AA02 - 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 °C 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).

Upon completion of the desilication experiment, the slurry was filtered using the previously described procedure. The resultant white desilication residue was dried overnight. The purified solution derived from the desilication was then used in the carbonation precipitation experiment.

In the precipitation step, high-purity CO_2 was introduced at a gas flow rate of 0.5 slpm. After approximately half an hour, the CO_2 gas purging was halted upon the appearance of a white aluminum hydroxide precipitate. Subsequently, a 24-hour aging process was started prior to separating the precipitates from the solution (as per the aforementioned filtration procedure).

The $Al(OH)_3$ precipitate obtained after filtration was placed in a drying overnight 60 °C overnight. The dried white powders were transferred to an Alsint alumina crucible (160×40×21 mm). Subsequently, the crucible was placed in a preheated Nabertherm N17/HR muffle furnace at 100 °C to initiate the calcination process. The calcination conditions were set at a constant holding temperature of 1000 °C for one hour with a heating rate of 10 °C/min. Afterwards, it was cooled down to room temperature at a rate of 5 °C/min, yielding in a final product of white alumina powder.

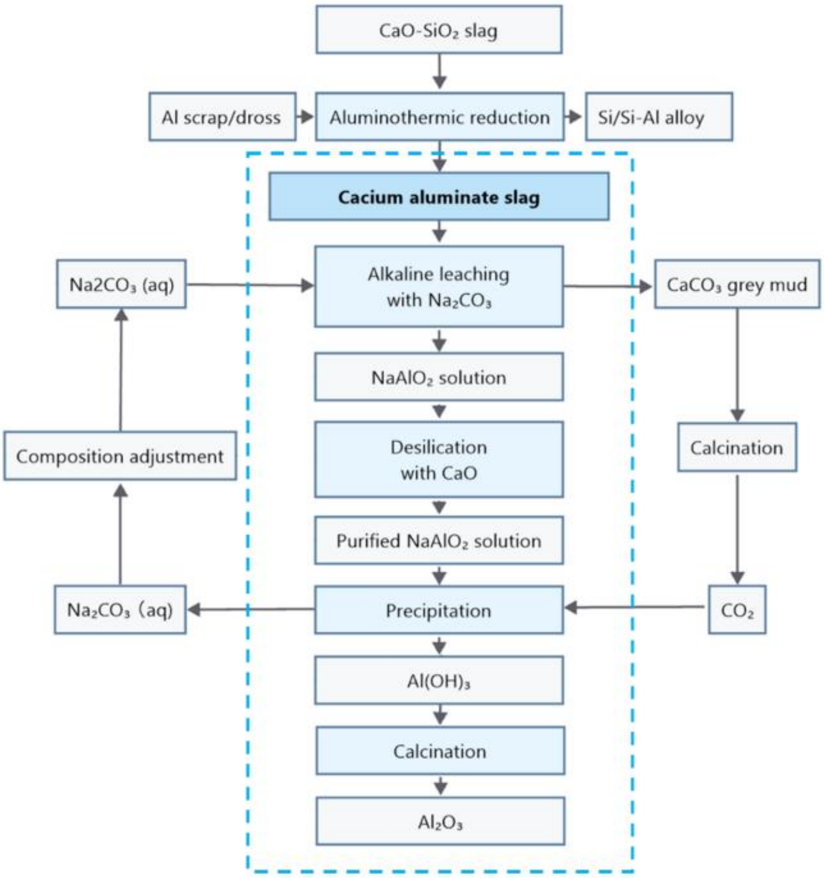

Figure 1. Flow chart of the SisAl process with alkaline leaching for alumina production, and with the procedures of the present work in the indicated dashed area.

All the solid products including the raw slags, grey mud, desilication residue, aluminium hydroxide, and alumina powers, were characterized by Bruker D8 A25 DaVinci™ X-ray Diffraction (XRD) machine with CuKα radiation (wavelength of 1.54 Å). The X-ray diffraction test was performed from 5 to 90° diffraction angle and using a step size of 0.013°. The subsequent qualitative analysis of the obtained XRD peaks were done by using DIFFRAC.EVA v.6 software. In addition, a Zeiss Supra 55-VP scanning electron microscope (SEM) was used for the microstructural characterization of the obtained powders. The elemental concentration in the corresponding liquor was measured by Agilent 8800 triple quadrupole high resolution inductively coupled plasma mass spectroscopy (ICP-MS).

3. Results and Discussions

3.1 Slag Leaching

Figure 2 illustrates the microstructure of the slag subjected to the hydrometallurgical treatment. It reveals a composition of two distinct phases: a matrix phase with a lower SiO_2 content and a phase presenting a porous structure with a higher SiO_2 content. Further XRD analysis (Figure 2 c) indicates that most of the SiO_2 in the slag precipitates out in the form of larnite (Ca_2SiO_4), while the primary mineral phase is krotite ($CaAl_2O_4$), which is suitable for alkaline leaching [6].

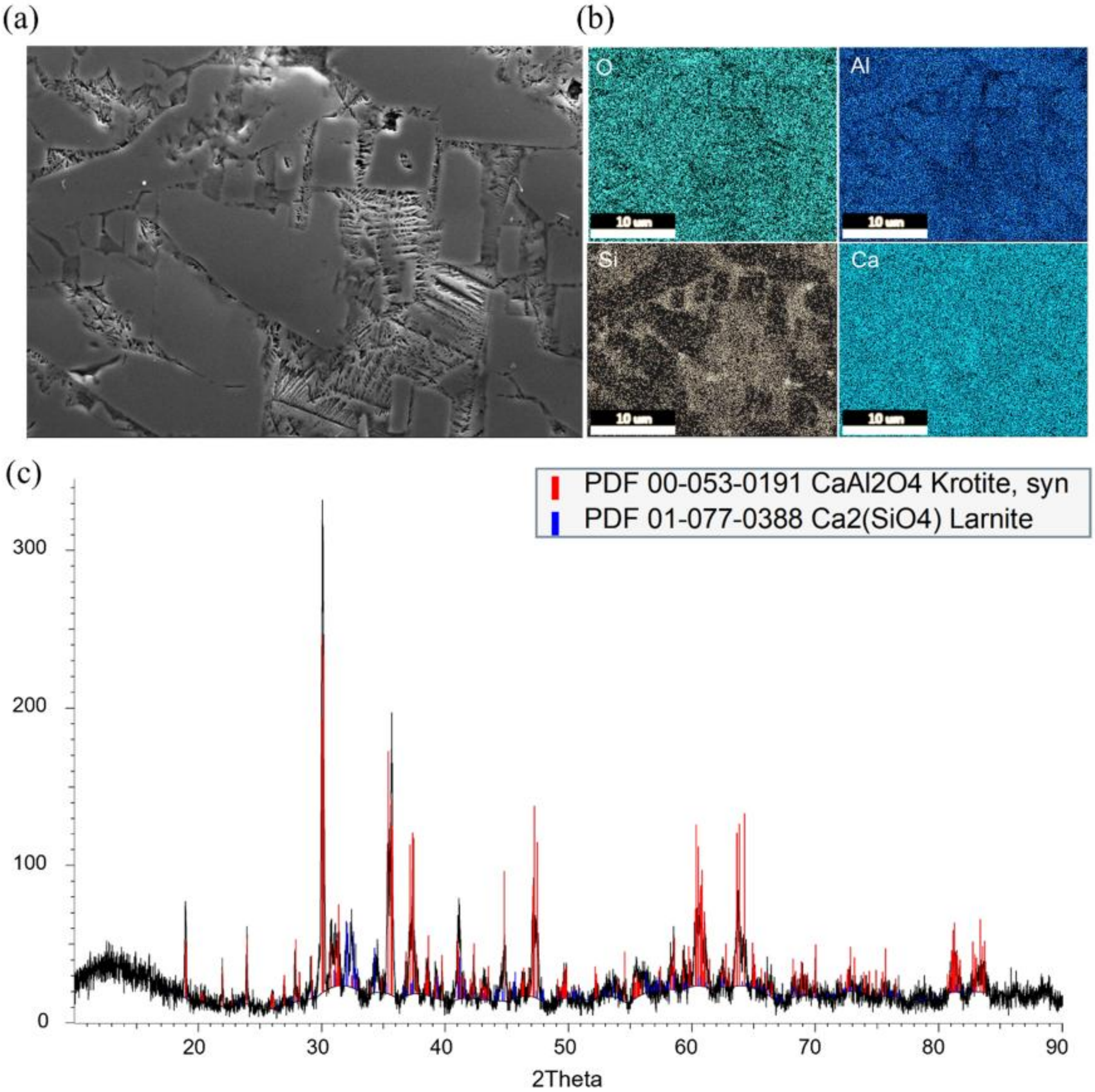

Figure 2. Characterization of the initial slag before leaching a) Backscattered electron image; (b) EDS elemental mapping results of the studied slag; (c) XRD results of the milled slag.

During the alkaline leaching process, the calcium aluminate in the slag readily dissolved into the sodium carbonate solution as per Equation (1), generating a $NaAlO_2$ solution and a calcium carbonate by-product, known as grey mud. In the SisAl process, the calcined grey mud can be recycled and reused as a calcium source for CaO-SiO_2 slagging raw materials, while the CO_2 produced can be utilized in the subsequent precipitation stage.

$$\mathrm{CaAl_2O_4}_{(s)} + \mathrm{Na_2CO_3}_{(aq)} \rightarrow 2\mathrm{NaAlO_2}_{(aq)} + \mathrm{CaCO_3}_{(s)} \tag{1}$$

To further assess the leachability of the slag, the concentration of Al and Si in the PLS and the extraction rates calculated using Equation (2), are demonstrated in Table 2. It can be noted that the corresponding Al and Si concentrations are respectively, 18.31 g/L and 0.35 g/L, reflecting an Al recovery of 66.5 %, while 6.85 % of Si is extracted into the $NaAlO_2$ liquor. Nearly all Ca was transformed into the grey mud in the form of calcium carbonate. As depicted in Figure 3 and Figure 4, further XRD analysis and SEM characterization of the grey mud reveal that most of the $CaCO_3$ is present as calcite, accompanied by a minor portion of vaterite. It is also seen that a substantial cubic calcite is adhered to the slag particles possibly forming a passivation layer, which in turn may limit the leaching progress.

$$\text{Al recovery (\%)} = \frac{\text{mass of Al in leachate}}{\text{mass of Al in slag}} \times 100\% \tag{2}$$

Table 2. Concentration of leachate and corresponding extraction rate of Al, Si, and Ca from slag.

	Al	Si	Ca
Concentration in leachate (g/l)	18.31	0.35	0.005
Extraction rate (%)	66.50	6.85	0.02

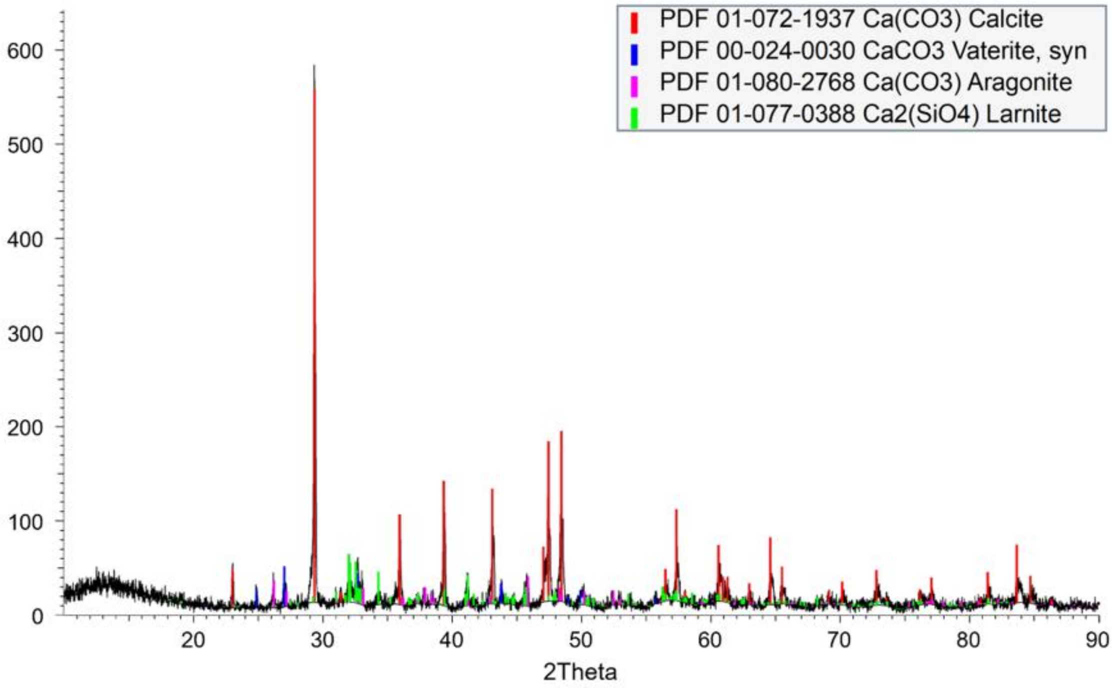

Figure 3. Grey mud characterization results by XRD.

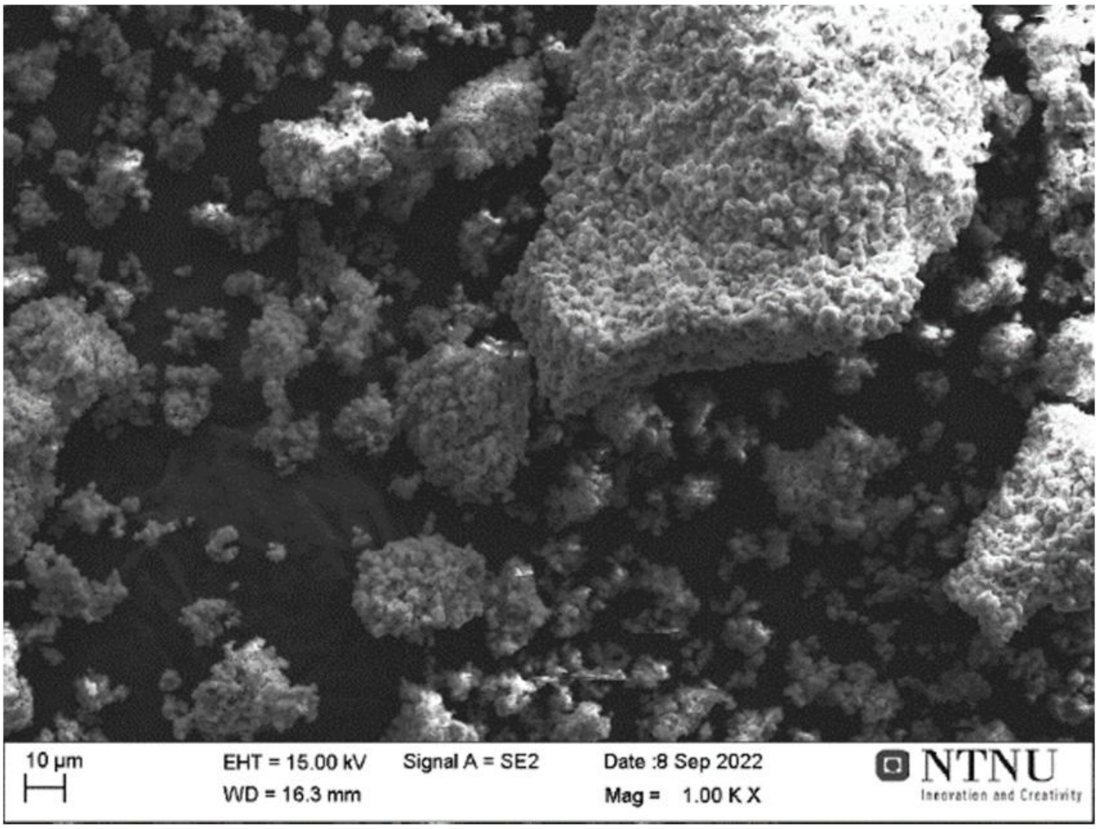

Figure 4. Grey mud characterization results by SEM.

3.2 Desilication

As a preliminary study, the common method of adding CaO was employed for desilication, with the amount of CaO added referencing prior research [7]. However, the XRD results shown in Figure 5, showing the composition of the desilication residue, indicate that most of the added CaO has reacted with the residual carbonate in the liquor forming calcite as the primary mineral phase in the desilication residue. Despite this, as listed in Table 3, it is worth noting that 42.39 % of Si was still removed, but this was accompanied by the co-removal of 22.62 % of Al.

According to the investigation of Mwase et al. [7], a possible Si removal mechanism has been proposed, as follows (equation 3):

$$\begin{gathered} 3\mathrm{Ca}^{2+} + 2\mathrm{AlO}_2^- + (3-\mathrm{x})\mathrm{H}_7\mathrm{SiO}_6^- + (\mathrm{x}+1)\mathrm{OH}^- \rightarrow \\ \mathrm{Ca}_3\mathrm{Al}_2(\mathrm{SiO}_4)_{3-\mathrm{x}}(\mathrm{OH})_{4\mathrm{x}} + (11-5\mathrm{x})\mathrm{H}_2\mathrm{O} \end{gathered} \tag{3}$$

Additionally, ’t's worth noting that the excessive amount of Na_2CO_3 in the solution could further restrict Si removal. This may be attributed to the following two reasons. First, the reaction of excess Na_2CO_3 with CaO could lead to an increase in the pH of the solution due to reaction (4), subsequently raising the solubility of SiO_2. Second, the presence of Na_2CO_3 could also facilitate the decomposition of the desilication products resulting in the re-dissolution of the Si according to reaction (5).

$$\mathrm{CaO}_{(s)} + \mathrm{Na}_2\mathrm{CO}_{3(aq)} + \mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{NaOH}_{(aq)} + \mathrm{CaCO}_{3(s)} \tag{4}$$

$$Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x(s)} + 3Na_2CO_{3(aq)} + (6-4x)H_2O \rightarrow 3CaCO_{3(s)} + 2NaAl(OH)_{4(aq)} + (3-x)Na_2(H_2SiO_4)_{(aq)} + (2x-2)NaOH_{(aq)} \quad (5)$$

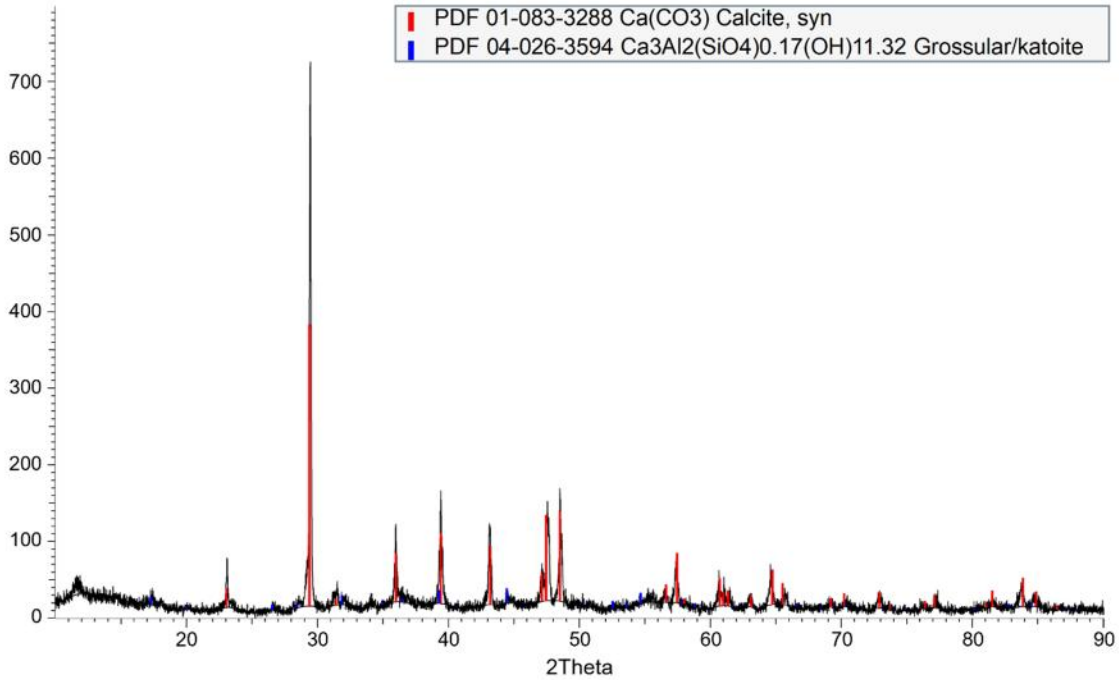

Figure 5. XRD results of obtained desilication residue.

Table 3. Concentration of desilication liquor and corresponding removal degree of Al and Si.

	Al (g/L)	**Si (g/L)**	**Solution volume (mL)**
Before	18.63	0.35	910
After	16.96	0.24	850
Removal degree (%)	22.62	42.39	-

3.3 Precipitation

The carbonation process is considered a complex heterogeneous process where gas, liquid, and solid phases are present [8]. According to equation (6), the hydrolysis of the sodium aluminate starts in the solution. With the sparging of CO_2 gas into the solution, the absorption and dissolution of CO_2 gas results in a decrease of the pH of the solution (equation (7)). Since the solubility of Al tri-hydroxide is reduced with decreasing pH, the precipitation reaction, as indicated in equation (8), is promoted.

$$NaAlO_{2(aq)} + 2H_2O_{(l)} = Na^+{}_{(aq)} + Al(OH)^-_{4\,(aq)} \quad (6)$$

$$CO_{2(g)} + H_2O_{(l)} \leftrightarrow CO^{2-}_{3\,(aq)} + 2H^+_{(aq)} \quad (7)$$

$$Al(OH)^-_{4\,(aq)} \leftrightarrow Al(OH)_{3(s)} + OH^-_{(aq)} \quad (8)$$

The overall reaction can be described as per the below (equation 9). The precipitated aluminum hydroxide can be observed as a white powder.

$$2NaAlO_{2(aq)} + CO_{2(g)} + 3H_2O_{(l)} \rightarrow 2Al(OH)_{3(s)} + Na_2CO_{3(aq)} \tag{9}$$

The key precipitation results are presented in Table 4 and Figure 6. It can be seen that after aging for one day at room temperature, 73.49 % of the Al was precipitated, accompanied by 72.67 % of Si as co-precipitate. According to the XRD results depicted in Figure 6, the resulting aluminium hydroxide is primarily in the form of bayerite with gibbsite as a minor constituent.

Table 4. Concentration of liquor before and after precipitation process and corresponding precipitation rate of Al and Si.

	Al (g/L)	**Si (g/L)**
Start	16.96	0.24
End	4.50	0.07
Precipitation rate (%)	73.49	72.67

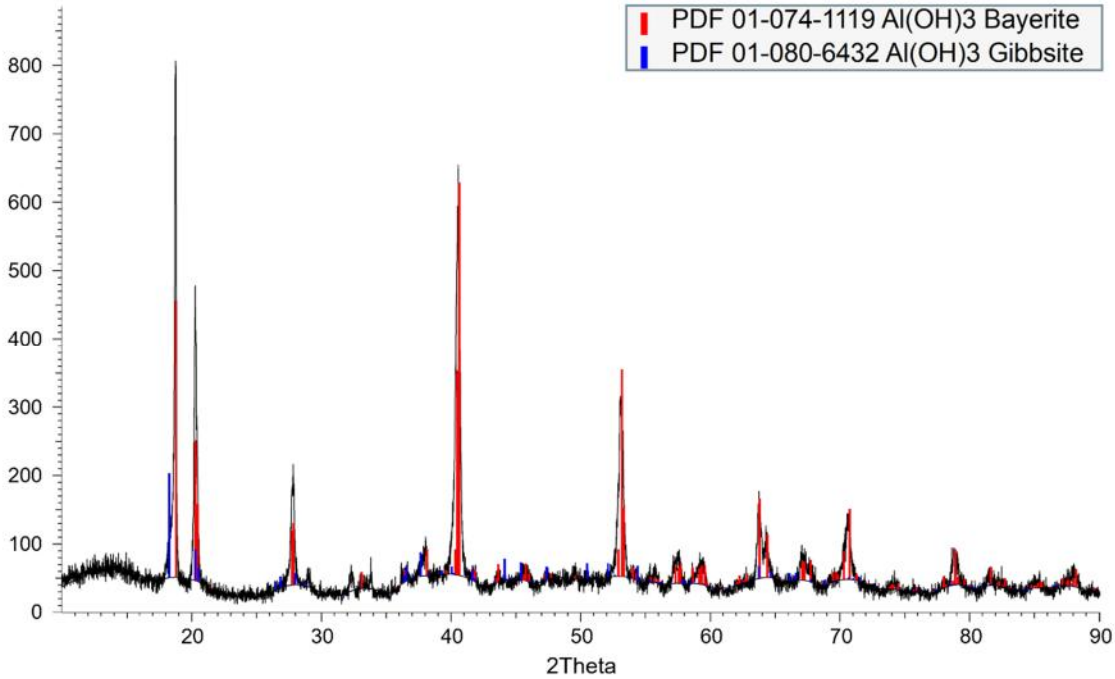

Figure 6. XRD results of the precipitated aluminium hydroxide.

3.4 Calcination

The composition of alumina obtained after calcination is presented in Table 5. It shows Al_2O_3 content of 90.5 %, along with 8.26 % Na_2O. This may indicate the possible presence of dawsonite, a byproduct resulting from excessive carbonization [8]. However, as presented in Figure 7, further XRD analysis indicates that the alumina produced in this experiment is in the form of η-Al_2O_3 accompanied with other amorphous products. In addition, as shown in Figure 8, despite the noticeable presence of large alumina particles can be seen, the overall particle size distribution still features a substantial quantity of fine powders. Thus, although this work aimed at investigating the feasibility of alumina production from the SisAl process, the results indicate that the precipitation and calcination processes require further optimization to fully meet the specifications for smelter-grade alumina.

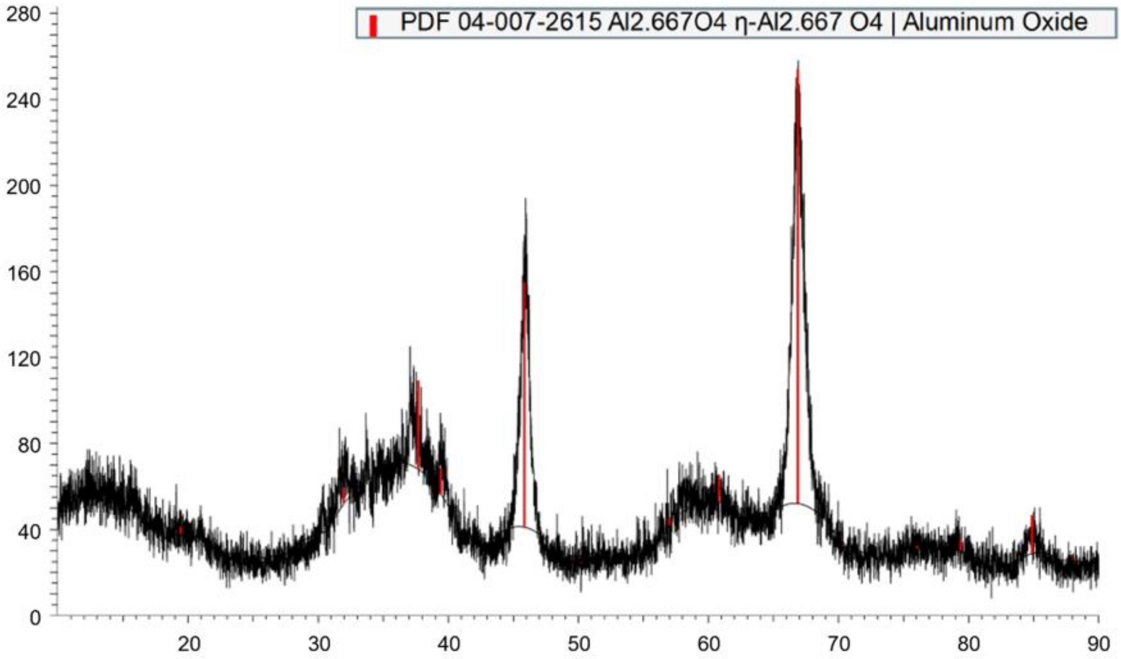

Figure 7. XRD results of obtained alumina powder.

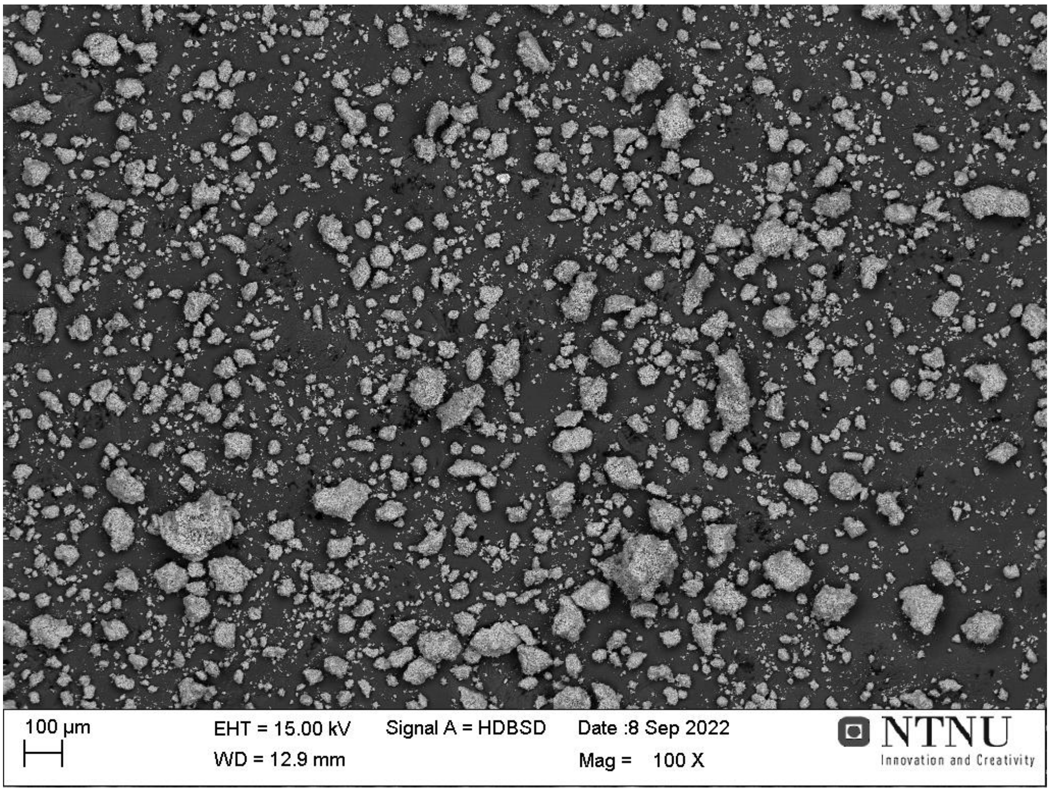

Figure 8. Obtained alumina powder morphology characterized by SEM.

Table 5. Chemical composition (in wt%) of obtained alumina measured by XRF.

Sample	CaO	Al_2O_3	SiO_2	Fe_2O_3	MgO	Na_2O
Alumina	0.05	90.5	1.14	-	-	8.26

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.

(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.

(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.

(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.

5. Acknowledgements

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