Iron Separation from Bauxite Through Smelting-Reduction Process

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Abstract
In the alumina production process through the dominant commercial Bayer process red mud, which is not consumable and causes serious environmental challenges is produced. Alternative sustainable process for bauxite treatment to alumina is the Pedersen process, which was patented in 1920s and was in operation in Norway for many years before closing down due to economic reasons. In this process, bauxite is smelted and reduced, which yields pig iron and a calcium aluminate slag. Alumina is further produced from the slag through a hydrometallurgical process. In the present study, different bauxites with different chemical compositions are smelted with lime and reduced by coke. The smelting reduction is studied through chemical analysis and microstructural study. It is shown that complete separation of iron from the slag is possible and in addition the process is effective for partial separation of the other impurities such as Ti, Si, V, from the Al₂O₃-containing slag.

Keywords
Bauxite • Bayer process • Pedersen process • Alumina • Smelting • Reduction • Pig iron • Slag

Introduction
Aluminum is the third most abundant element in the earth’s crust, 8.3 wt%, and the most common crustal metal [1]. Due to its chemical reactivity it only exists in oxidized form. The principal ore of aluminum extraction today is bauxite, although aluminum is found in other types of ores [1]. Aluminum is produced in three stages, first it is mined, then made into alumina (Al₂O₃) through the Bayer process, and finally the alumina is reduced to aluminium by the electrolytic process Hall-Héroult [1]. To produce one ton of aluminium it is needed two tons of alumina and approximately four tons of bauxite [2]. Figure 1 shows that global alumina production has doubled the last 15 years [3]. The increase in alumina production by Bayer process also increase the amount of the problematic waste product, red mud. It is a loss of iron from the bauxite ore, and although utilization of red mud is being investigated, it has not been solved. So the waste is growing in a rate of one to one and a half ton of red mud per one ton of alumina being produced [4]. It is, therefore, of high interest to look at an alternative method, that was used for over 40 years in Norway; the Pedersen Process. It eliminates the red mud problem, produces saleable grey mud, extract pig iron, has lower CO₂ emissions than Bayer, can be used for a wider range of bauxite types with a better overall alumina yield.

The purpose of the present work is to study the pyro-metallurgical part of the Pedersen process, which is believed to be a more sustainable process compared to Bayer process and is described in Section “Pedersen Process”. The main focus is about the distribution of the elements existing
in bauxites between the produced iron and slag phases under different process conditions.

**Bauxite**

Bauxite is mostly found in countries close to the equator, like Australia, China and Brazil being the top producers per 2015 [6]. Bauxite comes in a wide range of textures, colors and content, and is largely composed of a mixture of minerals that contains different amounts of hydrated aluminum oxides and impurities like iron oxide, silica and titanic dioxide [7]. Three types of minerals are found in bauxite: gibbsite, boehmite and diaspor. Gibbsite is an aluminium trihyrate (Al$_2$O$_3$.3H$_2$O), while boehmite ($\gamma$-AlO(OH)) and diaspor (α-AlO(OH)) are two forms of alumina monohydrate. Bauxite ore contains usually iron minerals such as goethite (FeOOH) and hematite (Fe$_2$O$_3$), titanium oxide in the form of ilmenite (FeTiO$_3$), silicon oxide (SiO$_2$), etc. The processing of the bauxites for alumina extraction is dependent on the ore composition and the presence of impurities like iron, silicon and titanium [7]. The most dominant being mined today is gibbsite and boehmite as they are more economical to process [2].

**Bayer Process**

The main commercial way to produce alumina is through the well-known Bayer process, patented by Carl Josef Bayer in Austria in 1888 [8, 9]. Typically, it produces smelter-grade alumina of 99.5% Al$_2$O$_3$ [10]. The process simple flowsheet is shown in Fig. 2. In this hydrometallurgical process, the bauxite is digested with a hot solution of caustic soda (NaOH) and lime (CaO). The main reactions in digestion yielding sodium-aluminate solution is shown in Eq. 1.

$$\text{Al}_2\text{O}_3(s) + 2\text{NaOH}(aq) \rightarrow 2\text{NaAlO}_2(aq) + \text{H}_2\text{O}(v) \quad (1)$$

The products of the digestion step are separated in a clarification process where undissolved impurities such as silica and iron settles as mud, which is called red mud residue [8]. Red mud is one of the largest industrial by-products today (3 billion tons in 2010) [11]. As it does not have a commercial value, several different methods is used for its deposition, including deep-sea disposal, lagooning and dry stacking and disposal. The trend today is to dry stack or use dry cake disposal [11]. Even so, the red mud can cause serious environment problems, as it has a high alkalinity [4]. The sodium-aluminate solution product is further treated and aluminum hydroxide is precipitated from the solution according to reaction described in Eq. 2.

$$\text{Al(OH)}_4^{-}(aq) + \text{Na}^+(aq) \rightarrow \text{Al(OH)}_3(s) + \text{Na}^+(aq) + \text{OH}^- (aq) \quad (2)$$

In the precipitation step a caustic solution is generated, which is reused in the digestion step after concentration control through an evaporation step for dewatering. The main product of the precipitation step is aluminum hydroxide Al(OH)$_3$. A portion of fine Al(OH)$_3$ particles are
separated and used in the precipitation step in order to improve the process kinetics. The aluminum hydroxide is further calcined in calcination furnace by using fuel i.e. methane and alumina is produced. The calcination reaction can be written as shown in Eq. 3.

$$2\text{Al(OH)}_3(s) \rightarrow \text{Al}_2\text{O}_3(s) + 3\text{H}_2\text{O} \ (v)$$  \hspace{1cm} (3)

**Pedersen Process**

Alternative process for alumina production is the Pedersen process, which has no red mud production problem. This process was patented in Norway in the 1920s by Harald Pedersen, and was used for over 40 years before it was closed down due to economic reasons [13]. It was developed to process ferruginous bauxites with high TiO$_2$ and SiO$_2$ content, as the Bayer process had limitations in processing these [8]. The first step in this process is the main difference compared to Bayer (see Fig. 3). Instead of digestion and clarification, resulting in red mud, the first step in the Pedersen process is to smelt bauxite, lime as flux and coke as reduction agent together, and the iron oxide is then reduced to molten iron and can be taken out and reused in ferrous industry [8]. The process does not only eliminate the red mud problem, but also one can extract pig iron. The main reactions for the smelting-reduction step are the reduction of iron oxides i.e. Fe$_2$O$_3$ (Eq. 4), and slag formation from bauxite and lime (Eq. 5):

$$2\text{Fe}_2\text{O}_3(s) + 3\text{C}(s) \rightarrow 4\text{Fe}(s) + 3\text{CO}_2(g)$$  \hspace{1cm} (4)
\[ \text{Al}_2\text{O}_3(s) + \text{CaO}(s) \rightarrow (\text{CaO} \cdot \text{Al}_2\text{O}_3)(s) \]  \hspace{1cm} (5)

As Fig. 3 shows, the produced calcium-aluminate slag, in the smelting-reduction furnace, is reduced in size by crushing or milling, before going through a wet stage process, with digestion and washing. The slag is digested by using a sodium carbonate solution, and this leaching stage can be chemically described in Eq. 6:

\[ (\text{CaO} \cdot \text{Al}_2\text{O}_3)(s) + \text{Na}_2\text{CO}_3(l) \rightarrow 2\text{NaAlO}_2(l) + \text{CaCO}_3(s) \]  \hspace{1cm} (6)

After the digestion step, the solution goes through a multiple step washing stages with thickeners, and a grey mud is extracted. As with pig iron, grey mud is a consumable by-product (cement, fertilizer, among others) [13]. The overall chemistry in this process is simple, but there is a large number of side-reactions which makes it complicated. In the precipitation section \( \text{CO}_2 \) is added to the \( \text{Na}_2\text{Al}_2\text{O}_3 \) solution in vessels containing slow moving stirrers, and alumina hydroxide precipitates [13] as described in Eq. 7:

\[ 2\text{NaAlO}_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \rightarrow \text{Al}_2(\text{OH})_3(s) + \text{Na}_2\text{CO}_3(aq) \]  \hspace{1cm} (7)

The sodium carbonate recycles back into the digestion step, while the precipitated alumina hydroxide is calcined to alumina powder [13] through the chemical reaction (Eq. 3) mentioned above.

**Experimental Procedure**

The employed experimental work in the present study is described as follows.

**Materials**

Three different types of bauxites were used in this study. The bauxites mainly contained the phases kaolinite (\( \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \)), gibbsite (\( \text{Al}(\text{OH})_3 \)) and hematite (\( \text{Fe}_2\text{O}_3 \)). The samples were delivered in ground and calcined form, and their chemical composition is presented in Table 1.

The experiments were done in graphite crucibles with 40 mm outside diameter, 32 mm inside diameter and 50 mm height. Three different mixture of materials were put in the crucibles.

1. Bauxites (A, B, C);
2. Bauxite B with added CaO;
3. Bauxite B with added CaO and coke.
Table 1  Chemical composition of bauxite samples in weight% on dry basis

<table>
<thead>
<tr>
<th>Bauxites</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>FeO</th>
<th>Total wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>55.75</td>
<td>33.50</td>
<td>6.25</td>
<td>1.75</td>
<td>2.74</td>
<td>100</td>
</tr>
<tr>
<td>B</td>
<td>59.77</td>
<td>15.93</td>
<td>21.84</td>
<td>2.46</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>C</td>
<td>71.53</td>
<td>17.50</td>
<td>8.93</td>
<td>2.03</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

Fig. 4  Induction furnace used for smelting-reduction experiments

The CaO, with purity around 98%, was mixed in order to obtain a 40% CaO and 60% Al₂O₃ slag, while the coke addition was 50% more than the stoichiometric required to complete the reduction of the hematite (2Fe₂O₃ + 3C = 4 Fe + 3CO₂(g)). The content of the coke was 97 wt% fix-C, 2 wt% ash and 0.41 wt% volatile matter. The bauxites were further ground in a vibratory disc mill, mixed and put in graphite crucibles for smelting.

Smelting-Reduction

The smelting-reduction experiments were done in an induction furnace illustrated in Fig. 4. A thermocouple type C was used for measuring the temperature. The thermocouple was covered in an insulating tube inserted in a graphite tube, and placed in the large graphite crucible in between the samples. The heating rate was approximately 20 °C/min up to 1600 °C, followed by keeping at this temperature for one hour. Then, the samples were cooled down very slowly at 5 °C/min to the room temperature.

SEM Analysis

All the samples (graphite crucibles containing metal and slag phases) were machine cut, imbedded in epoxy, grinded and polished. The crucibles were cut from the middle so that the cross section from bottom of crucible to the top of solidified slag can be studied. The microstructure and composition of the phases were studied by Scanning Electron Microscopy (SEM) supported by Energy Dispersive Spectroscopy (EDS).

Results and Discussion

The results of the smelting-reduction and SEM analysis are presented and discussed as follows.
Smelting-Reduction of Single Bauxites

All the bauxite materials became molten at the applied temperature (1600 °C) as observed from the crucibles top. It was observed that the smelted bauxites without any additions give porous structure, after cooling down to the room temperature. The complete melting of the all bauxites is proved with regard to the formation of a continuous slag matrix from all the samples as illustrated in Figs. 5, 6 and 7 for three types of bauxites. In these figures, the grey phase is slag and the bright particles distributed in it are metal particles. SEM study of the samples indicated that the sample containing highest amount of iron (sample B) is more porous. The SEM images (Figs. 5, 6 and 7) show that iron oxides were reduced to metallic iron in all samples. The images show that the amount and size of the iron particles is increased with increasing the iron oxide content of the bauxite. Moreover, the particles were equally distributed throughout the samples and not very large iron particles were found in the samples. This may be due to the high viscosity of the slag phases in all the samples, which are high in Al₂O₃.

EDS and X-ray mapping of the elements in the smelted-reduced bauxites clearly shows the complete iron oxide reduction as shown typically for the bauxite B in Fig. 8. As seen, there is almost no Fe in the slag phase, while it contains Al, Ti, Si, and O. Hence, we may say that the slag contains Al₂O₃, TiO₂ and SiO₂. In addition, partial

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Fig. 5 SEM images of smelted-reduced bauxite A which contained 6% iron oxide

Fig. 6 SEM images of smelted-reduced bauxite B which contained 22% iron oxide

Fig. 7 SEM images of smelted-reduced bauxite C which contained 9% iron oxide
separation of silicon and titanium oxides is observed, which shows that the slag matrix contains the both three oxides or a ternary $\text{Al}_2\text{O}_3$-$\text{TiO}_2$-$\text{SiO}_2$ slag, and the slag contains significant $\text{Al}_2\text{O}_3$-rich particles, most likely pure alumina particles.

**Smelting-Reduction of Bauxite with Lime**

By adding CaO into the bauxite (with CaO:$\text{Al}_2\text{O}_3 = 2:3$) significant differences were observed. The iron particles produced through the reduction have largely increased in size, and are positioned in the bottom of the crucible as illustrated in Fig. 9. This is due to the formation of a more fluid calcium-aluminate slag by using the flux compared to the smelting-reduction of only bauxite. The metal particles contain a lot of randomly distributed carbon flakes (Fig. 9), presumed to be from the graphite crucible in contact with the smelted iron (approximately 7 wt%). When the bauxite was smelted and reduced without CaO, the produced metal micro-droplets were surrounded by the slag phase and with no contact to the graphite crucible and therefore they did not contain significant amount of dissolved carbon, or graphite flakes after solidification. In contrast, when lime is used, the metal drops are settled in the bottom of crucible and they will get the carbon saturation level in contact with the graphite crucible. This carbon appeared in the form of graphite flakes in solidification due to the much lower solubility of carbon in solid iron. EDS analysis of the slag shows that it mainly contains Ca, Al, Si, O and Ti elements (Fig. 9). Carbon peak is from the sample coating by carbon, and the slag does not have significant carbon.

The microstructural analysis of the slag phase and X-ray mapping showed that the produced calcium-aluminate slag contains different phases with different amounts of the various oxides in them as illustrated in Fig. 10. Compared to the smelted-reduced bauxite without lime, there is no single $\text{Al}_2\text{O}_3$-rich phases in the slag and the co-existing phases contain other oxides as well. In Fig. 10 we see Ca and Mg elements, which were not observed when only bauxites were treated; Ca and Mg are originated from the consumed lime.

**Smelting-Reduction of Bauxite with Lime and Coke Addition**

Addition of coke does not seem to have an effect on the size of the pig iron particles. This may indicate that the process time as 60 min have been long enough for the reduction of iron oxides in the both experiments with or without coke. In principle, however, we expect to have faster reduction of the iron oxides with the addition of coke particles due to...
Fig. 9 SEM image of bauxite B smelted with CaO (on the left), and EDS analysis of the slag phase

Fig. 10 X-ray mapping of the slag phase produced through the smelting-reduction of bauxite B with lime

providing higher reaction interfacial area. Experiments in short reaction times may give better overview about the rate of iron oxide reduction.

The EDS and X-ray mapping of the elements of the bauxite samples smelted with lime show that vanadium, and titanium precipitate in a layer around the iron metal particle (Fig. 11), which are most likely carbides. These carbides are formed during the solidification of the metal phase from the dissolved Ti and V particles in the liquid iron as its mechanism presented elsewhere [5]. Obviously, an advantage of bauxite treatment through the smelting-reduction process is the partial removal of impurities such as Si, Ti, V, in addition to the complete removal of iron, which is very beneficial for further hydrometallurgical treatment of the produced calcium-aluminate slag and production of less process by product.
Fig. 11 X-ray mapping of a metal particle formed in the smelting-reduction of bauxite B with lime

**Conclusion**

The smelting-reduction of three types of bauxite with different amounts of iron oxides were carried out. In addition, the high iron-containing bauxite was treated through lime addition and lime + coke addition. The following results have been obtained:

(i) The smelting-reduction of bauxite is a feasible way to separate iron from bauxite and produce a high alumina slag as feedstock for further alumina production.

(ii) Complete reduction of iron oxides occurs, which yields pig iron. The separation of the produced molten iron phase from the slag is the best when lime is used, due to providing a low viscose calcium-aluminate slag.

(iii) Different phases co-exist in the slag depending on the lime addition. When bauxites without lime were treated, $\text{Al}_2\text{O}_3$-rich particles in an $\text{Al}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2$ slag matrix were formed. But, when lime was used, different three-four component slag phases were formed which all had different amounts of $\text{Al}_2\text{O}_3$.

(iv) The smelting reduction of bauxite with lime indicated partial removal of Si, Ti, V from the slag into the iron. Not significant difference between the samples with and without the use of coke was observed, indicating the fast reduction of iron oxides from the smelted bauxite, and calcium-aluminate slag.

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