

12. ALTERNATIVE PROCESSES AND RAW MATERIALS

The Bayer process holds an exclusive status as almost all of the world's metallurgical grade alumina is produced by this method. Although alternative processes have been developed and operated since the early 1900s, none has achieved the commercial success of the Bayer process. The only currently used alternative methods to produce alumina for metal production are the Nepheline- and lime-soda sinter processes, contributing a minor share of the global production.

Particularly during and immediately after World War II, and later in the 1960–1980s, several large scale initiatives were launched to investigate and develop alternative methods to the Bayer process for alumina production. These efforts were primarily motivated by economic factors or in order to be less dependent on foreign bauxites and instead utilize local non-bauxitic aluminum bearing raw materials. Most noteworthy are perhaps the sulphuric and hydrochloric acid processes, both which were successfully operated on a pilot-scale. Also the Pedersen process, which operated for 40 years on a commercial scale, should be noted.

The processes for alumina extraction can be categorized either as acidic or alkaline, as they make use of the increased solubility of aluminum at the extreme ends of the pH scale. In the alkaline processes, aluminum is dissolved from the parent mineral (sometimes a roasting pre-treatment is employed) to form an alkali aluminate and the impurities are separated (typically as alkali- and/or calcium aluminosilicates). Precipitation of gibbsite is carried out either by neutralization (often utilising CO_2) or hydrolysis, followed by calcination to produce alumina.

There are several variations on the acidic processes. Common to these processes is that the aluminum compounds are dissolved in a strong acidic solution and then separated as aluminum salts, typically after an impurity removal step. The aluminum salt is then thermally decomposed to form alumina and the acid captured and regenerated. The acidic processes have the advantages that other mineral valuables can be extracted with relative ease and most of the chemicals can be recovered.

Testifying to the vast interest in developing alternative methods the literature on this subject is abundant. The paper selection in this section covers some of the more rigorously investigated, best presented and seemingly promising alternative processes for alumina production. There are a number of interesting and well prepared papers that equally well could have been included in this section but that could not however be added due to space limitations. The reader is therefore referred to the recommended reading list for additional papers on this subject.

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ALUMINA PRODUCTION BY THE

PEDERSEN PROCESS - HISTORY AND FUTURE

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Over a period of about forty years (1928 - 1969), the Pedersen Process for the production of alumina was run in Høyanger, Norway, with an annual production of about 17,000 metric tons. This plant will be described in the paper.

With the present high quality trihydrate gibbsite ores in abundance, the Pedersen Process is less competitive than the Bayer Process. However, based upon inferior bauxite, say 20 - 40 % Fe₂O₃, a modern Pedersen Process could be the answer.

The Pedersen Process gives an excellent solution to the future demand for maximum utilization of useful ores. The waste-disposal problem is virtually eliminated with this process, because the pig-iron formed as a byproduct during the smelting process is of high quality and further the grey mud from the extraction step provides an excellent rawmaterial for a cement production.

Based upon these facts the lay-out of a modern Pedersen plant with an annual production of 200,000 metric tons is described.

Introduction

About 50 years ago, the late professor Harald Pedersen and his colleagues at The Technical University in Trondheim, Norway, developed a method for the production of alumina. This process was based upon the formation of a calciumaluminate slag which is readily soluble in a diluted sodiumcarbonate solution. From this solution aluminiumhydrate is precipitated out of the addition of carbon dioxide.

This method was successfully exploited by A/S Norsk Aluminium Company in Høyanger, Norway, where they operated such a plant with an annual capacity of 17,000 tons for about forty years. It was closed in the fall of 1969 due to economic reasons.

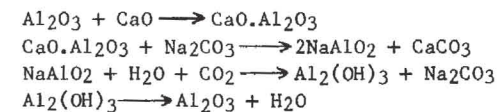
With the present high quality bauxite ores in abundance, this process is less competitive than the Bayer process. However, there are two important assets with the Pedersen process which might well give the process a future renaissance, viz.: -

- (i) The Pedersen process enables one to use a wide range of bauxite qualities with high silica and iron content, ranges far beyond the limitations of the present Bayer process.
- (ii) A total elimination of the red mud problem. In fact, the process calls for a complete utilization of the bauxite through the production of high quality pig-iron in the smelting process and further to use the grey mud as an important raw material for cement production.

This paper describes the plant in Høyanger. With the basis on our practical experience of running such a process, a rough outline of a modern Pedersen process with an annual capacity of 200,000 tons is presented.

THEORY

The overall chemistry in this process is basically very simple. However, due to a large number of sidereactions the complete set of chemical reactions taking place is numerous and complicated. The basic reactions are as follows:



The first reaction relates to the smelting process. Here it is important to compose a raw material charge which results in a slag which is easily soluble in a dilute sodium carbonate solution. The Rankine diagram which depicts the three component system CaO - Al₂O₃ - SiO₂, is here of great help. Experience has shown that a suitable slag is formed within a fairly restricted area including the monocalciumaluminate, CaO.Al₂O₃ which by crystallization moves towards the composite 12CaO.7Al₂O₃. The desired silica composition is 2CaO.SiO₂. The problem is that in this narrow range, a tertiary compound can be formed which is insoluble in a diluted lye solution, viz. gehlenite (2CaO.Al₂O₃.SiO₂). In order to avoid this, the raw material charge is made up with excess lime.

A typical slag analysis will be as follows:

Al ₂ O ₃ (%) :	48.5
FeO ₂ (%) :	1.5
SiO ₂ (%) :	4.5
TiO ₂ (%) :	3.0
CaO(%) :	42.5

DESCRIPTION OF PROCESS

The Pedersen process as it is described in this paper relates to the installation in Høyanger. A presentation of the raw materials used will be followed by a description of the smelting process and the wet-stage process.

1. Raw materials

This process of alumina production is based upon the following raw materials for which typical analyses are given.

Bauxite

The bauxite used in Høyanger was mainly imported from Greece. This was bohmite monohydrate, a typical analysis of which is given below: -

Loss on Ignition (%) :	12.7
SiO ₂ (%) combined ... :	3.1
TiO ₂ (%)	2.8
Fe ₂ O ₃ (%)	22.4
Al ₂ O ₃	58.5
Ratio $\frac{Al_2O_3}{SiO_2}$	18.9

We naturally preferred it as dry as possible and with a minimum of fines (-5 mm). A typical size analysis was as follows:

+ 50 mm:	0%
+ 25 mm:	30%
+ 10 mm:	40%
+ 5 mm:	10%
- 5 mm:	20%

Particularly detrimental to the smelting process was the amount of fines as these blocked the flow of furnace-gases resulting in small "volcanos".

Limestone

Limestone was supplied from our own quarries containing about 98% CaCO₃ and 0.5 - 1% SiO₂.

Coke

The quality of coke was most important to enable the furnaces to run on peak performance. Apart from lowest possible content of water, ash and particularly sulphur, the resistivity - determination of the coke was of great value for assessing its suitability. A typical coke analysis is as follows: -

H₂O (%) : 10
 Ash (%) : 10
 Sulphur (%)..... : 1
 Resistivity : 1300 ohm mm²/m

The resistivity was measured by a simple instrument of our own construction. The results were not absolute, but the relative values gave sufficient indication.

The size-analysis was another most important factor for good furnace performance, a typical analysis is given below

+ 38 mm : 0%
 + 19 mm : 70%
 + 9.0 mm: 20%
 - 9.5 mm: 10%

We aimed for a size between 20 and 10 mm.

2. Smelting Process

As already mentioned under "Theory", the three raw materials to be smelted together are weighed out in exact proportions. Under the raw material silo a manually operated mobile weighing machine measured out the quantities which were transported to silos above each of the two smelting furnaces. A typical composition of this charge to produce 1 ton of alumina, was as follows: -

Bauxite : 2,000 kg
 Limestone : 1,700 kg
 Coke : 250 kg

This gave roughly two tons of slag and about 250 kg of pig-iron.

While dealing with consumption figures here is included the additional components necessary to produce 1 ton of alumina:

Fuel oil (calcination and steam) 200-250 kg
 Caustic soda: 10 - 20 kg
 Sodium carbonate: 50 - 60 kg
 Electric power: 4000 - 4500 kWh

Each of the two smelting furnaces were run at 4MVA which was the limit of their capacity. The furnace was a normal three phase installation with electrodes of 700 mm diameter. The overall diameter was about 6 meters with a depth of 3 meters.

The furnaces were equipped with automatic electrode positioning; however, due to erratic operation because of inhomogeneous raw materials, the electrode adjustment was mainly by manual control.

The two furnaces were tapped every 6 hours, together producing roughly 100 - 110 tons of slag and 12 - 16 tons of pig-iron per day. The molten slag and pig-iron were tapped from the same hole, where the latter usually came at the end of the tapping so the separation did seldom cause any problem. The pig-iron was cast in 25 kgs blocks and sold as such. This was a high quality product as may be seen from the following analysis:

SiO₂ (%) : 0.15
 C (%) : 4.60
 Mn (%) : 0.10
 Ni (%) : 0.35
 Cr (%) : 0.45
 V (%) : 0.25
 Ti (%) : 0.35
 P (%) : 0.15
 S (%) : 0.05

The molten slag at 1500°C was collected in ladles each of two tons capacity. Here the slag was allowed to cool for about four hours before being emptied into a slag storage. This cooling was most important for ensuring a good slag quality, - too rapid cooling caused the formation of insoluble crystal compounds.

During the cooling process an expansion takes place resulting in a partial disintegration of the slag, thus aiding the subsequent size-reduction.

3. Size Reduction

The size reduction was carried out in three steps, i.e. a jawcrusher followed by a cone crusher before entering a ball-mill. The slag was reduced to about 98% - 200 mesh. After transportation to suitable silos the slag was now ready for further treatment.

4. Wet Stage Process

This stage comprises the leaching precipitation and calcination. Each will be dealt with under appropriate headings.

(i) Leaching-section (digestion)

This section consisted of eight vessels each of 200 cubic metres capacity with a slow-moving stirrer (3 r.p.m.) and circulating pump. The process was batchwise, the vessels being operated at different stages to allow a more or less continuous feed to a clarifier which treated the slag and lye mixture after the leaching process. The amount of slag to be added to the vessel was determined by analysis of the lye. Roughly we added about 5 tons of slag per 200 cubic metres of lye with a concentration of 15 g/l total alkaline. The first leaching step took 5 1/2 hours at 40°C and atmospheric pressure, after which time the lye had reached a concentration of about 13 - 14 g/l Al₂O₃. The slag/lye mixture was then emptied into a clarifier (area=95 m²). The overflow passed through Kelly filters and was pumped to the storage tank for "saturated" liquor.

The underflow from the clarifier was treated in a second leaching step using filtrate from the centrifuges as leaching agent.

From this second leaching step the solution was pumped to the washing series.

(ii) Washing-section

Here we had six thickeners working in parallel in a counter-current extraction process with fresh water at inlet. The water picked up alkali in this process, and by the time the fresh water had been through the series of six thickeners, it contained about 14 g/l total alkaline. This solution was then used in the first leaching step. The grey mud going in the opposite direction was eventually discharged into the sea with about 3.5 g/l total alkali and 1.5 - 1.8 g/l Al₂O₃ causing no damage to

marine life. The amount of grey mud discharged would be about 35,000 tons per year, i.e. 2 times the alumina production.

(iii) Precipitation-section

This was carried out in eight vessels each of 200 cubic metres capacity filled with a slow moving stirrer at 3 r.p.m. This was also a batch-process where the carbon dioxide was added to the vessel containing 200 cubic metres of "saturated liquor". This process was pH-controlled, the flow of carbon dioxide being automatically stopped when the pH = 11.5.

Now the mixture of precipitated aluminium hydrate and solution was passed via a tray-thickener and a centrifuge before entering the calciner.

(iv) Calcination-section

This was carried out in a conventional calciner, 62 m long with a diameter of 2 metres. The flue gas from the calciner was taken through an electrostatic precipitator and a wet scrubber. After compression this gas, containing about 8% carbon dioxide, was fed back into the process and used for precipitating the aluminium hydrate. In order to generate a sufficient amount of carbon dioxide it was necessary to operate the calciner at about 1250°C.

ALUMINA SPECIFICATION

The resulting alumina held the same specifications as that produced by the Bayer process, with the exception of silica, a typical analysis being:

Loss on ignition (%) :	0.07
H ₂ O	(%) : 0.07
SiO ₂	(%) : 0.11
Na ₂ O	(%) : 0.62
CaO	(%) : 0.21
Fe ₂ O ₃	(%) : 0.012
TiO ₂	(%) : 0.003
V ₂ O ₅	(%) : 0.004

A corresponding size analysis being

- + 100 mesh : 17%
- + 150 mesh : 27%
- + 200 mesh : 22%
- + 270 mesh : 16%
- + 325 mesh : 8%
- 325 mesh : 10%

Angle of repose: 31 - 34°

A MODERN PEDERSEN PROCESS

With the possibility of applying up-to-date engineering to a modern Pedersen process we have made some preliminary studies on a plant with an annual production capacity of 200,000 metric tons of alumina, and 60,000 tons of high quality pig-iron as a "by product". In addition there would be produced enough raw material (grey mud) for making some 500,000 tons of cement.

1. Smelting Process

In an up-to-date smelting section we plan the following:

- (i) 2 lime kilns each having a capacity of about 200,000 metric tons/year.
- (ii) Calcination of bauxite, about 400,000 tons capacity.
- (iii) Two electric furnaces each rated at 25 MVA arranged for continuous tapping. Due to the larger size and higher efficiencies of furnaces today the power consumed per ton of alumina produced will be halved compared with the consumption in the Høyanger installation. In addition it is important to take into account the pig-iron which is produced at the same time.

2. Size Reduction

A dual size-reduction unit will contain jaw- and cone crusher with a ball-mill based on a production of about 500,000 tons of slag/year.

3. Leaching-section

We still recommend to run this as a batch process to enable a close control of this most important step. We stipulate 9 stirred vessels of 1,200 cubic metres each fitted with stirrer and circulating pump. This process can be easily

operated from a control room, even though great care has to go into the selection of sensing devices because of scaling problems.

4. Clarifier-section

The sodium aluminate solution from the leaching section can be fed to two clarifiers, each with a settling area of about 350 m². A second leaching step is desirable and a dual counter current washing section advisable.

5. Precipitation-section

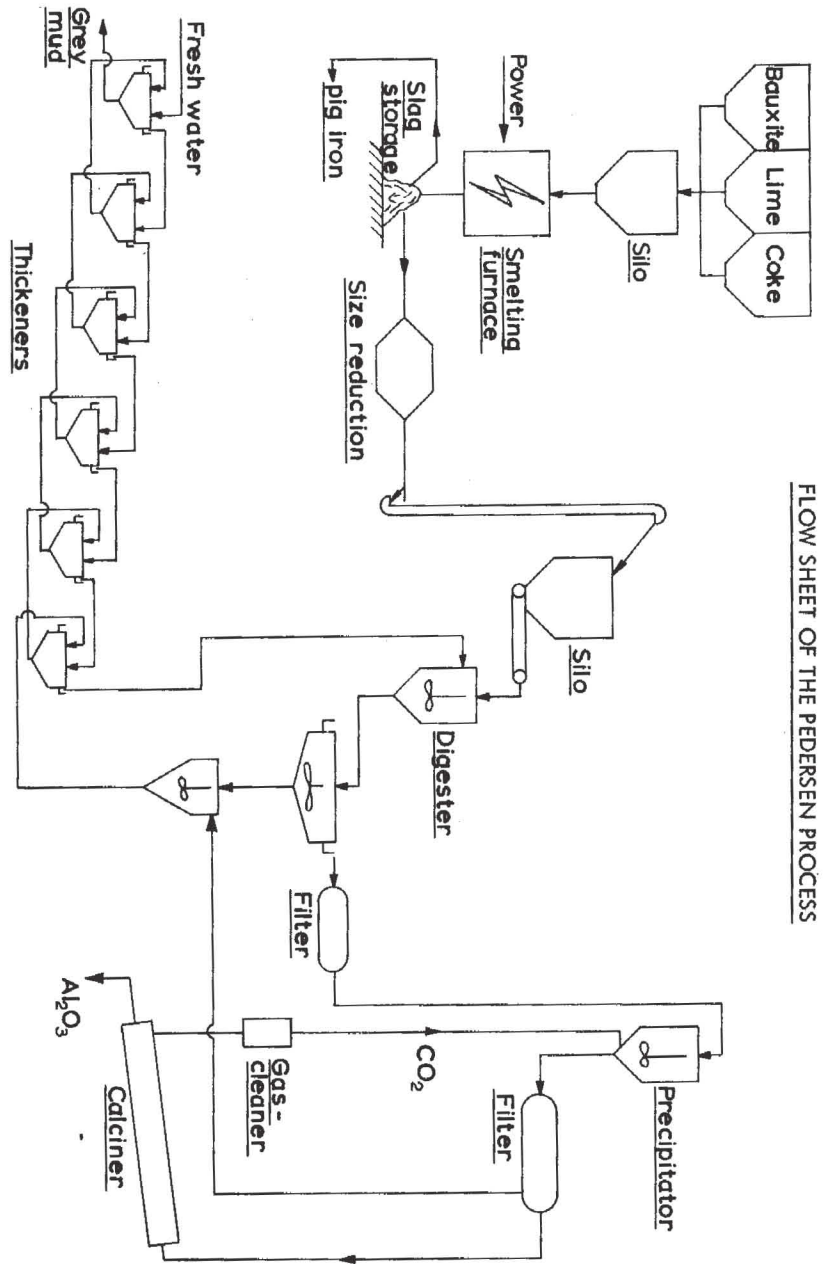
Again we will use a batch process with 8 stirred vessels each of 1,200 m³ capacity. This step will be pH-controlled and as such well suited for automatic control. The precipitated alumina hydrate could follow the present Bayer pattern with tray-thickeners, vacuum filters and calciner(s).

6. Grey mud

The amount of grey mud will be about twice the alumina production. The mud could be dried and calcined with any cheap high silica material available to produce a suitable cement.

Appendix

Flow sheet of the Pedersen process



FLOW SHEET OF THE PEDERSEN PROCESS