AA03 - Further Development of RUSAL's Alumochloride Technology for Alumina Production from Non-Bauxite Resources

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Abstract

RUSAL is currently developing an alumochloride process for the production of smelter grade alumina using kaolin clays from domestic Russian deposits. The outcome of this project will be significant cost reductions for the transportation of bauxites and alumina. The chemistry and a mass balance of the process, and the quality of smelter grade alumina produced were confirmed at mini-plant scale, and the design of a pilot plant has been completed. The proposed process is characterized by low operating costs, flexibility in the raw materials it can use, and the production of high-margin products. In the course of development, several technology directions and process flowsheets have been tested to reduce heat consumption and the concentration of product impurities such as iron and phosphorus, and including the closed cycles of intermediate products: calcium chloride, aluminum oxychlorides, hematite, etc. The most profound modernization is the replacement of the thermal decomposition of aluminum chloride hexahydrate by its neutralization with ammonia. Further development and integration of technology options will enable further improvements to the existing benefits of the process and enhance the cost-effectiveness of the alumochloride technology.

Keywords: Alumochloride process, smelter grade alumina, ammonium chloride, boehmite.

1. Introduction

Some aspects of the hydrochloric acid (alumochloride) process for alumina production from kaolin developed by UC RUSAL's Engineering & Technology Center have already been presented at previous ICSOBA conferences. A detailed description of the technology is documented in the relevant Russian patent [1]. The technology has been successfully tested at the specialized mini-plant, and as of today, the design of an industrial pilot plant has been completed. The new technology, named the 'Lainer' process (after Yuri A. Lainer - distinguished Soviet and Russian metallurgy researcher – who made valuable contributions to the development of an acid process for alumina production [2]), can be related to a number of hydrochloric acid (chloride) methods for the processing of aluminum non-bauxite raw materials [3].

In the almost forty years since the publication of this work, the following studies on this topic have been published: US Bureau of Mines [4], Orbite (Canada) [5], Nordic Mining (Norway) [6], Altech Chemicals (Australia) [7]. Shenhua Group (China's largest mining and power company), in partnership with the GAMI Institute, have achieved notable success in establishing an industrial pilot operation in Inner Mongolia [8]. The company has successfully carried out pilot tests of their proprietary hydrochloric acid process for coal fly ash processing and is planning to build an alumina refinery with capacity of 125 000 tpa using coal fly ash as a raw material.

Based on the analysis of all known conceptual solutions, this study has concluded that despite the lack of rigorous process testing, the paper by Australian researchers from the Commonwealth Scientific and Industrial Research Organisation (CSIRO), describes the technology that most closely corresponds to the "conventional chloride process for alumina production" [9].

Unlike all the above-mentioned technologies, RUSAL's method [1] comprises acidic and alkaline processes that are characterized by a fine balance of flows/streams and accumulated impurities resulting in lower heat consumption and lower operating costs compared to traditional sintering and similar alumochloride processes. This method enables the production of sandy smelter grade alumina (SGA) that complies with all current requirements of primary aluminum producers.

In the course of RUSAL's technology development, several variants to the main process have been identified which can provide additional energy savings and allow simplification of acid-resistant equipment.

2. Reducing energy consumption at ACH calcination

First of all, this study focused on the calcination of aluminum chloride hexahydrate (ACH), the most energy intense process area. Estimated heat consumption amounts to 2300 kCal/kg Al_2O_3 but when operating heat losses are accounted for, it increases to around 3250 kCal/kg Al_2O_3 [10]. As per the known process solutions, crystallized ACH was calcined in two stages; firstly at a temperature of 200–400 °C, and in a second stage, at a temperature of 900–1100 °C. Water vapor may be optionally injected to the second stage. Calcination was performed either under standard or under highly hydrothermal conditions. This results either in high residual chlorine in the product (~0.1 %), or increased alpha-phase content in alumina (> 70 %) when water vapor was fed into ACH calcination at 1000 °C. Such alumina is not suitable for smelting.

For this reason, an alternative solution was proposed [11], where water vapor is fed to the second ACH calcination stage at a comparatively low temperature. Laboratory tests showed that at temperatures between 150–450 °C with continuous water vapor supplied, and provided that the ratio between the total mass of the supplied vapor and the mass of the alumina product is between 0.2 and 5.7, the second ACH calcination stage allows the production of alumina with low chlorine and alpha-phase contents.

Thermal decomposition of aluminum chloride hexahydrate is a variant of its thermal hydrolysis but in the technical literature this process is usually referred to as calcination and represented by the following overall equation:

$$2AlCl_3{\cdot}6H_2O = Al_2O_3 + 6HCl + 9H_2O \quad (1)$$

In fact this process comprises a number of intermediate transformations of basic aluminum chlorides (oxychlorides) of different basicity and hydration degrees. Some of these intermediate are not necessarily sequential but can be presented as follows:

$$AlCl_3{\cdot}6H_2O \rightarrow Al(OH)Cl_2 + 5H_2O + HCl \quad (2)$$

$$Al(OH)Cl_2 + H_2O \rightarrow Al(OH)_2Cl + HCl \quad (3)$$

$$2Al(OH)_2Cl + H_2O \rightarrow Al_2(OH)_5Cl + HCl \quad (4)$$

$$Al_2(OH)_5Cl + H_2O \rightarrow 2Al(OH)_3 + HCl \quad (5)$$

solution by acid leaching. To minimize supply of additional water to the process circuit wash water from other areas, i.e. from Si-residue washing, can be used for water leaching of the roasted material. The iron chloride solution is directed to pyrohydrolysis. Thus, iron content in roasted alumina can be reduced to 0.006 %.

Ammoium chloride technology produces alumina with gradient porous structure of a cell-type [16] that can be used as a catalyst carrier, or sorbing agent with specific surface area of approx. 250 m^2/g or a dehumidifier with high moisture retention capacity especially as condensed water.

5. Conclusions

In the course of the development of a competitive alternative technology for alumina production from high-silica raw materials, RUSAL has developed and proven an effective basic method for production of smelter grade alumina at mini-plant scale. To improve its performance the following variants of the processes of this technology have been tested at laboratory scale.

1) To enhance Lainer technology, aluminum chloride hexahydrate is decomposed in the presence of water vapor (under hydrothermal conditions). This reduces fuel consumption and the process temperature to between 150-450 °C, while obtaining a product with low chlorine and alpha-phase contents.

2) Laboratory tests show that if the first stage of thermal decomposition is carried out until oxychlorides and amorphous aluminum hydroxide are formed, then part of these ACH incomplete decomposition products can be added to the alumochloride solution as seed before ACH crystallization to reach a pH of 1.6–2.2, preventing iron hydroxide precipitate from ingress to the crystallized product.

3) Experiments have shown that addition of calcium chloride to the Lainer circuit reduces heat consumption for rectification of recycled hydrochloric acid. This method also provides for significant (down to 0.0023 %) reduction of phosphorous pentoxide in alumina. Phosphorous pentoxide is a difficult impurity that easily passes from the raw material into the product in acid processes.

4) A variant of the alumochloride technology was proposed where the ACH thermal decomposition is replaced with treatment of this intermediate product with an aqueous ammonia solution. As a result, aluminum oxyhydroxide (boehmite) is formed and directed to production of calcined alumina. This ammonium chloride technology comprises two interconnected circuits, (hydrochloric acid and ammonium), and reduces energy consumption and improves alumina quality. The ammonium chloride process provides opportunities for further fine-tuning and obtaining value-added products.

All the above variants of upgraded alumochloride technology have potential to further improve the current version of the process. Further extensive lab and mini-plant scale tests are required before they can be integrated into more developed processes.

6. References

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