ACH Calcination and Spray Roasting: Opportunities for Closing Gaps Within the Chloride Route for Al_2O_3 Production

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https://doi.org/10.71659/icsoba2024-aa030

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 $AlCl_3$ for Al_2O_3 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_2O_3 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_2O_3 samples produced by two calcination methods: direct calcination of ACH precipitate and spray roasting after re-dissolving ACH or using another $AlCl_3$ 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 $AlCl_3$ solution was already presented as a technological alternative during the 3rd 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 filtration of the aluminium bearing solutions, the insolubility of 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 Al_2O_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].

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 $AlCl_3$ solution and calcination of ACH crystals. Through analysis of the physicochemical properties of the resulting Al_2O_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 α-Al_2O_3 along with broad diffraction peaks of γ-Al_2O_3 and δ-Al_2O_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 α-Al_2O_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 H_2O 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.

9. Acknowledgments

The authors are grateful for the support of Alessandro Della Rocca from Tenova Genova, for the discussions on the rotary hearth furnace opportunity for crystal calcination, and for the support of Frank Baerhold and Martin Brazda from Andritz Metals Vienna for the spray-roasted Al_2O_3 sample produced in their pilot unit and for their original picture from Becromal, Italy, $AlCl_3$ spray roaster.

10. References

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