

RECOVERY OF ALUMINA FROM NON-BAUXITE

ALUMINUM-BEARING RAW MATERIALS

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GeneralitiesThe situation regarding the presently used raw materials in the aluminum industry :

The present world production of aluminum amounts to about 14 million metric tons per year. This production is obtained by electrolysis of alumina which represents the raw material of this industry. Nearly the whole of the alumina produced is extracted from rich ores : bauxites and laterites. Taking into account that part of the alumina produced is used for other purposes than the production of aluminum, the consumption of bauxites and laterites amounts, at present, to about 100 million tons per year.

Rate of increase of the production of aluminum and the consumption of the ore reserves :

In view of estimating the development of the world consumption of aluminum, two assumptions can be made ; one may :

1. Assume an overall increase of 5.5 p.c. per year over 30 years, or
2. Assume a zero increase for the countries industrialized at present, and an increase for the countries in development, resulting in world consumption of about 20 kg Al per year and capita, as an average.

Taking into account the increase in population, these two assumptions lead sensibly to the same conclusion. By the

year 2005, the world consumption would be 5 times as high as at present. The consumption of rich ores would then reach the 500 million tons p.a. mark, which means that, if no other raw material is used, their reserves will be depleted between 2010 and 2030.

Distribution of bauxite and laterite ores in the world :

In fact, the known and economically exploitable reserves of bauxites and bauxitic laterites amount, according to the 1975 estimations, to 17 billion metric tons.

The most important regions are :

. Caribbean Islands	1 billion tons
. Central and South America	2-3 billion tons
. Africa	4-5 billion tons
. Australia	4-5 billion tons

The per cent shares in world bauxite and laterite reserves compared to aluminum production (for 1975) are given in Table I.

These figures reflect the long distances between the ore reserves and the aluminum producing and consuming regions.

With this respect, it is to be noted that the exploitations of the ore deposits are moving more and more from the coast to the interior, thus entailing problems of logistics and construction (on the new site), which puts more and more weight on the cost price of the raw material.

Conclusion :

The feeling that the world's reserves of rich ores should be preserved from too fast a depletion, as well as the desire of many countries to use their domestic raw materials, to save on foreign currency spending, and avoid paying heavy transport charges have, obviously, stimulated the research in view of using other raw materials for the production of alumina.

This has brought us to consider the nature of other raw materials and the importance of their reserves.

Other possible raw materials

The non-bauxitic raw materials may be divided, according to their treatment, into two categories : basic ores and acidic ores.

The basic ores include the silicoaluminates of the alkaline or alkaline-earth metals, such as the anorthosites and nephelines. These ores must be treated by alkaline-type processes, which we do not consider here.

Table I
Bauxite reserves and aluminum production in the world

Regions	"Bauxite" reserves	Aluminum production
. Europe	6 %	39.1 %
. North America ...	3 %	37.1 %
. Central and South America	20 %	2.3 %
. Africa	33 %	2.6 %
. Asia	5 %	16.0 %
. Oceania	33 %	2.9 %

The acidic category includes the silico-aluminous ores with low alkaline or alkaline-earth contents. Shales and clays belong to this category. Their reserves are enormous. Considering the USA as an example, their reserves of clays and kaolins amount to 9 billion tons, which represents 3 billion tons alumina. As to the coal shales separated from the coal by washing, they represent 30-60 weight per cent of the coal extracted. In 1973 the world production of coal was 2,200 million tons, which represents 600 to 1,200 million tons shales or 120 to 240 million tons alumina per year.

The processes studied for the treatment of this type of material use, for economic reasons, the major industrial acids : such as sulphuric, sulphurous, hydrochloric or nitric as reactants.

An examination of the various processes highlights the following points :

- . Only sulphuric acid can dissolve alumina without preliminary roasting or leaching above atmospheric pressure.
- . Only hydrochloric acid gives a salt which by thermal decomposition yields directly the acid reactant.
- . Only hydrochloric acid allows, through the crystallization of the salt, the easy separation of iron from alumina.

These points are the basis of the H⁺ Process which is described below :

Aluminium Pechiney H⁺ Process

This process allows the separation and extraction of alumina contained in the silicoaluminous materials such as clays, shales, carboniferous, bituminous and uraniferous shales. These ores essentially consist of silica (40-60 %), alumina (15-35 %), iron oxides (1-10 %), potassium oxides (0,5-5 %), magnesia, sodium oxides, lime and titania.

Process theory

The process is based on two basic ideas, the selective dissolution of alumina in a concentrated sulphuric acid solution, and the efficient purification of alumina as aluminum chloride hexahydrate. This salt may be pyrohydrolysed into alumina at a comparatively low temperature. The heat consumption for the thermal decomposition of the hexahydrated chloride is lower than that required for the sulphate or the nitrate. In addition, no reconversion of the acid reactant is needed.

The process flow-sheet, shows the classic unit operations

in hydrometallurgy :

1. Preparation of the ore.
2. Leaching of the ore to dissolve the alumina.
3. Solid-liquid separation to separate the impurities and the residues from the alumina containing liquor.
4. Washing of the residues with dissolution of the sulphates of the impurities. Recrystallization of the sulphates of the impurities and their removal.
5. Crystallization of the alumina as sulphate.
6. Conversion of the sulphate to chloride.
7. A sodium purification.
8. Separation of the sulphuric and the hydrochloric acids.
9. Thermal decomposition of the chloride hexahydrate to obtain alumina and the regeneration of the hydrochloric acid.

Description of the process

The process may be used for the treatment of a great number of ores by adapting the removal of the impurities, for each case. For this purpose, two ores have been chosen as examples : coal shales from a coal mine and kaolin clays from Georgia (USA).

Treatment of coal shales (see flow-sheet Figure 1) :

Preparation of the ore :

The ore undergoes a preliminary crushing and grinding. As the residual carbon content is a source of trouble during the leaching operation (reduction of the sulphuric acid into SO₂, and foam formation), we have to eliminate it by roasting the ore. The carbon content is sufficiently high to act as fuel for the whole operation. No additional fuel is required. The roasting allows the oxidation of the ferrous into ferric iron.

Leaching :

The ore thus prepared has the following typical composition. (See Table II).

This ore is brought into contact with a solution of sulphuric acid saturated with impurities under the leaching conditions. The oxides and metal silicates contained in the ore are converted to sulphates. The aluminum sulphate is dissolved whereas the sulphates of the impurities, with the exception of the sodium sulphate, remain insoluble like silica.

Table II

Typical composition of a coal shale

. Al ₂ O ₃	24.4 %
. Fe ₂ O ₃	7.8 %
. Na ₂ O	0.65 %
. K ₂ O	4.4 %
. MgO	1.9 %
. P ₂ O ₅	0.25 %
. TiO ₂	0.9 %
. SiO ₂	57.9 %

The sulphuric concentration varies around 50 %, the leaching temperature is approximately 130°C. The operation is carried out at atmospheric pressure.

The ore and the leaching liquor are fed continuously to the leaching reactors. Each reactor is a stirred vessel protected by an anticorrosive and antiabrasive lining.

The yield of dissolution of the alumina is higher than or equal to 90 %.

Solid-liquid separation :

During this operation, carried out by filtration, the aluminum containing sulphuric liquor is separated from the sulphates of the impurities and from the silica. The impregnating liquor which is rich in alumina is displaced by the mother liquor from the crystallization of the sulphate which is poor in alumina.

Treatment of the residues and separation of the impurities :

The previously separated solids are washed with water. During this washing, the sulphates of the impurities are dissolved again. The washed silica is separated, and the sulphuric solution containing the impurities is concentrated by evaporation of the washing liquor.

The evaporation is carried out as a continuous operation in a multiple effect evaporator.

The sulphates of the impurities crystallize, and are separated by filtration of their mother liquor which is recycled to the leaching circuit. The separation is carried out on a rotary vacuum filter. The main constituent of the sulphates of the impurities is the double ferri-potassic sulphate, insoluble in the liquors after leaching, and in the liquors after evaporation.

By thermal decomposition of the sulphates of the impurities we obtain sulphur oxides which are then reconverted to sulphuric acid to be recycled, and metal oxides. The potassium sulphate is not decomposed. It is extracted from the metal oxides and might represent a valuable by-product.

Crystallization of the aluminum sulphate :

The sulphuric acid solution, enriched with alumina after the leaching operation is separated from the residues and the impurities. It is vacuum flash-cooled to 75-80°C, and then fed continuously to the multi-stage crystallizers. Each vessel is equipped with a stirrer.

The vessels are protected by an anti-corrosive lining. Heat exchangers mounted in the crystallization circuit allow to control the temperature in each crystallizer. The temperature of the last one is approximately 40°C. By controlling

the sulphuric acid concentration of the leaching liquor and the temperatures of the crystallizers, a well crystallized aluminum sulphate is obtained. It is easily separated from the mother liquor by filtration on a rotary vacuum filter. The residual liquor impregnating the crystals is removed by washing on the filter.

The mother liquor is sent back into the circuit for ore leaching.

Crystallization of the aluminum chloride :

The aluminum sulphate separated in the previous step is not sufficiently pure for obtaining, through thermal decomposition, an alumina which meets the requirements for electrolysis. Furthermore, the thermal decomposition would be carried out at a high temperature, and the gas produced during this operation would have a high proportion of SO₂ which requires reconversion to sulphuric acid. For these reasons, the sulphate is transformed to chloride. This transformation is carried out by suspending or dissolving the sulphate in a hydrochloric acid solution obtained from the washing stage of the chloride. This mixture is then saturated with gaseous hydrochloric acid. The aluminum is separated as crystals of hexahydrated aluminum chloride, while practically all impurities remain dissolved. The chloride is washed on a filter with a hydrochloric acid solution obtained by absorption of the gas from the thermal decomposition of the chloride.

The crystallization of the chloride is carried out between 75 and 50°C, in stirred vessels provided with an anti-corrosive lining. The good contact between the gas and the liquid is achieved by quite a common device.

Sodium purification :

When the treated ore contains important quantities of sodium which are not entirely removed with the other impurities, a specific sodium purification is carried out. For this purpose, the mother liquor of the aluminum chloride previously separated by filtration is cooled by a few degrees, and saturated with hydrochloric gas. The sodium is separated as sodium chloride. The equipment used is of the same type as that used for the crystallization of the aluminum chloride.

Sulphuric-hydrochloric separation :

The separated liquor is a sulpho-hydrochloric solution. It yields first, by heating, in the degassing stage the hydrochloric gas used for the crystallization of the aluminum chloride and the sodium purification.

We obtain then by evaporation :

- . On one hand, a weak solution of hydrochloric acid used for the absorption of the gas from the thermal

decomposition.

- . On the other hand, a sulphuric acid solution free of hydrochloric acid. This solution is sent back into the leaching circuit.

These operations are carried out with anti-corrosive equipment. The temperatures are between 120° and 130°C.

Pyrohydrolysis - Calcining - Obtention of the alumina :

The aluminum chloride crystals previously separated undergo a pyrohydrolysis. We thus obtain an aluminum oxide of a high purity and the gas containing the hydrochloric acid which, by absorption, gives a hydrochloric solution used for the washing of the aluminum chloride.

The pyrohydrolysis of the aluminum chloride is realized in two steps :

- . In a first step at a comparatively low temperature (200 - 250°C), the thermal decomposition is accomplished at a rate of 90-95 %;
- . In a second step at a higher temperature (700 - 1200°C) the whole of the chlorine is eliminated, and the alumina produced has the desired physical properties as a result of the temperature control.

Treatment of kaolin clays from Georgia (see flow-sheet Figure 2) :

The treatment of kaolin clays by the H⁺ Process does not differ much from that used for roasted coal shales. Only two operations are different : the preparation of the ore and the separation of the impurities.

Preparation of the ore :

The kaolin clays are treated as they arrive from the ore deposit, they are neither dried nor roasted. A typical analysis of this raw material is given below (see Table III).

The preparation of the ore comprises shrinking and disintegration in a portion of the leaching liquor. The pulp obtained is directly fed to the leaching vessels.

Separation and treatment of the impurities :

Kaolin contains no potassium. Furthermore, the TiO₂/Fe₂O₃ ratio is much higher than in the coal shales. As the sulphates of these impurities are soluble in the liquors of the cycle, the impurities are removed by formation of double sulphates.

These salts crystallize when the mixture of the liquor from the washing of the residues and the mother liquor from the crystallization of the aluminum sulphate is concentrated by evaporation.

Table III
Typical composition of Georgia clay

Ore	Crude (undried)	Dried
Elements : (p.c)		
. Al ₂ O ₃	29.3	35.6
. Fe ₂ O ₃	0.75	0.95
. TiO ₂	1.5	1.9
. SiO ₂	35.8	44.8
. H ₂ O	31.3	14.10
. Miscellaneous	1.35	2.65

These salts are separated by vacuum filtration. They may be treated like the residues of the coal shales in order to recover the sulphuric acid and the reactant necessary for the formation of the double salts.

They may also be treated in view of separating the titanium oxide which might be considered as a useful by-product.

Properties of the alumina produced

The aluminum oxide obtained in this process has lower impurity contents than the alumina produced in the Bayer Process.

The comparative contents are indicated in table below. (see Table IV).

The temperature of the second step of pyrohydrolysis can be regulated so that the alpha alumina content of the alumina produced may vary from 15 to 95 per cent, corresponding to a BET surface area variation from 3 to over 100 m² p.g.

This alumina consists of agglomerates the dimensions of which can be adjusted by the size of the aluminum hexahydrated chloride crystals.

The size of the alumina particles will vary between 5 and 200 microns.

If this is necessary, they can be easily reduced by grinding to a size below 10 microns.

Uses of the alumina :

In addition to its use for aluminum production, thanks to its high purity and the versatility of its physical properties, this aluminum oxide is an ideal raw material for the ceramic industry and the catalyst manufacturing industry.

Comparison of the energy consumption of the different processes

Since the recent worldwide energy crisis has broken out, the consumption of energy in the different industrial processes has been considered of a major importance.

The total power consumptions of an alumina plant are given below for the different processes usable for different ores. These consumptions are expressed in thermies per ton alumina. They comprise the consumptions of electrical energy and of heat. (see Table V).

Present state of the development of the H⁺ Process

Laboratory studies on the H⁺ Process started in 1964.

Since 1968, pilot-plant scale unit operation have been

Table IV

Comparison of impurity contents in H⁺ Process vs. Bayer Process aluminas

Elements	Bayer alumina	H ⁺ alumina
	(ppm)	(ppm)
. Na ₂ O	4,000 - 7,000	< 100
. CaO	300 - 500	150 - 200
. Si	60 - 100	60
. Fe	100 - 250	< 50
. Ti	15 - 25	20 - 25
. Zn	30 - 100	< 5
. V	5 - 10	< 5

Table V
Total power consumption in various processes
for alumina production

	Power consumption Th. p. mt Al ₂ O ₃
. Bayer process on bauxite	3,000 - 4,000*
. H ⁺ process on clay or shales	6,500 - 9,500
. Nitric acid process on kaolin	11,500 - 12,000
. Hydrochloric acid process on kaolin...	12,000 - 12,500
. Sulphurous acid process on kaolin.....	10,000 - 11,000
. Lime-soda process on nepheline or anorthosite	12,000 - 14,000

* and 4,000 - 5,500 including the energy required for the production of caustic soda and lime used in the process.

carried out. In 1971, the whole of the pilot installation was built. Since that date this pilot plant having a capacity of 1 mt ore per day has been run on various raw materials.

In 1975, Aluminium Pechiney cooperating with Alcan Aluminum Ltd. has undertaken the building of a bigger experimental unit.

This unit will be put into operation in May 1976. From June 1976 on, the daily output shall be 15-20 metric tons Al₂O₃.

Summary

The expected demand for aluminum metal between the years 1975 and 2000, corresponds to a bauxite requirement of about 500 million tons. The present reserves of bauxite and laterite are estimated at 17 billion metric tons.

This underlines the need for economy in the use of bauxite, and for the development of a process which permits the recovery of alumina from non bauxite ores. The H⁺ Process allows the recovery of alumina contained in the silicoaluminous ores such as clays, shales and coal shales.

The basic ideas of the process are :

1. Selective dissolution of alumina in a concentrated sulphuric acid solution which avoids the preliminary roasting of the ore.
2. Conversion of aluminum sulphate into chloride and efficient purification of alumina in the form of aluminum chloride hexahydrate. This salt may be pyrohydrolysed at a relatively low temperature by indirect heating. The energy consumption of this pyrohydrolysis is lower than that needed for the sulphate or the nitrate. Furthermore, the regenerated reactant acid may be reused without any preliminary reconversion.

The alumina obtained by the process is of a very high purity. Operating and investment costs are competitive with present costs of the production of commercial grade alumina. The process has been demonstrated in an integrated pilot unit handling one ton of ore a day.

Aluminium Pechiney undertook, in cooperation with Alcan Aluminum Ltd. to build a new experimental plant. This plant will be on stream in June 1976 handling 100 tons of ore per day and producing 15 to 20 tons alumina.

