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THE AMMONOALUNITE PROCESS FOR PRODUCTION OF ALUMINA FROM CLAY

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The ammonoalunite process begins with two-stage sulfuric acid leaching of calcined kaolinitic clay. The clarified aluminum sulfate liquor is subjected to modest temperature autoclaving in the presence of ammonium ions to precipitate the ammonium analog of alunite, $NH_4Al_3(SO_4)_2(OH)_6$, in a hydrolysis reaction regenerating most of the acid needed in the leach. This acid liquor is recycled while the filtered ammonoalunite is thermally decomposed to alumina. Decomposition gases are scrubbed to recover ammonia and the remaining acid needed for leaching. Experimental results on precipitation parameters, thermal decomposition, energy consumption, and impurity control are given.

Introduction

The shortage of bauxite in the United States has led to several efforts to develop processes for utilizing kaolinitic clays to extract alumina suitable for Hall-Heroult reduction cells. These clays are plentiful in central Georgia, well located with respect to several U.S. reduction plants, and contain alumina concentrations similar to lower grade bauxites.

The various clay processes nearly always begin with calcination to meta-kaolin, which makes the clay more leachable. This is followed by leaching in either sulfuric, hydrochloric, or nitric acid. Precipitation of an intermediate compound usually follows, which is then calcined or otherwise thermally treated to generate alumina.

From leaching considerations alone, a sulfuric acid process is preferred over the other acids because of its lower reagent cost and reduced corrosion. However, sulfuric acid processes have encountered difficulties and high costs associated with recovery of alumina from the pregnant liquor and the regeneration of sulfuric acid for recycle to leaching.

This paper describes a new clay-alumina process based on sulfuric acid leaching. The novelty in the process lies in the precipitation of a new intermediate compound, ammonoalunite, which is subsequently calcined to alumina. The benefits of the process, compared with other sulfuric acid processes, are low energy consumption and immediate regeneration of most of the sulfuric acid during the hydrolysis reaction to produce ammonoalunite. The remaining sulfate and ammonia associated with the precipitate are emitted as gases during its calcination and are scrubbed for recycle to leaching. The process will be described along with its advantages and some of the difficulties with the process in its present, early stage of development.

Process Chemistry

At the outset, it is worthwhile reviewing some aspects of the chemistry involved with precipitation of aluminum compounds from sulfate liquors. Alum, $Al_2(SO_4)_3 \cdot 18H_2O$, can be precipitated from saturated hot solutions of aluminum sulfate on cooling or by evaporation of the water. The yield of alum on cooling is low and the resulting product contains a vast amount of chemically bound water. Consequently, calcination of this product requires large amounts of energy.

Neutralization of aluminum sulfate solutions to precipitate alumina does not permit the regeneration of the sulfate into sulfuric acid for recycle; hence, large amounts of sulfuric acid are wasted and this leads to an uneconomic process.

Heating aluminum sulfate solutions in an autoclave at sufficiently high temperatures can lead to the precipitation of basic aluminum sulfate, $(H_3O)Al_3(OH)_6(SO_4)_2$, but the yield at reasonable temperatures and operating pressures is low, leading to undesirable energy requirements and capital costs for autoclaves. In short, all of these approaches to the recovery of aluminum from aluminum sulfate solutions lead to uneconomic processes in competition with the Bayer Process or even with the best hydrochloric acid approaches to recovery of alumina from kaolin.

A better intermediate product is required--one that can be obtained in high yield from aluminum sulfate solutions with modest energy require-

ments, and one that contains very little water of hydration to minimize the subsequent energy consumption in calcination to alumina. It is mandatory that the process permit the recovery of sulfuric acid for recycle with minimum sulfate losses.

Hydrothermal processing of aluminum sulfate solutions requires considerable temperature and produces basic aluminum sulfate as already mentioned. If alkali metals are present in solution, the hydrolysis can occur at much lower temperatures to obtain the same yield. In the presence of potassium, the natural mineral alunite, $KAl_3(OH)_6(SO_4)_2$, results, while in the presence of sodium, natroalunite, $NaAl_3(OH)_6(SO_4)_2$, results. These processes occur so easily at modest temperatures that acid weathering of rocks commonly leads to the production of these minerals in nature. On the other hand, the difficult conditions for basic aluminum sulfate, which can be thought of as hydronium or hydrogen alunite, are rarely realized in nature. The use of alkali metals to produce various alunites cannot lead to commercial success because the alkali metal oxide is retained with the solid on calcination and provides gross contamination of the alumina product.

However, if ammonium ion is used, the result of hydrolysis is the ammonium analog of alunite, ammonoalunite, $NH_4Al_3(OH)_6(SO_4)_2$. This compound is not found in nature but it is easily crystallized in the laboratory under temperature conditions much milder than required to produce basic aluminum sulfate. The advantage of ammonoalunite is that the ammonium ion is released as a gas on calcination, which can be recovered by scrubbing and recycled. The ammonium ion is reused and is not a contaminant in the final alumina product.

Process Flowsheet

The ammonoalunite process flowsheet shown in Figure 1 consists of the following steps:

1. Leaching of calcined kaolin clay in the presence of recycled ammonium ion and sulfuric acid. Excess clay is used to neutralize acid and suppress iron solubilization.

2. Solid-liquid separation of the leach residue.

3. Hydrothermal precipitation of ammonoalunite in an autoclave train with concurrent regeneration of sulfuric acid.

4. Solid-liquid separation of ammonoalunite and recycle of the spent liquor to clay leaching.

5. Thermal decomposition of ammonoalunite crystals to gaseous ammonia, water, oxides of sulfur and solid alumina, with scrubbing of the gases by dilute clay-liquor slurry.

6. Purification of the calcined alumina product by a sulfuric acid wash, primarily to remove traces of phosphorus.

The ammonoalunite precipitation occurs with good yield at 150-250°C. Two-thirds of the sulfuric acid consumed in leaching aluminum is recovered in the ammonoalunite precipitation while one-third is recovered from thermal decomposition and scrubbing. Since both sulfuric acid and ammonia are

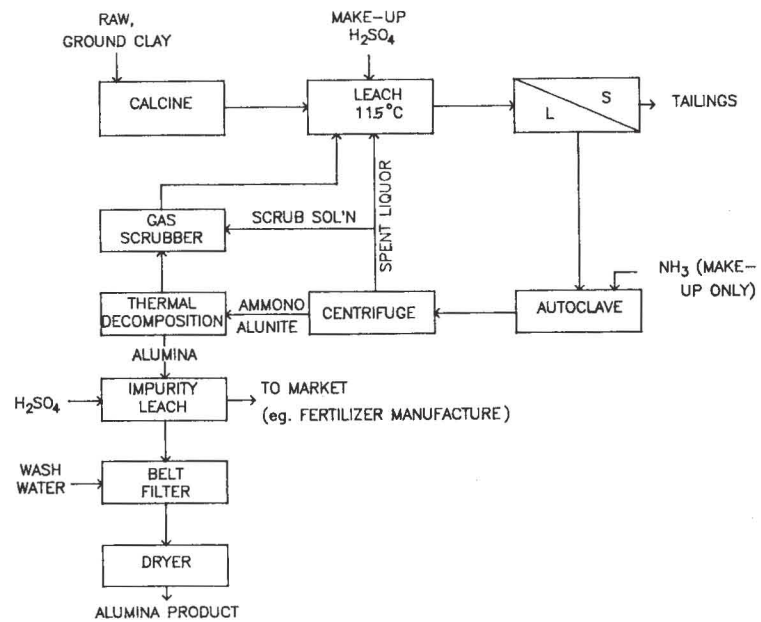

Figure 1 - FLOWSHEET FOR AMMONOALUNITE PROCESS

regenerated and recycled, purchased reagents are required only to make up entrainment losses. Simplified descriptions of the key chemical steps follow:

o Leaching

$$9H_2SO_4 + 3Al_2O_3 \cdot 2SiO_2 \longrightarrow 3Al_2(SO_4)_3 + 9H_2O + 6SiO_2 \quad (1)$$

o Hydrolysis (Ammonoalunite Precipitation and Acid Regeneration)

$$12H_2O + 3Al_2(SO_4)_3 + (NH_4)_2SO_4 \longrightarrow 2NH_4Al_3(OH)_6(SO_4)_2 + 6H_2SO_4 \quad (2)$$

o Ammonoalunite Decomposition

$$2NH_4Al_3(OH)_6(SO_4)_2 \xrightarrow{heat} 3Al_2O_3 + 2NH_3 + 7H_2O + 4SO_3 \quad (3)$$

o Gas Scrubbing and Recovery of Ammonia and SO_3

$$2NH_3 + 4SO_3 + 7H_2O \longrightarrow (NH_4)_2SO_4 + 3H_2SO_4 + 3H_2O \quad (4)$$

The major advantages of the ammonoalunite process are:

1. The ammonoalunite process requires lower autoclave temperatures and gives a much higher yield than the basic aluminum sulfate process.

2. The ammonoalunite, when thermally decomposed, releases ammonia and sulfur oxides as recoverable gases, whereas sodium and potassium alunite, when thermally decomposed, leave the alkali metal sulfate in the alumina product.

3. Ammonoalunite requires less energy to decompose than the various aluminum sulfate solids produced in other sulfuric acid processes. This is because aluminum sulfate solutions when crystallized form various hydrated alum compounds with much bound water such as:

$Al_2(SO_4)_3 \cdot 18H_2O$ (alum)

$NH_4Al(SO_4)_2 \cdot 12H_2O$ (ammonium alum)

$KAl(SO_4)_2 \cdot 12H_2O$ (potassium alum)

Experimental Ammonoalunite Precipitation Yields

Batch precipitation experiments were conducted in a Parr pressure reactor initially using synthetic solutions simulating leach liquor at pH about 2.5 and containing 30 gpl Al_2O_3. These liquors contained dissolved impurity concentrations at the following levels: 0.1 gpl Na_2O, 0.075 gpl K_2O, and 0.3 gpl P_2O_5. Subsequent experiments were conducted with natural calcined clay leach solutions in which iron control was a particularly important factor that will be discussed later.

The study of ammonoalunite precipitation focused on the effect of three variables: ammonia concentration, autoclave temperature, and reaction time. These variables determine the yield that can be obtained at reasonable industrial operating conditions. No excess sulfuric acid was used in the initial experiments because it is necessary to control dissolved iron in the leach by equilibrating the pregnant liquor with an excess of calcined clay.

The ammonia concentration in the autoclave feed solutions was varied relative to the alumina concentration. Molar concentration ratios of zero to three moles of ammonia per mole of dissolved alumina were tested and these results are presented in Figure 2. The purpose in varying ammonia concentration was to see if high molar ratios of NH_3:Al_2O_3 would drive the hydrolysis reaction to the right, increasing the ammonoalunite yield.

The autoclave temperature was examined to determine if reasonable industrial operating temperatures and pressures could be used to precipitate ammonoalunite. Temperatures were varied from 125-250°C. At these temperatures the pressures varied from 35-575 psia. The results of this test work are summarized in Figure 3. Note that potassium is more selectively precipitated than aluminum and that sodium and phosphorus are also precipitated. These are coprecipitated with ammonoalunite. Hydrolysis reaction time was also examined to determine if reasonably sized reactors could be used to precipitate ammonoalunite. The time was varied from one-half to three hours (Figure 4).

Figure 2 shows that as the concentration of ammonia increases, relative to the dissolved alumina concentration in the autoclave feed solution, the percentage of ammonoalunite precipitation increases. An ammonia-to-alumina molar concentration ratio of 3:1 precipitated 90% of alumina as ammonoalunite in this 200°C experiment. At the stoichiometric molar concentration ratio of 0.6:1, only 55% of the alumina contained in the feed precipitates as ammonoalunite at 200°C.

With an increasing ammonia/alumina concentration ratio, the solubility of ammonium alum decreases and ammonium alum may crystallize according to the following reaction:

$$(NH_4)_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow 2NH_4Al(SO_4)_2 \cdot 12H_2O \quad (5)$$

Ammonium alum crystallized from a solution prior to autoclaving would result in an alumina loss. To prevent crystallization of ammonium alum, the solution must be kept hot. Figure 5 shows the solubility of ammonium alum as a function of temperature for solutions with a molar NH_3:Al_2O_3 ratio of 2:1.

Autoclaving temperature is an important variable in ammonoalunite precipitation. The higher the autoclave temperature, the higher the percentage of precipitation. Figure 3 shows that 95% of the alumina contained in the solution can be precipitated at 250°C. Both the temperature and pressure are reasonable for an industrial process. However, it may be more cost-effective to use lower autoclaving temperatures and a lower NH_3:Al_2O_3 ratio and accept a recovery of Al_2O_3 as ammonoalunite significantly lower than 95% of the dissolved Al_2O_3 in the leach liquor. Because the spent liquor is recycled to the leach, all soluble Al_2O_3 not entrained with tailings will eventually be recovered in the precipitation autoclave.

The precipitation yield at various retention times presented in Figure 4 shows that the hydrolysis reaction is very rapid. At 200°C, 81% of the ammonoalunite precipitated within one-half hour. Only 83% had precipitated by the end of three hours. Hence, one-half hour residence time is adequate and further experiments may indicate a shorter residence time.

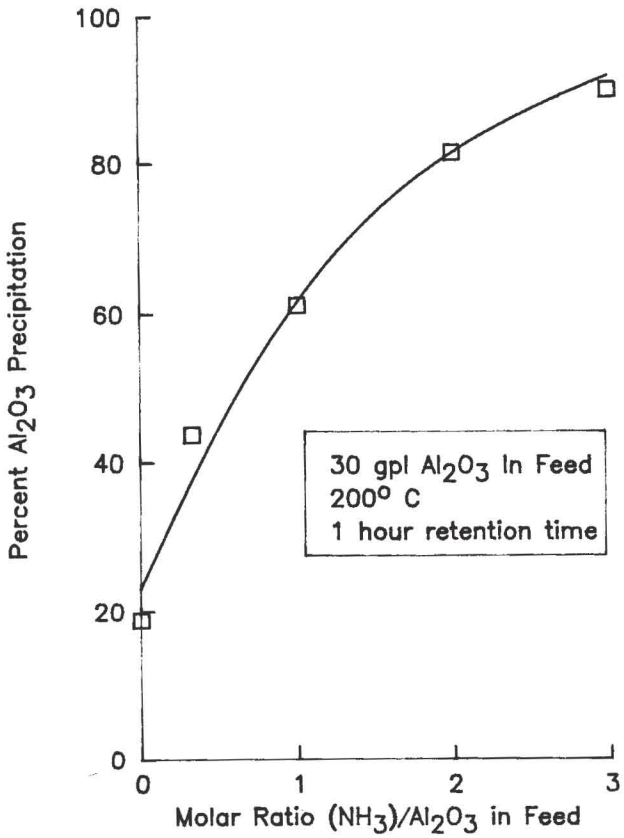

FIGURE 2 – NH_3 CONCENTRATION VS PERCENT PRECIPITATION

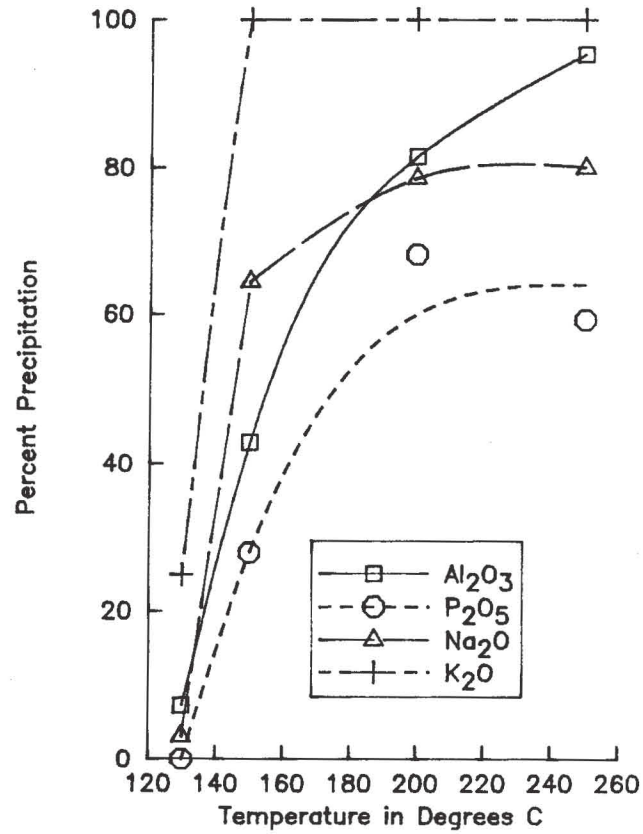

FIGURE 3 – PERCENT PRECIPITATION VS TEMPERATURE

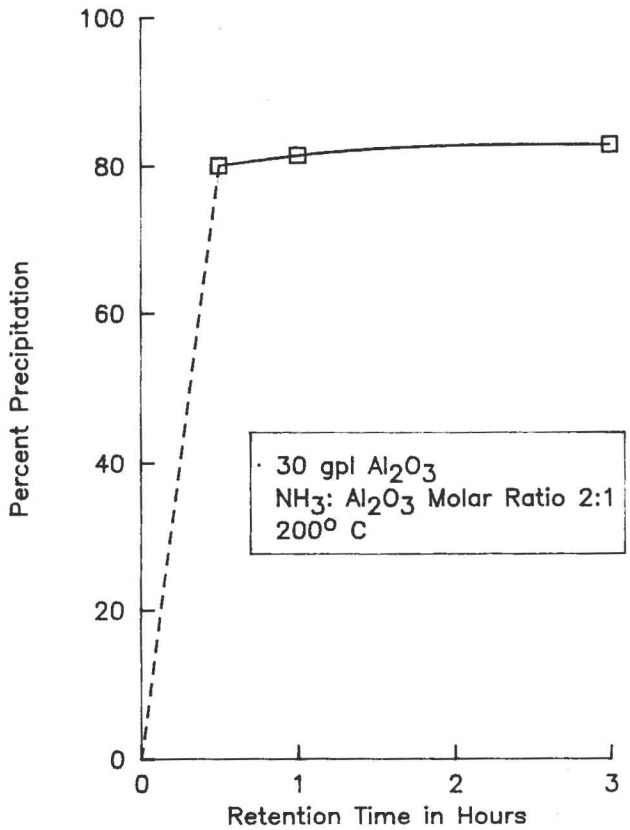

FIGURE 4 — PERCENT PERCIPITATION VS TIME

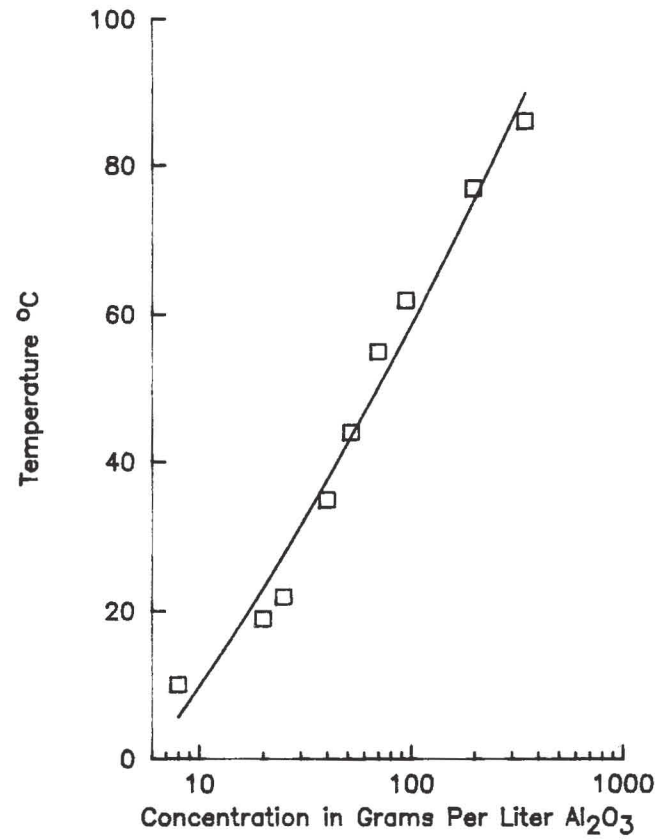

FIGURE 5 — SOLUBILITY OF $NH_4Al(SO_4)_2$ VS TEMPERATURE

Impurity Control

Phosphorus

The impurity concentrations used in making up the synthetic leach liquors used for the autoclave precipitation experiments were derived from an analysis of the feed clay and from extraction efficiencies obtained in prior laboratory work on sulfuric acid leaching of calcinced clay. Current Hall cell specifications (.001% P_2O_5) require removing only 90% of the P_2O_5 in alumina from ammonoalunite. Three general methods of impurity removal were tested in the laboratory. These methods are (1) precipitation of impurities prior to hydrolysis of ammonoalunite, (2) removal of impurities by leaching the ammonoalunite precipitate, and (3) removal of impurities by acid washing the calcined alumina product. Initial work on impurity removal consisted of selectively precipitating potassium, sodium, and phosphorus at lower autoclave temperatures. In the formation of alunites, potassium alunite precipitates first; i.e., at the lowest temperature; then sodium alunite, ammonium alunite, and finally hydrogen alunite precipitate. Seventy-five to 80% of the potassium, 45-50% of the sodium, and 15-20% of the phosphorus could be precipitated at 140°C. But, at this temperature, 25% of the aluminum also precipitates. Because too much alumina was rejected with the impurities, this method of impurity removal was abandoned.

The next step was to look at leaching impurities from the ammonoalunite. Leaching the precipitate with hot water had no effect. A hot acid leach removed 9% of the alumina and only a small portion of the impurities.

Impurity removal from the alumina, after thermal decomposition of ammonoalunite, appeared to be the most promising method of impurity removal. A hot water wash (98°C) of the alumina calcined at 1200°C removed 80% of the P_2O_5 and 40% of the Na_2O and K_2O. When using sulfuric acid at two normal concentration and 98°C to wash the calcined alumina, 2% of the alumina and essentially all of the impurities were removed, meeting specifications. The hot sulfuric acid wash is the recommended purification step at the present stage of process development for control of phosphorus. It should be pointed out that levels of sodium and potassium in the calcined ammonoalunite derived from clay leaching are within specifications for cell grade alumina, and strictly speaking, no treatment to control these impurities is expected to be required for most Georgia kaolinitic clays.

At the present time, the major drawback of the sulfuric acid wash of calcine clay is that for this step to remove phosphorus to cell specification levels requires that the ammonoalunite be calcined at a finishing temperature of 1200°C. At this temperature the calcined product was 100% alpha alumina. Calcination at 1000°C would be needed to provide a product that satisfies the requirements of dry scrubbing of fluoride vapors in Hall-Heroult reduction cells using an alumina dry scrubbing process, which has become prevalent in the industry. When the ammonoalunite is calcined at this lower finishing temperature the subsequent sulfuric acid washing removed 40% of the phosphorus.

Iron

Following the synthetic solution studies, calcined kaolin was leached with sulfuric acid, both with and without ammonium ion being present. This was followed by autoclave precipitation of ammonoalunite. These studies showed that iron was a serious contaminant of the resulting alumina. Later experimental work has shown that most of the iron can be removed if the leach slurry is heated to 115°C in the presence of excess calcined kaolin after leaching in order to neutralize the excess acid and precipitate iron, presumably as ammonium jarosite, $(NH_4)_2Fe_6(OH)_{12}(SO_4)_4$, which is the analog of ammonoalunite, with iron substituting for aluminum. Experimental conditions were obtained where most of the aluminum remained soluble while the majority of the iron is precipitated. Although these experiments have not been optimized in terms of temperature, residence time, ammonium content of the liquor, and amount of excess clay used, the results show that alumina containing iron of less than .2% could be obtained by adding additional clay to the leach liquor and reheating the slurry to 115°C for five hours. Much shorter residence times can be used at higher temperatures if precipitation of some alumina is acceptable.

Ammonoalunite Thermal Decomposition

In order to be a competitive process, the decomposition step must recover ammonia and sulfuric acid. The instability of NH_3 above 450°C dictates that it be recovered at a lower temperature. Industrial calcination of the ammonoalunite should occur in a process in which the material is gradually heated by countercurrent hot gas flow and heat exchange for maximum efficiency. For example, this would occur on passing the material countercurrently through a rotary kiln. A thermogravimetric analysis was run with gradual heating to study the decomposition process. The results are shown in Figure 6.

Forty percent of the weight loss occurred between 300 and 500°C. This initial weight loss corresponds to ammonia and water being driven off. The remaining weight loss occurred between 500 and 1000°C, and corresponds to the emission of sulfur oxides.

Energy and Cost Considerations

Although the process is far from optimized, some preliminary process engineering calculations were made to indicate whether the process had potential for being commercially competitive, if the phosphorus impurity problem could be resolved. This also identified major cost areas. Direct costs are approximately distributed with mining 15-20%, fuel 50%, and all other process costs 30-35%. Fuel usage is very important and concentrated in three major areas: calcination of the clay, heating solutions for autoclave precipitation of the ammonoalunite, and thermal decomposition of the ammonoalunite. Energy requirements for the autoclave depend on the yield of ammonoalunite, $NH_4Al_3(SO_4)_2(OH)_6$, that is obtained in the autoclave, and this in turn depends on the autoclave temperature. Fuel consumption, not including fuel equivalent of electric power used in the process, is about 26 million Btu per ton of alumina product. Although this is a very approximate number at this stage of development, it is less than required for other clay processes.

Conclusions

A laboratory investigation of the ammonoalunite process concept leads to the following conclusions:

1. Ammonoalunite can be precipitated with high conversion efficiency (up to 95% of dissolved aluminum at reasonable process conditions for an

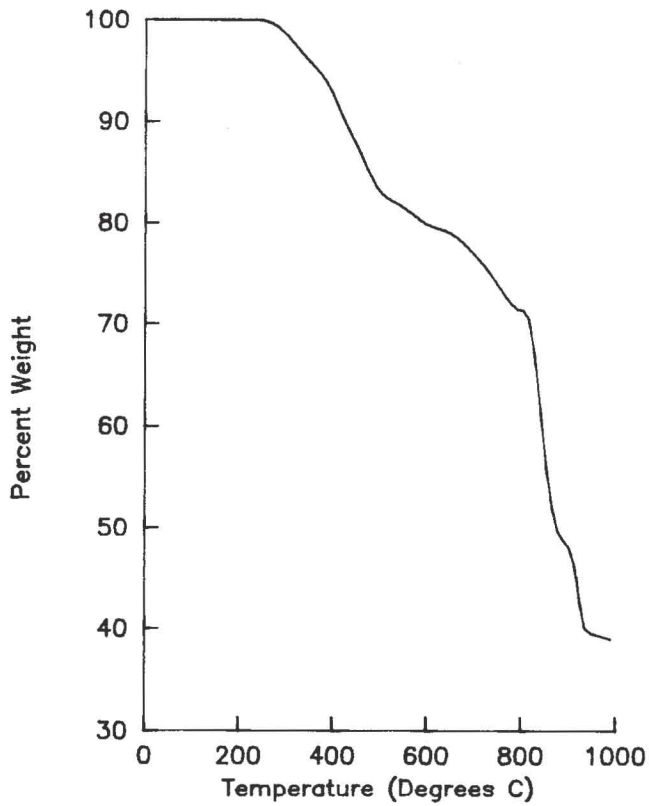

FIGURE 6 – THERMAL GRAVIMETRIC ANALYSIS DECOMPOSITION OF AMMONOALUNITE

industrial process). The optimum economic conditions may be at a somewhat lower yield and autoclave operating temperature.

2. Iron impurity levels can be adequately controlled by completing the leaching in an excess of calcined clay at a temperature of 115°C.

3. Two-thirds of the sulfuric acid needed is regenerated during the hydrolysis step and is easily recycled back to clay leaching. The remaining acid and ammonia associated with ammonoalunite crystals are recovered by scrubbing the ammonoalunite decomposition gas.

4. Sodium, potassium, and phosphorus can be removed from the product alumina to meet metallurgical specifications for Hall-Heroult cells by using a simple sulfuric acid wash of the calcined ammonoalunite (Al_2O_3). However, for this impurity removal to be sufficiently effective on phosphorus it is necessary that the alumina be calcined at a temperature where its BET surface area is not adequate to meet the specifications of fluoride dry scrubbing.

5. This process requires less energy and lower net reagent consumption when compared with other clay processes, but more energy than a modern Bayer plant with efficient heat recovery.

6. The process is less corrosive than clay processes based on hydrochloric acid or nitric acid.

7. The process does not appear at this stage to have any insurmountable environmental constraints; the slightly acidic silica tailings would have to be neutralized and impounded.