Alumina extraction from red mud by CaCO₃ and Na₂CO₃ sinter process

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Abstract

An investigation of the application of the CaCO₃ and Na₂CO₃ sinter process to extract alumina from red mud has been carried out. In the sintering stage, the optimal operating conditions have been obtained for highest extraction of alumina. The chemical composition of red mud is 16.07% Al₂O₃, 53.75% Fe₂O₃, 8.25% SiO₂, 3.83% Na₂O, 4.24% TiO₂, 0.15% V₂O₅, 0.157% MnO, 0.02% MgO, 0.085% Ga₂O₃, 0.007% ZnO, 0.099% K₂O and 11.83% LOI along with rare earth elements in ppm level. During the process of sintering-leaching the minerals and alumina phases present in red mud like gibbsite, gibbsite co-existing with boehmite, aluminosilicate, boehmite and sodalite is converted to soluble sodium meta-aluminate as well as stable phases of calcium ferrite, titanate and silicate. The effect of CaCO₃ and Na₂CO₃ additive, sintering temperature, sintering time and leaching time on the efficiency of alumina extraction from red mud were investigated. Studies show that it was possible to extract alumina from red mud with approximately 97.64% extraction efficiency at a sintering temperature of 1100 ºC for 4 hr with red mud, CaCO₃ and Na₂CO₃ in mole ratio of 1:0.20:0.25 followed by leaching with suitable caustic concentration. The formation of Na₂CaSiO₄, Ca₂SiO₄, CaTiO₃ and Ca₂Fe₂O₅ enhance alumina extraction efficiency. X-Ray diffractometer (XRD) and scanning electron microscopy (SEM) studied confirm the formation of Na₂CaSiO₄, Ca₂SiO₄, CaTiO₃ and Ca₂Fe₂O₅.

Keywords: Red Mud, Sintering, Leaching and Extraction.

1. Introduction

Aluminium can be extracted from bauxite, which is a compound of aluminium tri-hydroxide, iron oxide, silicon dioxide, kaolin and titanium. The first stage is to extract alumina (Al₂O₃) from the bauxite ore through the Bayer’s process, which is used with one or two exceptions, throughout the world. In this process, ground bauxite is treated with sodium hydroxide under heat and pressure forming sodium aluminate [NaAl(OH)₄], residue which is then purified and decomposed. As a result of decomposition, the aluminium tri-hydrate is calcined at 950-1200 ºC, thus yielding calcined alumina. The second stage is the electrolysis process. In the electrolysis cells, with the aid of a direct current, liquid aluminium is obtained from calcined alumina. The liquid aluminium, being alloyed when required is then cast into the desired moulds [1-3].

Red mud emerges as by-product from the caustic leaching of bauxites to produce alumina, and its major constituents are Fe₂O₃, Al₂O₃, SiO₂, Na₂O, TiO₂ and CaO, with little amounts of Zr, Y, Th, U and rare earth elements as trace constituents. Approximately 35-40% of the processed bauxite goes into waste as red mud. Red mud is the biggest problem in producing alumina. These waste present serious problems of storing and environmental pollution. Although studies in this area have been done since 1950, improved processes have mostly not been put into practice because of economic reasons [1-6]. The red mud has been accumulated at a rate of 2.7 billion tonnes annually throughout the world [7]. For a given aluminium production rate, the quantity of the red mud generated during the aluminium extraction process varies significantly depending on the original properties of the bauxite and the operating conditions of the Bayer’s process, and in particular, the process temperature [8]. Depending on the factors, between 1 and 2.5 tonnes of bauxite residue is generated per tonne of alumina produced. The disposal of the red mud is associated with pollution problems. Disposal of any solid waste is associated with space/real estate near industry, cost of disposal and pollution, which are now crucial factors. Obviously, these three factors are also associated with the red mud disposal. As the red mud contains a large amount of valuable chemicals, there is a need for developing a technology for the recovery of at least some of the important chemicals [9]. In the literature, a lot of different articles that explain the properties and the investigation of the red mud tailings can be met. One of them mentioned about the behaviour of Bayer’s
process, where the red mud was investigated under caustic concentrations of 10-30% to determine extraction of soda and alumina as a function of caustic ratio, CaO: SiO₂ ratio, water content, temperature and reaction time. Hydrothermal treatment of the red mud with lime at high temperatures (ca 300 °C) was found to be an effective method for the recovery of soda and alumina. Recoveries of 95% Na₂O and 70% Al₂O₃ was obtained [10]. Alyanak et al. [11] studied on the recovery of aluminium from the red mud of Seydisehir Aluminium Plant. They prepared a mixture composed of 26.6 wt% red mud, 37.2 wt% CaCO₃ and 36.2% Na₂CO₃.

In another article, gallium recovery methods applied to bauxite ores, during alumina production by the Bayer’s process, gallium movement and possible locations of gallium recovery were presented [12]. A different study was carried out by Smirnov et al. [13]. They worked on the sulphuric acid sorption recovery of scandium and uranium from the red mud with commercial and experimental resins. The red mud was investigated for the making of artistic glazes in ceramic. For this purpose, no additives and some fluxing materials such as read lead, ulexide, cryolite, borax, soda ash, etc. were added to the red mud at different proportions. Finally, the optimum conditions forming adventuring glazes were determined [14].

The red mud was also investigated to find out whether it can be used as a construction material or not. For this purpose, the red mud, a waste material of Aluminum Plant in Seydisehir, was mixed with clay, which was taken from the same region. This mixture was pressed and sintered at between 1000 and 1150 °C. It was stated that construction materials produced from the mixture had higher compressive strength and lower water absorption ratio compared with the related standards [14]. In another study, the structure of the red mud deposits of Seydisehir, Turkey was investigated by simple statistical analysis. It was shown that the ratio of the percent iron oxide (D₁) in the red mud to the mean percent iron oxide (D₂) was found to fit a linear function represented by plotting D₁/D₂ versus K₁/K₂ on double logarithmic paper. The relation in the form of a power function was D₁=1.0092D₂K₁-0.021 K₂-0.022 [16]. The thermal behaviour of the red mud was investigated in the literature. An extensive characterization of red mud was performed by thermal and x-ray diffraction analyses [17]. Dried red mud was substantially inert up to 900 °C, the loss of H₂O from aluminium hydroxides and of CO₂ from silico-alumino-carbonates being the only detectable effects [18].

Now, there were 2.70 billions of tonnes red mud was generated from alumina refinery plant of the world. These wastes were not investigated yet in any industrial process or used for material production as an additive. The aim of this study was to investigate it for alumina production, to decrease environmental problems and also to fulfil the future resource crisis likely occur.

2. Materials and Methods

2.1 Reagents and Apparatus

The red mud used in experimental studies was supplied from Damanjodi, Dist.-Koraput. The CaCO₃ and Na₂CO₃ used in experimental studies was supplied from Qualigens fine Chemicals, Bombay. The major elements were analysed by classical method as well as X-Ray Fluorescence Spectroscopy (Maker: Philips, Model: PW 2400). The minor elements were analysed by AAS ((Maker: Varian, Model: Spectra 220FS). The chemical compositions of red mud were written in table.1.

### Table 1: Chemical Analysis of Red Mud

<table>
<thead>
<tr>
<th>Chemical Constituents</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>SiO₂</th>
<th>Na₂O</th>
<th>CaO</th>
<th>V₂O₅</th>
<th>MgO</th>
<th>MnO</th>
<th>LOI at 1000 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range (%)</td>
<td>16-18</td>
<td>51-57</td>
<td>3-5</td>
<td>8-12</td>
<td>4-6</td>
<td>0.03-2.30</td>
<td>0.14-0.21</td>
<td>0.13-0.18</td>
<td>0.157-0.250</td>
<td>11-13</td>
</tr>
<tr>
<td>Typical (%)</td>
<td>16.07</td>
<td>53.75</td>
<td>4.24</td>
<td>8.25</td>
<td>3.82</td>
<td>1.48</td>
<td>0.15</td>
<td>0.02</td>
<td>0.157</td>
<td>11.83</td>
</tr>
</tbody>
</table>

2.2 Experimental procedure

An amount of 100g of red mud, 10g of CaCO₃ and 15g/20g/25g of Na₂CO₃ was mixed thoroughly and pulverised in a pulveriser, then the above mixture was sintered at temperatures of 900, 1000, 1100 °C for 1 to 4 hrs in a ceramic crucible in high temperature muffle furnace. An amount of 100 g of red mud, 15g of CaCO₃ and 10g/20g/25g of Na₂CO₃ was mixed thoroughly and pulverised in a pulveriser, then the above mixture was sintered at temperatures of 900, 1000, 1100 °C for 1 to 4 hrs in a ceramic crucible in a high temperature Muffle furnace. An amount of 100g of red mud, 20g of CaCO₃ and 10 g/20 g/25 g of Na₂CO₃ was mixed thoroughly and pulverised in a pulveriser, then the above mixture was sintered at temperatures of 900, 1000, 1100 °C for 1 to 4 hrs in a ceramic crucible in high temperature Muffle furnace. The sinter products was leached with 80 gpl caustic at 105 °C for 1 hr as shown in experimental set up Fig.1. The leached red mud was filtered after leaching. The amount of Al₂O₃ in leach solutions was determined by using titrometric method.

2.3 XRD Study

XRD analysis was done to detect the presence of different phases in the sinter red mud and leached red mud. XRD work was carried out on a Rigaku X-ray diffractometer, (Maker: Rigaku, Japan and Model: Dmax2200). The X-Ray diffractograms of sinter red mud and leached red mud were taken using Cu Ka (Ka =1.54186 Å) radiation at scan speed of 1°/min. and scan step of 0.02 with 2θ value from 5° to 70° at 30 mA and 20 mV.

2.4 SEM Study

The sinter red mud and leached red mud samples were coated with gold, palladium or carbon at 18 mA for 105 second. The morphological behaviours of coated samples and formation of sodium calcium silicate, di-calcium silicate, calcium titanate and calcium ferrite were studied by using Scanning Electron Microscopy (Maker: Leo, England and Model: Leo Electron Microscopy 430).

3. Results and Discussion

3.1 Sintering and Leaching Chemistry

The process involves adding CaCO₃ and Na₂CO₃ to the red mud and sintering at temperatures between 900 °C –1100 °C [19]. The Silica in the red mud reacts with calcium to form the relatively inert di-calcium silicate (equation: 1). The sodium, which is in the red mud added via sodium carbonate reacts with the alumina and Fe₂O₃ and forms the soluble sodium aluminate and sodium ferrite (Equation:2 & 3). The TiO₂, which is in the red mud, reacts with sodium carbonate forms sodium titanate (equation: 4). The titanium dioxide in red mud reacts with CaCO₃ forms calcium titanate (equation: 5) [20]. The sodium ferrite reacts with CaO forms calcium ferrite (equation: 6),

\[ \text{SiO}_2 + 2\text{CaO} \rightarrow \text{Ca}_2\text{SiO}_4 + \text{CO}_2 \]  
(1)

\[ \text{Al}_2\text{O}_3 + \text{Na}_2\text{O} \rightarrow 2\text{NaAlO}_2 \]  
(2)
\[
\begin{align*}
\text{Fe}_2\text{O}_3 + \text{Na}_2\text{O} & \rightarrow 2\text{NaFeO}_2 \\
\text{TiO}_2 + \text{Na}_2\text{CO}_3 & \rightarrow \text{Na}_2\text{TiO}_3 + \text{CO}_2 \\
\text{TiO}_2 + \text{CaCO}_3 & \rightarrow \text{CaTiO}_3 + \text{CO}_2 \\
2\text{NaFeO}_2 + 2\text{CaO} & \rightarrow \text{Ca}_2\text{Fe}_2\text{O}_5 + \text{Na}_2\text{O} \\
\end{align*}
\]

The sintered products were then leached in an alkaline solution (80gpl concentration) or water at 105 °C for 60 minutes to form NaAl(OH)₄ (Equation: 7). In the process of leaching the sodium aluminate solution is directed to the precipitation stage of Bayer’s process.

\[
\text{NaAlO}_2(s) + \text{Ca}_2\text{SiO}_4(s) + 2\text{NaFeO}_2(s) + \text{CaTiO}_3(s) + 3\text{H}_2\text{O} \rightarrow \text{NaAl(OH)}_4(aq) + 2\text{NaOH(aq)} + \text{Ca}_2\text{SiO}_4(s) + \text{CaTiO}_3(s) + \text{Fe}_2\text{O}_3(s) \\
\]

To produce high alumina extractions the decomposition of di-calcium silicate must be as low as possible. In practise the amount of silica recovered in the leaching step is too high as the Ca₂SiO₄ is not sufficiently stable under the leaching conditions \[22\] and silica extractions of around 15-20% \[23\] occur during leaching, trying up sodium and aluminium with the formation of Tri Calcium Aluminate, Hydro garnet and De-silication product. 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 trailed at Comalco to produce a Ca: Si ratio of one in the sinter product \[22\]. The potential benefits being to reduce 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 organic removal through liquor burning in the sinter step. However thermodynamics calculations and laboratory tests show that CaSiO₃ does not form under lime sinter conditions \[24\]. From the previous experiments it was thought that the following CaCO₃ sinter reaction was feasible (Equation: 8).

\[
\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \text{ (Sodalite)} + 2\text{CaCO}_3 + 4\text{NaOH} \rightarrow 2\text{Na}_2\text{CaSiO}_4 + 2\text{NaAlO}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} \\
\]

A similar lime sinter process is referred in a paper discussing the integration of coal combustion with lime sinter \[25\]. Reaction (8) 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 one CaCO₃ and Na₂CO₃ sinter process for use as a red mud treatment for recovery of alumina and compare with the current CaCO₃ and Na₂CO₃ sinter system of Ca: Si = 2.

### 3.2 Effect of Na₂CO₃ additive

The alumina extraction does not give an assessable change without Na₂CO₃ addition. A small variation in alumina extraction is pointed out when the Na₂CO₃ was increased from 10g to 25g as compared to red mud 100g at sintering temperature of 900 °C – 1100 °C as shown in Fig. 2 and Fig. 3. Inversely, addition of 20 and 25% Na₂CO₃ resulted to increase of alumina extraction at 900 °C –1000 °C. However, a sharp increase in alumina extraction was point out at sintering temperature of 1100 °C by increasing sintering time from 1 hr to 4 hrs as well as by increasing Na₂CO₃ from 10g to 25g as compared to red mud 100g as shown in Fig. 4. It can be generally said that increasing the amount of Na₂CO₃ additive and the calcinations temperature increased the extraction of alumina. The rate of the alumina extraction at 1100 °C is higher than at 900-1000 °C. High amount of Na₂CO₃ addition is not necessary. In order to get high alumina efficiency, only 17.24 wt% Na₂CO₃ addition is enough.
3.3 Effect of CaCO3 and Na2CO3 additive
When Na2CO3 addition is increased from 15g to 20g in 100g of red mud, the alumina extraction was enhanced from 79.80% to 82.79%. However the alumina extraction efficiency was reached to 86.66% with 20 wt% CaCO3 and 25 wt% Na2CO3 addition to this mixture in place of 10 wt% CaCO3. But the alumina extraction was reached to 97.64% with 20 wt% CaCO3 and 25 wt% of Na2CO3 addition to this mixture. The reason for increasing alumina extraction was the occurrence of insoluble di-calcium silicates (Fig. 5 & Fig. 6), because of CaCO3 addition and soluble sodium meta-aluminate (Fig. 5 & Fig.6), and of Na2CO3 addition in solid state. The alumina extraction efficiency was increased from 38.35% to 97.64% by increasing CaCO3 addition from 10 wt% to 20 wt%. Increasing the amount of CaCO3 more than 20 wt% decreased the increase of alumina extraction efficiency. It was understood from this result that the excess of CaCO3 reacted with a little amount of alumina in the solution and insoluble calcium aluminium silicates hydrates was formed. It was expressed in the literature that the formation of insoluble calcium aluminium silicates was occurred due to excessive sintering temperature/time and presence of excess of CaCO3 [26]. It was clarified that the addition of CaCO3 more than 20g was not necessary to recover high alumina ratio from the red mud. The addition of more than 20 g leads to only wasting of CaCO3. The amount of optimum Na2CO3 was determined as 25g in 100g of red mud (17.24 wt% Na2CO3 of the red mud) for solving enough alumina in the red mud. Since the addition of Na2CO3 in between 15g to 25g gives significant recovery of alumina.

3.4 Effect of Na2O/Al2O3 and CaO/SiO2 Molar ratio
The optimum range for alumina extraction corresponds to soda/alumina ratios of 1.2 to 1.3. Ratios greater than 1.3 are not necessary, and in fact they seem to be harmful. This is believed to be due to the formation of some insoluble compounds between soda and alumina. These data correspond to a constant value of Na2O/Al2O3 = 1.3. We can see that, with an increase in the CaO/SiO2 ratio, extraction increases up to CaO/SiO2 = 1.75 to 1.8 and then decrease thereafter. Here it is also seen that ratio equal to the stoichiometric values are not the optimum values as reported previously in the literature. From these results, it is known that the extractions of alumina are best with the soda/alumina and CaO/silica to obtain 1.3 and 1.8, respectively. Therefore, these ratios were adopted as standard for the subsequent experiments.

3.5 Effect of calcinations temperature and time for extraction of alumina
The alumina extraction efficiency increased from 38.35% to 68.13% by increasing sintering temperature from 900 °C to 1000 °C with sintering time of 2 hrs (Fig. 2 & 3). But there is no significant change in alumina extraction by increasing sintering temperature from 900 °C to 1100 °C with soaking time of 2 hrs and 3 hrs. The alumina extraction efficiency was increased from 61.11% to 97.64% by increasing sintering temperature from 900 °C to 1100 °C with soaking time of 4 hrs (Fig.4). Hence the optimum condition for dissolution of maximum alumina is 68.96% of red mud, 13.79% of CaCO3 and 17.24% Na2CO3, 1100 °C sintering temperature, 4 hrs calcinations time, -100+53 micron of the particle size distribution, leaching time 1 hr with 80 gpl caustic at 105 °C. Under these optimum conditions, the highest extraction efficiency of alumina was obtained as 97.64%.

In the synthetic CaCO3 and Na2CO3 sinter process, calcinations at 1100 °C under the above condition was found to produce the most stable sodium calcium silicate (SEM Fig.7), di-calcium silicate (SEM Fig.7), calcium titanate (SEM Fig.8) and calcium ferrite (SEM Fig.9 & 10) and which maximise the extraction of aluminium (97.64%). XRD scans (XRD Fig 5 & 6) show the target phases are present as described in Table 2 &3.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Synthetic new CaCO3-Na2CO3 sinter</th>
<th>Synthetic existing CaCO3-Na2CO3 sinter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target Phase</td>
<td>Na2CaSiO4 +NaAlO2</td>
<td>Na2CaSiO4 +NaAlO2 +NaFeO2</td>
</tr>
<tr>
<td>Phase Present in XRD</td>
<td>Na2CaSiO4 +NaAlO2</td>
<td>Na2CaSiO4 +NaAlFeO2 +NaFeO2</td>
</tr>
</tbody>
</table>

| Table 3: Formation of major phases confirmed by XRD during sintering of red mud followed by leaching |
|---------------------------------|------------------------------|--------------------------|
| Sinter Process | Formation of Major phases | Characteristic ‘d’ spacing (Å) |
| Red Mud + CaCO3 + Na2CO3 | Dicalcium Silicate | 2.90, 2.76, 2.21 |
| | Calcium Titanate (Pervoskite) | 2.70, 2.52, 2.87 |
| | Calcium Ferrite | 2.70, 2.67, 2.10, 1.84 |
| | NaAlO2 | 2.23, 2.52, 2.59, 2.64, 2.95 |
| | CaSiO3, CaV2O6 | 2.70, 2.67, 2.21 |
| | CaMnO3 | 2.67, 2.70 |
| | Hematite | 2.52, 2.70 |
| | Sodium Calcium Silicate | 2.64, 2.95, 1.48 |
| | Sodalite | 2.10 |
| | Cancrinite | 3.69, 4.62 |
| | Quartz | 4.26 |
Fig 5: XRD OF SINTERED RED MUD AT 1100 °C

Fig 6: XRD OF LEACHED SINTERED RED MUD AT 1100 °C

Fig 7: FORMATION OF Na₂CaSiO₄ and Ca₃SiO₄ (2KX)

Fig 8: FORMATION OF CALCIUM TITANATE (4KX)

Fig 9: FORMATION OF Ca₂Fe₂O₅ (1.09KX)
Fig 10: FORMATION OF Ca₂Fe₂O₅ (5.96K)

4. Conclusion
Studies showed that it was possible to extract alumina from the red mud with very high alumina extraction efficiency. The optimum operating conditions of the process were 13.79% CaCO₃ and 17.24% Na₂CO₃ addition of the red mud weight. The highest extraction efficiency of alumina was obtained as 97.64%. The highest extraction efficiency was achieved in this condition is due to formation stable phases like Na₂CaSiO₄ (d value-2.95 Å, 2.64 Å, 1.48 Å), Ca₃SiO₄ (d value-2.90 Å, 2.76 Å, 2.21 Å), CaTiO₃ (d value-2.70 Å, 2.52 Å, 2.87 Å), and Ca₂Fe₂O₅ (d value-2.70 Å, 2.67 Å, 2.10 Å, 1.84 Å). The alumina extraction efficiency reached with sintering at 1100 °C was higher than that at 900 °C. But 1100°C was chosen as an optimum sintering temperature. This temperature can be accepted as more economical, suitable and agreeable method for extracting maximum alumina from red mud and applicable to alumina refinery.

5. Acknowledgements
The author is thankful to Management of National Aluminium Company Limited, Damanjodi, Dist.-Koraput for their kind permission for publishing this research article.

6. Competing Interests
Authors have declared that no competing interests exist.

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