Alumina Recovery from Sodium Aluminate Solutions via Carbonation

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https://doi.org/10.71659/icsoba2025-aa009

Abstract

This study explores the recovery of alumina from sodium aluminate, sodium carbonate, and sodium hydroxide solutions resulting from the leaching of calcium aluminate slags generated from pyrometallurgical reduction of various ores/by-products for metallic iron, silicon, and manganese extraction within several EU-funded projects. Such calcium aluminate slags are leached with sodium carbonate, generating a pregnant leaching solution. The entire process is evaluated starting from the carbonation of the pregnant leaching solution, where alumina hydrates (aluminium hydroxides) are precipitated by purging carbon dioxide gas into the solution. The alumina hydrates are calcined to produce alumina (aluminium oxide), which is used for its dissolution in cryolite.

The research aims to highlight the key characteristics of this process and the challenges involved in producing smelter-grade alumina. In addition, critical aspects of the process, such as the removal of sodium ions from the hydrated precipitate, are assessed. These are instrumental in attaining the purity and quality of the alumina hydrate. The findings demonstrate the viability of processing industrial by-products into useful products with reduced environmental impact. This study provides information on the efficiency of carbonation and facilitates the development of more sustainable alumina production from alternative raw materials.

Keywords: Alumina hydrates, Alumina, Carbonation precipitation, Calcination, Cryolite dissolution.

1. Introduction

Aluminothermic processes are emerging as promising alternatives to traditional carbothermic reduction methods [1]. Unlike carbothermic reduction, which relies on carbon-based reductants and results in significant CO_2 emissions, aluminothermic reduction employs aluminium, preferably sourced from scrap or dross, as a reductant. This approach can substantially lower the greenhouse gas emissions, particularly if the aluminium used can be recovered downstream.

Depending on the process, calcium aluminate (CA) slags are a by-product of aluminothermic reduction processes. They are generated when aluminium reacts with oxides like dicalcium silicate slag, iron oxide, or other metal oxides in the presence of a calcium source. CA slags can also be produced from bauxite residue smelting for iron recovery. The composition and structure of CA slags can vary, but they typically contain significant quantities of aluminium oxide and depending on their phase composition and cooling conditions, can serve as secondary alumina sources. Efficient utilization of CA slags is crucial to maximizing resource recovery, minimizing waste, and promoting a circular economy [2].

CA slags can be leached with a sodium carbonate (Na_2CO_3) solution to produce a pregnant leaching solution (PLS), rich in sodium aluminate and a solid residue predominantly composed of calcium carbonate. Although this solution is often supersaturated, its alumina concentration (15–70 g/L Al_2O_3) is lower than that typically found in Bayer liquors (85–165 g/L Al_2O_3) [3]. In the Bayer process, only a relatively small portion of alumina is recovered via cooling crystallization; the rest remains in the recycled liquor. In contrast, carbonation, through pH-driven precipitation, can achieve high alumina recoveries, enhancing process productivity. Furthermore, CO_2 addition regenerates the Na_2CO_3 solution, allowing it to be reused for fresh slag leaching. Leaching CA slags with Na_2CO_3 yields a complex alkaline PLS, primarily composed of sodium aluminate ($NaAl(OH)_4$), sodium carbonate, and sodium hydroxide. The simplified leaching reaction – similar to the liquor causticization – done in the Bayer process is shown in Equation 1, though it varies with the specific CA phases:

$$CaO \cdot Al_2O_{3(s)} + Na_2CO_{3(aq)} + H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + NaAlO_{2(aq)} + CaCO_3 \downarrow \qquad (1)$$

When the resulting PLS is carbonated, alumina hydrates precipitate according to Equations 2−5. These reactions highlight the dynamic interplay between dissolved carbon dioxide, hydroxide ions, and aluminate species, ultimately leading to the formation of solid alumina hydrates.

$$CO_{2(g)} \rightarrow CO_{2(aq)} \qquad (2)$$

$$CO_{2(aq)} + OH^-_{(aq)} \rightarrow HCO^-_{3(aq)} \qquad (3)$$

$$HCO^-_{3(aq)} + OH^-_{(aq)} \rightarrow CO^{2-}_{3(aq)} + H_2O_{(l)} \qquad (4)$$

$$Al(OH)^-_{4(aq)} \rightarrow AlOH_{3(s)} \downarrow + OH^-_{(aq)} \qquad (5)$$

While carbonation offers a promising method for alumina hydrate recovery, several challenges must be addressed. High Na_2CO_3 concentrations in the solution, arising from incomplete leaching, excessive reagent use, or excessive CO_2 addition, can lead to the formation of dawsonite ($NaAlCO_3(OH)_2$), a sodium aluminate carbonate hydroxide. Dawsonite co-precipitates with alumina hydrates when Na_2CO_3 exceeds a critical concentration, reducing the purity of the final product and causing significant sodium losses [4]. Another concern is silicon co-precipitation. Silicate ions in the leach solution can lead to the incorporation of silicon into the precipitated product. Additionally, sodium ions may adsorb onto the surface of alumina hydrates, especially when sodium concentrations are high, further complicating downstream purification.

This study investigates the recovery of alumina from CA slags, a by-product of pyrometallurgical processes, via a carbonation-based route. The goal is to produce smelter-grade alumina (SGA) with a reduced environmental footprint. Key aspects examined include CO_2 consumption based on flow rate, the impact of seeding on particle size enhancement, the removal of residual soda and the calcination behavior of the alumina hydrates from alternative resources, contributing to a more sustainable and circular economy. Finally, the dissolution of the calcined alumina in cryolite is evaluated to assess its suitability for use in aluminium production.

2. Materials and Methods

2.1 Calcium Aluminate Slags

The results of the dissolution test are presented in Figure 7. Calcined aluminas from different raw materials are presented. The tested samples showed lower reactivities compared to the SGA sample, however, this is still within acceptable limits. Concerning the alumina sample originating from calcium silicate slag, the initial probe response was a sharp rise and fall before steadily increasing. This initial response does not correspond to the amount of dissolved alumina, indicating that the probe was disturbed by the alumina addition.

4. Conclusions

This study highlights key process insights for alumina recovery from calcium aluminate slags via sodium carbonate leaching and carbonation. CO_2 consumption experiments showed that higher gas flowrate accelerates precipitation but reduces gas utilization efficiency, as unreacted CO_2 exits the system more rapidly. Seeding with gibbsite promoted both primary nucleation and secondary crystal growth. Prominently, seeding also directed the precipitating phase toward gibbsite, matching the seed material and enhancing phase selectivity.

Although the precipitated hydrates exhibited high Al_2O_2 content, their Na_2O levels exceeded SGA limits. Water washing effectively reduced Na_2O content to near industrial tolerance (0.6%), though not fully within standard SGA specifications. Calcination revealed typical phase transitions toward α-alumina at 1200 °C, with slower kinetics attributed to residual sodium impurities. Despite this, the final products demonstrated good dissolution behaviour in molten cryolite, comparable to standard SGA, confirming its potential as a viable alumina source pending further impurity control.

To sum up, if desilication is applied prior to carbonation and sodium removal becomes more effective, reducing the need for extensive water washing, there is a clear potential for scalable and sustainable alumina production from calcium aluminate slags, with promising applicability in the aluminium industry. The remaining consideration is whether differences in precipitate morphology could pose operational challenges, which warrants further investigation.

5. Acknowledgements

This work has been completed in the course of the European Union's Horizon 2020 research and innovation programs: ENSUREAL (GA No 767533), SiSal Pilot under (GA No 869268) and HAlMan (GA No 101091936).

6. References

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