

CONF-980905--

**Technological and Economic Update on the
Nitrate to Ammonia and Ceramic Process**

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JUN 10 1998

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For presentation at
Spectrum '98, September 13-18, 1998
Denver, Colorado

and for publication in the
proceedings

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TECHNOLOGICAL AND ECONOMIC UPDATE ON THE NITRATE TO AMMONIA AND CERAMIC (NAC) PROCESS

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ABSTRACT

The Nitrate to Ammonia and Ceramic (NAC) process, which was developed several years ago at the Oak Ridge National Laboratory (ORNL), still remains relatively unknown. This is despite its simplicity in converting nitrate or nitrite to ammonia gas at high efficiency while forming a very useful hydrated alumina-based solid that binds most metals and nonmetals. Two recent Department of Energy (DOE)-contracted total life-cycle cost analyses, related to treating nitrate-based wastes at Hanford, Savannah River, and Oak Ridge, have shown that the NAC technology is only one-third to one-fourth the cost of vitrification, electroreduction, steam reforming, and plasma arc.

I. INTRODUCTION

Sodium nitrate-based wastes are common to many DOE facilities throughout the United States. Facilities exist at the Hanford, Washington, site; the Savannah River site; Melton Valley Storage Tanks at ORNL; and the Pad A Waste at Idaho Falls. The figures for 1984 indicate that more than 242,700 metric tons of nitrate wastes have been stored.

The nitrate anion in groundwater can pose a serious threat to the health of the public. For this reason, the Environmental Protection Agency (EPA) has set the nitrate concentration limit in drinking water at 44 ppm as nitrate, or 10 ppm as monatomic nitrogen (N).

II. NAC PROCESS PRINCIPLES

Aluminum is the third most abundant element in the earth's crust; only silicon and oxygen exceed its 8.1% abundance. Additionally, it is not found in a free form in nature as is the case for metals such as gold and silver. This reactivity occurs because the metal is not

thermodynamically stable in the presence of oxygen and quickly forms the oxide. The oxide coating, once formed, allows the aluminum to exist for a useful length of time in the earth's atmosphere.

In an aqueous medium, especially one that is distinctly alkaline, the protective oxide is sparingly soluble. Upon abrasion or partial solubilization of the oxide, the metal dissolves by reducing the hydrogen component of water to gaseous hydrogen or by reacting with some other reducible species that may be present, such as nitrate or nitrite.

The free energy change associated with the oxidation of aluminum (-378 kcal/g-mole) to its most stable, water-free oxide, alumina (Corundum), is quite large and exothermic. The thermodynamic driving force for aluminum metal to be oxidized or to function as a strong reductant is also evident by the fact that aluminum is present in nature as alumina, in bauxite ore.

The NAC nitrate reduction step is a type of electrochemical reaction that is related to the Hall-Herault process in which aluminum is produced today; that is, it is actually the latter process in reverse. Admittedly, a major difference is that it occurs in an alkaline, aqueous solution, rather than a water-free molten salt bath. In such an environment, the aluminum metal can be considered to function in a manner similar to that of a charged capacitor or battery, ready to release its energy during the reduction of nitrate to ammonia gas. Therefore, we have taken advantage of this source of stored electrons to reduce nitrate or nitrite ions to ammonia gas.

The addition of aluminum powder to a 50°C solution that is alkaline (pH >11.5) and contains ~4 to 6 M sodium nitrate produces a reaction that is associated with a rapid increase in temperature. During the early stage of the

reaction, the solution remains clear until following saturation, when a dense, white gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) begins to precipitate. The solids quickly settle to the bottom of the reactor, much like sand, after the mixer has been turned off.

As aluminum metal is added to an alkaline solution in the pH range of 12–14, the soluble aluminate anion predominates until, after a sufficiently large quantity of aluminum has been added, gibbsite precipitates. After the solution reaches this point, any further addition of aluminum metal causes the formation of highly insoluble gibbsite.

III. NAC PROCESS OPERATIONAL OVERVIEW

The alkaline, nitrate-based waste solution—in a closed and stirred reactor equipped with cooling coils to remove the heat of reaction—receives aluminum powders or ground aluminum scrap via an auger with weighing scale and totalizer. Addition of the aluminum to the reactor as larger particles reduces problems encountered with the fine, dry powder feed by preventing caking from water vapor condensation. The larger particles of aluminum also react more slowly than the fine powders and require less cooling and temperature control.

A. Experimental Conditions and Results

Experiments showed that aluminum can be pumped to the reactor as a slurry of aluminum powder and water, in addition to using a motorized auger. The water slurry feed has the advantage of adding needed water to the reactor to replace that taken up as the aluminum reacts to form crystalline gibbsite.

For 100% efficiency, 0.85 kg aluminum is required per kilogram of sodium nitrate treated.¹ When operating in the most efficient continuous mode in which solids are continually removed and filtrate is constantly returned to the reactor, ~99.5 % of the nitrate may be converted to ammonia gas. At steady state, it has been shown that a residual concentration of 1000 ppm nitrate remains in the system. If the amount of aluminum used is increased to 10% above theoretical, the steady-state concentration decreases to 50 ppm.²

The reactor requires a minimum temperature of 50°C to produce desirable kinetics but runs well in a wide range between 50 and 90°C. Reaction rates have been observed to typically be between 80 and 300 g NaNO_3 per liter of starting reactor volume per hour. Both the rate of addition

of aluminum and the rate of coolant flow through reactor coils are used to control the process.

In the reactor, the gibbsite precipitates constantly and exists in a solution of nearly saturated sodium aluminate. The aluminate anion removes most metals and nonmetals from solution, causing them to report to the insoluble gibbsite phase. The solid formed is very dense and sand-like—and consequently very easily filtered. The process does not form hydrogen gas until the concentration of nitrate falls too low. Even then, only 0.4 mole of hydrogen is formed per mole of sodium nitrate consumed. For this reason, a steady-state concentration of nitrate is maintained high enough to prevent any hydrogen formation.²⁻⁴

During the operation of the NAC reactor, one may add fine quartz powder as is used in making ceramics at the desired silica-to-alumina ratio such that the final solid may be pressed and fired to a ceramic. Ceramics with superior properties were produced as well as glasses from the reactor discharge.² The nepheline-glass ceramic formed with actual waste in the reactor showed that radioelements such as ^{85}Sr , ^{137}Cs , and ^{60}Co could not be detected in the American Nuclear Society (ANS) leach tests following the ANS 16.1 procedure. The ceramic product sintered well at 1200°C and produced a 70% volume reduction over the starting volume of a 4 M nitrate feed.^{2,5}

The ability to remove the reactor solids and make ceramics, glasses, or even hydraulic waste forms by the addition of phosphates to form aluminum phosphate-based waste forms makes the process a flexible one. Results of our work have consistently shown that the product exiting the reactor can be uniaxially pressed as any other ceramic to result in a 70% volume reduction based on the starting volume of the original 4 M waste solution. All the water associated with the waste solution is consumed by the aluminum to form hydrated oxide, requiring the addition of more water at times. The ammonia produced is far easier to handle than the NO_x produced during vitrification. The ammonia by-product can be handled in many different ways.

B. Utilization of Gaseous Ammonia

In laboratory tests the ammonia is scrubbed into dilute acid; however, this scrubbing option is only one of several that can be utilized for ammonia disposal or utilization. The following are a few possibilities that are "off-the-shelf" technologies:

- (1) The ammonia can be scrubbed into dilute acid to form ammonium salts.
- (2) The gas can be cooled and pressurized into liquid ammonia for reuse.
- (3) The ammonia can be burned in a heated, catalytic bed tower to form nitrogen and water vapor. (This is the preferred disposal scenario.)²
- (4) The ammonia can be reoxidized to form nitric acid for reuse on site.

IV. ECONOMIC LIFE-CYCLE COST COMPARISONS

The DOE contracted with Kapline Enterprises, Inc., (KEI) of Knoxville, Tennessee, to do both an independent technology comparison and a total life-cycle cost/benefit analysis of the NAC process technology.⁶ The result was a comprehensive comparison with vitrification and cement-based grouting of aqueous nitrate wastes at Hanford. The final document, available through the National Technical Information Services (NTIS), went far beyond its charter and provided a very thorough assessment of numerous technologies ranging from electroreduction to bionitrification with their respective shortcomings. The primary emphasis was upon life-cycle cost analysis of treating the vast quantities of Hanford nitrate-based waste, which average approximately 4.3 moles of nitrate per liter with a total mass, reported as sodium nitrate, of 2.2×10^8 kg.

The KEI life-cycle assessment assumed a plant that operated for 20 years, around the clock, with 60% availability. A Hanford feed throughput of 7.1 kg/h of waste solution was assumed and a treated volume of 600 million liters. Vitrification and grouting costs were extrapolated from comprehensive cost data presented in an EG&G report.⁷ During this cost analysis, KEI took into account disposal of the final waste forms (assuming Envirocare, shallow land, and engineered barrier), transportation costs, capital costs, operation and maintenance (O&M) costs, as well as off-gas treatment, which is substantial for NO_x , ranging from \$1000 to \$6000 per metric ton. Additionally, the ammonia off-gas produced from the NAC process and the aluminum required for the process were considered, providing a credit for DOE radioactively contaminated aluminum that was consumed in the NAC process.

The KEI life-cycle cost comparison between three types of final waste forms yielded costs of \$7 to \$9/kg NaNO_3 treated for the NAC technology, \$11/kg NaNO_3

for cement-based grouting, and \$30 to \$33/kg for vitrification. These figures are for final disposal at Envirocare (Utah). The KEI assessment stated that "NAC offers the most economical alternative to grouting, which does not truly solve the nitrate problem, it simply defers the problem to future generations." It was also concluded that "vitrification does not appear to be economical compared with NAC and grouting due to the high life-cycle cost," which is mostly due to high O&M costs.

A second, more recent economic assessment was performed by RCS Corporation of Aiken, South Carolina, for the Westinghouse Savannah River Company under a contract that was initiated in June 1997.⁸ This equally comprehensive report investigated complete life-cycle costs for a number of nitrate destruction technologies, including vitrification, NAC, electroreduction, steam reforming, plasma arc, and hydrothermal. Costs center around the construction and operation of a plant capable of 4 million gallons per year and a 6 M feed similar to Savannah River waste solution and operating over 25 years with 70% availability. The RCS independent evaluation took into account O&M costs, capital costs, permits, decontamination and decommissioning costs, and waste form disposal as well as off-gas treatment. The major O&M costs were independently estimated by RCS utilizing a Delphi approach and yielded cost figures even lower than a 1992 estimate prepared by ORNL's Central Engineering Organization, which yielded costs of \$2 to \$3/kg sodium nitrate treated.¹ The ORNL figures were based on a much lower aluminum use efficiency at that time when operating in a batch mode, while a continuous mode of operation would have decreased costs considerably. The RCS cost analysis produced a unit cost of \$0.37/kg sodium nitrate treated using the NAC technology with Savannah River waste solution.

Following a comparison of total life-cycle costs for the various technologies, the RCS report concluded that the NAC process had the most favorable economic technology. Vitrification life-cycle costs were found to be 2.8 times higher, while electrochemical reduction technologies developed at Savannah River Technology Center were 2.9 times higher; comparisons with plasma arc and steam reforming were also approximately 3 times higher. Since only nitrate treatment technologies were considered by RCS, grouting costs were not included for comparative purposes.

V. CONCLUSIONS

The NAC process has been proven to be a highly efficient chemical means for converting nitrate and nitrite

to ammonia gas at >98% efficiency while forming a solid product well suited for making a ceramic, glass, or a modified hydraulic waste form. Numerous economic cost analyses show that the technology is three times more economical than technologies such as vitrification and electroreduction while producing a more manageable ammonia gas by-product.

REFERENCES

1. A. J. Mattus, D. D. Lee, et al., *A Low-Temperature Process for the Denitration of Hanford Single-Shell Tank, Nitrate-Based Waste Utilizing the Nitrate to Ammonia and Ceramic (NAC) Process*, ORNL/TM-12245, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1993).
2. A. J. Mattus, D. D. Lee, et al., *A Low-Temperature Process for the Denitration of Hanford Single-Shell Tank, Nitrate-Based Waste Utilizing the Nitrate to Ammonia and Ceramic(NAC) or Nitrate to Ammonia and Glass (NAG) Process: Phase II Report*, ORNL/TM-12631, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1994).
3. A. J. Mattus, J. F. Walker, et al., *A Low-Temperature Process for the Denitration of Hanford Single-Shell Tank, Nitrate-Based Waste Utilizing the Nitrate to Ammonia and Ceramic (NAC) or Nitrate to Ammonia and Glass (NAG) Process: 1994 Summary Report for Bench-Scale Chemistry and Waste Forms*, ORNL/TM-12894, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1994).
4. A. J. Mattus, D. D. Lee, et al., "The Chemistry, Waste Form Development, and Properties of the Nitrate to Ammonia and Ceramic(NAC) Process," *Proc. Spectrum '94*, Atlanta, Georgia, August 14-18, 1994, p. 1286, American Nuclear Society, La Grange Park, Illinois (1994).
5. A. J. Mattus and D. D. Lee, "The Nitrate to Ammonia and Ceramic (NAC) Process—A Newly Developed Low-Temperature Technology," *Proc. Second International Mixed Waste Symposium*, Baltimore, Maryland, August 16-20, 1993.
6. Kapline Enterprises, Inc., Oak Ridge, Tennessee, *Aqueous Nitrate Waste Treatment: Technology Comparison, Cost/Benefit, and Market Analysis*, DOE/OR-2013, Prepared for the Department of Energy Office of Technology Development, January 1994.
7. F. Feizollahi and D. Shropshire, *Waste Management Facilities Cost Information for Mixed Low-Level Waste*, EGG-WM-10962, Idaho National Engineering Laboratory, March 1994.
8. M. Navetta, RCS Corporation, Aiken, South Carolina, *Evaluation of Nitrate and Nitrite Destruction/Separation Technologies*, Revision 0. Prepared for the Department of Energy, Westinghouse Savannah River Company, August 29, 1997.

M98001903



Report Number (14) ORNL/CP--95756
CONF-980905--

Publ. Date (11) 199805
Sponsor Code (18) DOE/ER, XF
UC Category (19) UC-400, DOE/ER

19980707 005

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