A TECHNOLOGICAL COMPARISON OF SIX PROCESSES FOR THE PRODUCTION

OF REDUCTION-GRADE ALUMINA FROM NON-BAUXITIC RAW MATERIALS

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Abstract

The U. S. Bureau of Mines, by means of a contract with Kaiser Engineers and with Kaiser Aluminum & Chemical Corporation as a subcontractor, has sponsored a technological and an economic evaluation of six candidate processes for the manufacture of alumina from certain U. S. raw materials other than bauxite. This paper describes each process. Flow diagrams and the total energy requirement for each process are included. Important characteristics affecting the economics of producing alumina by each process are discussed, and some presently unsolved technical problems are identified. The extraction of alumina from clay via hydrochloric acid with iron separation by solvent extraction, and the crystallization of intermediate $AlCl_3 \cdot 6H_2O$ through the introduction of HCl gas into the pregnant mother liquor, appears to be technically feasible and the most attractive of the six raw material/process combinations.

Introduction

This study is concerned with the producing of alumina from non-bauxitic domestic raw materials by means of six possible alternative processes. As an outgrowth of the long-term program of research on technologies for extracting alumina from domestic resources, the U. S. Bureau of Mines began on July 1, 1973, a mini-plant project to evaluate processes for recovering alumina from these resources. The purpose of the mini-plant project is to test and develop the most promising processes in a small scale pilot plant operation which would provide technical and economic data necessary for scaling up to commercial size plants and for making rational decisions for selecting the alumina process technology that should be used in a 10- to 50-ton-per-day pilot plant. Subsequently in January 1974, companies having an interest in producing alumina were invited by the Bureau of Mines to join the mini-plant project on a cooperative, cost-sharing basis. Ten companies joined the program which is being conducted at the Boulder City Engineering Laboratory of the Bureau of Mines.

On September 30, 1976, the Bureau of Mines awarded Contract Number J0265048 entitled "Alumina Process Feasibility Study and Preliminary Pilot Plant Design" to Kaiser Engineers in Oakland, California, with Kaiser Aluminum & Chemical Corporation as subcontractor. The work under this contract is divided into three consecutive tasks spanning a period of approximately 30 months.

This paper covers a part of the first of these tasks--Task 1. The objective of Task 1 was to construct technical and economic evaluations of each of six raw material/process combinations to permit comparison and nomination of the two appearing to offer the best potential for the production of alumina based on operable technology and at lowest cost. This paper describes and compares process technology. A companion paper describes and compares economics of the six combinations. The six conceptual raw material process combinations studied under this task are:

o Anorthosite/Lime – Sinter
o Alunite/Reduction Roast – Bayer Extraction
o Clay/Sulfurous Acid
o Clay/Nitric Acid
o Clay/Hydrochloric Acid (Evaporative Crystallization)
o Clay/Hydrochloric Acid (HCl Gas Induced Crystallization)

The basic technical and process data for the study was drawn from the published literature or was provided by the Bureau of Mines from data developed in the mini-plant program or in previous work. In addition, technical and economic information was drawn from other sources and from the experience of Kaiser Engineers and its subcontractor, Kaiser Aluminum & Chemical Corporation, although it will be evident to the knowledgeable reader that substantial amounts of information required for the design of a plant to produce alumina by any one of the six combinations was not available from any source. This problem was met by estimating the required information and/or by making assumptions. It is believed that this procedure, although not the most desirable, was sufficiently accurate to make possible the development of a useful comparison of the combinations.

Raw Materials

Aluminum is the third most abundant element in the crust of the earth and is present in many naturally occurring minerals and rocks. However, in general, more process work must be done, and the total cost of producing a unit of alumina from the raw material will therefore be higher: a) the lower the percentage of alumina in the raw material, b) the more strongly the alumina is chemically combined with other substances in the raw material, and c) the larger the number of components in the raw material which must be separated in order to obtain the alumina. The three raw materials included in the process/raw material combinations studied here appear on the basis of the above criteria to be the most promising which are available in large quantities within the borders of the 48 contiguous states.

Clay

Very large reserves of clay suitable for the production of alumina exist within the contiguous 48 states.

The primary mineral is kaolinite, the alumina content of which may be rendered almost completely acid-soluble by calcination at 1100° to 1500°F. The calcine is actually a better acid extractive process feed than total analyses indicate, because the minor constituent metal oxides tend to be in part derived from residual micas and feldspars in the clay. Metal oxides combined in these accessory minerals are only partially soluble in acid under the extraction conditions employed by the processes under discussion, thereby improving the soluble alumina to impurities ratio in the process liquor stream. Iron, unfortunately, occurs primarily in the clay either as free Fe_2O_3 or as a replacement for aluminum in the kaolinite lattice. In either case it is acid soluble.

The abundance of kaolinic clay, its high grade with respect to alumina, the ease with which the alumina may be rendered acid soluble, the possibility of rejecting the major unwanted constituent of the clay (silica) without reagent consumption, and the high ratio of acid soluble alumina to impurities combine to make kaolinic clay a preferred raw material, after bauxite, for the extraction of alumina.

Anorthosite

The crystalline rock anorthosite lies near the calcium-rich end of the soda-lime feldspar series which varies isomorphously in all proportions from albite, $NaAlSi_3O_8$, to pure anorthite, $CaAl_2Si_2O_8$. It is estimated that approximately 1.6×10^{11} tons of alumina, or much more than the total contained in all other minerals considered to be potential sources of alumina in the U.S., are available in reserves of anorthosite.

Thus it may be observed that anorthosite is a potential source of virtually unlimited amounts of alumina, provided that the problem of separating alumina from the primary impurities silica, lime, soda, and potassium can be solved on a basis competitive with the extraction of alumina from other less plentiful non-bauxitic materials. The difficulty of extracting alumina from anorthosite is increased by the fact that in anorthosite the alumina is in very strong chemical combination with the other constituents.

Secondary but major raw materials which have been employed in nearly all past efforts to extract alumina from anorthosite are limestone and coal. The U.S. is plentifully endowed with both of these materials, so no detailed discussion of them will be undertaken here.

Alunite

Alunite is a naturally occurring basic sulfate of potassium and aluminum made basic by the presence of alumina trihydrate in its molecule. The chemical formula of alunite may be written:

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 2Al_2O_3 \cdot 6H_2O.$$
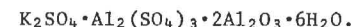
In naturally occurring deposits varying amounts of sodium substitute for potassium. Alunite appears to be formed as a result of solfataric action of hot acid waters upon feldspathic rocks. Much of the silica content of the original rock remains in admixture with the alunite; and it is important to note that although much of the silica may be in the form of quartz, some of it may be in the form of opal, which is chemically reactive to alkali. Slightly different conditions of alteration of the original rock may result in the gradation of alunite in an ore body into kaolinic clay, which also contains alkali-reactive silica.

Alunite has been used by various civilizations at least since the time of the Roman Empire as a source of potassium alum, but known deposits of it were too small to be considered as an important potential source of alumina. In 1970, however, a large deposit of alunite was discovered in Southwestern Utah. It is estimated that at least 100×10^6 tons of alumina, and possibly considerably more, are in place in alunite ore analyzing 5 to 20% Al_2O_3.

Alunite as compared with clay as a source of alumina suffers from the disadvantage that the percentage of alumina in known deposits as they naturally occur is relatively low, and there is no known practical industrial scale method of beneficiation. Additionally, provision must be made for the separation and utilization of the sulfate and potassium contents of the ore. These can be processed into saleable materials, but their unit values are low and they tend to be an economic burden rather than an advantage when alumina production is the primary goal.

The Raw Material/Process Combinations

Alumina from Anorthosite by Lime Sinter

A. *Introduction*

Development of a lime-soda sinter process began as long ago as

1902 when Adolf Kayser obtained a patent on a process for separating alumina from silica. Early work on lime-soda sinter processes was reviewed by Conley and Edwards, Frary, and Jeffries (1). Conley investigated the extraction of alumina from Pennsylvania nodular diaspore clay by a lime-soda sinter process (2). In this process clay was dry ground and then sintered with limestone and soda ash (sodium carbonate) to convert the alumina to sodium aluminate and the silica to dicalcium silicate. The sinter was leached with sodium carbonate solution to dissolve the sodium aluminate. The solution was then heated under pressure with lime to remove most of the silica that dissolved with the sodium aluminate. The purified solution was carbonated to precipitate alumina trihydrate which was then calcined to produce alumina.

During World War II the Defense Plant Corporation financed the construction of a 50-ton-a-day plant at Laramie, Wyoming, to produce alumina from anorthosite. Construction of this plant was almost completed when the program was terminated in 1945. In 1952 the Bureau of Mines modified the plant and operated it on an experimental basis. Operation of this plant was described in Bureau of Mines Bulletin 577(3). In this process crushed anorthosite and limestone were mixed and ground in a recycled soda solution in a ball mill. The wet mix was sintered and then wet ground with soda solution in a ball mill which served as the first leaching stage. The remaining process steps were similar to those used in the process treating Pennsylvania diaspore clay. The solution was heated under pressure with lime and then carbonated to precipitate alumina trihydrate.

The process evaluated herein is somewhat different than any of the previous studies in that it is an anorthosite/limestone sinter with no addition of soda to the sintering step. It cannot however be considered a true lime-sinter process, because the soda content of the anorthosite used in this study is equivalent to about 20 percent of the quantity required in the lime-soda sinter process. It therefore falls somewhere in between these processes. Information contained in Bureau of Mines RI 7068 was used extensively in evaluating this process (4).

B.   *Process Description*

A summary flow sheet is shown as Figure 1.

Preparation of Sinter Feed

This series of preparation steps includes crushing, wet grinding, wet classification, separation, partial drying, and pelletizing to produce an intimate blend of 98 percent minus 200 mesh anorthosite and limestone for sinter feed. The crushing section, consisting of jaw and cone crushers, prepares the anorthosite and limestone for subsequent wet grinding in ball or rod mills. The mill overflow is classified in a hydroseparator or wet cyclones with recycle of the coarse fraction to wet milling. The minus 200 mesh rock slurry is thickened with the aid of flocculant and dewatered using vacuum filters to a 17 percent moisture cake. The filter cake is partially dried in a rotary dryer which utilizes

Figure 1

ALUMINA FROM ANORTHOSITE VIA LIME SINTER
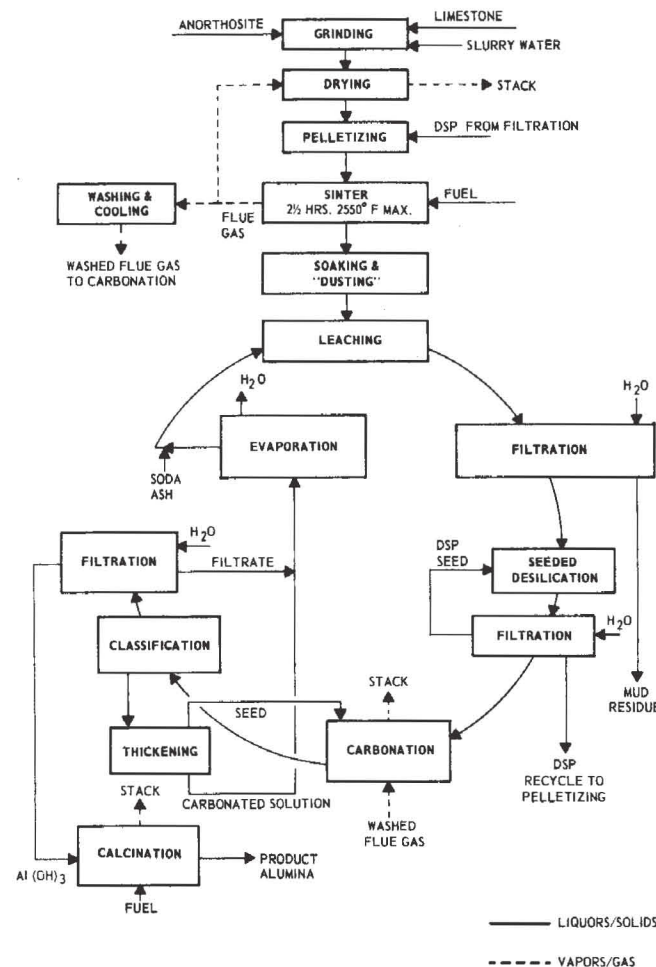
waste heat from the sinter kiln flue gases. The partially dried ground rock solids at 12 percent moisture are then pelletized to yield an intimate blend of anorthosite and limestone in the form of $\frac{1}{8}$ inch by $\frac{1}{4}$ inch diameter balls. A bleed stream of desilication product (DSP) from the desilication of pregnant liquor is also pelletized with the ground rock slurry.
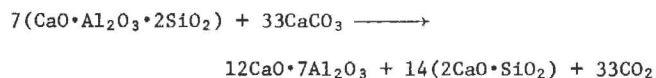
This preparation section is very important to the overall process as it must produce an intimate blend of anorthosite and limestone in the correct ratio so that it will react properly in the sintering kilns. A good sinter will, in turn, leach and process without gelation and yield a high alumina extraction. The control in the preparation section must be very precise to achieve this goal.

Pelletizing of the raw material mixture will require further investigation to determine the optimum pellet characteristics.
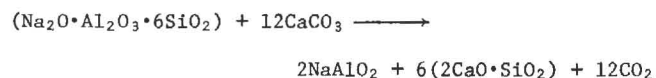
Sintering Operations

The pellets of anorthosite/limestone are fed to sintering kilns where they are heated to a maximum temperature of 2550°F. During a total retention of $2\frac{1}{2}$ hrs, the alumina and silica react with the limestone. The main reactions are represented as follows:

Anorthite:

$$7(CaO \cdot Al_2O_3 \cdot 2SiO_2) + 33CaCO_3 \longrightarrow$$

$$12CaO \cdot 7Al_2O_3 + 14(2CaO \cdot SiO_2) + 33CO_2$$

Albite:

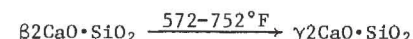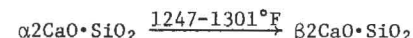$$(Na_2O \cdot Al_2O_3 \cdot 6SiO_2) + 12CaCO_3 \longrightarrow$$

$$2NaAlO_2 + 6(2CaO \cdot SiO_2) + 12CO_2$$

Excessive sintering temperatures and/or sintering times produce gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$). Alumina is not recoverable by leaching gehlenite. Excessive $CaCO_3$ in the sinter mix forms tricalcium silicate ($3CaO \cdot SiO_2$), a component of Portland cement which can cause gelation during the leaching step. Maximum alumina extraction requires maximum formation of $12CaO \cdot 7Al_2O_3$ with a minimum excess of $CaCO_3$. A very careful stoichiometric balance must therefore be obtained in mixing anorthosite and limestone for the sinter to achieve this maximum extraction and to avoid subsequent gelation.

The sintered product from the kilns is cooled in rotary coolers to a temperature of 1290°F.

Soaking and "Dusting"

The sintering step produces dicalcium silicate. Soaking in a rotary calciner at 1290°F for 15 to 30 minutes allows the α-form of dicalcium silicate to convert to the β-form. When the β-form is subsequently cooled rapidly to 577°F in another cooler, it converts

to the γ-form with a 10 percent increase in volume, which results in the disintegration of the sinter and the formation of "dust". The following equations represent these reactions:

$$\alpha 2CaO \cdot SiO_2 \xrightarrow{1247-1301°F} \beta 2CaO \cdot SiO_2$$

$$\beta 2CaO \cdot SiO_2 \xrightarrow{572-752°F} \gamma 2CaO \cdot SiO_2$$

This operation is described in a patent by Kapolyi (5).

There are several inhibitors noted for the above desired conversion of β to γ dicalcium silicate which tend to stabilize the β form. They are carbon, $3CaO \cdot SiO_2$, and the higher oxides of Cr, As, Mn, Te, P, Ge, and V. Excess Na_2O is also mentioned as a stabilizer.

It is desired that all the $2CaO \cdot SiO_2$ form dust less than 325 mesh. In practice, about 95 percent "dusting" has been achieved in laboratory batch experiments. The "dusting" yield however is quite variable and is greatly dependent on the proper ratio of anorthosite/limestone and sintering control. Without a good "dusting" yield, a prohibitive amount of coarse sinter would have to be recycled to the sinter kiln. Not enough information is currently available to indicate what happens to this recycle during resintering. If "dusting" yield is poor, the milling of sinter might become a requirement.

The "dusted" sinter is screened to remove plus 20 mesh particles which are recycled to the sinter kiln. The minus 20 mesh "dusted" sinter is conveyed to the leaching section.

Leaching

The dusted sinter is leached at 140°F for 30 minutes with a spent liquor solution from evaporation. The leaching solution will have a sodium carbonate concentration of approximately 170 g/ℓ and a residual Al_2O_3 concentration of approximately 10 g/ℓ. The slurry in the leach tanks will contain between 25 to 30% solids.

The main reaction during leaching is as follows:

$$12CaO \cdot 7Al_2O_3 + 12Na_2CO_3 + 5H_2O \longrightarrow$$

$$14NaAlO_2 + 12CaCO_3 + 10NaOH$$
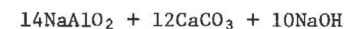
No flue gas (CO_2) is added to the leaching step in this process so as to allow for about 20 g/ℓ free alkali (as NaOH) to hold the alumina in solution. The pregnant liquor will contain approximately 50 g/ℓ Al_2O_3 and a total soda concentration of approximately 150 g/ℓ expressed as Na_2CO_3. It will also contain about 1 g/ℓ SiO_2 in solution. During the leaching operation, approximately 75 percent of the alumina in the anorthosite will be extracted.

Filters instead of thickeners are used to separate the insoluble residue from the pregnant liquor in order to avoid the problem of gelation. Literature and experience have shown that even when all precautions are taken to make a "good" sinter, gelation can still be a problem in anorthosite/limestone sinter processes. This process has been designed assuming that gelation will not occur. Gelation will however probably be the major operating problem in this process. The magnitude of this problem was shown during the Bureau of Mines experimental operation of the Laramie plant when operations had to be shut down to remove the solid mass with air hammers.

The filtered and washed leach residue consists of an enormous quantity of approximately 10 tons per ton of alumina which must be disposed of. This residue weight is approximately $\frac{2}{3}$ of the feed to the process. These solids also contain entrained liquor which makes the waste alkaline, therefore requiring environmental control measures in disposition.

Desilication

DSP (desilication product) seeded desilication is utilized in this process. The pregnant liquor from leaching contains approximately 1 g/ℓ SiO_2 in solution which must be removed before alumina is precipitated as the trihydrate. The pregnant liquor is desilicated by seeding with about 100 g/ℓ DSP solids and holding in stirred tanks at 212°F for 24 hrs. The desilicated slurry is filtered to remove the DSP solids, most of which are recycled back to desilication as seed. A bleed quantity of DSP equal to that which is removed by desilicating is washed and recycled to the sinter kiln to reclaim its soda and alumina value. The desilicated pregnant liquor will contain about 0.035 g/ℓ SiO_2.

Although data are not available on DSP seeded desilication for liquors of this composition, it is believed to be the best technology for this process.

Carbonation

The desilicated solution is carbonated to precipitate alumina trihydrate as shown in the following equation:

$$2NaAlO_2 + CO_2 + 3H_2O \longrightarrow Al_2O_3 \cdot 3H_2O + Na_2CO_3$$

Precipitation of the alumina is aided by adding alumina trihydrate seed crystals equivalent to 25 percent of the alumina that precipitates.

The seed crystals are recycled fines from the classification of the precipitate. The carbon dioxide gas is obtained from the sinter kiln stack gases after they have been scrubbed and cooled.

The carbonators are operated at 140°F and the retention time is 12 hrs. Sufficient carbon dioxide is added to precipitate 85 percent of the alumina in solution. Under these conditions approximately $\frac{1}{3}$ of the silica present in the liquor will precipitate.

The coarse alumina trihydrate crystals are separated from the fine seed crystals by hydro-classification. The coarse crystals are dewatered and washed on vacuum filters and conveyed to the calcination kilns. The fine seed crystals that remain in the hydro separator overflow are settled in thickeners and recycled to the carbonators. The carbonated overflow solution from the thickeners is pumped to soda ash recovery.

Calcination

The coarse alumina trihydrate crystals are calcined at 2000°F in rotary kilns to form alumina product as shown in the following equation:

$$Al_2O_3 \cdot 3H_2O \longrightarrow Al_2O_3 + 3H_2O\uparrow$$

The calcined alumina is conveyed to storage silos where it is held until shipped.

Soda Ash Recovery

The spent carbonated solutions are concentrated in multiple effect evaporators. Makeup soda ash is added as required to the concentrated solution from the evaporator and the solution is recycled to the leaching section of the process.

Flue Gas Processing

The carbon dioxide gas used to carbonate the desilicated pregnant liquor is obtained from the sintering kilns. The stack gas from the kilns contains carbon dioxide evolved from the decomposition of the limestone in the feed and from the combustion of the coal fuel. The dust is removed from the gas in cyclones and heat is recovered as 100 psig steam from waste heat boilers. After leaving the waste heat boilers, the gas is processed through Venturi scrubbers for washing and further cooling before use in carbonation or venting to the atmosphere.

Alumina Product Quality

The quality of alumina produced by this process should be equivalent to that produced in a Bayer plant. If the degree of carbonation is properly controlled, the silica content and the purity of alumina produced by carbonation should be equal to that produced by Bayer precipitation.

Considerable amounts of impurities may be introduced into the liquors dependent upon the analysis of the limestone, fuel, and anorthosite. Some form of impurity control may be required to remove them from the plant liquor. The effect of impurities other than silica and iron on the process are largely unknown.

Energy Requirements

The overall net energy requirement of 61.9 x 10^6 Btu/ton alumina is quite high even after utilizing waste heat from the sinter kiln

flue gases for all the steam requirements and the partial drying step before sintering. This high energy requirement of 58.0×10^6 Btu/ton Al_2O_3 that is required for the sintering step alone is due to the very large mass of anorthosite/limestone feed (17.4 tons/ ton of alumina produced).

Coal may be used for anorthosite/limestone sintering. The final product alumina calcination will require high grade fuel which will not compromise the product alumina quality.

Environmental Control

Because of the large quantity of waste leach residue generated by this anorthosite-lime sinter process, its disposal will be a serious problem. One method of discarding the waste solids would be the use of tailing ponds. However, the size of the ponds may be so large as to make this disposal method undesirable. It is estimated that the waste solids which must be disposed of will approach $\frac{2}{3}$ of the total plant feed or approximately 10,000 tons/ day on a dry basis. These solids will also contain some entrained liquor which will make them alkaline; therefore, runoff from any impoundment area must be treated.

The sinter kilns will require good dust removal equipment which will probably include wet scrubbers. SO_2 removal may also be required depending on the quality of coal used in the sinter kilns. Scrubber liquors will require impoundment and probably treatment for pH control.

Conclusions

The quality of alumina produced in this process should be equivalent to that produced in a Bayer plant. Further study may be required to characterize particular anorthosite ore bodies for minor impurities and to determine their effect on process impurity removal requirements.

The estimated net thermal energy requirement for this process is 61.9×10^6 Btu/ton Al_2O_3. This is very high even though waste heat from the sinter kiln flue gases is utilized for all steam and dry- ing requirements. This high energy requirement is due to the 58×10^6 Btu/ton Al_2O_3 estimated for the sintering step of this process. This large energy consuming step alone is almost prohibitive.

Gelation in the leaching section is potentially the most serious technical problem of this process. Although investigations indicate that gelation can be prevented by careful control of the sintering and leaching operations, the possibility that gelation may occur is a serious disadvantage of this process.

Disposal of the waste leach residue is also a serious problem in this process due to its sheer quantity. The waste solids which must be disposed of approaches $\frac{2}{3}$ of the total plant feed or approx- imately 10 tons per ton of alumina produced.

The recovery of alumina in the leach process is only 75%, which is poor.

Alumina from Alunite Via Reduction Roasting – Modified Bayer Extraction

A. *Introduction*

Interest in alunite as a raw material for the production of alumina has existed for many years and received renewed impetus during national emergencies that saw restrictions in the supply of bauxite or potash. Early investigators noted that the alunite com- ponent of an ore could be rendered quite chemically reactive by a relatively simple calcination at a moderate temperature. The potassium and sulfate contents of the alunite, which upon intensive study of alumina production alternatives prove to be a liability, at first appeared attractive and easily recoverable by simple known technology.

The development of alunite as a raw material for alumina was always handicapped until recently by the widely held opinion that reserves of high-grade alunite were small. The discovery about 1971 of much larger reserves in Utah containing 30% or more alu- nite led to renewed efforts to develop an economical process for extracting the alumina and other values. Information about the process developed as a result of these efforts has been obtained from a Draft Environmental Impact Statement filed by developers of the process (6) and other published literature, including particu- larly the Russian literature (7, 8, 9, 10, 11, 12, 13). Much effort has been expended in Russia on the development of a process for the manufacture of alumina from alunite.

B. *Process Description*

A summary flow sheet for the process being evaluated is shown as Figure 2.

#### Crushing, Conveying, and Storage of Raw Ore

Alunite has the chemical formula $KAl_3(OH)_6(SO_4)_2$, a density of 2.6-2.8, and a Mohs' hardness of 3.5-4. It is formed by the action of natural sulfuric acid solutions acting on rocks rich in potash feldspar, and occurs in massive form in admixture with the silica coproduct from decomposition of the feldspar. Varying amount of feldspar, kaolin, and other minerals may also be present. The first step in the processing of alunite ore therefore is to crush it from the as-quarried form to a size suitable for storage, conveying, and further size reduction in preparation for roasting.

Fine Crushing and Dry Grinding

It is expected that the most cost-effective technology for accomplishing the roasting or the ore will be the employment of fluidized solids techniques. The fine crushing and dry grinding operation accepts the coarsely crushed raw ore and reduces it to a controlled particle size distribution suitable for use in

ALUMINA, K$_2$SO$_4$ AND H$_2$SO$_4$ FROM ALUNITE VIA

REDUCTION ROASTING, MODIFIED BAYER EXTRACTION
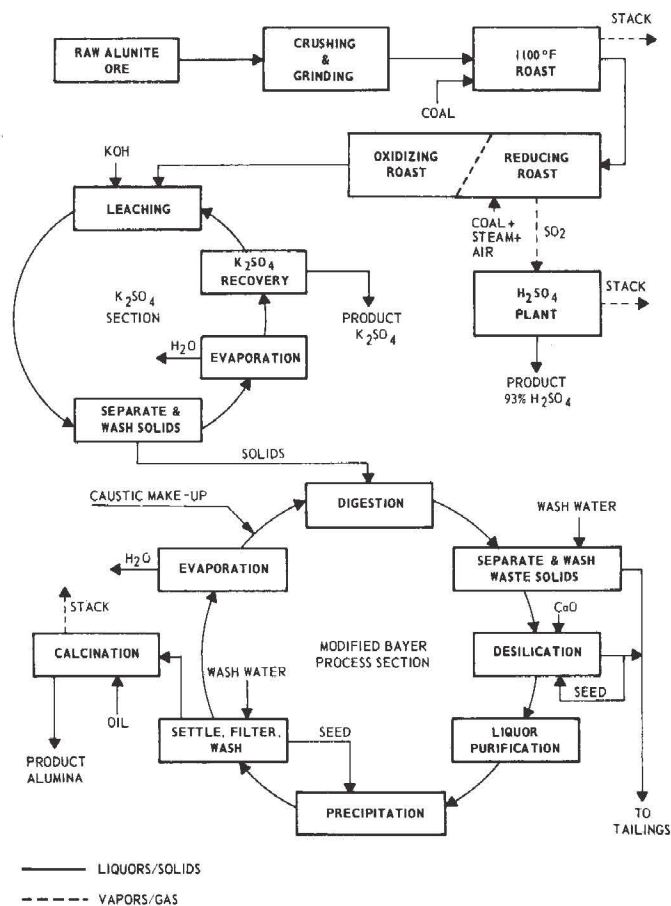
fluidized solids calciners.

First Roast for Removal of Free and Combined Water

The properly sized feed passes to the first fluidized bed roaster which is maintained at about 1100°F by the combustion of directly injected powdered coal and air. The overall chemical reaction for the removal of combined water may be represented by the equation:
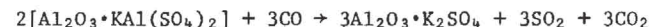
$$KAl_3(OH)_6(SO_4)_2 \longrightarrow Al_2O_3 \cdot KAl(SO_4)_2 + 3H_2O\uparrow$$

even though discrete units of Al$_2$O$_3$ probably do not actually exist in the calcine.

A residence time of two hours is postulated to insure complete removal of combined water from calcine leaving the roaster. It is possible that in commercial practice this roasting could be carried out in stages in order to obtain complete removal of the combined water (avoid short-circuiting of unreacted solids) with a much shorter total residence time.
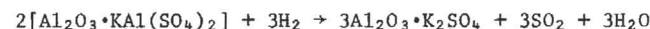
Particles of coal during combustion must attain temperatures far higher than 1100°F, but this apparently has no adverse effect upon the ore being calcined. Ash remaining in the calcine will be substantially inert in following process operations. Provided a temperature sufficient to achieve a reasonable calcination rate has been reached, insofar as can be determined from the literature, the calcination is not extremely sensitive to either temperature or residence time. It is however important to operate the calcination always under oxidizing conditions and below about 1300°F in order to minimize, in this step, decomposition of the sulfate in the ore. Fluidized solids techniques are known to be well suited for meeting the conditions described above that are required for this calcination.

Reducing Roast for Removal of Sulfate Associated with Alumina

Calcine from the preceding roast passes hot to a fluidized reducing roast operating, according to the Russian literature, adiabatically at about 1000°F with a one-hour residence time and using a mixture of CO and H$_2$ as the reducing agent. The overall desired chemical reactions are:

$$2[Al_2O_3 \cdot KAl(SO_4)_2] + 3CO \rightarrow 3Al_2O_3 \cdot K_2SO_4 + 3SO_2 + 3CO_2$$

or

$$2[Al_2O_3 \cdot KAl(SO_4)_2] + 3H_2 \rightarrow 3Al_2O_3 \cdot K_2SO_4 + 3SO_2 + 3H_2O$$

The degree of sulfur removal tends to increase with increasing roast temperature; but unfortunately the alumina also tends, with increasing roast temperature, to be converted to a caustic-insoluble form by a mechanism not fully understood. Again, fluidized solids techniques appear to offer the best means of closely controlling the roasting conditions so as to achieve the best possible sulfur removal while minimizing deactivation of the alumina.

The Russian literature reports approximately 80% sulfur removal with approximately 80% of the alumina remaining in the soluble form to be the best obtainable result.

Potassium hydroxide or ammonia equivalent to the unreduced sulfate associated with alumina must be supplied in a subsequent process operation, and the loss of as much as 20% of the alumina in the ore by conversion to a caustic-insoluble form is undesirable. The reduction roasting technique has been studied intensively in Russia. So far as is known, the technical difficulties described above associated with reduction roasting remain unsolved. Based on the amount of work reported on this subject, the prognosis for future solution is considered poor.

Reoxidizing Roast

The reducing roast tends to convert some oxides present in the ore--and particularly iron--to sulfides. These sulfides represent a loss of sulfur, and they would interfere with the operation of the Bayer process recovery of alumina. Solids discharged from the reducing roast are therefore delivered hot to a final fluidized roast under oxidizing conditions where the following reaction takes place:

$$2FeS + 3\tfrac{1}{2}O_2 \longrightarrow Fe_2O_3 + 2SO_2$$

This roasting step is reported to be directly fired with a small amount of powdered coal. The temperature is estimated to be 1100°F, and the residence time is estimated at 30 minutes.

Dissolve Potassium Sulfate

The reoxidized calcine is mixed with recycled hot K_2SO_4 solution wherein the K_2SO_4 component of the calcine dissolves:

$$3Al_2O_3 \cdot K_2SO_4 + Solution \longrightarrow 3Al_2O_3 + K_2SO_4 \text{ soln.}$$
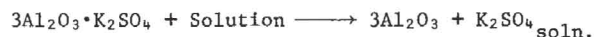
Potassium hydroxide is added to the recycle solution to dissolve unreduced sulfate associated with alumina, simultaneously freeing for solution existing K_2SO_4 present in the alunite calcine structure:

$$Al_2O_3 \cdot KAl(SO_4)_2 + 3KOH_{aq.} \longrightarrow Al_2O_3 \cdot Al(OH)_3 + 2K_2SO_4 \text{ aq.}$$

This procedure is effective for the removal of potassium and sulfate from the roasted solids.

Separate, Wash, and Remove Undissolved Solids

Solids remaining after leaching of the potassium and sulfate are mostly granular in nature. They may be filtered and washed on belt extractors.

Modified Bayer Process Dissolution of Alumina

The solids remaining after leaching and washing out sulfate

and potassium consist of approximately 20% alumina with the balance comprising primarily silica, together with small amounts of Fe_2O_3 and TiO_2. Some K_2SO_4 will also be present. These solids pass to a modified Bayer process using caustic soda to extract the alumina. It is necessary to design the Bayer extraction very carefully to maximize the extraction of alumina while minimizing solution of the relatively large mass of silica present, some of which is reactive. This is a technical problem requiring further study prior to the design of a demonstration plant for the production of alumina from alunite via this process.

Separate, Wash, and Remove Insolubles

The slurry from digestion is thickened in conventional thickeners. The thickener underflow is then washed in a multistage CCD system to recover the soda values before the mud is pumped to waste.

Liquor Purification

An amount of silica larger than would be acceptable in the product alumina, or than could be controlled by means of an economically acceptable bleed stream, is certain to be dissolved along with the alumina. Sulfate and potassium are also expected to build up in the recycling Bayer liquor unless means are provided for their control. Carbonates may also be present.

Control of dissolved silica will be provided by a desilication step in which the pregnant liquor is held at elevated temperature with gentle agitation for a period of hours in the presence of desilication product seed crystals. In a conventional Bayer process operation in the absence of lime, the seed crystals would grow, removing silica from the solution as a solid of the approximate expected composition:

$$Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \sim 2H_2O \cdot \tfrac{1}{3}Na_2O(\sim\tfrac{1}{2}CO_2,\sim\tfrac{1}{2}Al_2O_3)$$
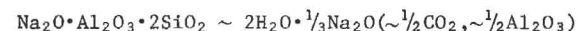
Thus, each unit of SiO_2 which must be removed from the solution would carry out of solution 1.0 units Al_2O_3 and 1.18 units soda. In the presence of lime it is expected that the normal desilication product will react partially to liberate soda and form hydrogrossularite, which has the approximate formula

$$3CaO \cdot Al_2O_3 \cdot YSiO_2 \cdot (6-2Y)H_2O$$

where Y may have a value ranging from slightly more than one to considerably less than one. The amount of lime stated in the Draft Environmental Statement may not be adequate for recovery of all of the soda in the desilication product, or some of this material may be nonreactive to lime. However, any significant loss of alumina and of soda in desilication product could impose a substantial economic penalty on the process. These potential losses emphasize the need for further study of the digestion operation with the goal of maximizing alumina extraction while minimizing the extraction of silica. Determination of the optimum relationship between the amount of desilication product seed recycled, lime addition, holding time, temperature, and intensity of agitation required to secure adequate desilication will also require further study.

The slurry at the conclusion of desilication will be classi-fied and thickened. An appropriate amount of seed will be returned to desilication. The net production of desilication product crys-tals will be sent to waste. A polish filtration must be provided for the pregnant liquor proceeding to precipitation.

The removal of sulfate from the recycling Bayer liquor will be required but has not been studied. Precipitation as $BaSO_4$ would be expected to provide acceptable control but would require provision for recovery and regeneration of the costly barium reagent.

Carbonate control may be achieved by causticization with lime or may be achieved with barium, again with the requirement of regen-eration if barium is used. Carbonate control has not been studied, and no provision has been made for it in the flow sheet. Similarly, there has been no study or provision made for the control of any organic carbon.

The extent to which potassium may build up in the recycling Bayer liquor, its effect on the operation of the Bayer extraction, and the amount of it which will appear in the product alumina for a given potassium level in the Bayer liquor have not been studied. Also unknown is the level of K_2O which may be tolerated in reduc-tion cell feed. Further study is required.

Alumina Trihydrate Precipitation

The precipitation of alumina trihydrate is expected to be accomplished much in the manner of conventional Bayer process tech-nology using seeded crystallization. Solid alumina trihydrate in the slurry leaving precipitation is classified in a settling operation. Slurry containing the coarser trihydrate particles is thickened and the underflow filtered. The solids are washed and sent to calcination. Slurry containing the smaller particle sizes is thickened with the underflow containing the seed returning to precipitation.

The precipitation and solid-liquid separation operations will be very similar to those carried out in a Bayer plant operating on bauxite provided that control has been achieved over the various impurities discussed above which may be present in the liquor to reduce their concentrations to the levels present during precipi-tation in a conventional Bayer plant. Hopefully, extraction of alumina can also be managed to present to precipitation a pregnant liquor of proper alumina and caustic concentration at the tempera-ture required to produce a product of requisite granulometry. Since this hope may not be entirely realized and economic considera-tions or technical necessity will dictate attempting to operate with liquor impurity levels different from those encountered in a Bayer plant operating on bauxite, the precipitation step will require further study using actual liquors derived from alunite processing on a cyclic basis before the design of a demonstration plant can be undertaken with confidence.

Alumina Trihydrate Calcination

Calcination of the washed alumina trihydrate can be accomplished using known technology in a manner similar to the calcination of trihydrate derived from bauxite. The use of fluidized solids tech-niques is the probable choice. A clean fuel such as oil is required for this direct-fired operation. No severe technical difficulties are expected.

Spent Liquor Evaporation and Recycle

Spent liquor from precipitation passes to multiple-effect evaporation where it is reconcentrated for water balance control of the Bayer process operation prior to recycle to alumina extrac-tion. Makeup caustic is added to the liquor proceeding to extraction.

It is believed unlikely that major technical difficulties will be experienced in evaporation of the spent liquor, but operation with differing levels of impurities than are present in conven-tional Bayer liquors could cause scaling, corrosion, or other problems. Study of the evaporation of spent liquor produced in a smaller-scale cyclic operation is recommended prior to the design of a demonstration alumina plant based on alunite in order to verify predicted conditions of operation.

Sulfuric Acid Production

Sulfur dioxide gas produced during the reducing roast is cooled, washed, dried, oxidized to SO_3 and then absorbed in 93% H_2SO_4 to make 98% acid. This acid passes to the gas drying step to regenerate 93% H_2SO_4, which is also the product acid.

Potassium Sulfate Evaporation

The combined potassium sulfate-bearing leach liquor and wash-ings are concentrated by multiple-effect evaporation for water bal-ance control of the potash recovery section and to prepare pregnant liquor for potassium sulfate recovery.

Potassium Sulfate Recovery

The solubility of K_2SO_4 decreases sharply with decreasing temperature. Hot concentrated pregnant K_2SO_4 solution from evapo-ration passes to a cooling crystallizer for the production of K_2SO_4 crystals. The crystals are recovered by centrifuging, dried, compacted, and sized to meet physical specifications set by the market place.

Some sodium is present as a substitute for potassium to a limited extent in the alunite molecule. This sodium appears in solution with the potassium, but is undesirable in the product K_2SO_4. Fortunately, the solubility of Na_2SO_4 changes very little with temperature, so that by proper control of operating conditions most of it can be held in solution during crystallization of the K_2SO_4. The concentration of Na_2SO_4 will therefore be enriched in the barren liquor remaining after recovery of K_2SO_4. A bleed stream is taken and sent to disposal at this point to control the buildup of Na_2SO_4. Unfortunately, the barren liquor still contains K_2SO_4, so the loss of a substantial amount of K_2SO_4 in the bleed

stream must be accepted. The remaining major fraction of the barren liquor is recirculated to K_2SO_4 leaching.

Energy Requirements

The net energy consumption is approximately 26×10^6 Btu/alumina because in addition to recovery of alumina by a modified Bayer process, there are substantial requirements for head-end processing before the feed enters the Bayer process. Overall energy requirements are increased because of the low grade of the ore with respect to alumina and the mediocre recovery of alumina; i.e., a relatively large mass of ore must be processed to recover a unit of alumina.

Energy requirements for both roasts and steam generation may be met by the combustion of coal if desired. A clean fuel such as oil must be used for the alumina trihydrate calcination.

Environmental Control

The Draft Environmental Impact Statement discusses environmental control problems encountered in the processing of alunite in considerable detail. In essence, impoundment is planned for all aqueous wastes. Scrubbing is planned for gases containing oxides of sulfur or dust. The environmental control measures described in the report, although costly, appear to be adequate. The presence of sulfur in the ore contributes in an important way to the total cost of environmental control due to the requirement for control of SO_2 emissions and waste water soluble sulfates.

Conclusions

Any process technology developed for the production of alumina from alunite, despite the proving of substantial reserves of alunite ore in Utah, can be of only limited applicability in a worldwide sense, because proven reserves of high-grade alunite are very limited in comparison with anticipated alumina requirements.

More steps are required in the manufacture of alumina from alunite than from some other alumina-bearing raw materials, because alunite contains (in addition to alumina) potassium, sulfate, and silica as major constituents. Capital and energy must inevitably be provided in any alumina process starting with alunite for process unit operations separating the potassium and the sulfate from the substantial amount of silica gangue, and from the alumina, and then for converting these by-products into some marketable form. It is important to note that the market values of sulfuric acid and potassium sulfate, the easiest forms in which to dispose of the sulfur and potassium, are low in relation to alumina.

For every ton of alumina produced from alunite, 1 ton of sulfuric acid and 0.73 ton of potassium sulfate will also be produced. The marketability of large tonnages of these materials raises questions as to what limitations these materials might place on the amount of alumina which could be produced commercially from alunite.

The total process energy consumption is approximately 26.1×10^6 Btu/ton alumina. It is advantageous that approximately 22.2×10^6 Btu of this, including both directly applied process energy and the requirement for steam generation may be supplied by the combustion of coal. The remaining 3.9×10^6 Btu are required for the direct-fired calcination of alumina trihydrate and must be supplied by the combustion of oil or other clean fuel.

Insofar as is known at the present time quantitative reduction of the sulfate associated with aluminum in the entering ore is impractical. Potassium hydroxide equivalent to this unreduced sulfate is therefore supplied in the leaching step following the reducing roast in order to solubilize the unreduced sulfate. This imposes a substantial economic penalty on the process, because the value of the potassium sulfate obtained from conversion of the potassium hydroxide is much less than the cost of this reagent.

It is expected that residual sulfate in the solids entering the Bayer section of the process will tend to build up in the recirculating Bayer process liquor. Some means for removal of this sulfate from the Bayer liquor will probably have to be devised.

Most of the silica gangue in the entering ore is present in a nonreactive form of relatively coarse particle size. However, opal and kaolin have been reported to occur in association with the Utah alunite deposit, and the nature of the geochemical process by which alunite is formed is such that these minerals are likely to be in close association in any alunite deposit. Both the opal and kaolin after calcination will be reactive towards the caustic Bayer liquor. Kaolin which dissolves will contribute some alumina towards the desilication product (DSP) losses. The solution of silica from the opal fraction will cause losses of both soda and alumina in the formation of DSP. These losses in the form of desilication product are expected to be substantial in the process being evaluated here.

The Bayer alumina extraction section of the overall process will require further study in order to meet reduction-grade alumina specifications while achieving an adequately high alumina extraction together with acceptably low soda and alumina losses in desilication. The control of other impurities which are expected to be more troublesome than in the Bayer extraction of alumina from bauxite will also require study. Another question requiring special mention is whether the presence of a small amount of potassium oxide in alumina produced from alunite will cause difficulties in reduction cell operation. A recent published report indicates that acceptable reduction cell operation can be achieved with this alumina, but further study is required.

Solids entering the Bayer process section are expected to contain only 15-20% extractable alumina. The relatively large amount of solids which must be handled, processed, washed, and discarded in order to obtain a unit of alumina is expected to contribute to high costs for the overall process.

It is considered probable, after the above-mentioned studies, that alumina meeting reduction-grade chemical purity and physical property specifications can be produced from alunite.

It is believed that the production of alumina from alunite can be engineered to meet applicable environmental regulations. The presence of sulfate in the alunite will contribute substantially to the cost of the provisions for environmental control.

The overall recovery of alumina from alunite by the process being evaluated is 80-85%. If alunite is to be a source of alumina, it appears desirable to design a process that would be capable of achieving a higher recovery of alumina from the ore, that would not require KOH, that would produce elemental sulfur rather than sulfuric acid, and that would more effectively deal with reactive silica. It is possible that an acidic process might be developed to achieve these goals, although no such process is known at present. Even if such a process were developed, it would be handicapped by capital and energy requirements for separation and recovery of the relatively low value potassium and sulfur, as well as by the low grade of the best alunite ore with respect to the valuable alumina.

Alumina from Clay Via Sulfurous Acid Extraction – Modified Bayer Refining

A. Introduction

The extraction of alumina from clay by means of sulfurous acid has interested many investigators since the latter part of the 19th Century because:

(1) Sulfurous acid is probably the cheapest acid industrially available.

(2) Acid consumed in reaction with iron can be recovered relatively easily.

(3) Aluminum sulfite may be decomposed hydrothermally at 320°F at a comparatively low energy requirement.

Sulfurous acid extraction of clay was carried to its greatest development in Germany, probably because of the unavailability of bauxite there during World War I and anticipation of the same problem in World War II. Sulfurous acid extraction was developed to the point where 8,000 tons/yr alumina were reportedly manufactured in Germany during World War II.

The literature describing the German process is primarily a series of U. S. patents which were issued beginning in the 1930's extending through 1941, an excellent description in Fulda-Ginsberg (14) and some older references tabulated therein. F. A. Peters, P. W. Johnson, and R. C. Kirby have translated the appropriate section of Fulda-Ginsberg. They have used the German experience, the patent literature, and the older references as the basis of U. S. Bureau of Mines Report of Investigations No. 5997, "An Evaluation of the Sulfurous Acid-Caustic Purification Process"(15). There is no known recent published work on sulfurous acid extraction of clay other than one or two Russian papers containing very little information (16). The process evaluated here is fundamentally the same as the one described in considerable detail in USBM RI No. 5997. The only

part of the process description to be given here therefore will be that which is pertinent to the present technical appraisal.

B. Process Description

A summary flow sheet for the process is given in Figure 3.

Calcination

Clay from the mine may be dried if necessary to render it amenable to materials handling and particle size control, following which it is sent to covered storage. Clay is withdrawn from storage and crushed/agglomerated as necessary. It next goes to calcination, which may be direct fired with any conventional fuel including powdered coal.

The rate of solution of clay in all acids is very greatly increased by calcination of the clay for 0.1-2 hrs in the temperature range 1200-1500°F. The reaction is:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \xrightarrow{\Delta H} Al_2O_3 \cdot\ +2SiO_2 + 2H_2O \uparrow$$

Kaolinite   Meta Kaolin

The literature indicates that all of each clay particle being calcined must reach temperature within the above limits in order for activation to occur but that conversion of alumina to the rapidly soluble form occurs in a very short time once the specified temperature range is reached. The required residence time in calcination is therefore largely determined by the size of particles calcined and by the rate of heat transfer to individual particles. Calcined clay particles may be held within the specified temperature range for reasonable periods of time without loss of alumina reactivity, but heating them above this range will cause rapid deactivation of the alumina. Calcination also removes free and combined water and destroys any organic materials which may be present in the clay as mined.

If coal is used for calcination, small particles of ash which may remain in the calcine are not expected to interfere with subsequent processing, because this processing must, in any case, provide for separation of impurities that might be introduced through the leaching of ash and because the particles of ash are expected to be rendered largely inert by the high temperature they will selectively attain during combustion.

An oil-fired rotary kiln is the accepted method of accomplishing this calcination and in practice requires approximately 5.5 x 10^6 Btu/ton alumina. A potentially better method of calcining the clay--but which is not yet proven for this application--is the employment of a fluid bed calciner. This technique could offer the following advantages.

(1) Reduction in thermal energy requirements by up to

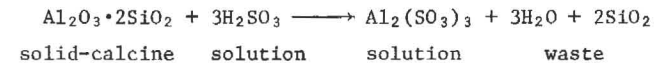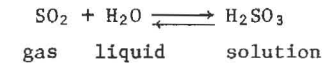Figure 3

ALUMINA FROM CLAY VIA SULFUROUS ACID EXTRACTION

1.5×10^6 Btu/ton alumina.

(2) Better control of and a more uniform calcination of the clay, making possible a higher alumina extraction from the clay.

(3) Delivery to the leaching process of a product calcine having an optimum particle size distribution for leaching and the subsequent solid-liquid separation, with savings in dilution water introduced during washing and capital costs.

(4) Possible capital savings in calciner cost due to decreased residence time.

The above comments apply to all acid processes involving clay calcination, but the use of fluidized solids calcination would appear to be particularly advantageous when leaching with sulfurous acid, because sulfurous is a weak acid and the extraction of alumina was always relatively poor. The major question about the use of fluidized solids techniques for calcination is whether the physical properties of the clay will permit the use of this technique without the generation of excessive amounts of fines having an uncertain degree of calcination.

Leaching

The overall reactions by which the aluminum is solubilized during leaching are:

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$

gas   liquid   solution

$$Al_2O_3 \cdot 2SiO_2 + 3H_2SO_3 \longrightarrow Al_2(SO_3)_3 + 3H_2O + 2SiO_2$$

solid-calcine solution   solution   waste

although the aluminum is only soluble in the presence of an excess of dissolved SO_2.

Sulfur dioxide has only a limited solubility in water, which decreases rapidly with increasing temperature at one atmosphere pressure. The amount of aluminum sulfite which can remain in solution is a direct function of the dissolved sulfur dioxide concentration. The rate of reaction of the calcined clay decreases with decreasing sulfurous acid concentration but increases with increasing temperature. Silica tends to dissolve in the leach liquor, but silica solubility is depressed with increasing dissolved alumina content. These partially conflicting factors led the German investigators to leach the clay semibatchwise in towers at 130°F and 9 atmospheres with about 17% dissolved sulfur dioxide. A maximum of 80% of the alumina was extracted under these conditions in 15 hours to produce a liquor containing a maximum of 60 gpl soluble alumina.

The German engineers chose these leaching conditions after very intensive investigation of the leaching process. It is still

possible that some form of more efficient leaching process could be developed, but this would take a great deal of effort and, even if successful, would not yield a decisive cost reduction. Otherwise, no way is known of improving upon the German approach. The leach can be accomplished as described but will be costly. Inevitable leaks of sulfur dioxide from the pressurized system will cause environmental problems that were ignored at the time the previous work was done but which would be very costly to solve today.

Blowdown

Slurry at the completion of leaching is passed into a blowdown tank for the purpose of removing excess SO_2 and reducing the pressure to atmospheric. The concentrated SO_2 evolved passes into the SO_2 recovery system from which it is eventually recompressed and returned to leaching.

Solid-Liquid Separation

German practice reportedly involved the use of a very large area of leaf filters, with washing in the filter. This would be a very costly operation today. Vacuum filtration is not applicable, because the consequent reduction in pressure would cause further SO_2 evolution and precipitation of alumina. Any contemplated application of sulfurous acid leaching today would almost surely involve an effort to develop a countercurrent decantation system for solid-liquid separation. This would probably be difficult in view of the known reactivity of the silica and the semicolloidal nature of at least a part of it. Unfortunately, the German reports give very little specific information on the properties of the silica residue.

Tailings Disposal

The residue from leaching, although consisting primarily of a reactive silica, is considered to have no value. It is pumped to disposal, probably in a mined-out clay pit. If an analysis of the tailings approximating that given in USBM RI 5997 can be attained, no special precautions would be necessary to insure isolation of tailings drainage water from the environment. Nothing is known about the suitability of sulfurous acid leach residue as subsoil.

First Autoclaving

The purpose of the first autoclaving of the primary liquor stream is to decompose under carefully controlled conditions the dissolved aluminum sulfite so as to produce an insoluble basic aluminum sulfite crystalline in form, and therefore filterable. The overall reaction is:

$$Al_2(SO_3)_3 + 6H_2O \longrightarrow (AlOHSO_3)_2 \cdot 4H_2O + SO_2 \uparrow$$

solution   semicrystalline
                  precipitate
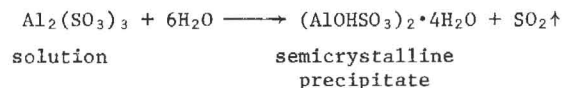
The combined leach liquor and washings from waste solid separation is pumped into heat exchangers where it is heated to 212°F

with heat recovered from acid vapor streams exiting both sets of autoclaves and the thickener overflow from the first autoclaving. The hot liquor is autoclaved for 2 hrs @ 212°F under three atmospheres SO_2 pressure with the direct addition of live steam to precipitate aluminum monobasic sulfite. Sulfur dioxide is evolved and passes to recovery.

The aluminum monobasic sulfite is reportedly crystalline and can be settled or filtered reasonably well although no quantitative data are available. It is thickened in the absence of air, with approximately 55% of the solution as overflow returning to leaching.

Second Autoclaving

A choice is possible at this point in the process between filtration and washing of the thickener underflow from the preceding step followed by mild calcination to produce a modified Bayer process feed, or a second autoclaving to decompose hydrothermally the basic sulfite produced in the first step. Fulda-Ginsberg reports that development of the hydrothermal decomposition, in which the trihydrate produced retains the crystal structure of the basic sulfite, was considered to be an important technical advance.

The overall reaction is:

$$(AlOHSO_3)_2 \cdot 4H_2O \longrightarrow 2Al(OH)_3 + 2SO_2 \uparrow + 2H_2O$$

Semicrystalline   Semicrys-   Gas   Liquid
precipitate   talline
                   precipitate
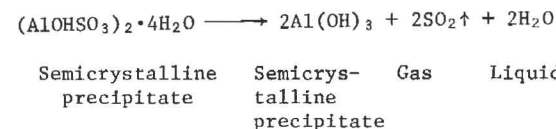
The thickener underflow from the preceding step is pumped first to heat exchangers and then into the second autoclave. This autoclave is maintained at 310°F and 7 atmospheres, primarily steam pressure, for at least 10 minutes by means of indirect steam heating. A mixture of SO_2 and steam boils off which, after some heat recovery, goes to the acid regeneration system.

The precipitation of alumina trihydrate in the second autoclaving as reported by the German investigators appears technically feasible, but no mention is made in Fulda-Ginsberg of difficulties probably encountered. Scaling of metallic surfaces is to be expected, and apparently the trihydrate readily adsorbed impurity metal hydroxides.

Filtration and Washing

The residual slurry is thickened, filtered, and washed to yield a crude trihydrate. The mother liquor is boiled at atmospheric pressure to recover some additional SO_2 and is then discharged to waste. No information is available, but it is known that the oxidation of S^{+4} to S^{+6} by the reaction

$$SO_3^= + \tfrac{1}{2}O_2 \longrightarrow SO_4^=$$
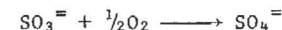
or by the disproportionation reaction

$$2H^+ + 3SO_3^= \longrightarrow 2SO_4^= + S^0 + H_2O$$
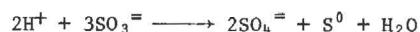
is a continuing problem throughout most of the steps in the manu-facture of alumina via sulfurous acid extraction. It is probable that this mother liquor contains sufficient dissolved materials--sulfur in a multiplicity of valence states in particular--to render it unacceptable for return to leaching, for use as acid absorber water, or as a discharge to the environment. An R&D effort will be required to determine what disposition can be made of this 13 mass units of liquor per mass unit of alumina product.

Technical Evaluation of Preceding Steps

The German effort to utilize sulfurous acid in the manufacture of alumina from clay is the only known reported actual experience with this acid and therefore is the only basis for technical evalu-ation of the foregoing steps. All of the steps appear reasonable although very little of the quantitative information that would be required for an engineering design of the process has been reported. It is concluded that the process could be operated as described but that the thermal energy requirements--with the possible exception of the clay calcination step--would be approximately the same as reported in German practice. Some improvement in crude alumina trihydrate product quality would probably be obtained from the use as raw material of U. S. kaolin, which is of a better quality than the German clay. The Germans did intensive research on the basic process to bring it to the present state of development. Environ-mental protection, which was of little or no concern in wartime Germany, would be a major problem today.

Acid Recovery System

Makeup sulfurous acid is provided by burning sulfur with air and then absorbing the SO_2 into water at 3 atmospheres. Approxi-mately 11.4 mass units water/mass unit alumina are required for this absorption. This water is rejected from the process as waste liquor from the settling-filtration following the second autoclav-ing; but if present day environmental considerations required treat-ment of this waste liquor involving evaporation, a substantial addi-tional process energy requirement for evaporation would result, because the amount of absorber water cannot easily be reduced.

Sulfurous acid produced at 3 atmospheres is pumped into a sec-ond absorber operating at 9 atmospheres in which it is combined with various recycle streams to prepare the leach acid.

Sulfur consumption is as high as approximately 20% on product alumina. An unknown fraction of the sulfur loss must be due to leakage from the pressurized system although it is very much to the German design engineers' credit that they succeeded in design-ing an almost totally closed system.

Another fraction of the sulfur loss is due to oxidation of SO_2 to $SO_4^=$ in solution. Some of the required oxygen undoubtedly comes from the air, but it is known that a large part of it comes from the reduction of SO_2 to elemental S. Sulfur compounds of other valences also formed to an unknown extent.

An operable acid recovery system incorporating provision for adding makeup can be designed on the basis of presently available information. Unfortunately, there is no known solution to the problem of sulfur disproportionation in the process, which is a major cause of sulfur consumption and which also interferes in the modified Bayer refinement as discussed below.

Modified Bayer Refining Process

The German investigators were never able to produce an alumina of reduction grade quality from the sulfurous acid process directly. Alumina trihydrate produced in the second autoclaving was therefore refined in a modified Bayer process. The removal of iron originally in the clay was deliberately avoided in order to facilitate the removal of titanium, chromium and vanadium by coprecipitation with iron in the Bayer treatment.

The alumina trihydrate from the second autoclaving was an exceptional Bayer process feed, reportedly going readily into solu-tion in caustic soda as one atmosphere and 140°-170°F with warming of the liquor from the heat of solution to 195°-200°F. The German feed contained approximately 10% Fe_2O_3 and 0.5% SiO_2, but feed pre-pared from lower iron content U. S. kaolin would undoubtedly con-tain substantially less iron. Not discussed in terms of its effect on the Bayer refining was 2-2.5% elemental sulfur produced by dis-proportionation. This sulfur is very finely divided and would be expected to dissolve in the Bayer process liquor. Special measures would be necessary for its control in a cyclic process. On the other hand, sulfite refined feed derived from calcined kaolin would contain no organics, which would tend to simplify the caustic puri-fication step.

The technology of the caustic purification step, with the exception of dealing with a feed containing reactive elemental sul-fur in the amount indicated, is well known; and a demonstration plant can be designed without additional pilot work. It is expected that demonstration plant design information required for sulfur control can be developed from bench-scale studies.

Alumina Product Quality

There appears to be no hope, based upon intensive German research, for producing alumina meeting reduction-grade specifica-tions without caustic purification. There appears to be no doubt that sulfurous acid extracted alumina which has been subjected to caustic purification will meet the chemical and physical properties specifications for reduction-grade alumina, and that such alumina will be interchangeable with Bayer alumina produced from bauxite.

Energy Requirements

Coal may be used for clay calcination and for the generation of steam. The final product alumina calcination, assuming that present day Bayer process technology is used, will require a high grade fuel which will not compromise the product alumina quality.

The total of 28.2 x 10 Btu/ton of alumina for the overall
process is high because the clay requires calcination, the maximum
soluble alumina loading which is possible in the leach liquor is
low, the hydrolysis of the intermediate aluminum salt is carried
out in two stages, and the primary product alumina is put into solu-
tion twice during the processing sequence. It is possible that the
heat requirement for clay calcination may be reduced by the employ-
ment of fluidized solids calcination. The requirement for steam
may probably be reduced a substantial but presently unknown amount
by extensive and innovative heat recovery design. On the other
hand, approximately 13 mass units of waste liquor/unit product alu-
mina are now planned to be discharged to the environment. If this
discharge cannot be accomplished under today's environmental pro-
tection standards without resort to a fuel-fired evaporative
process, a very substantial process energy requirement will be
added to the total.

Environmental Protection

Waste solids are expected to be disposed of in exhausted clay
pits. The properties of the solids as subsoil are not known, but
the water accompanying the waste solids is not expected to present
any particular problem. Iron and minor constituent metal oxides
will be discharged from the caustic purification section as a red
mud similar to Bayer process red mud but in much smaller quantities.
This mud will require impoundment in a manner similar to bauxitic
Bayer process red mud. The nature and disposition of caustic puri-
fication sulfur-bearing residues is unknown. The treatment required
and disposition of waste process liquor (as discussed in preceding
sections) is unknown.

The absorption of SO_2 into water is very difficult in the pres-
ence of inerts. This process has been carefully designed as a
totally closed system so as to avoid this problem. Leaks from the
pressurized processing system may however cause environmental
problems.

Conclusions

(1) Pressurized acid preparation, digestion, and two stages of
thermal hydrolysis are required.

(2) A relatively long period of time is required for the digestion
of calcined clay with sulfurous acid, even under pressure, and even
then only about 80% of the alumina is extracted.

(3) Air must be rigorously excluded from digestion, the two stages
of thermal hydrolysis and the thickening/filtration operations
associated with thermal hydrolysis in order to minimize the oxida-
tion of sulfite to sulfate. Even with exclusion of air, sulfate,
elemental sulfur and sulfur compounds of other valence states are
formed which together with other losses impose a makeup sulfur
requirement of up to approximately 20% by weight on alumina. Any
original advantage of inexpensive acid is lost by conversion of the
SO_2 to nonrecyclable forms.

(4) The process has very little ability to separate alumina from
impurity metal oxides in the entering clay, and silica is not
rejected adequately. Even after intensive study, a caustic purifi-
cation (modified Bayer) process appears to be required in order to
manufacture alumina meeting reduction grade specifications.
Alumina so prepared should be of excellent quality and interchange-
able with Bayer alumina produced from bauxite.

(5) Energy requirements are high despite the relatively low heat
of formation of aluminum sulfite from the oxides because of the low
solubility of alumina in the leach liquor, the employment of a two-
stage thermal hydrolysis, and the requirement that the primary
product alumina stream be put into solution twice. The energy
requirement will be substantially increased if it is found, as is
probable, that approximately 50% of the leach liquor, which in war-
time Germany was apparently simply discharged to the environment,
must be subjected to evaporation. A substantial amount of elec-
trical or other equivalent energy is required for gas compression.

(6) The low alumina loading achievable in process liquors will
influence both capital and operating costs.

(7) The relatively easy hydrothermal decomposition of the inter-
mediate aluminum sulfite is a distinct process advantage.

(8) Air and water environmental control problems, of little or no
concern at the time of the major thrust of process development,
would be difficult and costly to solve so as to meet today's
standards.

(9) The extraction of alumina from clay with sulfurous acid has
received intensive study in the past. There is no known body of
new technology which, if applied to sulfurous acid extraction,
could result in a major cost reduction. It is concluded that the
process as it exists is approaching the maximum state of development.

Alumina from Clay Via Nitric Acid Extraction

A.   *Introduction*

The first reported serious investigation of the use of nitric
acid in the manufacture of alumina took place in the early years
of the twentieth century in Norway where nitric acid was manufac-
tured by the Birkland-Eyde process employing inexpensive hydroelec-
tric power and where there are no deposits of bauxite. Natural
advantages of working in the nitrate system include the following:

(1) Iron has a very low solubility in solutions of aluminum nitrate
in which there are somewhat less than three moles of nitrate per
mole of aluminum.

(2) Aluminum nitrate in the presence of water is decomposed by heat
at fairly low temperatures to the oxide. This decomposition is
quantitative at higher temperatures with the result that no foreign
substance is introduced into the reduction cell due to incomplete
decomposition.

(3) Most, but unfortunately not all, of the nitrate volatilized during decomposition can be recovered as acid by direct condensation. Most of that not recovered in this manner may be recovered by installation of nitrogen oxide scrubbing/absorption equipment.

(4) Nitric acid is a strong acid. The solubility of silica in it is small, and silica precipitated upon the decomposition of meta kaolin by nitric acid tends to be nongelatinous and relatively easy to separate from the resulting solution.

(5) Aluminum nitrate, like other nitrates, is quite soluble in water, and its solubility increases sharply with increasing temperature. Up to almost 200 gpl alumina may therefore be carried in hot solutions, and process liquors are relatively free from scaling problems.

(6) Some purification will be achieved in the fractional crystallization of $Al(NO_3)_3 \cdot 9H_2O$.

The use of nitric acid received further impetus from development of the Haber process for ammonia and from the development of corrosion resistant alloys for apparatus construction. Intensive investigation in Germany prior to World War II culminated in the "Nuvalon" process, which was tested at what today would be considered a semicommercial scale. This process employed less than stoichiometric amounts of acid in relation to clay in order to minimize iron and titanium solubility. Leaching was done at elevated temperature under pressure in order to maximize alumina recovery in the presence of the reduced amounts of acid.

During the perior following World War II much was learned from the U. S. Atomic Energy program about the application of aqueous nitrate systems to hydrometallurgical processes. The mature development of the use of low-cost U. S. natural gas as a feed stock in the manufacture of ammonia reduced the cost of nitric acid to what was probably an all-time low in relation to the cost of other acids. Finally, the development of liquid ion exchange technology for the separation of iron from aluminum made possible abandonment of pressurized leaching while improving product alumina quality along with yields of alumina from the clay. These factors together with the need to develop a process for the manufacture of alumina from domestic resources probably have been responsible for development of the process which is the subject of this evaluation.

The evaluation is based primarily upon data derived from the May 1975 Boulder City mini-plant run, the work of Peters (17), and that of Margolin and Hyde (18). Other information has been supplied by the A. D. Little Company, and by the Idaho National Engineering Laboratory (INEL) (19).

B. *Process Description*

A summary flow sheet appears as Figure 4.

Figure 4

ALUMINA FROM CLAY VIA HNO$_3$ EXTRACTION
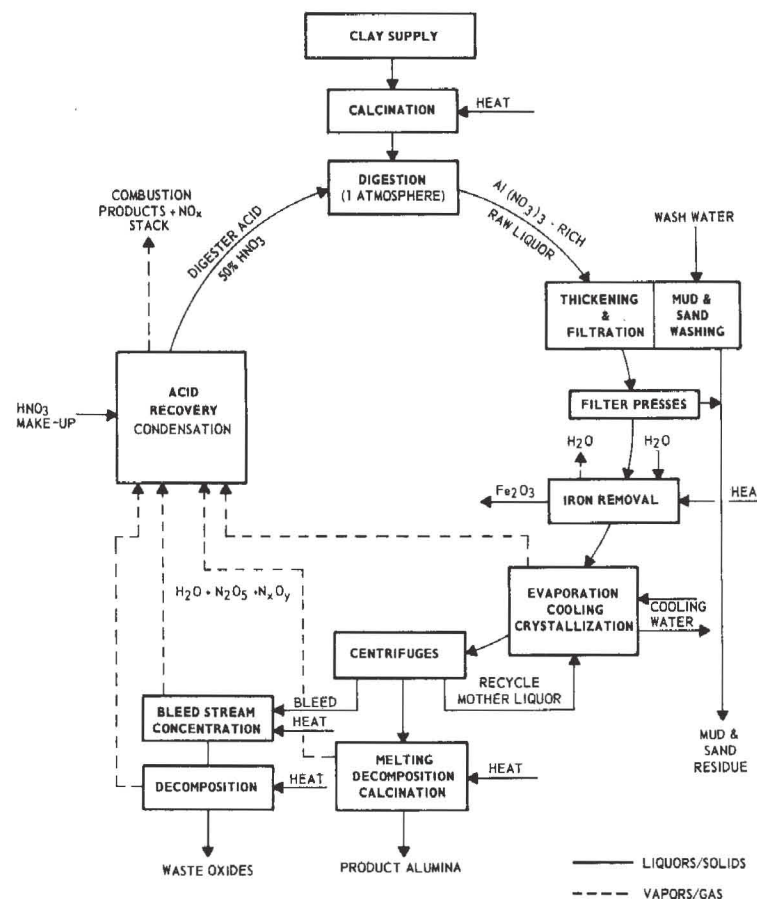
Calcination

Entering clay is first calcined as discussed under sulfurous acid extraction.

Leaching

The primary leaching reaction is:

$$Al_2O_3 \cdot 2SiO_2 + 6HNO_3 \longrightarrow 2Al(NO_3)_3 + 3H_2O + 2SiO_2$$
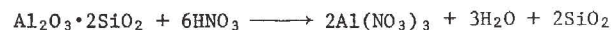
| Meta Kaolin | Solution | Solution | Waste |

Leaching in the process being evaluated is carried out using a small stoichiometric excess of acid at boiling and one atmosphere pressure for reasons discussed under solvent extraction.

The technology for leaching is well developed. It is expected that calcined clay and acid will be simultaneously and continuously metered into the first of a series of covered, gently agitated tanks. These tanks can be of carbon steel construction with a polymeric lining to protect the steel, and with an inner lining of acid resistant brick. The leaching reaction will be sufficiently exothermic to maintain the tanks at boiling. Some vapors comprising a mixture of HNO_3, H_2O, and NO_x arising from the boiling liquor will be conducted to a condenser. The HNO_3 and H_2O will be returned to the leaching system. The NO_x must be subsequently recovered in an absorber.

It is expected that 95% of the alumina content, about the same percentage of the iron content, and lesser percentages of minor constituent metal oxide impurities in the clay will dissolve during a 4-hr leach with 105% of the stoichiometric acid requirement at temperatures of 240°-250°F. The amounts and percentages of minor constituent impurity metal oxides which dissolve will depend in part upon the mineralogy of the specific clay.

Some published literature suggests that after much further research and development work it might be found practical to leach clay with this strong acid without prior calcination of the clay either at one atmosphere at boiling in the presence of some recycling dissolved fluoride as a catalyst, or at elevated temperature and pressure. Unfortunately, insufficient information was available to permit consideration of this potentially attractive approach in the present evaluation.

Solid-Liquid Separation

Undissolved solids in the slurry emerging from the leach must be separated from the leach liquor, washed as free as economically possible of adhering liquor, and then conveyed by some means to a tailings disposal area, which will probably be a clay pit in the vicinity where mining has been completed. The technology required for the engineering design of this operation is well known, provided that the following are known as well: the relative amounts of liquor and solids, the particle size distribution of the solids,

their amenability to flocculation and the settling rate of the flocculated particles, the degree of dissolved solids recovery required, the density, and viscosity of the solutions. Enough is known about the properties of the residue and solution produced by nitric acid leaching of Georgia clay to make possible the <u>preliminary</u> engineering design of a multistage countercurrent decantation washing system.

Much work remains to be done on optimizing the residue solid-liquid separation operation. This will also require further study of leaching, because initial acid concentration, leach time, and even the manner in which the calcined clay and entering acid are initially mixed can influence the physical properties of the silica leach residue. The design of a leaching system tending to preserve the particle size distribution in a calcined feed clay of selected particle size distribution could permit the initial separation as sand of a substantial mass fraction of the silica. An effective flocculant could greatly reduce the required settler area. No problem appears to exist that would actually prevent operation of the process, but the amount of dilution water introduced to the process in actual operation could vary substantially, influencing both energy costs and the capital required for subsequent evaporation. There could also be a wide variation in the capital requirement for settler/filters.

Iron Removal by Solvent Extraction

The U. S. Bureau of Mines and the A. D. Little Co. have proposed the removal of dissolved iron from the leach liquor by solvent extraction with a mixture of di-ethyl-hexyl phosphoric acid (DEHPA) and tri-butyl phosphate (TBP) in kerosene solvent. Stripping is accomplished by contacting the iron-loaded organic phase with hydrocholoric acid. The iron passes back into the aqueous phase as an anionic chloride complex with simultaneous regeneration of the organic phase for recycle.

There is little doubt that the solvent extraction step will remove iron to produce a primary liquor stream meeting the iron specification, but some important technical problems with respect to this method of iron separation remain unresolved. The iron loaded into the organic phase coextracts some nitrate from the primary leach liquor. Aqueous hydrochloric acid is required for stripping, but chloride and nitrate ions must be kept separated in order to avoid their interaction which would result in loss of reagent together with severe corrosion problems. The iron-loaded organic phase must therefore be washed with water to ensure the complete removal of nitrate before contact with the hydrochloric acid stripping solution. Some residual iron in the stripped organic complexes with HCl and thereby carries some of the chloride into the organic phase. The regenerated organic must again be washed with water to remove this chloride and avoid carrying it back into the primary nitrate liquor stream.

These three aqueous streams represent important losses of nitrate, organic extractant, and alumina occurring in combinations which cannot be discharged to the environment. A possible use for

the first nitrate wash solution may be to wash waste solids.

The iron-bearing, used HCl solution is first treated with H_2SO_4 and then evaporated to produce a waste $FeSO_4$ sludge and recover most of the HCl.

The second chloride wash solution, because of its chemical nature, will be difficult to process for recovery of its constituents, and the method of doing so is not known. The reprocessing/utilization of these streams is an important problem that requires solution before nitric acid could be employed commercially in the extraction of alumina from clay.

The use of this solvent extraction also presents a hazard in that an operational upset could cause the introduction of chloride into the acidic primary nitrate liquor with consequent severe metallic corrosion problems.

The alternative to removal of iron by solvent extraction is to leach the calcined clay with a substoichiometric quantity of nitric acid at elevated temperature and pressure to repress the solubility of iron while maximizing that of alumina, or to add back a portion of substoichiometric nitrate solution prepared by distillation to a quantity of leach liquor prepared by stoichiometric leaching at atmospheric pressure and then autoclave the mixture for a period of time to precipitate iron. It is presumed that the German investigators, since the solvent extraction technique was not known at the time of their work, thoroughly studied both variations of substoichiometric iron rejection before choosing pressurized leaching. In either case, lengthy pressurized treatment of the primary liquor stream at elevated temperatures, with the attendant technical problems and costs, is required. Unfortunately, insofar as can be determined, the achievable iron rejection also is inadequate in terms of present day Fe_2O_3 specifications in the product alumina without resorting to multiple crystallizations of the $Al(NO_3)_3 \cdot 9H_2O$. Consequently, solvent extraction was the iron removal method chosen for the process being evaluated. Data on iron removal via solvent extraction was available from the U. S. Bureau of Mines mini-plant.

Evaporation

Evaporation under vacuum removes from the solvent extraction raffinate approximately 2.7 mass unites H_2O/unit product alumina. The condensate contains approximately 0.5% HNO_3.

Crystallization

The preceding vacuum evaporation yields a liquor which at temperatures lower than those prevailing in the evaporator is supersaturated with respect to aluminum nitrate. This liquor is cooled evaporatively in at least two stages of crystallization to prepare $Al(NO_3)_3 \cdot 9H_2O$. The crystals are recovered by centrifuging and then may be washed with 50% nitric acid. The used wash acid would go to leaching. The major part of the centrifugate is recycled to evaporation, but a fraction of it is diverted as a bleed stream in order to control the buildup of minor constituent metal nitrates. This

bleed stream may, of course, be subjected to further evaporation and crystallization to reduce losses of $Al(NO_3)_3 \cdot 9H_2O$, the impure crystals so recovered being redissolved in the primary leach liquor. Subsequently, the bleed stream is processed for recovery of contained nitrate values.

A recent patent indicates that the amount of the bleed stream may be substantially reduced and final crystal purity improved by operating with a higher level of impurities in the crystallizer and producing slightly impure crystals. These crystals are then redissolved in pure water from which $Al(NO_3)_3 \cdot 9H_2O$ is recrystallized. The recrystallized material is washed with water, which is also used countercurrently to wash the crystals initially produced. This procedure is virtually certain to achieve both of the above objectives but at a considerable cost for increased capital and energy for evaporation.

Results from the mini-plant studies and the teachings of the patent referred to above suggest that the separation factor between aluminum and other metals is not high, although there is little doubt that the crystallization can be engineered to produce $Al(NO_3)_3 \cdot 9H_2O$ crystals of the required purity. Insufficient data are available in the published literature to evaluate the optimum number of crystallizations versus bleed stream losses, so for the purposes of Task 1, the process evaluated has been based upon the U. S. Bureau of Mines flow sheet employing a single crystallization and at the same size bleed stream as has been assumed in evaluating the hydrochloric acid processes. Additional crystallization studies would be required prior to a demonstration plant design to determine the optimum trade-off between crystal growth rate per unit crystallizer volume, crystal size, washing procedure and amount of wash liquid, the number of crystallizations, consequent evaporation, and the size of the bleed stream.

Decomposition

It is expected that $Al(NO_3)_3 \cdot 9H_2O$ crystals of requisite purity will be melted at 165°F in their water of crystallization. The resulting liquor will be sprayed onto existing alumina particles in a series of indirectly heated beds fluidized by recycled decomposition products, or by stream. The film of liquid acquired by any given particle in this rapidly circulating hot bed will decompose almost instantaneously to form an onion-skin-like layer of oxide containing only a fraction of the nitrate originally present. The amount of residual nitrate in the bed product is an inverse function of the temperature at which the bed is operated and the solids residence time.
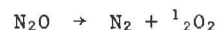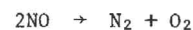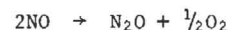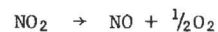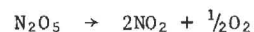
In practice, in order to obtain the highest thermal efficiency and to minimize exposure of the nitric acid/nitrogen oxide vapors to high temperatures, the decomposition will probably be carried out stagewise with the solids subjected to increasing temperatures in succeeding stages as decomposition is carried to completion. It is expected that the final stage of decomposition will be carried out in a direct-fired fluid bed under slightly reducing conditions at 1500°F to destroy the last traces of nitrate in the product alumina.

The idealized overall reaction for the decomposition is:

$$2Al(NO_3)_3 \cdot 9H_2O_{(l)} \rightarrow Al_2O_{3(c)} + 6HNO_{3(g)} + 15H_2O_{(g)}\uparrow$$
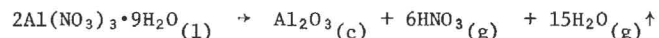
The estimated net energy requirement for this reaction is approximately 20.8 x 10^6 Btu/ton alumina.

Some undesired gas phase reactions also occur to varying degrees dependent upon the temperature and the residence time of the gases within the decomposer, the composition of the gaseous phase, and possibly upon catalytic properties of the alumina itself or of metal surfaces within the decomposer:

$$2HNO_3 \rightarrow N_2O_5 + H_2O$$

$$N_2O_5 \rightarrow 2NO_2 + \tfrac{1}{2}O_2$$

$$NO_2 \rightarrow NO + \tfrac{1}{2}O_2$$

$$2NO \rightarrow N_2O + \tfrac{1}{2}O_2$$

$$2NO \rightarrow N_2 + O_2$$

$$N_2O \rightarrow N_2 + {}^1_2O_2$$

The oxides of nitrogen are thermodynamically unstable at ambient temperature and at all temperatures encountered in the decomposer; if thermodynamic equilibrium was attained, decomposition to N$_2$ and O$_2$ would be virtually complete. Fortunately, the kinetics for decomposition reactions yielding the elements are such that only a small amount of decomposition to the elements normally occurs excepting at temperatures higher than those required for carefully designed decomposition. N$_2$O$_5$, NO$_2$, and NO also can be at equilibrium with each other, O$_2$, and H$_2$O. Increasing the temperature shifts these equilibria sharply in the direction of oxides with lower oxygen content whereas lowering it shifts the equilibria in the direction of the higher oxides/liquid acid. It is therefore desirable to operate the decomposer at the lowest possible temperature and with the shortest possible gas residence time to minimize the decomposition of nitric acid and any higher oxides of nitrogen, but it is also possible to reconstitute acid from NO and NO$_2$ in the presence of O$_2$ and H$_2$O in the acid condenser/absorber. N$_2$O$_5$ requires only the presence of H$_2$O.

Nitrogen oxides which have decomposed so as to form N$_2$O or N$_2$ cannot be reoxidized and recovered as acid in the condenser/absorber and are irretrievably lost. N$_2$O usually does not form in the absence of a reducing agent, but small amounts of it formed by an unknown mechanism were observed in gases exiting a decomposer operated at 750°F by the Idaho National Engineering Laboratory (INEL). The decomposition of NO to N$_2$ is reported to be very slow at temperatures below about 1200°F. Detection of the formation of N$_2$ is difficult, because it is inert and because under process conditions a substantial amount of N$_2$ derived from air is likely also to be present. The easiest way to detect loss of nitrate by decomposition to N$_2$ is usually by difference.

Nitrate decomposition studies carried out by INEL at 750°F, a higher temperature than would be used when one of the goals would be maximum nitrate recovery, did permit construction of a nitrogen balance. Calculations based upon gas analyses and other data obtained from INEL showed decomposition to N$_2$ and O$_2$ of approximately 14% of the nitrate fed to a decomposer operating at 750°F. A material balance for a decomposition process operating at 400°F showed the disappearance of 7.4% of the nitrate fed to decomposition. The evidence is quite strong that the decomposition of some nitrate to N$_2$ and N$_2$O does, in fact, take place. A possible explanation for the observation of larger losses of nitrate by decomposition to N$_2$ than would be expected from reported studies of the decomposition of nitrogen oxides is catalysis of the decomposition by the large mass of reactive alumina, or by metal surfaces present in the decomposer at any given time. Another possible explanation is a decomposition reaction mechanism which produces N$_2$ and O$_2$ directly. Some further reduction of nitrate loss to N$_2$ may be possible by careful engineering of the decomposition process or by means of some presently unknown technique, although 400°F for various reasons is probably close to the minimum temperature practical for industrial scale decomposition.

There is little doubt that Al(NO$_3$)$_3$·9H$_2$O melted in its water of crystallization can be decomposed to Al$_2$O$_3$ using fluidized solids techniques with indirect heating of the bed; INEL has already accomplished this at what would today be considered pilot scale. They operated a liquid NaK heat transfer system as a heat source for decomposition for approximately 40,000 hours with very little corrosion on the NaK side or other problems and also experienced no significant corrosion/erosion on the nitrate side of the heat transfer surfaces over the same period of time. INEL also solved successfully the problems of introducing a viscous liquid into the bed, and of controlling bed particle size.

The INEL effort was unconcerned about the recovery of nitrate. Required before the construction of a demonstration plant for the manufacture of alumina via nitric acid extraction from clay is the development of a decomposer-acid recovery design capable of producing reduction-grade alumina with an acceptable nitrate recovery, and verification of the cost, operability, and acid recovery for the design.

Bleed Stream Treatment

Filtrate from the recovery of Al(NO$_3$)$_3$·9H$_2$O crystals is saturated with respect to Al(NO$_3$)$_3$, which together with free HNO$_3$ comprises approximately 45% by weight of this stream. It is unfortunate that this is the least disadvantageous stream from which to withdraw the bleed stream taken for the control of soluble impurities other than iron, because taking the expected required amount of bleed will result in rejection along with impurities of a substantial amount of previously dissolved alumina. It is probable that further study of the crystallization and/or washing the product crystals with concentrated acid would provide the basis for reducing the size of the bleed stream while still meeting product specifications. The amount of reduction achievable and the effort required are unknown.

It is also probable that the amount of bleed stream taken relative to alumina production may be reduced when the raw material is a clay containing only very small amounts of acid soluble accessory minerals, or if the accessory minerals present are only slightly soluble in the acid. Conversely, as examples, the presence of acid soluble potassium and phosphate minerals would tend to increase the bleed stream requirement, because the potassium and phosphorus specifications for the product alumina are very low. The effect of accessory minerals in specific clays on the bleed stream requirement has not been studied to date. It probably would be economical to evaporate, cool, and possibly even chill the bleed stream to recover for recycle a fraction of its contained aluminum nitrate. Impure crystals so obtained would be redissolved in the primary liquor stream prior to evaporation.

It is expected, in order to recover the contained nitrate values, that the bleed stream will be decomposed in a process and apparatus very similar to the one used for final product recovery. In this case a waste solid oxide will be produced suitable for disposal. The amount of bleed stream to be processed per unit of final product obviously will have an important bearing on total energy consumption per unit of final product. All of the comments in the previous section pertaining to further study of $Al(NO_3)_3 \cdot 9H_2O$ decomposition apply equally to decomposition of the waste stream.

Acid Recovery

Acid which is present in the vapor phase as HNO_3 may be recovered by simple condensation. Nitrate which has undergone decomposition to oxides of nitrogen will require a more complicated absorption system. The proportion of nitrate present in decomposer off-gases as HNO_3 will tend to increase as the temperature of decomposition is decreased and with increasing partial pressures of steam. The use of auxiliary steam will facilitate both decomposition and acid recovery but will increase energy costs for provision of the steam and for later removal by evaporation of the added water. Thermal decomposition should be studied in conjunction with acid recovery to optimize these interrelated operations. It would be necessary to do this study before designing a nitric acid alumina demonstration plant.

Energy Requirements

The total net thermal energy required by the process is 37.0 x 10^6 Btu/ton alumina. Gross fuel energy requirements will be somewhat higher. The energy requirement for clay calcination may be reduced somewhat by employing fluidized solids rather than rotary kiln calcination. Coal may be used as the energy source with either method of calcination but with the requirement of some development work. The energy required for evaporation may be reduced to some extent if the leaching-solid-liquid separation system is studied further to optimize it, thus minimizing primary liquor dilution. Coal will probably be used to generate steam required for evaporation.

The heat required for nitrate decomposition is by far the largest process energy input. Coal may be employed as fuel to supply the indirectly fired major part of the decomposition heat load. A relatively small amount of clean fuel will be required for the final direct fired, higher temperature, reducing calcination which removes the final traces of nitrate from the product alumina.

A substantial amount of heat may be recovered from the condensation of nitric acid vapors produced by aluminum nitrate and waste nitrate bleed stream decomposition. This heat may be used in evaporation although its utilization will require innovative engineering design effort. Such effort is expected to be worthwhile, because utilization of this heat offers a significant capital as well as operating cost savings.

The energy requirement for bleed stream treatment will vary in accordance with the amount of bleed actually required. This would be determined from sustained cyclic process operation.

Environmental Impact

The extraction of alumina from clay via nitric acid will require total impoundment of the waste solids from leaching in order to prevent loss to the environment of nitrates/nitric acid remaining in the waste solids which will be discarded. Spillage and dilute solutions of nitrates will require similar containment. It is possible that very dilute solutions of nitrates ultimately recovered from the drainage of waste solids or from other sources may be returned to the process as wash water, nitrogen oxide absorber water or in some other way. In some climates an excess of these solutions could be concentrated by solar evaporation in open ponds prior to return to the process.

Alternates include, but are not limited to, use of the waste nitrate solutions as agricultural irrigation water or reduction of the nitrate to elemental nitrogen by soluble organic materials such as methanol followed by disposition of the remaining water to the environment.

A small amount of gaseous nitrogen oxides will be produced during leaching by the oxidation of ferrous to ferric iron. A much larger--but presently unknown--quantity of nitrogen oxides will be produced by nitrate decomposition. Under conditions wherein these oxides are not in admixture with large quantities of combustion gases, recovery of them by absorption employing known technology to meet existing environmental control standards is possible. It is not known but is doubtful whether a sufficient degree of recovery can be achieved at an acceptable cost of nitrogen oxides from decomposition that are mixed with combustion products.

Alumina Product Quality

There are no known published alumina analyses from a nitric acid extraction process operated under industrial conditions in accordance with the flow sheet being evaluated here, but product analyses from the mini-plant operation give reason to believe that,

with refinements in the process and some changes in materials of construction to avoid the presence of metallic corrosion products, reduction-grade alumina chemical specifications can be met. As stated in a preceding section, the ratio of the bleed stream to primary alumina product required to meet reduction-grade specifications when working with a specific raw material may vary.

The extent to which nitrate may be economically removed from the alumina product is not known. It is expected that any residual nitrate will be expelled upon addition of the alumina to the reduction cells. The presence of NO_x in the cell off-gases would require additional provision at the reduction plant for environmental control. Such provision would be costly.

Conclusions

The following conclusions are offered in regard to the production of alumina from clay via nitric acid extraction:

(1) The price of ammonia used as the primary raw material in the manufacture of makeup nitric acid has escalated by a factor of at least 4 in the last 7 years. This escalation is due in large part to the decreasing availability and increasing cost of natural gas. It is a trend which can only continue.

(2) The energy requirement for producing alumina via nitric acid extraction is relatively high. This is because:

(a) Aluminum nitrate nonahydrate forms in the crystallization step relied upon for rejection of impurity metals other than iron. Decomposition of the nonahydrate requires a large amount of heat.

(b) The chemical nature of the process requires that all of the water in which the aluminum nitrate is dissolved as it passes out of the leaching step must eventually be vaporized.

(c) Water must be added to the process in the absorption of nitrogen oxides and very probably in thermal decomposition to inhibit the decomposition of nitrate to nitrogen oxides. Any water so added is supplied as steam and then must subsequently be removed by evaporation.

(d) Hydrochloric acid solution used to regenerate organic solvent in iron removal is regenerated by sulfuric acid treatment followed by distillation. This distillation requires a substantial amount of energy.

(3) Environmental control will be relatively costly. The nitrate ion does not normally occur naturally in groundwater and is very undesirable even in extremely small concentrations. The oxides of nitrogen are undesirable air pollutants and are costly to control.

(4) The nitrate group is not stable under some conditions that cannot be avoided in the process, with the result that a fraction of the nitrate present decomposes to various oxides of nitrogen

during the processing cycle. This acts to increase the process capital as well as energy requirements. Additionally, there will be in practice an unavoidable loss of nitrate by decomposition to the lower oxides of nitrogen and to elemental N_2. The amount of this loss has not been precisely established, because the process has not yet been operated with a sufficiently accurate material balance. Such a loss could easily be large enough to have economic significance.

(5) The selection of organic polymeric materials available for handling nitric acid and nitrate solutions is restricted by the chemical nature of the nitrate group. Metallic materials of construction are available for handling nitric acid and its salts but only in the absence of chlorides. The latter are ubiquitous in the natural waters on the surface of the earth, and could also be introduced into the primary liquor stream of the process being evaluated by an upset in the iron removal section, thus presenting a possibility for severe corrosion of metals in contact with the liquor stream.

Alumina from Clay via Hydrochloric Acid Extraction - Evaporative Crystallization

A.   *Introduction*

Interest in the use of hydrochloric acid as a means of extracting alumina from clay has existed since the turn of the century. Early investigators noted that:

(1) It was relatively easy to operate the leaching process so as to obtain almost quantitative separation of silica, and the silica was in a form which could be filtered and washed easily.

(2) Hydrochloric acid is an aggressive reagent which, after clay calcination, will dissolve up to 98% of the alumina in many U. S. kaolin clays with 2 hours leach time at the boiling temperature and at atmospheric pressure.

(3) The leaching process is exothermic, making it easy to reach and maintain the boiling temperature.

(4) Iron in the clay dissolves in about the same proportion as alumina. Titanium, sodium, potassium, calcium, and magnesium present in small amounts in accessory minerals tend to have much lesser, but variable, solubility in hydrochloric acid.

(5) High solution loadings of up to 200 g/ℓ dissolved alumina are possible in the chloride system.

(6) Aluminum chloride hexahydrate can be crystallized from solution in a simple crystal of controlled particle size distribution. Only one hydrate forms, and the crystals are readily washed. Complex salts containing other substances do not form easily.

(7) Aluminum chloride hexahydrate decomposes without melting in its water of crystallization at comparatively low temperatures,

although not completely excepting at higher temperatures.

(8) Hydrogen chloride is a very stable chemical compound. Chloride volatilized from aluminum chloride hexahydrate during thermal hydrolysis is completely converted into hydrogen chloride.

(9) Properties of the system $HCl-H_2O$ are well known, and properties of the systems $M_xCl_y-HCl-H_2O$ for the metals of interest are known to a lesser but sufficient extent to allow the design of evaporators, crystallizers, acid recovery units, etc. Virtually complete recovery of HCl is possible if suitable conditions are chosen.

(10) The solubility of chlorides tends to increase with increasing temperature. Scaling problems on heat transfer surfaces are therefore eliminated or greatly reduced.

An important characteristic, recently discovered, is that virtually all of the metallic elements in the periodic system with the exception of sodium, potassium, calcium, magnesium, and aluminum form anionic chloride complexes. Iron, in particular, may be separated as an anionic chloride complex from the aluminum by solvent extraction using an appropriate organic extractant. Nonvolatile organic extractants are available, which are almost insoluble in the aqueous phase, and which may be regenerated for reuse by stripping the iron chloride into a very dilute solution of hydrochloric acid. The iron-aluminum separation problem was a major barrier to the production of alumina from clay via hydrochloric acid extraction prior to development of the new solvent extraction technique.

Materials of construction for tanks, piping, pumps, heat transfer surfaces, valves, and other equipment presented a nearly insuperable problem before and during World War II, which was the last previous time of widespread interest in the extraction of alumina from clay. Fortunately, there have been major developments in corrosion resistant polymeric materials--both as linings and in solid form--since that time. Zirconium, titanium, tantalum or tantalum coatings, and resin impregnated graphite are available as corrosion resistant heat transfer surfaces in contact with acidic chloride solutions. A selection of metals protected by the development of oxide films may be used in the presence of HCl and H_2O above the dew point and under other specified conditions. It is believed possible today to design a plant using hydrochloric acid as an extractant which will operate with an acceptable level of maintenance expense.

B. *Process Description*

USBM RI 6133 (20) evaluates five hydrochloric acid processes for the extraction of alumina from clay, all of which have been rendered obsolete by the anionic chloride iron separation solvent extraction technology recently reported in USBM RI No. 8188 (21). The process evaluated here has been constructed primarily from information contained in RI 6133 and other technical literature cited in the bibliography which is a part of RI 6133, but taking

advantage of the improved iron separation method of RI 8188. Azeotropic breaking distillation is employed in treating the crystallizer bleed stream. This latter process has been described in the U. S. patent literature and in Eastern European technical literature (22).

A summary flow sheet is given by Figure 5.

Calcination

Entering clay is calcined in the same manner as for processes employing sulfurous or nitric acids as the aluminum extractant. All of the comments made in the evaluations of the processes employing those acids as extractants--and in particular to the possible development of fluidized solids clay calcination--apply equally when employing hydrochloric acid as the extractant.

Leaching

Alumina dissolves during leaching:

$$Al_2O_3 \cdot 2SiO_2 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O + 2SiO_2$$

Calcined clay   Solution   Solution   Solid waste

The tanks employed for leaching may be constructed of mild steel with a polymeric lining, protected against abrasion and excessive temperature by an inner brick lining. Free-standing fiberglass-reinforced plastic (FRP) tanks, also protected by a brick lining, are a possible alternative. The tanks will have sealing covers so that vapors generated by the heat of reaction may be contained and conducted to a condenser. Gentle agitation will meet the objectives of assuring adequate access of acid to all of the solid particles while avoiding, insofar as practical, attrition of the clay particles during leaching. It is further expected that the leaching will be accomplished cocurrently in three to five stages at one atmosphere at the boiling temperature with solution extraction of 90-98% of the total entering aluminum within a total residence time of about 2 hours.

Adequate information is available today for the design of a leaching operation that will operate successfully using calcined clay. Some additional study is desirable to develop a design which will minimize feed particle attrition. This is important in minimizing the production of fines, which would make the subsequent solid-liquid separation and residue washing step more difficult and costly.

It is possible that further study would show the leaching of uncalcined clay with hydrochloric acid to be practical, either in the presence of some recycling fluoride as a catalyst or at moderately elevated temperature and pressure or both. Insufficient information is available to permit inclusion of this method of leaching in the process evaluation at this time.

Figure 5

ALUMINA FROM CLAY VIA HCL EXTRACTION
EVAPORATIVE CRYSTALLIZATION
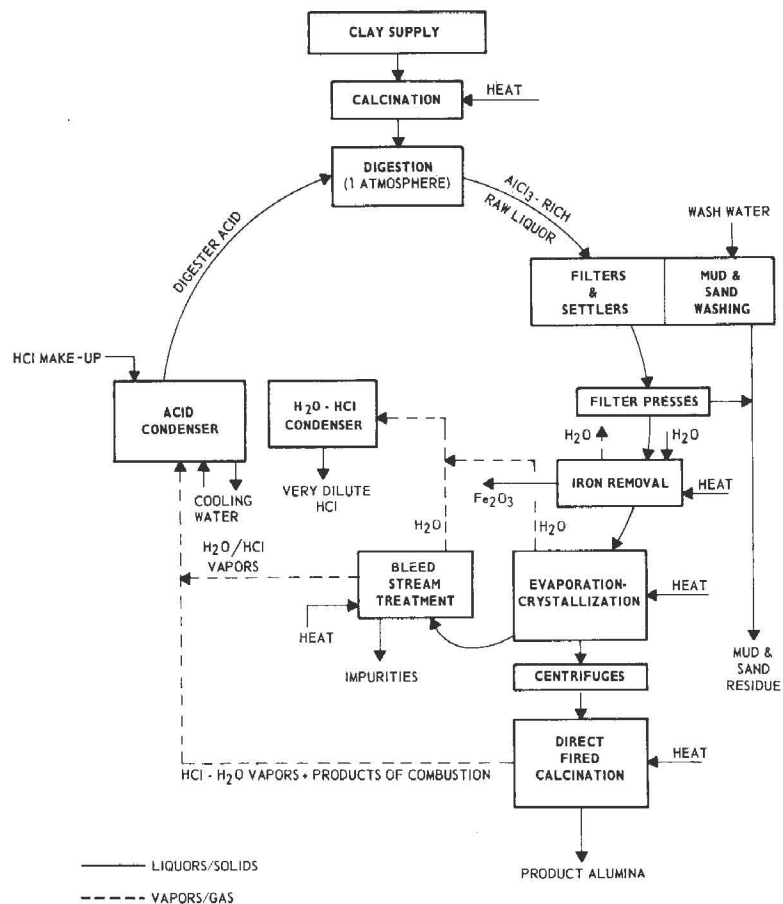
Solid-Liquid Separation

The amount of waste solids is large enough to require, under optimum conditions, a substantial capital investment in the separation, washing, and solids handling operations and to require the introduction of a substantial amount of waste solids wash water into the process. This wash water must later be removed by evaporation in order to maintain the process water balance.

Enough is known about the properties of the residue and solution produced by hydrochloric acid leaching of U. S. kaolin clay to make possible the engineering design of a solid-liquid separation system which would operate. Much work however remains to be done on optimizing the solid-liquid separation in terms of the capital cost for the operation and the dilution water introduced. This must, as in the case of nitric acid leaching, be done in conjunction with design of the leaching operation, because the characteristics of the solids emerging from leaching will control the solid-liquid separation.

Iron Removal

The removal of iron at this point is desirable to insure that it does not enter crystallization, thereby insuring its exclusion from the final product. Removal of iron prior to evaporation also makes possible entering crystallization with a pregnant liquor containing a higher concentration of dissolved alumina.

The first step in iron removal is quantitative oxidation of the iron to the ferric state in order to render it amenable to solvent extraction. It is recommended that this be accomplished by means of elemental chlorine, which oxidizes ferrous iron very quickly according to the reaction

$$Fe^{++} + \tfrac{1}{2}Cl_2 \longrightarrow Fe^{+++} + Cl^-$$

The oxidation process can be readily monitored and an excess of chlorine avoided through the well-developed use of an oxidation potential measurement. A further advantage of chlorine as an oxidant is that it is converted to chloride which supplies part of the overall process chloride makeup requirement.

The U. S. Bureau of Mines has described (21) an excellent separation of iron from aluminum which comprises a multistage countercurrent solvent extraction of ferric iron into a mixture of certain amine hydrochlorides dissolved in an organic solvent.

The reaction for formation of the anionic chloride complex is:

$$FeCl_3 + Cl^- \longrightarrow FeCl_4^-$$

and for the extraction is:

$$FeCl_4^- + R'RNH^+Cl^- \longrightarrow R'RNH^+FeCl_4^- + Cl^-$$

aqueous   organic   organic   aqueous

The equipment used was mixer-settlers. The organic was regenerated for recycling in a similar multistage operation by stripping it into water containing just enough hydrochloric acid to avoid precipitating basic ferric compounds.

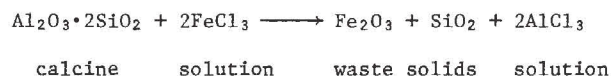The equation for the stripping step is:

$$R'RNH^+FeCl_4^- + water \longrightarrow R'RNH^+Cl^- + FeCl_3$$

organic   organic   aqueous
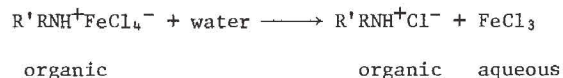
The strip solution produced during regeneration of the organic extractant is acidic and contains approximately 3.5% ferric chloride. This solution, for purposes of this process evaluation, was presumed to be concentrated by multiple effect evaporation to approximately 50% ferric chloride, at which concentration it is sprayed onto particles of iron oxide in a direct-fired fluid bed at a temperature of approximately 1500°F. The ferric chloride immediately decomposes:

$$2FeCl_3 + (n + 3)H_2O \xrightarrow{\Delta H} Fe_2O_3 + 6HCl\uparrow + nH_2O\uparrow$$

solution   solid   (vapor)   (vapor)
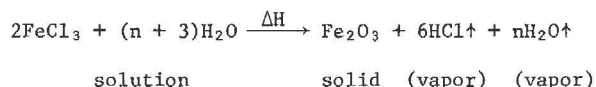
The vapors plus inerts and combustion products pass to acid recovery and the iron oxide goes to waste disposal.

An alternate and preferred method of processing the iron extract has been developed from the work of Marburg (23). The $FeCl_3$ strip solution is heated to boiling and then slurried with calcined clay containing alumina in approximately 50% excess for the reaction:

$$Al_2O_3 \cdot 2SiO_2 + 2FeCl_3 \longrightarrow Fe_2O_3 + SiO_2 + 2AlCl_3$$

calcine   solution   waste solids   solution

The Fe_2O_3 tends to precipitate on the surface of and within the pores of the insoluble portion of the calcined clay particles, producing a readily filterable waste solid. Experimentally, it was found that 99.5% or more of the iron can be removed from the iron extract by adding an amount of calcined clay containing a 50% excess of contained alumina in relation to iron and by holding the slurry at boiling for 2 hours. An equivalent amount of aluminum goes into solution replacing the iron as indicated in the above equation.

The dilute $AlCl_3$ slurry is added to the waste residue washing system at an appropriate point, rejecting Fe_2O_3, SiO_2, and unreacted clay to tailings along with acid insolubles from the primary leaching step. Very little or no Fe_2O_3 is expected to redissolve at this point, because nearly all of the acid originally added to leaching was consumed during that step, and because of the dilution. Any soluble iron forming or present will, of course, be removed in the subsequent solvent extraction of the primary liquor stream.

This method of iron separation-extract treatment rejects the iron from the overall process as oxide without consumption of reagent and at only a very small expenditure of energy. Acid used to leach iron is returned to the process in the form of $AlCl_3$. A small amount of $AlCl_3$ either coextracted with $FeCl_3$ or mechanically carried over into extract, along with organic either dissolved in or mechanically entrained in the extract, is also returned to the process.

It is expected that the above-described overall approach to iron rejection will reduce the cost of rejecting iron from clay raw materials containing any reasonable amount of iron to a low percentage of the total cost of producing alumina from the clay.

Evaporation

Concentration of the iron-free pregnant liquor to saturation brings the liquor to the point where crystallization of $AlCl_3 \cdot 6H_2O$ may begin. It also provides a means of rejecting water, thus helping to maintain the overall process water balance.

Approximately 9.6 mass units of water/unit of product alumina, along with all of the free dissolved HCl, are removed by evaporation from the iron-free leach liquor (including diluted leach liquor recovered by washing the waste solids) to produce a solution containing about 31% total dissolved chlorides, primarily aluminum chloride. This evaporation may be done under vacuum in order to utilize heat recoverable in other sections of the process.

Acid vapors produced during evaporation may be totally condensed, or may be condensed stagewise, to obtain a liquid acid the concentration of which will depend upon the ratio HCl:H_2O in the vapor entering the condenser and the pressure (temperature) at which the condenser is operating. Under the circumstances existing during concentration of the pregnant liquor, it will be possible by stagewise condensation to recover all of the hydrogen chloride in the vapor as liquid acid of at least 10% HCl and to recover the remainder as water of pH ≥ 5 suitable for reuse in the process.

Crystallization

Cooling crystallization is not effective for producing $AlCl_3 \cdot 6H_2O$, because the solubility of aluminum chloride decreases only slightly as the temperature is decreased. The saturated solution from the evaporators is therefore continuously passed into evaporative crystallizers where all of the water in which the aluminum chloride is dissolved (in excess of that required for the formation of $AlCl_3 \cdot 6H_2O$) is evaporated under controlled conditions. This induces supersaturation, with the consequent formation of crystals.

Heat is absorbed when $AlCl_3 \cdot 6H_2O$ crystals form. This crystallization process requires a substantial amount of heat, because heat must be supplied both for evaporation of the water and for formation of the crystals.

Ideally, only water vapor and $AlCl_3 \cdot 6H_2O$ crystals would leave

the crystallizer. In practice a mother liquor bleed stream must also be taken out in order to control the buildup of soluble impurities entering the crystallizer.

Crystal Recovery

The $AlCl_3 \cdot 6H_2O$ crystals may be separated from the crystallizer mother liquor by either vacuum filtration or centrifuges. Some mother liquor will inevitably adhere to the crystals; this mother liquor can probably provide the bleed stream required for control of minor constituent impurities in the crystallizer. The crystals are therefore washed with 35% hydrochloric acid, in which aluminum chloride has a very low solubility, to free them of adhering mother liquor.

Decomposition

The crystals next pass to thermal decomposition. $AlCl_3 \cdot 6H_2O$ crystals decompose very rapidly when heated to temperatures above about 375°F approximately in accordance with the reaction

$$2AlCl_3 \cdot 6H_2O \xrightarrow{\Delta} Al_2O_3 + 6HCl\uparrow + 9H_2O\uparrow$$
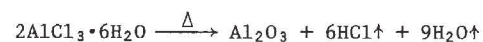
but the decomposition does not proceed within a reasonable time to a composition of residual chloride of <0.1% unless a final calcination temperature of approximately 1650°F is attained. The presence of a high partial pressure of steam facilitates removal of the chloride. It appears that alumina can be produced which will meet or exceed all specifications for chemical purity with the possible exception of the present target specification for residual chloride. It also appears possible that alumina can be produced which will have a suitable surface area, which will dissolve readily in the reduction cell cryolite bath, and which will have an acceptable particle size distribution.

The thermal decomposition process is energy intensive, requiring approximately 14.5×10^6 Btu/ton product alumina if it is assumed that the alumina leaves decomposition at 1300°F and that the gaseous products exit at 600°F. No provision is included in the above requirement for steam that may be supplied in the final stage(s) of decomposition. The required thermal energy may be supplied by direct contact of the crystals with hot combustion products; but if this option is chosen, a clean fuel is required. If indirect heating is selected, a suitable heat transfer medium and heat transfer surface material of construction must be chosen.

The published literature describes the employment of Herreschoff-type furnaces, rotary kilns, and fluid beds, both directly and indirectly fired, for accomplishing the decomposition. Further development of equipment for carrying out the thermal decomposition operation, even if a direct-fired decomposition employing a clean fuel is chosen, is required before an economically competitive demonstration plant can be designed. This process evaluation is based upon the employment of direct-fired decomposition.

Acid Recovery

The recovery of hydrochloric acid from hot vapors is simpler than for nitrogen or sulfur-based acids, because no decomposition of hydrogen chloride occurs at any process temperature and because of the great affinity of hydrogen chloride for water.

The equilibrium partial pressure of HCl over water containing small percentages of HCl is extremely low even at the normal boiling temperature of such solutions, and the volatility of HCl in relation to water decreases with decreasing temperature. A maximum boiling azeotrope exists at one atmosphere in the system $HCl-H_2O$ at 20.2 wt. % HCl. The equilibrium partial pressure of HCl gas in contact with the liquid increases very rapidly with increasing concentration in the liquid above the azeotrope, and as a consequence of this the normal boiling point of solutions above the azeotrope decreases very rapidly with increasing HCl concentration.

The above properties determine the conditions of operation which are possible for the acid recovery system. The three important factors in the recovery of hydrochloric acid from condensing vapors are the ratio $HCl:H_2O$, the temperature at which the system is operating, and the amount of inert gases which are present. Virtually complete recovery of HCl is possible from the gases exiting a direct-fired thermal decomposition of $AlCl_3 \cdot 6H_2O$. A countercurrent flow condenser may be used to condense the decomposer off-gases and produce approximately 20% HCl while rejecting excess H_2O vapor and inert gases.

Bleed Stream Treatment

Mother liquor adhering to the $AlCl_3 \cdot 6H_2O$ crystals, withdrawal of which also serves the purpose of removing soluble minor constituent impurities from the process, is recovered after washing of the crystals. An additional amount of crystallizer mother liquor may be diverted to bleed stream treatment as dictated by process requirements for impurity control. Further treatment of this very acidic mixture has three functions:

(1) rejection of soluble impurities other than iron from the process,

(2) recovery as fresh concentrated wash acid of the HCl values,

(3) rejection of water from the process.

The washings are mixed in a stripping column with a hot, concentrated, recycling stream of previously separated waste alkali and alkaline earth metal chlorides so as to prepare after mixing, on an HCl-free basis, a solution approximately 60% H_2O and 40% waste chlorides. The presence of the high metal chloride concentration is known to greatly increase the volatility of the HCl in relation to H_2O, the latter having a great affinity for the dissolved $MgCl_2$ and $CaCl_2$. Almost pure HCl vapor exits the top of the column, whereas the bottom liquid contains only a small amount of HCl but

nearly all of the H_2O in the washings being processed.

Concentrated HCl vapor from the top of the column passes into an absorption column where it increases the concentration of a side-stream of acid from the primary absorber from 20-22% to 35%. This becomes fresh wash acid. The somewhat diluted waste chloride stream passes to an evaporator where it is reconcentrated. The major fraction of the reconcentrated waste chloride stream is recycled to stripping, but the net production is withdrawn for further treatment described below. Acidic vapors proceed to the primary acid condenser for recovery of contained HCl, the associated water vapor being rejected to the stack.

The chemical engineering principles involved in the addition of a third component to a two-component system in order to make possible separation of the original two components by distillation is well known. There is reportedly one commercial installation in the U. S. of this method for separating HCl and H_2O. Other commercial installations have been reported in Eastern Europe, and a partially analogous operation has been reported in Israel. There appears to be very little doubt that the method is operable, but piloting is recommended prior to design of a demonstration plant to solve problems that may arise due to the presence of aluminum chloride, the possible formation of double salts, etc. The pilot study should be based upon a recirculating waste chloride solution of a composition that would be derived from a particular clay.

Sulfuric Acid Treatment of Waste Chlorides

The net production of concentrated waste chlorides is treated with sulfuric acid equivalent to the alkali and alkaline earth metals present (but not equivalent to alumina) and calcined. Representative reactions occurring are:

$$CaCl_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HCl\uparrow$$

$$2AlCl_3 + 3H_2O \longrightarrow Al_2O_3 + 6HCl\uparrow$$

The HCl produced is relatively concentrated and is sent to concentrated acid absorption. The mixture of sulfates and alumina is waste.

The technology of the calcination of chlorides with sulfuric acid to produce metal sulfates plus HCl is well known. No further development work is necessary prior to design of a demonstration plant.

Energy Requirements

The total net energy requirement for HCl extraction-evaporative crystallization is 31.4×10^6 Btu/ton Al_2O_3.

It is important that the direct-fired thermal decomposition of $AlCl_3 \cdot 6H_2O$, although technically simpler than an indirect-fired decomposition because it avoids the need for heat transfer surfaces

and media, will require a clean fuel which probably will be oil. This will be costly in view of the large heat requirement for this process section.

Waste heat may be recovered from the condensation of hydrochloric acid by innovative design in the acid recovery section. This heat could be employed in vacuum evaporation to reduce the amount of steam otherwise required.

Steam requirements can be met by coal-fired boilers.

Environmental Control

It will be necessary to construct as a closed system with respect to the environment those plant sections where hydrogen chloride is present in order to safeguard the health of the workment, avoid excessive maintenance costs, avoid acid losses, and meet anticipated emission standards. Fortunately, this task is made easier by the great affinity of hydrogen chloride for water. Covered leach tanks, for example, can be vented to the atmosphere through a condenser. Filters must be covered but also can be vented to the atmosphere through a condenser/scrubber.

Recovery of hydrogen chloride to meet air pollution control requirements can be assured in the acid recovery section.

Waste solids from leaching will comprise silica, a small amount of unreacted clay, and small amounts of unreacted accessory minerals. The silica will not be excessively hydrated, and these waste solids should make a good subsoil. It will undoubtedly be desirable to return them to mined-out areas for disposal, but provision will have to be made eventually to return to the process small amounts of chloride remaining in them. Other waste solids from the process are iron oxide and a mixture of metal sulfates with alumina. The sulfate-alumina mixture will require disposal in a manner such that the sulfates will not be leached out or where the presence of dissolved sulfate will not be objectionable. The quantity of sulfates produced in relation to alumina will be small.

Heat entering the process is largely rejected to the atmosphere in combustion gas streams or by means of cooling towers. The process does not produce a liquid effluent other than the water present in the waste leach solids.

Alumina Product Quality

Experimental evidence based upon literature, some laboratory work, and some mini-plant results all indicate that the chemical purity of chloride process alumina with respect to metals has the potential of being considerably higher than Bayer process aluminas. The extent to which chloride may be economically removed from such aluminas, and the actual extent to which reduction plant operations will require its removal, are not known with certainty at this time. Phosphate is a material present only in small amounts in the entering clay, but the P_2O_5 specification in reduction-grade alumina is very low, and very little is known about the path of phosphate

through the processing cycle. Further study will be necessary to determine the best method of meeting the P_2O_5 specification.

Tests on small quantities of chloride process alumina have shown that it can be produced to meet present day specifications for surface area and water absorption. This alumina also appears to dissolve very readily in molten cryolite. It will be possible to produce $AlCl_3 \cdot 6H_2O$ crystals in a particle size distribution appropriate as the precursor to the finished alumina. Assuming that a decomposition process can be developed which--in addition to meeting other requirements--will minimize attrition, it is probable that the particle size distribution specification can also be met. The finished alumina will be less dense than Bayer alumina, but chloride process alumina can be produced with a constant density.

Alumina from Clay Via Hydrochloric Acid Extraction – HCl Gas Induced Crystallization

A. *Introduction*

All of the salient characteristics of hydrochloric acid as an extractant that were discussed under "Alumina from Clay Via Hydrochloric Acid Extraction - Evaporative Crystallization" apply equally to hydrogen chloride precipitation, but there is one very important addition.

F. A. Gooch discovered and in 1896 obtained U. S. Patent No. 558,725 covering the crystallization of $AlCl_3 \cdot 6H_2O$ from concentrated solutions of aluminum chloride by dissolving hydrogen chloride gas into the solutions (24). Gooch also proposed recycling the mother liquor (hydrochloric acid) remaining after crystallization back to leach more aluminum although his and subsequent efforts to utilize his discovery failed, because there was no way--other than distilling all of the mother liquor--to separate iron. Gooch and subsequent investigators were also beset with what were in those times insuperable materials of construction, heat transfer, and materials handling problems--particularly in attempting an indirectly heated decomposition of the $AlCl_3 \cdot 6H_2O$ crystals. The last serious investigations of the extraction of alumina from clay with hydrochloric acid and utilizing hydrogen chloride-induced crystallization of $AlCl_3 \cdot 6H_2O$ that have been published took place during World War II (25, 26).
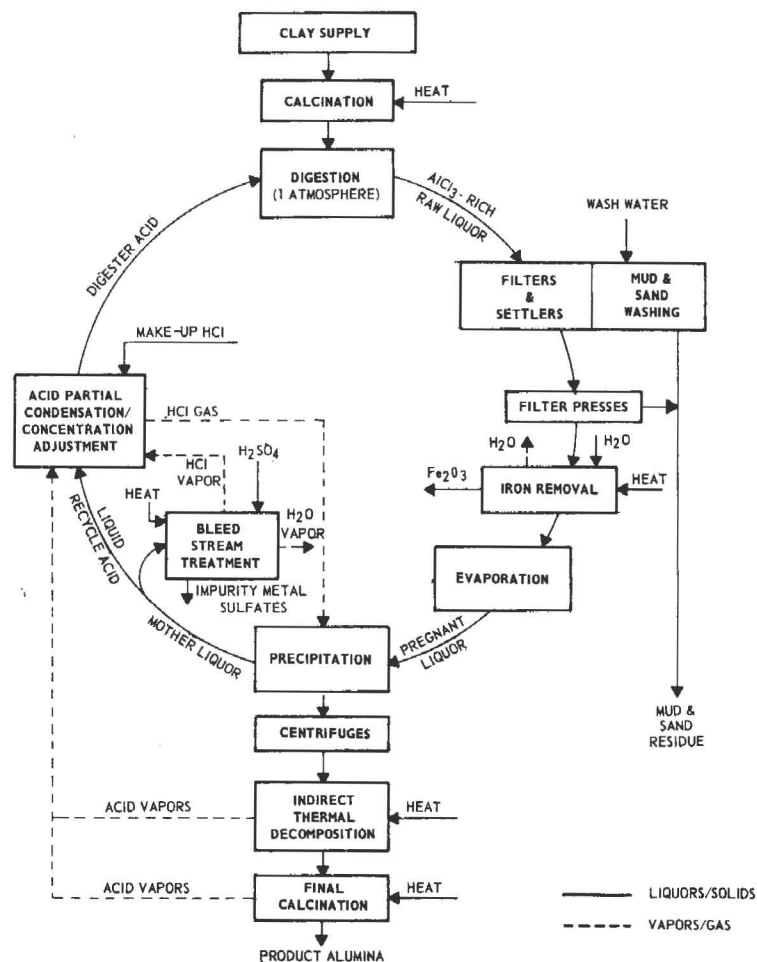
B. *Process Description*

A summary flow sheet of the process appears as Figure 6.

Clay Calcination

Entering clay is calcined in the same manner as for processes employing nitric or sulfurous acids as the alumina extractant. All of the comments made in the evaluations of the processes

ALUMINA FROM CLAY VIA HCl EXTRACTION HCl PRECIPITATION

employing those acids as extractants--and in particular about the possible development of fluidized solids clay calcination, if this clay is to be calcined--apply equally when employing hydrochloric acid as the extractant.

Leaching

The leaching operation--except for the use of somewhat more concentrated acid containing some recycled dissolved aluminum chloride, which therefore will produce a more concentrated solution of aluminum chloride than if 20% acid without recycling aluminum chloride is used as the extractant--is the same as previously described under hydrochloric acid extraction - evaporative crystallization.

Solid-Liquid Separation

The solid-liquid separation operation is expected to be the same for either variation of hydrochloric acid extraction.

Iron Removal

The previously described iron removal step, the processing to convert the iron extract to solid iron oxide, and the disposition of the waste solids are the same as described for evaporative crystallization.

Evaporation

The evaporation step is the same as for the evaporative crystallization process, excepting that as a consequence of using a higher concentration of leach acid, only approximately 1.9 mass units of water/unit product alumina must be removed in evaporation to enter crystallization with a saturated solution of $AlCl_3$.

Crystallization

Hydrogen chloride gas dissolves readily over a useful range of temperatures at a pressure of one atmosphere or less into aluminum chloride solutions. Starting with a saturated aluminum chloride solution, $AlCl_3 \cdot 6H_2O$ is crystallized as hydrogen chloride dissolves so as to maintain a virtually constant molality in the solution with respect to chloride until the aluminum chloride solubility is depressed to approximately 6.5% in the presence of 25.6% HCl. The solubility of aluminum chloride may be further depressed to 0.7% at 35.5% HCl. The solubility of aluminum chloride changes very little with change in temperature although the equilibrium partial pressure of hydrogen chloride in contact with aluminum chloride solutions changes very rapidly with change in temperature. The solubility of potassium chloride in solutions containing approximately 25% HCl and saturated with $AlCl_3$ is approximately 2% and that of sodium chloride is about 1%. The solubilities of calcium and magnesium chlorides are depressed by the addition of HCl but remain quite high. The solubilities of other metallic chlorides which form complexes tend to increase with increasing concentrations of hydrogen chloride. Existing data are of doubtful applicability to the complex system produced by the cyclic leaching of naturally

occurring clay. The industrial application of hydrogen chloride induced crystallization of $AlCl_3 \cdot 6H_2O$ will benefit from the development of further knowledge about solubility relationships in complex liquors.

Struthers-Wells Corporation representatives have stated that because of the concentration-growth-nucleation relationship existing in the crystallizer, it will not be economically practical to produce $AlCl_3 \cdot 6H_2O$ crystals of a useful particle size distribution below a concentration of about 6.5 wt. % aluminum chloride. This concentration corresponds to recovery as crystals of about 85% of the dissolved aluminum chloride entering crystallization and has been chosen as the operating condition for this evaluation. Struthers-Wells has also suggested carrying out the crystallization in at least two stages in order to hold the solids content of the slurries at easily manageable levels.

Struthers-Wells has operated, on a small pilot scale as a part of the mini-plant program, the hydrogen chloride crystallization of $AlCl_3 \cdot 6H_2O$. They were able to produce good crystals of controlled particle size distribution and were optimistic about scale-up of the crystallization operation.

Very little quantitative data are available in regard to the concentration of various impurity metal chlorides which may be present in the mother liquor during crystallization without incorporation of these impurities into the lattice of the crystals to such an extent that alumina produced from the crystals would not meet chemical purity specifications. It may be inferred from the older literature that adequately pure crystals of $AlCl_3 \cdot 6H_2O$ can be produced in the presence of rather substantial amounts of impurities and that reduction-grade alumina purity specifications can be met if the crystals are grown carefully to avoid inclusions of mother liquor and are washed so as to remove adhering mother liquor adequately.

Crystal Recovery

The $AlCl_3 \cdot 6H_2O$ crystals may be separated from the crystallizer mother liquor by either the use of centrifuges or by vacuum filtration. Both the mother liquor and the wash acid will have substantial vapor pressures at the filtration temperature. It will probably be desirable to use a centrifuge in order to eliminate any possibility of flashing and to reduce the quantity of wash acid adhering to the crystals to the lowest possible value. The centrifuge or filter will have to be totally enclosed, and provision will have to be made either for recirculating air drawn through the cake or for scrubbing HCl from the air before discharging it to the environment.

Mother liquor washed from the crystals in admixture with wash acid is conveniently sent to leach acid preparation where the mixture becomes part of the recycle leach acid.

Decomposition

The chemistry of the thermal decomposition step and the

theoretical energy requirement to accomplish it are, of course, the same irrespective of the method of $AlCl_3 \cdot 6H_2O$ crystal preparation. When employing HCl-induced crystallization of $AlCl_3 \cdot 6H_2O$, it is desired to carry out at least 90% of the decomposition by means of indirect heat so that the vapors produced by decomposition--which overall will contain approximately 57.4 wt. % HCl along with 42.6% H_2O and no combustion products--may be partially condensed to produce the major fraction of the HCl gas required in crystallization. The water content of the vapors is recovered as 35% acid, useful for washing $AlCl_3 \cdot 6H_2O$ crystals, after which it may be easily stripped down to leach acid concentration to produce the remainder of the HCl gas required for crystallization.

Little information is available with respect to the rate and mechanism of the thermal decomposition process as a function of temperature. A search must be made for materials of construction for heat transfer surfaces that will give satisfactory service at various temperatures above the dew point. Several metals, including zirconium and even aluminum appear to offer corrosion resistance at temperatures not much higher than the dew points for aqueous systems containing their metallic chlorides. High nickel-chromium content metals appear to offer corrosion resistance, as well as mechanical strength at higher temperatures.

It may be necessary to complete the decomposition of the $AlCl_3 \cdot 6H_2O$ at a temperature high enough so that no practical material having adequate mechanical strength with suitable resistance to corrosion will be available for use as a heat transfer surface. In this case it will be necessary to use a direct-fired fluid bed for the last stage of calcination. It is known that the presence of an atmosphere comprising primarily steam lowers the temperature necessary, at a constant decomposition time, to reduce the chloride level to a given value.

It is believed, taking all of the foregoing into consideration, that the design of industrial-scale indirectly heated decomposition equipment is possible.

Acid Recovery

The acid recovery operation comprises three sections: a wash acid preparation section producing 35% wash acid and HCl gas for use in crystallization; a leach acid preparation section which produces leach acid and hydrogen chloride gas; and a dilute HCl condensation section.

(1) <u>Partial Condensation to Obtain Concentrated Acid Plus Hydrogen Chloride Gas</u> – The vapor stream from the indirectly heated decomposer containing approximately 57% HCl is divided between the leach acid and wash acid preparation sections. The part of it entering the wash acid preparation section passes countercurrently to 25% acid, in a direct contact partial condenser. The acid stream is heated to 220°F by selective condensation of the vapor so that the vapor stream exiting the partial condenser contains 90% HCl and 10% H_2O. The 220°F acid is externally cooled to

175°F and recirculated. The vapor stream plus the net production of acid from this condenser are fed cocurrently to a cooled falling film absorber producing 35% acid at 140°F and 98% HCl gas. This gas returns to crystallization, and the acid is used for washing $AlCl_3 \cdot 6H_2O$ crystals.

(2) <u>Leach Acid Preparation</u> – Used wash acid, concentrated HCl vapors from bleed stream treatment, acid of 10-20% concentration that may be available, and the recycling mother liquor are blended with the remainder of the concentrated HCl vapor that was not used to prepare wash acid. The heat content of the vapor is utilized by controlling heat removal from the system to prepare as a bottom product hot liquid acid containing the amount of dissolved hydrogen chloride desired for recirculation to leaching, and as a top product the balance of the hydrogen chloride gas required in crystallization.

The leach acid preparation section consists of two direct contact packed towers. The concentrated vapors enter the bottom of the first of these, which is irrigated by a recirculating stream of cooled leach acid, plus used wash acid. Partial condensation/stripping occurs to produce 91% hydrogen chloride gas as a top product and an excess of 25% leach acid as the bottom product.

External cooling must be used to remove the heat developed by condensation of HCl and H_2O vapors. One goal of the design of this section was to make possible eventual reuse of this heat in a low temperature application such as evaporation at reduced pressure.

Vapors exiting the first tower enter the second one, which is irrigated with the used wash acid before this acid joins the crystallizer mother liquor in irrigating the first tower. The second tower functions almost adiabatically. The top product from this tower is 99% hydrogen chloride gas, which meets the balance of the requirement for crystallization.

(3) <u>Dilute Acid Condensation</u> – Vapors from the direct contact evaporation/decomposition of waste chloride solutions pass to a dilute acid condenser in which they pass countercurrently to a film of descending dilute acid on the inside of externally cooled tubes.

The exact ratio H_2O:HCl is not presently known for the dilute HCl streams to be dealt with, so it has been assumed that the HCl content of these gases may be recovered as 10% acid.

Bleed Stream Treatment

A portion of the filtrate from the final stage of intermediate product $AlCl_3 \cdot 6H_2O$ crystallization is withdrawn from the process for the control of soluble impurities other than iron. It is estimated that withdrawal altogether of approximately 5% of the final crystallizer mother liquor (filtrate) will be required. The treatment of the bleed stream is somewhat different than when evaporative crystallization is employed due to the production of wash acid in the acid recovery section as described above. Bleed stream treatment does have the same goals as described under evaporative crystallization.

The first treatment of this stream is saturation with hydrogen chloride gas at 120°F to reduce the solubility of $AlCl_3$ below 1%. The $AlCl_3 \cdot 6H_2O$ crystals obtained will not meet particle size nor purity specifications for feed to decomposition but will be filterable. They are filtered, recovered, and redissolved in the iron-free leach liquor proceeding to evaporation.

Once the $AlCl_3 \cdot 6H_2O$ has been recovered, the mother liquor is mixed with waste chlorides, stripped of its HCl content, and then concentrated by evaporation as described under evaporative crystallization.

Sulfuric Acid Treatment of Waste Chlorides

The net production of concentrated waste chlorides is treated with sulfuric acid equivalent to the alkali and alkaline earth metals present (but not equivalent to alumina) and calcined as was described under evaporative crystallization. The previous recovery of $AlCl_3 \cdot 6H_2O$ will decrease the proportion of Al_2O_3 in the waste oxides in comparison with the evaporative crystallization waste oxide stream.

Energy Requirements

The net energy requirement for HCl extraction-HCl induced crystallization is approximately 23.5×10^6 Btu/ton alumina. Energy has been provided in this total for concentration by conventional multiple effect evaporation of the iron extract followed by thermal decomposition of the concentrate, although the alternate approach to iron extract treatment described under evaporative crystallization is expected to be employed if a demonstration plant is built.

Heat required for evaporation is low in this process due to the higher acid concentration employed in leaching, and because the free water in which the $AlCl_3 \cdot 6H_2O$ is dissolved, less the bleed stream, is not evaporated.

The nature of the process requires that the thermal energy intensive $AlCl_3 \cdot 6H_2O$ decomposition be carried to about 90% completion using indirect heat. A concomitant advantage is that relatively inexpensive fuels (including coal) may be used to provide the indirect heat. A maximum of 1.5×10^6 Btu in the form of clean fuel such as oil may be required in a final decomposition stage. The use of direct vs. indirect heating in the final decomposition stage has not yet been decided, and the exact heat requirement in this stage cannot be precisely determined.

The energy requirement for purposes of this evaluation does not include any provision for the use of recovered heat, but heat may be recovered from the condensation of hydrochloric acid by innovative design in the acid recovery section. This heat could be employed in vacuum evaporation to reduce the amount of steam otherwise required, and its utilization will also result in capital savings. Additional heat rejected directly to cooling towers may possibly be utilized on a single-effect basis for evaporation of water from dilute solutions, thus reducing steam

requirements. Remaining steam requirements can be met by coal-fired boilers. It is expected that after some development work, entering clay can be calcined using coal as the heat source.

Environmental Control

Environmental control considerations for HCl-induced crystallization are essentially the same as for evaporative crystallization.

Alumina Product Quality

Comments pertaining to this subject made under evaporative crystallization also apply to this process.

Technical Comparison of the Six Raw Material Process Combinations

Following is a summarized technical comparison of the six process-raw material combinations described above. Costs for the production of alumina by these six raw material-process combinations inevitably will be a quantitative expression of part, but not all, of the information summarized below.

Alumina from Anorthosite Via Lime Sinter Process

(1) Anorthosite was originally attractive as a possible alumina source, because enormous reserves exist and because it is reasonably high in alumina grade. However, approximately two units of limestone must be provided for each unit of anorthosite to make sinter feed, with the result that the total amount of sinter feed per unit of alumina produced becomes quite large. The quality of the limestone is also very important.

(2) Both the limestone and anorthosite must be very finely ground and proportioned with great accuracy to secure a satisfactory sinter; the grinding is energy intensive and the accurate blending difficult.

(3) The sintering process is very energy-intensive.

(4) It is very questionable whether decrepitation ("dusting" of the sinter into fine particles) can be secured by controlled cooling of the sinter on an industrial scale. Fine sinter particle size is required for leaching of the alumina values.

(5) There is no known practical solution to the problem of gelation, the possibility that solids undergoing leaching or settling may set up into a hard, concrete-like mass.

Alumina from Alunite/Reduction Roast - Bayer Extraction

(1) Mine-run alunite ore is low grade with respect to alumina,

requiring the processing of at least eight units of ore per unit of alumina.

(2) The key front-end step, reduction roasting, appears capable of removing by reduction under optimum conditions only about 85% of the $SO_4^=$ associated with alumina. Even under these conditions a substantial fraction of the alumina is rendered caustic-insoluble.

(3) Unreduced sulfate associated with aluminum must be removed by leaching with dilute KOH or NH_4OH. K_2SO_4, originally a part of the alunite structure, is removed in the same leach.

(4) The process of solfataric alteration of feldspathic rocks, which creates alunite, is likely to create kaolinic clay and reactive silica in close association with it. Alumina and soda losses as desilication product in the modified Bayer section of the process may be considerably higher than the values used in preparing the operating cost estimates. It may be difficult to make product specifications due to possible problems in desilicating the pregnant liquor adequately.

(5) The process as discussed here produces three products, namely, alumina, potassium sulfate, and sulfuric acid, all of which must either be marketed or disposed of economically.

(6) Known reserves of alunite are small in comparison with reserves of alumina in other non-bauxitic aluminous materials and are very restricted in geographic location.

Alumina from Clay Via Sulfurous Acid Extraction

(1) Sulfur dioxide is a gas exhibiting only limited solubility in water; in addition, sulfurous acid is a weak acid. The consequences are:

    (a) Pressurized leaching of calcined clay for a relatively long period of time is ncessary to secure even a comparatively low alumina extraction.

    (b) The alumina concentration of the leach acid solution is comparatively low.

    (c) Most of the sulfurous acid section of the process must be operated under elevated pressure.

(2) The relative instability of aluminum sulfite permits the hydrothermal precipitation of alumina trihydrate which is advantageous. However, the sulfurous acid process section offers no means of separating iron or other impurity metals in solution, and even the separation of silica is incomplete. Hydrothermal precipitation of first a basic sulfite and then the trihydrate occurs in the presence of at least a part of these impurities. Consequently, no way is known to produce alumina trihydrate via sulfurous acid extraction that is pure enough to meet reduction-grade specifications without subsequent purification by means of a modified Bayer process.

(3) Sulfur in aqueous solutions as $SO_3^=$ disproportionates to sulfate and sulfur relatively easily. In practice, this occurs during autoclaving. These chemical reactions cause substantial sulfur losses, processing difficulties in the Bayer refining section, and environmental control problems.

(4) Energy requirements are relatively high because of the need for two processes: a sulfurous acid process plus a modified Bayer process. The main energy users are the sulfurous acid autoclaving sections.

(5) The equipment required to put all of the alumina into solution twice, once in H_2SO_3 and once in NaOH, results in high capital cost.

Alumina from Clay Via Nitric Acid Extraction

(1) This process employs nitric acid as the primary leaching reagent which is more costly and is expected to increase in cost relative to hydrochloric acid.

(2) The relative instability of the nitrate group results in some unavoidable nitrate losses as N_2 and N_2O.

(3) No fully satisfactory method of iron removal is known to be available. The use of ion exchange creates large streams containing HNO_3 and HCl. The use of substoichiometric HNO_3 leaching would require a considerable amount of additional equipment.

(4) The apparent poor separation factor in crystallization may require either a large crystallizer bleed stream or multiple $Al(NO_3)_3 \cdot 9H_2O$ crystallizations. Optimization of the crystallization section of the process would require extensive further study.

(5) This process requires that all H_2O in which $Al(NO_3)_3 \cdot 9H_2O$ is dissolved be evaporated.

(6) The heat requirement for decomposition of $Al(NO_3)_3 \cdot 9H_2O$ is approximately 50% greater than for decomposition of $AlCl_3 \cdot 6H_2O$.

(7) The oxidizing nature of nitric acid is likely to cause metallic corrosion problems in the presence of even small amounts of chlorides unavoidably introduced from a variety of sources.

(8) Environmental control problems include the elimination of nitrate losses to groundwater and removing NO_x from stack gases to meet environmental requirements.

Alumina from Clay Via Hydrochloric Acid Extraction - Evaporative Crystallization

(1) The process has been expressly designed for U. S. clays which are readily soluble in hydrochloric acid after an activating calcination and which have high ratios of acid-soluble alumina to acid-soluble metallic oxide impurity contents in the entering clay. The process can accommodate, with only minor increases in processing costs, reasonable amounts of silica and other acid-insoluble

impurities which reduce the grade of many otherwise good U. S. clays. It can accommodate, with modest increases in processing cost (because of the nature of the iron rejection process employed) clays containing somewhat increased amounts of acid soluble iron. Processing costs will increase more rapidly with increasing ratios of acid soluble alkali and alkaline earth metal oxides to acid soluble alumina in the entering clay.

(2) Hydrochloric acid as a primary extractive reagent is likely to remain stable in cost. In addition, Cl_2 employed to oxidize ferrous iron to the ferric state eventually reports as makeup HCl. It is possible, especially with some raw materials, that this latter source could provide all required makeup HCl.

(3) Hydrochloric acid is chemically stable under all process conditions. HCl vapor produced by thermal decomposition of $AlCl_3 \cdot 6H_2O$ may be recovered by condensation/absorption in water. Equilibrium partial pressures of HCl over dilute solutions of HCl are low, simplifying the recovery of HCl diluted with inert gases.

(4) A significant breakthrough in the use of hydrochloric acid as a leaching reagent is the recent availability of a solvent extraction system for iron removal which permits production of alumina with a satisfactory iron content. This method enjoys the advantage of using very dilute HCl to strip the iron from the loaded organic solvent.

(5) Only one hydrate, $AlCl_3 \cdot 6H_2O$, is formed upon crystallization of aluminum chloride from aqueous solution. This hydrate does not melt in its water of crystallization and requires only approximately $^2/_3$ the heat for decomposition as is required for $Al(NO_3)_3 \cdot 9H_2O$.

(6) It is expected that only a single crystallization of the $AlCl_3 \cdot 6H_2O$ will be required for soluble impurity control in the product alumina although optimization of the crystallizer process section will require a considerable amount of additional study prior to design of a demonstration scale plant.

(7) The endothermic decomposition of $AlCl_3 \cdot 6H_2O$ may be carried out by direct contact between hot combustion product gases and the crystals undergoing decomposition. However, the presence of combustion product gases in admixture with the gaseous products of the decomposition increases the cost of equipment required for subsequent condensation of acid, and economically limits the concentration of the recovered acid to approximately 20% HCl. Additionally, in recent years the cost of clean fuel for the $AlCl_3 \cdot 6H_2O$ decomposition has risen dramatically in comparison with the cost of other fuels such as coal which are suitable energy sources only when the combustion products do not come into direct contact with the product alumina.

A considerable amount of further study and pilot scale development work would be required prior to the design of a cost-effective direct fired thermal decomposition process section.

(8) The 20% HCl recovered in the acid condenser is not suited to washing $AlCl_3 \cdot 6H_2O$ crystals because of their substantial solubility in acid of this concentration. Condenser acid to be used for crystal washing would require fortification to approximately 35% HCl.

(9) In the evaporative crystallization process all of the water in the leach liquor must be vaporized. This results in a considerably higher evaporation load compared to the HCl process using HCl gas to induce crystallization.

(10) This process has the advantage of simpler technology in the salt decomposition phase.

(11) Its most important disadvantages in comparison with HCl leaching (HCl gas induced crystallization) indirect-fired decomposition are the higher evaporation requirement and the questionable future availability of a clean fuel for the direct-fired thermal decomposition step.

Alumina from Clay Via Hydrochloric Acid Extraction - HCl Gas Induced Crystallization

(1) Process characteristics 1 through 6 inclusively, as listed under HCL-Evaporative Crystallization, apply equally to this process.

(2) After the crystallization step, the crystals of $AlCl_3 \cdot 6H_2O$ are separated from the mother liquor. This mother liquor is recycled to the leach step as liquid and does not go through the vapor phase as with the evaporative crystallization process. This characteristic reduces the amount of evaporation required in this process compared to the HCl process using evaporative crystallization.

(3) This process requires HCl gas of at least 95% concentration for precipitation of $AlCl_3 \cdot 6H_2O$. The most practical way to produce this gas in the required amount is partial condensation of vapor rich in HCl and containing at most only small amounts of noncondensibles. This, in turn, requires that at least 90% of the thermal decomposition of the $AlCl_3 \cdot 6H_2O$ be accomplished without mixing the HCl/H_2O gaseous decomposition products with combustion products.

An extensive program of development effort to obtain design information must be carried out before the design of a demonstration scale, indirectly fired decomposer can be undertaken with confidence. However, there is reason to believe the design and construction of such equipment is possible.

(4) To reduce the impurities in the product alumina the $AlCl_3 \cdot 6H_2O$ crystals must be washed free of mother liquor. The 35% hydrochloric acid produced by partial condensation of the gases leaving the indirectly fired decomposer is used for this purpose because of the low solubility of the crystals in acid of this concentration.

(5) The HCl induced precipitation technique may be employed to minimize alumina losses in the bleed stream. Subsequently, distillation in the presence of a high concentration of waste chlorides should permit almost complete recovery of HCl in the bleed stream.

(6) The condensation of acid in the absence of inerts and exo-thermic operation of the primary crystallizer permits recovery of heat at temperatures high enough to be useful in evaporation or distillation, with the possibility of some reduction in the total process heat requirement.

(7) The primary disadvantage of this process is the requirement for development of indirectly fired decomposition equipment. Since questions of long-term availability and added cost of clean fuel may eventually require the development of an indirectly heated decomposer capable of firing with coal for any acid process, this disadvantage may be short term only.

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