PRECIPITATION OF MONOHYDRATE ALUMINA
IN THE BAYER PROCESS

Prof. A. Kontopoulos, Dr. D. Panias, Ass. Prof. I. Paspaliaris

NATIONAL TECHNICAL UNIVERSITY OF ATHENS
UNIVERSITE LIBRE DE BRUXELLES
HELLENIC ALUMINA INDUSTRY

CONTRACT JOE3-CT95-0003

PUBLISHERABLE FINAL REPORT

January 1996 to June 1997

Research funded in part by
THE EUROPEAN COMMISSION
in the framework of the
Non Nuclear Energy Programme
JOULE III
PRECIPITATION OF MONOHYDRATE ALUMINA IN THE BAYER PROCESS
1. Abstract

The Bayer process is universally applied for the production of alumina from bauxites. In the current industrial practice, established for over 100 years, the process has three main steps: Digestion, where bauxite is digested with caustic soda at elevated temperature and pressure to produce aluminate liquor, containing alumina in the form of \(\text{Al(OH)}_4^-\); precipitation, where the aluminate liquor is hydrolysed at 55 - 60°C to produce crystalline alumina trihydrate, \((\text{gibbsite}, \text{Al}_2\text{O}_3.3\text{H}_2\text{O})\) and calcination, when gibbsite is calcined at 1000 - 1200°C to produce alumina: \(\text{Al}_2\text{O}_3.3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}\). The Bayer process is energy intensive, requiring approximately 12GJ/t alumina. The calcination step absorbs 3 GJ/t alumina, or 25% of the total Bayer process.

The objective of the current project was the development of a highly innovative modification of the Bayer process, whereby aluminium monohydrate (boehmite, \(\text{Al}_2\text{O}_3.\text{H}_2\text{O}\)) rather than the trihydrate is the product of the precipitation stage. This modification will result in significant energy savings during the calcination stage because (a) the enthalpy of dehydration of boehmite to alumina is lower by 1.1 GJ/t alumina compared to that of gibbsite, and (b) the quantity of material to be calcined will be reduced by 20% per t alumina, as only one rather than three moles of water are associated to one mole of alumina. The energy saving in calcination of boehmite is estimated to be 34.8 kg/t of alumina for fuel oil and 7.2 kWh/t of alumina for electricity. This corresponds to 40-50% less fuel or electricity consumption compared with gibbsite calcination for the same alumina production. For a typical Bayer process plant with a capacity of 1.000.000 tpa alumina, this represents energy savings of 35000 t of fuel oil per year.

In the present project the condition of boehmite precipitation from aluminate liquors have been studied in detail. A theoretical model predicted boehmite solubility in caustic solutions has been developed and also validated by the experimental data of boehmite solubility in such solutions. Detail kinetic analysis of experimental data has been carried out and a kinetic equation has been established. This equation has been incorporated into a new simulator and used to develop the optimum processing flow sheet for the precipitation section. Finally, a technological and economical evaluation of the new process has been carried out to. The main results of the research performed are the following:

- Boehmite is precipitated from supersaturated sodium aluminate solutions at atmospheric conditions in the presence of boehmite seed.
- The % yield of the new boehmite precipitation process is very close to this achieved in the current gibbsite precipitation process.
- Precipitated boehmite is characterized as “floury” type.

The market potential of the new process appears to be very extensive as it may be applied not only in new plants but also in existing ones with minor modifications. EU companies currently producing 5.580.000 tpa of alumina and companies around the world currently producing 39.420.000 tpa alumina are the target market of the process.

2. Partnership
### 3. Objectives

The main objective of this project is the reduction of energy consumption for the production of alumina by suitable adaptation of the Bayer process.

Energy costs constitute about 35% of the alumina price. Since most of the alumina plants use either oil or natural gas to meet their energy demands they are been subjected to the rapidly increasing prices of the energy sources. Therefore, the reduction of the energy costs in the coming years, is the most important task for the alumina industry.

Total energy requirements in modern alumina plants amounts to about 12 GJ/t of alumina produced. Of this, 3 GJ/t Al₂O₃, representing 25% of total energy consumption, is used for calcination, which takes place in rotary kilns, flash calciners or fluid-bed reactors.

Taking advantage of the significant difference in the enthalpy of the dehydration reactions of gibbsite and boehmite and the reduction in weight of the material to be calcined, the energy consumption during the calcination stage can be reduced to 1.2 GJ/t Al₂O₃, representing more than 60% energy reduction in the calcination stage and more than 15% total energy savings in the Bayer process.

### 4. Technical description

Chemical modeling of the system Al₂O₃-Na₂O-H₂O was initially carried out and the stability area of boehmite and gibbsite as well as the solubility of boehmite in sodium hydroxide solutions was determined as a function of temperature and alkali concentration. Experimental determination of boehmite solubility in caustic solution as a function of temperature and sodium hydroxide concentration was also carried out. The experimental data have been used for the validation of the theoretical model. The model predictions are shown in table 1 while a comparison between experimental and theoretical solubility values is shown in table 2.
Table 1: Predicted boehmite solubility values, grAl₂O₃/L, in caustic solutions

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Initial caustic concentration, grNa₂O/L</th>
<th>60</th>
<th>80</th>
<th>100</th>
<th>120</th>
<th>140</th>
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<td></td>
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<td>25.2442</td>
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<td>38.8096</td>
<td>45.1454</td>
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<td>28.5889</td>
<td>36.6783</td>
<td>43.6234</td>
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<tr>
<td>120</td>
<td></td>
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<td>56.1910</td>
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<td></td>
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<tr>
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<td>73.7785</td>
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</tbody>
</table>

Table 2: Comparison between theoretical and experimental boehmite solubility values

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Theoretical values gAl₂O₃/L</th>
<th>Experimental values gAl₂O₃/L</th>
<th>Deviation %</th>
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<tr>
<td>90/120</td>
<td>34.3419</td>
<td>35.7940</td>
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<td>120/80</td>
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</tr>
<tr>
<td>100/100</td>
<td>32.5191</td>
<td>34.6443</td>
<td>-6.1</td>
</tr>
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</table>

The model predicts accurately the boehmite solubility values with a deviation not exceeding 10%. It seems that the model has the tendency to gently underestimate the solubility values but the final results are within the acceptable margins.

Precipitation of boehmite from supersaturated aluminate liquors have been experimentally studied. The effect of a number of parameters such as precipitation temperature and time, concentrations, quantity and quality of boehmite seed, additives and application of ultrasonic waves on the physical properties of the product and on the extent of the reaction have been investigated in detail. The effect of the main process parameters are shown in figures 1, 2 and 3.

The precipitation of boehmite from sodium aluminate solutions is a slow process like the gibbsite precipitation from similar solutions. The precipitation process is accelerated by the use of seeding material. Therefore, the preparation of boehmite seed material is very important. Two types of seeds were prepared. The first type, called F seed, were prepared by thermal decomposition of gibbsite at 250°C for 48h. The second type, called A seed, were prepared by hydrothermal transformation of gibbsite to boehmite at 180°C for 3h.
Figure 1: Effect of temperature on boehmite precipitation from a sodium aluminate solution with caustic concentration 120g/L as a function of time.

Figure 2: Effect of caustic concentration on boehmite precipitation from a sodium aluminate solution at 110$^\circ$C as a function of time.
Figure 3: Effect of seed ratio on boehmite precipitation from a sodium aluminate solution at 110°C as a function of time.

During the precipitation experiments the F seed was proved ineffective. Therefore, the A seed was used for most of the boehmite precipitation experiments.

The main results from precipitation experiments are the following:

- Boehmite is precipitated from supersaturated sodium aluminate solutions in the presence of boehmite seed not only at elevated temperatures, higher than the boiling point of aluminate solution, but also at atmospheric conditions, temperatures lower than 100°C.

- Boehmite can be precipitated (a) isothermally at temperatures higher or equal to 90°C (b) non isothermally with the “flash cooling” procedure at temperatures lower to 90°C but higher than 70°C.

- The yield of boehmite precipitation is 35 - 40%. This yield is very close to this achieved in the current gibbsite precipitation practice.

- The boehmite precipitation is practically ceased when an apparent boehmite solubility value is established in the solution. As the real boehmite solubility is much lower than the apparent boehmite solubility, the precipitation yield can be drastically increased if the kinetic inhibitions are overcome.

- The precipitated boehmite is characterized as “floury” type as it has the granulometry of -47µm.
Mathematical modeling of boehmite precipitation process was carried out and the following preliminary kinetic equation has been established.

\[
\frac{dC_{pr}}{dt} = 1.85 \times 10^{13} \left( C_{Na_2O} \right)^{-1.8} \left( SR \right)^{0.5} \cdot e^{-\frac{E_a}{RT}} \left( C - C_e \right)^2
\]

Where,

- \( C_{pr} \) = amount of precipitated boehmite per volume of solution defined as gAl₂O₃/L.
- \( C_e \) = Apparent equillibrium concentration of solution defined as gAl₂O₃/L.
- \( C \) = Al₂O₃ concentration at time \( t \) expressed as gAl₂O₃/L.
- \( t \) = Precipitation time, hours
- \( C_{Na_2O} \) = Initial caustic concentration in the solution, gNa₂O/L
- \( SR \) = Initial Seed Ratio, (gAlOOH/L)/(gAl₂O₃/L)
- \( E_a \) = Activation Energy, 21.15 Kcal/mol
- \( R \) = Ideal gas constant, 1,987 cal/K.mol = 8,314 J/K.mol
- \( T \) = Absolute Temperature, K

The major conclusions drawn from the preliminary kinetic study of boehmite precipitation are the following.

- The activation energy of boehmite precipitation is 21.15Kcal/mol which is about 50% higher from the activation energy of gibbsite precipitation.
- The initial caustic concentration of the solution has negative effect on the rate of precipitation reaction. As the caustic concentration decreases the reaction rate increases.
- The seed ratio significantly affects boehmite precipitation. Seed ratio values higher than 1.76 have no effect on boehmite precipitation rate.
- Boehmite precipitation follows second order reaction kinetics as in the case of the gibbsite precipitation.

A more advanced kinetic analysis of boehmite precipitation process gave the following kinetic differential equation. This kinetic equation reveals the self-decelerated character of the boehmite precipitation reaction and also the effect of the Na₂O excess on the precipitation rate.

\[
\frac{dC}{dt} = \frac{K_S}{1 + L(C_{e} - C)} \left[ \left( \frac{C_e - C}{C_0 - C_{e}} \right) \left( 1 - 0.036(C_{e} - C) \right) - C \right] = \frac{D}{e} \left( C - C_e \right)
\]

The parameters in the above equation have the following values:

L=122, K=10⁴ and D/e=4.5x10⁻².

Two types of kinetic inhibitions have revealed. The first inhibition is responsible for the event that boehmite can not be precipitated isothermally at temperatures lower than 90°C. This type of inhibition is in accordance with the high activation energy (21.15 Kcal/mol) of boehmite precipitation which is about 50% higher than the activation
energy of gibbsite precipitation. The second inhibition is responsible for the event that boehmite precipitation rate is practically eliminated while the remaining supersaturation degree in the solution is enough high. This observation is in accordance with the self-decelerated kinetic which is revealed after the kinetic analysis of the process. The last observation can be attributed to the passivation of the boehmite grains due to water adsorption on the grain’s surfaces. The second type of inhibition is observed at any temperature and not only at lower temperatures.

The mathematical model have been incorporated into a new simulator developed by the research team of NTUA and used to develop the optimum processing flow-sheet for the precipitation section.

Finally, a preliminary technological and economical evaluation has been carried out to compare the boehmite precipitation process with the existing gibbsite one.

5. Results and conclusions

The main exploitable result of the project is a new innovative process. The new process is a highly innovative variation of the Bayer process whereby, at the precipitation step, alumina monohydrate (Al$_2$O$_3$.H$_2$O) rather than trihydrate is precipitated at atmospheric conditions. The main feature of this process is the production of a material requiring substantially lower amounts of energy during the calcination stage. The technical characteristics of the new process are the following:

- Precipitation of the monohydrate alumina (Boehmite) from supersaturated sodium aluminate solutions is carried out at temperatures lower than 100°C.

- Precipitation of the monohydrate alumina (Boehmite) from supersaturated sodium aluminate solutions is carried out with cooling, starting the procedure at temperatures close to, but lower, than 100°C.

- In a process variation, precipitation of the monohydrate alumina (Boehmite) from supersaturated sodium aluminate solutions is carried out with cooling, starting the procedure at temperatures close to but lower than 100°C, and with simultaneous use of ultrasounds at a frequency varying between 20-50kHz.

- The alumina concentration in the supersaturated sodium aluminate solution is typically, but not exclusively, varying between 80-200g/l with best value 132gAl$_2$O$_3$/l.

- Caustic concentration in the supersaturated sodium aluminate solution, expressed as grams of Na$_2$O per liter of solution, is typically, but not exclusively, varying between 50-250g/l with best value 120g/l.

- The precipitation of the monohydrate alumina can be carried out without boehmite seed addition in the aluminate solution. In this case, a time consuming induction period is observed.
In a process variation, precipitation of the monohydrate alumina (Boehmite) from supersaturated sodium aluminate solutions is carried out in the presence of boehmite seed. In this case, the precipitation process is drastically accelerated. The initial seed ratio (SR), grams of added boehmite/grams of dissolved alumina, is typically, but not exclusively, varying between 0-5 with best value 1.76.

The precipitation of the monohydrate alumina can be carried out with or without glycerol or any other alcohol addition at concentrations varying between 0-5mol/kg boehmite seed.

The new process has many advantages, the most important of them is the significant energy savings during the calcination stage for the following reasons:

(a) the enthalpy of dehydration of boehmite to alumina is significantly lower than that of gibbsite.

\[
\begin{align*}
\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} &\rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \quad \Delta H = 187 \text{ KJ/mole Al}_2\text{O}_3 \\
\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} &\rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \quad \Delta H = 72 \text{ KJ/mole Al}_2\text{O}_3
\end{align*}
\]

This means energy savings of about 1.1 GJ/t Al$_2$O$_3$.

(b) As boehmite contains one mole of water against three for gibbsite, the amount of the material to be calcined will be reduced by 360 kg/t of alumina produced. This will result in additional energy savings of the order of 0.7 GJ/t Al$_2$O$_3$ as well as in increase of the calciner productivity.

The energy consumption during the calcination stage is reduced to 1.2 GJ/t Al$_2$O$_3$, representing more than 40% energy reduction in the calcination stage and more than 10% total energy savings in the Bayer process.

The partners of the project consortium have already submitted a patent application to Greek Patent Organization. A detailed description of this project output is shown in the following table 3.

<table>
<thead>
<tr>
<th>Kind</th>
<th>Application No</th>
<th>Owner</th>
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<td>Patent</td>
<td>970100253/24-6-1997</td>
<td>Project Consortium</td>
<td>Prof. A. Kontopoulos</td>
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6. Exploitation plans and anticipated benefits

The new process is a highly innovative variation of the Bayer process for the precipitation of boehmite under atmospheric conditions and the calcination of the precipitated boehmite to produce anhydrous alumina. This variation of the Bayer
process can be easily applied to the existing alumina production plants by suitable modification of the plant operating conditions and also to the design of new ones. As, the alumina production is almost exclusively performed by the Bayer process, it is expected that the new process will be accepted by the European and world-wide alumina industry. Besides the use for the production of smelter grade alumina, the boehmite produced is expected to be applied in various other industrial sectors, expanding this way the potential applications of the process.

Approximately 90% of anhydrous alumina produced by the Bayer process is used for the production of primary aluminium by the Hall-Heroult process (metallurgical grade alumina). The remainder (non-metallurgical grade alumina) is used for the production of refractories, abrasives, ceramics, cement, whiteware, aluminium chemicals, flame retardants, detergent zeolites, adsorbents and fillers. Therefore, the demand for alumina depends mainly on the trends of the aluminium sector.

The world alumina and primary aluminium production is estimated to be approximately 45 and 20 million tons, respectively. 12.5% of the alumina production and 18% of the aluminium production are produced in EU. The market corresponding to this world alumina and aluminium production is 30 billion ECU; EU accounts for approximately 10 billion ECU.

Up to 2000, the demand for metallurgical grade alumina is expected to rise at a rate of 3% per year, while this for non-metallurgical alumina is expected to increase at a rate higher than 4% per year. This increase will mainly concern alumina-graphite refractories for continuous casting processes, low-cement monolithics, alumina-rich monolithic ladle linings, fused alumina abrasives and micronised reactive alumina for ceramics. Finally, the production of alumina for detergent zeolites is estimated to increase by 12% per year. These estimates have already stimulated alumina industry to increase their production capacity. It is expected that this increase in production capacity will be focused in Australia, South America and Asia, where the alumina production cost is low.

The potential energy savings from the application of the proposed process are 1.8 GJ/t $\text{Al}_2\text{O}_3$, which are equivalent to 43 kg fuel oil/t $\text{Al}_2\text{O}_3$ or 11 ECU/t $\text{Al}_2\text{O}_3$. As the EU annual alumina production is approximately 5.6 Mt. alumina, the potential energy savings are estimated to be 61.5 MECU annually.

Based on these figures, the potential market in Europe and world-wide to which this technology is addressed is several billion ECU.
Diagram to illustrate potential applications of the project

New Boehmite Process

- Metallurgical Grade Alumina
- Non Metallurgical Grade Alumina
- Non Calcined Alumina

- Activated Alumina
  -Adsorbents
  -Catalysts

- Specialty Calcined Aluminas
  - Refractories
  - Abrasives
  - Ceramics
  - Whitewares
  - Glass and Enamels

- Fillers