

High-purity Alumina Production Prospect from Alternative Raw Materials

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Abstract

This study investigates a method for producing high-purity alumina (HPA) from non-conventional raw materials, namely bauxite. Various aluminosilicate raw materials, including bauxite tailings, aluminium silicate slags, nepheline-syenite, kaolin samples, and calcium aluminate slags, have been examined as alternative sources for alumina production. The leaching efficiency of these alternative raw materials using hydrochloric acid (HCl) was assessed based on aluminium recovery and the filtration properties of the residues. The precipitation of aluminium chloride hexahydrate (ACH), as a precursor for HPA, was studied in the pregnant leach solutions (PLS) generated from calcium aluminate slag leaching with HCl. During this process, HCl gas is used to precipitate ACH by the salting out phenomenon, and this step must be repeated several times to achieve the desired alumina purity. The study focuses on optimising aluminium recovery while minimising HCl gas consumption during the ACH precipitation process. After precipitation, ACH is calcined to produce HPA, with its purity verified. The results indicate that processing alternative raw materials using the described technologies can provide a sustainable and flexible approach for manufacturing HPA in an environmentally and resource-efficient manner.

Keywords: High-purity Alumina, Alternative Raw Materials, HCl Process.

1. Introduction

High-Purity Alumina (HPA) serves as an essential material in various high-tech applications, including light-emitting diodes (LEDs), lithium-ion batteries, and scratch-resistant glasses [1]. Traditionally, HPA production has primarily relied on bauxite, or bauxite derivatives, as the primary raw material [2]. However, this dependency presents several challenges:

- **Resource Depletion:** The limited availability of high-quality bauxite reserves raises concerns about long-term supply sustainability.
- **Environmental Impact:** Bauxite mining and the subsequent Bayer process significantly contribute to environmental issues, including deforestation, habitat destruction, and the generation of red mud waste.
- **Geopolitical Constraints:** The concentration of bauxite reserves in specific regions can lead to supply chain vulnerabilities and market monopolies [3].

In light of these challenges, there is an increasing interest in exploring alternative, non-bauxite raw materials for HPA production along with the utilization of Bayer by-products [4, 5]. Materials such as bauxite tailings, aluminium silicate slags, nepheline-syenite, kaolin, and calcium aluminate slags are potential options. These alternatives offer abundant and underutilised sources

of aluminium and align with the principles of waste valorisation and circular economy by transforming industrial by-products into valuable resources.

The extraction of aluminium from these alternative feedstocks requires a departure from the conventional Bayer process. Given the complex mineralogy of aluminosilicate materials, an acid leaching approach, particularly using hydrochloric acid (HCl), is more effective. The acid route facilitates the dissolution of aluminium-bearing phases, enabling efficient recovery while avoiding silicon dissolution. Moreover, the subsequent precipitation of aluminium chloride hexahydrate (ACH) from the pregnant leach solution (PLS) serves as a precursor to HPA, providing a streamlined production pathway [6, 7].

This study investigates the feasibility of producing high-purity alumina (HPA) from alternative raw materials using the aluminium chloride hexahydrate (ACH) process. As a core focus, HPA production from calcium aluminate (CA) slag is experimentally demonstrated. In parallel, the potential of alternative raw materials is evaluated, with their suitability for HPA production discussed based on the findings from CA slag processing. This investigation aims to provide a sustainable and flexible pathway that reduces reliance on bauxite and addresses both environmental and geopolitical challenges.

2. Materials and Methods

This section presents materials characterisation, along with the procedures and analytical techniques used.

Elemental chemical analysis of the produced aqueous solutions was conducted using a PerkinElmer Optima 800 Optical Emission Spectrometer.

X-ray diffraction (XRD) analysis was conducted using a Miniflex 600 Rigaku diffractometer with Cu-K α radiation (40 kV, 15 mA). Phase identification was performed with Bruker™ Diffrac EVA software, utilising the ICDD™ Diffraction databases PDF-4+ 2023 and PDF-4 Minerals 2023 [8].

Wet chemical analysis techniques were used to determine the chemical composition of the precipitates and calcined alumina samples. In more detail, calcined samples were fused with a mixture of Li₂B₄O₇/LiBO₂ and then dissolved into an HNO₃ solution. Precipitate samples, as hydrated salts were directly dissolved in H₂O. For the analysis of the liquid phases, the PerkinElmer Optima 8000 ICP-OES was used, along with a BWB XP Flame Photometer.

The calcium aluminate slag used was the product of the aluminothermic reduction of a calcium silicate slag with aluminium dross (containing 72 %wt. Al) in a graphite crucible at 1650 °C for 1h. Its chemical analysis is presented in Table 1.

Table 1. Chemical analysis of the slag used in this research work.

Al ₂ O ₃	SiO ₂	CaO	MgO	Na ₂ O	Fe ₂ O ₃	Total
51.2 % ± 1.2 %	9.0 % ± 0.7 %	40.0 % ± 2.2 %	0.3 % ± 0.2 %	0.2 % ± 0.1 %	0.1 % 0.2 ± 0.01 %	101.1 % ± 1.6 %

The analysis and dissolution of calcium aluminate slag has been thoroughly investigated in prior research [9, 10], and a summary is given in Table 2. Consequently, this study focuses on the detailed analysis and discussion of the subsequent precipitation and calcination processes applied to the optimal solution derived from the leaching campaign.

Table 2. Aluminium dissolution and major impurity concentrations from different alternative raw materials.

Raw Material	Kaolin	Nepheline Syenite	Bauxite Tailings	SiO ₂ Slag	CA Slag
Al concentration (g/L)	21.7	5.66	36.8	28.16	40.7
Dissolution degree (%)	56.30	62.16	92.88	96	91.9
Major impurities (g/L)					
Si	0.03044	0.0776	0.0769	0.04	0.35
Fe	0.465		25.2	10.36	0.07
Ti	0.077		0.0804		
K	1.02	0.79			
Na	0.622	4.02			0.005
Ca				21.78	42.6

2.1 ACH Precipitation

For the HCl(g) sparging crystallisation experiments, a glass reactor was utilised, equipped with a PTFE lid featuring openings for gas inlet and outlet. A constant flow of pure HCl(g) was maintained using a gas mass flow controller. To calculate the theoretical amount of HCl(g) needed to reach the saturation point, the free HCl content of the PLS was measured with a standard NaOH solution in an auto-titrator. The conditions applied are presented in Table 3, while the starting solution concentration is depicted in Table 2.

Table 3. Conditions for HCl sparging.

HCl(g) flow (mL/min)	Stirring Rate (rpm)	Temperature (°C)	Reached HCl concentration(M)
600	300	20	10

ACH was filtered from the acid solution and washed with puriss acetone at room temperature. It was then redissolved in deionised water at a 1:1.8 w/w ACH/water ratio, which was then used for the subsequent HCl gas sparging step.

2.2 Calcination to Al₂O₃

A two-step calcination process was implemented. Initially, a low-temperature step was conducted to transform ACH into amorphous transition alumina, as depicted in Figure 1, by selectively removing HCl(g). Subsequently, under high-temperature conditions, crystalline α -Al₂O₃ is formed, as depicted in Figure 2.

The experimental conditions and setup utilised are detailed in Table 4. Previously published work marked the used conditions as the optimum [9].

Table 4. Applied conditions in calcination steps.

Calcination Step	Retention Time (h)	Temperature (°C)	Amount (g)/Material	Set Up
1 st	1	400	30 /ACH	tube furnace with N ₂ gas constant flow
2 nd	1	1200	~6.3/Al ₂ O ₃	muffle furnace, under open-air conditions

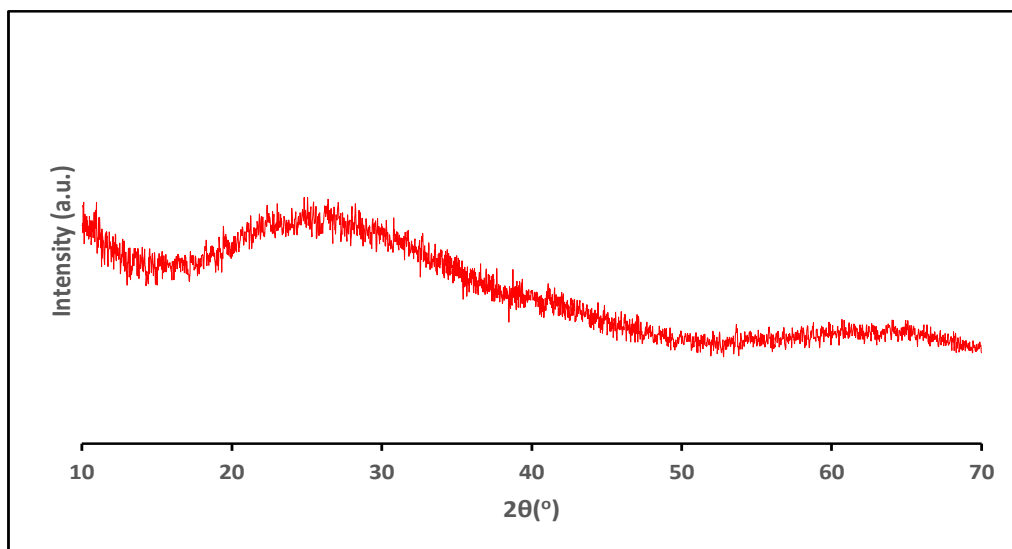


Figure 1. XRD pattern of the calcined ACH from the 1st calcination step.

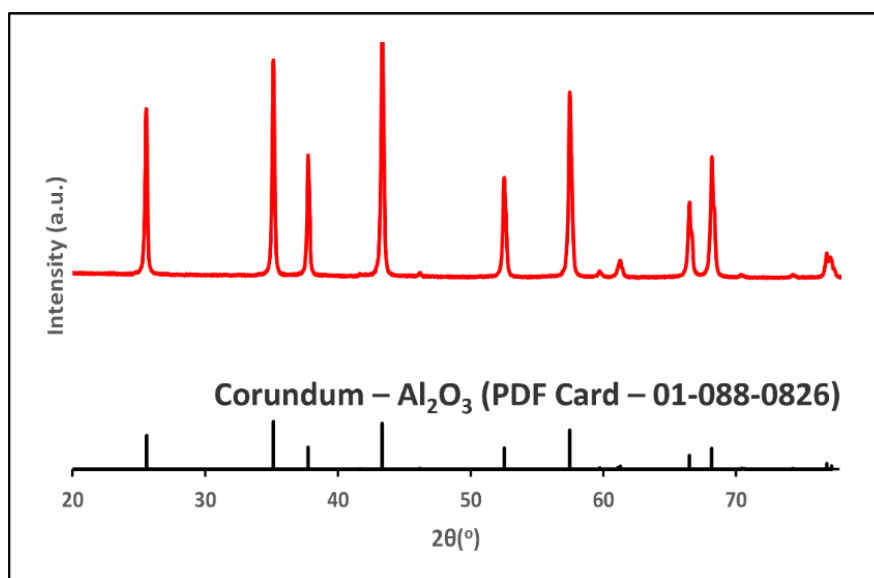


Figure 2. XRD pattern of the calcined ACH from the 2nd calcination step.

3. Results and Discussion

3.1 HPA Production from a Calcium Aluminate-slag Solution

Figure 3 illustrates the precipitation behaviour of key elements – Al, Na, Ca, Si, Mg, and Fe – from the pregnant solution as a function of the free-HCl concentration in the solution. The left y-axis shows the precipitation degree for Al and Na, while the right y-axis tracks the precipitation of Ca, Si, Mg, and Fe.

At free-HCl concentrations up to 3 M (mol/L), sodium precipitates sharply, achieving over 65 % removal, while aluminium remains predominantly in solution, while the rest of the metals are almost entirely left in solution. Under these conditions, sodium can be selectively removed from the solution with minimal loss of aluminium. By increasing the free-HCl concentration beyond 5M, aluminium begins to precipitate significantly, whereas the other metals exhibit very low precipitation rates, less than 5 %. Based on these results, a two-stage precipitation process is

proposed: The first stage involves maintaining free-HCl concentration until 3 M to remove more than 60 % of sodium, along with 17 % of aluminium; the second stage increases free-HCl concentration to 8 M where aluminium massively precipitates as ACH, contaminated by minor amounts of other metals, primarily iron. This two-stage process achieves the lowest possible contamination levels in the produced ACH while maintaining high aluminium recovery calculated as the percentage recovered mass of Al from the PLS, ensuring optimal purity (99.982 %) and yield (82 %) in the final product, as illustrated in Figure 4.

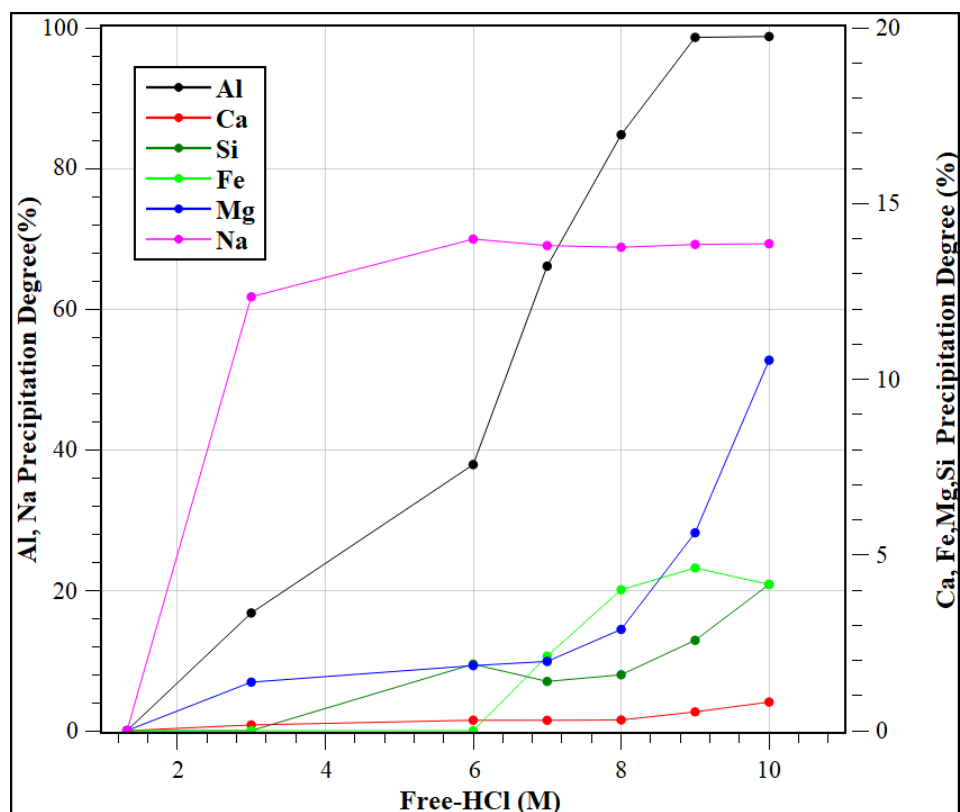


Figure 3. Precipitation behaviour of major elements as a function of free-HCl concentration.

The purity threshold for high-purity alumina (HPA) applications, such as sapphire substrates, light-emitting diode (LED) production, lithium-ion battery separators, and advanced technical ceramics, is established at 99.99 % (4N), as indicated by the dashed red line in Figure 4. To achieve this standard, an HPA purification step is necessary. The HPA produced from the two-stage process undergoes redissolution in deionised water, followed by an HCl(g) sparging step until an 8M free-HCl concentration is reached in the solution. The resulting purified HPA achieves a purity of 99.994 %, surpassing the 4N threshold, as shown in Figure 2; however, this comes at the expense of aluminium recovery, which decreases to 70 %.

The results highlight that the HPA production process must be carefully designed by balancing two competing factors: HPA purity and aluminium recovery, depending on the end-user requirements for the HPA product.

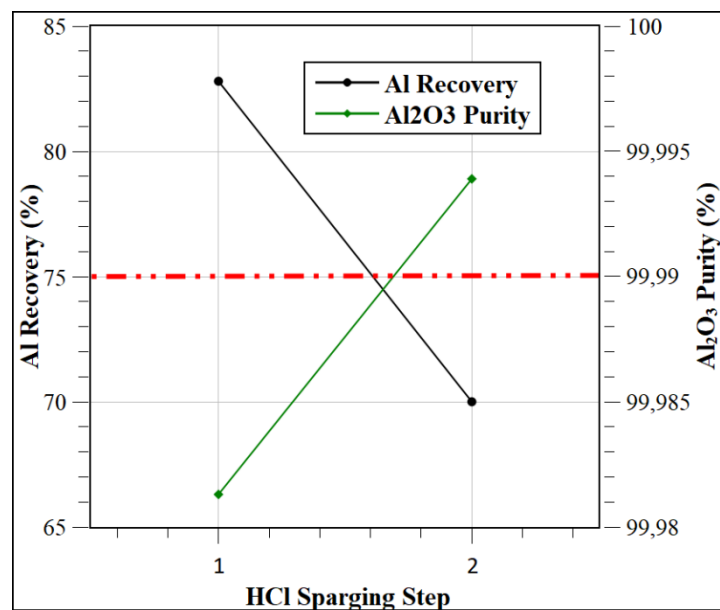


Figure 4. Effect of HCl sparging steps on Al recovery and Al₂O₃ purity.

The process outlined above distinguishes itself from previously documented methods by prioritising reduced hydrochloric acid (HCl) consumption, even if this results in a decrease in aluminium recovery. Earlier studies [11, 12] utilised multiple HCl sparging steps to maximise aluminium recovery, achieving rates above 90 %. However, these methods considerably increased HCl(g) usage, energy demand, and process complexity. Conversely, minimising the number of sparging steps reduces reagent costs and environmental impact, while accepting a modest reduction in aluminium recovery as a compromise. This approach enhances the sustainability of the process and improves its potential economic viability, given that the cost of the initial raw material is much smaller than the price of the final HPA product. The sodium-rich precipitate in the first stage can also be calcined and used as feedstock in the Bayer process. Based on chemical analysis, it meets low ACH purity (94.36 %) with Ca (0.8 %) and Na (0.0466 %) being the major contaminants.

3.2 Feasibility of HPA Production from Other Alternative Raw Materials

Calcium Aluminate (CA) slag has been identified as a viable raw material for HPA production. Such slags can be derived from various processes, including (i) bauxite residue (BR) reductive smelting for iron recovery, as examined in the REMOVAL Project [13], (ii) aluminothermic reduction of calcium silicate slags to produce silicon, assessed in the SISAL Project [14], and (iii) aluminothermic reduction of manganese ore to produce manganese, analysed in the HALMAN Project [15]. Additionally, alternative aluminosilicate materials such as kaolin, nepheline-syenite, and bauxite tailings (solid waste produced during the mining and beneficiation processes of certain bauxite sources) were investigated in the ALSICAL Project [16] as raw materials for alumina production via a hydrometallurgical HCl route. Furthermore, SiO₂-rich slags produced through the reductive smelting of bauxite residue with SiO₂ as a flux were studied in REMOVAL and ALSICAL projects as potential raw materials for alumina production through an HCl route.

The leaching behaviour of some of these materials has been thoroughly researched in previous publications [17–19]. All materials were leached with an azeotropic HCl solution (5.9M), at 90°C under different raw material/leaching agent ratios and retention times, depending on the specific properties of each material. A summary of the aluminium dissolution degree as well as the composition of the PLS achieved under optimal conditions is presented in Table 2. The PLS from

the leaching of CA slag used in the experimental work detailed in section 3.1 is also shown for comparison.

CA slag (containing approximately 51 % Al_2O_3) demonstrated a high aluminium dissolution rate of 91.9 % and the highest Al concentration in the PLS at 40.7 g/L, making it a highly productive source. Among the alternatives, bauxite tailings (containing about 38.9 % Al_2O_3) and SiO_2 slag (containing about 25 % Al_2O_3) showed notable Al concentrations of 36.8 and 28.16 g/L, respectively, and higher dissolution rates than CA slags (> 92 %), indicating potential productivity. Kaolin and nepheline-syenite exhibited significantly lower Al dissolution degrees and consequently lower Al concentrations, suggesting limited output without further optimisation. Pretreatment of materials might enhance their dissolution behaviour and ultimately result in high Al-bearing PLS. Preliminary trials on the mechanical activation of kaolin showed promising results [20].

The analysis of experimental trials on CA slag has yielded significant insights into effective purification strategies that could be applicable to other alternative raw materials. In the CA slag process, high calcium concentrations (42.6 g/L) were successfully managed through controlled precipitation. This technique could similarly address the high calcium content in SiO_2 slag solutions. Moreover, silicon, present at relatively low concentrations across all materials (0.03–0.35 g/L), did not interfere with downstream processing. Iron, which appears at elevated levels in bauxite tailings (25.2 g/L) and SiO_2 slag (10.36 g/L) and therefore holds high potential to contaminate high purity alumina (HPA), was effectively removed from the HPA produced from the CA slag pregnant leach solution (PLS) using acetone washing [9] – a method that could be adapted for these materials. Additionally, the high sodium and potassium contents found in the PLS originating from kaolin and nepheline-syenite could be addressed by employing the selective precipitation stage developed for CA slag, wherein a treatment until 3 M free-HCl enabled early-stage sodium removal. These findings underpin a theoretical framework for impurity management in alternative feedstocks, demonstrating that techniques proven effective in CA slag treatment may be transferable with appropriate modifications.

4. Conclusion

This study showed that high-purity alumina (HPA) can be produced from calcium aluminate slag using a process that reduces HCl consumption while achieving 4N purity with aluminium recovery. Compared to methods with multiple HCl sparging steps, this approach provides a more sustainable and resource-efficient pathway.

Future research should aim to experimentally apply these techniques to other alternative raw materials, such as bauxite tailings, SiO_2 slag, nepheline-syenite, and kaolin. It will be crucial to adjust processes according to their specific impurity profiles and solubility behaviours. Furthermore, scaling up the proposed process and assessing its economic and environmental performance will be vital for promoting its industrial application.

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