ACID EXTRACTION PROCESSES FOR NON-BAUXITE ALUMINA MATERIALS

C.A. Hamer

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ABSTRACT

A number of acid extraction processes for recovering alumina from non-bauxite materials are reviewed from strictly technical considerations. These processes are based on leaching with sulphuric, hydrochloric or nitric acids, purifying the leachates, recovering aluminum salts and calcining to produce alumina. Sulphuric acid processes include those which use potassium and ammonium alums, aluminum sulphate, basic aluminum sulphate, combination processes utilizing both sulphuric and hydrochloric acids and some which have caustic purification following acid leaching. The variety of processes differ in their approach to removing impurities and in the method of recovering snd treating the hydrated aluminum salts. Methods are described in sufficient detail to indicate their major technical advantages and disadvantages.

Some comments are made on acid processes for the principal potential Canadian non-bauxite sources, i.e., anorthosite, high alumina-containing coal wastes and low grade clays. No process described in the report is entirely satisfactory and none so far can produce alumina as cheaply as the Bayer process for bauxite. Economic aspects of the acid processes are to be covered in a forthcoming report.

PROCEDES D'EXTRACTION AUX ACIDES DE L'ALUMINE A PARTIR DE MATERIAUX AUTRES QUE LA BAUXITE*

par

C.A. Hamer**

RESUME

Un certain nombre de procédés d'extraction de l'alumine par réactions avec des acides, à partir de matériaux autres que la bauxite, sont étudiés en se fondant sur des considérations strictement techniques. Ces procédés sont basés sur la lixiviation à l'aide d'acide sulfurique, chlorhydrique ou nitrique, suivie d'une purification des produits résultants, puis de la récupération des sels d'aluminium; ces sels sont ensuite calcinés pour produire de l'alumine. Les procédés faisant appel à l'acide sulfurique comprennent les procédés utilisant les aluns de potassium et d'ammonium; le sulfate d'aluminium, le sulfate basique d'aluminium; les procédés combinatoires utilisant les acides sulfurique et chlorhydrique et certains procédés pour lesquels la lixiviation à l'acide est suivie d'une purification dans une solution de soude caustique. Ces procédés diffèrent dans leur méthode d'élimination des impuretés et dans la méthode de récupération et de traitement des sels d'aluminium hydratés. Les méthodes sont décrites avec suffisamment de détails pour indiquer leurs principaux avantages et inconvénients techniques.

On commente les procédés aux acides pour l'extraction à partir des principales sources possible canadiennes autres que la bauxite, c'est à dire l'anorthosite, les résidus de charbon à haute teneur en alumine et les argiles à faible teneur. Aucune des méthodes décrites dans ce rapport n'est entièrement satisfaisante et aucune, à l'heure actuelle, ne peut produire de l'alumine de façon aussi économique que le procédé Bayer sur le minerai de bauxite. Les aspects économiques des procédés aux acides feront l'objet d'un autre rapport.

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FIGURES

FIGURES (Con't)

INTRODUCTION

In the past 50 to 60 years, numerous patents and papers have been published on the processing of low-grade alumina-bearing minerals to alumina using acid extraction techniques. Although aluminous minerals are soluble to some extent in practically all acids, sulphuric, hydrochloric and nitric acids are the more commonly used. With low-alumina high-silica minerals, the separation of alumina from silica is more readily achieved with acid processes in which silica is sparingly soluble, than with alkaline processes in which silica is significantly soluble. Conversely, with high-alumina low-silica minerals, i.e., a typical bauxite, the alkaline Bayer process is the cheapest method of extracting alumina.

The magnitude and variety of processes developed attest to the difficulties involved with acid techniques: difficulties in removing iron which is generally soluble in acids, difficulties in removing the small but still significant amount of silica which is soluble in some solutions, difficulties with acid recovery and regeneration, difficulties in handling and calcining aluminum salts, most of which contain considerable amounts of water of hydration and, finally, the need for acid resistant equipment.

This paper does not attempt to review all processes described in the literature but rather concentrates on those which have been developed and tried in the laboratory or pilot plant, if not on an industrial scale, and which are representative

of general techniques. The methods are discussed in sufficient detail to point out major strengths and weaknesses. They are described under the general categories of sulphuric, hydrochloric and nitric acid leaching. Sulphuric acid processes, for example, include the production of alumina from potassium and ammonium alums, aluminum sulphate and basic aluminum sulphate. Also included are "combination" processes such as the Pechiney H Plus method which utilizes sulphuric and hydrochloric acids, and others which utilize acid leaching followed by caustic purification.

The aluminous material available for treatment has an effect on the choice of process. Although many processes have been designed to treat high alumina clays, some specific processes have been developed to take advantage of particular impurities in the material. Canada does not possess known reserves of high alumina clays. Potential alumina materials in Canada are anorthosite, clays and shales associated with coal, and possibly some lower grade clay deposits. Some comments on processes to extract alumina from these materials are included at the end of the paper.

This review has been prepared to record some of the information compiled as part of the CANMET Minerals Research Program on Non-Bauxite Sources of Alumina. Some of the techniques described are the basis of work being conducted at CANMET, e.g., the acid leaching of melted and quenched anorthosite, and the fluosilicic acid catalysed hydrochloric acid leaching of anorthosite. A nitric acid, a hydrochloric acid and a sulphuric-sulphurous acid process are included in the current United States

Bureau of Mines' Alumina Miniplant Program on which CANMET has observer status.

SULPHURIC ACID

Sulphuric Acid Processes

Sulphuric acid has the advantage of being the cheapest commercial acid available. It has a relatively low vapour pressure and is less chemically aggressive than either nitric or hydrochloric acid. Materials of construction for use with sulphuric acid are fully developed, as are methods for acid recovery and regeneration.

In these processes, alumina-bearing materials which may have been preconditioned, e.g., by crushing and dehydrating, are leached with sulphuric acid. Aluminum, iron and alkaline metals are dissolved as sulphates. Major difficulties are involved with the removal of iron and the effective separation and decomposition of the aluminum sulphate salts.

Hydrated aluminum sulphate, $Al_2(SO_4)_3 \cdot 18H_2O$, does not readily crystallize from solution into manageable crystals. On evaporating, an aluminum sulphate solution becomes increasingly more viscous and finally results in a sticky, viscous mass of microscopic, mushy crystals. To filter and wash impurities from this material is practically impossible. Various techniques have been devised to circumvent these problems.

Kretschmar developed a process to extract aluminum sulphate produced by sulphuric acid leaching of clay (1,2). This

process involved an interrupted vacuum crystallization technique
to separate large aluminum sulphate crystals from the iron-con-
taminated leachate. The procedure was to concentrate the dilute
aluminum sulphate solution until the mushy crystals formed.
Fresh dilute aluminum sulphate solution was then added to partially
dilute and dissolve the mush. This in turn was reconcentrated
until the mush reformed. The dilution and concentration cycle
was continued until the crystals grew to sufficient size to allow
effective separation and washing. A double crystallization was
necessary to produce an iron-free product. However, the efficiency
of the crystallizer operation was relatively low.

Saeman of Olin Mathieson Chemical Corporation, developed
a vacuum crystallizer incorporating a fines elutriation zone to
grow large (-16+30 mesh) pure aluminum sulphate crystals (2).
Providing the initial iron content was not excessively high and
carried out in the presence of excess acid, this technique for
growing large crystals was sufficient to purify the product.
Because of the controlled size of the crystals, it was claimed
possible to dehydrate the crystals, without fusion or melting, in
a rotary dryer by increasing the temperature from 95° up to $200^{\circ}C$
over a 90-minute period.

The growth of large crystals permits the separation of
aluminum sulphate from the iron-contaminated liquor. Under most
conditions a double precipitation would be necessary to ensure
the reduction of, not only iron, but also silica and alkali
sulphates. Peters et al. reviewed three techniques for separating
iron and aluminum: removal of iron in electrolytic cells using

mercury cathodes, removal of iron by chemical precipitation as
an iron-manganese complex, and precipitation of the alumina from
an aqueous-ethanol solution leaving iron in solution (3). These
methods were expensive in both capital and operating costs. The
present day solvent extraction techniques probably offer more
efficient and less expensive routes to iron removal.

The North American Coal Company set up an experimental
facility in 1962 to produce 40,000 tons/year of hydrated aluminum
sulphate from sulphuric acid leaching of coal shales (1,4). It
was claimed that careful control of concentration and temperature
in the digestion stage left all of the silica, iron and other
metal oxides as insoluble residue. The strongly acid leach
liquor was cooled to crystallize fine aluminum sulphate crystals.
Aluminum sulphate seed crystals were probably added to promote
crystal growth. The acidic crystals were separated by centri-
fuging, neutralized, and shipped for kraft paper manufacture.
The company had intended to decompose some of the aluminum
sulphate to alpha alumina for aluminum production. This program
of recovering aluminum sulphate from coal wastes has been
terminated for reasons unknown.

Despite all the work to produce alumina via aluminum
sulphate, there does not appear to be any one process that has
proven effective and used commercially. The flow chart in Fig. 1
represents a general sulphuric acid process to produce alumina
via normal aluminum sulphate.

Figure 1. Sulphuric acid-solvent extraction process


```
                          CLAY, COAL REJECTS
                                 │
                                 ▼
                           ┌─────────────┐
                           │ DEHYDRATION │────────────▶ H₂O
                           └─────────────┘
                                 │
                                 ▼
       SULPHURIC ACID ────────┌─────────┐
                              │  LEACH  │
                              └─────────┘
                                 │
                                 ▼
                           ┌─────────────┐
                           │ FILTRATION  │────────────▶ RESIDUE
                           └─────────────┘
                                 │
                                 ▼
                        ┌───────────────────┐
                        │   IRON REMOVAL    │────────▶ IRON
                        │ SOLVENT EXTRACTION│
                        └───────────────────┘
                                 │
                                 ▼
                        ┌────────────────────┐
                        │   CRYSTALLIZATION  │
                        │ AS ALUMINUM SULPHATE│
                        └────────────────────┘
                                 │
                                 ▼
       H₂SO₄ WASH ─────────┌─────────────┐
                           │ FILTRATION  │──────────▶ TO ACID RECOVERY
                           └─────────────┘
                                 │
                                 ▼
                        ┌─────────────────┐
                        │ LOW TEMPERATURE │────────▶ H₂O
                        │   DEHYDRATION   │
                        └─────────────────┘
                                 │
                                 ▼
                        ┌──────────────────┐
                        │ HIGH TEMPERATURE │────────▶ ACID VAPOUR
                        │   CALCINATION    │          TO RECOVERY
                        └──────────────────┘
                                 │
                                 ▼
                              ALUMINA
```
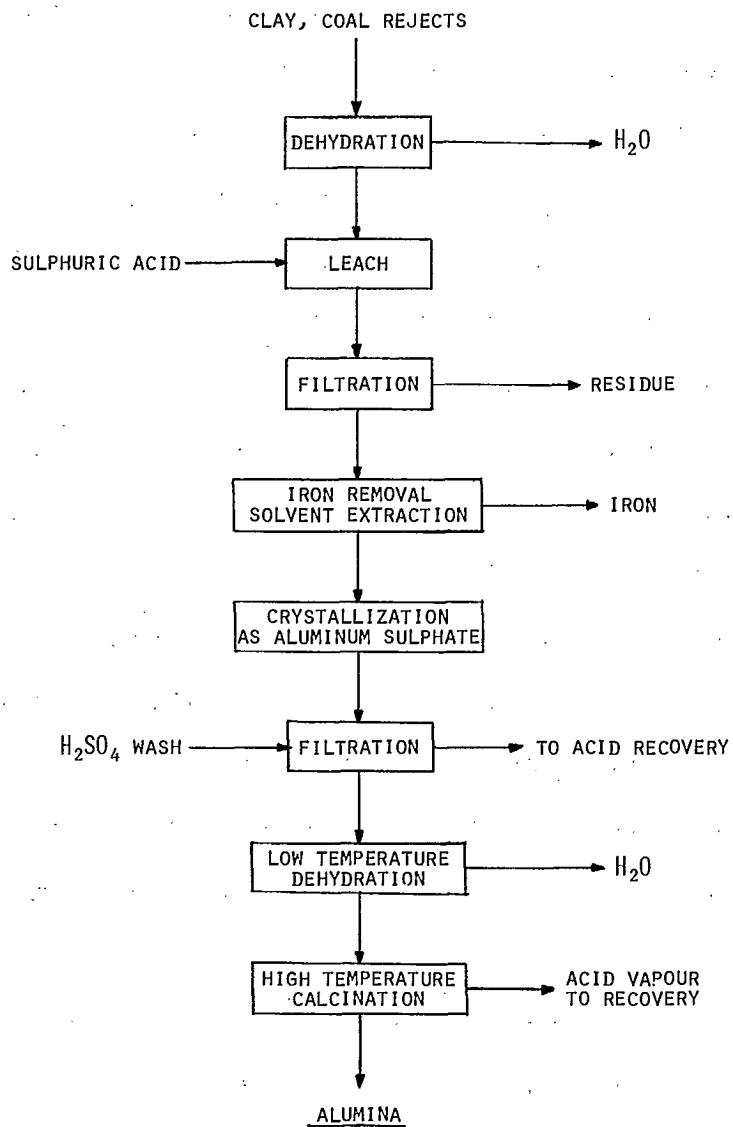
Potassium Alum Processes

A variety of processes have been proposed wherein
aluminum is crystallized as a double alum salt, i.e., as
potassium or ammonium aluminum sulphate. These salts can be
recovered as large, manageable crystals from sulphuric acid
leaches thus eliminating the difficulties of crystallizing
aluminum sulphate. Recovery of alum is the usual procedure
where the alumina material contains considerable amounts of potas-
sium, e.g., alunite $KAl_3(SO_4)_2(OH)_2$. During the Second World War,
pilot plants operated in the United States using the Kalunite pro-
cess, Fig. 2, and some work was also done on it in Russia (5).

Recently a consortium of three companies - Earth Sciences
Inc., National Steel Corp. and the Southwire Co.-started an
alunite pilot plant based on a Russian-developed process (6-7).
The flowchart of this process is shown in Fig. 3. It is inter-
esting that the alumina is extracted by caustic digestion followed
by desilication and precipitation as hydrated aluminum oxide, and
not as an alum.

Processes have been investigated wherein potassium
sulphate was added to the aluminous material to make up for the
potassium deficiency and subsequently crystallize potassium alum.
One such process was evaluated by Peters et al. (8) on clay and
another was examined by CANMET, then known as Mines Branch of
EMR (9) on shale. In the USBM process, shown in Fig. 4, calcined
clay is leached with a sulphuric acid-potassium sulphate solution.
An excess of clay neutralizes the solution to precipitate most of
the iron during leaching. After filtering, the dissolved iron
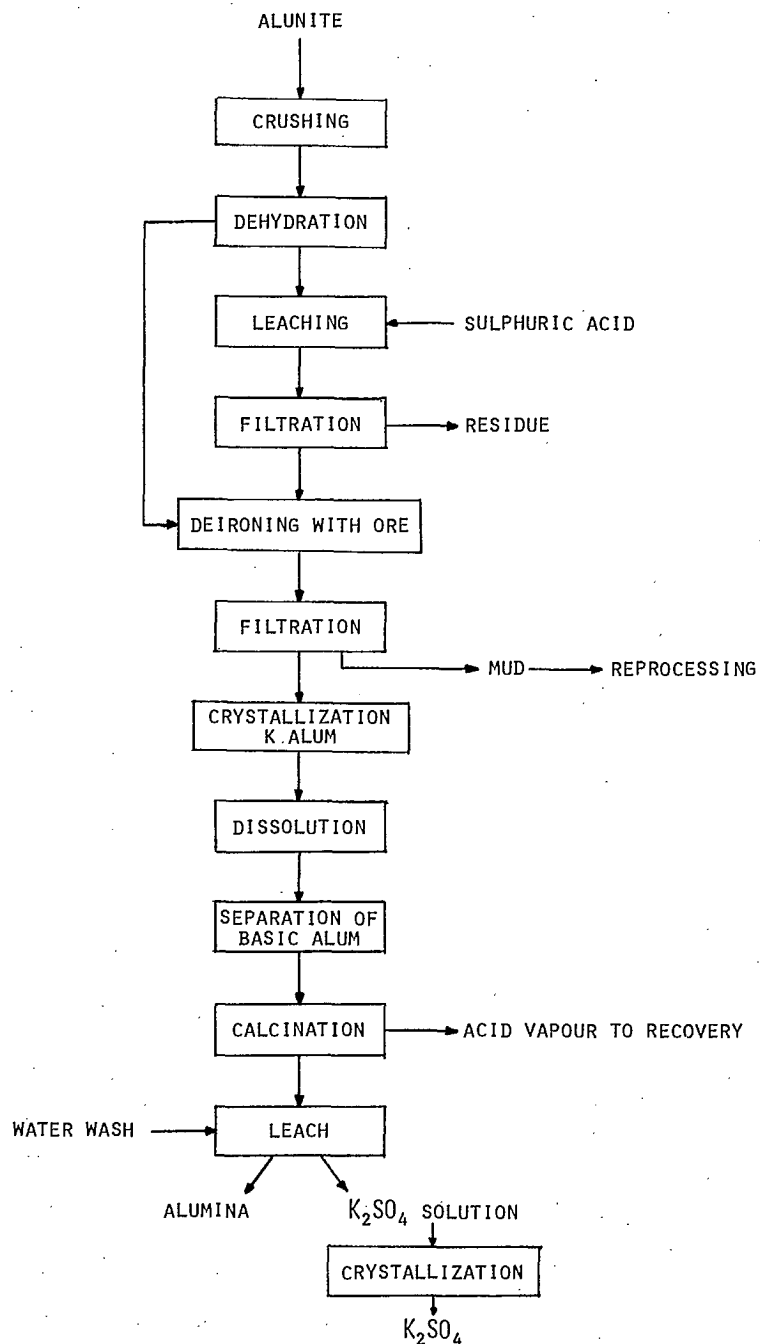
Figure 2. Kalunite process

```
                        ALUNITE
                           │
                           ▼
                     ┌───────────┐
                     │  CRUSHING │
                     └───────────┘
                           │
                           ▼
          ┌──────────┌────────────┐
          │          │ DEHYDRATION│
          │          └────────────┘
          │                │
          │                ▼
          │          ┌────────────┐
          │          │  LEACHING  │◄──── SULPHURIC ACID
          │          └────────────┘
          │                │
          │                ▼
          │          ┌────────────┐
          │          │ FILTRATION │───► RESIDUE
          │          └────────────┘
          │                │
          │                ▼
          └───►┌────────────────────┐
               │ DEIRONING WITH ORE │
               └────────────────────┘
                           │
                           ▼
                     ┌────────────┐
                     │ FILTRATION │
                     └────────────┘
                           │
                           └──────► MUD ──────► REPROCESSING
                           │
                           ▼
                  ┌───────────────┐
                  │ CRYSTALLIZATION│
                  │    K.ALUM      │
                  └───────────────┘
                           │
                           ▼
                     ┌────────────┐
                     │ DISSOLUTION│
                     └────────────┘
                           │
                           ▼
                  ┌───────────────┐
                  │ SEPARATION OF │
                  │  BASIC ALUM   │
                  └───────────────┘
                           │
                           ▼
                     ┌────────────┐
                     │ CALCINATION│───► ACID VAPOUR TO RECOVERY
                     └────────────┘
                           │
   WATER WASH ────►  ┌────────────┐
                     │   LEACH    │
                     └────────────┘
                        │      │
                        ▼      ▼
                   ALUMINA   K₂SO₄  SOLUTION
                                     │
                                     ▼
                          ┌────────────────┐
                          │ CRYSTALLIZATION│
                          └────────────────┘
                                     │
                                     ▼
                                   K₂SO₄
```
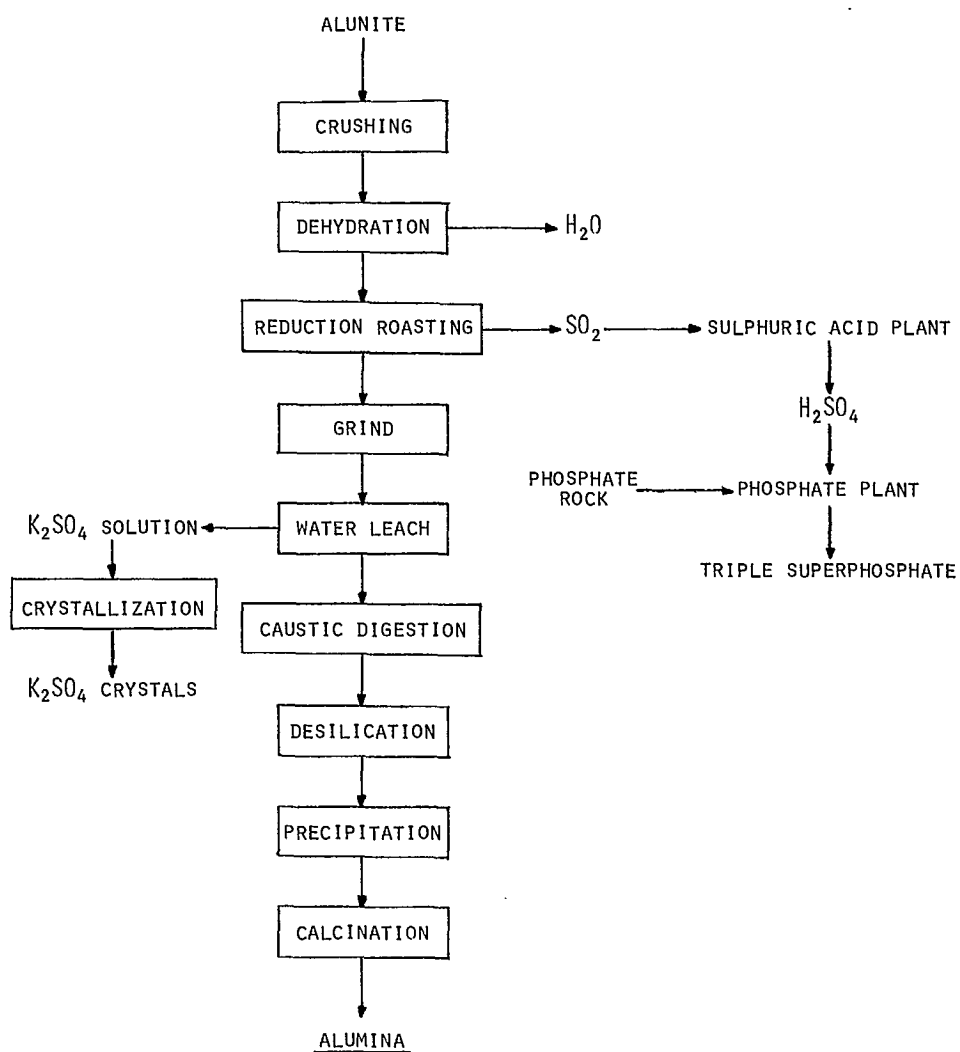
ALUNITE

CRUSHING

DEHYDRATION

LEACHING ← SULPHURIC ACID

FILTRATION → RESIDUE

DEIRONING WITH ORE

FILTRATION

→ MUD ──→ REPROCESSING

CRYSTALLIZATION K.ALUM

DISSOLUTION

SEPARATION OF BASIC ALUM

CALCINATION → ACID VAPOUR TO RECOVERY

WATER WASH → LEACH

ALUMINA K_2SO_4 SOLUTION

CRYSTALLIZATION

K_2SO_4

Figure 3. Alunite process

```
                              ALUNITE
                                 │
                                 ▼
                          ┌──────────────┐
                          │   CRUSHING   │
                          └──────────────┘
                                 │
                                 ▼
                          ┌──────────────┐
                          │  DEHYDRATION │──────────▶ H₂O
                          └──────────────┘
                                 │
                                 ▼
                   ┌─────────────────────────┐
                   │   REDUCTION  ROASTING    │────▶ SO₂ ──────▶ SULPHURIC ACID PLANT
                   └─────────────────────────┘                          │
                                 │                                      H₂SO₄
                                 ▼                                       │
                          ┌──────────────┐         PHOSPHATE            ▼
                          │    GRIND     │         ROCK ──────▶ PHOSPHATE  PLANT
                          └──────────────┘                              │
                                 │                                      ▼
                                 ▼                           TRIPLE SUPERPHOSPHATE
  K₂SO₄ SOLUTION ◀───── ┌──────────────┐
                        │  WATER LEACH  │
       │                └──────────────┘
       ▼                       │
  ┌───────────────┐            ▼
  │ CRYSTALLIZATION│   ┌──────────────────┐
  └───────────────┘    │ CAUSTIC DIGESTION│
       │               └──────────────────┘
       ▼                       │
  K₂SO₄ CRYSTALS               ▼
                        ┌──────────────┐
                        │  DESILICATION│
                        └──────────────┘
                               │
                               ▼
                        ┌──────────────┐
                        │ PRECIPITATION│
                        └──────────────┘
                               │
                               ▼
                        ┌──────────────┐
                        │  CALCINATION │
                        └──────────────┘
                               │
                               ▼
                            ALUMINA
```

Figure 4. Potassium alum process USBM
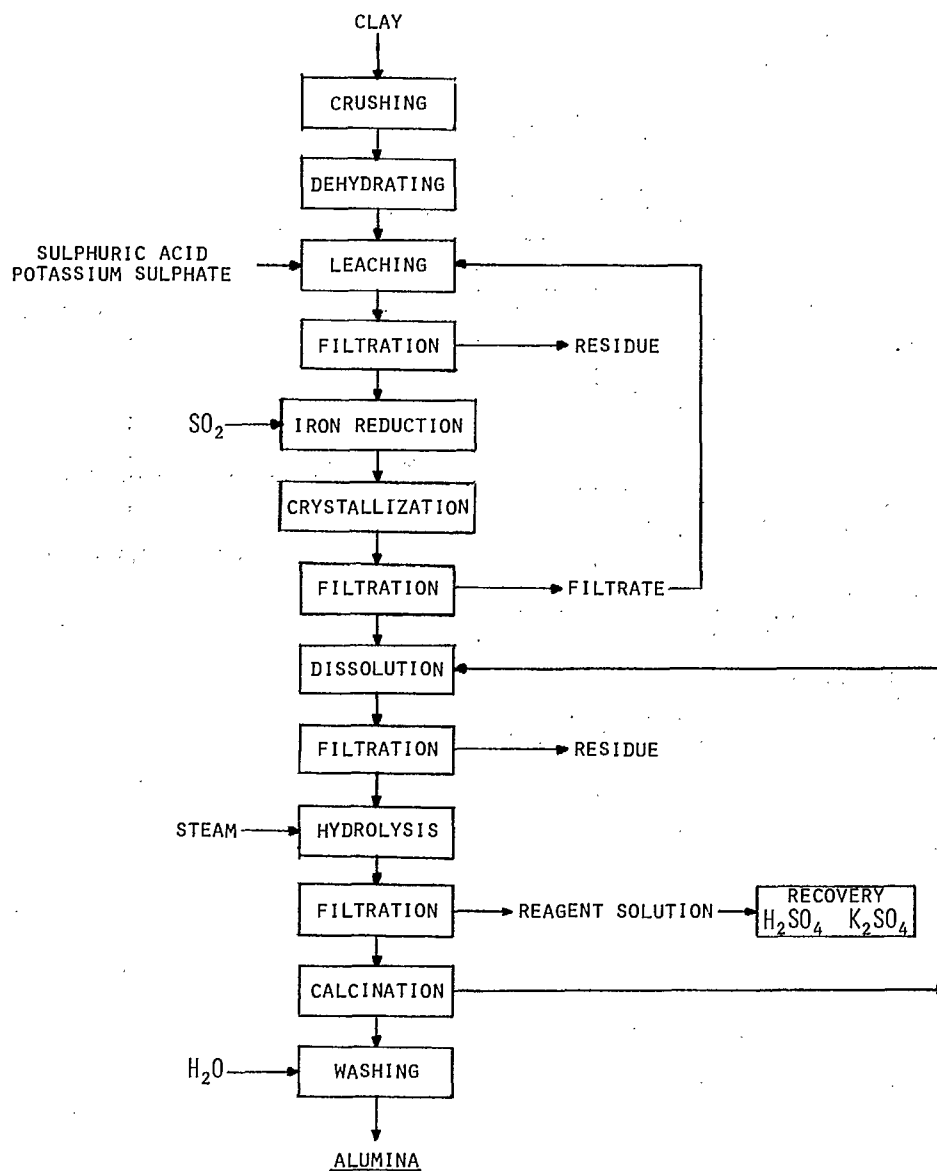
is reduced to the ferrous state by SO_2 to prevent precipitation when the potassium alum is crystallized. The crystals are dissolved in dilute alum solution, filtered to remove insolubles, and then steamed in autoclaves to precipitate basic alum. The basic alum is dehydrated and calcined. The calcine is water washed to remove potassium sulphate from the alumina.

The Canadian process shown in Fig. 5 is based on shale which is roasted with sulphuric acid and then leached with a weak acid solution (9). The pH of the leachate is raised with lime to hydrolyse most of the iron. After filtering, potassium sulphate is added to crystallize alum. This alum is purified either by double or single crystallization followed by a solvent extraction on the crystal slurry with Primene JM to remove residual iron. The purified alum is then decomposed, washed to remove potassium sulphate, and calcined. In both these processes, the necessity of adding and recycling potassium sulphate would add to the cost. Considerable washing of the calcined product is necessary to reduce the potassium to an acceptable 0.01% K_2O in the alumina, and of course this solution would have to be concentrated to recover the potassium sulphate.

The crystallization of the aluminum salt as potassium alum overcomes the difficulties associated with the crystallization of aluminum sulphate. However, both normal potassium alum and aluminum sulphate in crystal form are associated with large amounts of hydrated water, e.g., $K_2Al_2(SO_4)_4 \cdot 24H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$ from the viewpoint if materials handling, there are between 6.6 and 9.3 weight units of hydrated salt for every unit of alumina.

Figure 5. Potassium alum process - CANMET, formerly Mines Branch of EMR
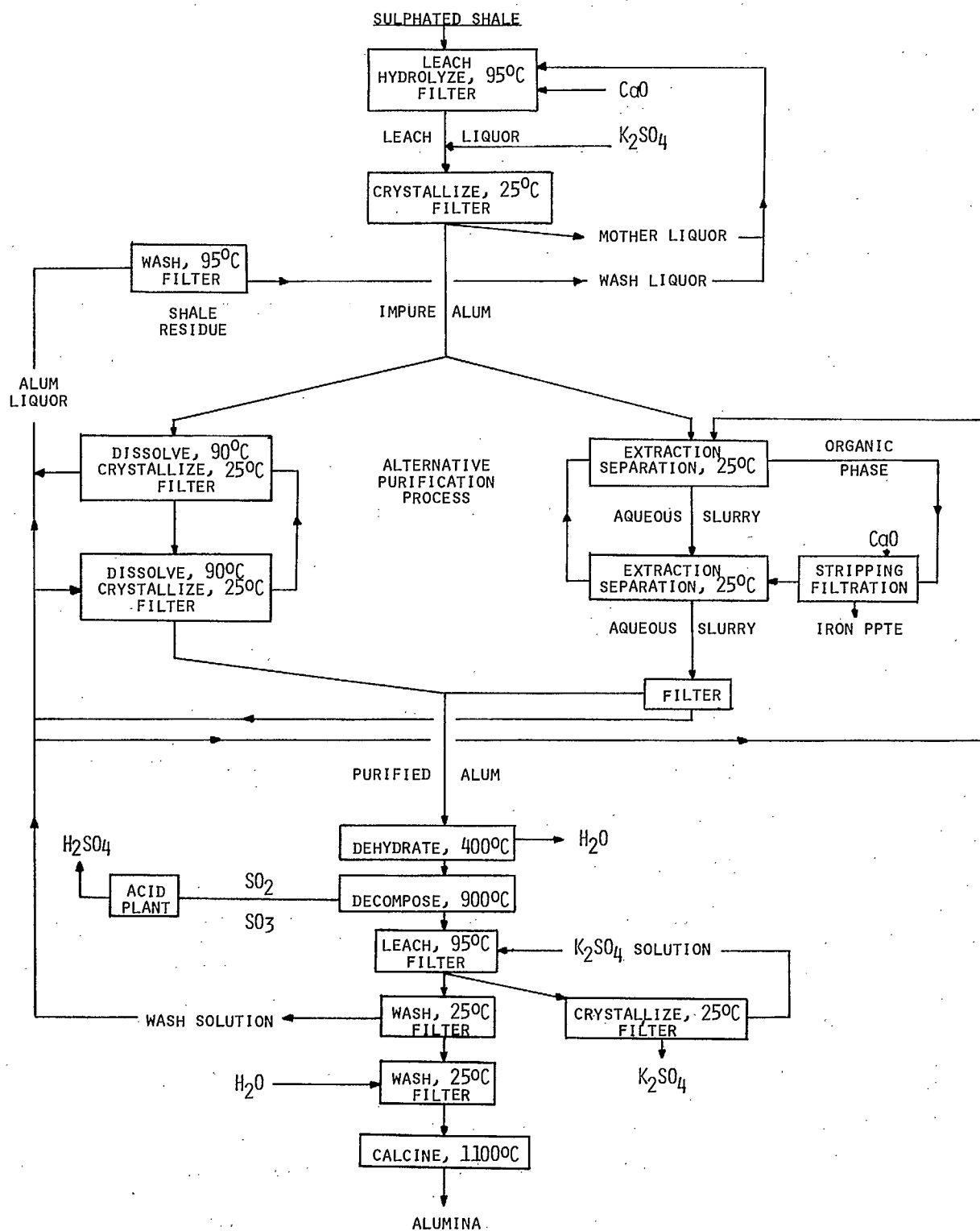
Considerable energy is consumed to drive off the water and sulphur oxides. Additionally, when these salts are heated, they melt into a viscous mass which, with poor heat transfer rates, tend to foul up equipment. Therefore, any alum process should aim to produce a basic salt which has less associated SO_2 and H_2O and does not melt on heating.

Ammonium Alum Processes

Alumina can be extracted and recovered via an ammonium alum salt. Peters et al. describes two such processes (10). One is based on Buchner's Aloton process in which aluminous material is pressure-leached with ammonium bisulphate solution. In the other, the feed material is roasted with ammonium sulphate and leached with water or dilute acid.

In the ammonium bisulphate process, Fig. 6, dehydrated clay is leached with a solution of 85% ammonium bisulphate and 15% ammonium sulphate. At 90°C and atmospheric pressure, about 85% of the alumina in the clay dissolves in 8 hours. After the residue is discarded, the iron, which also dissolves during leaching, is reduced to the ferrous state with a 50% ammonium sulphite - 50% ammonium bisulphate solution. Ammonium alum is separated by vacuum crystallization, re-dissolved and re-crystallized. The purified alum is then dissolved in 40% ammonium sulphate and treated with 20% aqueous ammonia in autoclaves at 100°C to pre-cipitate alumina trihydrate. The trihydrate is filtered, washed and calcined to Al_2O_3 at 1100°C.

Figure 6. Ammonium bisulphate process
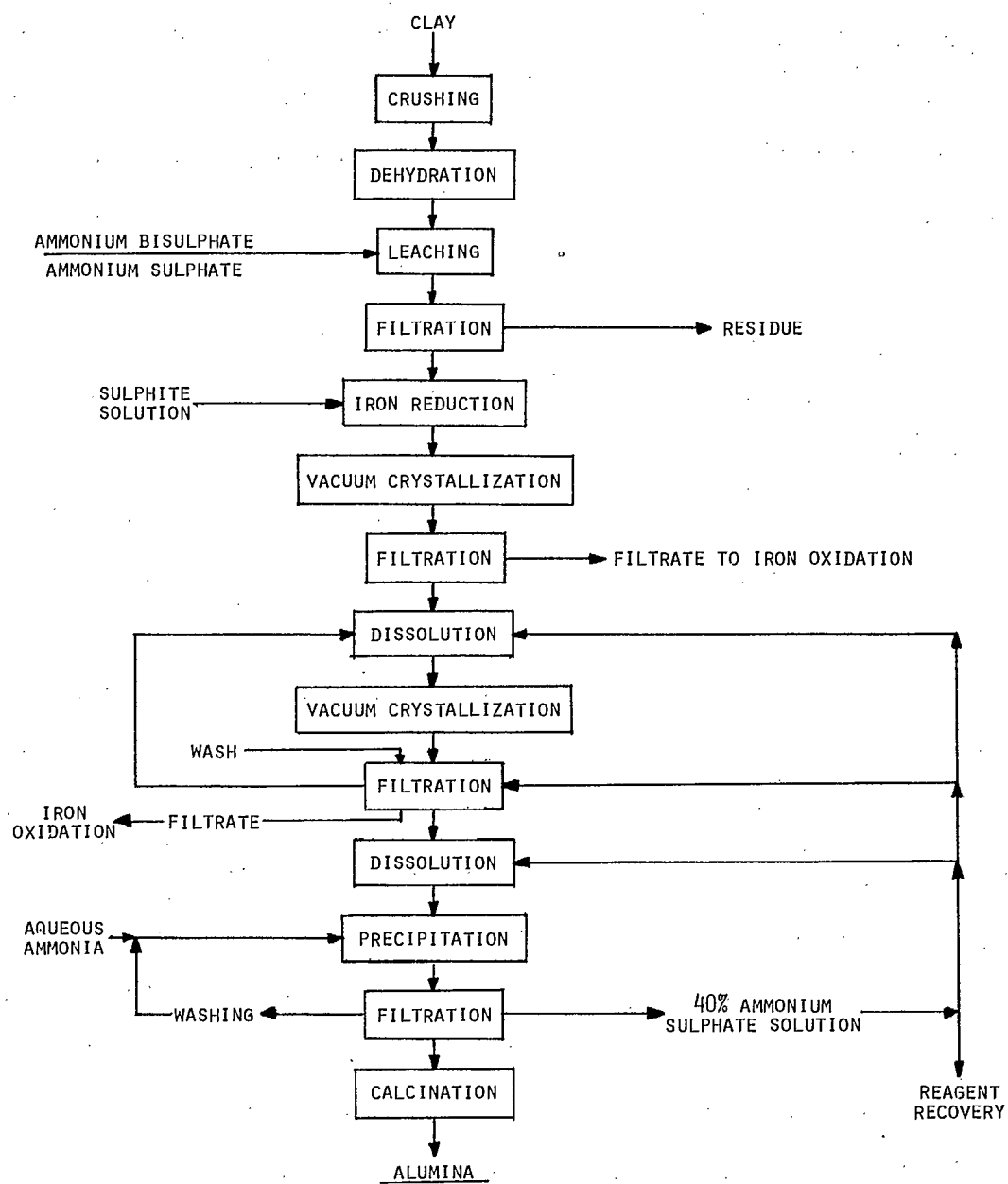
In the ammonium sulphate roasting process, finely ground clay is mixed with ammonium sulphate in a 1:6 ratio of alumina:ammonium sulphate. The mixture is pelletized and sintered at 400 to 450°C. The resulting sinter is crushed and leached in 0.5 to 3.0% sulphuric acid. The residue is discarded and the solution treated in the same manner as in the ammonium bisulphate process.

Basic Aluminum Sulphate Processes

Several acid processes have been proposed whereby alumina is separated from the mother liquor by crystallization of basic aluminum sulphate salts. These processes have some advantage over alum or aluminum sulphate methods since they produce, by means of hydrolysis, basic crystalline salts which have lower water of crystallization, less associated sulphate, and are practically insoluble in water.

One such process developed by T. R. Scott of the Commonwealth Scientific and Industrial Research Organizations, is shown in flowsheet form in Fig. 7 (11,12). Two stage counter-current leaching is used. Ore is added to the second stage (modification) to convert the acidic alum sulphate from the first stage (digestion) to basic aluminum sulphate. Some iron is precipitated in this weak acidic second stage at a pH of 3.5. Leaching of the ore is completed in the strongly acidic first stage at 180°C and at a pressure of 1030 kPa (150 psig). Iron remaining in the basic aluminum sulphate solution is reduced to the ferrous state with SO_2 to prevent its precipitation in the hydrolysis stage. At this stage the solution is heated to 220°C to

Figure 7.   Scott-CSIRO process
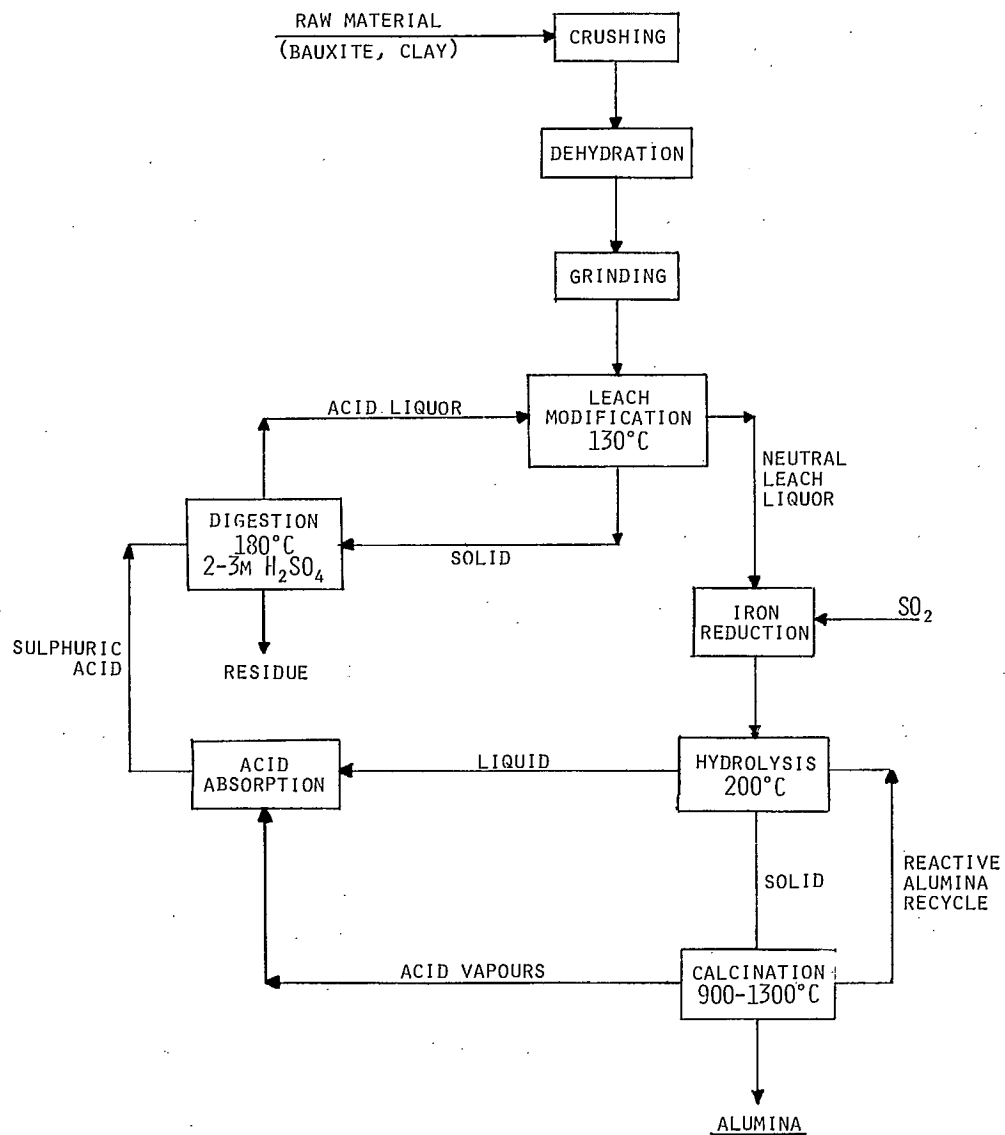
precipitate basic aluminum sulphate $3Al_2O_3 \cdot 4SO_3 \cdot 9H_2O$. The addition of reactive alumina to the hydrolysis stage increases the yield of basic salt to about 80%. This material is fairly insoluble in water and can be filtered and washed.

By comparison with other alum processes, the basic aluminum sulphate has only 2.5 weight units of hydrated salt per weight unit of alumina. On calcining, there is less water to be removed and less SO_2 to be recovered than with alum processes. However, alkaline metals present in the ore reduce yield as they also precipitate during the hydrolysis stage as alunites and carry down three aluminum ions with each sodium and potassium ion. Scott reported that there is some problem reducing iron to an acceptable level. Another disadvantage is the need to recycle large amounts of active alumina from calcining back to the hydrolysis stage as seed to increase the hydrolysis yield. This recirculation of materials would increase energy requirements.

Barrett et al. (13) evaluated a sulphurous acid-sulphuric acid process, shown in Fig. 8, whereby clay is leached with sulphurous acid to produce aluminum sulphite, and the residue from this operation is then leached with sulphuric acid to produce aluminum sulphate. The two separate leach solutions are combined so that four moles of aluminum sulphite react with one mole of aluminum sulphate to form a basic aluminum sulphate $5Al_2O_3 \cdot 3SO_3 \cdot 32H_2O$. Steam is added to the reaction vessel, driving off SO_2 and precipitating basic aluminum sulphate. Ferric iron impurities are reduced to ferrous sulphate in the same reactions so that the resultant basic salt contains some iron, silica and other impurities.

Figure 8.   Sulphurous acid-sulphuric acid process
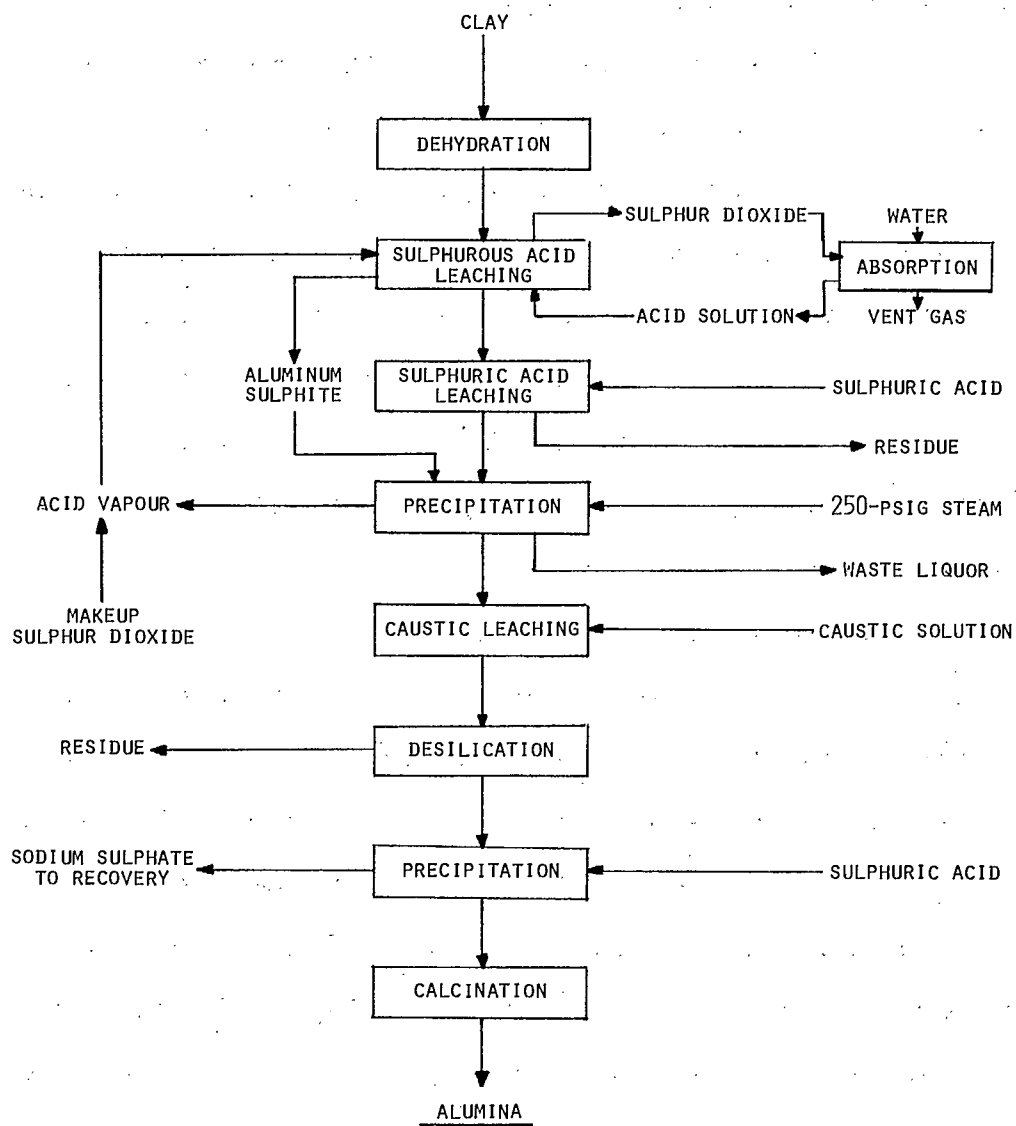
A caustic purification is used to reduce impurities to an acceptable level. The basic salt is dissolved in sodium hydroxide as sodium aluminate. Iron, precipitated as the hydroxide, and silica, as an insoluble sodium aluminium silicate, are removed by autoclaving for 6 hours at $150^{\circ}C$ and 500 kPa.

After filtering to remove the insoluble impurities, the sodium aluminate is reacted with sulphuric acid to precipitate alumina trihydrate which is then calcined to alumina. Recovery of acid and caustic is quite complex. Sodium sulphate solution from the precipitation of alumina trihydrate is concentrated and electrolysed in diaphragm cells to sodium hydroxide and sulphuric acid which are then separately concentrated. This recovery technique is yet to be performed on a large scale.

Pechiney H Plus Process

Aluminum Pechiney developed a process for leaching shales and clays with strong sulphuric acid and then precipitating and purifying aluminum chloride hexahydrate from the sulphate liquor with hydrochloric acid gas (14,15). The flowchart for this process, shown in Fig. 9, is rather complex, but all impurities are accounted for and removed so that the end alumina product is purer than that of the Bayer process. Alcan Aluminum Ltd. is a partner with Pechiney in the development and construction of a 20-ton Al_2O_3 per day pilot plant in France.

If the ore contains considerable combustible organics and carbon, it is roasted in an oxidizing atmosphere without additional fuel. A clay or schist is not preroasted. Leaching is accomplished in 1 to 4 hours with an excess of 65% sulphuric

Figure 9. Pechiney H Plus process
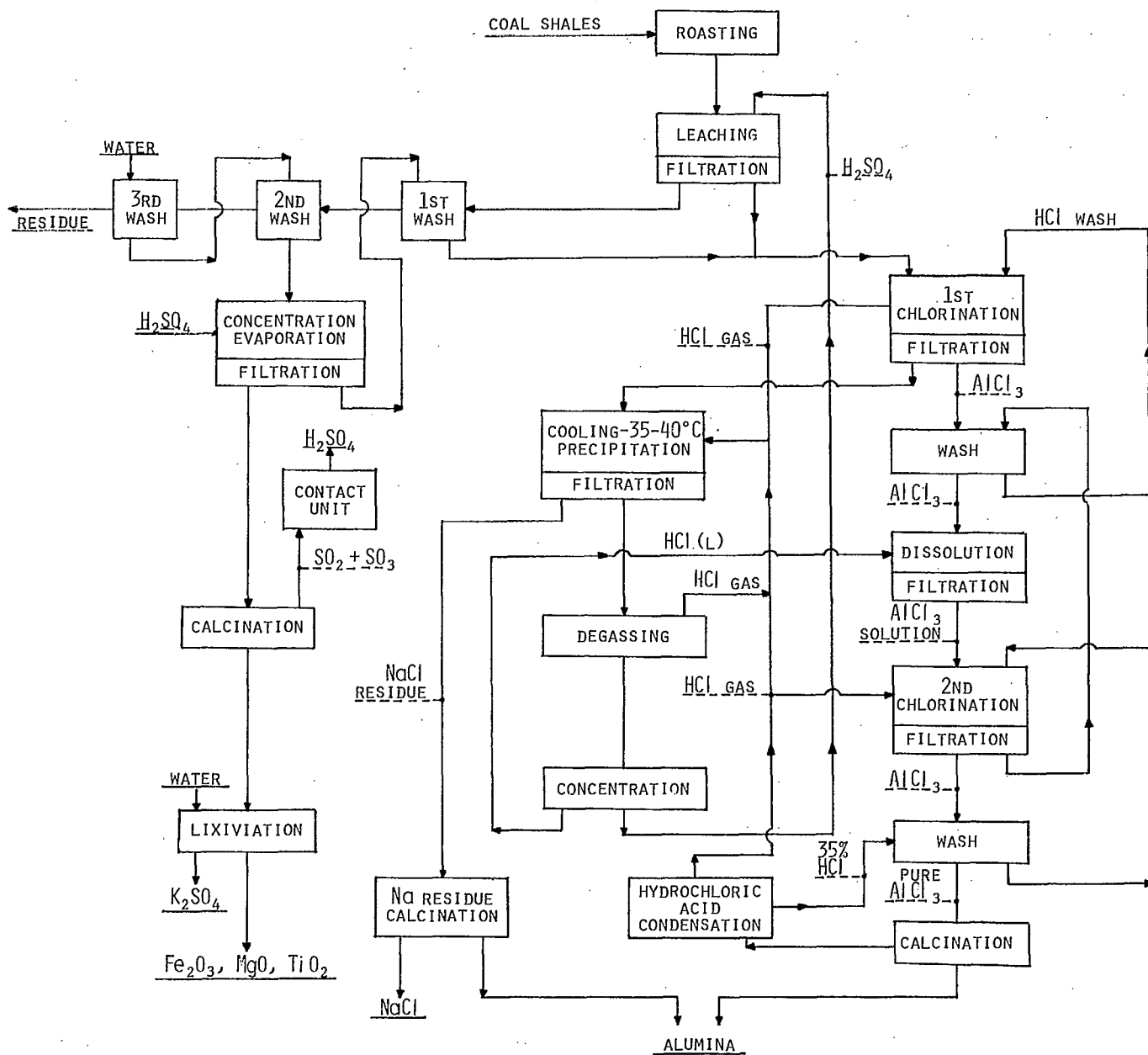
acid at 140°C. Because the impurities are less soluble in concentrated acid than in dilute acid, all the silica, 90% of the titania, and 80% of the alkali metals remain with the residue. Iron from preroasted ore is in the oxidized state and is converted to ferric sulphate that combines with potassium sulphate to form a double salt which is only slightly soluble in strong sulphuric acid. With ore which is not preroasted, the iron is in the ferrous state and must be oxidized to ferric sulphate with chlorine gas before it will combine with potassium as an insoluble salt.

The residue from the leach is washed in three counter-current washes. The filtrate from the second wash contains much of the iron and potassium which is insoluble in concentrated acid but becomes soluble in the more dilute wash. This wash is concentrated to precipitate the sulphates which are removed by filtering. The filtrate is used as the wash for the digestion residue and then joined with the mother liquor from the digestion.

This mother liquor is diluted to approximately 40 g/l Al_2O_3 and cooled to 40°C. Additional cooling is required while saturating the solution with hydrochloric acid gas to precipitate aluminum trichloride hexahydrate. Most of the impurities remain in solution. The precipitate is filtered, washed with hydro-chloric acid, heated and dissolved in dilute acid, filtered again to remove any insolubles, cooled, and reprecipitated with hydro-chloric acid gas.

In an alternative method, not shown in Fig. 9, the mother liquor is processed through multistage crystallizers.

By careful control of temperatures and sulphuric acid concentration well crystallized aluminum sulphate is obtained. After filtering, the mother liquor is returned to the leach circuit. The impure aluminum sulphate is dissolved in hydrochloric acid wash solution and then sparged with hydrochloric acid gas to precipitate aluminium trichloride hexahydrate.

The mother liquor from the first precipitation and filtration is further cooled to $30-35^{\circ}C$ with the addition of more gas to precipitate sodium chloride. Following removal of the solid chlorides, the solution is heated to drive off hydrochloric acid gas which is returned to the circuit. The resultant sulphuric acid solution is cooled to $115-120^{\circ}C$ and chlorine is injected to oxidize any ferrous to ferric sulphate which then precipitates with potassium as an insoluble salt. These salts are calcined to recover SO_2 and SO_3, for sulphuric acid, and Fe_2O_3 and K_2SO_4.

The purified aluminum trichloride hexahydrate is heated to $1100^{\circ}C$ to produce alumina and hydrochloric acid. The resultant alumina is somewhat finer and purer than that obtained by the Bayer process.

HYDROCHLORIC ACID

Hydrochloric Acid Processes

Hydrochloric acid is one of the more chemically aggressive of the commercial acids and as a result can extract alumina from many alumina-bearing minerals at high yields with

relatively short leach times. Advantages of using hydrochloric
acid are the ease of filtration of slurries and the relative
ease with which aluminum trichloride hexahydrate can be recover-
ed and decomposed. Its aggressiveness necessitates the use of
corrosion resistant plastics, rubber and glass-lined vessels
and piping.

Peters et al. reviewed five hydrochloric acid processes,
the major differences being the method used to remove iron from
the solution and the subsequent treatment to obtain anhydrous
alumina (16). Calcined clay or other aluminous material is
leached at about 100^OC, generally at atmospheric pressure, with
15 to 25% hydrochloric acid. Practically all the aluminum and
iron passes into solution as soluble chlorides, along with most
of the alkaline metals and a small amount of silica.

Iron can be removed from the leach liquor by solvent
extraction. Ferric chloride is readily extracted in ethyl or
isopropyl ether cyclohexanone and amines. The ferric chloride
is stripped from the solvent which is then recycled. The iron-
free aluminum chloride is crystallized in evaporators as aluminum
trichloride hexahydrate. These crystals are separated from the
liquor and are calcined to alumina and HCl gas (Fig. 10).

A second method, first patented by Gooch in 1896,
precipitates aluminum trichloride hexahydrate from the leach
solution with hydrochloric acid gas (16). Because of the low
solubility of aluminum chloride in strong hydrochloric acid
solutions compared with other chlorides such as iron, calcium,
potassium and magnesium, an effective separation of aluminum

Figure 10.   Hydrochloric acid-solvent extraction process
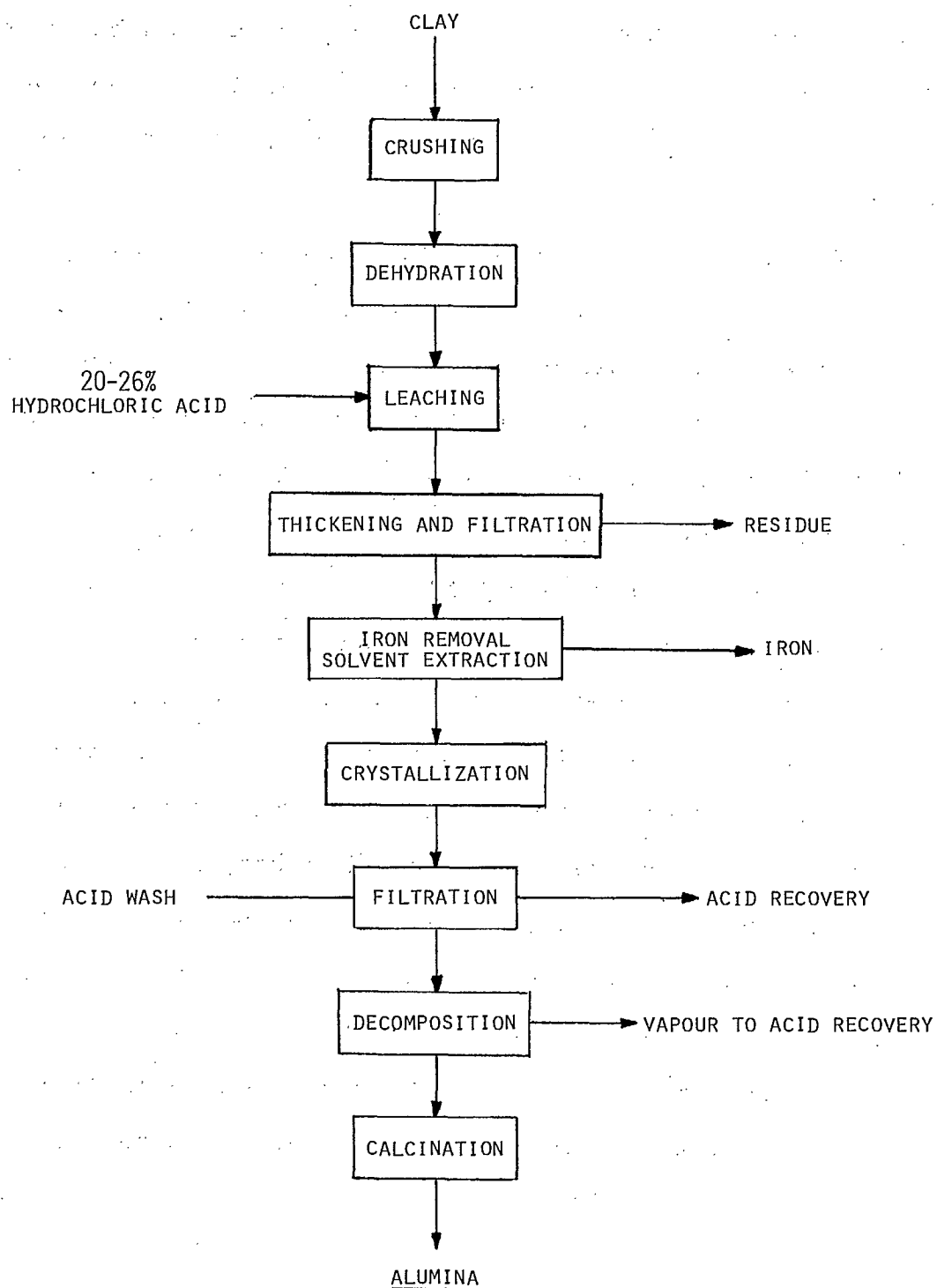
chloride can be made from these impurities. Sodium, if present, may precipitate along with the aluminum chloride. Cooling is required to remove heat evolved from the dissolution of the hydrochloric acid gas.

From the author's practical experience, a single gas precipitation will not produce aluminum trichloride hexahydrate of sufficient purity to obtain cell-grade alumina on calcining. Some silica will have dissolved in the initial leach, particularly if the leach were done in a relatively dilute acid, e.g., 15% HCl. As the leach liquor is made more acidic with hydrochloric acid gas, silica will come out of solution. To remove other impurities such as iron would require excessive washing with strong acid. Consequently, aluminum chloride from a single gas precipitation requires additional purification. This could be done by dissolving the aluminum chloride in dilute hydrochloric acid, filtering to remove insolubles such as silica, and reprecipitating the aluminum chloride with more hydrochloric acid gas. Such a procedure reduces the impurities such as iron and calcium by a further factor of about 10 so that the resultant calcined product is very pure.

Alternatively, as suggested by the USBM, the aluminum chloride from a single gas precipitation could be redissolved and subjected to solvent extraction to remove iron, and the aluminum chloride subsequently recrystallized by evaporation. At present, the USBM is operating a miniplant for hydrochloric acid leaching of clay. In this operation, iron is removed by solvent extraction before aluminum chloride is crystallized.

Aluminum trichloride hexahydrate will be precipitated in a continuous crystallizer or by gas sparging.

Two techniques, patented by Anaconda, employ caustic purification (16). In one process, the hydrochloric acid leach liquor, containing ferric chloride, is evaporated to produce an impure aluminum chloride which is subsequently calcined to an impure alumina. This alumina is treated by a modified Bayer process wherein it is dissolved in caustic, filtered to remove the insoluble impurities such as iron, cooled and seeded to precipitate alumina trihydrate, and calcined to pure alumina.

The second Anaconda process takes the crude alumina produced in the same manner as above and sinters it with limestone and soda ash to form sodium aluminate. The sodium aluminate is leached in water, filtered, precipitated as alumina trihydrate with carbon dioxide, and calcined. Both Anaconda processes require three and four sintering operations at high temperatures, compared with the usual two (clay dehydration and alumina calcination), and therefore would result in high fuel energy consumption.

A hydrochloric acid leach process catalysed by a small amount of fluosilicic acid has recently been patented by a German company (17). High alumina clay and even anorthosite can be attacked without being preconditioned by dehydrating or melting and quenching (in the case of anorthosite) which represents a considerable energy saving. The fluosilicic acid disrupts the alumina-silicate bonds and allows the alumina to dissolve in solution. Leaching is carried out in 15 to 25% hydrochloric acid

and 1 to 5% fluosilicic acid near the boiling temperature for one to three hours. After filtering, iron is removed by solvent extraction and the alumina trichloride hexahydrate precipitated by hydrochloric acid gas.

Preliminary experimental results have recently been reported by Ni et al. (USSR) on HCl leaching in which regeneration of HCl and the decomposition of $AlCl_3$ are accomplished electrochemically with the use of ion exchange membranes (18). The prepared ore (high-silica bauxite, clay, ashes) is leached with 14 to 18% HCl to dissolve aluminum, iron and vanadium. The separated silica residue can be used in the building industry. The iron and vanadium compounds are separated from the solution by tributyl phosphate. Separation of free HCl is effected in a multicell electrodialysis apparatus with ion exchange membranes. A further step includes electrochemical decomposition in ion-exchanging membranes in which $AlCl_3$ serves as catholyte and H_2SO_4 as anolyte and the result of which is aluminum oxychloride and regenerated HCl. After roasting the aluminum oxychloride, a fine-grained alumina is produced, free of alkali, iron and silica, which is suitable for aluminum electrolysis or for sorbants and catalysts. It is noted in the report that this process is more expensive than alkali leaching.

NITRIC ACID

Nitric Acid Processes

There are two approaches to nitric acid leaching of aluminous materials, the first being to use an excess of acid

which dissolves most of the aluminum and iron, and the second being to use a deficiency of nitric acid, i.e., less than the stoichiometric amount required to convert all the aluminum to aluminum nitrate nonahydrate. Under the latter condition, little iron is dissolved and that which is dissolved can be precipitated. The alumina extraction is lower because there is insufficient acid to react with all the alumina. By comparison with other acids, nitric acid processes require longer leach times and are often done under pressure.

Although some early work was done with nitric acid leaching of aluminous material, the first major pilot plant operation was the Nuvalon process in Germany. This process was evaluated by the USBM (19). Calcined clay is digested with 30% nitric acid for six hours at 160°C and 580 kPa (85 psig) pressure. Less than stoichiometric nitric acid is used to dissolve 85% of Al_2O_3, producing a slightly basic aluminum nitrate solution in which the iron is almost insoluble. The leach solution and residue are held in thickeners for approximately 14 hours where additional aluminum nitrate hydrolyses to the basic form. Any iron that initially dissolves, also hydrolyses and precipitates as the hydroxide.

After filtering, normal aluminum nitrate nonahydrate is crystallized out of the solution in vacuum crystallizers leaving a basic liquor which is recycled. The crystalline material is calcined to alumina at 500°C. A steam atmosphere is maintained to promote the formation of nitric acid. Alumina is converted to the required alpha phase by calcining at 1100°C. By careful
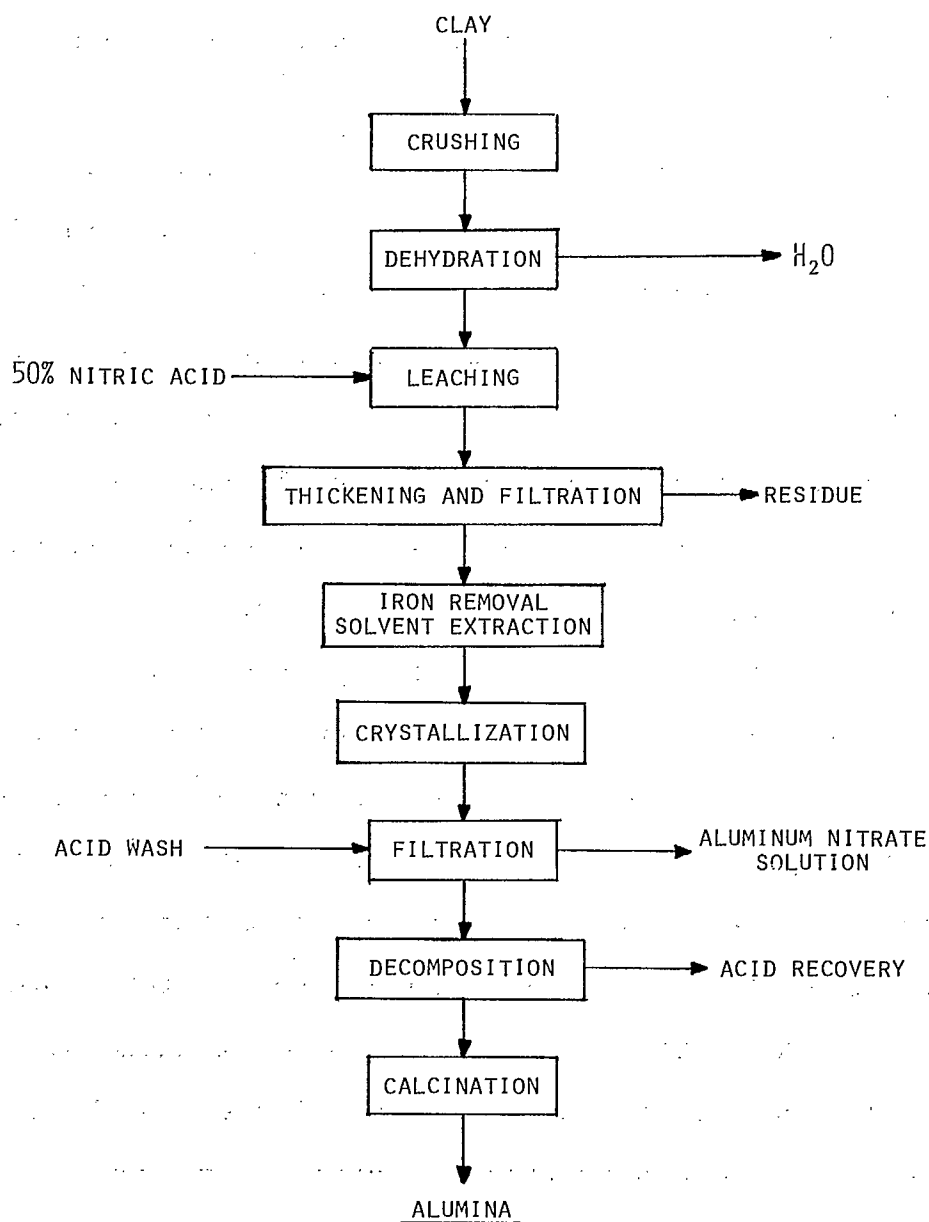
control of the digestion stages, acidity, time and temperature,
it is reported that 80 to 90% of the alumina can be extracted
and that the resultant product contains 0.03% Fe_2O_3 and less than
0.01% SiO_2 (16).

A process developed by Arthur D. Little Inc. was the
basis for a 1974-75 evaluation by the USBM in their miniplant
project (20). Calcined clay is leached at an acid concentration
of 50 to 55 wt % nitric acid at 125°C for four hours at atmospheric
pressure. Slightly over 90% of the alumina dissolves using 95%
of the nitric acid required to react with all the alumina to
form normal aluminum nitrate. Some iron dissolves. After
separation from the residue, the liquor is subjected to solvent
extraction to reduce the iron to an acceptable level.

The iron-free solution is concentrated in vacuum
evaporators to crystallize 85% of the alumina nitrate as nona-
hydrate. The crystals are separated, washed with nitric acid,
and then heated to 400°C to decompose aluminum nitrate and
recover nitric acid vapour. Final calcining to 1100°C produces
alpha alumina. The USBM has also decomposed aluminum nitrate
nonahydrate in a fluid bed reactor. Acid losses in the mini-
plant operations were higher than expected, which would result in
a higher cost product than was anticipated.

The Allied Chemical Corporation developed a process
whereby aluminous material in the form of clay was pressure
leached at 160-220°C and 550 kPa for 0.5-2 hr with 15-30% nitric
acid (21). Only 65% of stoichiometric requirement of nitric acid
to convert the aluminum to $Al(NO_3)_3 \cdot 9H_2O$ was used. Consequently,

Figure 11. Nitric acid-solvent extraction process

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                              CLAY
                               │
                               ▼
                        ┌──────────────┐
                        │   CRUSHING   │
                        └──────────────┘
                               │
                               ▼
                        ┌──────────────┐
                        │  DEHYDRATION │────────────▶ H₂0
                        └──────────────┘
                               │
                               ▼
 50% NITRIC ACID──────▶ ┌──────────────┐
                        │   LEACHING   │
                        └──────────────┘
                               │
                               ▼
                  ┌───────────────────────────┐
                  │  THICKENING AND FILTRATION │────▶ RESIDUE
                  └───────────────────────────┘
                               │
                               ▼
                    ┌──────────────────┐
                    │   IRON REMOVAL   │
                    │ SOLVENT EXTRACTION│
                    └──────────────────┘
                               │
                               ▼
                    ┌──────────────────┐
                    │  CRYSTALLIZATION │
                    └──────────────────┘
                               │
                               ▼
 ACID WASH ───────────▶ ┌──────────────┐         ALUMINUM NITRATE
                        │  FILTRATION  │────────▶     SOLUTION
                        └──────────────┘
                               │
                               ▼
                        ┌──────────────┐
                        │ DECOMPOSITION│────────▶ ACID RECOVERY
                        └──────────────┘
                               │
                               ▼
                        ┌──────────────┐
                        │  CALCINATION │
                        └──────────────┘
                               │
                               ▼
                            ALUMINA
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alumina extraction was only 65%; however, the ratio of $Al_2O_3:Fe_2O_3$ was 2440:1.

Boehmite $Al_2O_3 \cdot H_2O$ was precipitated from this basic aluminum nitrate solution by hydrolysis (22). After being diluted to a nitrate concentration of less than 25%, the solution was heated in an autoclave to 190-210°C to precipitate all the free alumina as boehmite. The solution was seeded to promote increased crystal size. The nitric acid, formed by dissolving N_2O_5 in water, and the $Al(NO_3)_3$ solution were recycled to treat fresh ore. With these processes there is no requirement for acid gas recovery. Additionally, as there is only one water of hydration combined with the alumina, the energy requirements and materials handling in calcining to alumina would be considerably less than with many other processes.

GIPKL Process

A Russian nitric acid process produces alumina and a byproduct nitrate salt fertilizer. Finely ground, roasted, kaolin is processed with nitric acid either in a percolator or in a diffusion apparatus at 90°C for 7 to 20 hours. After filtering to remove the residue, the solution is treated with active pyrolusite, MnO_2, to remove the iron. This portion of the process is inefficient because the pyrolusite must be recovered and regenerated, some manganese dissolves to contaminate the solution and iron removal is not total. A solvent extraction-ion exchange approach would remove iron more effectively. The iron-free solution is then neutralized with gaseous ammonia and steamed to 12% Al_2O_3. The solution is cooled and treated with ammonia to

precipitate aluminum hydroxide which, after washing, is calcined

to alumina. The ammonium nitrate solution is steamed to obtain

NH_4NO_3 crystals as fertilizer. In this process both ammonia and

nitric acid are consumed to produce over 5 tons of fertilizer to

1 ton of Al_2O_3. Consequently the operation would have to be

associated with both nitric acid and ammonia plants and have a

distribution system for a very large amount of fertilizer.

COMMENTS

Technical Considerations

This paper considers only technical aspects of a number

of acid processes; the economic evaluations will be considered in

a future report. From the foregoing brief descriptions of a

variety of processes, it is obvious that some are more practical

than others, particularly with respect to Canadian resources;

e.g., a potassium alum process would not be viable without a

source of alunite as feed stock. Insufficient information is

available to make a judgement on some processes, particularly

those reported in the Russian literature. No single process

described is perfect and none can produce alumina as cheaply as

the Bayer process for bauxite.

Many of the earlier processes used complex techniques

for solving the problem of iron contamination. Recent advances

in solvent extraction technology have simplified the removal of

iron so that it is no longer the major problem. However, because

permissible impurity levels in cell-grade alumina are low, other

impurities can cause difficulties. For example, the target specification for silica is 0.025 wt %, and although silica is relatively insoluble in acids the amount present can often be several times the maximum limit. Similarly the complete removal of nitrates, sulphates and chlorides from aluminum salts during calcination to alumina may prove difficult. Depending upon the nature of the aluminous material there is a possibility of the heavier elements, such as nickel, chromium, lead, etc., being in excess of the target specifications. Because solvent extraction is relatively selective, many of these impurities are not removed during the iron extraction.

An efficient crystallization method will usually serve to purify the aluminum salt. In most cases, a double crystallization will result in a product which readily meets the alumina target limits. Sometimes a combination of solvent extraction and careful crystallization will be sufficient. The successful technique is dependent upon the aluminous source material and its inherent impurities. The more soluble impurities present in the material the greater the likelihood that a double crystallization approach will be required.

Alternatively, the aluminous material may be leached in acid and recovered as an impure aluminum salt or alumina. This impure material can then be treated in a caustic media and recovered by a modified Bayer approach. These techniques generally give rise to complex flow sheets and reagent recovery systems.

The choice of acid process is not obvious. Although sulphuric acid is the cheapest, problems associated with

crystallizing and dehydrating aluminum sulphate are still major. There are no reports in the recent literature of any serious work being conducted with this acid alone. The H Plus process uses sulphuric acid as a leaching agent but recovers the aluminum as a hydrated chloride. The USBM miniplant program intends to evaluate sulphurous acid leaching, but will subsequently recover the alumina in a caustic media.

Previous cost evaluations by the USBM indicated that a nitric acid approach similar to the A.D. Little process was the most economical method for recovering alumina from clay. This process has recently been evaluated in the miniplant program; however, the results have not yet been published.

Hydrochloric acid is the most aggressive of the common acids and hence leach duration is relatively short. The recovery and decomposition of aluminum trichloride hexahydrate is the least complex of the acid processes. The extraction of alumina from clay with hydrochloric acid is presently being evaluated in the miniplant program. In general, the major effort of industry appears to centre around processes utilizing either nitric or hydrochloric acids.

Canadian Resources

As previously mentioned, Canada does not have known deposits of high alumina clay. Most of the processes discussed were devised in other countries which possess material such as kaolinite. Canada's present resources appear to consist mainly of anorthosite, clays associated with coal wastes, and low grade clays.

Anorthosite is the largest single potential alumina
resource, but this rock is not normally soluble in acid. It can
be made acid soluble by melting and then quenching the anortho-
site in an amorphous state (23). However, the melting point is
in the vicinity of 1500°C which makes this approach unattractive
from the viewpoint of energy consumption. Alumina can be
extracted from anorthosite using a lime sinter, lime-soda sinter
or a hydrochemical method, but all these are alkaline techniques
and beyond the scope of this report. Pressure leaching with
nitric acid has been tried but only a 50% yield was reported.
The addition of a small amount of hydrofluoric or fluosilicic
acid to a hydrochloric acid leach of ground anorthosite may
have some promise. Laboratory experiments conducted by the
author have given 90% alumina extraction; however, more work
needs to be done, particularly on the recovery of acid chlorides
from the contaminated waste acid liquor.

The extraction of alumina from coal wastes is dependent
on the nature of the deposit. There are some advantages to using
this material as it is already mined and partially crushed as
part of the coal operation. There may be sufficient carbon
present to provide the thermal energy required to dehydrate the
clay and also to reduce the iron oxides sufficiently so that they
may subsequently be removed magnetically. Fly ash from conven-
tional coal firing is not amenable to acid treatment because it is
in a sintered form. There is a possibility that ash from fluidized
bed combustion of coal, at lower firing temperature, could be
attacked by acids to extract alumina. Work is planned on the

extraction of alumina from fluidized bed combustion of a high-ash coal in the near future.

Both coal wastes and low grade clays, after suitable pretreatment, could be treated by sulphuric, nitric or hydrochloric acid leaching.

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