

# Alkaline alumina recovery from bauxite residue slags

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## Abstract

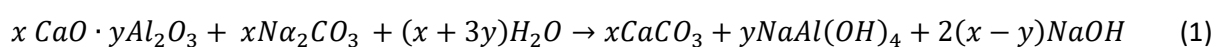
A calcium aluminate (CA) slag of modelled composition, originating from the reductive smelting of Greek bauxite residue (BR) from the Aluminium of Greece facility, was hydrometallurgically treated with a Na<sub>2</sub>CO<sub>3</sub> solution, with a 5% S/L ratio, for Al extraction. 60-minute leaching tests were performed at atmospheric pressure and a temperature range of 25 to 90 °C, with and without the addition of 10% NaOH. Driven by earlier research, a series of 5-minute leaching tests were also performed at the optimum temperature to highlight aspects of the leaching mechanism. More than 75% of the total Al extracted is dissolved in this time but total wt% extraction from the slag ranges between 35%-41%, with the maximum achieved at 90 °C. The coating of particles with CaCO<sub>3</sub> was confirmed as the main inhibitor of Al extraction. Addition of NaOH had minimal effect in Al extraction but enhanced Si extraction.

## Introduction

Europe remains a major importer of Al and EU28 countries import approximately 50% of their aluminium ingot requirements. At the same time primary Al production in Europe (EU28 & EFTA) has remained flat for almost a decade<sup>1</sup>. Moreover, the operating alumina refineries, along with many legacy sites, are filled with the accumulated tailings of decades long production of alumina by the Bayer Process, the so-called Bauxite Residue (BR). The socioeconomic and environmental consequences of BR are a growing concern among the industry players, states of alumina producing countries and the greater public. This has led to a wide range of research activity for the re-use of BR in different sectors, one of which is the metallurgical industry. Due to the high content of Fe in BR, there is focus on the treatment of BR to recover Fe, with or without the subsequent extraction of Al. The challenges of such processes have been reviewed recently by Klauber et al<sup>2</sup>.

Nonetheless, the possibility of economic extraction of Al from BR could prove of vital importance for the EU with its growing dependency on imports of this key commodity, as previously mentioned.

A collaboration between RWTH Aachen University and NTUA has actively engaged in the extraction of Fe and Al from BR. The aim of this work, as summarised by Tam Wai Yin et al.<sup>3</sup>, was a >95% recovery of Fe and the production of a calcium aluminate (CA) slag containing mostly the  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  phase. This phase, along with other calcium aluminates, is leachable in  $\text{Na}_2\text{CO}_3$  solutions<sup>4</sup> – a strategy employed by various alternative processes to produce alumina, such as the Pedersen Process<sup>5</sup> and the Lime-Sinter Process<sup>6</sup>. The overall chemical action is described by the generic reaction (1) shown below:



Al recovery from this type of slag reached 43% after atmospheric pressure leaching tests were performed in the temperature range of 40 - 90 °C and  $\text{Na}_2\text{CO}_3$  concentrations ranging from 50 to 300 g/L. The main inhibitor to the progression of leaching appears to be the build-up of an insoluble  $\text{CaCO}_3$  surface on the slag particles. This work was a continuation of earlier research by Kaußen and Friedrich<sup>7</sup>, who employed a Bayer-type leaching of slags from German BR. Employing pressure leaching with 200 g/L NaOH Al recoveries reached 50%. Increasing the NaOH concentration to 500 g/L and temperatures over 250 °C, around 90% of the Al was extracted, but the conditions were not suitable for industrial application. The Laboratory of Metallurgy in NTUA has continued working on this research area with slags originating from the reductive smelting of Greek bauxite ore. Several steps have been made to better understand the chemical processes taking place<sup>8,9</sup>. Highlights of this work include the confirmation of  $\text{CaCO}_3$  precipitation on the surface of particles and the non-efficient precipitation of alumina hydrates by carbonation, from a PLS with high  $\text{Na}_2\text{CO}_3$  concentration. The last observation poses a strict limit on the concentration of  $\text{Na}_2\text{CO}_3$  in the leaching stage.

Since the optimisation of pig iron production from Greek BR has been achieved, the goal of the ongoing research is to map the effect of different parameters in the hydrometallurgical treatment of the slag phase. Should the results prove to align with corresponding results obtained from CA slags originating from bauxite smelting, it will be a step forward towards deciphering the fundamental chemical principles that dictate the extraction of Al and Si from these materials. In this paper we present the initial results of Al and Si extraction from a CA slag of optimised composition, originating from the reductive smelting of Greek BR. The

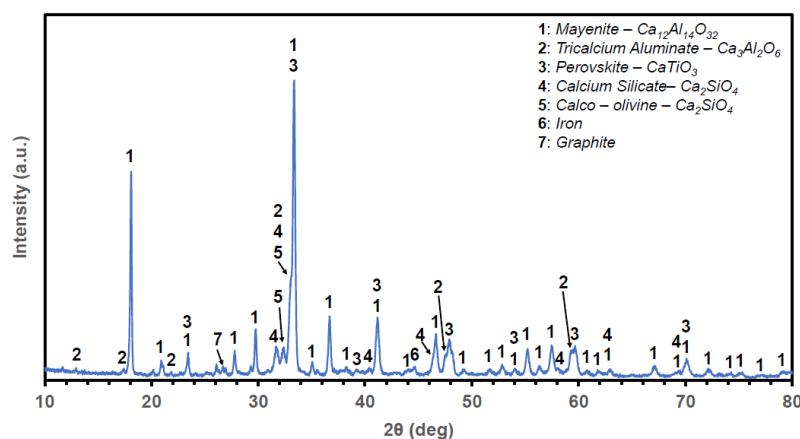
effects of temperature and NaOH addition to the Na<sub>2</sub>CO<sub>3</sub> leaching solution are presented.

## Materials and Methodology

BR received from the Aluminium of Greece was dried at 105 °C for 24 h to remove moisture and a batch of the dried sample was retrieved to be mixed with lime (commercial purity, 95% CaO) and lignite coke (containing 87 % C). The ratio of raw materials of the mixture was 1.5kg BR, 600 g lime (40% addition) and 150g coke (10% addition). The mixture was then fed into a 100 KVA DC electric arc furnace, operated at about 5 kW, and smelted batch wise in a graphite crucible at 1500-1550 °C for an hour. Upon completion, the melt was poured into a refractory mould to cool and solidify into distinct slag and metal phases. The slag and metal were separated and weighed. The slag was crushed and milled. All slag particles passed through the 250µm sieve. The chemical composition for the main oxides expressed in elemental form is shown in Table 1 and the X-ray diffractogram of the slag in Figure 1. The main phases are calcium aluminates, silicates and titanate.

**Table 1.** Elemental chemical analysis of calcium aluminate slag used in this study

| Element | Ca | Al | Si | Ti | Fe | Na | Mg  |
|---------|----|----|----|----|----|----|-----|
| wt%     | 35 | 16 | 5  | 3  | 1  | 2  | 0.5 |



**Figure 1.** Powder X-ray diffractogram of calcium aluminate slag used in this study.

For the leaching tests a Parr 4563 reactor was used, equipped with a 600 mL capacity vessel made from Inconel alloy, a heating mantle, and a Teflon custom-made lid. The lid is designed with openings and sockets which allow (a) the attachment of a condenser for condensing vapours, (b) the immersion of a

thermocouple and mechanical stirrer (c) the insertion of solids, (d) the drawing of samples and (e) the immersion of electrodes for pH measurement. The heating mantle, thermocouple and mechanical stirrer are connected to a PLC unit which allows for the control of the operating parameters. Leaching tests were performed in atmospheric pressure conditions. After each test, the solution was separated from the solids with filtration by a Buchner funnel. Samples were taken and analysed by AAS.

In this study we present the effect in Al and Si extraction of temperature and NaOH addition to the Na<sub>2</sub>CO<sub>3</sub> leaching solution. All leaching tests were conducted with a 5% S/L ratio (10g slag in 200mL solution), in a moderate stirring rate of 300rpm for a duration of 60 minutes. Na<sub>2</sub>CO<sub>3</sub> concentrations was stable at 71 g/L, which corresponds to the exact molar amount needed for the complete conversion of the Ca content of the slag to CaCO<sub>3</sub>, according to equation (1). This amount is a theoretical starting point, as our previous work established that high amounts of Na<sub>2</sub>CO<sub>3</sub> in the PLS push the system away from the precipitation of Al(OH)<sub>3</sub>. A NaOH addition of 10% in excess (on the basis of the equivalent Na<sub>2</sub>O as carbonate) was chosen as a starting point, to register its effect on Al and Si extraction. Finally, driven by previous experience, a series of 5-minute leaching tests were conducted at the optimum leaching temperature. Tests and the corresponding parameters tested are shown in Table 2.

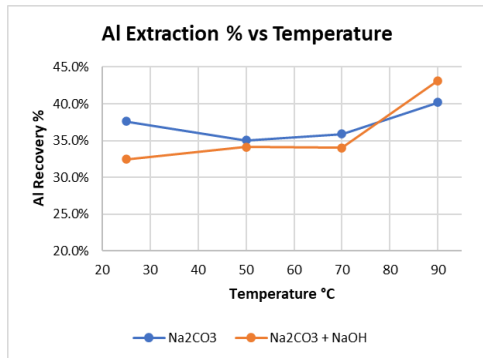
**Table 2.** Leaching tests and corresponding parameters tested in this study

| Test | Parameter      | S/L Ratio | Stirring Rate | Na <sub>2</sub> CO <sub>3</sub> (g/L) | NaOH (g/L) | Na <sub>2</sub> O (g/L) | Temperature (°C)  |
|------|----------------|-----------|---------------|---------------------------------------|------------|-------------------------|-------------------|
| 1    | Temperature    | 5%        | 300 rpm       | 71                                    | 0          | 41.5                    | 25, 50, 70, 90    |
| 2    | NaOH addition  |           |               |                                       | 5.5        | 45.8                    | 25, 50, 70, 90    |
| 3    | 5-minute tests |           |               |                                       | 0          | 41.5                    | Optimum of test 1 |

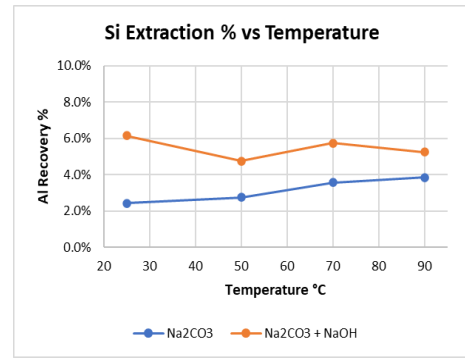
## Results and discussion

### Dependence of Al & Si extraction on temperature

The wt% extraction of Al as a function of different leaching temperatures is shown with the blue line in Figure 2a. It is observed that temperature does not act as a crucial factor for Al extraction when Na<sub>2</sub>O remains in low concentrations. For all temperatures, the extraction ranges between 35% - 41%. Maximum Al extraction is achieved at 90 °C.



**Figure 2a.** Al extraction in Na<sub>2</sub>CO<sub>3</sub> solution (blue line) and in Na<sub>2</sub>CO<sub>3</sub> +10% NaOH (orange line) at different temperatures



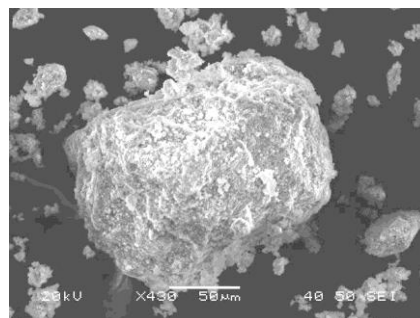
**Figure 2b.** Si extraction in Na<sub>2</sub>CO<sub>3</sub> solution (blue line) and in Na<sub>2</sub>CO<sub>3</sub> +10% NaOH (orange line) at different temperatures

The orange line in Figure 2a presents the wt% extraction of Al with the addition of NaOH at the same temperatures. Slightly raising the caustic concentration of the solution has minor contribution to the overall extraction of Al and only at 90 °C. Although this result seems counterintuitive at first, it is the extraction of Si that completes the picture. These results are shown in Figure 2b where, for all leaching temperatures, the 10% NaOH addition aided the extraction of Si. Therefore, even if the small contribution of NaOH to the extraction of Al at high temperatures is somewhat positive, the co-dissolution of Si at higher rates diminishes any positive effects.

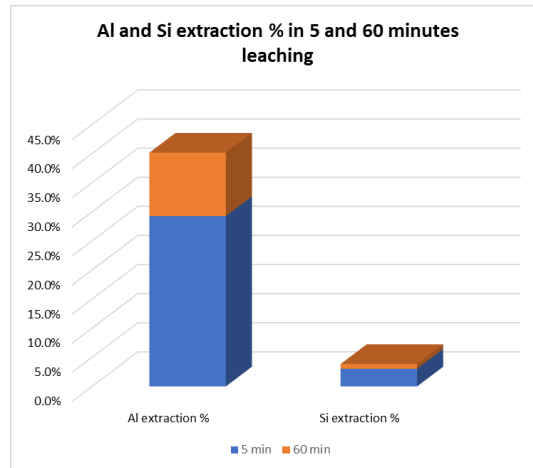
### Dependence of Al & Si extraction on time

Based on previous work with CA slags, two distinctive features of the leaching process have been confirmed:

- CaCO<sub>3</sub> precipitates on the surface of slag particles, hindering further dissolution of Al
- The rates of Al dissolution in the initial stages of extraction are rapid



**Figure 3.** CaCO<sub>3</sub> coated slag particle after 60min leaching with Na<sub>2</sub>CO<sub>3</sub> at 70 °C



**Figure 4.** Extraction in wt% of Al and Si during the first 5 minutes of leaching and in 60 min, under the same experimental conditions

To confirm that the slag originating from BR smelting behaves in the same manner (a) the leaching residues were observed with a Scanning Electron Microscope to verify the presence of  $\text{CaCO}_3$  coating and (b) targeted 5-minute leaching tests in the optimum temperature of 90 °C were conducted to verify the rapid extraction rates prior to the formation of the  $\text{CaCO}_3$  coating. Figure 3 presents the typical  $\text{CaCO}_3$  coating observed in slag particles, whereas in Figure 4 the wt% extractions of Al and Si in the 5 minutes of leaching are compared with the corresponding extraction in 60 minutes. It is observed that more than 75% of the total Al and Si extraction in the first hour of leaching takes place in just 5 minutes.

## Conclusions

It was confirmed that CA slags originating from the reductive smelting of BR present similar leaching features as the ones from bauxite ore smelting, regardless of their lower Al and higher Si content. Al extraction at ambient pressure and low  $\text{Na}_2\text{O}$  concentrations is practically independent of temperature, although at higher temperatures a slight increase is observed. Addition of 10% NaOH to the leach solution has minor contributions to extraction of Al and only at 90 °C but it enhanced Si extraction. The precipitation of  $\text{CaCO}_3$  on the surface of particles was confirmed as the main inhibitor of what would otherwise be a rapid extraction process, as proved by the fast rates of Al extraction in the 5 minutes of leaching, where more than 75% of the total Al extracted is dissolved. Despite the fast kinetics, total Al extraction ranges between 35% - 41%, with the maximum achieved at 90 °C. Work on profiling the effect of the remaining leaching parameters is ongoing.

## Acknowledgements

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