ON THE RECOVERY OF CAUSTIC AND ALUMINA FROM BAUXITE RESIDUES BY LEACHING

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Abstract

The dissolution of caustic and alumina from three bauxite residue slurries by leaching with water was investigated. The experiments were performed with different leaching ratios, and the leaching results were evaluated with respect to the total and relative concentrations of the main compounds. The results of the study help to understand how different bauxite residues behave in the presence of excess water. In the alumina industry, the leaching behavior of caustic compounds and aluminium is of major practical importance, and the results of the study should be taken into account when planning improved alkali recovery systems and reuse of the residue. To make a difference between the leached sodium and caustic compounds, linear relationships between the caustic concentrations calculated based on sodium and OH analyses are presented for the slurries. Additionally, the paper shows that the results of routine chemical analyses for bauxite residue slurries clearly depend on the applied procedure of sample preparation.

Introduction

The production of alumina from bauxite ore by the Bayer process generates large quantities of highly alkaline waste called bauxite residue, which is of serious environmental concern. It is estimated that approximately 120 million tonnes of bauxite residue are produced in the world annually.\textsuperscript{1} Leaching of harmful compounds from the disposed residue remains a challenge which can be partially resolved by washing the bauxite residue carefully prior to disposal. In addition to alkaline compounds such as NaOH,\textsuperscript{2} the leaching of heavy metals can cause problems,\textsuperscript{3} although the leachable alkali may be of a greater concern.\textsuperscript{4} There are also some valuable compounds, such as metals, which can be recovered by using the same washing techniques at various pH.

The objective of this study is to evaluate the dissolution of different bauxite residue solids by diluting the slurry with water to see how the dissolution is affected by the
dilution ratio. This evaluation is primarily based on the concentration of dissolved sodium, but also on the concentrations of dissolved aluminium and total caustic.

Materials and Methods

Characteristics of the slurries

Three bauxite residue slurries obtained from industrial alumina production sites were investigated. All the slurry samples were taken from the underflow of the last wash thickener of the residue washing train.

The most essential characteristics of the slurries are presented in Table 1. The methods of analysis are described below. The pH values of the slurries were measured with a WTW pH 340i pH meter. The total solids contents (TS) of the slurries were measured by drying the slurry and filtrate samples at 105 °C and 180 °C, respectively, to dryness. The sodium concentrations were measured with atomic absorption spectroscopy (AAS). Particle size distributions (PSD) were measured with a Malvern Mastersizer 3000 laser diffraction particle size analyser.

Table 1: Characteristics of bauxite residue slurries

<table>
<thead>
<tr>
<th>Slurry</th>
<th>pH (-)</th>
<th>TS (g/kg)</th>
<th>TDS** (g/kg)</th>
<th>Density (kg/m³)</th>
<th>CNa*** (g/kg)</th>
<th>D₁₀ (µm)</th>
<th>D₅₀ (µm)</th>
<th>D₉₀ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry I</td>
<td>13.20</td>
<td>442</td>
<td>52</td>
<td>1363</td>
<td>27.2</td>
<td>0.87</td>
<td>6.9</td>
<td>235</td>
</tr>
<tr>
<td>Slurry II</td>
<td>12.92</td>
<td>330</td>
<td>8</td>
<td>1290</td>
<td>2.3</td>
<td>0.90</td>
<td>2.6</td>
<td>17</td>
</tr>
<tr>
<td>Slurry III</td>
<td>13.46</td>
<td>483</td>
<td>86</td>
<td>1450</td>
<td>33.3</td>
<td>0.90</td>
<td>3.9</td>
<td>27</td>
</tr>
</tbody>
</table>

**Total solids in slurry
***Total dissolved solids in the liquid phase of slurry

The elemental composition of each oven-dried slurry was measured with a scanning electron microscope (Jeol JSM-5800 SEM-EDS). The results of the SEM-EDS analyses are shown in Table 2.

Table 2: Average elemental composition of bauxite residue slurries, in wt%

<table>
<thead>
<tr>
<th>Slurry</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>Al</th>
<th>Si</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry I</td>
<td>1</td>
<td>39</td>
<td>11</td>
<td>10</td>
<td>5</td>
<td>1</td>
<td>10</td>
<td>23</td>
</tr>
<tr>
<td>Slurry II</td>
<td>1</td>
<td>39</td>
<td>8</td>
<td>10</td>
<td>7</td>
<td>4</td>
<td>3</td>
<td>28</td>
</tr>
<tr>
<td>Slurry III</td>
<td>1</td>
<td>37</td>
<td>11</td>
<td>13</td>
<td>7</td>
<td>1</td>
<td>3</td>
<td>27</td>
</tr>
</tbody>
</table>
Experiments and equipment
The leaching tests were performed by using liquid/slurry (L/S) ratios of 0:1, 1:1, 1:5, and 1:10. In some cases, Na was analysed after reducing the pH to below 1 with 14 wt% HNO$_3$ solution. In addition to the leaching experiments, the pH of the slurries with and without the presence of solids was investigated. Clear filtrates were produced from each slurry by filtering the slurry through Whatman 42 filter paper. Five grams of slurry or filtrate was then diluted with water for several times, to obtain a final L/S ratio of 1000. After each dilution step, the samples were shaken and allowed to stabilise for 15 minutes before measuring the pH.

Definitions
The results of thermometric titration are discussed below with respect to the total caustic content of the liquid samples. The total caustic is defined as the total hydroxyl ion content comprising 1) the free hydroxyl ion content and 2) one mol hydroxyl ion per mol aluminate.

Results and Discussion

Particle size distributions
The particle size distribution in each bauxite residue slurry was measured in order to understand how much the dilution of the samples affects the size of the solids. The results are shown in Figures 1a-c.

![Figure 1](image)

**Figure 1:** Particle size distribution of each slurry at different dilution ratios

When the slurry samples were diluted with water, the size of particles in Slurries II and III did not change to a measurable extent, whereas the solids in Slurry I may have been affected slightly (Figure 1a). On the basis of Figures 1a-c, it is easy to conclude that dissolution of the flocs is not very significant when leaching is performed with increasing quantities of water without the presence of an acid.
Reduction of pH

Reduction of the pH is possibly the most important effect when a bauxite slurry is diluted with water. The pH has a great influence on the dissolution of alkali and metals from the residue. Bauxite residues have significant acid neutralising capacity, which makes the reduction of the pH challenging in practice. The reduction of the pH with an increasing dilution factor, with and without the presence of solid particles, is shown in Figure 2.

![Figure 2: Effect of L/S ratio and presence of suspended solids on the pH of bauxite residue samples. The L/S ratio is presented with linear (a) and logarithmic scales (b)](image)

Dissolution of Sodium and Aluminium

Figures 3a-b show clearly that the liquid phase of the sample is mainly responsible for providing the water-soluble sodium under the applied conditions. Figures 3c-d present similar results for aluminium, which is dissolved from the suspended solids of all slurries (Figure 3d). The extent of Al dissolution depends on the applied L/S ratio. The concentrations of dissolved sodium in the samples prepared by using 14 % HNO₃, measured similarly as above, are presented for various L/S ratios in Figures 3e-f. When a bauxite residue slurry is diluted with an acidic solution, the buffering solids dissolve gradually with the pH reduction. The observations regarding the dissolution of Na when the sample was prepared for analysis with acid can probably be associated with the dissolution of desilication products. A general conclusion from the sodium dissolution experiments is that leaching with water alone is not always effective at recovering sodium from the solid phase of bauxite residue slurries. Aluminium seems to be easier to recover without a significant reduction of the pH.
Figure 3: Concentrations of sodium (a-b) and aluminium (c-d) at different dilution ratios, with respect to the mass of slurry (a, c) and mother liquor ML (b,d). Concentrations of sodium in the samples and in the liquid phase of the samples when the samples were prepared by using 14 % HNO₃ (e,f).

**Dissolution of caustic compounds**

Thermometric titration was applied to investigate how large a proportion of the total sodium is leached from the caustic compounds. The comparison of atomic absorption spectroscopy and thermometric titration presented in Figure 4 provides useful information about the origin of sodium. It is clear to see that about 30 and 10 % of the sodium in the case of non-diluted Slurries I and III, respectively, comes from other sources than caustic compounds which release hydroxyl groups. However, the proportion of caustic increased when the samples were diluted with water.
Figure 4: Comparison of analysis results obtained by AAS and thermometric titration, expressed as Na$_2$O

Conclusions

The leaching behaviour of sodium, aluminium and caustic from bauxite residues was found to depend strongly on the applied L/S ratio. The leaching properties also varied with the composition of the slurry. The relative concentrations of total sodium, aluminium and caustic concentrations were clearly influenced by the L/S ratio as well. Preparation of samples by using an acidic solution instead of water increased the dissolution of Na from the solid phase.

References