

Alumina Extraction from a Pennsylvania Diaspore Clay by an Ammonium Sulfate Process*

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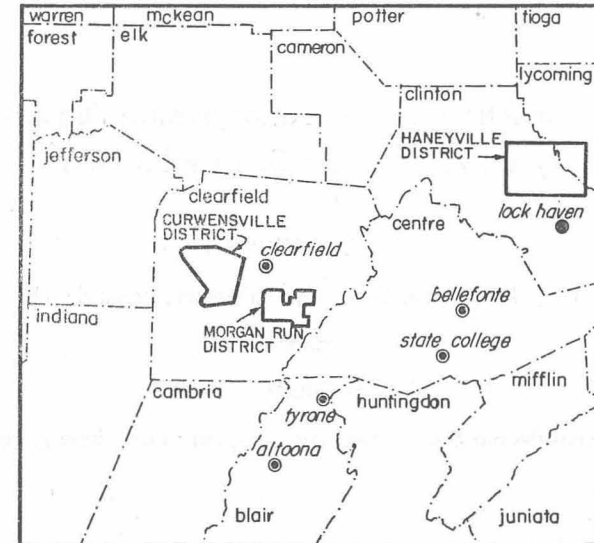


Fig. 1. Location of diaspore clays in central Pennsylvania (see ref. 3).

A method is proposed for the extraction of alumina from the minerals diaspore, kaolinite and boehmite, the major alumina minerals in Pennsylvania diaspore clay. The conditions required for optimum alumina extraction and minimum ammonium sulfate loss as determined for the alumina minerals are applied to a naturally occurring diaspore clay. The proposed flowsheet thus obtained is examined in its parts and such variables as particle size, ammonium sulfate to alumina mole ratio, roasting temperature, roasting time, heating rate, leaching conditions, and purification methods are discussed.

Introduction

Although the major portion of the aluminum produced today comes from alumina processed by the Bayer process, certain reasons warrant investigation of new source materials and new methods for processing these materials. Some of these reasons are as follows.

1. Aluminum is the most abundant metallic element in the earth's crust; therefore, it occurs in most rocks and minerals.

2. Bauxite, which is formed by lateritization, occurs mainly in hot humid climates; therefore, certain industrial nations are without a domestic supply.

3. Because certain nations lack a domestic supply of bauxite, there is the added cost of transportation and the fear of losing this supply during political upheavals and war.

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4. The constantly increasing demand for aluminum may lead to a scarcity of bauxite in the future.

5. Certain nonbauxite deposits may have an extremely high alumina content and yet be unsuitable for use in other industries.

The investigation discussed herein was prompted by the last of these reasons. It has been known for many years that a high-alumina diaspore clay occurs in Pennsylvania.^{3,5} The Pennsylvania diaspore clay occurs in three areas in central Pennsylvania as shown in Figure 1. The clay in these deposits is of three general types.⁵ One portion containing high alumina and less than 3% ferric oxide is suitable for use in the refractory industry. Another portion with 40 to 70% alumina and 5 to 25% ferric oxide content would be a potential feed for aluminum extraction and was used in this investigation. The third type is a high-iron flint clay containing 35 to 39% alumina and 3 to 25% ferric oxide.

Of all the aluminum-bearing rocks and minerals, the nonbauxite type most often investigated as a source of alumina has been clay. Due to their high-alumina content (20 to 70%) and widespread occurrence, clays have been investigated as a possible source of aluminum since the beginning of the aluminum industry in 1854.⁴ Clays, unlike bauxite, have a relatively high silica content which limits the use of the Bayer process for extracting their alumina. Generally other processes, either

acid or alkaline in nature, are considered, each having certain advantages and limitations. In alkaline processes, silica is a serious contaminant and usually the temperatures required for optimum alumina recoveries are higher than in acid processes. On the other hand, iron removal, which is a problem in the acid processes, gives little trouble in alkaline processes. Acid processes require specially constructed equipment.

During World War II, clays from the Pennsylvania high-alumina diaspore deposit near Clearfield were investigated for alumina extraction by the lime-soda method.³ The results were technically encouraging, but the costs made the method noncompetitive. The high temperatures required (1000–1250°C) and the need for desilicating the leach liquors greatly added to the costs.

The purpose of this investigation was to determine if the alumina in the Pennsylvania diaspore clay could be extracted by the ammonium sulfate process. In this process, clay and ammonium sulfate are mixed and fused to convert the alumina to a water-soluble double salt of ammonium sulfate and aluminum sulfate (ammonium alum). The alum thus formed is leached with a hot solution of dilute sulfuric acid and the alum is crystallized from the clarified liquor causing an initial purification. After further purification, alumina is precipitated by adding the alum crystals to an ammonium hydroxide solution made by passing the exhaust gases from the roasting reaction through water.

The acid ammonium sulfate process was accepted as offering a possibility for future commercial application for a number of reasons. The temperatures required for extraction were lower than in the alkaline processes. Iron, which was a serious contaminant, could be more easily removed than silica which interfered in the alkaline processes. Ammonium sulfate, which was recovered and recycled, is abundant at a moderately low cost as a coke furnace by-product.

Related Literature

Many early investigators attempted to produce a pure alumina by fusion with ammonium sulfate. As early as 1909, a U.S. patent was issued to Rinman⁹ in which he claimed that a water soluble alum could be produced by heating kaolin, feldspar, or bauxite with ammonium sulfate at 250–400°C. The alum was said to crystallize in a high degree of purity without filtering. In 1917 a Swedish patent was issued to Hultman⁶ which claimed to produce a crystalline alum by fusing clay and acid potassium or ammonium sulfate. A U.S. patent was issued to Whittington¹⁴ in 1925. This patent described a process in which bauxite or clay was heated with ammonium sulfate to temperatures of 525–560°C until

ammonia ceased to be given off. The aluminum sulfate was water soluble while the iron was said to convert to the insoluble oxide.

A semicommercial process, patented in the United States in 1924, using ammonium sulfate was developed in Germany by Buchner.² The first stage of this operation consisted of heating solid ammonium sulfate in a suitable vessel so that ammonia was driven off converting the sulfate to bisulfate. The ammonia was collected and used elsewhere in the process. Clay was treated with the fused bisulfate and a little water in a digester at temperatures around 200°C resulting in a slurry of ammonium aluminum sulfate, ammonium iron sulfate, and insoluble material. An excess of hot saturated solution of ammonium sulfate was added to this slurry which was then filtered. On cooling, the ammonium alum crystallized in a state of very high purity, while the iron salts remained in solution in the excess ammonium sulfate. Aluminum hydroxide was precipitated by adding the alum crystals to an ammonia solution containing two or three times the theoretical quantity of ammonia. The ammonia and ammonium sulfate were used cyclically.

In a later work, Seyfried¹¹ used a similar process for processing clays from the area around Castle Rock, Washington. Raw clay was roasted in a rotary kiln at 750°C and crushed. The calcined clay was then leached with molten ammonium bisulfate which was manufactured at the pilot plant. The temperature of the leach was 106°C or the boiling point of the slurry. Since ferrous iron did not interfere with alum crystallization, ammonium sulfite was added to the pregnant liquor before cooling to crystallize the alum. Crystallization recovered about 77% of the alumina present in the clay and approximately 8% remained in solution. Alumina was recovered by redissolving the alum crystals in a 50% aqueous ammonia solution. The ammonia and ammonium sulfate were again used cyclically.

St. Clair,¹² working with a clay from the western United States, preferred to roast the clay-ammonium sulfate mixture. The mixture was baked at temperatures between 360 and 400°C for 2 hr. Ammonia losses were said to be negligible in this temperature range, but at higher temperatures the ammonium sulfate decomposed. It was also found that particle size was important, especially for hard dense clays. The roasted product was leached at 70°C with water having a slight excess of ammonium sulfate, or in dilute sulfuric acid solutions to keep the resulting alum from hydrolyzing. The alum solutions formed were ideal for crystallization, since a saturated solution of ammonium alum contained 126 g of Al₂O₃ per 1000 g of water at 90°C and only 16.5 g of Al₂O₃ per 1000 g of water at 20°C. Aluminum hydroxide was precipitated with aqueous

ammonia produced from the gases evolved during baking. The ammonia and ammonium sulfate were used cyclically.

Raw Material

According to Foose,⁵ the high-alumina refractory clays of central Pennsylvania are all under-clays associated with carboniferous coal beds. The nodular or diaspore-bearing clays are limited to the Mercer horizon of the Pottsville series. The clays occur in lenticular masses which have a wide range of thickness.

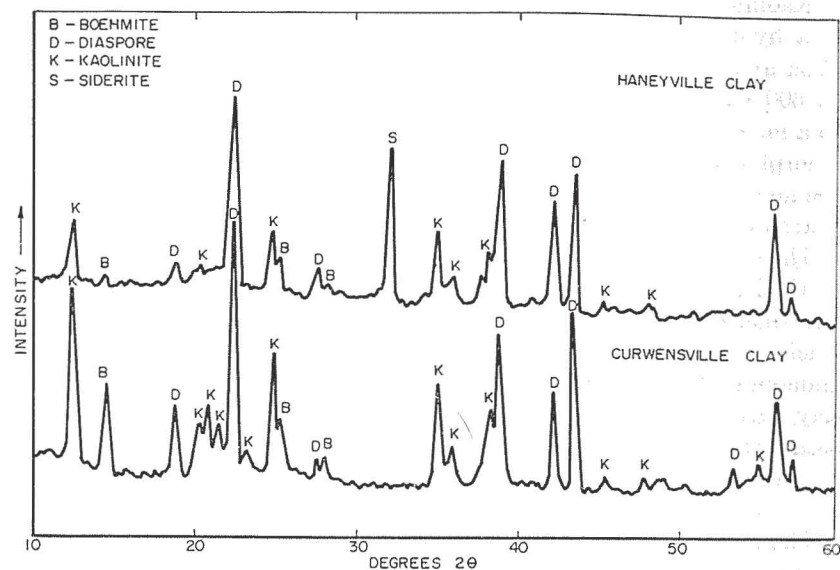


Fig. 2. X-ray diffraction patterns of some Pennsylvania high-alumina clays.

X-ray diffraction showed that the alumina is present as the minerals diaspore (β -alumina monohydrate), kaolinite, and boehmite (α -alumina monohydrate), as shown in Figure 2. Boehmite generally occurs in small amounts but some samples have been reported which analyze up to 15% boehmite.¹ The alumina content of these clays generally ranges from 40 to 70%. The particular samples used in this investigation were collected near Lock Haven, Pennsylvania, in the Haneyville district. Chemical analysis of this sample shows the following values (in %): SiO_2 , 13.59; Al_2O_3 , 56.13; Fe_2O_3 , 9.47; TiO_2 , 3.12; H_2O (105°C), 0.16; and loss on ignition 16.40.

The mineral proportions were estimated by use of x-ray diffraction to be about 75% diaspore, 20% kaolinite, and 5% boehmite.

The minerals diaspore and boehmite pose a special problem since on heating to dehydration they convert to insoluble species. According to Pask and Davies,⁸ the dehydration reaction for both these minerals takes place at about 550°C. Schwiersch,¹⁰ however, found that dehydration actually began at 340°C. On dehydration, diaspore converts to corundum while boehmite converts first to an amorphous species and then to γ -alumina. All of these species are relatively insoluble in sulfuric acid.

Kaolinite which is the only true clay mineral found in the clay deposit is a hydrated aluminum silicate with the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Pask and Davies⁸ found that the dehydration of kaolinite takes place at 600°C. Some workers feel that on dehydration kaolinite converts to a mixture of amorphous alumina and silica, while others feel that an amorphous compound known as metakaolinite is formed. At any rate the material formed by the dehydration of kaolinite is soluble in sulfuric acid as shown by Pask and Davies.⁸

The characteristics of the minerals contained in the clay dictated the method used for extracting the alumina. Since diaspore and boehmite and their dehydration products are insoluble, the method proposed by Buchner² in which the raw or calcined clay was extracted with molten ammonium bisulfate could not be used. In the present investigation, the clay was roasted with solid ammonium sulfate similar to the method used by St. Clair.¹²

Procedure

The raw clay was crushed and ground to minus 60 mesh. The ground clay was then mixed with solid ammonium sulfate in glass containers agitated by mixing rolls. After mixing, a small amount of water was added to the clay-ammonium sulfate mixture to insure binding, and the mixture was pelletized. Pelletizing was conducted with a Carver laboratory press using a stainless steel mold. The pellets were 3 cm in diameter and ranged between 4 and 4.5 cm in height which gave a pellet weighing between 45 and 50 g. The pellets were dried at 110°C for 12 hr and weighed before roasting. Using the total weight of the pellet, the percentage of alumina in the raw material, and the ammonium sulfate-alumina mole ratio in the pellet, the alumina and ammonium sulfate content of each pellet was calculated.

After the pellets were prepared, they were placed in hard-baked ceramic crucibles and roasted in a muffle furnace. The furnace was

brought to temperature and the pellet inserted. Temperatures were measured with a Chromel-Alumel thermocouple inserted in the roasting zone of the furnace. In certain tests in which a controlled heating rate was used, the pellets were placed in the cold furnace and the temperature was increased at a controlled rate. Duplicate samples were tested. When roasting was conducted in a controlled atmosphere, the pellet was crushed and the three-to-ten mesh particles were roasted. These were placed in a ceramic boat and were roasted in a tube furnace with gas flowing through the tube.

After roasting, the charge was air cooled, crushed and ground with a mortar and pestle. A small aliquot of the roasted product was taken for x-ray analysis. The remainder was stored in sealed glass containers prior to extraction. Extraction of the roasted product was conducted in a 500-ml three-neck distillation flask.

After extraction, the slurry was filtered while hot through a Buchner funnel using Schleicher and Schuell Blue Ribbon filter paper. The residue was washed several times with hot water. The filtrate was diluted to 500 ml and kept for alumina and sulfate analysis. Alumina was analyzed by an acid-base back-titration method using a centrifuge; sulfate was analyzed by the gravimetric barium sulfate method. The solids were kept for x-ray analysis.

Results and Discussion

The investigation was conducted in two phases. First, research was conducted to determine the proper conditions for the extraction of alumina from the minerals occurring in the clay. For this part of the investigation, the minerals diaspore, kaolinite, and boehmite were obtained in the purest form available. The diaspore used was a high-grade naturally occurring material from near Rosebud, Missouri. The kaolinite was a naturally occurring kaolin from Dry Branch, Georgia. The boehmite used was a synthetic product manufactured by the Aluminum Co. of America. The second phase of the investigation was the application of information gained in the first part to one of the Pennsylvania diaspore clays.

The results can be best discussed by presenting the proposed flow sheet, Figure 3, and elaborating on those portions which were found to be most important. Like most flow sheets it can be broken down into a number of stages for discussion. The stages are: (1) crushing and grinding; (2) mixing and pelletizing; (3) roasting; (4) leaching and primary crystallization; (5) alum purification; and (6) alumina precipitation, calcining, and ammonium sulfate crystallization.

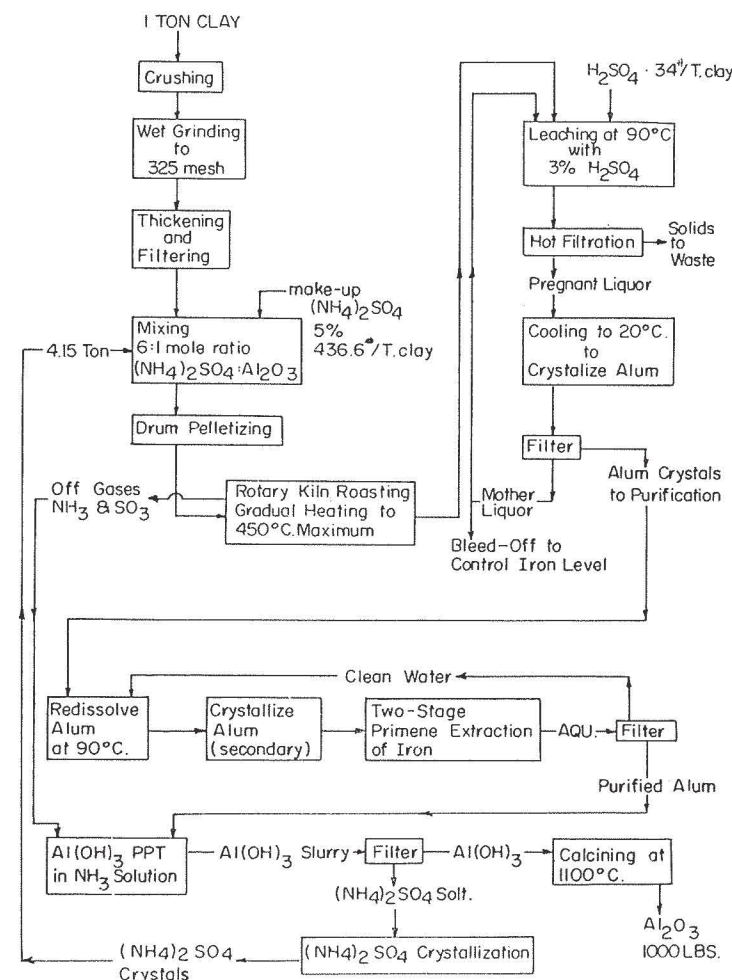


Fig. 3. Proposed flow sheet.

Crushing and Grinding

The equipment for the crushing and grinding stages would be similar to that used in existing plants that treat a product ground to a fine size such as the 325-mesh size required in this flow sheet. A primary and secondary crushing would definitely be necessary, and since the final size required is so fine, a tertiary crushing stage would not be unexpected.

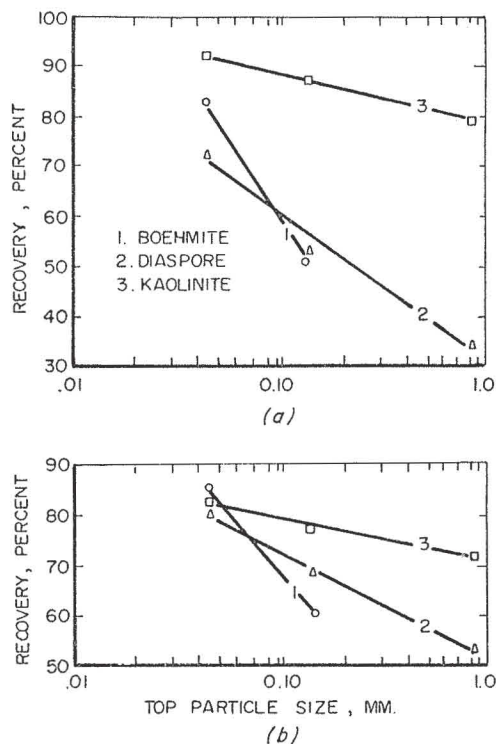


Fig. 4. Effect of particle size on (a) alumina and (b) ammonium sulfate recovery. Roasting at 450°C for 2 hr.

Grinding would be with a wet ball mill in closed circuit to insure the final size. A thickening and filtering stage would follow grinding.

Alumina extraction and ammonium sulfate recovery were found to be dependent on the particle size of the material as can be seen in Figure 4. The ammonium sulfate recovery curves presented in all the figures represent that portion of the ammonium sulfate which was recovered in the roast, and the loss was a combination of the actual loss through decomposition and some sublimation. The actual loss of ammonia, as determined by St. Clair,¹² varied from 0.14–1.48% from 200–400°C but increased rapidly to 3.90% at 450°C.

Both alumina and ammonium sulfate recovery increased proportionally with decreasing particle size of the alumina raw material. The rate of increase varied with the material and appeared to be dependent on the hardness of the material. As the hardness of the raw material

increased, the importance of grinding increased. The information presented in Figure 4 is for the alumina minerals; however, the Pennsylvania diasporite clay gave results similar to those for boehmite. The slope of the line was steeper than for the kaolinite or diasporite minerals.

Mixing and Pelletizing

The product from the filter of the grinding circuit would contain sufficient water to make a paste during the mixing stage. At this point recirculated and make-up ammonium sulfate would be added to the clay to make a mixture with 6 moles of ammonium sulfate for each mole of alumina. Make-up ammonium sulfate would amount to 5% of the total amount used. After mixing, the wet mixture would be fed to drum pelletizers.

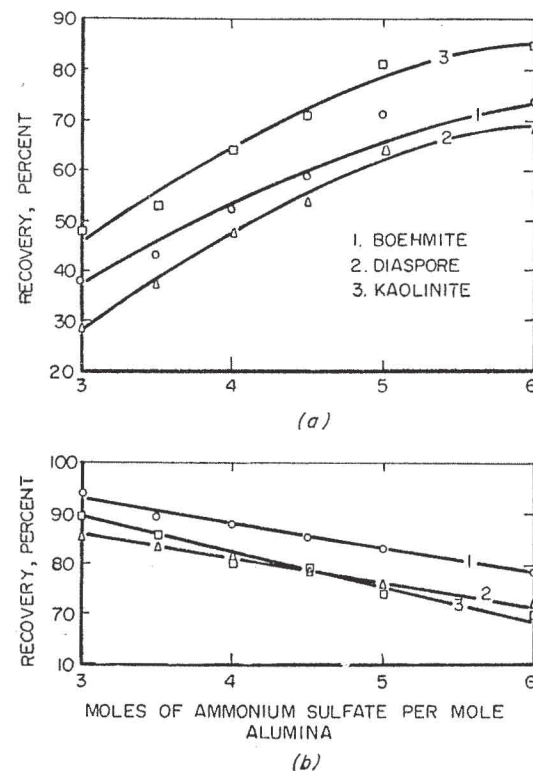
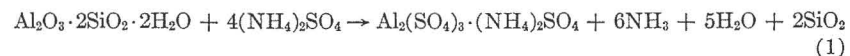
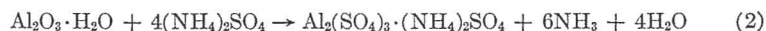


Fig. 5. Effect of the amount of ammonium sulfate on (a) alumina and (b) ammonium sulfate recovery. Roasting at 450°C for 2 hr.

The overall reaction between kaolinite and ammonium sulfate is as follows:



The reaction between ammonium sulfate and diaspore or boehmite would be:



Both reactions are endothermic. St. Clair¹² found the heat of reaction for eq. (1) to be 320,900 cal/mole of alumina at 25°C. According to these equations, 4 moles of ammonium sulfate are required for each mole of alumina in the raw material. Figure 5 shows that alumina recovery increases with an increased ammonium sulfate-alumina mole ratio and begins to level off only above a mole ratio of 5:1. This can be explained by the sublimation loss of ammonium sulfate. The amount of ammonium sulfate left in the roast is not sufficient to form the alum unless an excess is added before roasting.

When this information was applied to the Pennsylvania diaspore, an additional problem was present. The Pennsylvania diaspore contained much more iron than any of the minerals, and the double sulfate of iron and ammonia formed in preference to the alum. X-ray diffraction patterns of a roast containing an ammonium sulfate-alumina mole ratio of 5:1 indicated the major phase was the double sulfate of iron and ammonia. In addition, the leached residue of this roast contained considerable diaspore and kaolinite. When a mole ratio of 6:1 was used, there was sufficient ammonium sulfate present to react with both the iron and alumina plus the desired excess. X-ray examination of this roast showed the predominant phase to be desired alum. The leached residue was found to contain only traces of diaspore.

Testing indicated that pelletizing was relatively unimportant as far as alumina and ammonium sulfate recovery were concerned. However, since the clay would have to be ground to minus 325 mesh, it would be necessary to use pelletizing to prevent the loss of fines in the escaping gases. It is, therefore, proposed to use a drum pelletizer in the flow sheet following the mixing stage.

Roasting

Roasting would be conducted in a rotary kiln. Tests conducted using a flowing gas over the roasting charge indicated that the loss of ammonium sulfate was greatly increased causing a corresponding decrease in

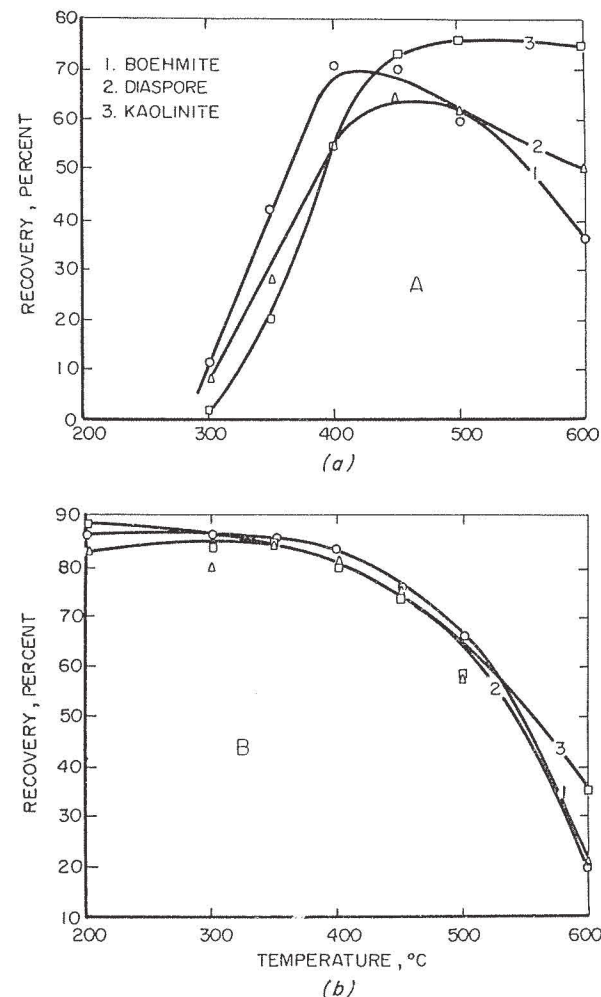


Fig. 6. Effect of roasting temperature on (a) alumina and (b) ammonium sulfate recovery. Roasting time, 2 hr.

alumina recovery. The possibility of using a fluidized-bed type of roaster was eliminated for this reason.

Figure 6 shows alumina and ammonium sulfate recovery as a function of roasting temperature. Both diaspore and boehmite exhibit a maximum alumina recovery. The decrease in recovery on heating above this temperature is caused by the formation of the insoluble species discussed

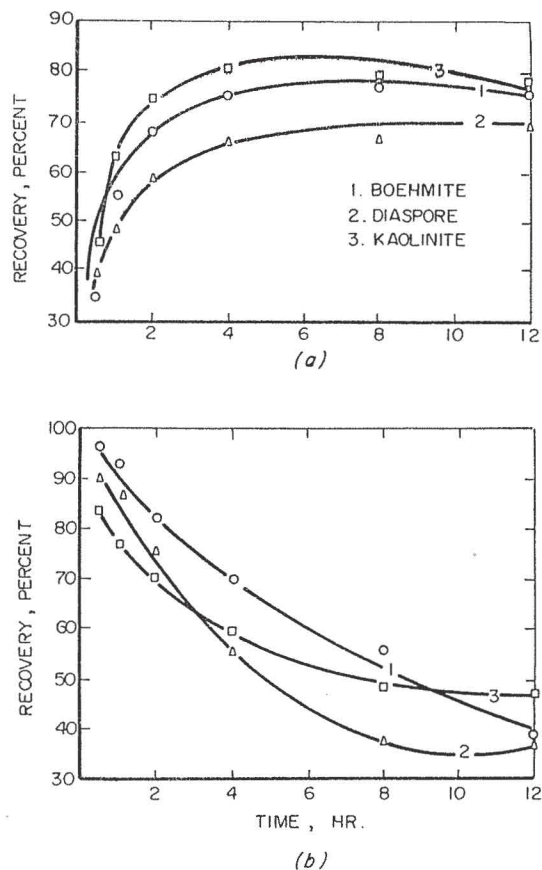


Fig. 7. Effect of roasting time on (a) alumina and (b) ammonium sulfate recovery. Roasting temperature 450°C for kaolinite and diasporite, 400°C for boehmite.

previously. X-ray diffraction patterns of the leach residue at each of these temperatures indicated the formation of corundum and γ -alumina at temperatures above 450°C. Alumina recovery from kaolinite levels off above 450°C but does not decrease as it does with the monohydrates. X-ray diffraction studies indicated the formation of alum at 300°C for kaolinite-ammonium sulfate mixtures, whereas the alum did not appear until 350°C for boehmite and diasporite roasts. Testing of the Pennsylvania diasporite clay indicated that 450°C was the best roasting temperature.

Figure 7 indicates that a roasting time of 4 hr was required to achieve maximum alumina recovery from the three minerals. As can be seen in

Figure 7b, ammonium sulfate recovery decreased in almost direct proportion with increasing time. X-ray diffraction studies of the roasted product indicated the decomposition of the alum to aluminum sulfate after roasting for more than 4 hr at 450°C.

In order to achieve optimum alumina recovery without excessive ammonium sulfate loss, it was proposed to roast the mixtures using a controlled heating rate. With this approach, the mixture could be

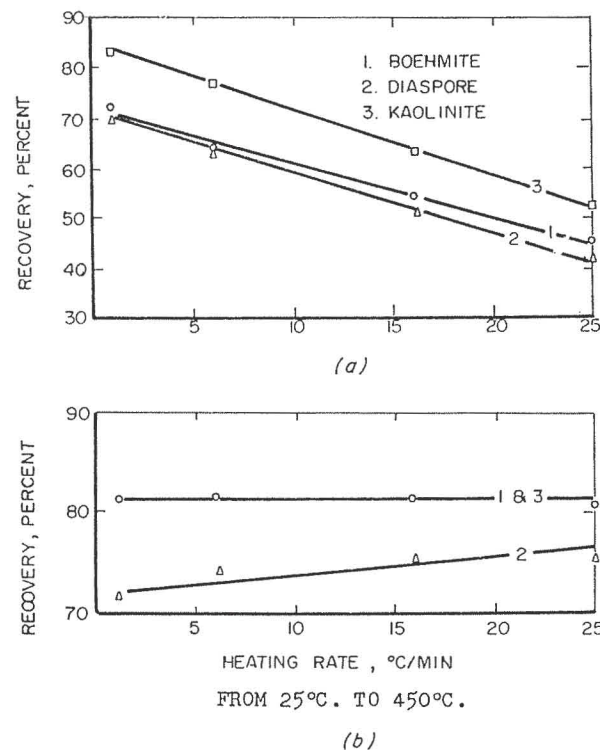


Fig. 8. Effect of heating rate on (a) alumina and (b) ammonium sulfate recovery.

roasted for the desired length of time without subjecting it to maximum temperature for the entire length of time. Figure 8 indicates that alumina recovery increased with a decreasing heating rate but more important is that ammonium sulfate recovery remained relatively independent of heating rate. Even at a heating rate of 1°C per minute, when the mixture was roasted for a total of 8 hr, ammonium sulfate recovery was the same as that obtained after roasting for 1 hr at 450°C.

After considering the variables involved in the roasting reaction, the roasting stage of the flow sheet can be proposed. Roasting would be conducted in a rotary kiln using a controlled heating rate of about 1°C per minute. The temperature would be varied from 250°C at the inlet end to 450°C at the outlet so that the pellets would be in the furnace for a total of 4 hr, including one-half hour at maximum temperature. The kiln lining would of necessity be composed of acid-proof brick, probably carbon brick; and an arrangement for collecting and directing the exhaust gases would be required.

Leaching and Primary Crystallization

The roasted product would be leached in brick and lead-lined leaching tanks in a 3% solution of sulfuric acid for one-half hour at 90°C. Using a pulp density so that there is 1 liter of solution for every 100 g of alumina in the feed, 925 gal of water and 0.34 lb of sulfuric acid would be added in the leaching tank for every ton of clay processed. Following leaching, the slurry would be filtered and washed at 90°C. The clarified liquor would then be cooled to 20°C to crystallize the alum.

Leaching tests on the mineral and diasporic clay roasts indicated that a leaching temperature of 90°C gave maximum alumina recovery. As the leaching temperature was increased above 90°C, recovery decreased due to loss of water by evaporation and hydrolysis of the alum. A slightly acidic leach solution was required to prevent loss of alumina by hydrolysis. An acid strength of 3% sulfuric acid was found to be adequate. Maximum alumina recovery was obtained after leaching for one-half hour. Alumina recovery was affected very little by changing the pulp density of the leach slurry. There was a slightly higher recovery in the very dilute slurries. According to the International Critical Tables,⁷ 126 g of alumina, as the alum, are soluble in 1000 g of water at 90°C. By using a pulp density in which there are 100 g of alumina per 1000 g of water, the alum will be readily soluble.

Alum Purification

The alum crystals from the initial crystallization contain about 8% iron. After the initial crystallization, the alum crystals would be redissolved in water at 90°C and recrystallized in the secondary crystallization stage. At this point the crystals contain about 0.6% iron. The alum crystals and their mother liquor would then go through a two-stage amine extraction. After the amine extraction, the aqueous phase would be filtered, the water being sufficiently pure to redissolve more alum,

and the alum crystals would be sent to precipitation. The organic phase would be regenerated by stripping with an alkali.

The method proposed for alum purification in this flow sheet was not investigated by the authors but was studied by Thomas and Ingraham.¹³ Using a potassium alum produced from shale, they reduced the iron content from 0.4% to as low as 0.001% with amine extraction. The amine used in their work was a primary amine designated as Primene JM-T which is available commercially from the Rohm & Haas Co.

Another method of eliminating iron was investigated by the authors; however, the results are not complete. The approach used was to leach the roasted product in a sulfur dioxide atmosphere, thereby reducing ferric iron to ferrous which will not crystallize with the alum. The method succeeded in producing an initial alum with 0.4% iron and could undoubtedly have been lowered further by changing conditions. However, since there was a loss in alumina recovery due to hydrolyzing and difficulty in filtering the slurry, testing was discontinued. These problems could probably be overcome by further testing.

Alumina Precipitation and Ammonium Sulfate Crystallization

Purified alumina would be precipitated by adding the pure alum crystals to an ammoniacal solution made by passing the exhaust gases from the roasting stage into water. St. Clair¹² and many other workers have proved that if the concentration of ammonia in the solution is sufficiently high (about three times the theoretical quantity), the resulting aluminum hydroxide is easily filtered. The slurry from precipitation would be filtered, the solids would be calcined to pure alumina at 1100°C in a rotary kiln with an overall recovery of about 89%, and the filtrate would be sent to ammonium sulfate crystallization. Ammonium sulfate would be crystallized by evaporation with about 95% of the ammonium sulfate being recovered and recycled to the mixing stage. Ammonia gas would also be collected and recycled at this point.

Conclusions

This investigation proved that clays containing the monohydrate minerals, diasporic and boehmite, can be successfully treated for their alumina content by the acid ammonium sulfate process. The particle size of the clay is important, particularly for hard materials. The roasting temperature required is critical since the monohydrate minerals convert to insoluble species above 450°C. Since the optimum roasting temperature and time required cause excessive loss of ammonium sulfate, an

amount of ammonium sulfate in excess of the theoretical amount is required. Improved alumina and ammonium sulfate recoveries can be obtained by controlling the heating rate during the roasting stage. The product obtained by roasting clay and ammonium sulfate, which was proved to be ammonium aluminum sulfate, is readily soluble in hot water although a slight excess of sulfuric acid is desirable to prevent loss of alumina by hydrolysis. Iron can be eliminated from the alum crystals to some extent by leaching in a sulfur dioxide atmosphere. However, the increased complexity and loss of alumina by hydrolysis make this method of iron removal less attractive. The method using solvent extraction proposed by other workers would apparently be more satisfactory.

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Discussion

O. Wicken (Harbison-Walker Co.): Did you consider potassium sulfate leaching instead of ammonium sulfate? If so, why did you choose ammonium sulfate?

J. W. Fetterman: Ammonium sulfate was chosen because of its availability as a by-product from coal coke ovens in the area. Potassium sulfate was considered, but the method of processing would have been considerably different from that described.