Alumina Production from CaO-Al_2O_3-SiO_2 Slag Produced in SisAl Process

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Abstract

The global pursuit of sustainable silicon and alumina production has led to the development of the SisAl process, an innovative zero-waste approach to produce both alumina and silicon utilizing secondary raw materials such as Al dross and scrap. In the SisAl process, an exothermic aluminothermic reduction is initiated using calcium silicate slags and Al-based reductants. This reaction results in the formation of a silicon alloy and CaO-Al_2O_3-SiO_2 slags, while the SiO_2 content can be quite low and in the range of a few mass percentages. The produced slag undergoes a series of hydrometallurgical treatments encompassing leaching, desilication, precipitation and calcination to finally yield alumina from the slag.

In this work, an alumina rich CaO-Al_2O_3-SiO_2 slag containing krotite and larnite phases was obtained from a pilot scale SisAl aluminothermic process. The produced slag was subsequently subjected to hydrometallurgical treatment after milling to -150 µm. The alkaline leaching process involved treating 100 g of the milled slag powder with 60 g/L Na_2CO_3 solution at 90 ºC for a duration of 90 minutes. The leaching residue, or 'grey mud', was analyzed using X-ray Fluorescence (XRF), demonstrating a good Al recovery rate. Following this, a desilication stage was performed by introducing CaO powder into the separated $NaAlO_2$ solution under the same condition. Later, CO_2 gas was sparged into the desilicated solution to precipitate aluminum hydroxide at room temperature. The carbonation ceased with the appearance of the first precipitate, and the solution was left to age for 24-hours. XRD results revealed that the formed precipitate consist of predominantly bayerite with minor amounts of gibbsite present as well. The final stage involved the calcination of the precipitated $Al(OH)_3$ yielding alumina white powders. This study offers valuable insights into the potential of the SisAl slag processing to produce alumina in a sustainable and efficient approach.

Keywords: Alumina production, Leaching, Desilication, Precipitation, Aluminum hydroxide.

1. Introduction

Alumina is the most commonly used technical ceramic and the exclusive industrial feedstock for the primary aluminium production. For more than 130 years, the well-established Bayer process has been widely used for the production of smelter grade alumina. However, an increasing awareness and understanding of some of the limitations of the Bayer process have received increased attention in recent years. First, not all bauxite ores are suitable for the Bayer process, as only those with a high concentration of Al_2O_3 and a high mass ratio of Al_2O_3 to SiO_2 (A/S). In addition, from the environmental perspective, the Bayer process produces a significant amount of red mud, a hazardous waste with limited commercial applications for recycling or utilization. It is estimated that the global red mud inventory was around 4 billion tonnes in 2020, and there is an additional 120-150 million tonnes of red mud waste accumulated annually.[1]

In response to the global pursuit of sustainable silicon and alumina production, the innovative SisAl process (https://www.sisal-pilot.eu) has been developed and patented [2–5], enabling the production of Si, Si-Al alloys, and alumina of various grades. In the SisAl process, secondary raw materials such as aluminum scrap and/or aluminum dross are employed as feedstock for the aluminothermic reduction to reduce the SiO_2 in CaO-SiO_2 slag. The resulting products include Si or Si-Al alloys as the metal phase with various purity grades, along with a CaO-Al_2O_3-(low) SiO_2 slag. The produced slag can be further treated through hydrometallurgical processes, namely, alkaline leaching, desilication, and precipitation to produce alumina of differing purity levels.

In the present study, an alumina-rich CaO-Al_2O_3 slag was obtained through the pilot-scale SisAl aluminothermic reduction process. The microstructure of the slag sample was initially investigated to identify its constituent phases. Subsequently, the leachability of the slag was assessed through alkaline leaching experiments. CaO powder was introduced to further enhance desilication from the sodium aluminate containing *pregnant leaching solution* (PLS), followed by a carbonation process to precipitate $Al(OH)_3$. Finally, the $Al(OH)_3$ was calcined to yield the final alumina $Al(OH)_3$ $Al(OH)_3$ product.

2. Experimental

The flow chart of hydrometallurgical and pyrometallurgical treatment conducted in this study is depicted in Figure 1. In this study, an alumina rich calcium aluminate slag was produced through a pilot-scale SisAl process test operated by Elkem in Kristiansand, Norway. The composition of obtained slag sample was analyzed using X-ray Fluorescence (XRF) analysis by Degerfors Laboratorium AB, Sweden, and is presented in Table 1.

Table 1. Chemical composition (in wt%) of calcium aluminate slag produced by the pilot-scale test.

Sample	CaO	Al_2O_3	SiO_2	Fe_2O_3	MgO	Na_2O
Initial slag	36.5	52.0	10.8	0.51	0.13	< 0.01

Prior to the hydrometallurgical treatment, the slag lumps were milled to powders (< 150 µm) using Retsch Vibratory Disc Mill RS200 with tungsten carbide units. 100 g slag sample was then weighted and introduced into a jacketed glass reactor for alkaline leaching with 1 L solution using 60 g/L Na_2CO_3, prepared from deionized water and reagent grade Na_2CO_3 (> 99.95 %, Sigma-Aldrich). The leaching temperature was kept at 90 °C rigorously maintained through a heat transfer system involving the circulation of silicon oil within the reactor jacket. The slurry was uniformly agitated at a rate of 400 rpm by employing a stainless-steel overhead stirrer equipped with a paddle impeller. This agitation speed ensured the homogeneity of the slurry throughout the experiment. To maintain a consistent volume within the reactor, a glass condenser equipped with a cooling system was attached at its apex. The leaching period was fixed at 90 minutes.

Once the leaching process was completed, the remaining slurry was cooled, and vacuum filtered using a büchner funnel. The resultant filter cake, referred to as grey mud, was subsequently placed in a drying oven and kept at 60 °C overnight.

Concurrently, following the leaching experiments, desilication experiments were performed with the addition of 6 g reagent grade CaO powder (99.9 % purity, Sigma-Aldrich) into the pregnant leaching solution. The same jacketed glass reactor was employed and the desilication conditions were set with identical experimental conditions as in the leaching process (ie a temperature of 90 °C and a stirring speed of 400 rpm for a duration of 90 minutes).

4. Conclusions

This preliminary investigation aimed at evaluating the feasibility of alumina production from an alumina-rich calcium aluminate slag produced from the pilot-scale SisAl process test. The obtained results demonstrate the feasibility of this innovative method for alumina production; however, additional research is needed to improve our understanding and further optimize the process which is also summarized below:

> (1) The precursor slag used for the leaching and further processing in this study was predominantly composed of krotite, with minor amounts of larnite present as well. The nearly complete leaching of the slag resulted in an appreciable aluminum extraction rate demonstrating good reactivity during the leaching step. However, further optimization of the leaching process remains necessary for the appropriate leaching conditions such as Na_2CO_3 concentration, leaching temperature, and leaching time for the slags produced from the pilot-scale experiments. The resultant by-product, known as grey mud, was primarily comprised of calcite.
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> (2) The desilication process used in this study resulted in the formation of a substantial amount of calcite, reflecting the process requires further optimization of both refining temperature and additive type and proportions.
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> (3) The precipitation of aluminum hydroxide could be achieved through a combination of carbonation and aging at room temperature. The precipitated $Al(OH)_3$ was predominantly in the form of bayerite with minor amounts of gibbsite. Further improvement of the carbonization control during the precipitation process is still essential to prevent the formation of dawsonite. Meanwhile, appropriate seeding addition and aging time control are also vital to facilitate the optimal precipitate formation with adequate particle size.
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> (4) The final calcination stage yielded the formation of alumina powders, however, further optimization such as heating rate, holding temperature, and holding time are still important to yield alumina suitable for smelting.

Overall, the preliminary results presented and conclusions derived from this research prove the feasibility of alumina production from the pilot-scale SisAl process, and offer important insights which will aid in the further optimization and refinement of the process.

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