Combined carbothermic reduction of bauxite residue and basic oxygen furnace slag for enhanced recovery of Fe and slag conditioning

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Abstract

Bauxite residue (BR) usually contains substantial amounts of Fe and Al however the extraction of these elements from BR is not economically viable due to relatively low levels in comparison to primary sources. Basic oxygen furnace slag (“BOF”, also called LD-converter slag) finds applications in industry; however, a sizeable amount is landfilled. In this study, a combined carbothermic reduction of BR and BOF slag was undertaken to increase the Fe produced and recovered to the metal phase. Lignite coke was the selected reducing agent due to its local availability. Furthermore, the high CaO content of BOF slag in combination with the available Al₂O₃ from BR favoured the attainment of a low melting slag. The slag was found to be enriched in oxides of ignoble elements, and the slag concentrate could be an attractive resource for valuable elements recovery. The preliminary smelting experiments and modeling work carried out for the carbothermic reduction of BR under BOF-slag addition confirmed an increase in produced metallic iron, values as high as 26% in comparison to fluxing with conventional fluxing agents were reported. Furthermore, there is feasibility for higher production of iron. Slag characterisation by mineralogical means showed that there is potential for refinement in the conditioning of the produced slags for downstream recovery of valuable elements including Al and Ti.

Introduction

Bauxite residue also referred to as red mud is an important by-product in the extraction of alumina via the Bayer process. In 2014, approximately 140 million tonnes of BR were produced, with an estimated 3 billion tonnes of stockpiled bauxite residue.¹ Effort into finding sustainable uses of BR spans over a century and numerous technically successful trials, however, the economics are usually unfavourable.¹² Consequently, only a small fraction of BR is used in a productive manner and the bulk of the material is disposed as waste. Disposal of BR is a problem due to a combination of the following: fine particle size, high alkalinity and large amounts as mentioned previously. According to the European Commission, BR is classified as a non-hazardous waste (Commission Decision 2000/532/EC).³
The red colour of BR is mainly attributed to the contained Fe in the form of hematite; other elements that are contained in considerable amounts in BR include oxides of Al, Ti and Si. Furthermore, smaller concentrations of elements including REEs, Sc, Ga, Cr, Ni and V can be found in BR. This renders BR a potential valuable secondary resource.

According to a thermodynamic evaluation the carbothermic smelting of BR would reduce the contained Fe, Ni, Na, Cr and V oxides to their metallic states in the temperature range 1400 to 1600 °C, reporting to the pig iron product except for the highly volatile Na which either stabilises in the slag with alumina or leaves the melt as gaseous Na. Furthermore, with an increase in temperature Si and Ti could also be reduced to a smaller extent and report to the pig iron product. The highly stable oxides report to the slag phase. The operating temperature and reductant amount have a direct influence on the extent of reduction and consequently dictate the distribution of elements between slag and pig iron. High temperatures or fluxing agents are a requirement for carbothermic smelting of BR due to the high alumina content that reports to the slag. Fluxes can also condition the slag for downstream processing, and examples of fluxes used for smelting of BR include lime, silica sand and wollastonite.

Literature reports about slag leaching post carbothermic reduction of BR under lime fluxing for Al recovery. Leaching of the slag for recovery of other valuable elements including Ti, REEs and Sc is reported in literature.

BOF slag is the main by-product generated during converter steelmaking. With the rapid growth in the steel industry over the past decades, the volume of BOF slag generated has increased tremendously. Disposal of the slag is a burden to the steel industry. Therefore, recycling of BOF slag is desirable to the steel industry for sustainability. BOF slags are mainly used as aggregates for road construction and as agricultural fertilizers. The chemical composition of BOF slag is dictated by the impurities present in the hot metal. The main constituents in BOF slag include oxides of Fe, Ca, Si, Mn and Mg. Carbothermic reduction of BOF slag for extraction of metallic Fe has been reported in literature. Complete utilisation of BOF slag to extract Fe and use the remaining gangue components (residual slag) would lead to achieving zero-waste for BOF slag.

In the current study, a preliminary investigation to recover Fe into a metal product (pig iron) from two industrial waste resources (BR and BOF slag) through a smelting process is investigated. The high CaO content of the BOF slag is a suitable flux for the BR, as the major gangue component of BR is Al₂O₃, which is characterised by high melting temperature and high viscosity and also to
compensate the neutralisation effect of FeO for SiO$_2$ and TiO$_2$ when Fe is formed. The produced slag concentrate can be utilised downstream for the recovery of Al and other valuable elements contained in BR by hydrometallurgical means.

**Experimental procedure**

The BR used for the experiments was sourced from an alumina producing facility in Greece and the BOF slag was sourced from a steel producing facility in Germany. The BR was dried over a period of 24 hours at 105 °C. A locally sourced lignite coke with a fixed carbon content of 87 wt% was used as the reducing agent during the smelting testwork. A significant amount of BOF slag was necessary to introduce sufficient fluxing of the BR, and to introduce a further resource in the form of Fe oxide for the smelting. As such, the additions of BOF slag and lignite coke were 30% and 10% of the BR, respectively. For baseline comparison, an experiment using lime (CaO = 95%) as a flux was used. The recipe for this reference experiment was as follows: lime (30% of the BR), and lignite coke (10% of the BR). Batch masses of 1.5 kg of BR with the additions as detailed above were prepared for the smelting tests. They were conducted in a refractory lined 100 KVA DC electric arc furnace (EAF), with a graphite crucible for containment of material during smelting. The smelting tests were conducted at 1500 °C for a holding time of 1 hour.

At the end of each experiment the power supply to the furnace was switched off, and the molten material was poured into a refractory lined mould for intermediate cooling, where the metal collects at the bottom of the mould. The cooled material was separated into slag and metal and then weighed. The products were subsequently prepared for analysis. The as received dried, BOF slag and produced slag samples were analysed by X-ray fluorescence (XRF) for bulk chemical analysis. Moreover, the BR and the milled slags were analysed via X-ray Diffraction (XRD) for mineralogical characterisation. The metal product was analysed by spark spectrometry. Furthermore, using as an input, BR, lignite coke and BOF slag, the thermochemical equilibrium composition of the system at 1500 °C was calculated using FactSage 6.4 Equilibrium module. The chemical composition of the raw materials and product streams (both experimental and theoretical) are presented in Table 1.

The ternary phase diagram detailing the final slag from the preliminary carbothermic reduction experiments and from the theoretical calculations as predicted by FactSage 6.4 for a system of varying Al$_2$O$_3$, CaO and SiO$_2$ composition and constant TiO$_2$ composition at 7.5 wt% (other BR slag oxides are omitted from the calculation detailing the liquid phase between 1200 and 1800 °C) is shown in
Figure 1. The main component of BR, namely Al₂O₃, occupies the lower left corner of the ternary phase diagram, and this region is characterised by high liquidus temperatures. Similarly, BOF slag has a high liquidus temperature due to high CaO content. The phase diagram below shows that low melting slags are achievable via fluxing of BR with BOF slag as detailed in the phase diagram.

Table 1. Chemical composition of the feed materials of interest (bauxite residue and BOF slag) and product streams (slag and metal)

<table>
<thead>
<tr>
<th>Components (wt%)</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bauxite residue</td>
<td>43.5</td>
<td>24</td>
<td>10.2</td>
<td>5.5</td>
<td>5.6</td>
<td>2.0</td>
</tr>
<tr>
<td>BOF slag</td>
<td>23.1</td>
<td>1.4</td>
<td>45.1</td>
<td>14.4</td>
<td>1.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Slag 1 (baseline exp.)</td>
<td>1.7</td>
<td>33.8</td>
<td>49.0</td>
<td>6.9</td>
<td>6.9</td>
<td>0.2</td>
</tr>
<tr>
<td>Slag 2 (30% BOF slag-exp.)</td>
<td>3.7</td>
<td>34.5</td>
<td>31.6</td>
<td>15.7</td>
<td>7.8</td>
<td>2.9</td>
</tr>
<tr>
<td>30% BOF slag (Theoretical)</td>
<td>3.6</td>
<td>35.1</td>
<td>31.7</td>
<td>15.2</td>
<td>7.4</td>
<td>2.4</td>
</tr>
<tr>
<td>40% BOF slag (Theoretical)</td>
<td>3.4</td>
<td>32.5</td>
<td>35.0</td>
<td>15.8</td>
<td>7.0</td>
<td>2.3</td>
</tr>
<tr>
<td>50% BOF slag (Theoretical)</td>
<td>3.5</td>
<td>30.2</td>
<td>37.5</td>
<td>16.2</td>
<td>6.6</td>
<td>2.1</td>
</tr>
<tr>
<td>Metal 1 (30% Lime)</td>
<td>0.6</td>
<td>0.01</td>
<td>0.3</td>
<td>0.1</td>
<td>0.1</td>
<td>4</td>
</tr>
<tr>
<td>Metal 2 (30% BOF slag)</td>
<td>0.1</td>
<td>0.32</td>
<td>0.46</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 1. Ternary phase diagram as predicted by FactSage 6.4 for a system of varying Al₂O₃, CaO and SiO₂ compositions and constant TiO₂ composition of 7.5 wt% detailing the liquid phase between 1200 and 1800 °C
Results and Discussion

The chemical analyses of both slags report a low residual Fe remaining in the slag, an indication of good Fe recovery to the metal even at the applied small scale. Furthermore, the Al\textsubscript{2}O\textsubscript{3} content of both slags was successfully diluted rendering both slags molten at the targeted operating temperatures of between 1500 and 1550 °C (see Figure 1). Contamination of the metal by elements contained in the feed materials seem minimal for both metal products; this could be partly attributed to the low but significant residual Fe in the slag which could suppress the reducing potential in the system. The elemental recoveries of the major elements are summarised in the Table 2.

Table 2. Elemental distribution to product streams (wt% of mass fed)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Product</th>
<th>Fe</th>
<th>Al</th>
<th>Ca</th>
<th>Ti</th>
<th>Si</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>30% Lime</td>
<td>Slag</td>
<td>2.9</td>
<td>105.6</td>
<td>95.0</td>
<td>92.4</td>
<td>94.1</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>Metal</td>
<td>87.9</td>
<td>-</td>
<td>-</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>90.9</td>
<td>105.6</td>
<td>95.0</td>
<td>93.2</td>
<td>94.1</td>
<td>7.5</td>
</tr>
<tr>
<td>30% BOF-slag</td>
<td>Slag</td>
<td>5.0</td>
<td>96.8</td>
<td>91.3</td>
<td>90.1</td>
<td>109.6</td>
<td>97.9</td>
</tr>
<tr>
<td></td>
<td>Metal</td>
<td>91.5</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>1.8</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>96.5</td>
<td>96.8</td>
<td>91.3</td>
<td>90.3</td>
<td>111.4</td>
<td>97.9</td>
</tr>
</tbody>
</table>

The main gangue components (Al, Ca, Ti and Si) are collected to the slag as expected. High total recoveries of elements, close to 100%, for the main elements found in BR namely Fe, Al and Ca, Ti and Si are an indication of a good mass balance characterised by accurate chemical analyses and accounted for masses. Although the recovery of Al to the slag is over 100%, this is acceptable as it is only about 5% over complete recovery of Al. Sodium undergoes reduction during the smelting reduction as a function of the reducing potential, and the volatile sodium reports to the off-gas stream. However, this is suppressed under acidic conditions as Na activity in the slag tends to be lower than under basic conditions. This explains the low Na recovery to the slag under lime fluxing, and high Na recovery under BOF-slag fluxing. Slags with high Na content could be limited in terms of possible applications.

High Fe recoveries to the metal were achieved, and it must be noted that some metal entrainment in the slag was observed. When the entrained Fe in the slag is accounted for, recoveries of Fe in excess of 95% to the metal are achievable. The Fe contained in the BOF slag is also reduced during smelting, and Figure 2 details the mass percentage of Fe to BR reporting to the metal stream as a function of flux addition. The Fe recovery to the metal is fixed at 96% for all the cases to represent realistic prediction.
In the baseline case for every 100 kg of BR processed, 29 kg of Fe report to the metal. The addition of 30% BOF slag results in 34 kg of Fe reporting to the metal, and equates to a 16% increase in comparison to the baseline case. Furthermore, at 50% BOF slag additions, the iron reporting to the metal increases to 37 kg for 100 kg of processed BR and this represents a 26% increase in the produced Fe that reports to the metal.

The combined smelting of the BR with BOF slag has an effect in the slag and metal chemistry as shown earlier. For further characterisation of the slag, especially when considering using the slag for downstream processing to recover valuable elements, the mineralogy of the slag becomes important. The XRD patterns for BR, baseline slag and BOF slag fluxed slag are presented in Figure 3.

The XRD patterns demonstrate that the BR was transformed minerallogically during the smelting process. Furthermore, the two slags show slightly different mineralogical results. The main slag phases formed from the baseline case are calcium aluminate and gehlenite as can be seen in Figure 3, while for BOF slag fluxing the formation of calcium silicates over calcium aluminates is favoured. The presence of calcium silicates and specifically dicalcium silicate phases in these BR slags could be exploited, as slow cooling of such slags could promote the phase change of dicalcium silicate from beta to gamma form, producing a self-disintegrating slag due to the expansion associated with the phase change as reported in literature. This could prove useful as a self-disintegrating slag would...
require minimal sample preparation for the downstream leaching for valuable metals recovery.

Ti is contained in the CaTiO$_3$ phase for both slags. The mineralogy of these slags is comparable to slags reported in literature for the recovery of Al hydrometallurgically$^8,9$. The presence of dicalcium silicates, also supported by the high SiO$_2$ content of the slags, slow cooling could be investigated post smelting, targeting self-disintegrating slags for downstream leaching.

**Figure 3.** XRD patterns of BR and the produced slag concentrates after the smelting process

**Conclusions**

Combined smelting of BR and BOF slag was successfully undertaken. The resulting slag has a lower melting point which allows for lower operating temperatures. Experimental results were in good agreement with the theoretical prediction of the smelting process for the combined smelting of BR and BOF slag. Furthermore, the combined smelting resulted in higher Fe throughput in comparison to the baseline case where BR was fluxed with lime. An increase in Fe throughput as high as 26% was predicted under the combined smelting of BR and BOF slag and higher Fe throughput figures are possible since the flux additions of BOF slag during smelting were relatively conservative. This could improve the attractiveness of a combined smelting of these two materials as a source of Fe. The produced metal phase including impurities from the proposed smelting process will be studied further as the quality of the produced metal is important for its tailoring for the market.
Despite dilution slags with high Al$_2$O$_3$ content were achieved from the smelting tests. Furthermore, an enrichment of Ti to the slag phase was reported. Ti was found to be contained in perovskite. The mineralogy of the slags from combined smelting of BOF slag and BR confirmed that the slags mainly contain gehlenite and calcium silicates, while calcium aluminate and gehlenite containing slag was confirmed for the baseline case. The produced slag could serve as a concentrate for recovery of valuable elements including Al and Ti via hydrometallurgical treatment or conditioned further for optimal recovery of the valuable elements.

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