon)

INEEL:

- Sodium bearing waste
- Newly generated liquid wastes
- Tank heels and sludges
- V-Tank sludges
- Reprocess calcine

West Valley:

- Orphan nitrate LAW