

## ACH Calcination and Spray Roasting: Opportunities for Closing Gaps Within the Chloride Route for Al<sub>2</sub>O<sub>3</sub> Production

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### Abstract

The chloride route for alumina production has recently gained renewed interest in R&D and industry. The EU-funded “SisAl Pilot” (no 869268) exemplifies this, utilizing HCl and AlCl<sub>3</sub> for Al<sub>2</sub>O<sub>3</sub> production. Using HCl allows for alternative raw materials such as anorthosite, kaolin, and by-products such as bauxite residues or fly ash to be utilized for alumina production. A 1977 study by the US Bureau of Mines identified the chloride route as a promising alternative to the Bayer process. As of late, this alumina production method has been used to produce specialized alumina products such as polishing suspensions.

However, handling HCl poses significant challenges, particularly in the roasting step where aluminium chloride hexahydrate (ACH) is converted to Al<sub>2</sub>O<sub>3</sub> and HCl, with subsequent capture and recycle of the HCl. Scaling this process to an industrial level presents additional difficulties, such as feeding solid material into a reactor in an HCl gas atmosphere.

This paper aims to reintroduce this technology to the alumina community and to demonstrate the properties of Al<sub>2</sub>O<sub>3</sub> samples produced by two calcination methods: direct calcination of ACH precipitate and spray roasting after re-dissolving ACH or using another AlCl<sub>3</sub> source. One sample is produced by acid processing of calcium aluminate slag together with ACH precipitation, and the other by direct spray roasting of a Polyaluminiumchloride (PAC) solution. X-ray diffraction (XRD) and scanning electron microscope (SEM) analyses are used to examine their distinctive properties.

**Keywords:** Alumina, Calcination, Chloride route, Spray roasting, Specialized alumina products.

### 1. Context and present situation

The alumina industry is dominated by the Bayer Process, which has been the primary technology for over a century. Virtually all significant alumina plants utilize this process, and it remains the sole technology employed in new installations. However, the efficiency of the Bayer Process is contingent upon access to bauxites of a specific quality [1]. While such raw materials are available, their supply is finite. Moreover, current global challenges underscore the risks associated with relying on a single type, grade, or source of raw material in the production of a globally important metal like aluminium [2].

Efforts to diversify the raw materials available for alumina production and to develop novel processes capable of treating alternative materials began in the latter half of the last century. Initiatives such as those undertaken by the US Bureau of Mines explored various opportunities at pilot scale [3].

After years of investigation, the chloride route emerged as one of the most promising alternatives. HCl leaching presents a viable option for a wide range of aluminium-containing raw materials, including kaolin, anorthosite, and even waste materials such as fly ash or bauxite residue from the Bayer Process [4, 5]. The chloride route offers favourable prospects for the purification of the alumina fraction and the possibility of HCl regeneration to recover chlorides, enabling chloride recycling within the process. Spray roasting of an  $\text{AlCl}_3$  solution was already presented as a technological alternative during the 3<sup>rd</sup> International Congress of ICSOBA in 1973, with a plant in Italy successfully operating for approximately 40 years. This method, having proven its durability and effectiveness, deserves renewed attention from the alumina industry.

A specific advantage of the HCl acidic process route is that silica has a low solubility in HCl. Consequently, employing this approach ensures that under optimal process conditions the produced alumina remains uncontaminated by silica. Additionally, the process avoids losses of the main process agent/utility, further enhancing its efficiency and economic viability.

By considering these advancements and alternative processes, the industry can mitigate the risks associated with the finite supply of high-quality bauxite and the geopolitical and economic challenges of relying on a single type of raw material. The application of the chloride route for alumina production from aluminosilicate resources that are readily available in global scale can potentially contribute towards a more sustainable and resilient aluminium value chain.

## 2. Challenges

HCl has several advantages in comparison with other acids for the processing of kaolinitic clays and similar aluminosilicate materials, including the availability of HCl and its competitive cost, the effortless filtration of the aluminium bearing solutions, the insolubility of  $\text{TiO}_2$  and the available process alternatives for Fe removal by ion exchange or solvent extraction techniques. On the other hand, from the standpoint of impurity co-dissolution, the leaching of the alkali (Na, K, etc.) and alkaline earth impurities (Ca, Mg, Ba, etc.), as well as phosphate impurities is unavoidable. The dissolution of Si and Ti is limited. Most of the aforementioned impurities can traditionally be controlled by precipitation or by bleeding of the leach solution. In either case, the process costs and corresponding efficiencies of Al extraction are affected negatively. For this reason, the purity of the aluminosilicate raw material is of the utmost importance.

The most challenging impurities are Fe and Si as they can both precipitate with the aluminium salt and thus affect the purity of the  $\text{Al}_2\text{O}_3$ . As mentioned above the dissolution of Si is limited and usually does not pose an issue when the quality of the aluminosilicate raw material is high. Fe on the other hand is the most challenging impurity and can be found from two sources: (a) as an impurity in the raw material and (b) as an impurity from the corrosion attack of HCl on the equipment of the industrial facility. The latter has been recognized as the most critical issue opposing the further development of chloride processes for alumina production [6]. The HCl route does not allow for the selective leaching of alumina, as seen in the Bayer process. Instead, many other elements, including alkaline, earth alkaline, and non-precious metals, are co-dissolved. Despite these challenges, well-established purification steps can achieve smelter grade alumina (SGA) purity and beyond. Technologies such as HCl sparging, discussed in detail by Argyn and coworkers in the context of ACH crystallization, are considered promising for addressing these purification challenges and advancing the technology [5].

HCl is a highly corrosive agent, particularly affecting the most widely used construction material – globally iron. Even high-grade iron-based materials are not resistant to HCl, leading to various types of corrosion, including aqueous corrosion and pitting.

By taking the advantage of using experience for construction materials of the chemical industries, HCl becomes manageable even at industrial plant size.

The following statements should give a rough summary of what has to be considered when dealing with HCl at industrial plant size:

- polymers, polymer coatings or rubber-based materials are in general resistant against HCl
- Steel in in general not resistance against HCl higher concentrations (+15 wt.%) in its dissociated form
- Steel in in general resistance against HCl in gas form which makes pyrohydrolysis process possible under certain conditions
- Specific operations considering higher temperatures together with dissociated HCl or Cl-salts are challenging for the process industry and special materials like niobium, tantalum or silica carbide have to be used.

In general, it can be mentioned that most types of polymers, polymer coatings or rubber-based materials are resistant against HCl in its dissociated form in liquid phase. The resistance of steel-based construction materials against HCl solutions is in general weak. However, the resistance of steel-based construction materials against HCl in gas phase is, in comparison, quite good. This circumstance is crucial for the pyro hydrolysis process that is being considered in this paper.

In liquid phase HCl is in a dissociated form, which causes high corrosion rates of iron-based materials, although special alloys are reported to have considerable resistance to aqueous HCL. However, in a process environment with HCl in gaseous phase, and no condensation or dissociation, steel-based materials can be widely used.

To address the challenges of using HCl in chemical processes, it can be concluded that HCl can be effectively used in environments where cost-effective polymers are available or where condensation can be avoided. However, in temperature ranges between 100 °C and 300 °C, the situation becomes more challenging. In these conditions, specialized materials such as tantalum, niobium, titanium, fluoropolymers, ceramics, or even alpha alumina are required.

The HCl route is not an approach where alumina is leached selectively, as it happens within the Bayer process. Many other elements like the alkaline, earth alkaline and non-precious metals are co-dissolved. There are, however, well know purifications steps available that allow to reach smelter grade alumina (SGA) purity and above. A detailed explanation of HCl sparging in by Argyn and coworkers [5] while discussing ACH crystallisation explains why this technology is the most promising.

### 3. State of the art

There are specific HCl routes available for different feed materials. Within these process approaches, alumina can be either the main product or a byproduct [7]. In any case, all these processes have several aspects in common. Generally, the process starts with HCl leaching and the separation of the non-dissolvable fraction, such as silica. Afterwards, one or several purification steps are carried out to obtain aluminium chloride and other metal chloride fractions. These procedures are well documented in the literature [8].

There are two possible states in which the purified, pretreated  $AlCl_3$  can be applied to the hydrolysis/calcination stage:

- In aqueous state, as an  $\text{AlCl}_3$  salt solution, with a maximum saturation point of 31.1 wt.% [9] at ambient temperature.
- As a solid hydrate chloride salt, specifically ACH crystals produced by the HCl sparging process and containing some remaining surface moisture from the saturated HCl solution.

In the case of alumina production, aluminium chloride must be converted to alumina; the released HCl will again find applications in leaching or purification steps in the process.

This work specifically examines the available roasting processes. The key questions addressed include: What technologies are available on an industrial scale? What throughputs are achievable? What is the current development status of these technologies? What are the expected properties of the products after roasting?

Using the chloride route for  $\text{Al}_2\text{O}_3$  production, which involves the roasting of ACH crystals to obtain  $\text{Al}_2\text{O}_3$ , offers several advantages. Firstly, the process allows for the recovery and recycling of HCl, reducing the need for fresh acid and minimizing waste. Secondly, the chloride route can produce high-purity alumina, due to the relative ease of obtaining a pure  $\text{AlCl}_3$  solution based on removing excipients and other impurities. This same purification is possible when recrystallizing and precipitating ACH crystals. Both steps are essential for producing pure  $\text{Al}_2\text{O}_3$  for applications requiring superior material properties. Thirdly, the roasting of ACH can be conducted at different temperatures (depending on targeted phase  $\alpha$ ,  $\gamma$ ,  $\delta$ ), which can potentially optimize energy consumption within the chloride route under specific conditions that are not comparable to those of the Bayer process.

To investigate the raw materials, this paper discusses two primary technologies: (i) calcination of ACH precipitate and (ii) spray roasting of  $\text{AlCl}_3$  concentrated solution. The aim is to show what is available technologically, and less to compare the specific properties of the generated products.

#### 4. ACH Crystals

The solubility of  $\text{AlCl}_3$  in an aqueous solution can be reduced by adding HCl to the solution. The thermal decomposition of aluminium chloride hexahydrate (ACH) to produce alumina is a straightforward process, like the state-of-the-art production of MgO from the calcination of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . In this approach, ACH is precipitated from the acidic solution [10-11]. Different pyrometallurgical technologies that have been used by various projects studying and implementing this route include indirectly heated fluidized beds and indirectly heated rotary kilns, all working with varying degrees of success. [12].

The ACH crystal route is more appealing than spray roasting from the perspective that it contains less water to be evaporated, leading to lower energy consumption. In table 1, preliminary mass and energy balance simulations results, calculated using HSC-Outotec, for the calcination of ACH or solubilized  $\text{AlCl}_3$  to produce  $\text{Al}_2\text{O}_3$  are showcased. The obtained values demonstrate the different energy requirements for the calcination of ACH (cases a and b) or pure  $\text{AlCl}_3$  (case c), and the effect of different fuels, reveal that the primary energy expenditure is the increase of water content. This further demonstrates that the ideal technology suitable for a decreased energy consumption is the one which requires less water to manage the input stream combined with the choice of an ideal fuel. Furthermore, both roasting technologies are scalable, allowing the production of higher throughputs. This is crucial when scaling up to industrial level and opens the field to investigate other issues, such as the obtention of smelter-grade alumina (SGA). A rough estimation on the energy consumption upon the calcination of aluminium chloride and aluminium chloride hexahydrate, taking into consideration different fuels and electrical consumption, has been evaluated.

**Table 1. Non-indicative first values on the energy per kg of SGA in a generic calciner at T = 500 °C.**

Energy Required in m <sup>3</sup> fuel or kW per kg of Al <sub>2</sub> O <sub>3</sub> produced						
	Fuel	CH <sub>4</sub> [Nm <sup>3</sup> /kg]	CH <sub>4</sub> [Nm <sup>3</sup> /kg]	H <sub>2</sub> [Nm <sup>3</sup> /kg]	H <sub>2</sub> [Nm <sup>3</sup> /kg]	Electrical [kWh/kg]
	Oxidant, AF	Air, AF = 9.5	O <sub>2</sub> , AF = 2	Air, AF = 2.5	O <sub>2</sub> , AF = 0.5	-
(a)	AlCl <sub>3</sub> ·6H <sub>2</sub> O <sub>(s)</sub> 45 % abs water	0.72	0.62	2.32	2.03	4.91
(b)	AlCl <sub>3</sub> ·6H <sub>2</sub> O <sub>(aq)</sub> (65 wt%) 64 % abs water	1.10	0.94	3.51	3.07	6.74
(c)	AlCl <sub>3</sub> in water (30 wt%) 70 % abs water	1.59	1.36	5.08	4.44	10.77
Fuels considered are pure methane (LHV=36 MJ/m <sup>3</sup> ) with air or pure oxygen, or H <sub>2</sub> (LHV=11 MJ/m <sup>3</sup> ) with air or pure oxygen at stoichiometric combustion. (a) Solid stream containing only ACH crystals; (b) Wet cake ACH crystals (65 wt%) and water (35 wt%); (c) Solution containing pure anhydrous AlCl <sub>3</sub> dissolved in water (S/L = 30/70).						

However, handling ACH poses challenges due to its properties — a corrosive, hygroscopic, and sticky material both during handling and calcination. Therefore, identifying the appropriate process technology is crucial to avoid corrosion of the different pieces of equipment.

Considering the material properties generated in a static bed, it's worth mentioning a calcination technology that could achieve these roasting conditions and gently process the crystals. The rotating hearth furnace or rotating hearth calciner technology involves placing the material on a moving bottom and transferring it through the furnace or kiln. This allows for precise temperature control in the furnace, with minimal mechanical stress compared to other technologies where particles are constantly in motion like e.g. in a fluidised bed. The SEM analysis showed that the shape of the ACH crystal remains even when the porosity seems to increase during chemical conversion and HCl and H<sub>2</sub>O release.

This approach could be likened to the currently tested simplified model of having the ACH in a static bed in a muffle furnace. Currently, discussions are taking place to possibly execute the calcination of ACH in a rotary hearth furnace (RHF). Tenova<sup>®</sup> has kindly provided us with a photo of the current industrial equipment that is likely to be used to process these materials (Figures 1 and 2) in the future at industrial scale.



Figure 1. Rotary hearth furnace calciner, ©TenoVA.

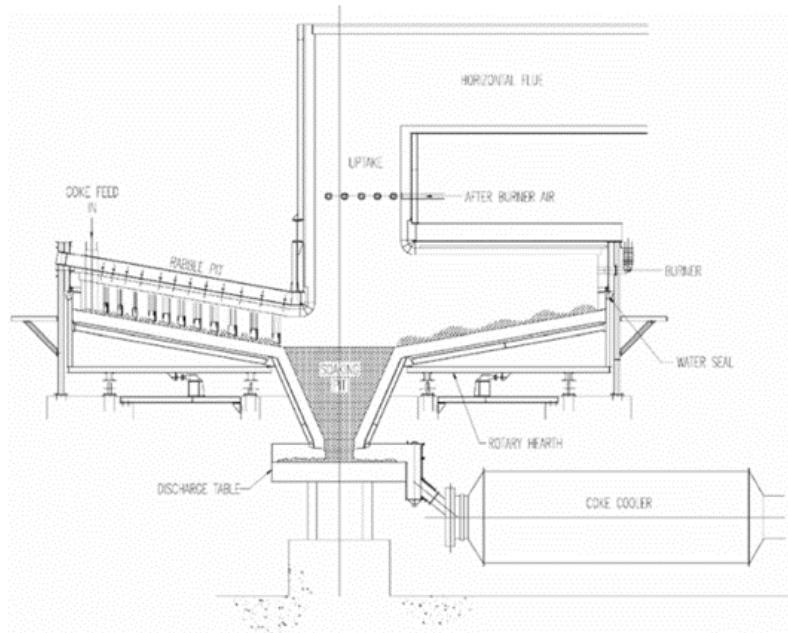
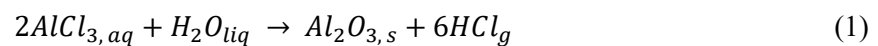


Figure 2. Rotary hearth furnace calciner scheme, ©TenoVA.

## 5. Liquid

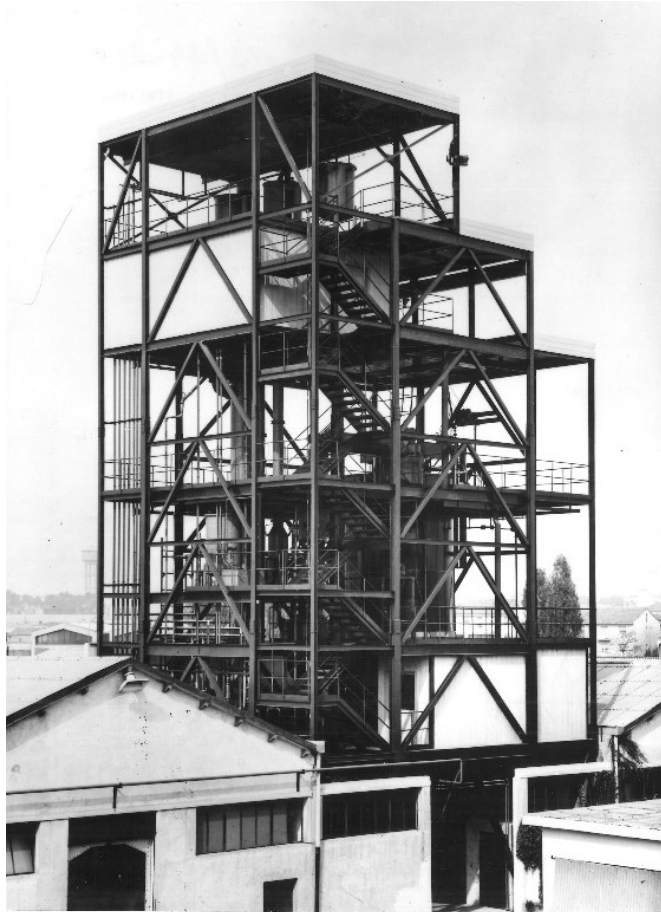
One option that was already presented at the 3<sup>rd</sup> ICSOBA in Nice is the spray roasting process [13]. In the spray roasting method, a concentrated  $AlCl_3$  solution is atomized and subjected to high-temperature roasting. This process is industrial proven and is also scalable for industrial production considering state of the art of up to 4 t/h of alumina. It also offers efficient recovery of HCl, which can be recycled back into the leaching process (as is conducted in several cases, namely MgO and  $Fe_2O_3$  production) [14].

In this case, a reactor similar to a spray dryer is used, but which operates at a significantly higher temperature range. The  $AlCl_3$  solution is sprayed into the reactor and during the way from the top to the bottom the drops evaporate and will be calcined / pyrohydrolyzed so that the following global chemical reaction can take place:



It is a counter-current flow process, with the hottest temperature zones in the reactor reaching 800 to 900 °C. The generated alumina is a mixture of alpha, gamma, and delta phases and exits the system from the bottom of the reactor. HCl fumes produced during the process exit the reactor from the top and are then water quenched. Subsequently, the HCl is separated from the inert and combustion gases using washing columns, achieving a strength close to the azeotrope of HCl (~ 20 %wt).

Figure 3 illustrates the plant presented at the 3<sup>rd</sup> ICSOBA, which operated successfully in the industry for approximately 40 years.



**Figure 3. Italian AlCl<sub>3</sub> spray roaster plant in operation from 1970<sup>th</sup> to early 2000s,  
©Andritz Metals, Vienna.**

Figure 4 shows a first draft of a spray roaster plant process flow diagram for Al<sub>2</sub>O<sub>3</sub> and how it could be built today, while still following the same philosophy as the original one.

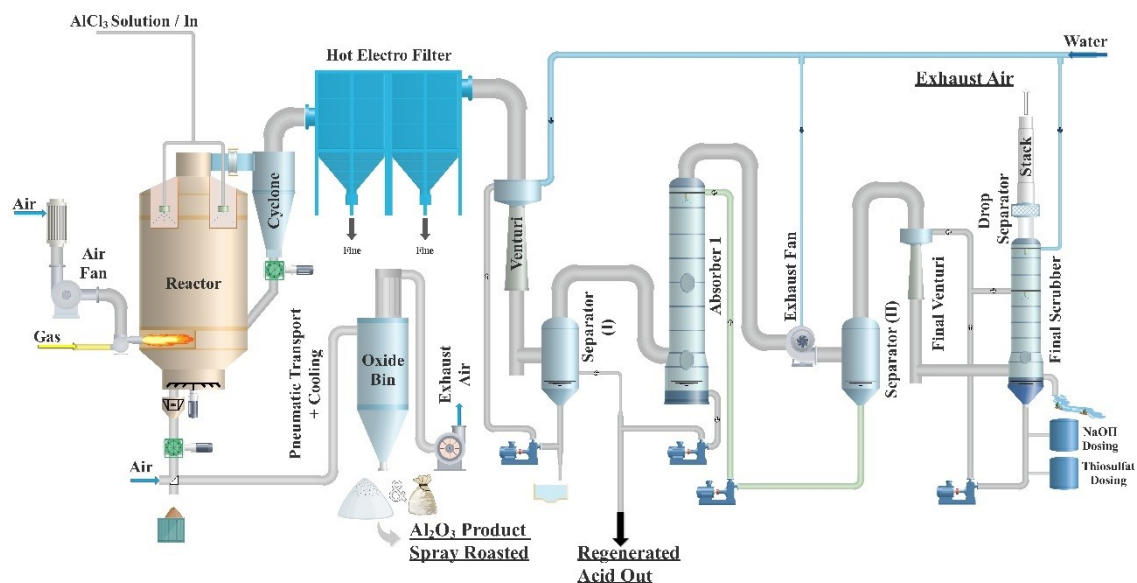


Figure 4. Process flow diagram Al<sub>2</sub>O<sub>3</sub> Spray roaster plant.

Spray roasting is a widely used technology in the steel industry to recover HCl from spent pickling baths and produce hematite powder as a by-product. This process is also implemented on an industrial scale for synthetic magnesia production from magnesia chloride. The largest units built thus far, particularly in the case of magnesia production, have had a feed flow to the reactor ranging up to 30 m<sup>3</sup>/h and a MgO production rate of 3 to 4 t/h. Given these precedents, it's conceivable that current plants handling alumina could achieve similar magnitudes. While these volumes are certainly not comparable with today's Bayer plant throughputs, and considering the limits in upscaling, the feed material flexibility is a significant advantage that allows one plant to deal with different resources as well as focusing on special products. A "Mini Mill" concept must be further investigated, since it counterbalances the current approach using the advantage of economy of scale.

## 6. Materials and Methods

Experiments were conducted to compare two Al<sub>2</sub>O<sub>3</sub> samples produced through: 1) by calcination of ACH crystals generated through HCl(g) sparging precipitation, and 2) a spray roasting process using an AlCl<sub>3</sub> solution. The experimental conditions for the thermal treatment are summarized in Table 2.

Table 2. Experimental conditions on the production of Al<sub>2</sub>O<sub>3</sub> via two technologies: Spray roasting and calcination.

Al <sub>2</sub> O <sub>3</sub> production method	Precursor synthesized by	Conditions of Al <sub>2</sub> O <sub>3</sub> production
Calcination of ACH	HCl <sub>(g)</sub> sparging precipitation in AlCl <sub>3</sub> /CaCl <sub>2</sub> solution	<ol style="list-style-type: none"> <li>Starting solution concentration: 41 g/L Al, 43 g/L Ca, 350 ppm Si, 70 ppm Fe, 250 ppm Mg, &lt;10 ppm Na</li> <li>Sparging crystallization at 20 °C, 300 rpm stirring rate, 600 ml/min HCl flowrate, HCl concentration at the end of the process 10M</li> <li>Purification by redissolving the ACH of step 2 and performing precipitation at the same conditions as in Step 2</li> </ol>

Al <sub>2</sub> O <sub>3</sub> production method	Precursor synthesized by	Conditions of Al <sub>2</sub> O <sub>3</sub> production
		<p>4. Calcination of ACH produced in step 3 in two (2) stages.</p> <ul style="list-style-type: none"> <li>• Stage 1: Calcination in a tube furnace, retention time 1 h at 400 °C, average heating rate 8 °C/min, inert atmosphere N<sub>2</sub></li> <li>• Stage 2: Calcination at a muffle furnace, retention time 1 h at 1200 °C, average heating rate 8 °C/min</li> </ul>
Spray Roasting of AlCl <sub>3</sub> solution	Technical grade PAC Solution	<p>Starting solution concentration: 20–25 wt.% AlCl<sub>3</sub> in water (approx. 250–320 g/L).</p> <p>The solution is sprayed into the reactor of the industrial pilot unit [15] following the concept shown in Fig 4, which contains different temperature levels as in more details explained in the reference [16].</p> <ol style="list-style-type: none"> <li>T = 450 °C at the reactor top outlet</li> <li>T = 700–800 °C at the burner level</li> </ol>

The Al<sub>2</sub>O<sub>3</sub> products are examined by laser particle size analysis, XRD, and SEM to determine their phase composition, particle size, and morphology.

In more detail, the XRD patterns were collected using a MiniFlex 600 benchtop diffractometer (Rigaku, Tokyo, Japan) equipped with a D/tex ultra detector. The diffractometer operated at 40 kV and 15 mA (600 W) with Cu-K $\alpha$  radiation (Ni-filtered). Diffraction data were collected from 10 to 120° (2 $\theta$ ), in 0.02° (2 $\theta$ ) steps and at a rate of 5° (2 $\theta$ ) per minute. The mineralogical composition of the materials examined was determined using DIFFRAC EVA V5.1 software (Bruker AXS, Karlsruhe, Germany) and the ICDD databases PDF-4+ 2023 and PDF-4 Minerals 2023[17]. Particle size analysis was performed with a Partica LA-960 V2 laser scattering particle size distribution analyser. Electron microscopy was performed on a JEOL 6380LV scanning electron microscope.

## 7. Results and Discussion

### 7.1 Analysis of Al<sub>2</sub>O<sub>3</sub> Sample Produced from ACH Calcination

The X-ray diffractogram of the Al<sub>2</sub>O<sub>3</sub> sample produced by the ACH precipitation/ACH calcination process is shown in Figure 5. The calcination conditions were listed in Table 1 previously. A near complete transition to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was achieved for this sample under the conditions applied. As indicated by the sharp diffraction peaks, the material is well crystallized. Figure 6 presents a typical  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particle produced by the ACH calcination process. Especially in Figure 6(b), discontinuities in the crystal structure can be observed. Y. Yang et al. have microscopically examined the transformation of ACH crystals to Al<sub>2</sub>O<sub>3</sub> and also observed the transformation of the ACH particles to regular hexagonal prisms in temperatures above 175 °C, similar to that shown in Figure 6b.[18] Moreover, they also note the appearance of cracks on the surface of the particle, similar to the ones observed in our sample. They attribute these cracks to the escape of gaseous HCl and H<sub>2</sub>O from the interior of the particle. At the same time, it is known that the alumina calcination process is pseudomorphic and the cracks observed could additionally be attributed to the phase transformation reactions. Compared to the spray roasting process, the particle size distribution of Al<sub>2</sub>O<sub>3</sub> produced by ACH calcination depends on the particle size of the original ACH particles. As a result, the particle size of the sample presented in this work had D(0.5) value of 65  $\mu$ m and its D(0.9) value was 124  $\mu$ m approximately.

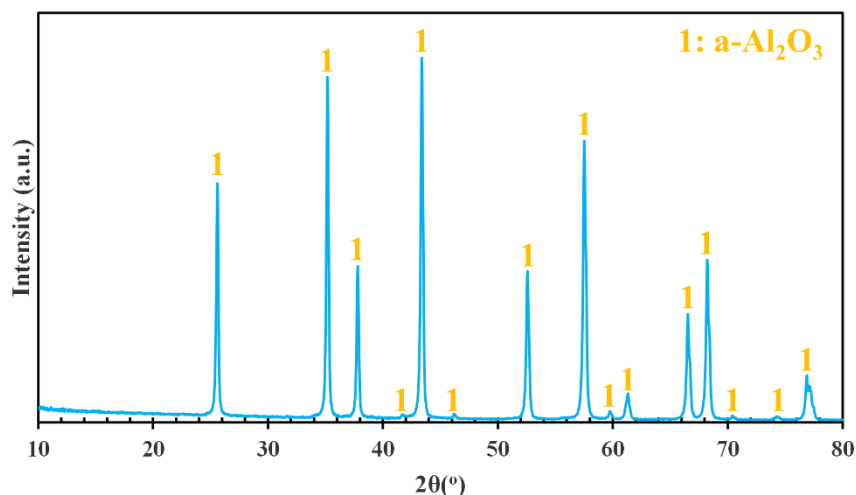


Figure 5. Qualitative XRD analysis of  $\text{Al}_2\text{O}_3$  produced from ACH calcination.

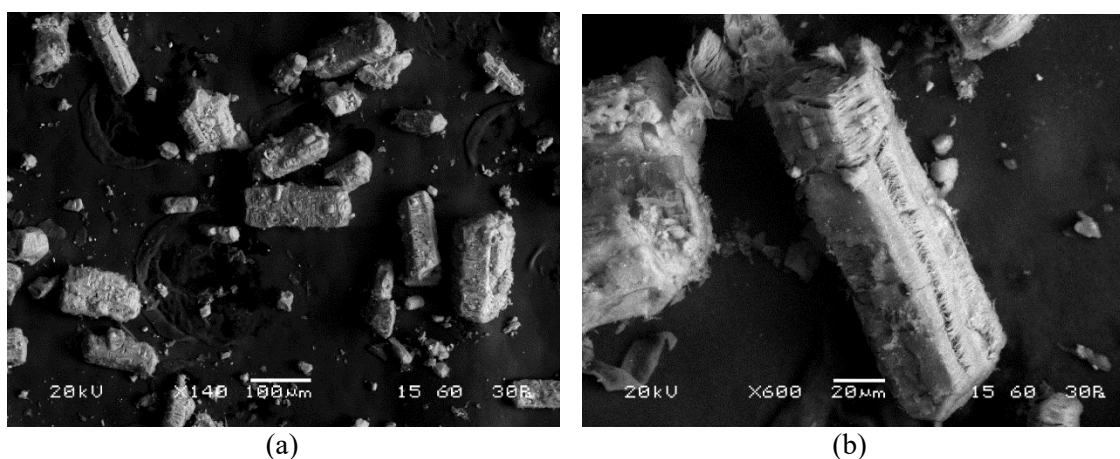


Figure 6. (a)  $\alpha\text{-Al}_2\text{O}_3$  produced by ACH calcination that was studied in this work. Most of the particles are in the form of hexagonal prisms (b) Detail of an  $\alpha\text{-Al}_2\text{O}_3$  particle produced by ACH calcination. Discontinuities in the structure are observed.

## 7.2 Analysis of Spray Roasted $\text{Al}_2\text{O}_3$ Sample

The X-Ray Diffractogram of the spray roasted  $\text{Al}_2\text{O}_3$  sample is shown in Figure 7. The spray roasted  $\text{Al}_2\text{O}_3$  is predominantly an amorphous material (X-Ray Indifferent). This is to be expected considering the maximum temperature of spray roasting (Table 2). Nonetheless, it is interesting to note that some crystalline phases have already been formed. In more detail, the most noticeable phase identified is  $\alpha\text{-Al}_2\text{O}_3$ , while some broad diffraction peaks of  $\gamma\text{-Al}_2\text{O}_3$  and  $\delta\text{-Al}_2\text{O}_3$  were also detected. As the calcination temperature values leading to the formation of these aluminas are different ( $\alpha\text{-Al}_2\text{O}_3$  is synthesized at temperature values over  $1100\text{ }^\circ\text{C}$ , while  $\gamma\text{-Al}_2\text{O}_3$  and  $\delta\text{-Al}_2\text{O}_3$  below  $800\text{ }^\circ\text{C}$  and  $950\text{ }^\circ\text{C}$  respectively), their existence is an indication of non-uniform calcination conditions in the reactor.

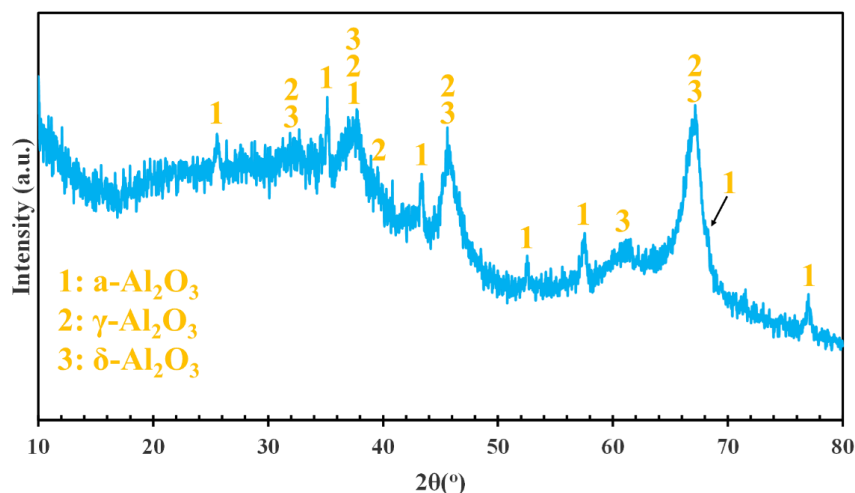


Figure 7. Qualitative XRD analysis of spray roasted  $\text{Al}_2\text{O}_3$ .

As mentioned earlier, the most prominent characteristic is the amorphicity observed in the alumina sample produced through the spray pyrolysis technique. This is indicative of the fast calcination and low retention time approach of the spray pyrolysis process. In addition, the size of the  $\text{AlCl}_3$  solution droplets entering the reactor is, probably, also a crucial factor, although it could not be extensively studied in this research. The microscopic examination of the sample produced by the pyro-hydrolysis process showed marked differences in the morphology of the particles, compared to the previous sample. Porous particles of irregular shape were mostly observed, as shown in Figures 8a and 8b. Finally, the particle size analysis of the material determined that its  $D(0.5)$  value is  $15\ \mu\text{m}$  and its  $D(0.9)$  is  $37\ \mu\text{m}$  approximately.

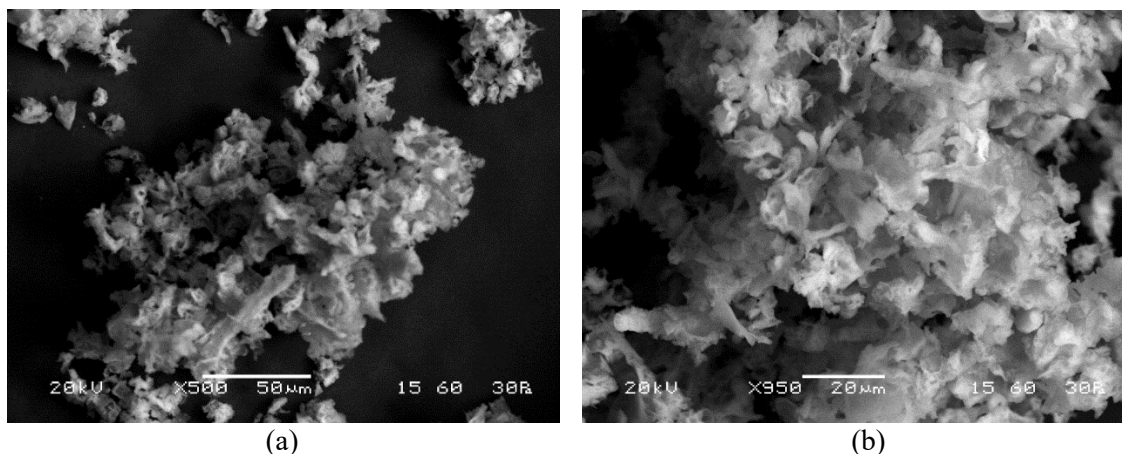


Figure 8. (a) Spray roasted alumina studied in this work. The absence of well-defined crystal structures is evident. (b) Detail of previous image, showing an irregularly shaped morphology.

By comparing the crystallographic and particle size and morphology properties of these two alumina samples, certain aspects of the effects of the thermal processes applied are immediately observable. The spray roasting process produces a fine, amorphous product. Its morphology is irregular and a mixture of  $\gamma$ -,  $\delta$ - and  $\alpha$ - $\text{Al}_2\text{O}_3$ . This could be attributed to both the low retention time and non-uniform temperature conditions in the reactor. Whether a further, separate thermal treatment of the material could yield a more uniform and crystalline product is a potential area of investigation. On the other hand, the low particle size and amorphous nature would make it more easily dissolvable in wet chemical systems, which could also be a potential future application.

The ACH calcination process, as mentioned earlier, has been previously studied in the production of MGA, resulting in a crystalline material. The particle size and morphology of the product are strongly influenced by the hydrometallurgical process of ACH precipitation preceding the calcination. Therefore, the ACH route appears more suitable for producing crystalline alumina and is under investigation for various applications. However, the high HCl consumption required for ACH production, the regeneration of HCl during calcination, and the behaviour of the product during electrolysis are issues that warrant further exploration. Additionally, determining the chlorine content of both products is a crucial factor that should be investigated.

## 8. Conclusions

In this study, we investigated two distinct technologies for alumina production: spray roasting / pyro hydrolysis of  $\text{AlCl}_3$  solution and calcination of ACH crystals. Through analysis of the physicochemical properties of the resulting  $\text{Al}_2\text{O}_3$  samples, the following conclusions can be drawn:

1. The spray roasting process yielded an amorphous alumina product with an irregular morphology. XRD analysis revealed the presence of  $\alpha\text{-Al}_2\text{O}_3$  along with broad diffraction peaks of  $\gamma\text{-Al}_2\text{O}_3$  and  $\delta\text{-Al}_2\text{O}_3$ , indicating non-uniform calcination conditions. The particle size distribution of the spray-roasted alumina was fine, making it potentially suitable for applications requiring dissolution in wet chemical systems.
2. The ACH calcination process, under the conditions applied, produced crystalline alumina with well-defined crystal structure and crystallites. XRD analysis confirmed a near complete transition to  $\alpha\text{-Al}_2\text{O}_3$  under the applied conditions. The crystals produced in the calcination process showed a hexagonal prismatic shape, which has been also observed in literature. There were also cracks observed in the structure which could be attributed to the evolution of HCl and  $\text{H}_2\text{O}$  gases during the early stages of calcination and to the pseudomorphic nature of the phase transformations of the different transition alumina.

The comparison of these two alumina samples highlights distinct advantages and challenges associated with each technology. However, ACH handling poses challenges due to its corrosive and hygroscopic properties, requiring careful process optimization.

Further research is needed to optimize process parameters, enhance product quality, and explore potential applications of both spray-roasted and ACH-derived alumina in diverse industrial sectors. While spray roasting can be seen as proven technology will the RHF's will also need some more work to make them fit for high HCl environments. Fine-tuning the technology and unique properties of each technology allows the alumina industry to advance toward more efficient and sustainable production methods.

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