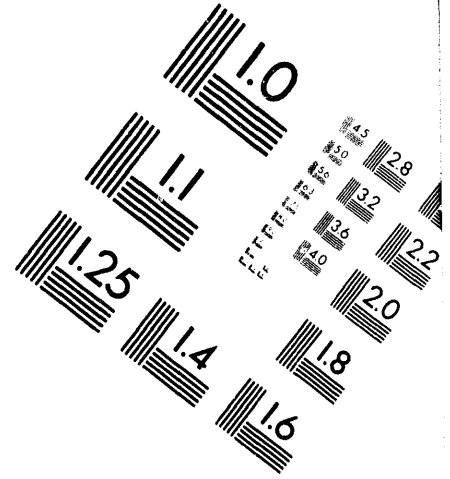
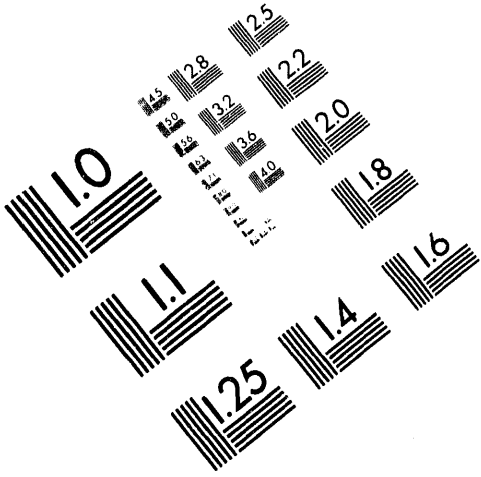




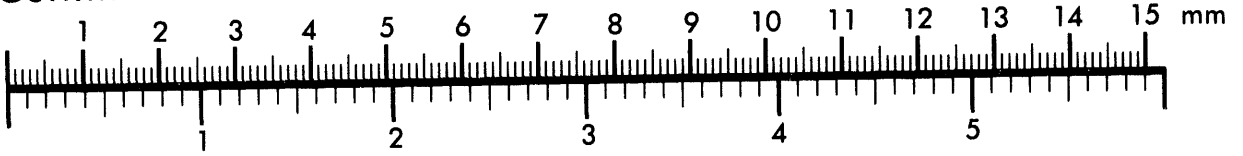
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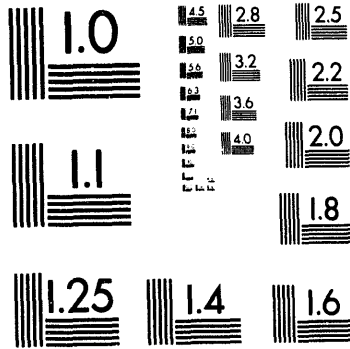
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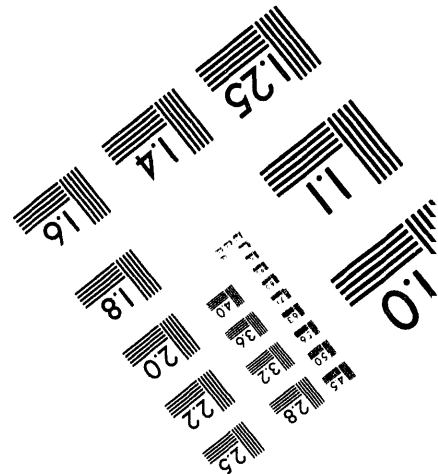
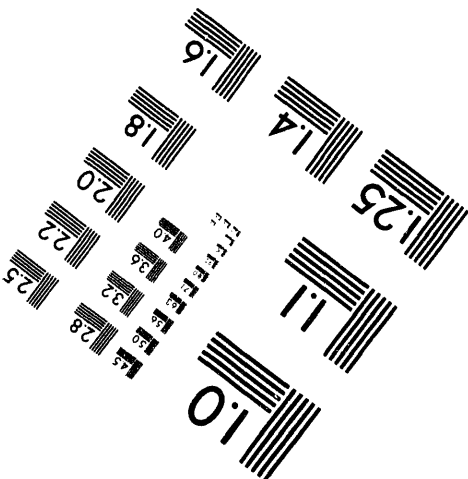
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## THE CHEMISTRY, WASTE FORM DEVELOPMENT, AND PROPERTIES OF THE NITRATE TO AMMONIA AND CERAMIC (NAC) PROCESS

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### ABSTRACT

A process for the conversion of alkaline, aqueous nitrate wastes to ammonia gas at low temperature, based upon the use of the active metal reductant aluminum, has been developed at the Oak Ridge National Laboratory (ORNL). The process is also well suited for the removal of low-level waste (LLW) radioelements and hazardous metals which report to the solid, alumina-based by-product. The chemistry of the interaction of aluminum powders with nitrate, and other waste stream metals is presented.

The by-product of the NAC reaction is insoluble, hydrated alumina (gibbsite). This by-product is combined with the proper ratio of silica in the form of 40-micron quartz and can then be thermally processed into either a glassy ceramic or high-alumina glass. The development of the final waste form is discussed, and the benefits of producing desired mineral phases are explained.

The chemistry of the process yields an added bonus in addition to converting nitrate to ammonia; that is, it also precipitates most cations from solution, forming "highly" insoluble aluminates. This ability of aluminate to form precipitates results in enhanced leaching resistance, comparable to glass. Leaching results using actual ORNL radioactive waste, and hazardous waste simulants are discussed including the NRC's ANS 16.1 leach test, and the EPA's

\* Managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under contract DE-AC05-84OR21400.

### Toxicity Characteristic Leaching Procedure (TCLP) test.<sup>1,2</sup>

Construction of a pilot-demonstration-scale system to prove the nitrate destruction portion of the Nitrate to Ammonia and Ceramic (NAC) process and product formation is under way. The reaction of nitrate-based solution with aluminum powder will occur in a single-stage, continuous-stirred-tank, back-mix reactor. The reactor will operate initially at 0.2 l/min but will be capable of operating at 1 l/min at between 50 to 70 °C.

### I. INTRODUCTION

The NAC technology is being developed in support of the Underground Storage Tank Integrated Demonstration (UST-ID) at DOE's Hanford site and is funded through the Office of Technology Development (OTD). The radioactive, nitrate-based supernates contained in 149 single-shell tanks (136 M L of liquid and sludge), and 28 double-shell tanks (95 M L of mostly liquid) may utilize the NAC technology.

Aluminum metal is not found in a metallic state on the surface of the earth even though it is the third most abundant element in the earth's crust. This is because aluminum is not thermodynamically stable in the presence of water and oxygen and is readily oxidized to alumina ( $Al_2O_3$ ) with a very favorable free energy change of -378 kcal/g-mole based upon the formation of corundum.

Because this metal is so readily oxidized (that is, functions as a reductant), it is a good source of stored energy in the form of three available electrons per gram-atom of aluminum. This energy is taken

advantage of in a number of processes, and for example is the major component in the solid fuel of the space shuttle in combination with ammonium perchlorate, and in thermite reactions for melting, or softening metals. The high energy density of this metal has even been studied for use in electric vehicles by Aluminum Company of America (ALCOA) in cooperation with Lawrence Livermore National Laboratory to power a vehicle for one year using only 0.2 m<sup>3</sup> of aluminum.<sup>3,4</sup>

Aluminum, like other metals such as zinc and magnesium, is capable of even reacting with water to form hydrogen gas and their respective metal oxides. Aluminum is slow to react at intermediate pH values (pH 5-8) but reacts quickly with the evolution of hydrogen and heat at both low pH (acid) and high pH (basic). In the intermediate pH regime, the dense protective oxide on the surface of aluminum protects it well, and as a result we are able to manufacture and use this metal in our daily lives.

Since nearly all Department of Energy nitrate-based wastes are stored as alkaline solutions to minimize corrosion concerns, they can be expected to react with aluminum powders or shot despite aluminum's protective oxide. As a result, upon adding aluminum powders to an alkaline (pH > 12.5) nitrate and nitrite-based waste in a stirred reactor we find that the aluminum quickly dissolves exothermically and preferentially reduces nitrate or nitrite to ammonia gas. The ammonia formed is not very soluble in the hot, saline, alkaline solution and is readily swept from the process reactor.

## II. CHEMISTRY OF THE NAC PROCESS

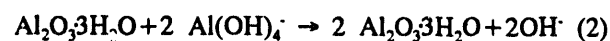
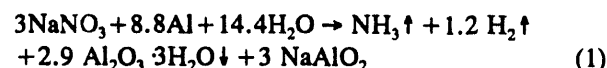
The NAC process utilizes the energy stored in the active metal aluminum to chemically reduce nitrate, and nitrite when present, in alkaline solutions to ammonia gas.<sup>5,6</sup> This reduction occurs at an efficiency of between 91 to 97 % based upon the formation of ammonia from nitrate, with efficiency primarily dependent upon the nitrate concentration. In solutions which are preferably at or above a pH of 12.5, the efficiency remains in this range until the concentration of nitrate is lowered to below approximately 5-10 g/L. Below this concentration range the efficiency begins to drop since the relative concentration of nitrate to that of water (~ 55 M) favors the metal reacting with the water to form hydrogen gas.

Equation 1 as written represents this reaction between aluminum and nitrate at 90 % efficiency

based upon the formation of ammonia and has been demonstrated to operate as high as 95-97 %. Based upon an efficiency of 90 %, aluminum consumption is 0.9 kg/ kg NaNO<sub>3</sub> converted. Presently, aluminum metal in the form of powders, in the size range of 0.1 to 1 mm are used. The metal can be added to the waste feed solution just prior to entering the stirred, back-mix reactor or directly to the reactor itself.

In the reaction, the solution in the reactor becomes saturated in aluminate (AlO<sub>2</sub><sup>-</sup>) upon adding enough aluminum, and an equilibrium is then established between the aluminate anion and continuously forming insoluble gibbsite. As depicted in reaction 2, the crystalline gibbsite (ΔG<sub>r</sub> = -555 kcal/g-mole) serves as a seed for driving the removal of this anion and releasing free hydroxide. Initially, amorphous gibbsite (ΔG<sub>r</sub> = -272 kcal/g-mole) forms but then ages to form more of the dense (2.4 g/cc) crystalline product. Both forms of gibbsite are extremely insoluble, with the crystalline form being less soluble than the freshly formed amorphous product; with solubility products at low ionic strength of 10<sup>-36</sup> and 10<sup>-33</sup>, respectively.

The hydroxide formed combines continuously with the newly formed aluminum III cation as the metal reacts, and in this way serves to moderate a too rapid rise in the free hydroxide concentration. Hydroxide is however formed when aluminum reacts with water which competes with nitrate and nitrite as an electron acceptor. Hydrogen production is not observed until the nitrate concentration drops to below 5-10 g/L, this fact can not be inferred from the overall reaction shown by equation 1 which implies that hydrogen is always co-produced.



crystalline + aluminate → amorphous + hydroxide  
gibbsite seed gibbsite

At pH's lower than approximately 7, aluminum speciation becomes exceeding complex, for many polymeric cationic forms co-exist, such as Al<sub>13</sub>(OH)<sub>34</sub><sup>+3</sup> and Al<sub>7</sub>(OH)<sub>17</sub><sup>+4</sup>, however at high pH such as employed here, the aluminate anion predominates. This predominance of the aluminate anion in saturated or supersaturated solution in the

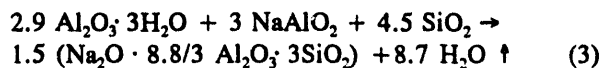
reactor allows it to precipitate most metals, and many radioelements.

## II. WASTE FORM DEVELOPMENT

The alumina-silica-based solid produced during the reaction has the versatility of being converted to either at glassy ceramic or high-alumina glass.

### A. Glassy Ceramic

The products from reaction 1 above, when combined with silica at a molar ratio of silicon to sodium of 1.5 : 1 can be processed into a glassy ceramic. The formation of this glassy ceramic from reaction 1 product can be represented by equation 3. Upon calcining and sintering, the nepheline-based ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) mineral phase formed in this reaction immobilizes otherwise mobile sodium, with 50 molar percent excess silica added than required to form this mineral phase.



Upon producing the ceramic, a 70 % volume reduction is obtained based upon the starting volume of a 4 M  $\text{NaNO}_3$  based waste feed solution. This favorable volume reduction compares with at least a 40-50 % volume increase if the nitrate-based aqueous waste were solidified in cement-based grout.

Ceramic product produced to date for laboratory testing has been found to densify well at approximately 1300 °C. The nepheline-based product can be classified as a glassy ceramic with a ceramic primary phase and a glassy grain boundary secondary phase.

### B. High-Alumina Glass

By the addition of more silica and a variety of fluxing agents such as: lime, magnesia, fluorite or oxides of boron it is possible to produce a glass from solids produced in the NAC process. Because the presence of alumina in glass tends to increase the viscosity, work is in progress to develop a flowable, high sodium, high alumina glass. Studies to investigate the potential to form a stable glass are currently in progress at ORNL using Hanford site surrogate waste solution.

## III. LEACHING CHARACTERISTICS

The amount of silica added to the solids centrifuged from the reactor slurry as shown in equation 3 is based upon the alkali metal content of the waste solution, which for the Hanford waste is primarily limited to sodium and potassium. Although the formula for the nepheline mineral is based upon one mole of silica per mole of sodium, sodium leaching experiments revealed that a 50 % molar excess of silica worked best.

Leach tests over 90 days in deionized water were used to evaluate the performance of various ratios of silica to sodium and aluminum use as well. The Nuclear Regulator Commissions ANS 16.1 leaching procedure was employed to generate effective diffusion coefficients and sodium fractional release from sintered glassy ceramic forms.

As shown in table 1 below, using the theoretical amount of aluminum to reduce nitrate, in combination with a molar ratio of silica to total sodium of 1.5 : 1 yielded the best results. Despite the fact that the glassy ceramic contained approximately 10 w/o Na, only 0.02 % leached over the 90 day duration of the ANS 16.1 test. This result corresponds to a normalized, effective diffusion coefficient of  $10^{-16}$   $\text{cm}^2/\text{s}$  or a leach index of 16 upon taking the negative logarithm. Based upon these results, 50 % excess silica is used above that theoretically required to form the nepheline mineral phase to aid in binding the sodium cation.

Table 1- Percentage sodium leached over 90 days.

| Si:Na | Aluminum Use Times Theoretical |       |
|-------|--------------------------------|-------|
|       | 1 X                            | 2 X   |
| 0.5:1 | 14.7                           | 12.09 |
| 1:1   | 0.28                           | 0.50  |
| 1.5:1 | 0.02                           | 0.05  |

Having established the desired ratio of silica to alkali sodium and the amount of aluminum to use in the reaction with nitrate it was of interest to see how well radioelements from our Melton Valley Storage Tank (MVST) waste would be bound in the glassy ceramic. The MVST waste comprises a transuranic sludge with a LLW supernate above, and is therefore similar to that of the Hanford wastes. The LLW supernate was denitrified utilizing the NAC process on the bench top and solids were dried and then

microwave sintered at 1300 °C to form glassy ceramic discs for leach testing in accordance with the ANS 16.1 method in deionized water.

The glassy ceramic waste forms produced were leached over 90 days in deionized water to study the release of radioelements <sup>85</sup>Sr, <sup>137</sup>Cs, <sup>60</sup>Co and <sup>65</sup>Zn. Despite lengthy counting times using gamma spectroscopy, results showed nondetectable concentrations of all radioelements over the 90 days, with the exception of <sup>137</sup>Cs. The cesium activity in the leachates was found to be just above background and required extended counting times using the Accuspec multi-channel analyzer employing an intrinsic germanium detector from Princeton Gammatech.

The leach tests were extended past the required 90 days to 240 days to further observe the <sup>137</sup>Cs leaching characteristics. The last leaching interval, between 30 days and 240 days yielded interval leach indices ranging between 14.2 to 15.5, with average interval indices ranging between 12.2 to 13.7 for the three replicates.

The leaching performance for cesium constantly improved with time over the 240 day duration of the leaching test. This is partly the result of a dependence upon matrix dissolution followed by diffusion of the mobile cesium cation into the leachate solution. This type of release mechanism and resulting performance is typical of glasses. Cesium release was also partially controlled by the solubility of the cesium-based nepheline phase which not only incorporates sodium and potassium but also the cesium cation as well.

The ability of the glassy ceramic to immobilize hazardous waste components, regulated by the EPA, is also of interest since the Hanford tank waste also includes some of these hazardous waste species. For this reason, surrogate solution containing enough of the hazardous species to permit a 100 g sample of product to contain enough hazardous metals to fail the test by two orders of magnitude were prepared for use. Two types of product were tested. Solids produced following denitration were oven dried and tested without conversion to a glassy ceramic form by calcination and sintering. In addition, calcined and sintered ceramic was prepared and crushed prior to use in the TCLP test. The results for both unsintered and sintered product are shown in table 2.

Table 2- TCLP leaching test results, ppm.

| Species | Limit | Unsintered | Sintered |
|---------|-------|------------|----------|
| Ag      | 5     | 0.59       | 0.017    |
| Ba      | 100   | 35         | 1.8      |
| Cd      | 1     | 0.067      | 0.010    |
| Cr      | 5     | 0.024      | 0.093    |
| Ni      | *     | *          | 0.047    |
| Pb      | 5     | 0.73       | 0.11     |
| Hg      | 0.2   | 0.32       | **       |
| Se      | 1     | 0.20       | **       |
| As      | 5     | 0.44       | **       |

\* Expected future addition to TCLP test

\*\*Not present due to expected volatility

As table 2 data show both unsintered and sintered solids passed the TCLP test. The fact that such metals are readily bound in the solid phase, in a very insoluble form, is a consequence of having saturated or supersaturated aluminate in the NAC reactor. In the presence of aluminate, most metal cations form spinels of the general form M(II) M<sub>2</sub>(III)O<sub>4</sub>, where M represents metal. In nature, well known forms such as ZnAl<sub>2</sub>O<sub>4</sub>, MgAl<sub>2</sub>O<sub>4</sub>, or even [Fe(II)(Mg)]Cr<sub>2</sub>(III)O<sub>4</sub> (chromite) exist where chromium takes the place of aluminum which is germane to the NAC chemical system.<sup>7</sup>

Such spinels are so inert that they are insoluble in boiling mineral acids as well as even hydrofluoric acid. The alkali spinels such as sodium or potassium aluminate are quite soluble in contrast to insoluble alkaline earths such as magnesium or calcium aluminate. Magnesium aluminate is so chemically and thermally stable that it is employed in the manufacturing of crucibles. The aluminates of calcium, barium and magnesium are voluminous and thermally inert up to temperatures as high as 2000 °C. For this reason, it is preferred to process alkaline wastes which contain a minimum of soluble alkaline earth cations. Maintenance of a waste feed solution pH of 12.5 or higher ensures that little calcium or magnesium remains in solution. The upper concentration limit for the alkaline earths in the feed has not yet been established or the potential for problems during sintering when forming glassy ceramics.

#### IV. PILOT PLANT DEMONSTRATION

The design of the equipment for a pilot demonstration of the nitrate destruction portion of the NAC process has been initiated. A schematic diagram of the proposed pilot facility is presented in figure 1. The reaction will take place in a single-stage, stirred, backmix reactor. Crystalline silica powder (quartz) will be added to the reactor or in the waste solution feed. Aluminum powders, obtained commercially or from contaminated, shredded aluminum scrap will be injected under pressure into the reactor. A continuous centrifuge and recycle system will be used for removing the solid reaction products (gibbsite, silica and sodium aluminate) from the recycle stream. The reactor will be cooled by circulating slurry from the reactor through a heat exchanger. The ammonia offgas generated will be scrubbed into dilute sulfuric acid to form ammonium sulfate salt, but may also be catalytically oxidized to nitrogen and water vapor as shown in figure 1.

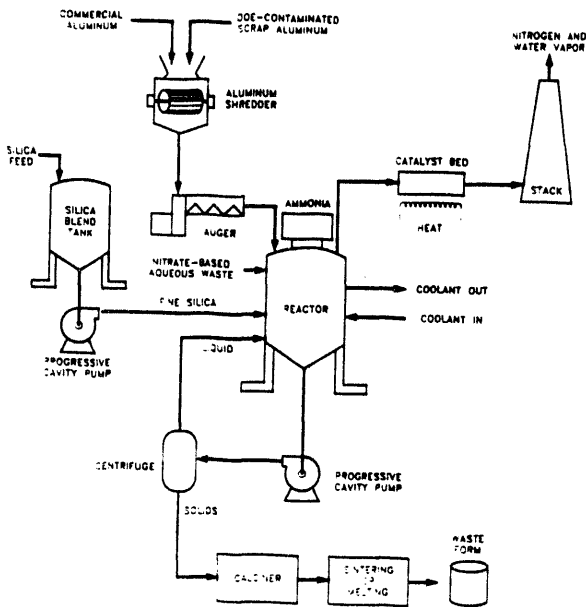


Figure 1- General schematic drawing of the NAC pilot process.

The initial design for the pilot plant is based upon processing a 3.1 molar nitrate feed at 0.2 L/min, but is capable of processing up to 1 L/min. Solids removed from the centrifuge will be converted to glassy ceramic and/or high alumina glass for laboratory testing.

#### ACKNOWLEDGMENTS

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Development.

#### REFERENCES

1. American Nuclear Society, Measurement of the Leachability of Solidified Low-Level Radiactive Wastes, Method ANS 16.1, (1981).
2. Toxicity Characteristic Leaching Procedure, Federal Register, 51 (114), June 13, (1986).
3. Development and Demonstration of Process and Components for the Control of Aluminum-Air-Battery Electrolyte Composition Through the Precipitation of Aluminum Trihydroxide, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-15503, May 11, (1982).
4. Maimoni, A., Crystallization of Aluminum Hydroxide in the Aluminum-Air Battery: Literature Review, Crystallizer Design, and Results of Integrated System Tests, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53843, March 31, (1988).
5. Mattus, A.J. and Lee, D.D., The Nitrate to Ammonia and Ceramic (NAC) Process- A Newly Developed Low-Temperature Technology, Proceedings of the Second International Mixed Waste Symposium, Baltimore, MD, August 16-20, (1993).
6. Mattus, A.J., "Process for Reducing Aqueous Nitrate to Ammonia", US Patent 5,266,174, Nov.30, (1993).
7. Ryshkewitch, Eugene, Oxide Ceramics-Physical Chemistry and Technology, Academic Press, New York, pp 257-264 (1960).



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