

**Technical Review of the Applicability of the  
Studsvik, Inc. Thor<sup>sm</sup> Process to INEEL SBW**

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## EXECUTIVE SUMMARY

Approximately 1,000,000 gallons of liquid waste, termed sodium-bearing waste (SBW), resulting from a variety of processes (e.g., laboratory operations and decontamination processes) are stored temporarily in 300,000-gallon underground storage tanks at the U.S. Department of Energy's (DOE's) Idaho Site, also known as the Idaho National Engineering and Environmental Laboratory (INEEL).

A 1998 Modification to Notice of Non-compliance Consent Order issued by the State of Idaho directed DOE to cease use of the tanks for storing the liquid waste by December 31, 2012. As part of the necessary actions to comply with this date, DOE Idaho Operations Office (DOE-ID) issued for public comment a draft environmental impact statement evaluating various alternatives for treatment/disposal of the SBW and their associated impacts.

This report summarizes actions, findings, and recommendations of a Tanks Focus Area (TFA) Review Team recently chartered to evaluate the technical feasibility and, to the extent possible, cost incentives of the Studsvik, Inc. (Studsvik) steam-reforming technology for treating retrieved SBW. Studsvik recently submitted a technical proposal to DOE-ID to demonstrate the plant-scale and actual application of steam-reforming technology to denitrate both surrogate and actual SBW at the Studsvik facility in Erwin, Tennessee. Receipt of this technical proposal prompted DOE-ID to request that the TFA organize a Review Team to conduct an in-depth evaluation of the technical feasibility and cost incentives, if any, of steam reforming for treating SBW.

Based upon the findings of their evaluation, the Review Team concludes the following:

1. Steam reforming of SBW will not generate a waste form qualified for direct disposal in a high-level waste (HLW) repository.
2. There are marginal technical incentives for steam reforming of SBW to generate a waste form for direct disposal in the Waste Isolation Pilot Plant (WIPP) as a Remote-Handled transuranic (TRU) waste. However, uncertainties related to waste type (HLW or TRU), the status of Resource Conservation and Recovery Act requirements at WIPP, the impacts of long-term storage of the steam-reformed product, and cost of a facility that satisfies safety requirements at INEEL appear to outweigh the technical incentives.
3. Steam reforming of SBW to produce a solid feed for subsequent vitrification appears to be a technically viable option if the presence of chemicals added or created during reforming is shown to not adversely impact melter reliability and if there is an incentive for partitioning sulfate to the off-gas stream.

Thus, the Review Team recommends the following actions:

1. DOE-ID should vigorously maintain and pursue direct vitrification as the baseline technology for treating and immobilizing SBW.

2. DOE-ID should not pursue further steam-reforming initiatives for treatment of SBW to produce waste forms for direct disposal in a federal HLW repository or in WIPP.
3. DOE-ID should follow a multistep process with appropriate go/no go decision points to properly evaluate further steam reforming of SBW to produce an interim solid form suitable for subsequent vitrification. A decision on the current Studsvik proposal to conduct tests with surrogate and actual SBW in their Erwin, Tennessee, facility should be delayed pending the results of the multistep process.
4. Although somewhat outside the scope of this review, the Review Team recommends that DOE-ID consider the application of steam reforming to the treatment of the off-gas that would be generated by direct vitrification of the SBW.

## Acronyms

CH <sub>4</sub>	methane
CO	carbon monoxide
CO <sub>2</sub>	carbon dioxide
DOE	U.S. Department of Energy
DOE-ID	DOE Idaho Operations Office
EIS	environmental impact statement
HEPA	high efficiency particulate air (filter)
HLW	high-level waste
H <sub>2</sub> O	water
INEEL	Idaho National Engineering and Environmental Laboratory
LLW	low-level waste
NaOH	sodium hydroxide
SBW	sodium-bearing waste
RH	remote-handled
RCRA	Resource Conservation and Recovery Act
TFA	Tanks Focus Area
THOR <sup>sm</sup>	Thermal Organic Reduction
TRU	transuranic
WIPP	Waste Isolation Pilot Plant
WIPP-WAC	Waste Isolation Pilot Plant Waste Acceptance Criteria

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## 1.0 Introduction

Approximately 1,000,000 gallons of liquid waste, termed sodium-bearing waste (SBW), resulting from a variety of processes (e.g., laboratory operations and decontamination processes) are stored temporarily in 300,000-gallon underground storage tanks at the U.S. Department of Energy's (DOE's) Idaho Site, also known as the Idaho National Engineering and Environmental Laboratory (INEEL). Estimates of the composition of the wastes now stored in the tanks are provided in DOE 1999a. SBW may be classified as transuranic waste after a "waste incidental to reprocessing" determination is made (DOE 1999b).

A 1998 Modification to Notice of Non-compliance Consent Order issued by the State of Idaho directed DOE to cease use of the tanks for storing the liquid waste by December 31, 2012. As part of the necessary actions to comply with this date, DOE Idaho Operations Office (DOE-ID) issued for public comment a draft environmental impact statement (EIS) evaluating various alternatives for treatment/disposal of the SBW and their associated impacts (DOE 1999c).

This report summarizes actions, findings, and recommendations of a Tanks Focus Area (TFA) Review Team recently chartered to evaluate the technical feasibility and, to the extent possible, cost incentives of the Studsvik, Inc. (Studsvik) steam-reforming technology for treating retrieved SBW. Steam-reforming technology, as embodied in the Studsvik Thermal Organic Reduction (THOR<sup>sm</sup>) process, involves reaction, in a fluidized bed, of selected candidate radioactive wastes with steam and certain reductants/additives, to produce a small volume of inorganic residue essentially free of nitrates and organic materials. Primarily because only limited technical information (Studsvik, 2000a) was available, steam-reforming technology was not initially considered as an option to carry forward to the final EIS and Record of Decision (PNNL 2000).

Studsvik recently submitted a technical proposal (Studsvik 2000b) to DOE-ID to demonstrate the plant-scale and actual application of steam-reforming technology to denitrate both surrogate and actual SBW at the Studsvik facility in Erwin, Tennessee. Receipt of this technical proposal prompted DOE-ID to request that the TFA organize a Review Team to conduct an in-depth evaluation of the technical feasibility and cost incentives, if any, of steam reforming for treating SBW.

## 2.0 Findings, Conclusions, and Recommendations

This section collects and summarizes the Review Team's findings, conclusions, and recommendations concerning the application of the Studsvik steam-reforming technology to SBW. Two candidate applications are addressed:

- Treatment to produce a waste form suitable for direct disposal either as a HLW or as a transuranic (TRU) waste.
- Treatment to produce an interim solid-waste form suitable as feed to a vitrification process.

### 2.1 Findings

General findings and findings specific to the two candidate applications of steam reforming are discussed in this section. Section 5.0 of this report discusses findings and uncertainties in greater detail.

#### 2.1.1 General

1. Although several highly significant technical uncertainties remain unresolved, the Review Team believes that application of the Studsvik steam-reforming process to SBW would satisfactorily denitrate the waste to yield a product consisting of dry inorganic salts. Major technical uncertainties include:
  - a. Limited experience in applying steam-reforming technology to surrogate SBW and no experience with actual SBW.
  - b. Propensity for and frequency of agglomerate formation during steam-reforming operations.
  - c. Absence of a suitably demonstrated remote method for dealing with agglomerates.
  - d. Hygroscopic nature of the steam-reformed product and potential consequences to the acceptability of the product for long-term interim storage, vitrification, and/or disposal in a repository.
  - e. Limited understanding of partitioning of certain key chemicals and radionuclides (e.g., sulfate,  $^{137}\text{Cs}$ ,  $^{99}\text{Tc}$ ) between the process off-gas and the final steam-reformed product.
  - f. Unspecified technology for separating mercury from the steam-reforming process off-gas and converting it to a form suitable for disposal.

- g. Technical challenge of modifying the present Studsvik steam-reforming equipment design and facility to permit safe and reliable remote operations and maintenance consistent with the administrative dose limits at INEEL.
  - h. Lack of a methodology for satisfactorily accommodating the presence of chemical components (e.g., alumina, carbon, elemental iron, SiC) that may be present in the steam-reformed product at levels that compromise effective vitrification.
2. The Review Team was not able to judge if there is an economic incentive to implement a steam-reforming process at INEEL to treat SBW due to the sparse facility and operating-cost information available, and because of high uncertainties in the cost of upgrading the Erwin, Tennessee plant design to meet INEEL standards.

### 2.1.2 Production of a Waste Form for Direct Repository Disposal

The Review Team found that there is no strong technical incentive to implement a steam-reforming process over direct vitrification for treating SBW to produce a waste form suitable for direct disposal in a federal HLW repository or at the Waste Isolation Pilot Plant (WIPP). Specifically:

1. If SBW is classified as HLW, the steam-reformed product would not qualify for disposal in a federal HLW repository. Currently, borosilicate glass and spent fuel are the only HLW forms qualified for final repository disposal. Even if these current waste form qualification requirements were eliminated, the high solubility and hazardous chemical constituents would probably preclude the steam-reformed product as an acceptable waste form.
2. If the SBW is classified as a TRU waste, the steam-reformed product may qualify for disposal as remote-handled (RH) TRU waste in WIPP. However, there are several obstacles to such disposal, any one of which alone or in concert with another could prevent disposal of the steam-reformed product in WIPP. These include:
  - The SBW may be determined to be HLW and not a TRU waste, thereby requiring compliance with the requirements of the federal HLW repository.
  - The State of New Mexico may initiate legal action to prohibit or indefinitely delay shipment of waste containing hazardous chemical constituents to WIPP.
  - Delays in shipping may result in extended interim storage of the packaged steam-reformed product. This could raise safety questions and issues because of the potential for the product to hydrate and generate gas through radiolysis of residual water and organics.
3. According to Studsvik estimates (Studsvik 2000b), steam reforming of SBW would generate 505 to 750 cubic meters of product compared to 440 cubic meters of monolithic glass logs produced by direct vitrification (PNNL 2000). Studsvik personnel suggested that the steam-reformed product could be fused to substantially reduce its volume. The fusion step would

add to the overall complexity and cost of treating the SBW; would involve complicated remote handling of a highly radioactive, dispersible powder; and would not, at least for SBW classified as HLW, produce a waste form suitable for repository disposal.

### **2.1.3 Production of an Interim Solid Form for Subsequent Vitrification**

1. The Review Team noted that the dry powder produced by steam reforming of SBW may be a suitable feed for vitrification. Vitrification of a solid, denitrated SBW, rather than liquid SBW, could simplify melter off-gas equipment and improve melter throughput rates.
2. The Review Team also noted that it may be technically feasible to adjust steam-reforming process conditions to partition much of the sulfate in the SBW feed to the off-gas stream as SO<sub>x</sub>. Sulfate is known to be a feed component that may limit the loading of other waste components in borosilicate glass waste form or result in a corrosive layer of molten salt in the melter. Hence, removal of at least some of the sulfate from the SBW by steam reforming may reduce the volume of SBW glass produced. However, the Review Team is not yet convinced that the level of sulfate in the SBW is high enough to be a deterrent to its direct vitrification.
3. Steam reforming of SBW to generate a solid feed for subsequent vitrification would present several technical problems that would need resolution. Specifically:
  - Secondary wastes generated in the steam-reforming process that contain halides, sulfate, mercury and other metals would need to be treated and disposed of.
  - The product from the steam-reforming process may need to be oxidized further (to destroy carbon and elemental iron) before vitrification.
  - The product from the steam-reforming process contains alumina, which, because of its relatively high density and refractory nature, may settle in the melter and interfere with vitrification operations.
  - Operating a melter with a solid feed instead of a liquid feed would require additional solids-handling capability and moving parts that could add greatly to problems encountered in operation and maintenance of a liquid-fed melter. The hygroscopic nature of a solid feed is an added complexity.
  - Variability in the concentration of chemicals added to or created in the steam-reformed SBW will probably require blending, sampling, and analysis to ensure reliable melter performance and an acceptable glass product.

## 2.2 Conclusions

Based upon the findings summarized in Section 2.1, the Review Team concludes:

4. Steam reforming of SBW will not generate a waste form qualified for direct disposal in a HLW repository.
5. There are marginal technical incentives for steam reforming of SBW to generate a waste form for direct disposal in WIPP as a RH-TRU waste. However, uncertainties related to waste type (HLW or TRU), the status of Resource Conservation and Recovery Act (RCRA) requirements at WIPP, the impacts of long-term storage of the steam-reformed product, and cost of a facility that satisfies safety requirements at INEEL appear to outweigh the technical incentives.
6. Steam reforming of SBW to produce a solid feed for subsequent vitrification appears to be a technically viable option if the presence of chemicals added or created during reforming is shown to not adversely impact melter reliability and if there is an incentive for partitioning sulfate to the off-gas stream.

## 2.3 Recommendations

The Review Team recommends the following actions:

5. DOE-ID should vigorously maintain and pursue direct vitrification as the baseline technology for treating and immobilizing SBW.
6. DOE-ID should not pursue further steam-reforming initiatives for treatment of SBW to produce waste forms for direct disposal in a federal HLW repository or in WIPP.
7. DOE-ID should follow a multistep process with appropriate go/no go decision points to properly evaluate further steam reforming of SBW to produce an interim solid form suitable for subsequent vitrification. A decision on the current Studsvik proposal to conduct tests with surrogate and actual SBW in their Erwin, Tennessee, facility should be delayed pending the results of the multistep process. These steps include:
  - Commission, fund, oversee, and document an engineering study, using the best available data, to compare the technical and economic incentives and advantages of a combined steam reforming and vitrification process versus direct vitrification of liquid SBW. A key objective of this study is to determine if the quantities of sulfate known or anticipated to be present in SBW will present problems in direct vitrification. Advantages and disadvantages of methods other than steam reforming for dealing with excessive amounts of sulfate, e.g., reduced glass loadings and blending of SBW batches, should be discussed and evaluated. The engineering study should also compare and evaluate advantages and disadvantages of operating a vitrification facility with a solid feed versus a liquid feed.

- In parallel with the recommended engineering study, commission and fund Studsvik to prepare a technical proposal, including a proposed schedule and costs, for conducting a structured series of small-scale tests with surrogate SBW at the Hazen Research Inc. facility in Golden, Colorado. The objectives of these tests are to establish (a) general technical feasibility of a steam-reforming process for treating SBW, (b) the degree of partitioning of feed components to the off-gas stream and steam-reformed product, both with and without addition of aluminosilicate clays to the steam-reforming process, and (c) the need for and quantities of additives to ensure safe, reliable steam reforming.
  - Decide, on the basis of the results of the comprehensive engineering study and merits of the proposed tests, whether to implement all or parts of the test program proposed by Studsvik.
  - If a decision is made to revise and implement the test program, use the results of the tests to update the engineering study and, if steam reforming still appears attractive, decide if the baseline technology for treating SBW should be changed.
8. Although somewhat outside the scope of this review, The Review Team recommends that DOE-ID consider the application of steam reforming to the treatment of the off-gas that would be generated by direct vitrification of the SBW. Steam-reforming technology may offer certain technical and/or economic advantages. These include (a) reducing the NO<sub>x</sub> concentration of the off gas stream over conventional melter off-gas treatment technologies, (b) treating acidic scrubber solutions to destroy nitrate and organics, and (c) rendering other chemicals non-hazardous, thereby eliminating a hazardous secondary waste stream.

## **3.0 Independent Review**

This section identifies the membership of the Review Team, its scope, and the methodology it used to assess the feasibility of steam reforming of SBW.

### **3.1 Review Team Members**

The Review Team consisted of four members:

- Wallace W. Schulz, Consultant, W2S Co., Inc., Hanford Retiree, Team Chairman
- Joseph A. Gentilucci, Consultant, JAG Technical Services, Inc., Savannah River Retiree
- James E. Miller, Sandia National Laboratories
- Russell L. Treat, Consultant, Dade Moeller and Associates, Inc.

Mr. Schulz also serves as Chair of the TFA Technical Advisory Group. The remaining team members are experienced chemical engineers with substantial experience in nuclear waste treatment technologies. Resumes of the Review Team members are provided in Appendix A.

### **3.2 Review Scope**

The initial scope of this review, as stated in a written communication from Mr. Thomas Brouns, Manager, TFA Technical Team, was to "... conduct an independent technical review of a technical proposal they (i.e., DOE-ID) have received from Studsvik, Inc. on a steam-reforming system to process SBW. The objectives of the review are to determine the technical feasibility and applicability to SBW and cost realism of the proposed system." In a subsequent telephone conversation with the Review Team, Mr. Joel Case, Director, Idaho Nuclear Technology and Engineering Center Waste Programs, confirmed that the review should address the general technical applicability of the Studsvik steam-reforming system to the SBW. Mr. Case added that the review should evaluate the applicability in the case of the future classification of SBW as HLW or as TRU waste. Mr. Case also reaffirmed his desire for the Review Team to identify costs and potential cost savings offered by steam-reforming technology over alternative processing methodologies, e.g., direct vitrification and radionuclide separations, to the extent achievable.

It is important to note that the review was concerned solely with the application of steam reforming to SBW; the potential application of the technology to other wastes at INEEL or elsewhere in the DOE complex was not addressed.

### **3.3 Assessment Methodology**

The Review Team and several DOE-ID and INEEL site contractor personnel visited the Studsvik processing facility in Erwin, Tennessee, on August 24, 2000, to tour the facility and engage in technical discussions with Studsvik personnel. Relevant Studsvik reports and brochures

(Studsvik 2000a; Studsvik 2000b)<sup>(a)</sup> were provided before the visit. Also, before the visit, the Review Team submitted various written questions (Appendix B) to Studsvik concerning steam-reforming technology and Studsvik's experience with the technology. These questions and the Studsvik responses to them (see Appendix B) formed the basis for the technical discussions.

Additional questions orally posed to Studsvik personnel during the visit are included in Appendix C. Studsvik's responses are reflected in the evaluation of the steam-reforming application to SBW provided in Section 5.0.

The Review Team met the day following the visit in Johnson City, Tennessee, to formulate findings and recommendations and to prepare draft sections of this report. Further report preparation was accomplished in Richland, Washington, on August 28–30 by Msrs. Schulz and Treat. Comments and suggestions from the other team members were solicited, addressed, and incorporated in the final manuscript.

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(a) Letter: Transmittal Studsvik, Inc. Demonstration Process, Mr. Brad Mason to Mr. Darryl Siemens, Columbia, South Carolina (1998).

## 4.0 Description of the Studsvik THOR<sup>sm</sup> Process

This section describes the current application of the Studsvik steam-reforming technology and its potential application to SBW. A description of the chemistry of steam reforming and nitrate destruction is provided in Appendix D.

### 4.1 Current Application

Studsvik's THOR<sup>sm</sup> process is used at a commercial facility located in Erwin, Tennessee, for reducing the volumes of low-level waste (LLW), primarily spent organic ion exchange resins. In the currently deployed process, waste is fed directly to the steam reformer either as a slurry via a metering pump or as shredded solids through a lock hopper. The reforming reactor consists of a vertical vessel containing a fluidized bed of alumina sand that is designed to operate at temperatures of up to 800 °C. For safety reasons and to ensure containment of steam-reformed product and gases within the processing equipment, the bed operates at a negative pressure. Heat is supplied to the bed through the injection of superheated steam. Additional energy is supplied by injecting oxygen into the bed where it reacts exothermically with reductants present in the waste or added to the waste. The temperature of the bed is thus controlled by adjusting the inlet temperature of the fluidizing steam and by regulating the amount of oxygen and reductant injected.

Water fed into the pyrolyzer as a component of the waste is converted to superheated steam. Organic compounds are broken down through thermal processes (pyrolysis) and through reaction with the high-temperature steam and oxygen. The gaseous effluent exiting the top of the bed consists primarily of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), hydrogen (H<sub>2</sub>), and water (H<sub>2</sub>O). Smaller amounts of organic compounds, e.g. methane (CH<sub>4</sub>), and volatile metals, e.g. mercury (Hg), may also be present. The fine solids (<100 microns) resulting from the pyrolysis/reforming reaction are disengaged from the larger alumina particles that constitute the semi-permanent bed in a cyclone at the top of the reactor and are entrained in the gas flow. The fine solids include the dried inorganic portion of the injected waste as well as small amounts of fixed carbon and abraded particulates from the bed.

The fluidized bed is designed to be operated such that less than 5% of the total bed weight is due to waste solids to ensure that the inert part of the bed acts as a large heat sink, thereby avoiding problems with agglomeration caused by the presence of low-melting salt eutectics in the waste. Recovery from an agglomeration of the bed media involves cooling the bed and washing the media with hot water. The dissolved salts are then returned to the waste feed tank for reprocessing. The bed is then dried and re-fluidized through the injection of superheated steam. Alternately, a water-wash screw conveyor has been designed for installation on the bottom of the bed. Operation of the screw would augment the de-agglomeration process.

The solid products that elutriate from the pyrolyzer/reformer are collected on the surface of ceramic filter elements. The filter elements are periodically backpulsed with nitrogen to recover the solids. The hot product gases pass through the filter to an oxidation chamber and evaporator where energy is recovered by evaporating excess water from spent scrubber solution. The concentrated scrubber solution is filtered to remove insoluble materials and then dried to produce

a salt product for final disposal. The cooled gases pass out of the evaporator to the scrubber where acid gases (sulfur and halogens) are neutralized by sodium hydroxide (NaOH). The gases then pass through the demister and water-recovery condenser before entering the blower. The blower compresses the gases to atmospheric pressure and forces them through the ceramic thermal converter where combustible gases (CO, H<sub>2</sub>) are oxidized at 1000–1100 °C. Finally, the gases are cooled, filtered in the baghouse and high efficiency particulate air (HEPA) filtration system and released through a monitored vent stack.

## 4.2 Application of the THOR<sup>sm</sup> Process to SBW

The SBW stored at INEEL is an acidic solution of sodium and aluminum nitrates that contains smaller amounts of other cations and anions. The process proposed by Studsvik for processing SBW is similar to the currently operating process at Erwin, Tennessee. In the proposed steam-reforming process, cations would be primarily converted to a powdery form composed principally of carbonates and/or aluminates. Volatile anions and cations exiting the reformer process would be converted to dried salt. Nitrate ions would be reduced to nitrogen while reducing agents would be oxidized to carbon monoxide, carbon dioxide, and water.

The primary unit operation of the proposed process is the fluidized alumina bed reactor. The reactor would be operated in an autothermal mode at subatmospheric pressure. The bed would be fluidized through the injection of superheated steam. The SBW, after mixing with sucrose, would be fed to the reactor. Solid carbon would be fed separately as a reactant in the steam-reforming process. Additional additives, such as aluminosilicate clay (kaolin type), may also be added to alter the physical and chemical properties of the final product. Water in the waste would be vaporized to superheated steam. Nitrates would exothermically react with the sucrose and carbon to yield H<sub>2</sub>, nitrogen (N<sub>2</sub>), CO, CO<sub>2</sub>, and water. Additional energy would be supplied to the bed by injecting oxygen to react with the carbon sources. Adjusting the inlet temperature of the fluidizing steam and the amount of oxygen injected would enable control of the temperature of the bed. Organic compounds in the waste would be broken down through thermal processes (pyrolysis) and through reaction with hot nitrates, steam, and oxygen. Reforming reactions with the carbon sources would produce H<sub>2</sub>, CO, and CO<sub>2</sub>. Additional oxygen would be fed at the top of the bed to convert most of the CO and H<sub>2</sub> to CO<sub>2</sub> and water, respectively.

The fluidized bed would be designed to be operated such that less than 5% of the total bed weight is due to waste solids to avoid problems with agglomeration. Studsvik anticipates that as many as three bed agglomerations a year could occur. A hot-water wash system is the anticipated method for recovery from an agglomeration event. The resulting hot wash solution would be returned to the waste feed tank. The bed would then be dried and re-fluidized through the injection of superheated steam.

The fine solid-waste products, including small amounts of fixed carbon and alumina fines from the bed, would be separated from the larger semi-permanent fluid-bed particles in a cyclone above and internal to the reactor. The resultant vapor stream would be passed through ceramic candle filters where the solids would be separated from the vapors. The filter candles periodically would be backpulsed with nitrogen to recover the solids, which would then be packaged for disposal. These solids would be combined with larger particles that occasionally

would be discharged from the bottom of the fluid bed reactor. Together these solids would make up the primary steam-reformed product.

The vapor stream exiting the ceramic candle filters would be processed through a quencher where acid gases would be neutralized. The heat content of the vapor stream would be used to concentrate the resulting salt solution to about 20 weight percent solids. The concentrated solution would be processed to dryness in a spray dryer and then packaged as solid salt particles. The vapor from the dryer would be combined with building air exhaust before HEPA filtration. The water vapor from the scrubber would be condensed and cooled. The gases exiting the condenser would pass through a demister and bag house before being treated with air in a thermal converter. The thermal converter is an electrically heated high-temperature system that would convert the CO and H<sub>2</sub> to CO<sub>2</sub> and water. The vapors exiting the thermal converter would be passed through a HEPA filter and a cooler before being discharged to the atmosphere through a monitored vent stack.

## 5.0 Evaluation of the Application of Steam Reforming to SBW

This section provides an assessment the feasibility of steam reforming of SBW. Uncertainties and risks in two different SBW processing options that include steam reforming as part of each option are also presented. This evaluation served as the basis for the summary of findings, conclusions, and recommendations presented in Section 2.0.

### 5.1 General Feasibility

The current steam-reforming process operated by Studsvik has been demonstrated to be effective in processing spent ion exchange resins and other LLWs from commercial nuclear reactors. Studsvik has not performed large-scale reforming of nitrate solutions, although Studsvik cited several industrial applications and tests that substantiate Studsvik's assertions that steam reforming is applicable to SBW and that most of the nitrate in the waste would be reduced to nitrogen. Although Studsvik's Erwin, Tennessee, plant has only been in operation for 1 year, the staff possess the relevant backgrounds and technical knowledge to understand the application of the technology to SBW. The Review Team could not have completed this evaluation without the expertise demonstrated by Studsvik in its submitted documents and in answers to questions before and during the Review Team's visit on August 24, 2000.

Several unresolved concerns remained after the plant visit. Studsvik previously identified many of the concerns and proposed to resolve them in a testing program (Studsvik 2000b). One of those concerns is the absence of an adequate understanding of the competing steam-reforming and off-gas treatment reactions. This understanding is necessary to establish a process material balance, which is needed to support decision making and cost estimates regarding the technology. Many assumptions about the effectiveness of the technology must be made because of the absence of an adequate material balance. However, sufficient analogous experience exists to support preliminary decision making and cost estimating.

Areas of greatest concern in the steam-reforming application to SBW include (a) the degree of partitioning of sulfate to the steam-reformer off gas, (b) recovery and treatment of vaporized mercury, (c) the potential for and recovery from agglomeration of the steam-reformer bed, (d) the effect of additives to the steam-reformer reactor that carry over into downstream processes, (e) the suitability of the highly soluble steam-reformed product and secondary wastes for disposal, (f) selection of alloys to accommodate the highly corrosive process off gases, and differences in commercial and DOE safety standards. These concerns are discussed below; some are further discussed in Section 5.2.

Partitioning of sulfate (as  $\text{SO}_x$ ) to the off-gas stream is of interest because of concern expressed by INEEL staff that higher levels of sulfate may be present in SBW than previously thought. The higher levels may limit the waste loading in glass, thereby increasing glass volume, processing time, and costs. Studsvik estimated that about half of the sulfate in the SBW would be partitioned to the off-gas stream. Studsvik reported, based on the experiences of a major supplier of industrial processing equipment (Dorr-Oliver), that the addition of aluminosilicate clays may enhance sulfate partitioning by preferentially reacting with sodium.

An adequate method of recovering Hg from the off-gas stream is of interest because of the high concentration of Hg in the SBW. The recovered Hg must be treated. Several treatment options are available, but these have not been demonstrated under the conditions created by processing SBW in a steam reformer.

Studsvik projected that the steam-reformer bed would become agglomerated and require cleanout at a frequency of about one to three times per year. Studsvik predicted that recovery by flushing the agglomerates with hot water would be successful due to the highly soluble nature of the steam-reformed SBW. High solubility should ensure that the agglomerates can be readily decomposed into alumina sand and salt solution. Studsvik also suggested that aluminosilicate clays could be added to the reformer bed to react with low-melting, agglomerate-forming sodium salts in the SBW, thereby ensuring a very low potential for forming agglomerates in the bed. The high alumina content of the clay could substantially increase the amount of glass that would be formed if the steam-reformed SBW is to be vitrified, however.

Several chemicals not present in the SBW are expected to be present in the steam-reformed product. These include alumina from alumina sand added to create the bed, carbon from activated carbon and sucrose added to react with the water and nitrate, possibly small quantities of elemental iron formed by the reduction of iron compounds in the SBW during steam reforming, and, occasionally, silicon carbide from broken filter candles. These chemicals may have adverse impacts on the vitrification process as discussed later.

The process off gases will be highly corrosive due to the presence of phosphate, sulfate, and halides; this problem is in common with the direct vitrification process off-gas system, however.

Studsvik reported substantially higher annual worker doses than received by most workers within the DOE complex. The higher doses are a consequence of a design philosophy that reflects the realities of being competitive in the commercial nuclear sector. Design upgrades, especially in the reformer reactor, filter, and product handling systems, will be required to meet the administrative dose limits at INEEL.

## **5.2 Processing Options**

Two SBW processing options that include steam reforming as a processing element are (a) generation of a steam-reformed product that is suitable for direct disposal and (b) generation of an interim product that is suitable for vitrification. The processes for these two options would begin with steam reforming, but would end with different treatment steps to satisfy the acceptance criteria for disposal and the specifications for melter feed, respectively. Findings for these two options are discussed below.

### **5.2.1 Direct Disposal**

The physical characteristics of the steam-reformed SBW product are expected to be similar to those of commercial steam-reformed products, i.e. a powdery material with a density of about 0.9 g/cc. Such a product would not comply with the requirements for disposing of HLW in a federal repository (DOE 1999d). These requirements include consolidation of particulates into a

non-dispersible form that (a) does not support combustion, (b) generates essentially no gas and pressure (< 22 psia), (c) contains no detectable organic materials, and (d) is not subject to regulation under RCRA.

The powdery product of the steam-reforming technology would not satisfy the particle-consolidation requirement. The presence of carbon, carbonate, and small quantities of water, organics, and metals in a leachable chemical form also raises serious doubts about the ability of this waste form to satisfy the other requirements. Fusing the particles by the application of pressure and/or steam may create a consolidated waste form as required, but the potential for complying with the other requirements would not be improved appreciably.

DOE-ID is currently seeking a determination of the designation of SBW (HLW or TRU) in accordance with the waste incidental to reprocessing process defined in DOE 1999b. As such, compliance with the federal repository requirements for HLW may not be necessary. However, the significant TRU fraction of steam-reformed SBW would be sufficient to require disposal at WIPP in accordance with the Waste Isolation Pilot Plant Waste Acceptance Criteria (WIPP-WAC) (DOE 1999e). While the disposal requirements at WIPP are less demanding than those for the federal HLW repository, there are two major uncertainties that should be resolved before committing to any process that generates a waste form that satisfies requirements of the WIPP-WAC, but not those of the federal HLW repository:

1. The likelihood that SBW will be determined TRU waste through the waste incidental to reprocessing process remains highly uncertain. The issue remains at the discussion stage, and there appears to be only limited activity devoted to an early determination.
2. Partial RCRA compliance at WIPP is apparently being enforced by the State of New Mexico, despite the exemption from RCRA's Land Disposal Requirements. This enforcement could lead to the need for further treatment of steam-reformed SBW, or it may result in an indefinite, extended period of interim storage of the packaged product. Corrosion and pressurization of containers during extended storage has been a chronic problem in the DOE complex. Extensive testing may be necessary to establish RCRA compliance and an acceptably low level of corrosion and gas generation.

### **5.2.2 Preparation of Steam-Reformed Feed for the Vitrification Process**

Steam-reformed SBW may be a suitable feed for vitrification. Advantages of using steam reforming to produce melter feed include:

1. Partitioning sulfate to the off-gas stream would ensure that sulfate does not unduly limit the mass loading of SBW in the glass formulation nor cause a corrosive molten salt layer to form in the melter.
2. Destruction or partial destruction of organic compounds that contribute to the "listed" status of SBW would occur, which may enable RCRA-delisting of the salt waste recovered from the off gas stream.

3. The aqueous component of SBW would be eliminated; thereby reducing the load on the melter and the melter off-gas system and potentially improving the stability of the glass-making process.
4. The steam-reformed SBW could be stored and later processed in the same vitrification system that may be used to process calcine stored at INEEL.
5. Destruction of nitrates by steam reforming would eliminate the requirement for treating NO<sub>x</sub> emissions in the melter off-gas system.

These advantages are further discussed below:

The need to partition sulfate to the off-gas stream as SO<sub>x</sub> has not been established. During a meeting of an expert panel and INEEL personnel in June, 2000, to assess selected technologies for treating SBW and calcine (PNNL 2000), INEEL personnel reported that 38% simulated SBW oxide had been loaded in glass. During the visit to the Studsvik facility on August 24, 2000, INEEL personnel reported that recent analyses of sulfate in SBW were higher than originally thought. INEEL personnel also reported that the sulfate levels ranged by a factor of about three from lowest to highest concentration. The Review Team believes that it would be prudent for INEEL to reassess SBW loadings in glass in light of the new sulfate data so that the merits of sulfate partitioning can be better evaluated. The expert panel at the June, 2000, meeting recommended homogenizing the SBW tanks so as to reduce the need for process testing, the level of glass qualification testing required, and the demands on the processing equipment for processing a variable waste composition (PNNL 2000). Homogenizing the SBW may also enable the maximum waste loading in glass to be achieved and eliminate the need for sulfate partitioning or other sulfate-removal processes.

INEEL personnel reported to the expert panel during the June, 2000, meeting that the SBW contained several organic solvents that rendered the waste as being listed under RCRA. The effectiveness of steam reforming in destroying the solvents to a level that meets the Environmental Protection Agency's treatment standards is unknown, but may be achievable with a proper reformer design. Meeting these standards is a key element of delisting the steam-reformed secondary salt waste stream and permitting its disposal.

Removing the aqueous component of SBW by steam reforming would reduce the load on the glass melter by eliminating the need for the melter to serve as an evaporator as well as to fuse the other waste components and additives into a glass product. A smaller melter and off-gas system would be needed in this case. Operation of the off-gas system also may be made more stable by eliminating the component (water) that contributes most to variability in gas rates exiting the melter. Elimination of nitrates by steam reforming would also simplify operation of the off-gas system since the need to control NO<sub>x</sub> emissions would be eliminated. The smaller melter and off-gas system also may be suitable for processing both steam-reformed SBW and calcine because the physical characteristics of these wastes are expected to be similar.

Disadvantages of steam reforming of SBW to produce a feed for vitrification include:

1. Materials added or created during steam reforming may adversely impact melter performance.
2. The steam-reformed product may lose its free-flowing characteristics due to its hygroscopic nature.
3. The life-cycle cost of a steam reformer/vitrification system is probably higher than the life-cycle cost of direct vitrification.

These disadvantages are further discussed below:

Materials added to the steam-reformed product or created during steam reforming include alumina sand from the reformer bed, carbon from activated carbon, sugar added to support the reforming and autothermal reactions in the reforming process, silicon carbide from broken filter candles, and possibly small amounts of elemental iron and other easily reduced metals.

Studsvik projected that carryover of alumina from the bed would constitute about 4% of the total mass of the steam-reformed SBW. The alumina sand is very refractory and relatively high in density (~3.8g/cc vs. ~2.5g/cc for glass). Thus, the alumina will resist dissolution in the glass and probably will settle to the bottom of the melter where it may accumulate. Accumulated alumina may disrupt the flow of electrical current in the melter and reduce the residence time for melting the waste and glass-reforming additives. Results may include shortened melter life and a glass product that is not fully melted.

Studsvik projected that about 4% carbon would be present in the steam-reformed SBW product. Glass-making experience within the DOE complex has shown that wastes with similar carbon contents can cause the reduction of certain metal oxides and salts to their elemental states. The reduced metals are much denser than glass and will settle rapidly to the bottom of the melter where they will coalesce into pools. The metal pools are especially corrosive to the refractory brick at the bottom of the melter and, if allowed to build up, will eventually cause the melter to fail due to electrical short-circuiting through the pools or due to the refractory drilling action caused by electrical coupling to the pools. Reduced iron in the steam-reformed SBW and perhaps the silicon carbide will also contribute to the potential for corrosion and electrical short-circuiting. A possible solution to the presence of carbon and reduced iron is oxidation in a reactor before feeding the steam-reformed SBW to a melter. Testing would be required to evaluate the magnitude of the metal reduction problem and the effectiveness of potential solutions.

The relative fractions of alumina, carbon, iron, and silicon carbide in the steam-reformed product will vary over time as a function of variability in the operating parameters of the reformer. The magnitude of this variability is unknown, but is probably high enough to require blending, sampling, and analysis of large batches of the steam-reformed SBW to guarantee reliable melter operation and an acceptable glass product for repository disposal. Thus, it is unlikely the reformer and melter cannot be directly coupled, i.e., the freshly produced steam-reformed

product probably cannot be fed directly to a melter. An intermediate solids handling system is probably required. This system would convey the steam-reformed solids to silos for interim storage; blend, sample, and analyze blended solids batches; establish the glass formulation and reduction/oxidation (redox) conditions for reliable melter operation; and feed the blended solids batch in the required proportion with the glass-forming and redox control chemicals. Operating and maintaining such a solids handling system under the remote conditions required to ensure acceptable worker doses at INEEL would be a significant challenge.

The need for steam reforming and additional solid handling in the combined steam-reforming/vitrification system probably equates to higher capital costs than for a direct vitrification system. The higher number of unit operations probably equates to higher operations and maintenance costs as well.

The steam-reformed SBW contains a high concentration of sodium salts known to be hygroscopic. This characteristic may cause the steam-reformed SBW to agglomerate in the storage silos unless precautions are taken to prevent exposure of the material to room air. Some agglomeration of the calcine at INEEL, which has a much lower sodium content than SBW, has been observed (NAS 1999).

Disposal costs will be proportional to the amount of waste glass that will be produced. The amount appears to depend on whether the sulfate level in SBW significantly limits waste loading in the glass. An evaluation of sulfate concentrations in the SBW and the impact of sulfate on glass production can then be compared to any benefits of sulfate partitioning by steam reforming.

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**APPENDIX A**  
**Resumes of Review Team Members**

**JOSEPH A. GENTILUCCI**

**Profession:** Chemical Engineer

**Education**

1953 B.A. – Chemical Engineering, Lafayette College, Easton, PA.  
Magna Cum Laude  
Rank: 1st. of 16 Chemical Engineers  
3rd. of 125 Engineers  
8th. in Class of 315  
Honorary Societies:  
Phi Beta Kappa  
Tau Beta Pi

**Professional Experience**

Sept 1993 – Present Independent Contractor  
JAG Tech Services, Inc.  
127 Savannah Drive  
Aiken, S. C. 29803-5833

May 1978 – Mar 1994 Westinghouse Savannah River Company  
and E. I. du Pont de Nemours and Co., Inc.  
Savannah River Site  
Aiken, S. C. 29808  
Supervisor: J. F. Ortaldo

Jan 1975 – Jan 1978 Inland Chemical Corporation  
P.O. Box 36, 1702 Winter Street  
Fort Wayne, Indiana 46801  
Supervisor: R. R. Elston, President

June 1953 – Jan 1975 E. I. du Pont de Nemours and Co., Inc.  
Orange, Texas and Niagara Falls, N. Y.  
Supervisor: D. Sanders  
Low Density Polyolefins Division  
Superintendent (Orange, Texas)

**Patent**

Patent No. 3,502,734 – Process for partially chlorinating methyl chloride and/or methylene chloride, R. M. Baird, P. K. Baumgarten, J. A. Gentilucci (assigned to E. I. du Pont de Nemours and Co.)

## Amplification of Resume of Joseph A. Gentilucci

### **Employment Highlights**

Sept 1993 to Present  
JAG Tech Services, Inc.

Established JAG Tech Services, Inc. as an S Corporation to provide consulting services associated with the preparation and/or review of technical programs and procedures and perform independent evaluations of existing technical programs. Past contracts have been associated with:

- Two with Los Alamos Technical Associates relative to the Hanford Double Shell Tank Program and the Tank Waste Remediation System Process Configuration Alternatives Review.
- A fiscal 1995 through 1997 contract with Westinghouse Hanford Company on Down Selection of High Level Melter Alternatives, Redirection of Development Programs for Low Level Melter Alternatives and technology liaison with the Savannah River Site.
- Consulting services to the Lockheed Martin Hanford Company on their waste treatment programs and technology liaison with the Savannah River Site through fiscal year 1998.
- SGN Eurisys Services Corporation on vitrification and technology programs
- Mississippi State University on development of test facilities for establishing an accredited test facility.
- A short term contract with PNNL in 1998 on a DOE sponsored technical review of the Phase 1 submittals from private industry on the Privatization of Hanford Waste Disposal.
- COGEMA Engineering on canister storage costs and concepts
- Lockheed Martin Hanford Company on review of Cs and Sr processing concepts.

Current contracts are in place:

- With Pacific Northwest National Laboratories to participate in the Technical Review Group for Immobilization associated with the Tank Focus Area program through December 1999.
- With Westinghouse Savannah River Site on technology programs related to the operation of the Defense Waste Processing Facility through December 1999.
- With Concurrent Technologies Corporation to participate in an External Independent Review of the Readiness of the Office Of River Protection and their contractors to Privatize the disposal of nuclear wastes at the Hanford Site.

May 1978 to Mar 1994  
Westinghouse Savannah River Company & E. I du Pont de Nemours Co.

For the sixteen years I was associated with the Defense Waste Processing Facility (DWPF). During that time, this multi-billion dollar program for the vitrification of highly radioactive waste, was brought from the conceptual phase through design, construction and is currently in operation. My participation in this program started with the writing of the first basic data report on the conceptual facility including the tank farm requirements for feed preparation and its relationship to DWPF operation. I then went to San Francisco to open the liaison office with Bechtel National who was the Architectural Engineer on the Project. I later returned to the

Savannah River Site where I continued as liaison and then assumed responsibilities for construction liaison and establishing the construction quality verification program. I then initiated the first phases of the field component testing program and established the basic testing requirements for bringing the facility through simulated feed operation to radioactive operation. These assignments not only covered the testing and operating requirements but also involved demonstration of glass product quality to meet the Federal Repository requirements. I later assumed responsibilities for Technical Advisor to the Joint Test Group in the Start Up Organization which was assigned to direct the testing of the facility. My last assignment was Manager of Process Engineering for the DWPF. In this assignment, I was responsible for maintaining the overall technology assurance and configuration of the process including directing technical experimentation programs required to support operations. In addition, I was responsible for technology exchanges with the Hanford Waste Vitrification Plant and other vitrification facilities such as Pamala, Cogema and Sellafield. During this period I also directed and participated in many operational activities such as establishing manpower requirements, job assignments, presenting overview training, future project budgeting and resolution of technical problems.

Jan 1975 to Jan 1978  
Inland Chemical Corporation

Inland Chemical Corporation was a privately owned corporation specializing in the reclamation of solvents from waste streams. As Director of Process Development, I was responsible for improvement of process equipment, procedures to maximize the yield of recoverable solvents and plans to optimize the throughput capabilities of the plants. As new waste streams were uncovered, I was responsible for evaluating the potential for recovery within the existing equipment or determining modifications to permit recovery. On large waste streams, I was responsible for developing overall process schemes including sizing of major equipment and evaluating the economic potential for the process. These assignments required coordination between sales, manufacturing and the customer.

June 1953 to Jan 1975  
E. I. du Pont de Nemours and Co., Inc.

In my last assignment, assistant division superintendent, at du Pont, I was responsible for supervising more than 100 men including wage roll, foremen and supervisors in the manufacture of polyolefin resins on a multi unit installation. These responsibilities included; personnel administration, estimating production capabilities and costs, manufacturing the desired products to specification at the desired rates in a safe and economical manner, determining the adequacy of proposed expansions to meet future commitments, and obtaining the necessary support from other organizations such as technical and maintenance to accomplish these objectives.

Other assignments (in reverse order with time) with du Pont were:

- Sr. Technical Supervisor, Elvax Liaison
- Sr. Technical Supervisor, Chlorine Products
- Sr. Engineer, Chlorine Products Expansion and Startup

Supervisor, Startup of Chloromethanol Process  
Engineer, Chlorine Products Expansion and Startup  
Supervisor, Step I and II THF and ZFC Catalyst  
Supervisor, Step II THF and ZFC Catalyst  
Supervisor, Sodium Perborate and Per Compounds  
Staff Engineer, Sodium Products Construction Liaison  
Supervisor, Sodium Peroxide  
Supervisor, Chloromethanol Products  
Engineer, Chlorine Products

## VITA of JAMES E. MILLER

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James Miller graduated from Texas A&M University with a B.S. in Chemical Engineering in 1986. He then attended the University of Texas at Austin and received a Ph.D. in Chemical Engineering in 1992. He began his work at Sandia National Laboratories in 1992 in a post-doctoral position where he studied oxidation catalysts derived from hydrous metal oxides. In 1993 he joined Sandia as a Senior Member of the Technical Staff to work on radioactive waste processing technologies. He led technical efforts to develop steam-reforming technologies for organics destruction, and highly selective inorganic ion exchange materials for waste separations (an R&D 100 award winning technology that has been utilized on commercial scales). He has been involved in the evaluation of catalysts for coal liquefaction and upgrading of coal and petroleum liquids (hydrotreating/hydrocracking) and has recently focused his efforts on the development of catalysts for oxidative dehydrogenation and lignin (biomass) utilization.

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## RUSSELL L. TREAT

### Education/Qualifications

1969 B.S. Chemical Engineering – Washington State University,  
Over 30 years of experience in project and program management, line management, engineering, including 24 years in the analysis, design, testing, and operations of Hanford single-shell tank (SST)/double-shell tank (DST) systems and associated retrieval, treatment, and closure technologies. Pioneered the development of the joule-heated glass melting process, the Hanford grouting process, and a patented barrier for closing SSTs. Have “hands on” experience in the retrieval of waste from Hanford SSTs and in operating a plutonium processing facility.

### Professional Experience

Associate with Dade Moeller & Associates (Specializing in Occupational and Environmental Sciences)  
1845 Terminal Drive, Suite 140  
Richland, Washington 99352  
(509) 946-0410 Extension 120  
Fax (509) 946-4412

Most recently Mr. Treat managed the \$50 million/year Waste Feed Delivery System Definition Program in support of the River Protection Project at the Hanford Site.

He managed the \$7 million/year, 100 full-time equivalent Hanford Waste Technology Program for Pacific Northwest National Laboratory (PNNL), which included the grout, performance assessment, SST characterization, SST ferrocyanide studies, and DST Waste Retrieval Programs. Also he served as project manager of Foster Wheeler’s \$25 million Environmental Restoration and Waste Management (ERWM) support project for Westinghouse Hanford Company (WHC), overseeing activities such as the \$2.5 million design of a hydrogen mitigation test assembly for tank SY-101. Mr. Treat started Foster Wheeler’s office in Richland in 1989 and managed up to 31 staff.

His experience is divided between DOE contractors (Atlantic Richfield Hanford Company [ARHCO], PNNL, and MAC Technical Services [MACTEC] for 18 years) and commercial enterprises (ALCOA, Foster Wheeler, and Dade Moeller for 12 years), providing understanding and balance in the methods employed by both the DOE and commercial sectors.

Mr. Treat served on numerous expert panels, including SST/DST technologies, Hanford grout, and design of the Idaho National Engineering and Environmental Laboratory PREPP facility, and has more than 35 technical publications and presentations, most relating directly to SST/DST wastes. In addition he authored a chapter on in-situ vitrification in a book on waste solidification and stabilization technologies published in 1997.

## **Accomplishments**

***Program Manager for Hanford Tank Waste Feed Delivery Program.*** Mr. Treat developed and implemented management systems for the Tank Waste Retrieval and Disposal Program (TWRD), including the strategy for satisfying the needs for both Defense Nuclear Facility Safety Board (DNFSB) 92-4 specifications and project-level specifications. Mr. Treat developed the strategy for the Program's reliability, availability, and maintainability evaluation, including the failure modes and effect analysis, recovery mode analysis, and Monte Carlo analysis of schedule risks.

***Project Engineer for the Commercial High-Level Waste Vitrification Project.*** Mr. Treat designed, procured components for, oversaw the construction of, and operated two joule-heated glass melters. The largest of the melters, the pilot-scale melter (with modifications) was recently in use at PNNL. Completed successful startup and operation two weeks ahead of schedule and \$500,000 under budget. The melter worked as designed on the first startup attempt. Also led a \$1 million preconceptual design and cost study of a high-level vitrification process against ten other high-level waste (HLW) processing alternatives.

***Project Manager/Engineer for the Savannah River Vitrification Project.*** Mr. Treat served as project manager of a \$300,000 project that involved the calcination/vitrification and liquid-fed vitrification of simulated high-level Savannah River Plant waste. Vitrified high-iron, high-alumina, and average composition wastes using the joule-heated and in-can melting methods. Canisters of glass were destructively examined to evaluate the homogeneity of the vitrified product.

***Project Engineer for the Hanford HWVP.*** Mr. Treat developed remote sensors and a liquid waste feeder for the Hanford pilot-scale joule-heated melter. Remote sensors included (1) a differential resistivity sensor capable of monitoring for the presence of unacceptable levels of floating molten salt phases, (2) a conductivity probe capable of sensing glass foam in the melter plenum, and (3) a conductivity/temperature probe capable of indicating glass pouring rates. He also developed the Air-Displacement System (ADS), a remote-designed pulse pump capable of reliably delivering thick waste slurries to the glass melter. The ADS is the reference Hanford Site and West Valley Demonstration Site (WVDS) pump.

***Project Engineer for the Commercial High-Level Waste Alternative Waste Form Solidification Project.*** Mr. Treat designed, built, and operated several pilot-scale HLW processing systems including (1) glass marble machine; (2) disk pelletizer; (3) chemical-vapor-deposited coatings and plasma-torch-deposited coatings on marbles and pellets; (4) elevated temperature and pressure autoclave for curing grouted waste; (5) furnace for sintering ceramic pellets; and (6) uniaxial hot press for ceramic pellets. The waste forms resulting from these processes were analyzed for leachability, volume-reduction effectiveness, and other parameters, which were compared to those for glass.

***Project Manager for the Rocky Flats Plant Transuranic Waste Solidification Alternative Project.*** Mr. Treat developed preconceptual designs and life-cycle cost estimates for eight solidification processes, including joule-heated glass melting, in-can glass melting, glass

marbles, drummed concrete, cold-pressed hydraulic cement, cold-pressed sintered ceramic, and basalt glass-ceramic.

***Project Manager for the Hanford Environmental Restoration Support Programs Project.***

Mr. Treat provided technical oversight and review of four Best Available Radionuclides Control Technology (BARCT) and Toxic BACT (TBACT) evaluations, including those for HWVP. Also developed data and documentation on radioactive air emissions and treatment for the Plutonium-Uranium Extraction (PUREX) and U/VO<sub>3</sub> Plant to comply with the Washington State Department of Health Radioactive Air Emissions Program. Also, Mr. Treat contributed to the conceptual design bases and successful fair-cost estimate for the 200 East Area Effluent Treatment Facility (ETF) to be used by BNFL Inc., for treating secondary liquid effluent waste, and provided cost estimating assistance to WHC in support of the construction change control process. He led the design and procurement of the initial vapor extraction system for Hanford's successful Expedited Response Action that removed several hundred tons of carbon tetrachloride from the soil.

***Task Leader for SST Leak Detection, Monitoring, and Mitigation (LDMM).*** Mr. Treat developed the strategy and criteria for determining the level of risk-based allowable leakage from SSTs during sluicing. In addition, he developed a decision logic for selecting Tank Waste Remediation System (TWRS) retrieval, LDMM, and closure technologies. The selection was based on the projected risk associated with leakage, the current condition of the tanks and waste in each tank, and the cumulative impacts of other waste sources gradiently aligned with the tank and other factors.

***Task Leader for TWRS Waste Treatment Testing Options Study.*** Mr. Treat evaluated four options involving differing levels of testing of TWRS baseline pretreatment and vitrification technologies prior to initiating detailed design. The evaluation included an innovative assessment of technology risk based on the likelihood and consequences of technology failure of the various levels of technology testing assumed. The cost impacts of these evaluated risks were compared to the cost impacts of the schedule delays necessary to accommodate the various testing levels. The conclusions of the study were presented to and supported by the DOE Pretreatment Sub-Technical Advisory Panel.

***Project Manager for U.S. Nuclear Regulatory Commission (NRC) Volume-Reduced Waste Forms Project.*** Mr. Treat led a team of scientists and engineers who developed data on bitumen and cement waste forms to demonstrate compliance with the requirements of the NRC branch technical position on waste forms. Work focused on solidified low-level waste (LLW) incinerator ash.

***Project Manager for Best Available Treatment Evaluation of Project C-018H Waste Water Treatment Alternatives.*** Mr. Treat evaluated 15 different low-level radioactive waste water treatment technologies and processing and disposal options for the secondary waste produced during operation of the 200 East Area ETF. Technologies evaluated included reverse osmosis, ion exchange, precipitation, flocculation, evaporation, granular activated carbon, ultraviolet oxidation, drying, cementation, and French drains.

***Process Control Engineer for ALCOA.*** Mr. Treat served as process control engineer for a high-capacity (500 tons per day) commercial aluminum smelter. The aluminum smelter included 774 smelting vessels, each heated electrically to approximately 1,000°C and coupled to central off-gas cleaning systems. The heating occurred as a consequent of passing current through molten salt, a concept similar to joule-heated glass melting. Design and implemented several mechanical improvements, saving several million dollars per year.

***Project Manager for the Hanford Grout Program.*** Mr. Treat led PNNL's \$7 million grout project for five years. During this time, conceived the grout mixing and pumping system that became the heart of the Hanford Grout Facility constructed in Hanford's 200 East Area. To demonstrate the feasibility of this system, designed, procured, built, and tested a quarter-scale prototype of the grout system. Operated the prototype around the clock, producing 22,000 gallons of simulated grouted waste. The grout was fed as it was produced to a trench where its flow properties could be measured. Also conducted the risk assessment for disposed radioactive grout. This risk assessment served as the basis for the risk assessment included in the Part B Permit Application for the Hanford Grout Facility.

***Process Engineer for Hanford Tank Farm Process Engineering.*** Mr. Treat developed and demonstrated a modified waste pump in an SST. The use of the pump increased retrieval of waste heels by 30 percent. He also developed a remote radiation sensor that enabled real-time feedback to the effectiveness of waste retrieval operations. In addition he designed a restricted intake pump that minimized vortexing and loss of positive suction head. The pump was successful in retrieving 7,000 gallons of liquid waste from a leaking SST that could not be recovered using conventional pumps.

***Process Engineer/Supervisor for Z Plant (now Plutonium Finishing Plant [PFP]) Process Engineering.*** Mr. Treat was responsible for all process engineering related to Miscellaneous Treatment Operations at Hanford's Z Plant, now PFP. These operations included preparation of feed for subsequent solvent extraction and ion-exchange operations for recovery of plutonium, uranium, and americium. Specified radiochemical and chemical analyses at Z Plant's Analytical Laboratory as a means of verifying the level of process control and conformance to operating specifications and standards. He participated in two startups of plutonium oxide line operations. He prepared safe operating procedures (SOP) for these operations and audited conformance to the SOPs. In addition he supported the causal assessment of the explosion of Z Plant's americium-241 ion exchange column in 1977.

***Project Engineer for the Underground Storage Tank Integrated Demonstration Project.*** Mr. Treat evaluated the engineering and remote-operable feasibility of three candidate pretreatment processes for TWRS waste: Cs-137 ion exchange, the nitrate to ammonia and ceramic process, and the nitrate biological destruction process. He was the lead author of a feasibility study of 14 alternatives for the remote retrieval of wastes from SSTs, with emphasis on the use of subsurface barriers to minimize leakage during retrieval by sluicing. The feasibility study included an assessment of life-cycle costs (total present net worth) and a risk assessment based on projected groundwater contamination. Related the costs and risks in an innovative cost benefit analysis. The work was presented to and endorsed by a review panel that included members of the National Academy of Sciences. The work was

subsequently presented to the Washington State Department of Ecology (Ecology), resulting in a reversal of Ecology's position on the need for subsurface barriers. WHC was granted an award fee for the work by the U.S. Department of Energy, Richland Operations Office, which noted that the effort "exceeded expectations." He also planned and contributed to the development of a TWRS technology screening model that evaluated new technologies against the TWRS baseline based on life-cycle cost, risks, and operations safety.

**Publications**

Mr. Treat has more than 35 technical publications and presentations.

WALLACE W. SCHULZ

PROFESSIONAL OBJECTIVE

Nuclear Consultant: Provide valuable, authoritative counsel on nuclear waste management/disposal and chemical separations technology to government, industrial, and academic organizations.

OUTSTANDING STRENGTHS

Recognized world-class authority on nuclear chemical separations and waste disposal technology.

48+ years broad experience in all parts of back-end of nuclear fuel cycle.

Experienced technical consultant to management.

Creative/innovative. An idea person. Twenty-one patents.

Prolific writer. Eleven books, 100+ journal papers and research reports.

Excellent communicator and mentor.

Highly qualified technology evaluator and analyzer.

OVERVIEW OF PROFESSIONAL EXPERIENCE

<u>Dates</u>	<u>Organization</u>	<u>Highest Position</u>
1988-Present	W2S Co., Inc.	President/consultant
1987-1988	Westinghouse Hanford Co.*	Advisory Scientist
1977-1987	Rockwell Hanford Co.*	Sr. Scientific Advisor
1969-1977	Atlantic Richfield Hanford*	Principal Chemist
1965-1969	Battelle Pacific Northwest Laboratory*	Sr. Research Scientist
1950-1965	General Electric Co.-Hanford*	Research Scientist

\*Prime contractors to the U.S. Department of Energy (or its predecessor agencies, e.g. Atomic Energy Commission) at the Hanford Site.

WALLACE W. SCHULZ RESUME, page 2

EDUCATIONAL BACKGROUND

University of Nevada  
Reno, Nevada

B.S. (1949), M.S. (1950)  
Major: Chemistry

*Other Training:* Joint Center for Graduate Study, Richland, WA (1950-1975), completed coursework equivalent to Ph.D. degree.

HONORS AND AWARDS

Rockwell International Corporation "Engineer of the Year", 1987.

Glenn Seaborg Award in Actinide Separations, 1987.

IR-100 Awards, 1984 & 1987.

Westinghouse Hanford Co. "Signature Award", 1990.

American Chemical Society-Richland Section, "Chemist of the Year", 1986.

Plenary Lecturer, International Solvent Extraction Conference, Moscow, USSR, 1988.

Member Phi Kappa Phi Honorary Society.

Listed in American Men of Science.

MEMBERSHIPS AND AFFILIATIONS

American Nuclear Society

American Chemical Society: Industrial & Engineering Chemistry Division (Technical Program Chairman 1991-Present; Chairman, 1988); Separation Science & Technology Subdivision (Chairman, 1985).

The Metallurgical Society

Sigma Xi

References and publications available on request.

## **APPENDIX B**

**TFA Independent Technical Review – Studsvik, Inc. Technical  
Proposal (No. 2K-5000, 7/13/00)**

# Technical Review Team Information Needs

## Questions for Studsvik, Inc.

The following questions from the TFA Review Group have been reviewed and the additional information provided by Studsvik as requested.

### General

1. **Question:** Can THOR process acidic (1.-1.5 M HNO<sub>3</sub>) SBW directly or is it necessary to neutralize acid in the SBW? What is the acceptable pH range for liquid feeds to THOR?

**Answer:** THOR can process acidic SBW directly with no need to neutralize acid in the SBW. The HNO<sub>3</sub> acid will be volatilized upon injection into the fluidized bed. The NO<sub>3</sub> will be converted to nitrogen gas the same as other nitrates in the SBW. The hydrogen released in the bed will be consumed by oxidation to form water. The hydrogen to water reaction utilizes oxygen from the nitrate reduction.

There is no absolute pH limitation as long as the waste feed system and fluid bed injector are designed to handle the corrosive feed. Commercially available corrosion resistant metals can provide suitable long-term service.

2. **Question:** Studsvik, Inc. literature (1998) described a “portable, skid-mounted THORmps 2430 System”. Does this equipment still exist? If so and if there were a need, could this equipment be shipped to the DOE Idaho site or to any other DOE site for joint operation by DOE contractor/Studsvik, Inc. personnel?

**Answer:** The THOR transportable processing system has been only conceptually designed. Studsvik postponed full commercial development until the Studsvik Processing Facility (SPF) completed the first year of commercial operation. Studsvik plans to restart the engineering of the modular, transportable fluid bed processing system later this year. The portable system should easily handle a wide variety of organic and nitrate wastes and could be moved from site to site as needed. Studsvik would welcome the opportunity to work with DOE contractors at DOE facilities for processing wastes streams that cannot be shipped to a central processing plant.

3. **Question:** What are the allowable concentration limits of components in the waste as defined by current permits, licenses, and limits of the technology (e.g., those that pertain to controlling corrosion, process efficiency, etc.)? What components in the SBW may be close to or outside the limits?

**Answer:** The State of Tennessee permits for the Studsvik Processing Facility do not prescribe limits on waste components other than radionuclides. The SPF is not currently licensed to receive, handle or process mixed wastes. Studsvik anticipates obtaining an EPA Treatability Study permit to allow the SPF to receive and process up to 10,000 lbs

of actual INTEC SBW waste. Testing with actual SBW would occur following a series of tests that will utilize non-radioactive SBW simulant as feed to the denitration fluid bed.

The SBW simulant for the demonstration test can have similar compositions to the actual SBW. Inasmuch as Studsvik will utilize a currently installed fluid bed system at the SPF, it is proposed the chlorine and fluorine constituents be excluded from the initial scoping test runs (Series one tests) due to the highly corrosive nature of these gases in the existing fluid bed. The second series of simulant tests will contain chlorine and fluorine at typical concentrations. A production facility for processing the SBW would be designed for high chlorine and fluorine waste.

The denitration fluid bed system shares a common off-gas handling system with the SPF's large ion exchange resin processing fluid bed. The commingling of the off-gases from both fluid bed systems precludes the use of mercury, cadmium and lead in the simulant. This is necessary to prevent generation of a mixed waste salt in the off-gas scrubber system.

For processing the actual INTEC SBW, Studsvik will shutdown and isolate the ion exchange processing system and utilize only the denitration fluid bed system. This will minimize the volume of scrubber salts that will probably be considered mixed waste due to the content of mercury, lead and cadmium in the actual SBW.

From a review of the latest INTEC SBW tank farm inventory that provides the composition of the SBW, it appears that the post-processing, denitrated residue may not be mixed waste as the heavy metals should partition to the scrubber salt and the non-volatile chromium will be in the non-hazardous trivalent state. The impact of the wide variety of radionuclides on a mixed waste designation for the final reformed residue is unknown at this time.

There are no components in the SBW that should pose any processing problems for THOR. The presence of chlorine, fluorine, and phosphate will require the use of special alloys that are commercially available. The future full-scale fluid bed system will be designed with replaceable liners to mitigate potentially high corrosion in the free board of the fluid bed.

4. **Questions:** What problems were encountered and how were they overcome in obtaining the necessary permits and licenses?

**Answer:** Studsvik obtained its State of Tennessee radioactive materials license and air permit in a 4 to 6 month period of time. The license process was straight-forward with no unforeseen issues or problems. There were a variety of questions and concerns raised by the State of Tennessee that were answered to the satisfaction of all parties. Since the SPF is not licensed to receive mixed waste, the licensing process was uneventful and received little public reaction from the community and residential neighbors. Studsvik must still

obtain the Treatability Study permit for processing the actual INTEC SBW waste at the SPF.

## Process Operation

5. **Question:** What is the potential for alkali slagging in the pyrolysis reformer when processing SBW? Is there any potential at all? If so, please describe the status of technology for remote removal of the alkali slag. Where are buildups of slags and other deposits likely to occur? What is the expected frequency of cleanouts? What are the expected and historical dose rates and total doses incurred by staff during cleanout? How will "elutriating" the fluidized bed minimize buildups?

**Answer:** The SBW waste includes several components that can lead to agglomerations or "slagging" in the fluid bed, in particular: sodium, potassium, boron, nitrates, and sulfates. All of these components are common to the ion exchange resin wastes that the SPF has successfully processed.

Nitrates do not form agglomerations in the THOR process as the nitrates are quickly reduced to nitrogen gas. Sodium and potassium (cations) form salts with certain anions in the bed. Typical salts that could be generated in the bed by SBW components include: NaCl, KCl, NaF, KF, Na<sub>3</sub>PO<sub>4</sub>, K<sub>3</sub>PO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, and KBO<sub>2</sub>.

The borate salts are of no concern due to the very small quantity of boron in the SBW and the high volatility of boron chloride and fluoride. The phosphates should pose little agglomeration concern as phosphorous and most phosphorous compounds are highly volatile and should largely partition to the gas phase. However, should sodium and potassium phosphates occur, they have very high melting points. The high melting point phosphate salts should increase the melting point of any Cl, F, or SO<sub>4</sub> eutectic salts that form. The calcium in the SBW will also form Cl, F and SO<sub>4</sub> salts that will tend to raise the melting point of any salt eutectics that may form. The sodium and potassium sulfate salts tend to form eutectic mixtures with silicate and chloride salts that when combined, melt at lower temperatures than the pure salts. The absence of silicates in the SBW and the use of alumina media in the bed further reduce the potential for agglomeration formation. Studsvik has extensive experience with sulfate salts and how to avoid and remove agglomerations in the fluid bed. Only testing can confirm the formation and behavior of eutectic salt mixtures.

Studsvik utilizes multiple techniques to prevent or limit agglomerations in the fluid bed resulting from eutectics that have potential to melt at 600 to 650 °C, as discussed below.

1. The fluid bed material comprises pure alumina beads that are inert to sodium and potassium fluxing.
2. The fluid bed is operated in a strongly reducing mode that serves to reduce the majority of sulfate to volatile SO<sub>2</sub> and H<sub>2</sub>S.
3. Heat is generated in the bed to eliminate hot heat transfer surfaces such as electrical heaters that will become coated with melted salts and ultimately fail.

4. The fluid bed is operated with high fluidizing velocities that elutriate the solid reaction products out of the bed. Operating the fluid bed in an elutriating mode assures that the bed contains less than 5% by weight SBW solids. The presence of such a small inventory of salts in the bed limits the potential for formation of agglomerations.
5. The fluid gas nozzles are operated at very high velocity imparting a self-cleaning action as the high velocity steam impacts the media at the bottom of the bed knocking accumulated deposits off the media, thereby continuously cleaning the alumina media.
6. The bed can be operated continuously below 600 °C, which is below the eutectic mixture softening point of all known sulfate eutectics.
7. The addition of metered quantities of CaO and/or aluminum nitrate could be considered to eliminate the formation of low melting point eutectics. The addition of such additives would increase the final waste volume by 10% to 30% and would be considered only if the above techniques prove inadequate.

In addition to the above in-bed techniques, Studsvik has designed a water wash conveyor that can be installed on the bottom of the fluid bed. If a major agglomeration event occurs, the fluid bed is cooled down and the media is washed with hot water. The hot water flows out the bottom of the bed and is returned to the waste feed tank. The washed media is then dried by starting up the fluid gas supply and gradually increasing the fluid gas temperature to dry all moisture from the media. Alternatively, the media can be removed out the bottom by using the water-wash conveyor on the bottom of the fluid bed. The conveyor is provided with integral electric heaters to fully dry the media for reuse. By this means agglomerations can be removed and the media cleaned for reuse without the need for any personnel exposure or contact maintenance. A full-scale, water-wash conveyor is available for inspection at the SPF. The water-wash system works because almost all low melting point eutectic salts are very soluble in water.

Agglomerations typically form near the bottom of the fluid bed on the inside surface of the vessel wall and on the instrument rack installed in the middle of the bed. Studsvik has had to manually remove 5 or 6 agglomerations in the large ion exchange resin processing fluid bed over the past year, until the above techniques were fully developed. Manual cleaning of the bed resulted in 1 to 1.5 manrem of personnel exposure. Typical bed radiation levels run from 200 to 500 mrem/h when feeding ion exchange resin slurry with radiation levels of 2 to 150 R/h contact dose rates. With the water-wash conveyor installed, no exposure is anticipated. We would expect one to three agglomeration events per year that would be remotely removed as discussed above.

6. **Question:** Has Studsvik, Inc. any plant-scale experience in operating the THOR process with actual radioactive waste of a composition similar to SBW?

**Answer:** Studsvik has not operated the SPF's large-scale fluid bed systems with high nitrate wastes. The proposed demonstration test will utilize Studsvik's CR fluid bed, 18 inch inside diameter. The CR fluid bed could process the 5,050 cubic meters of SBW in

12 years, assuming 75% on-line processing time. It is anticipated that a 30 to 36 inch diameter THOR fluid bed could process the entire SBW inventory in a four year period.

7. **Question:** What is the function of the "Thermal Converter"? Is the oxidizing system catalytic? Is fuel addition required? Table 4 in the document describing the denitration test shows 0.65% other gases. Do any of these cause emissions concerns, e.g. benzene?

**Answer:** The Thermal Converter oxidizes any carbon monoxide and hydrogen that may exit the fluid bed. The fluid bed is provided with an autothermal (oxygen) gas injection manifold in the top of the bed. The injection of small quantities of oxygen in the top of the bed, serves to oxidize the majority of the hydrogen and carbon monoxide generated by the steam-reforming reaction inside the bed. It is estimated that the carbon monoxide and hydrogen concentrations leaving the bed will be approximately 2% and 1%, respectively. The Thermal Converter is designed to complete the oxidation of these gases. The low hydrogen and carbon monoxide levels exiting the bed are well below the low limits of flammability.

The Thermal Converter is a ceramic filled matrix, refractory lined vessel that is provided with integral electrical heaters to maintain the matrix temperature. Air is added to provide oxygen needed for full oxidation of the remaining carbon monoxide and hydrogen. The unit is non-catalytic and operates at 800 to 1000 °C. This type of Thermal Converter is commercially available from several vendors and has proven very reliable with very little maintenance.

The "other" gases shown as <0.65% include methane, ethane, ethylene, and a number of minor acid gases that will be removed by the scrubber. There is no potential for emissions of cyclical hydrocarbons such as benzene, as the process uses no hydrocarbons and the SBW contains no hydrocarbons. Only low-molecular weight gases that can be formed by steam-reforming carbon can exist or be formed.

8. **Question:** Section 3.2 of the Technical Proposal first diamond has mix tank to add solid reductant, what are the solid, granular reductants and solid waste feeds mentioned in 3<sup>rd</sup> diamond?

**Answer:** Sucrose (common sugar) is an additive that is mixed with and co-fed with the SBW feed. The solid reductants that are added to the fluid bed may include a variety of solid carbon products. Generally, granular activated carbon is the main or only solid reductant. There is the possibility of adding other inorganic additives with the solid reductant such as CaO, however, the use of such additives is not believed to be necessary.

9. **Question:** Will the addition of nitrates raise additional corrosion concerns. How will they affect the heating elements?

**Answer:** The nitrates are quickly (<one second) converted to nitrogen gas in the fluid bed. Nitrates will have no impact on corrosion in the THOR systems. There are no

heating elements inside the fluid bed as eutectic salts tend to melt and stick to the hot heating surfaces and ultimately lead to heater failure.

10. **Question:** Describe more precisely the mechanism of disengaging the solid products from the fluidized sand. I assume it is a mechanism that relies on differences in density. What are the expectations for  $\text{NaNO}_3$  to react with the sand bed? The formation of sodium silicates seems to be a possibility under the reaction conditions. The document dated April 12, 2000 includes a paper that describes a “washing system” for the sand, but this is not included in most of the flow diagrams. How critical to operation is this unit, and how would the addition of large quantities of  $\text{NaNO}_3$  be expected to impact this operation?

**Answer:** Elutriation is the disengagement method used for stripping fine solids from a bubbling fluidized bed. The mechanisms that make this happen include: 1) solid products generated from the reactions are small particles (<100 micron size), 2) gas velocities in the bed are sufficiently high that the fine product particles are carried out of the bed by the gas as the gas velocity exceeds the settling velocity of the particles in the up-flowing gas, and 3) sand media size and density are selected and gas velocities are controlled such that the sand has a settling velocity greater than the gas up-flow velocity. The sand media will then stay resident as a semi-permanent bed.

The formation of sodium silicates is not possible as Studsvik utilizes a pure alumina bead media as the bed material.

The water-wash system is briefly described in Answer No. 5 above.

11. **Question:** There is reference in the April 12 document to operating under autothermal conditions. Does this imply that some amount of air is cofed to balance the endothermic reforming process? When feeding nitrate and sugar, I would expect that the process will be exothermic. How will this impact the operating parameters?

**Answer:** The THOR steam reformer is operated in an autothermal mode. This means that oxygen is injected into the bed to provide any required energy through oxidation of the solid reductant (carbon). Autothermal gas (oxygen) is also injected into the top of the bed to oxidize the in-bed-generated carbon monoxide and hydrogen. The steam fluidizing gas superheat temperature is lowered or additional water is injected into the bed to maintain the desired bed temperature if there is excess energy generated in the bed from the oxidation of carbon monoxide and hydrogen and the reduction of nitrates by the oxidation of the carbon reductant. If there is not sufficient energy generated in the bed, additional oxygen is added to oxidize the carbon reductant to provide the needed heat. By this means bed temperatures are easily controlled during start-up, for all waste feed injection rates and for any waste feed composition, including injection of flush water. This method of energy generation and control is identical to that employed by the SPF's current operating fluid bed. Operation is simple, energy efficient, and reliable.

A preliminary heat balance has been performed on the full-scale fluid bed system. The evaluation shows that a small amount of additional energy will be required in the bed to make up for the heat needed to evaporate and superheat the water in the SBW feed.

12. **Question:** The flow diagrams show separate pyrolyzer and reformer beds, while the text seems to indicate the use of a single bed. Which is it for this case?

**Answer:** The THOR denitration process utilizes a single fluid bed. A two stage pyrolyzer and reformer system was installed at the SPF, however, the use of both fluid beds in series was found to be unnecessary. The SPF uses only a single stage fluid bed for processing of ion exchange resin slurries. The second, smaller CR fluid bed is the unit proposed for performance of the SBW denitration demonstration.

## Off Gas

13. **Question:** What is the anticipated distribution of any Tc-99 in SBW, i.e., percent of Tc-99 in off gas and percent in final inorganic residue? Can Tc distribution profile be changed significantly by changing the type and amount of reductant, i.e., sucrose, etc., added during process operation? Is it possible to drive more than 99% of the Tc-99 to the inorganic residue?

**Answer:** The SPF ion exchange resin feed contains minor levels of Tc-99. We have been unable to do a mass balance on the Tc-99 as the actual levels of incoming Tc-99 are only scaled off of other radionuclides at the nuclear power stations that generate the resin waste. Whether the Tc-99 can be fully or partially partitioned to the off-gas is unknown. It is very unlikely that the volatility of Tc-99 can be changed by adjusting the amount of reductant, as the reductant input is controlled by the denitration reaction and energy needs in the bed. The presence of free chlorine and fluorine will have a much greater influence on the volatility of Tc-99 as  $TcCl_6$  and  $TcF_6$  are highly volatile. Technetium oxide is not volatile. Only testing can determine the influence that the halogen gases will have on the Tc volatility.

14. **Question:** It is our understanding that one of the key by-products of the THOR process is flammable synthesis gas. It is also our understanding that this by-product must be destroyed (oxidized) by reaction at temperatures as high as 1200 C.

**Answer:** The composition of the off-gas from the THOR steam-reforming process will be approximately as shown in the following table. The process off-gas is non-flammable due to the small concentrations of carbon monoxide and hydrogen. This off-gas does need to be fully oxidized prior to release to convert the carbon monoxide to carbon dioxide. The Thermal Converter, described above, serves this function.

Off-Gas Component	Concentration (% by Vol.)
H <sub>2</sub> O (Steam)	84
CO <sub>2</sub>	11
CO	2
N <sub>2</sub>	1
H <sub>2</sub>	<1
Other	1
Total	100

15. **Question:** We foresee that routine oxidation of the synthesis off gas at 1200 C could be a difficult process to control and operate safely. Please discuss Studsvik, Inc. experience with this particular unit operation and also discuss any alternative treatment for synthesis gas which could be/has been considered.

**Answer:** The operation of the Thermal Converter is discussed in Answer No. 5 above. There are over 1,000 installations of ceramic matrix thermal converters (oxidizers) in the U.S.A. These units have an excellent history of performance. There are over 100 electrically heated, ceramic matrix units. The keys to successful operation are to remove all particulates and minimize the presence of acid gases in the off-gas stream. Particulates, if not removed, will tend to accumulate in the ceramic matrix and eventually cause gas channeling and uneven temperatures. Acid gases, if not removed, will accelerate heater element corrosion in the thermal oxidizer. Studsvik has successfully operated a non-ceramic thermal oxidizer at the SPF for the past year at temperatures of 1000 to 1100 °C. The SB Heater at the SPF will be part of the plant tour.

16. **Question:** Will Studsvik measure and report compositions of all constituents of concern in the off-gas when it conducts testing with simulants and actual SBW? Constituents of concern include all flammable components, all corrosive species, entrained solids, and key volatile radionuclides and chemicals.

**Answer:** Studsvik plans on maintaining a calibrated CEMs on-line thorough all test runs. There will be two CEMs, one on the outlet of the fluid bed ceramic filter and one on the outlet of the off-gas system - downstream of the scrubbers. The principal components that will be monitored downstream of the fluid bed are: NO<sub>x</sub> (NO, NO<sub>2</sub>), CO, CO<sub>2</sub>, O<sub>2</sub>, Cl<sub>2</sub>, SO<sub>2</sub>, and THC (Total Hydrocarbons). Gas bag samples will also be periodically taken downstream of the fluid bed ceramic filter and analyzed for a wide variety of gases including: H<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>S, SO<sub>2</sub>, NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, HCN, HF, HCl, Cl<sub>2</sub>, and THC.

Solids samples will be taken periodically from the filter vessel solids outlet during the simulant runs and analyzed for Al, B, Ca, CO<sub>3</sub>, Cl, Cr, F, Fe, K, Mn, Mo, Na, Ni, NO<sub>3</sub>, SO<sub>4</sub>, and Zr. Solids samples will be taken twice from the filter vessel solids outlet during the actual SBW and analyzed for Al, B, Cd, Ca, CO<sub>3</sub>, Cl, Cr, F, Fe, K, Mn, Hg, Mo, Na, Ni, NO<sub>3</sub>, Pb, SO<sub>4</sub>, and Zr as well as for all radionuclides. Scrubber water samples will be taken twice during the actual SBW run and analyzed for the above components as well as all radionuclides.

17. **Question:** There is reference to Hg recovery in several documents. Is this an issue for the SBW? If so, how is it accomplished? What technology will be used to recover mercury and what is its anticipated effectiveness?

**Answer:** Mercury is an issue in processing the actual SBW as it will partition to the off-gas. The scrubber will remove soluble forms of mercury as well as elemental mercury. Volatile forms of mercury (at ambient temperature) will be exhausted from the SPF with other non-condensable off-gases. Studsvik plans no special process for recovery of the mercury in the scrubber solution during the demonstration program.

Suitable mercury recovery processes will need to be a part of the full-scale plant, however, this work is currently outside the scope of the proposed Studsvik demonstration program. There are several commercially available mercury recovery and stabilization processes to select from.

18. **Question:** What are the features of the "explosion-proof design"? How is the system monitored and inspected for leaks of potentially flammable gases? What safety limits and other requirements are imposed in your license?

**Answer:** The entire THOR processing system is maintained under a slight negative pressure during processing operations. There is no potential for leakage of potentially flammable gas mixtures during normal operations. Upon a loss of the on-line process blower it is possible for the thermal system to experience slight positive pressures. Such an event is minimized by the use of redundant process blowers and providing an emergency backup generator to power the blower during a loss of off-site power.

The first level of defense against potential hazards of flammable gases is to not generate them. It is impossible for flammable mixtures to form in the THOR process unless there is a major, simultaneous failure in the both the oxygen injection system and on-line CO, NO<sub>x</sub>, and O<sub>2</sub> monitor systems located on the outlet of the fluid bed ceramic filter.

The second level of defense is that the THOR process can be quickly and completely shutdown in seconds. A significant advantage of the THOR process is that no gaseous or liquid fuels are used to provide heat in the fluid bed. Therefore, upon process shutdown, the off-gas flow can be quickly stopped in less than 10 seconds by isolating the waste feed injection and the steam and autothermal gas input. Due to the very low inventory of waste in the fluid bed, when the steam flow stops, the production of off-gases also ceases within seconds.

The third level of defense is to design the entire high temperature portion of the process system as explosion-proof. This means that the fluid bed and ceramic filter vessels and piping are designed and built to safely contain any postulated explosion. For example, the fluid bed vessel is an ASME designed and stamped pressure vessel that can contain the full, maximum explosion pressure wave with no pressure boundary failure or damage. Thus even after the worst case event - an explosion- the vessel can be placed back in

service without pressure boundary repairs. The piping between vessels and all vessels nozzles are interconnected with ANSI flanges rated to contain an explosion pressure pulse. The use of ANSI flanges and high pressure and temperature rated gaskets assures absolute system integrity.

The licenses for the SPF do not specifically recite any requirements related to safety other than the state safety requirements for radiation and radioactive materials release to the environment. Studsvik has made commitments to the State of Tennessee and in the approved SPF operating procedures that define what safety measures will be utilized and what conditions will require a plant shutdown if certain safety systems are unavailable.

## **Final Inorganic Residue (Product)**

**19. Question:** Please describe and discuss expected key physical properties, e.g., particle size range, bulk density, respirable fines fraction, etc. of the inorganic residue which would result from application of the THOR process to SBW.

**Answer:** The reformed solid product that will be removed from the fluid bed ceramic filter will have the following estimated properties. The melted product properties are also estimated below.

### Elutriated Product - Dry Powder:

Particle Size Range:	90% 20 to 200 micron, 8% 3 to 20 micron, 2% <3 micron
Bulk Density:	880 to 1,040 kg/cumeter (55 to 65 lbs/cuft)
Respirable fines:	10-50 %
Total Weight:	570 to 650 metric tons
Total Volume:	550 to 740 cubic meters

### Melted Product - Fused Block:

Particle Size Range:	Bulk Monolith (no particles)
Bulk Density:	1920 to 2400 kg/cumeter (120 to 155 lbs/cuft)
Respirable fines:	None
Total Weight:	545 to 620 metric tons
Total Volume:	220 to 320 cubic meters

**20. Question:** What is the final product composition? What is the expected radionuclide content and the radiation dose? In particular are there any by products of the reducing agent or any of the fluid bed constituents? Are there any listed wastes formed during the process? Studsvik, Inc. literature indicates some proprietary additives are used in the THOR process operation. Do the additives remain with the inorganic residue? If so, would such additives increase the RCRA metal content of the inorganic residue produced by application of the THOR process to INEEL SBW?

**Answer:** The only additives that are anticipated for the THOR denitration of SBW are the addition of sugar and granular activated carbon in the fluid bed. Therefore, there will

be no increase in the RCRA metal content of the inorganic residue. No listed wastes are formed.

A small portion of the carbon reductant will carryover with the residue. As the large activated carbon granules are consumed the granules will eventually be reduced in size to where the small carbon particle is elutriated out of the fluid bed. A small fraction of the alumina fluid bed media will also carryover to the final product despite the presence of a high efficiency cyclone assembly integral to the fluid bed. The carbon and alumina media carryovers are estimated below.

The following table provides the anticipated composition of the final, reformed, solid residue from the THOR fluid bed system. The compositions shown below depend upon the following major factors that can only be determined from actual testing due to competing reactions between potential products; aluminum nitrate conversion ratio to  $Al_2O_3$  or  $NaAlO_2$ ; calcium affinity for formation of  $CaCl_2$ ,  $CaF_2$  or  $CaSO_4$ ; and volatility of  $SO_4/SO_2$  versus formation of  $Na_2SO_4$ .

Compound	Composition
$Na_2CO_3$	32%
$NaAlO_2$	30%
$K_2CO_3$	8%
$Al_2O_3$	5%
$Na_2SO_4$	4%
$CaCl_2/F_2$	4%
$Al_2O_3$ (Media)	4%
C (Reductant)	4%
Zr	3%
$NO_3$	1%
Other	5%
Total	100% by Wt.

The final residue will contain essentially all radionuclides except for the following radionuclides that exhibit higher volatility or form non-condensable gases: H-3, C-14, I-129, Rn-219/220, Cd-113m, In-115, Sn-119m/121m/126, Te-123, Tl-207/208/209, Pb-209/210/211/212/214, Bi-210m/210/211/212/213/214, Zn, Po-210/211/212/213/214/215/216/218, Se-79, Rb-87, Ru-106, and Nb-94/93m. The partitioning of the following radionuclides is unknown at this time: At-217, FR-221/223, Am-241/242m/242/243, and Cf-249/250/251/252. Additional factors to consider are that many metals are more volatile in the chloride and/or fluoride form, such as Tc-99, and Sb-126, however, the carbonate forms are less volatile. With the excess of carbon dioxide in the fluid bed, there is a high probability of forming less-volatile carbonates with many of the radionuclides. Only testing can determine the relative volatility of such radionuclides in the complex SBW mixture.

21. **Question:** What are the expected quantities, compositions, physical properties, and types of secondary wastes expected in the SBW steam-reforming process? What additional treatment may be necessary to prepare the secondary wastes for disposal?

**Answer:** The secondary processing wastes from the process include: dried scrubber salts and activated carbon for mercury adsorption. Acid gases will be removed in the scrubber and neutralized with sodium hydroxide to form sodium salts. Mercury will need to be handled separately. The estimated quantities and properties of the scrubber salts are shown below:

Scrubber Salt Product - Dry Powder/Granules:

Particle Size Range: 95% 20 to 200 micron, 5% <20 micron  
 Bulk Density: 880 to 960 kg/cumeter (55 to 60 lbs/cuft)  
 Respirable fines: 5-20 %  
 Total Weight: 32 to 70 metric tons  
 Total Volume: 30 to 75 cubic meters

Melted Salt Product - Fused Block:

Particle Size Range: Bulk Monolith (no particles)  
 Bulk Density: 1920 to 2400 kg/cumeter (120 to 150 lbs/cuft)  
 Respirable fines: None  
 Total Weight: 20 to 66 metric tons  
 Total Volume: 12 to 35 cubic meters

Compound	Composition Minimum	Composition Maximum
Na <sub>2</sub> SO <sub>4</sub>	4,500	13,500
Na <sub>3</sub> PO <sub>4</sub>	4,500	18,000
NaNO <sub>3</sub>	4,500	22,000
NaF	4,500	11,000
NaCl	2,500	5,500
Total	20,500 kg	70,000 kg

If the scrubber salts were to be buried at a commercial burial site, such as Barnwell, the only requirements are that the salt would have to be packaged in an approved high integrity container and the powder would have to be made non-dispersible. The salt could be wetted or bound in a matrix to make it non-dispersible. The preferred alternative would be melting to achieve a non-dispersible product.

22. **Question:** What is the estimated water/hydrate content of the inorganic residue which would remain after application of the THOR process to INEEL SBW? How long could this residue be stored under ambient conditions of temperature, pressure, and humidity at the Idaho site without excessive hydration? Is the steam-reforming product (unfused) expected to be and remain a dry free-flowing material, or over time, will it absorb moisture from the air and lose its free-flowing characteristic

**Answer:** The reformed residue as it is transferred from the THOR process will have <0.2% water, no hydrates, and is a free-flowing powder. The dried scrubber salts will have <2% water and may have some hydrates when transferred from the salt dryer. The scrubber salt is a free-flowing granular/powder solid. The principal constituents in both the reformed residue and scrubber salts are sodium salts such as Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, etc. which readily form hydrates. The residue and scrubber salts will readily pick up moisture from the atmosphere and form large blocks or chunks. In order to keep the residue and scrubber salts as free-flowing solids, it will be necessary to store them in sealed containers or tanks that will not "breathe" with fluctuations in ambient temperatures and pressure. Alternatively, the tanks could be sealed and a dry gas purge placed on the tanks to prevent atmospheric pressure changes from drawing in moist outside air.

### **Additional Documents Needed From Studsvik, Inc.**

23. **Request:** Page 2 of Studsvik, Inc.'s Technical Proposal states that the test equipment is about 1/3<sup>rd</sup> scale of the Idaho needs. Page 6 claims "no further need for "scale up" testing". Please provide information where Studsvik, Inc. has defined the 3X scale up parameters.

**Response:** Studsvik's demonstration program will utilize the SPF's THOR CR fluid bed as described above. The CR fluid bed has the capacity to process the 5,050 cubic meters of INTEC SBW over a 12 year operating period. Studsvik understands that the DOE desires to process the waste over an approximate 4 year period. In order to process the SBW in four years, a fluid bed system that has three times higher throughput than the CR fluid bed will be needed. The PYR fluid bed at the SPF has five times higher throughput than the CR fluid Bed.

Following the successful completion of the Studsvik 1/3<sup>rd</sup> scale demonstration program, no additional denitration testing would be required prior to designing and constructing a full-scale SBW processing plant. Typical fluid bed scale-up factors range from 100:1 for well know operations to 10:1 for unique applications. The 3:1 scale-up factor from the CR fluid bed to full-scale SBW denitration is very conservative.

24. **Request:** Page 6 of the Technical Proposal claims use of current radiological equipment. Please provide estimates of how the radiation field from Idaho wastes compares to the radiation levels currently processed by the facility.

**Response:** Studsvik has received and processed a variety of ion exchange resin wastes from nuclear power stations at the SPF. Typical resins have contact dose levels of 1 to 150 R/h upon receipt at the SPF. The resins are commingled and processed on a batch basis. Each batch of resin has contact radiation levels of up to 30 R/h. The reformed residue powder has contact radiation levels of 15 to 40 R/h. The SPF is provided with heavy concrete and steel shielding to maintain personnel exposures ALARA. The plant is designed for remote emptying or flushing of piping and tanks to allow contact maintenance.

From the information available to Studsvik, it appears that the SBW has contact radiation levels of 10 to 15 R/h. The resin slurry and residue that we process and package have radiation levels up to 2 or 3 times higher than the SBW with some resins having over 10 times higher dose rates.

25. **Request:** Pg. 11, Section 3.2 of the Technical Proposal refers to a Denitration Flow Diagram in Attachment 4, no such attachment was provided. Please obtain.

**Response:** Studsvik will provide copies of the referenced Denitration Flow Diagram with this transmittal.

26. **Request:** Attachment 3 of the Technical Proposal refers to a document under separate cover but does not identify the document. Please identify and provide.

**Response:** Studsvik will provide copies of the referenced Studsvik Processing Facility description with this transmittal.

## Questions for DOE-Idaho

27. Based on data from the Alternatives study on tank WM 183, we get 660K sodium nitrate vs. the 1122K shown on Page 4 of 7/13/00 Technical Proposal. Please confirm validity of the page 4 data.
28. Based on the way Section 5.0 of the Technical Proposal is written, cost of the program will be defined after DOE tells them what to do. Please describe/clarify DOE's approach.

**Studsvik's Response:** Studsvik will discuss budgetary pricing during our technical discussions in Erwin for the scope of work outlined in our technical proposal. The intent of the wording of Section 5.0 of the technical proposal was to indicate that Studsvik desired to work with DOE to ensure that the program as proposed will ultimately answer all of the questions that DOE may have concerning deployment of the THOR technology. We do not anticipate that this will be significantly different from what we have proposed, however, we recognize that additional test runs may be desired or additional reports may be requested.

The first step of the program, prior to issuance of a contract, would be to meet with appropriate DOE representatives and "conform" our proposal and subsequent pricing to the exact DOE needs.

29. Studsvik, Inc. requested INEEL to provide "complete characterization" of the SBW to be shipped to Studsvik's facilities for steam reforming. Can Studsvik, Inc. be more definitive to ensure that INEEL can meet the characterization needs without incurring unnecessary costs?

30. Does DOE-Idaho expect this product to meet a disposal criteria, if so, what?

## **APPENDIX C**

### **Questions for Studsvik Process Technology**

## Questions for Studsvik Process Technology

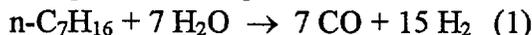
- What are the properties and composition of the salt waste?
- Can a silicate based ash product from the Studsvik process be formed?
- What are the engineering data for the interim storage design of Studsvik product, transport and thermal properties?
- Is Studsvik compliant with MACT requirements?
- What is the fate of phosphate, sulfate and chloride in the Studsvik process?
- Can Studsvik equipment be remotely maintained?
- What is the fate of Hg in the Studsvik process? Will it poison the catalyst in the thermal converter? Is it collected and handled separately from the salt waste?
- What is the quantity of filter material that may be in the ash product material?
- What is the Cs retention in the Studsvik product? What is the quantity of Cs retained in the Studsvik product? Is there a requirement for Idaho to remove Cs and keep it out of the salt cake waste?
- How much carbon is on the ash product?
- What NO<sub>x</sub> level can we expect out of the fluidized bed?
- What is the reliability data on the Erwin Studsvik plant?
- What is the degree of denitration in the solid product?

## **APPENDIX D**

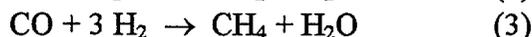
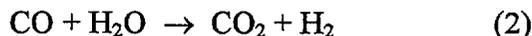
### **Steam-Reforming Chemistry and Nitrate Destruction**

## Steam-Reforming Chemistry and Nitrate Destruction

Steam reforming is a versatile process that destroys organic materials through reaction with steam. Steam reforming has been used on a large scale by the petrochemical industry to produce hydrogen for at least 65 years. More recently, the process has been commercialized as an alternative to incineration for waste treatment. The chemistry of steam reforming can be simply illustrated by the reaction of n-heptane with superheated steam.



CO reacts further with both steam and H<sub>2</sub>.



Consumption of CO and H<sub>2</sub> drives reaction (1) strongly towards products. In addition, because the reaction of steam with organics is highly endothermic, steam-reforming reactions can be driven essentially to completion by operating at an appropriately high temperature. If air or oxygen is included in the reaction mixture, the process can be autothermal. That is, the exothermic reaction with oxygen can be used to balance the endothermic reaction with steam. The formation of the relatively stable carbon and poly- nuclear aromatic byproducts can be almost completely suppressed by operating with a moderate excess of steam.

If the organic material being reformed contains halogens, phosphorus, or sulfur atoms, mineral acids are also formed (e.g., hydrochloric acid, phosphorous acid, phosphoric acid, and hydrogen sulfide) unless inorganic materials capable of scavenging these species are present<sup>a,b</sup> Organic nitrogen is converted to N<sub>2</sub><sup>a</sup> and organic oxygen is converted to CO or CO<sub>2</sub>.

In principle, all organic compounds can be steam-reformed. The process has been demonstrated on a number of organic liquids (e.g., simple hydrocarbons, alcohols, ketones, and chlorocarbons), a variety of polymeric organic materials (paint residues, caulks, shredded paper, plastics, and wood products; organics adsorbed on soils, debris, activated carbon and ash), and even coal<sup>c</sup> and cellulosic wastes.<sup>d</sup>

Nitrate salts will thermally decompose, even in the absence of reducing agents (see below). The complete thermal decomposition of NaNO<sub>3</sub> is not well-understood. Thermodynamic analysis indicates that N<sub>2</sub> and O<sub>2</sub> are the thermodynamically favored products and should be formed

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<sup>a</sup> M. R. Nimlos and T. A. Milne, *Environ. Sci. Technol.*, **26**, 545 (1992).

<sup>b</sup> M. Nimlos and T. Milne, "Preliminary Screening of Steam-reforming Efficacy of Rhodium Catalysts for Destroying Halon 1301 (CF<sub>3</sub>Br)," Letter Report to Sandia from SERI dated June 28, 1990.

<sup>c</sup> *Chemistry of Coal Utilization, 2nd Suppl. Vol.*, M. A. Elliott, Ed., Wiley-Interscience, New York, 1981, p. 1500.

<sup>d</sup> M. J. Antal et al., *A Study of the Steam Gasification of Organic Wastes*, Final Progress Report to the U.S. Environmental Protection Agency, Princeton University, Princeton, NJ, 1979.

instead of  $\text{NO}_x$  if a kinetic pathway exists for their formation and the system is allowed to come to thermodynamic equilibrium. In practice, thermal decomposition of nitrates generally produces  $\text{NO}_x$  as the primary product. However, rapid heating to very high temperatures (2200 °C) does result primarily in the formation of  $\text{N}_2$  and  $\text{O}_2$ .<sup>a</sup>

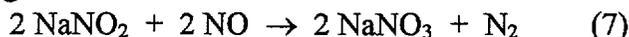
There is general agreement in the literature that at lower temperatures the first reaction in the thermal decomposition of  $\text{NaNO}_3$  is the loss of oxygen to form  $\text{NaNO}_2$ .



In fact, at higher temperatures (600-750 °C), the equilibrium between  $\text{NaNO}_3$ ,  $\text{NaNO}_2$ , and  $\text{O}_2$  has been studied and quantified.<sup>b</sup> The mechanism of interest therefore becomes the decomposition of  $\text{NaNO}_2$ . The decomposition of  $\text{NaNO}_2$  has been reported as probably first producing  $\text{NO}_x$ .<sup>c</sup>



The  $\text{NO}_x$  can then undergo further reactions.<sup>d</sup>



At least reaction 9 is reversible. The net result of the secondary reactions 7-9 is the production of  $\text{NaNO}_3$  and  $\text{N}_2$ . When coupled with the decomposition of  $\text{NaNO}_3$  to  $\text{NaNO}_2$ , the net result is the conversion of  $\text{NaNO}_3$  to  $\text{Na}_2\text{O}$ ,  $\text{N}_2$ , and  $\text{O}_2$ . In the presence of steam,  $\text{Na}_2\text{O}$  will convert to  $\text{NaOH}$ ; in the presence of  $\text{CO}_2$  it will convert to  $\text{Na}_2\text{CO}_3$ .

Many other reactions, some involving the direct conversion of  $\text{NaNO}_3$  to products other than  $\text{NaNO}_2$ , have been postulated in the literature.<sup>e</sup>  $\text{N}_2\text{O}$  has also occasionally been reported as being a product of nitrate decomposition.<sup>f,g</sup> Although reaction mechanisms were not reported,  $\text{N}_2\text{O}$  can be produced from  $\text{NO}_x$ , especially in the presence of a catalyst or a reducing agent such as  $\text{SO}_2$ .<sup>h</sup>

The reactions above illustrate one possible route for  $\text{NaNO}_3$  decomposition. In reality, it is likely that many of the above reactions occur in parallel with others such as the reaction of nitrogen dioxide to nitric oxide and oxygen.

<sup>a</sup> L. J. Meile and A. J. Johnson, "Waste Generation Reduction - Nitrates FY 1982 Status Report," Rockwell International, RFP-3465, DOE/TIC-4500 (Rev. 72), January 1984.

<sup>b</sup> E. S. Freeman, *J. Phys. Chem.*, **60**, 1487 (1956).

<sup>c</sup> C. C. Addison and N. Logan, "Anhydrous Metal Nitrates," *Adv. Inorg. Chem. Radiochem.*, **6**, 71 (1964).

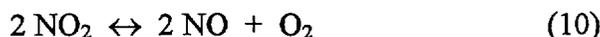
<sup>d</sup> K. H. Stern, *J. Phys. Chem. Ref. Data*, **1**, 747 (1972) and references therein.

<sup>e</sup> C. M. Kramer et al., *High Temperature Science*, **16**, 257 (1983).

<sup>f</sup> H. R. Bartos and J. L. Margrave, *J. Phys. Chem.*, **160**, 256 (1956).

<sup>g</sup> R. W. Brown, J. H. Lippiat, D. Price, D. C. A. Izod, *Intl. J. Mass Spect. Ion Phys.*, **16**, 101 (1975).

<sup>h</sup> A. N. Hayhurst and A. D. Lawrence, *Prog. Energy Combust. Sci.*, **18**, 529 (1992).



Ultimately, the final mix of gaseous products from the thermal decomposition of nitrate, i.e., the ratio of  $\text{NO}_x$  to  $\text{N}_2$  in the product stream, depends on a number of chemical and physical factors, such as residence times and flow patterns in the reaction vessel.

Reacting nitrates with reducing agents is a more direct and efficient route to producing  $\text{N}_2$  rather than  $\text{NO}_x$  as a final decomposition product. A large number of chemical reducing agents have been examined for the denitrification of aqueous solutions. These chemicals include iron metal,  $\text{Fe}^{2+}$ ,  $\text{N}_2\text{H}_2$ , glucose, CO, formaldehyde,<sup>a,b</sup> formic acid,<sup>c</sup> sugar,<sup>d</sup> and urea.<sup>e</sup> Nitrate ions can be reduced to ammonia (and sometimes  $\text{N}_2$ ) with aluminum<sup>f,g</sup> or iron<sup>h</sup> powder, depending on the pH of the solution. Thermochemical reduction has also been applied to dry nitrate wastes. Ammonia and ammonium compounds have been reported to reduce nitrates directly to  $\text{N}_2$  at temperatures of 300-600 °C.<sup>i</sup> Coke (carbon) has also been successfully used to directly reduce nitrates to  $\text{N}_2$  although higher temperatures were required.<sup>a</sup> The reaction of sodium nitrate and coke is representative of the thermochemical processes.



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<sup>a</sup> F. C. Gunderloy Jr., C. Y. Fujikawa, V. H. Dayan, S. Grid, "Dilute Solution Reactions of the Nitrate Ion as Applied to Water Reclamation" Technical Report No. TWRC-1; FWPCA: Cincinnati, OH 1968.

<sup>b</sup> F. C. Gunderloy Jr., R. I. Wagner, V. H. Dayan, "Development of a Chemical Denitrification Process" Technical Report No. EPA 17010EEX/10/70; U.S. Environmental Protection Agency, Water Quality Office: Washington, DC, 1970.

<sup>c</sup> R.F. Bradley,, C.B. Goodlett "Denitration of Nitric Acid Solutions by Formic Acid" DP-1299; Savannah River Laboratory: Aiken, SC, 1972.

<sup>d</sup> L. A. Bray "Denitration of Purex Wastes with Sugar" HW-76973; Hanford Atomic Products Operation: Richland, WA, 1963.

<sup>e</sup> J. L. Cox, R. T. Hallen, M. A. Lilga; *Environ. Sci. Technol.*, **28**, 423 (1994).

<sup>f</sup> A. P. Murphy, *Nature*, **350**, 223 (1991).

<sup>g</sup> A. J. Mattus D. D. Lee "The Nitrate to Ammonia and Ceramic (NAC) Process - A Newly Developed Low Temperature Technology" CONF-930873-18; Oak Ridge National Laboratory, Oak Ridge, TN, 1993.

<sup>h</sup> I.F. Cheng, R. Muftikian, Q. Fernando, N. Korte; *Chemosphere*, **35**, 2685 (1997).

<sup>i</sup> J. M. Dotson, T. E. Peters, U. S. Patent 3,862,296 (1975).

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