

A VARIATION OF THE RED MUD LIME SINTER PROCESS

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Abstract

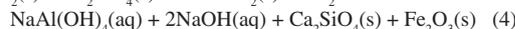
The red mud lime sinter process can be used in combination with the Bayer process to recover sodium and aluminium from the red mud waste and direct it back to the process stream. This is facilitated by the high temperature reaction of lime and DSP in the red mud to produce an insoluble dicalcium silicate and a soluble sodium aluminate. A variation of the red mud lime sinter process using half the limestone of existing methods has been investigated. The calcium to silicon ratio was reduced from 2 to 1 producing a sodium calcium silicate ($\text{Na}_2\text{CaSiO}_4$) rather than the dicalcium silicate (Ca_2SiO_4) insoluble phase produced in the existing lime sinter method. Synthetic lime sinter products were investigated to understand the phases produced during calcination at varying temperatures and the chemistry of extraction. The target phases were seen in XRD and the highest extractions were produced from a sinter temperature of 1100°C. A two-stage (65°C/2 mins, 95°C/16 hrs) water leaching process was found to be most effective for extraction. Sodium and aluminium extractions were 99% and 91% respectively. The experimental method devised was then used to treat red mud and the target phases were produced. An extraction of sodium and aluminium of 94% and 87% respectively was achieved. Silicon extractions were below 2%. Production benefits include sodium hydroxide and lime savings, liquor burning, increased aluminium extraction and reduced cost of waste handling.

1 Introduction

Methods of aluminium and sodium recovery from red mud have been around for many years due to the requirement of some refineries to process very high silica bauxites. The most common method to process red mud or very low grade ore is the 'lime sinter process'. The process involves adding lime (CaCO_3) to the ore and calcining at temperatures above 1100°C (King 1980). The silica in the ore reacts with calcium to form the relatively inert dicalcium silicate (1). The sodium, which is in the ore or added via soda ash or sodium carbonate, reacts with the alumina and forms the soluble sodium aluminate (2) (Lecis, Gaudi 1962).

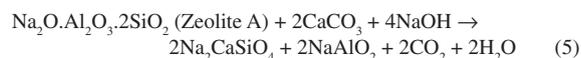


The product is then leached in an alkaline solution or water and the sodium aluminate solution is directed to the precipitation stage of the Bayer process.



To produce high aluminium and sodium extractions the decomposition of dicalcium silicate must be as low as possible. In practise the amount of silica extracted in the leaching step is too high as the Ca_2SiO_4 is not sufficiently stable under the leaching conditions (Hartshorn 2000) and silica extractions of around 15–20% (Likuan 1993) occur during leaching, tying up sodium and aluminium with the formation of TCA, hydrogarnet and DSP. The opportunity exists for a process to treat red mud to separate aluminium and sodium from silica, producing an adequately stable insoluble phase for leaching and therefore yielding greater extractions.

An alternative method of lime sinter has been trialled at Comalco to produce a Ca:Si ratio of one in the sinter product (Hartshorn 2000). The potential benefits being to halve raw material costs and to give a more stable insoluble phase. Also the extra sodium needed could be provided by spent liquor creating the potential for organics removal through liquor burning in the sinter step. However, thermodynamic calculations and laboratory tests show that CaSiO_3 does not form under lime sinter conditions (Osborne 1997). From previous experiments it was thought that the following lime sinter reaction was feasible.



A similar lime sinter process is referred to in a paper discussing the integration of coal combustion with lime sinter (Rayzman, Filipovich 1999). Reaction (5) shows that soluble sodium aluminate and sodium calcium silicate are produced. The sodium associated with sodium calcium silicate must also be recovered in the leaching step. The objective of this project was to investigate the use of a Ca:Si ratio of one lime sinter process for use as a red mud treatment for the recovery of aluminium and sodium and compare this with the current lime sinter system of Ca:Si = 2.

2 Experimental

Lime sinter products with varying chemical compositions were prepared to gain an insight into the thermodynamics and chemistry of the lime sinter process. Both the existing (Ca_2SiO_4) and new ($\text{Na}_2\text{CaSiO}_4$) method of lime sinter were tested for comparison in initially synthetic and then red mud lime sinter mixtures. Synthetic mixtures were produced using SiO_2 , CaCO_3 , Na_2CO_3 (all analytical grade) and Zeolite-A which were ring-milled, pressed into pellets and calcined and phases confirmed by XRD and ICP analysis. Synthetic Phases with iron present were then made using Fe_2O_3 . The red mud lime sinter mixtures were produced similarly, adding CaCO_3 and Na_2CO_3 to bauxite residue. The temperature of calcination was varied to optimise extraction. Leaching with water and spent liquor was undertaken in a water bath at varying times and temperatures, again to optimise extraction.

3 Results and Discussion

In the synthetic lime sinter stage, calcination at 1100°C was found to produce the most stable sodium calcium silicates and dicalcium silicates which maximised the extraction of aluminium and sodium. XRD scans show the target phases are present as described in Table 1.

Table 1: Major phases present in XRD scans of 1100°C sinter products

Experiment	Synthetic new lime sinter		Synthetic existing lime sinter	
Target Phase	$\text{Na}_2\text{CaSiO}_4 + \text{NaAlO}_2$	$\text{Na}_2\text{CaSiO}_4 + \text{NaAlO}_2 + \text{NaFeO}_2$	$\text{Ca}_2\text{SiO}_4 + \text{NaAlO}_2$	$\text{Ca}_2\text{SiO}_4 + \text{NaAlO}_2 + \text{NaFeO}_2$
Phases present in XRD	$\text{Na}_2\text{CaSiO}_4 + \text{NaAlO}_2$	$\text{Na}_2\text{CaSiO}_4 + \text{Na}_2\text{AlFeO}_4$	$\text{Ca}_2\text{SiO}_4 + \text{NaAlO}_2$	$\text{Ca}_2\text{SiO}_4 + \text{Na}_2\text{AlFeO}_4 + \text{Ca}_2\text{Fe}_2\text{O}_5$

The existing lime sinter product ties some calcium up with iron due to the formation of $\text{Ca}_2\text{Fe}_2\text{O}_5$. This meant that extra calcium was added to ensure the maximum amount of silica was reacted with the calcium and not with sodium or aluminium. At 1100°C, instead of sodium aluminate and sodium ferrite forming, $\text{Na}_2\text{AlFeO}_4$ formed in products with iron present.

For the synthetic new lime sinter system without iron it was found that a two stage water leach (65°C/2 min, 95°C/16 hrs) was required to gain maximum Na and Al extractions due to the decrease in Al in solution over time as shown in Figure 1.

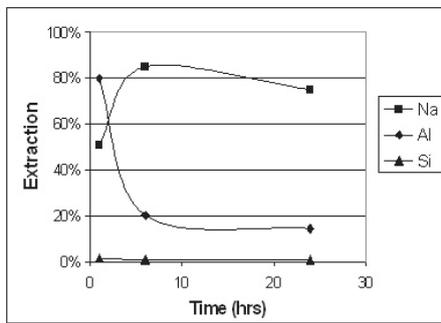


Figure 1: Single Stage Extraction over Time

This allowed the removal of the majority of the aluminium before the decomposition of the sodium calcium silicate and subsequent reaction to form DSP, hydrogarnet or TCA. To ensure leaching conditions were the same for both systems the two stage process was also employed for the existing lime sinter products. The results of extractions for the sinter products without iron are displayed in Figure 2.

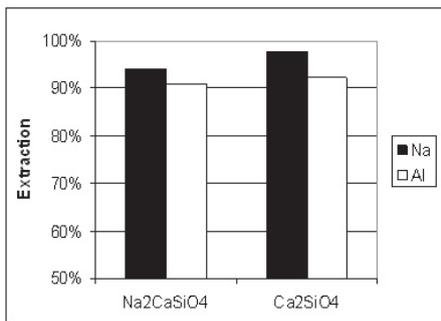


Figure 2: New vs Existing Synthetic Lime Sinter without Iron

When Iron is introduced to the system there are effectively two soluble phases ($\text{NaAlO}_2 + \text{NaFeO}_2$) in which the ratio of soluble sodium to soluble aluminium increases. The results in Figures 3 and 4 show the benefit of the new lime sinter method in terms of aluminium extraction.

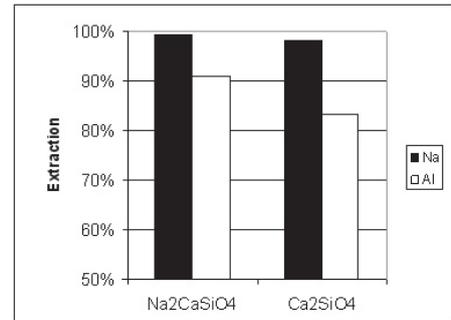


Figure 3: New vs Existing Synthetic Lime Sinter

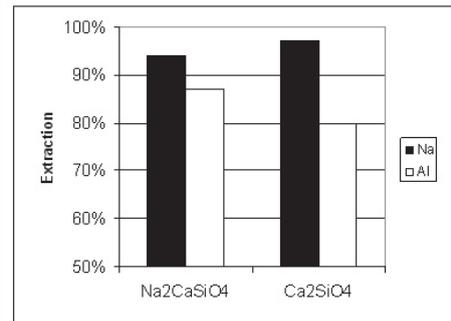


Figure 4: New vs Existing Red Mud Lime Sinter

Much of the sodium and all of the aluminium is extracted from the existing lime sinter process in the first stage. The second stage merely completes the leaching of sodium. In the new red mud lime sinter extraction the resultant solids have a sodium content of 2.7% compared to the 14.6% sodium content of the red mud. The aluminium levels have been reduced from 22.9% to 3.14%. A more stable sodium calcium silicate would increase these extractions and could be achieved with the optimisation of sinter temperature and leach conditions.

A simulation of the second stage leach, which in the new process aims to recover the sodium from the sodium calcium silicate, produced highly concentrated caustic solutions (up to 320g/L). The extraction was of a synthetic $\text{Na}_2\text{CaSiO}_4$ calcined at 1100°C and leached with 200g/L caustic solution. The high caustic concentration may be due to the stabil-

ity of the decomposition products which have a Ca:Si of 1 rather than 2. This is a significant result and should be investigated further.

When leaching the red mud lime sinter products the greater aluminium extraction in the new process was evident however there was less sodium extracted. This may be overcome with further optimisation of the mole ratios of reactants in the lime sinter step. The high silicon extraction that has been reported (Likuan 1993) was not seen during this project with most experiments producing a silicon extraction of less than 2% for both the new and existing processes. This may be due to the accuracy of the mole ratios, which can easily be targeted in laboratory conditions compared to in plant conditions where an assay of the red mud to be sintered with lime is unlikely to have taken place.

4 Conclusions

The new lime sinter method with a Ca:Si of one proved to be an effective procedure in recovering the sodium and aluminium from red mud with minimum silicon extraction. The problems with high silica extraction using the existing lime sinter method were not evident which may be due to the difference in mole ratio accuracy between laboratory and plant. The advantages of the new lime sinter process include a decrease in limestone and NaOH purchases, increased aluminium extraction and possible organics removal through liquor burning. The potential for producing a concentrated sodium hydroxide solution from the second stage leach is also a major benefit of this system.

References

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