

CARBOTHERMIC REDUCTION OF RED MUD IN AN EAF AND SUBSEQUENT RECOVERY OF ALUMINIUM FROM THE SLAG BY PRESSURE LEACHING IN CAUSTIC SOLUTION

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Abstract

The research work presented in this paper is focused on the recovery of alumina from red mud, which is obtained from bauxite during the Bayer process. The procedure employed is carbothermic reduction of iron-oxide in the red mud using an electric arc furnace (EAF) followed by pressure leaching of the slag with sodium hydroxide solution. The reduction experiments included except of coke the addition of lime based on the silica content of red mud. The leaching experiments variables include NaOH concentration, temperature and leaching time. In certain leaching experiments there were also investigated the additions of defined amounts of sodium carbonate (Na_2CO_3) and sodium fluoride (NaF) in the caustic solution, while the solid-to-liquid ratio of 1:10 was standard, and optimised leaching conditions were obtained. The characterisation of the initial red mud, as well as of the slags and the leach residues was carried out by X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS) and X-ray diffraction (XRD).

Introduction

The red mud used in the experiments contains large amounts of alumina bearing minerals, mostly gibbsite which offers the possibility for conventional alumina extraction via high pressure caustic leaching. Nevertheless 27 wt% Al_2O_3 in total is much lower than the alumina content in natural bauxite ores and therefore an intermediate step seems to be necessary to enrich the alumina content in a generated concentrate by separating other undesired compounds. Considering the entire analysis of the experimentally used red mud given in Table 1 it becomes obvious that the selective removal of iron oxide by carbothermic reduction is the most promising opportunity to achieve a metal phase which is saleable as a product and obtain a slag phase which is enriched in alumina. In order to improve the leaching efficiency, lime is added directly in the smelting step. Like many authors

already mentioned, lime reacts with (sodium) aluminium silicates to calcium silicates and thus liberate the alumina for leaching.^{1,2} The alumina concentrate is afterwards leached with sodium hydroxide solution (NaOH) in order to dissolve the alumina selectively from the other components. Common literature reports the precipitation of dissolved aluminium in caustic solutions in presence of dissolved silicon as sodalite or cancrinite.^{1,2,3} To avoid the aluminium loss in these compounds the addition of fluoride as reactant for silica and especially dissolved silicon is examined. As a chemical compound with good solubility NaF is chosen for the experiments. Moreover Z. Li² reports almost 100 % aluminium recovery by using concentrated sodium hydroxide solutions and therefore the experiments are conducted with sodium concentrations in common ranges of 15-20 wt% NaOH and up to 50 wt%.

Table 1: Chemical composition of the used red mud and the obtained products

Component	Red mud, wt%	Slag, wt%	Leach residue wt%
Fe ₂ O ₃	29.5	1.2	0.6-0.9
Al ₂ O ₃	27.0	39.9	2-5
SiO ₂	13.1	18.4	20-21
TiO ₂	8.0	11.0	16-18
CaO	3.8	29.1	35-38
Na ₂ O	7.0	2.8	7-10

Experimental Setup

The red mud with the composition shown in Table 1 was dried at 105 °C for 24 h and the agglomerated cake was subsequently crushed to lumps of 5-40 mm size. Together with lignite coke (containing 88 wt% carbon) and lime (commercial purity 95 wt% CaO) the material was fed into a 100 kVA AC electric arc furnace. The amounts of the used admixtures correspond to a coke-to-red mud ratio of 1:10 and a lime-to-red mud ratio of 1:4. In total 3.5 kg of material have been smelted per batch in a graphite crucible of 1.5 l volume at a temperature of 1600-1700 °C. The entire melt was then tapped into a steel mould and due to the density difference between slag and metal phase, the phases separate in the mould before solidification. Thereafter the slag was separated from the metal phase manually and for further processing the slag was ground and milled until the preferred granulometry for leaching (90-120 µm) was achieved.

In the second step the alumina enriched slag was put into a titania vessel and leached with caustic sodium hydroxide solution (15-50 wt% NaOH) and in some experiments a mixture of sodium carbonate (10 wt% means 120-140 g/l depending

on the NaOH concentration) and NaF (20 g/l) for 3 h at different temperatures varying from 170 °C to 250 °C. The solid/liquid ratio was kept constant at 1:10 (50 g slag/500 ml solution). In total the leaching step had a duration of 5 h including 90 min heating to desired process temperature, 180 min leaching at process temperature and 30 min cooling down to 50 °C. In order to measure the leaching progress samples of the leaching liquor have been taken in 1 h intervals beginning after 90 min by reaching the process temperature. The filtration of the leach solution was done by vacuum filtration to separate the leach liquor from the solid content (leach residue). For analysis the residue was washed with distilled water and afterwards dried at 105 °C for 13 h.

The samples of slags, the leach residues and also the leaching solutions were analysed by X-ray fluorescence (XRF) and by inductively coupled plasma mass spectrometry (ICP-MS).

Results and Discussion

It can be seen from Figure 1 that especially the temperature has big influence on the aluminium recovery. At sodium hydroxide concentrations of 200-300 g/l, as commonly used in the Bayer process, the aluminium recovery is at 170 °C only 40 %. By increasing the temperature to 200 °C and 250 °C the recovery can be improved to 50 % and almost 80 %, respectively. By increasing the concentration of sodium hydroxide the recovery can be pushed further towards 95 %. In this case, the aluminium concentration in the final leaching residue was reduced to 2 wt% (converted into Al_2O_3) from initially 39.9 wt% in the slag phase before leaching.

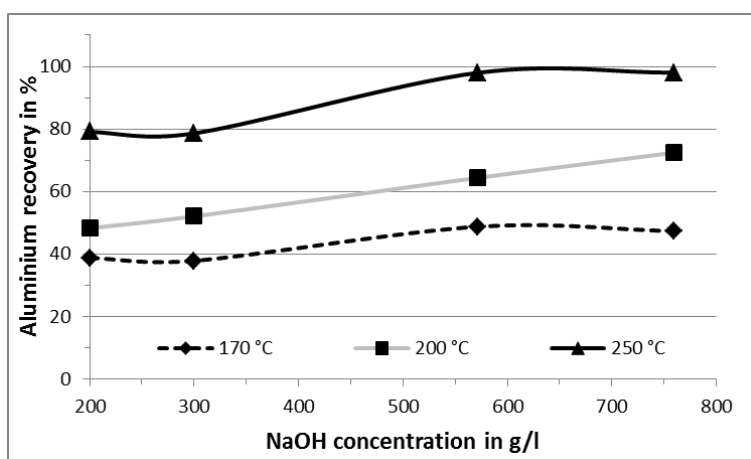


Figure 1: Effects of temperature and sodium hydroxide concentration on the leaching efficiency

Nevertheless higher sodium hydroxide concentrations and thus more aggressive conditions result in the dissolution of minor elements. Especially iron and silica are dissolved as well and affect the purity of the leach liquor and the subsequently crystallised aluminium hydroxide from the liquor.

The effects of the addition of sodium hydroxide and NaF are shown in Figure 2. In comparison to Figure 1, leaching without any additives, the aluminium recoveries are almost comparable or slightly decreased. As a positive effect the dissolved silica in the liquor is effectively diminished at low NaOH concentrations of 200 g/l. In these cases the silicon concentration in the liquor can be reduced to values around 50 mg/l instead of concentrations around 200 mg/l in conventional leaching without fluoride addition. At higher NaOH concentrations the effect is less visible. It becomes obvious that especially at the beginning fluoride ions dissolve large portions of silica but after 3-4 h of leaching the concentration of dissolved silicon ions is drops to the same levels as in leaching experiments without fluoride addition.

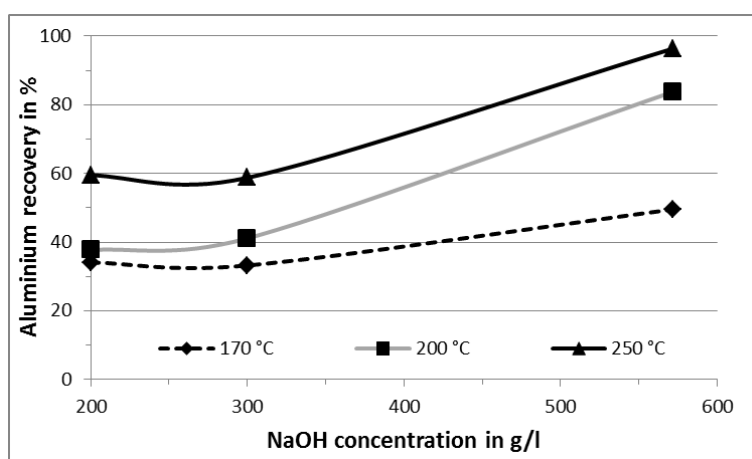


Figure 2: Effects of temperature and sodium hydroxide concentration on the leaching efficiency in presence of 10 wt% Na₂CO₃ and 20 g/l NaF

Conclusions

The recovery of aluminium from high alumina and high silica containing slag by caustic pressure leaching is strongly affected by temperature and also affected by the concentration of sodium hydroxide. As mentioned in literature,¹ the use of concentrated sodium hydroxide solution can increase the yield from 80 % to 95 % at 250 °C, solid/liquid ratio 1:10. But thereby the dissolution of other compounds like iron and silicon is accelerated as well and the use of additives, in this case especially NaF to avoid the silica dissolution, benefits only in the later stage of leaching and especially at lower NaOH concentrations of about 200-300 g/l.

For further information, x-ray diffraction patterns of slag and leaching residue, detailed figures and composition of the yielded metal phase, the full paper will be published soon in “Journal of Sustainable Metallurgy”.

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References

1. P. J Cresswell and D. J. Milne, “A Hydrothermal Process for Recovery of Soda and Alumina from Red Mud”, in *Light Metals 1982*, Metallurgical Society of AIME, Edited by J.E. Andersen, Warrendale, Pa, USA, 227–238, 1982.
2. Z. Li, Z. Yifei, Z. Vi, “Extraction of Alumina and Sodium Oxide from Red Mud By a Mild Hydro-Chemical Process”, *J. Hazard. Metals*, **172** 1629-1634 (2009).
3. M. C. Barnes, J. Addai-Mensah, A. R. Gerson, “The Kinetics of Desilication of Synthetic Spent Bayer Liquor Seeded with Cancrinite and Cancrinite/Sodalite Mixed-Phase Crystals”, *J Cryst Growth*, **200** 251-264 (1999).

