

Thermal Denitration

Tanks Focus Area



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Thermal Denitration

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Tanks Focus Area

Demonstrated at
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Richland, Washington

Demonstrated at
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Idaho Falls, Idaho



Purpose of this document

Innovative Technology Summary Reports (ITSRs) are designed to provide potential users with the information they need to quickly determine whether a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that prospective users consider a technology.

Each report describes a technology, system, or process that has been developed and tested with funding from the U.S. Department of Energy's (DOE) Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. ITSRs are intended to provide summary information. References for more detailed information are provided.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published ITSRs are available on the OST Web site at www.em.doe.gov/ost under "Publications."

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SECTION 1 SUMMARY

Technology Summary

Background

Fuel reprocessing activities over the past 50 years at the Idaho Chemical Processing Plant (ICPP), renamed the Idaho Nuclear Technology and Engineering Center (INTEC), resulted in four categories of radioactive waste (Nenni and Boardman 1997):

- alumina calcine waste,
- zirconia-blend calcine waste,
- discarded aqueous and organic wastes from the uranium extraction process, and
- aqueous sodium-bearing acidic waste (SBW).

Historically, SBW was mixed with aqueous waste from extraction processes and pure aluminum nitrate, and the mixture fed into in a fluidized-bed calciner, where it was converted to free-flowing granular solid oxides (referred to as “calcine”). The calcination process heats a substance to a high temperature but below the melting or fusing point, causing one or more of the following: loss of moisture, reduction, or oxidation. Calcine is stored on site in vented silos called “bin sets.” Currently, the waste inventory at INTEC includes 4,386 cubic meters of calcine waste and over 1,000,000 gallons of sodium-bearing acidic waste (TFA 2000).

A 1995 settlement agreement between the State of Idaho and the U.S. Department of Energy (DOE) required that all sodium-bearing waste (SBW) be calcined by December 31, 2012. Waste that is calcined presents less environmental risk than liquid waste. Additionally, all high-level waste (HLW) was to be treated and suitable for transport to a federal repository by 2035 (Boardman 1997).

In December 1999, the DOE Idaho Operations Office issued a draft environment impact statement (EIS) for HLW and facilities disposition for public comment. The EIS identified five alternatives for the treatment, storage and disposal of SBW, calcine, and other HLW generated at INEEL (DOE 1999). Within the EIS, it was noted that the 1995 settlement agreement milestone was changed by a 1998 modification that now requires DOE to cease use of the pillar and panel tanks by June 30, 2003 and cease use of the remaining tanks by December 31, 2012. This change requires the tanks to be emptied of their contents to a residual waste “heel” (definition of “cease use”) but does not specify a required treatment.

Problem

The presence of nitrate compounds in an aqueous waste feed stream to a treatment process can result in: (1) lower performance of the final waste form (for a grout process) or (2) high emissions of nitrogen oxides (for a thermal process such as vitrification).

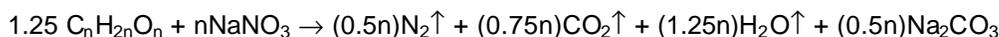
Solution

The addition of a carbon-based reductant (e.g., sugar) to a nitrate-containing feed stream into a thermal treatment system has been shown to achieve higher levels of denitration at lower temperatures and at a faster processing rate relative to a baseline process without the reductant (Smith et al. 1999). This innovative variation to the calciner flowsheet previously used at INEEL is termed Thermal Denitration. This approach is sometimes also referred to as Thermo Chemical Denitration.

How It Works

Thermal denitration uses temperatures between 300 °C and 500 °C and a carbon-based reductant to decompose the nitrate and nitrite salts to nitrogen gas and oxides of nitrogen. Thermal denitration is a three-step process: (1) evaporation of the acidic liquid, (2) decomposition of the highly volatile components, and (3) chemical interaction of the waste components and the added mixture to form a solid. During denitration, heat can be added via in-bed fluidization and/or direct heating, depending on the maximum temperature required.

Previous testing by researchers at the Pacific Northwest National Laboratory (PNNL) and others (Staples et al. 1999; Staples et al. 2000) has successfully demonstrated thermal denitration of low-level and high-level waste simulants using carbon-based reducing agents. The denitration reaction for nitrate and a carbohydrate proceeds as follows:



Potential Markets

- Calcine solids at INEEL,
- Nitric acid and high nitrate salt content waste streams stored at the Hanford site, Oak Ridge Reservation (ORR), and Savannah River Site (SRS) that do not have time-critical deadlines set for treatment and disposal,
- Wastewaters containing high concentrations of nitrates and nitrites, and
- High-activity waste with high sodium content at West Valley Demonstration Project

Advantages over Baseline

- 75% net increase in the waste processing rate (increase operating temperature of calciner from 500°C to 600°C),
- 33% reduction in the amount of pure aluminum nitrate that must be added to feed material,
- 5% projected decrease in nitrogen oxides (NO_x) emissions, and
- a decrease in carbon monoxide (CO) and unburned hydrocarbon emissions.

Demonstration Summary

Bench-Scale Demonstration

Bench-scale development tests conducted at PNNL involved the addition of sugar to the liquid waste simulant as it was fed into the rotary calciner (Figure 1). The purpose of the sugar was to increase the processing rate at lower operating temperatures. The major objective was to generate data to define the optimum conditions for demonstrating a technically viable and cost-effective approach to condition low activity waste (LAW) for immobilization. The simulated waste material used for testing represented the LAW at INEEL generated from separating SBW at INTEC.



Figure 1. Bench-scale rotary calciner with quartz reactor.

Key Results from the PNNL Demonstrations

Significant results from bench-scale testing:

- Higher levels of denitration can be achieved. With thermal denitration at 700°C for 8 hours, denitration efficiencies of 60% to 75% have been achieved with LAW. With reducing agents, greater than 90% denitration has been achieved at less than 300°C in 20 minutes.
- Approximately 50% to 70% of the nitrates destroyed were converted to N₂, with the remaining fraction converted to N₂O and NO_x. During typical calcination, the materials are typically heated to about 600°C, which causes the majority of nitrates to decompose to nitrogen oxides (principally NO_x) with a minimum generation of N₂.

INEEL Pilot-Scale Demonstrations

INEEL conducted pilot-scale cold (non-radioactive) testing using the existing 10-cm calciner pilot plant to demonstrate and develop empirical data on two processing options that showed potential for increasing the processing rate and throughput of LAW at INEEL (Boardman 1997; Nenni and Young 1997):

- Addition of carbon-based reductant to feed and
- Addition of aluminum compounds to feed.

The 10-cm calciner pilot plant validation tests were successfully completed, demonstrating both processing options. The results were compared to the standard 500°C high aluminum nitrate addition baseline technology. The product and effluent streams from the validation tests were characterized to help elucidate the process chemistries, provide insights on the optimum mode of operations, and investigate potential environmental permitting issues.

Key Results from the INEEL Demonstration

- Both processing options provided effective denitration and produced a free-flowing product (free-flowing product is desirable for transferring and ease of mixing purposes), while significantly reducing the amount of aluminum nitrate that must be added to the feed.
- The use of aluminum compounds showed greater promise for implementation because of ease of retrofit to the existing INEEL New Calcine Waste Facility and because of less safety and environmental concerns.
- Thermal denitration technology would be more difficult to permit and operate because of increased emissions of carbon monoxide and increase in unburned hydrocarbon relative to baseline levels.
- Aluminum nitrate is the preferred diluent additive for processing SBW. It reacts chemically with the alkali metals to form stable aluminates, it is commercially available, and it can be blended with SBW without causing precipitation in the feed system.
- An aluminum-to-alkali ratio (AAR) of 1:1 or higher promotes complete product denitration in the process feed at temperatures of 600°C or higher.

Commercial Availability

The hardware and associated equipment (fluid bed denitrator, rotary kiln, screw dryer, pumps, blowers, and off-gas treatment systems) to assemble a complete thermal denitration system exist..

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Other

All published Innovative Technology Summary Reports (ITSRs) are available on the Office of Science and Technology (OST) Web site at www.em.doe.gov/ost under "Publications." The Technology Management System (TMS), also available through the OST Web site, provides information about OST programs, technologies, and problems. The Tech ID for Thermal Denitration is 2371.

SECTION 2 TECHNOLOGY DESCRIPTION

Overall Process Definition

Bench-Scale Rotary Calciner at PNNL

Demonstration tests were performed in a small, bench-scale rotary calciner to observe and quantify the physical behavior of the waste feed during and after denitration, the dynamics of the denitration technique in a form that would be applicable to pilot- and full-scale systems, and the off-gas characteristics. The experiments were conducted with a bench-scale calciner equipped with off-gas analysis equipment. The calciner consisted of a 4-inch-diameter quartz reactor held between two nonrotating, stainless steel pillow blocks. The quartz reactor has nine dimples, approximately 1 inch in diameter and 0.5 inch deep, used as mixing flights when the unit is in operation. The quartz reactor has surrounding it a 1-zone clamshell heater with insulating collars. A schematic of the system is shown in Figure 2 (Smith et al. 1999).

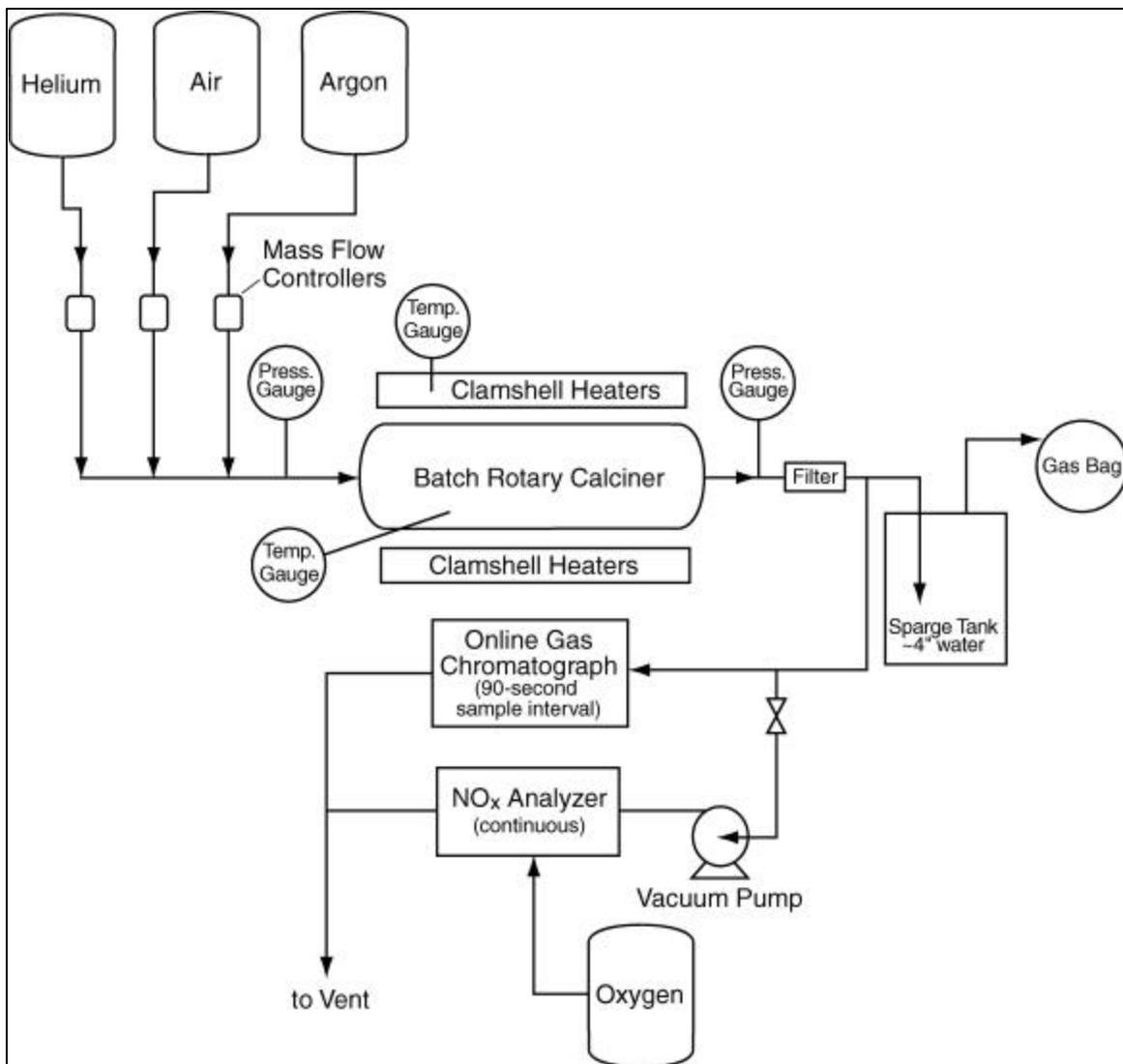


Figure 2. Schematic of PNNL bench-scale rotary calciner.

Pillow blocks are fitted with ground-glass-style ball joints that are greased and held together with spring clamps to maintain a gas-tight seal while allowing the reactor to rotate. A direct chain drive is used to rotate the reactor at four revolutions per minute. The outlet arm of the reactor is packed with quartz wool to keep fine particulates from exiting the reactor chamber. The front pillow block is fitted with type-K thermocouple that extends into the center of the reactor and is bent down to drag in the calcined material as the reactor rotates. The block is fitted with a magnahelic gauge and an inlet for the sweep gas. The rear block is assembled with a magnahelic, a particulate filter on the gas exit line, and a large-diameter blowdown tube submerged in 4 inches of water to allow excess gas to be collected if the reactor exceeds 4 inches of water pressure during operation.

10-cm Calciner Pilot Plant at INEEL

The 10-cm Calciner Pilot Plant is located in Building CPP-637 at INTEC. A schematic diagram of the 10-cm calciner vessel is shown in Figure 3 (Nenni and Young 1997). The calciner vessel consists of three sections: the plenum with the distributor plate, the reaction zone, and the disengagement section. The distributor plate is a perforated plate design. The reaction zone is located above the distributor plate and has a 10-cm internal diameter and a height of approximately 38 cm. The reaction zone is constructed from 310L stainless steel so that it can withstand elevated temperatures. The feed and fuel atomizing nozzles are located in the reaction zone. The feed is atomized with air and the fuel with oxygen. The disengagement section is located above the reaction zone and is approximately 117 cm in height. The internal diameter of the disengagement section widens from 10 to 15 cm in the base of the disengagement section. The disengagement section and the plenum were constructed from 304L stainless steel. Product continually overflows from the vessel through the overflow line that extends approximately 8 cm into the disengagement section. The product is collected in the product collection vessel. The vessel off-gas (VOG) stream from the calciner discharges at the top of the disengagement section (approximately 145 cm above the distributor plate) into the off-gas system.

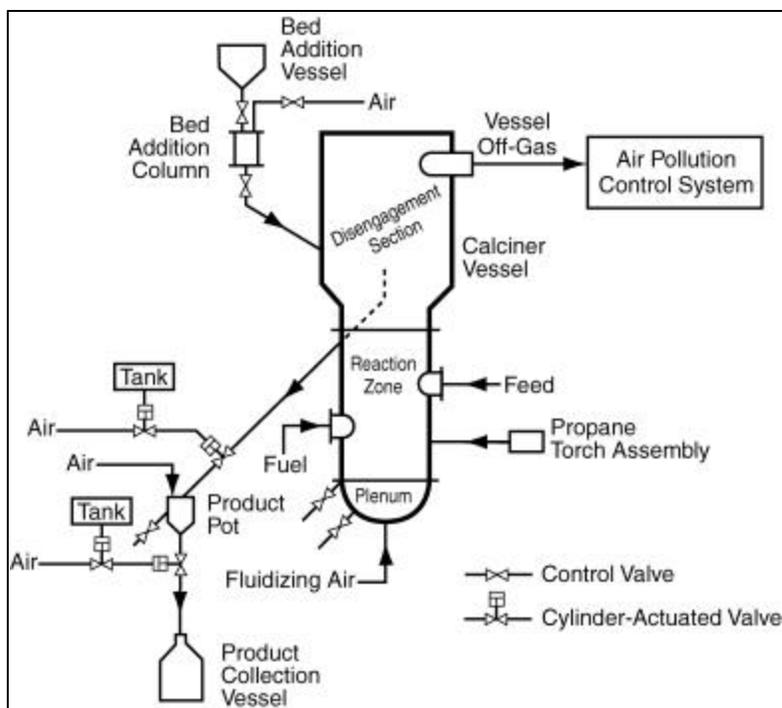


Figure 3. The 10-cm calciner vessel.

The VOG passes through a primary cyclone, where entrained particle fines are removed from the gas stream and are collected in a fines collection vessel. The VOG is then quenched in a venturi scrubber using nitric acid to cool the stream and remove any remaining entrained particle fines. Downstream of the venturi scrubber, a secondary cyclone removes acid droplets and small particle fines from the gas stream. The acidic vapors from the secondary cyclone drains into a scrub collection vessel. Acid from the collection vessel is continually recycled to the venturi scrubber. The off-gas stream is further cooled upon passing through a main condenser. The condensate is removed from the gas stream by a final cyclone. The off-gas stream passes through a final condenser before being discharged into the pilot plant enclosure ventilation system (not shown, but typical of air pollution control system design).

System Operation

- The denitration unit and associated equipment is designed for a 55% total operating efficiency.
- The waste is blended with recycled quench liquor and additives and atomized as feed to a fluidized-bed denitration unit operating at 650°C.
- The denitration unit is fired with kerosene and oxygen, and fluidization is maintained with the addition of preheated air.
- The denitration unit off-gas is first treated by a cyclone to remove fine particulates entrained in the off-gas stream.
- The fines and denitrated solids are air-conveyed to the solid storage bin.
- The off-gas is further treated through an acid quench, venturi scrubber and separator, demister, and filter prior to entering the nitrogen oxides and ammonia reactor and finally through the LAW Treatment Facility stack.

Materials and Labor

- Chemicals—Aluminum nitrate nonahydrate, calcium nitrate, boric acid, nitric acid, ammonium, kerosene, oxygen, and water.
- Materials—Fluidized-bed denitrator, feed tank, storage tanks, collection tanks, preheaters, scrubbers, quench towers, demister vessels, separators, pumps, filters, mixers, ventilation system, and exhaust fans.
- Labor—The 30-cm pilot-scale calciner requires over 500 person-hours to operate per test, and operating costs for a single test currently exceeds \$100,000 (Boardman 1997).

Secondary Waste Considerations

The 30-cm pilot-scale calciner generates over 1000 gal of liquid waste per test. However, much of this liquid waste can be used as make-up liquid and recycled in the quench liquid, venturi scrubber, and the demister system that are major parts of air pollution control system (Boardman 1997).

Concerns/Risks

- Regulatory acceptance and permit approval of denitration technology is questionable because of the high acid concentration off-gas emissions and strict requirements in the new Maximum Achievable Control Technology (MACT) rule for hazardous air pollutants.
- Increased flash evaporation of the feed material results in the generation of more particulate fines in the off-gas. The impact of this development may not be fully understood until tested in a full-scale unit.
- Higher operating temperatures of the denitration unit may result in increase corrosion of the fluidized-bed vessel and piping system. This stress on the unit may increase maintenance costs and increase down time, which may cause the cost analysis of this technology to be unfavorable in comparison to other potential options for waste treatment.

Many of the concerns and risks related to thermal treatment systems and their operations are clearly defined and explained in greater detail in Assistant Secretary for Environment, Safety and Health, Office of the Deputy Assistant Secretary for Nuclear and Facility Safety 1999 and U.S. Environmental Protection Agency 1998.

SECTION 3 PERFORMANCE

Demonstration Plan

PNNL Bench-Scale Calciner System Operation and Performance

The bench-scale calciner at PNNL is equipped with off-gas analysis equipment. Tests were performed to observe and quantify the physical characteristic and the dynamics of the thermal and thermochemical denitration processes as related to off-gas generation and cost-effective stabilization of residue solids. A portable on-line gas chromatograph (GC) was available during some tests for evaluating the off-gas from the reactor. In other tests, a sample port on the exit line of the reactor was used, and gas samples were removed through a septum via a gas-tight syringe. The samples were then taken to a nearby laboratory and analyzed for N₂, O₂, CO₂, H₂, and CH₄ using a standard laboratory GC (Smith et al. 1999).

The tests were conducted using a LAW simulant (Table 1) formulated to mimic LAW streams at INEEL. The simulant was mixed with an inert material (Micro-Cel E) and a reducing agent (glycolic acid or sugar). The inert material was added to inhibit the formation of a molten slag and thus prevent fluidization. The reducing agent was added to lower the melting and reacting temperature, reduce stress on the system components, and convert more of the nitrate (NO₃⁻) to nitrogen gas (N₂) rather oxides of nitrogen (NO_x).

Table 1. LAW simulant waste composition

Element/ anion	Concentration (moles/L)	Element/ anion	Concentration (moles/L)	Element/ anion	Concentration (moles/L)
Al ⁺³	1.9E-01	Hg ⁺²	2.43E-04	Zr ⁺⁴	5.01E-04
B ⁺³	5.67E-03	K ⁺	5.31E-02	As ⁻³	1.05E-05
Ca ⁺²	7.08E-02	Mn ⁺²	3.47E-03	Ba ⁺²	1.52E-11
Cd ⁺²	8.5E-04	Na ⁺	5.16E-01	Mo ⁺⁶	6.09E-17
Cl ⁻	7.74E-03	Ni ⁺²	3.40E-03	Pb ⁺²	6.02E-10
Cr ⁺³	8.60E-04	NO ⁻³	2.58E+00	Se ⁺⁴	5.57E-06
Cs ⁺	1.37E-08	PO ₄ ⁻³	4.15E-03	H ⁺	1.32E+00
F ⁻	2.03E-02	SO ₄ ⁻²	1.36E-02	CO ₃ ⁻²	5.66E-02
Fe ⁺³	6.32E-03	H ⁺	1.32E+00	NaNO ₂	2.28E-04

For each of the tests, simulated LAW was mixed with the diluent, and then the reductant was added. The resultant product was a solid, as the diluent tended to absorb most of the free liquid from the LAW bottoms simulant. The mixture was then added directly to the calciner. The reactor was rotated and purged with air or argon to which a 4% helium stream was added. This method was used to track the evolution of gaseous products in the reactor. The reactor contents were slowly heated to a predetermined setpoint, and the temperature and pressure were monitored during heating. As a general rule, the temperature elevation was performed quickly, and it was slowed down or stopped during observed events such as water removal, smoking, pressure excursions, and ignition. Temperatures were recorded for such events, and then the temperature elevation continued to a predetermined temperature, after which the reactor was held at the selected temperature and then cooled. Following the tests, the resulting material was weighed, collected, and sent for analysis for total organic carbon (TOC) and for nitrates.

Results

- Thorough contact between the nitrate-bearing waste and the reductant must be achieved to yield high nitrate reduction. This fact is illustrated in comparing Run 1 with Runs 2–5. In Run 1, the feedstock was prepared by loading the LAW bottoms simulant in a 4:1 ratio onto the Micro-Cel E diluent. This

slightly moist mixture was then partially dried until about 50% of the mass (as water) was removed. After drying, the reductant (in dry form) was mixed with the simulant and then loaded into the reactor. In subsequent tests, the dry reductant was added directly to the moist simulant/Micro-Cel E mix, which allowed some of the sugar to dissolve into the moist waste form. The mixture was then added to the reactor, and further commingling occurred during the heating cycle while water was still present in the waste. Runs 2–5 provided more complete denitration than the first run, where the reductant was added to a dry mixture (Table 2).

Table 2. Summary of feed conditions for rotary calciner runs with LAW simulant

Run number	LAW simulant (g)	Inert type	Inert wt (g)	Wt of nitrate in feed (g)	Reductant type	Reductant wt (g)	Total wt of feed (g)	Final wt of product (g)
1	12.50	MCE*	3.13	3.41	Sucrose	1.96	9.82	4.82
2	16.06	MCE	4.01	4.38	Sucrose	2.59	22.66	4.46
3	16.06	MCE	4.01	4.38	Glycolic acid	4.46	24.53	6.26
4	22.48	MCE	5.62	6.13	Glycolic acid	6.27	34.37	8.67
5	20.92	MCE	5.23	5.71	Sucrose	3.28	29.43	5.52
6	4.64	fly ash	1.16	1.27	Sucrose	0.73	3.53	1.34
7	4.78	fly ash	1.20	1.30	Sucrose	0.75	3.64	1.35
9	24.22	MCE	6.05	6.61	Sucrose	3.81	23.55	7.24

*Micro-Cel E

- The data indicate that the sucrose reductant yielded slightly higher nitrate reduction than the glycolic acid. Run 2 (sucrose reductant under argon) had a final nitrate reduction level of 99.8%, whereas Run 3 (glycolic acid reductant under argon) had a final nitrate reduction level of only 90.6%. Initially, it was believed that disparity between the nitrate reduction levels could be explained by the fact that the glycolic acid test was taken up to a maximum temperature of only 350°C, whereas the sucrose test was taken up to a maximum temperature of 550°C. However, testing in Runs 5 and 6 (sucrose as reducing agent) indicated that 97% to 99% nitrate reduction occurs without exceeding 370°C. Thus, there was a slight performance improvement using sucrose over glycolic acid for testing with respect to achieving denitration. Residual TOC in the final product was related to the maximum temperature achieved in the test. The lowest TOC readings (Runs 2 and 5) occurred in tests that ended above 600°C, while the highest TOC readings occurred in the other tests that had maximum temperatures between 370°C and 550°C, likely due to volatilization of excess reductant that occurred at higher temperatures (see Table 3).

Table 3. Summary of rotary calciner runs with LAW simulant

Run number	Reductant mixing condition	Cover gas	Maximum temperature (°C)	NO ₃ removed (%)	Residual nitrate (ppm)	Residual TOC (ppm)
1	Dry	Air	610	77	160,000	100
2	Moist	Argon	550	99.8	1,800	1,000
3	Moist	Argon	375	90.6	66,000	7,200
4	Moist	Air	575	96	26,000	1,100
5	Moist	Argon	630	99.6	4,200	310
6	Wet	Argon	370	99	11,000	980
7	Wet	Argon	232	97	28,000	1,130
9	Dry	Argon	270	NA	NA	NA

10-cm Pilot-Scale Calciner System Operation and Performance

Five scoping tests were conducted using the 10-cm calciner to evaluate the elevated-temperature and sugar-additive flowsheets. The initial test, SBW-BL-1, was conducted using the baseline flowsheet and was completed to serve as a comparative reference for the alternative flowsheets. Two high-temperature denitration tests, SBW-HT-1 and SBW-HT-2, were conducted to compare the effects of temperature and AAR variations. Two sugar-additive denitration tests, SBW-SA-1 and SBW-SA-2, were also completed to compare the effects of varying the AAR. SBW-SA-2 resulted in massive cluster of material in the bed and was discontinued before the test was completed. Table 4 lists some of the major operating parameters and measured results of key characteristics from waste processing using the 10-cm pilot-scale calciner (Nenni and Young 1997).

Table 4. Key operating parameters and measured physical/chemical properties of processed waste using the 10-cm pilot-scale calciner

Run description	SBW-BL-1	SBW-HT-1	SBW-HT-2	SBW-SA-1	SBW-SA-2
Temperature, °C	500	650	600	500	500
Actual AAR	3.54:1	0.98:1	1.48:1	1.04:1	
Feed rate, L/hr	1.9	2.0	1.5	1.5	1.63
Total feed calcined, L	76	76	88	68	24
SBW processed, L	14	33	30	23	
Weight percentage of NO ₃ in final bed	16	4.1	4.2	7.4	
Product/fine weight ratio	1.2	2.6	13.3	2.0	
NO ₃ /Na+K mole ratio in final bed	0.72	0.077	0.092	0.15	
Weight percentage undissolved in 8M HNO ₃	8.9	4.5	4.7	6.5	
Weight percentage undissolved in 2M HNO ₃	40	2.9	7.6	2.4	
Percentage of CO in off-gas stream	0.7	0.7	0.5	4.8	

Results

- The products of the alternative flowsheets were more soluble in 2M HNO₃ and 8M HNO₃ than the baseline flowsheet. This is an indication that the calcine product will be easier to prepare and make ready for final treatment and/or transport.
- The high-temperature flowsheets resulted in the lowest nitrate content in the product with corresponding higher amounts of nitrate in the fines (compare to the sugar-additive flowsheet). This phenomenon should increase the calcine product susceptibility to final treatment and decrease the amount of filler material required to produce a suitable waste form. It would also decrease the waste volume.
- The feed rate of kerosene required to achieve 600°C was approximately the same as the feed rate to maintain the bed temperature at 500°C. A higher temperature can be achieved without increasing the quantity of kerosene required, meaning that the kerosene cost does not increase at the elevated temperatures.
- The off-gas data show that CO emissions rates decreased at the higher temperatures but increased during sugar-additive denitration. CO emissions are critical in permitting a thermal treatment process.
- The sugar-additive flowsheet resulted in a significantly higher level of unburned hydrocarbons than did the elevated-temperature flowsheet. The unburned hydrocarbons could potentially inhibit the permitting of this process.

Additional test data and results on the comparison of high-temperature and organic reductant thermal denitration of INTEC waste using a bench-scale rotary reactor is included in Pao 1998 and Marshall 1998.

SECTION 4 TECHNOLOGY APPLICABILITY AND ALTERNATIVES

Competing Technologies

This section examines the potential flowsheets developed and implemented either as a pilot-scale or full-scale system for removing nitrates and nitrites from waste streams (Table 5). The basic principle for each of the systems reviewed is similar, with minor differences in mode of operation, equipment specifications, or the type of waste the system was designed to treat. The flowsheets or treatment systems were evaluated based on the following criteria (Smith et al. 1999):

- ability to meet state and federal requirements for licensing, permitting, and operating thermal treatment systems;
- maturity of the technology;
- operability;
- ease of integration into existing INEEL facilities;
- safety and environmental considerations; and
- design considerations (availability of system components, process capabilities, etc.).

Table 5 Comparison of competing technologies

Technology	Developer	Basic principle	Status/comments
Fluid bed calciner (baseline)	INEEL	Uses a high-temperature fluid bed reactor to convert nitrate to nitrogen gas and oxides of nitrogen.	Was operated at INEEL for many decades. Existing system was not able to meet the required throughput to process the projected low-level waste inventory. Compliance with new provisions of the Clean Air Act would require substantial expenditures for air pollution controls. Requires minor modifications to existing equipment.
Fluid bed calciner with sugar added	PNNL and INEEL	Uses a fluid bed reactor and a reducing agent (sugar) to convert nitrate to nitrogen gas and oxides of nitrogen at a lower temperature than the baseline method uses.	Has the potential to convert a greater percentage of the nitrate to nitrogen gas, therefore reducing the cost of the air pollution controls. Requires minor modifications to existing equipment.
High-temperature dryer/rotary kiln	Various	Uses an evaporator, dryer, and rotary kiln to sequentially remove nitrate in several stages.	Has not been pilot-tested but employs proven technologies, thus has high probability of success. None of the equipment proposed is currently in use at INEEL.
COGEMA direct-injection rotary kiln	COGEMA	Uses a COGEMA rotary kiln to remove nitrate via a reducing agent (sugar). Process is proprietary, so specifics are unknown.	Has been used in France for many years. None of this equipment is currently in use at INEEL. Operation of rotary kiln is well understood and has good safety record.
Glycine Nitrate Process	PNNL	Uses a rotary kiln to remove nitrate via a reducing agent (glycine).	Has been used by Seattle Specialty Ceramics to produce ceramic powder. Only limited testing and production on specific metal nitrates have been conducted. None of this equipment is currently in use at INEEL.

Bureau of Mines briquette	Bureau of Mines	Uses an evaporator, mixer, brick former, and rotary kiln to sequentially remove nitrate in several stages. Sugar and nitrate react within each pellet in the rotary kiln. Calcined pellets are then grouted.	Limited pilot-testing has been accomplished using an INEEL characteristic simulant waste. None of the proposed equipment is currently in use at INEEL.
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Additional resources that identify and review competing and innovative technologies in the early research and development stage and that were not listed in the table include Jantzen et al. 2000 and Kirkham and Herbst 2000. A series of bench-scale testing was also performed to identify a candidate glass to determine the feasibility of the vitrification process on an INEEL HAW fraction from a zirconia calcine separation (Vienna et al. 1999).

Technology Applicability

Thermal denitration may be applicable to aluminum calcine waste, zirconium calcine waste, and mixed calcine waste at INEEL and aqueous acidic waste containing high concentrations of nitrates and nitrites in waste tanks at the Oak Ridge Reservation, Savannah River Site, and Hanford Site. This technology is most cost-effective and advantageous when (1) the nitrate/nitrite concentration of the waste stream is high and direct immobilization using grout technologies is impractical because a stable waste form would be difficult to obtain and (2) direct vitrification is impractical or cost-prohibitive.

Patents/Commercialization/Sponsor

The Glycine Nitrate Process developed by PNNL has been awarded several patents (Aksay et al. 5,061,682; Maupin et al. 5,705,132) and received an R&D 100 Award for being one of the top 100 new technologies of 1992 as determined by *Research & Development Magazine*. In addition, the process also received a Federal Laboratory Consortium award for Excellence in Technology Transfer in 1993.

SECTION 5 COST

Methodology

OST is involved in demonstrating and validating the performance and cost data associated with promising and innovative technology systems and components of systems that target urgent environmental opportunities and needs. This section examines costs directly associated with thermal denitration processes: pumps, denitrators, preheaters, and off-gas treatment processes.

Cost Analysis

Capital and Operating Costs

Table 6 shows the capital costs of a thermal denitration system, and Table 7 shows the capital costs of the air pollution control system required to treat the emissions from the thermal denitration system (Flour Daniel, Inc. 1997).

Table 6. Capital costs for denitration equipment

Equipment description	Material unit cost (\$)	Labor cost (\$)	Total cost (\$)
Cyclone (21-CY-1102)	25,000	4,084	29,084
Pneumatic ejector (21-EJ-1101)	10,000	2,060	12,060
Air preheater (21-HE-1101), 211 kW	25,000	4,084	29,084
Ejector preheater (21-HE-1104), 44 kW	25,000	4,084	29,084
Quench/recycle/bleed pump (21-P-1101), 64,000 L/hr	10,000	2,060	12,060
Scrubber feed pump (21-P-1102), 3,000 L/hr	8,000	1,729	9,729
Nitric acid pump (21-P-110), 72,000 L/hr	10,000	2,060	12,060
Aluminum nitrate pump (21-P-1111), 602 L/hr	5000	1,030	6,030
Boric acid pump (21-P-1112), 110 L/hr	3,000	662	3,662
Kerosene pump (21-P-1113), 338 L/hr	3,000	662	3,662
Anhydrous ammonia pump (21-P-1114), 65.3 L/hr	3,000	662	3,662
Calcium nitrate pump (21-P-1115), 8.6 L/hr	2,000	441	2,441
Liquid waste collection tank (21-T-1105)	640,000	69,681	709,681
Fluidized-bed denitrator (21-V-1101), includes off-gas quench tower, demister vessel, venturi scrubber, and separator	1,500,000	245,007	1,745,007
Total (denitration process system)			2,607,308

Cost Conclusions

The capital cost for a denitration unit and associated components is approximately \$2.6 million, and the capital cost for the off-gas treatment system is approximately \$2.9 million, making the total capital cost for a full-scale thermal denitration system and the off-gas treatment unit approximately \$5.5 million. INEEL estimates that the annual operating cost for a denitration facility is approximately \$3.2 million.

Table 7. Capital costs for off-gas treatment process system

Material description	Material unit cost (\$)	Labor cost (\$)	Total cost (\$)
SCR feed blower (23-BL-1104)	15,000	2,232	17,232
Stack blower (23-BL-1105)	15,000	2,232	17,232
Exhaust roughing filters (23-FL-1101), 2 required	30,000	9,289	39,289
Exhaust HEPA filter (23-FL-1102, first stage), 2 required	30,000	9,289	39,289
Exhaust HEPA filter (23-FL-1103, second stage), 2 required	30,000	9,289	39,289
Exhaust preheater (23-HE-1101), 2 required	50,000	4,930	54,930
SCR feed preheater (23-HE-1102), 270 kW	25,000	2465	27,465
Exhaust preheater (23-HE-1103), 46 kW	25,000	2465	27,465
NO _x reactor heat exchanger (23-HX-1104)	105,000	11,448	116,448
NO _x reactor, primary (23-V-1107)	38,000	6,221	44,221
NO _x reactor, secondary (23-V-1108)	38,000	6,221	44,221
NH ₃ reactor (23-V-1109)	38,000	6,221	44,221
Plantinized-bed reactor (23-V-1110)	38,000	6,221	44,221
Type H-1 HEPA filter, 50,000 cfm	400,000	75,000	475,000
E-5C HEPA filter trains, @ 12/cfm	1,080,000	108,001	1,188,001
E-5C HEPA filter, @ 3/cfm	270,000	27,035	297,035
Blowers, 10 required, 9000 cfm each	85,060	8,500	93,560
E-5C inlet to cells, 50,000 cfm	250,000	24,747	274,747
Total (air pollution control system)			2,883,864

The U.S. Environmental Protection Agency (EPA) and air pollution industry experts have estimated that the cost of the Best Available Control Technology for NO_x abatement is approximately \$35,400 per ton of NO_x removed. PNNL has demonstrated that the sugar-additive denitration process can reduce the formation of NO_x by 30% to 40% and determined that the cost to prevent the formation of NO_x using this process is approximately \$360/ton. This is nearly a 100-fold cost reduction when compared to NO_x abatement. PNNL reports that the thermal denitration process can reduce the volume of waste by a factor of 3 to 8, which means a substantial reduction in storage requirements or volume of waste to be treated and disposed (Smith et al. 1999).

SECTION 6 REGULATORY AND POLICY ISSUES

Regulatory Considerations

The National Environmental Policy Act (NEPA) of 1969 requires that all federal agencies prepare a detailed statement on the potential environmental effects that a major proposed federal action may have on the quality of the environment. Table 8 lists the federal, State of Idaho, and other DOE regulations and requirements applicable to the construction and operation of the thermal denitration technology (Flour Daniel, Inc. 1997).

Table 8. Relevant federal and state regulations*

Media or type of stream	Permit, approval, or requirement	Regulation(s)	Regulatory agency
NEPA	NEPA documentation	10 CFR 1021 (NEPA)	DOE
Nonradioactive air emissions	New stationary source/NOC/PTC	40 CFR 60 (CAA)	IDHW, EPA
Hazardous waste air emissions	Treatment, storage and disposal facilities	40 CFR 264/265, Subpart AA and BB (RCRA)	IDHW, EPA
Radioactive air emissions	NESHAPs	40 CFR 61 Subpart H (CAA), IDAPA 16.01.01	IDHW, EPA
Hazardous waste treatment, storage, and disposal	Hazardous waste permit (RCRA Part A and B)	40 CFR 264 (RCRA), 40 CFR 265, 40 CFR 270	IDHW, EPA
Land disposal of radioactive, hazardous and mixed waste	Technical standards, LDRs (universal treatment standards)	40 CFR 268, IDAPA 16.01.05 (RCRA, LLWPA)	IDHW, NRC, EPA
Solid waste	Solid waste handling permit	IDAPA 16.01.06	IDHW, EPA

*Acronyms are defined in Appendix B.

DOE and the State of Idaho entered into a consent order on November 1, 1995 that provides for compliance with all federal and state requirements applicable to hazardous waste, including the Hazardous Waste Management Act (Idaho Code 39-4401) and the Federal Facilities Compliance Act (Public Law 102-386).

Emissions and Effluents

The thermal denitration unit gaseous emissions are discharged from the facility stack. Emissions are estimated or calculated based on waste stream characterization and process rate because direct measurement of the pollutants can be difficult.

- The level of NO_x emissions from a waste with high nitrate content can mask the other constituents from detection by standard monitoring equipment. INEEL has developed an approved EPA sampling and monitoring strategy that overcomes this NO_x masking problem and achieves MACT compliance.
- Tritium is emitted from the stack during the processing of mixed wastes. Emissions of tritium at INEEL are presently far below the allowed release limit. INEEL estimated that the dose from tritium at the site boundary during waste processing is about 6.5E-06 mrem/year.
- The emissions from the denitrator unit must comply with the National Ambient Air Quality Standards or Prevention of Significant Deterioration increments, especially the site limits for NO_x emissions.

Key Regulatory Issues

It is necessary to interact with the regulators on several key issues to establish the plausibility of the regulatory pathways laid out in Table 8:

- LAW from calcine will be mixed with grout for disposal. Designation of the LAW as Class A waste requires either a treatment variance (because the calcine waste feed material is defined as HLW) or designation by NRC as incidental waste. To determine whether the variance must be obtained, it is first necessary for DOE to communicate with NRC regarding designation of the residual LAW as incidental waste. If designated as incidental waste, the LAW is no longer regulated by NRC rules. If not designated as incidental waste, then a treatment variance will be required for the LAW fraction from the calcine waste since it will be grouted. Under the treatment variance scenario, NRC and EPA maintain jurisdiction over the LAW from calcine processing and are likely to require the disposal site to meet performance objectives set out in 10 Code of Federal Regulations (CFR) 61 and DOE Order 435.1.
- Disposal of LAW as low-level waste (radioactive and not hazardous) requires approval so the wastes can be disposed of as nonhazardous waste in the tank farm tanks prior to conventional closure. This step requires a DOE waiver from the disposal sites requirements of DOE Order 435.1.
- The denitration units are designed to meet the incinerator standards, 40 CFR 264 Subpart O. The operating requirements must demonstrate compliance with performance standards during trial burn. Operating limits specified include CO levels in the stack's exhaust, waste feed rate, combustion temperature, and combustion gas velocity.

Safety, Risks, Benefits, and Community Reaction

Several potentially significant safety issues exist with implementation of the thermal denitration technology. These issues include release of toxic gases, fires or explosions, and release of radioactivity or hazardous material. A preliminary assessment of the issues and potential preventive and mitigative controls and features are addressed in Table 9 (Flour Daniel, Inc. 1997).

Technologies and processes that require elevated temperatures have received excess scrutiny from the regulators and stakeholders because of the increased risks for fire and explosion and because of the volume and type of off-gas emissions generated. Technologies that include thermal processes continue to receive consideration for implementation and deployment because of the potential to greatly reduce the volume of waste required for disposal and lower costs for disposal.

Table 9. Preliminary safety analysis of thermal denitration facility

Activity or process	Safety condition	Causes	Material at risk	Immediate consequences	Potential safety features	Category
Kerosene storage tank	Fire	Leaking tank, spill during loading	Kerosene	Fire	Design tank to prevent spill and fire	S2*
Anhydrous ammonia storage tank	Release of toxic gas	Leaking tank, release during loading	Ammonia	Release of toxic material	Design tank to prevent spill; design loading port to prevent releases	S3
Fluidized-bed denitrator	Fire	Higher than design temperature, H ₂ accumulations, unplanned chemical mix	Sodium-bearing waste, calcine	Fire	Temperature monitor, air mix monitor, limits on amount of material	S3
Fluidized-bed denitrator	Release of radioactive material	Failure of vessel due to high pressure, corrosion, high temperatures	Sodium-bearing waste, calcine	Release of radioactive material	Temperature monitor, pressure monitor	S3
Denitration feed tank	Release of radioactive material	Leak	Low-activity waste	On-site or off-site dose	Design of tank	S3
Denitration pump	Release of toxic material	Spray	Low-activity waste	On-site or off-site exposure	Design of pump, spray guard	S3
Filter	Toxic or radioactive material release	Failure of filter; gas leak around filter	Toxic or radioactive material	Release of toxic or radioactive material	Change filter periodically, monitor filter performance	S2
NO _x removal	Release of NO _x	Failure of reactor vessel; failure of system to remove gas	NO _x	Release of NO _x	Monitor NO _x system performance	S2

*S0 – Negligible on-site and off-site impact on people and the environment.

S1 – Minor on-site impact and negligible off-site impact on people and the environment.

S2 – Major on-site impact on people and the environment; only minor off-site impact.

S3 – Major on-site and off-site impact on people and the environment.

SECTION 7 LESSONS LEARNED

Implementation Considerations

To cost-effectively implement thermal denitration processes, several factors must be considered:

- Denitration of wastes containing high concentration of nitrates and nitrites is a preconditioning step to the final treatment options and disposal. Treatability studies should be continued to determine the optimum nitrate destruction level criteria when correlated to final treatment options, waste durability, and cost. The denitration facility should be designed and engineered based on these evaluations and not on the assumption that zero or near-zero residual nitrates produce the best waste performance.
- Higher temperatures will increase vessel and piping stress and may increase corrosion in the fluidized-bed vessels. An economic assessment of upgrading the material construction of the vessels and piping should be performed.
- The elevated temperature during thermal denitration process increases flash evaporation of the feed material, which results in generation of fine particles. Generation of fine particles may cause the solids to agglomerate and create transfer and handling problems. The impact of these phenomena may not be fully understood until tested on a full-scale unit.
- Adequate control of the off-gas from the denitrator-fluidized bed at the elevated operating temperature of 650°C requires significantly larger quench liquor flows than the baseline technology (at 500°C). It may be necessary to place parallel train quench towers to ensure adequate processing of the gases.
- The need for applying a postcombustion unit to destroy aromatic compounds may be required because kerosene is used as the primary source of fuel for the denitration unit. Kerosene may generate products of incomplete combustion. The use of cleaner fuel or plasma torch to heat the denitration unit may obviate the need for a postcombustion unit.

Technology Limitations and Needs for Future Development

- Concern exists over the creation of polyaromatic and/or hazardous organic compounds as the result of incomplete combustion of the fuel oil used in the denitration process. Consideration should be given to the use of propane or other clean, indirect heating methods, such as plasma heating of the fluidizer air, to minimize the potential formation of these hazardous constituents. Thoroughly defined off-gas characterization is essential prior to start of denitration system design.
- An on-line monitor needs to be developed to measure the levels of hazardous air pollutants and criteria pollutants (NO_x, CO, and unburned hydrocarbons) emitted from the denitrator. The emissions data will help address design and permitting needs to comply with MACT rule and other EPA requirements.
- Thermal denitration of some wastes may generate a significant volume of toxic and corrosive off-gases. A cost-effective method to treat or render these emissions harmless is needed.

Technology Selection Considerations

- Thermal denitration is a technically viable and effective approach to condition waste containing a high content of nitrate salts, aluminum calcine waste, and zirconium calcine waste.
- This technology has the advantages of high throughput capabilities (75% over standard calcinations technology), a 5% decrease in NO_x emissions, and a decrease in CO and unburned hydrocarbon emissions.
- Waste volume can be reduced by up to a factor of 8 from its initial volume, depending on nitrate salt content.

APPENDIX A REFERENCES

- Assistant Secretary for Environment, Safety and Health, Office of the Deputy Assistant Secretary for Nuclear and Facility Safety. 1999. *Waste Vitrification Systems Lessons Learned*. Washington, D.C.: U.S. Department of Energy.
- Boardman, R. D. 1997. *Alternative Calcination Development Status Report*, INEEL/EXT-97-00654. Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory.
- Flour Daniel, Inc. 1997. *ICPP Waste Treatment Facilities Feasibility Study Report*. Idaho Falls, Idaho.
- Goozner, R., S. Alkinburg, and W. Drinkard. 1996. *A Process to Denitrify Radioactive Waste Streams, Phase I Final Report to U.S. DOE*, SBIR Grant No. DE-FG02-95ER81952. Charlotte, N.C.: Drinkard Metalox.
- Hickman, R. G. 1992. *Hanford Tank Wastes; Salt Splitting FY92 Activities*, UCRL-ID-111983. Livermore, Calif.: Lawrence Livermore National Laboratory.
- Jantzen, C. M., et al. 2000. *Crystalline Phase Separation in Phosphate Containing Waste Glasses: Relevancy to Vitrification of INEEL High Activity Waste*, WSRC-TR-2000-00339. Aiken, S.C.: Savannah River Technology Center.
- Kirkham, R. J., and A. K. Herbst. 2000. *Suitability of Silica Gel to Process INEEL Sodium Bearing Waste*. Idaho Falls, Idaho: Bechtel BWXT Idaho, LLC.
- Krapukhin, V. B., E. P. Krasavina, and A. K. Pikaev. 1997. *Crystallization of Sodium Nitrate from Radioactive Waste*, PNNL-11616 UC-2030. Richland, Wash.: Pacific Northwest National Laboratory.
- Marshall, D. W. 1998. "Recommendation for a LAW Denitration Pilot Plant DWM-03-98." LMITCO interdepartmental communication D. V. Croson dated September 29.
- Nenni, J. A., and R. D. Boardman. 1997. *Thermal Denitration and Mineralization of Waste of Waste Constituents*, CONF-970537-INEL/CON-97-00507. Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory.
- Nenni, J. A., and L. J. Young. 1997. *Status Report for Alternative Calcination Scoping Tests*. Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory.
- Pao, J. 1998. "Comparison of High Temperature and Organic-Reductant Thermal Denitration of INTEC Low-Activity Waste in a Bench Scale Rotary Reactor." INEEL interdepartmental communication to J. H. Valentine dated December 24.
- Pao, J. 1998. "Summary of High Temperature and Organic Additive Thermal Denitration of INTEC Low Activity Waste." INEEL interdepartmental communication to D. V. Croson dated September 28.
- Sevigny, G. 1996. *Letter Report: Evaluation of Dryer/Calciner Technologies for Testing*, PNNL-10979 UC-910. Richland, Wash.: Pacific Northwest National Laboratory.
- Smith, H. D., et al. 1998. *Denitration of High Nitrate Salts Using Reductants*, PNNL-12144. Richland, Wash.: Pacific Northwest National Laboratory.
- Staples, B. A., et al. 1999. *The Preparation and Characterization of INTEC HAW Phase 1 Composition Variation Study Glasses*, INEEL/EXT-98-00970 Rev. 1. Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory.

Staples, B. A., et al. 2000. *The Preparation and Characterization of INTEC Phase 2b Composition Variation Study Glasses*, INEEL/EXT-99-01322. Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory.

Steele, D. F. 1990. "Electrochemical Destruction of Toxic Organic Industrial Waste," *Platinum Metal Review* 34(1): 10–14.

Tanks Focus Area. 2000. *Assessment of Selected Technologies for Treatment of Idaho Tank Waste and Calcine*, PNNL-13268. Richland, Wash.: Pacific Northwest National Laboratory.

U.S. Department of Energy. 1999. *Idaho High-Level Waste and Facilities Disposition, Draft Environmental Impact Statement*, DOE/EIS-0287D. Idaho Falls, Idaho.

U.S. Environmental Protection Agency. 1998. *On-Site Incineration: Overview of Superfund Operating Experience*, EPA-542-R-97-012. Washington, D.C.

Vienna, J. D., et al. 1999. *Glass Formation for INEEL Zirconia Calcine High Activity Waste*, PNNL-12202. Richland, Wash.: Pacific Northwest National Laboratory.

APPENDIX B ACRONYMS AND ABBREVIATIONS

AAR	aluminum-to-alkali ratio
CAA	Clean Air Act
CFR	Code of Federal Regulations
CO	carbon monoxide
DOE	U.S. Department of Energy
EIS	environmental impact statement
EPA	Environmental Protection Agency
GC	gas chromatograph
HLW	high-level waste
ICPP	Idaho Chemical Processing Plant
IDAPA	Idaho Air Pollution Authority
IDHW	Idaho Department of Health and Environment
INEEL	Idaho National Engineering and Environmental Laboratory
INTEC	Idaho Nuclear Technology and Engineering Center
ITSR	Innovative Technology Summary Report
LAW	low-activity waste
LDR	Land Disposal Restriction
LLWPA	Low-Level Waste Performance Assessment
MACT	Maximum Achievable Control Technology
NEPA	National Environmental Policy Act
NESHAP	National Emission Standards for Hazardous Air Pollutants
NOC	notification of construction
NO _x	nitrogen oxide(s)
NRC	Nuclear Regulatory Commission
OST	Office of Science and Technology
PNNL	Pacific Northwest National Laboratory
PTC	permit to construct
RCRA	Resource Conservation and Recovery Act
SBW	sodium-bearing waste
STCG	Site Technology Coordination Group
TFA	Tanks Focus Area
TMS	Technology Management System
TOC	total organic carbon
TTP	Technical Task Plan
VOG	vessel off-gas stream