Reductive Smelting of Red Mud for Iron Recovery

Frank Kaußen*, and Bernd Friedrich

DOI: 10.1002/cite.201500067

The reductive smelting of red mud is calculated and investigated regarding the necessary amount of reduction agents and the final composition of the pig iron phase and the mineral (slag) phase as products of the process. Liquidus temperatures of slags with three different compositions are calculated during the reduction process and in dependency of the remaining sodium content in the slag. All calculations were done with FactSage and the results are confirmed by smelting experiments in a lab scale electric arc furnace.

Keywords: Bauxite residue, Carbothermic reduction, Iron recovery, Red mud

Received: June 02, 2015; revised: August 10, 2015; accepted: August 31, 2015

1 Introduction

Red mud is the so-called bauxite residue after the solid-liquid separation from alkaline high pressure leaching of aluminum bearing bauxite ore. Depending on the composition of the primary mineral deposit, 4 – 7 t bauxite are necessary to gain 2 t alumina in order to produce 1 t aluminum [1]. The leaching process is very selective on the extraction of aluminum and gallium and the undissolved minerals remain in the residue. Due to its high hematite content, the bauxite residue has a reddish color and is, therefore, called red mud.

With each ton of primary produced aluminum, 1 – 2.5 t red mud are generated [2, 3]. The composition of red mud varies strongly dependent on the composition of the original bauxite and the employed process parameters (digestion temperature, caustic concentration, digestion time, etc.). Tab. 1 shows the average ranges in composition of commonly produced red muds. It can be seen that the predominant phases are iron compounds like hematite or goethite which can be easily recovered by carbothermic reduction.

Literature reports many different ways of reductive sintering with magnetic separation [4 – 6] or recently microwave assisted carbothermic reduction [7]. But in many cases red mud has been smelted. Thereby red mud is mixed with fluxes and coke and either pelletized or directly smelted. The pellets are heated up and get pre-reduced before the temperature was raised above the liquidus temperature to assure a complete fusion of the material. Thereafter the metal phase is easily separated and the remaining and crushed slag can undergo a subsequent magnetic separation to recover the remaining small pig iron droplets in the slag [8, 9]. But the mixture can also be smelted directly like it was successfully done for instance during the recent research project ENEXAL [10]. In many cases lime or dolomite are used as additive to lower the slag viscosity and improve the slag handling [11, 12]. According to the selection of additives and the choice of cooling conditions a self-disintegrating slag phase can be obtained which is further treated in order to recover the remaining valuable metals like aluminum or titanium in a subsequent leaching process [11, 13]. Especially Logomerac [12] and Ziegenbalg [13] conducted experiments of red mud smelting with pig iron recovery in an electric arc furnace. The composition of the gained pig iron is shown in Tab. 2.

The use of red mud as a substitute or in addition to iron ore is not realized yet due to the high alkaline content of the slag which causes serious problems with the refractory of installed blast furnaces. Moreover, the alkaline content is a criterion for the further utilization of the produced slag and limits the range of applications for example in the construc-

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Table 1. Composition of different red muds and composition of the raw material used in the experiments.

<table>
<thead>
<tr>
<th>Component</th>
<th>Average red mud</th>
<th>Red mud Lünen (Germany)</th>
<th>After re-leaching</th>
<th>After re-leaching with CaO (CaO/SiO₂ ~ 0.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>30 – 50</td>
<td>29.5</td>
<td>35.5</td>
<td>34.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10 – 20</td>
<td>27</td>
<td>18.3</td>
<td>17.7</td>
</tr>
<tr>
<td>SiO₂</td>
<td>5 – 20</td>
<td>13.1</td>
<td>14.9</td>
<td>15</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3 – 15</td>
<td>8</td>
<td>9.3</td>
<td>9</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3 – 7</td>
<td>7</td>
<td>9.3</td>
<td>9.1</td>
</tr>
<tr>
<td>CaO</td>
<td>1 – 8</td>
<td>3.8</td>
<td>4.7</td>
<td>7.7</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>–</td>
<td>0.35</td>
<td>0.41</td>
<td>0.4</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>–</td>
<td>0.22</td>
<td>0.25</td>
<td>0.27</td>
</tr>
<tr>
<td>SO₃</td>
<td>–</td>
<td>0.47</td>
<td>0.5</td>
<td>0.58</td>
</tr>
</tbody>
</table>

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following test trials. 

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fluorescence and the aluminum values in Tab. 1 are con-

mite). The exact aluminum content is measured by X-ray 

X-ray diffraction patterns show the predominant phases are 

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high amounts of remaining alumina. In the past, high 

The original composition is shown in Tab. 1 and indicates 

vapor re-oxidizes in the off-gas stream \([15]\).

immediately evaporates. According to Eq. (2) the sodium 

metallic sodium is very low (897 °C \([14]\)) and means that 

reduced sodium at process temperatures of >1400 °C 

immediately evaporates. According to Eq. (2) the sodium 

vapor re-oxidizes in the off-gas stream \([15]\).

\[
\text{Na}_2\text{O}_{(\text{liq,sl})} + \text{C}_{(s)} \rightarrow 2\text{Na}_{(g)} + \text{CO}_{(g)} \quad (1)
\]

\[
4\text{Na}_{(g)} + \text{O}_{2(g)} \rightarrow 2\text{Na}_2\text{O}_{(s)} \quad (2)
\]

Ziegenbalg reports that it is, therefore, possible to reduce the alkaline content in the slag after the reducing treatment to levels below 0.1 wt % in total.

This work is aimed on the theoretical investigation and partly practical verification of the smelting behavior of three different bauxite residue mixtures. Special focus is set on the final composition of metal and slag phase and the calculated physical properties of the slag with regard to the liquidus temperature and viscosity as the main important characteristics.

## 2 Materials

The examined red mud comes from the landfill of the former “Vereinigte Aluminiumwerke” near Luënen, Germany. The original composition is shown in Tab. 1 and indicates high amounts of remaining alumina. In the past, high throughputs and cheap but poorly digestible bauxites as raw material prohibited a high alumina recovery. Therefore, X-ray diffraction patterns show the predominant phases are hematite and still aluminum hydroxides (gibbsite and boehmite). The exact aluminum content is measured by X-ray fluorescence and the aluminum values in Tab. 1 are converted into alumina as quite common in literature. Therefore, the sum of all components does not reach 100 %. This original red mud from landfill is one material for the following test trials.

Moreover, the entire research project includes a recovery of the main parts of the remaining alumina content. Thereby the red mud from the landfill is leached a second time employing the Bayer process with optimized parameters. From this second leaching a red mud originates with the composition called “after re-leaching” (see Tab. 1) which is also examined for iron recovery.

The third examined raw material for carbothermic iron recovery experiments is presented in the last column of Tab. 1. In this case small amounts of lime are added during the second leaching of the initial red mud in order to increase the recovery of alumina in the leaching step. Experiments confirmed an increased alumina yield of about 10 % since the molar ratio CaO/SiO₂ increased from 0.31 in the initial red mud to 0.5 by the addition of lime. Thus, the remaining leaching residue is increased in its lime content while the other constituents are slightly diluted.

## 3 Prior Calculations and Simulations

During the reductive smelting process the entire material will be smelted and transferred into a liquid state. Thus, the mineralogical composition of the raw material is totally destructed, crystal water is driven out and the minerals such as sodalite, calcium aluminate or perovskite are dissolved and diluted in the molten slag.

The reaction temperature is assumed as 1650 °C in order to assure a superheat of the slag accompanied by low slag viscosities. Moreover, the experiments are conducted in an electric arc furnace. This furnace type is preferred due its easy operation and low off-gas volume. But the temperature distribution inside the furnace is not homogeneous. The desired temperature is 1550 °C, but in the arc spot temperatures of 1650 °C are most likely.

According to Eqs. (3) and (4) for the carbothermic reduction of the entire hematite content the needed carbon amount per kg input material is calculated as 66.5 g in case of the original red mud, 80.1 g and 78.3 g in case of the re-leached red mud with lime addition.

\[
\text{Fe}_2\text{O}_3_{(\text{liq,sl})} + \text{C}_{(s)} \rightarrow 2\text{FeO}_{(\text{liq,sl})} + \text{CO}_{(g)} \quad (3)
\]

\[
\text{FeO}_{(\text{liq,sl})} + \text{C}_{(s)} \rightarrow \text{Fe}_{(\text{liq})} + \text{CO}_{(g)} \quad (4)
\]

However, this calculation neglects the loss of reducing agents due to the co-reduction of other slag components like sodium oxide (see Eq. (1)) and the formation of sub-

oxides. In this case the comparable high titania content can be partially reduced to the trivalent state as TiO₂. These titania reductions are well known from ilmenite smelting processes and follow Eq. (5). The relation between the FeO content and the amount of formed TiO₂ is shown in Eq. (6).

\[
2\text{TiO}_2_{(\text{liq,sl})} + \text{C}_{(s)} \rightarrow \text{Ti}_2\text{O}_3_{(\text{liq,sl})} + \text{CO}_{(g)} \quad (5)
\]

\[
\text{Ti}_2\text{O}_3_{(\text{liq,sl})} + \text{FeO}_{(\text{liq,sl})} \rightarrow 2\text{TiO}_2_{(\text{liq,sl})} + \text{Fe}_{(\text{liq})} \quad (6)
\]

Pistorius [16] calculated the equilibrium from Eq. (6) for pure ilmenite slags and compared it with the observed

| Table 2. Pig iron composition in experiments by Logomerac [12] and Ziegenbalg [13]. |
|-----------------|-----------------|-----------------|
| C               | 3.8 – 4.5       | 4.2 – 5         |
| Si              | 0.5 – 3         | 0.3 – 0.6       |
| Ti              | 0.1 – 0.3       | 0.2 – 0.7       |
| Cr              | 0.2 – 0.4       | –              |
Ti₂O₃/TiO₂ distribution in real industrial ilmenite smelter slags. It is shown that the Ti₂O₃/TiO₂ ratio increases with decreasing FeO content up to ~3 at 1650°C and carbon saturation in contact with metallic iron containing 2 wt% carbon. Higher temperatures increase this ratio. Nevertheless, industrial slags show lower ratios concluding that the equilibrium is not reached due to the influence of other slag components.

Moreover, the produced pig iron phase has an absorption capacity of carbon. The dimension of these secondary reactions is calculated with the modeling software FactSage® (version 6.4). The results are exemplarily shown in Figs. 1 and 2.

It can be seen from Fig. 1 that firstly the hematite is reduced to FeO. At about 15 g carbon addition the co-reduction of titania to Ti₂O₃ starts but stagnates on a low level. Only 15–35 % of the titania is reduced to Ti₂O₃. By adding 26 g carbon per kg re-leached red mud, the hematite is almost completely converted into FeO (remaining Fe₂O₃ content < 0.9 wt%). If the addition of the reducing agent is further increased, a phase of metallic iron will be produced and the FeO content of the slag declines. At about 80 g carbon addition the FeO activity descends rapidly and the titania activity increases dramatically which leads to a significant titania reduction. At 87.5 g carbon addition the iron oxide content in the slag is below 1 wt %, so the reduction is completed.

Higher additions of reducing agents result in a contamination of the metal phase as shown in Fig. 2. The metal phase firstly forms after the addition of 26 g carbon and at about 80 g addition carbon is even dissolved in the metal phase. At about 90 g carbon addition the silica reduction to...
metallic silicon that is collected in the metal phase starts and at about 96 g carbon the reduction to titanium slightly begins (threshold 0.1 wt %). Thus, due to the co-reduction of titania and the carbon dissolution in the metal phase 88 g of carbon are needed in case of the treatment of re-leached red mud, which is about 110 % of the amount calculated by the simplified calculation only considering Eq. (1). The same calculations can be made for the also tested red mud directly from the landfill and the re-leached red mud with lime addition. FactSage \(^2\) predicts in these cases a carbon demand of 72.5 (109 %), and 86 (110 %) g per kg raw material (% regarding the stoichiometric reduction of Fe\(_2\)O\(_3\)), respectively.

The second diagram of Fig. 1 shows the slag composition during the reduction of re-leached red mud with lime addition. It can be seen, that a miscibility gap occurs which divides the slag at the end of the reduction process into two slag phases and separates a \(\text{Ti}_2\text{O}_3\)-rich fraction of slag.

By decreasing the iron content of the slag, the composition changes and thereby the liquidus and, thus, the process temperature is affected. As Fig. 3 indicates, the slag reduction can be basically divided into four stages. At first Fe\(_2\)O\(_3\) is reduced to FeO. In the second stage half of the formed FeO is reduced to metallic iron without any effect on the liquidus temperature. With advancing FeO reduction in the third period the slag is largely enriched in alumina and titania which leads to the formation of refractory mineral phases. In stage four undesired co-reductions of silica and titania take place due to the carbon excess. It becomes obvious that processing of the original red mud efforts the highest process temperatures due to the high alumina content. With increasing amount of bivalent iron during the advancing reduction, high melting FeAl\(_2\)O\(_4\) (hercynite) spinels occur and set the liquidus temperature up to 1500°C. With decreasing activity of FeO, due to the reduction to metallic iron, the percentage of hercynite in the slag diminishes and the high alumina content leads to the formation of alumina corundum phases which keep the liquidus temperature on a high level of about 1450°C. Above 75 g (113 % stoichiometric with regard to Fe\(_2\)O\(_3\) reduction) carbon addition per kg red mud silica reduction takes place and the liquidus temperature increases dramatically due to the high alumina activity.

Re-leached red mud has a slightly lower liquidus temperature. Due to the highest amount of iron oxide in the tested raw materials firstly the formation of magnetite takes place during the reduction process and leads to an increase of the liquidus temperature. Thereafter again the hercynite phase determines the liquidus temperature. But due to the lower alumina concentration in the re-leached red mud, the lower hercynite activity allows a low liquidus temperature level of about 1350°C. With removal of the iron oxide from the slag the relative amount of the minor components lime and titania increases and leads to the formation of perovskite and subsequently the liquidus temperature raises again until a separation into two slag phases takes place at the end of the reduction.

The processing of re-leached red mud with lime addition proceeds quite similar to the leached red mud. During the first half of the process the added lime dilutes the dominating magnetite and hercynite phases and lowers the liquidus temperature to 1330°C. But during the second half of the reduction process the comparably higher lime activity leads to a strong driving force of perovskite formation resulting in a steep surge of the liquidus temperature. At the end again the miscibility gap of the slag system forms two liquid slag phases and the liquidus temperature drops as a consequence.

The calculated final slag compositions after the iron oxide removal are presented in Tab. 3. Basis for the calculations is a carbon excess of 5 g kg\(^{-1}\) raw material in order to lower the remaining FeO content in the slag to a level of 0.3 wt % and allow an almost complete iron recovery. Moreover, the melt was permanently in contact with the used graphite crucible and the graphite electrode, thus, a higher reduction potential is assumed.

As already mentioned in the introduction the slag viscosity plays an important role for the handling during the process. Many empirical models exist to predict the viscosity of conventional slag systems. Most of them are calcium-silica based [17,18] but a very popular model made by Urbain [19] and partially extended by Kondratiev [20] works also with the \(\text{Al}_2\text{O}_3\)-\(\text{SiO}_2\)-CaO system. Unfortunately the other slag components like TiO\(_2\) and Na\(_2\)O are treated as minor elements. However, as shown in Tab. 1 the red mud contains almost 10 wt % TiO\(_2\) and Na\(_2\)O and especially the valence of the amphoteric component titania (TiO\(_2\) or \(\text{Ti}_2\text{O}_3\)) is not considered sufficiently. These lacks make it impossible to apply any of these models. FactSage\(^2\) has the opportunity to calculate viscosities as it is done for the proceeding iron reduction in
Fig. 4. It can be seen that slag viscosity will increase heavily in the third stage of the reduction process if the basic acting FeO content is totally removed and the high silica content makes the slag thick. In addition, the viscosities for the calculated final slags after iron removal are calculated and presented in Tab. 3.

### 4 Experimental Setup

The slag must not be contaminated by the used refractory and the aim of all experiments was a complete reduction of iron oxide. Therefore, the raw material was smelted in a graphite crucible with the dimensions of 150/120 mm outer/inner diameter and 200 mm depth. To minimize the graphite consumption of the crucible due to the carbon absorption by the slag and to cover the melt from reoxidizing at the surface, approx. 200 g (depending on the hematite content of the raw material) of lignite coke with a grain size below 1 mm have been fed together with 3200 g pre-dried and lumpy raw material of a particle size of 10 – 30 mm.

All experiments were conducted in a tiltable AC electric arc furnace, which is presented in Fig. 5. Although the setup with one top electrode made of graphite in combination with a water-sprayed copper bottom electrode is typical for DC mode, the furnace was driven without a rectifier. In order to establish a good electrical contact, a thin layer of graphite powder was put between the bottom electrode and the graphite crucible. The electrical power during the smelting process was 12 – 15 kW. A process temperature of 1600 °C was aspired and controlled discontinuously by a pyrometer. Actually the temperatures varied from 1600 °C to 1700 °C. The feed rate of the input material was continuously 2500 g h⁻¹. After 90 min the whole material has been fed and the melt was hold for additional 10 min to complete the hematite reduction. Afterwards the entire melt was tapped into a steel mold, in which metal and slag phase were separated due to the settling behavior of the higher density metal droplets.

### 5 Results and Discussion

Red mud as a hydrometallurgically pretreated lateritic residue still contains volatile compounds like the crystal water of (aluminum-) hydroxides (loss of ignition of red mud is about 10 wt %). In combination with the high hematite amount, which is carbothermically reduced, a lot of gaseous products are formed and have to leave the melt. Therefore, the slag tends to foam and the furnace must be fed carefully and on a constant low feed rate.

The slag resulting from the landfill smelting is easy to handle, even after the removal of iron. However, the slag resulting from the test trials with re-leached red mud is very difficult to handle, sticky and pasty in its viscosity. The high

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Table 3. Comparison of the predicted slag composition with obtained slag from experiments calculated at 1650 °C with 5 g kg⁻¹ input material carbon excess according to the stoichiometric amount. All data in wt % and calculated with FactSage® 6.4.

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>FeO</th>
<th>Viscosity [Pa s]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Red mud</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FactSage®</td>
<td>47.5</td>
<td>22.3</td>
<td>6.7</td>
<td>10.6</td>
<td>12.4</td>
<td>0.3</td>
<td>0.271</td>
</tr>
<tr>
<td>Experiment</td>
<td>48.8</td>
<td>22.6</td>
<td>7.5</td>
<td>9.4</td>
<td>12.2</td>
<td>0.6</td>
<td>–</td>
</tr>
<tr>
<td><strong>Re-leached</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FactSage®</td>
<td>34.2</td>
<td>27.1</td>
<td>8.7</td>
<td>14</td>
<td>14.6</td>
<td>0.3</td>
<td>0.363</td>
</tr>
<tr>
<td>Experiment</td>
<td>34.3</td>
<td>26.8</td>
<td>8.9</td>
<td>14</td>
<td>15.1</td>
<td>2.2</td>
<td>–</td>
</tr>
<tr>
<td><strong>Re-leached with lime</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FactSage®</td>
<td>31.8</td>
<td>26.5</td>
<td>13.6</td>
<td>12.7</td>
<td>14.2</td>
<td>0.35</td>
<td>0.319</td>
</tr>
<tr>
<td>Experiment</td>
<td>32.1</td>
<td>25.4</td>
<td>13.7</td>
<td>13.8</td>
<td>14.5</td>
<td>2.5</td>
<td>–</td>
</tr>
</tbody>
</table>
viscosity hinders bubbles of gaseous reaction products, e.g., CO, Na and SiO to ascend through the melt and leads, moreover, to a bad separating and settling of iron droplets in the melt. Therefore, the results from the smelting experiments show high values of sodium oxide in the slag phase and the iron content is also slightly increased. Although the iron content in Tab. 3 is given as FeO, it is assumed that most of the iron in the experimental slag originates from unsettled metal droplets which are entrapped in the slag. Moreover, titania is partly reduced to TiO2 and, therefore, the titania values are given calculated as TiO2. Lime decreases the slag viscosity visibly and in case of the re-leached red mud with lime, the slag handling is much better.

The obtained results are summarized in Tab. 3 for the slag phase and in Tab. 4 for the metal phase. FactSage® was used to calculate the expected phase compositions. A basic parameter for the calculation is 1650 °C, as the temperature near the arc spot in the electric arc furnace is intended to be. Furthermore a closed system (no exchange of atmosphere) was assumed at atmospheric pressure (1 bar). These conditions imply that the created atmosphere above the melt is quickly saturated with gaseous sodium and stops the volatilization of the entire sodium content. This model seems to be contradictory to the real process since the exhaust suction leads to a continuous exchange of atmosphere. Nevertheless, due to the dimensions of the crucible (narrow and deep) and the rapid smelting procedure with a short holding time of 10 min the exchange of atmosphere is low. Therefore, it can be seen that the calculated compositions are in good agreement with the experimental obtained results.

The high amount of sodium oxide forms with alumina NaAlO2, which is dissolved in the slag phase, reduces the sodium activity and makes it more difficult to reduce the sodium oxides. Due to the calculation as closed system the FactSage® model predicts higher alkali amounts in contrast to the observations of Ziegenbalg [13], who unfortunately does not describe his experimental process in detail. But it is assumable that he had longer holding times or a better exchange of atmosphere. To verify his results, the system was recalculated as an open system with permanent exchange of atmosphere. Then even FactSage® predicts an asymptotic decline of the sodium content in slag.

Fig. 6 shows the volatilization of sodium in an open system. In this calculation argon mixed with a slightly reducing CO atmosphere is purged at atmospheric pressure and 1650 °C above 1 kg red mud melt. It can be seen that the sodium content in the slag decreases with increasing exchanged volume of atmosphere. In order to confirm the calculations with open system conditions, test trials with additional holding time of about 20 – 30 min have been conducted and confirm, that the sodium oxide content in the slag could be reduced to values < 3 wt %. A low sodium con-

<table>
<thead>
<tr>
<th>Landfill</th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Cr</th>
<th>Ti</th>
<th>Al</th>
<th>P</th>
<th>S</th>
</tr>
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<td>1</td>
<td>0.6</td>
<td>0.86</td>
<td>0.06</td>
<td>0.01</td>
<td>0.45</td>
<td>0.2</td>
</tr>
<tr>
<td>Experiment</td>
<td>93.0</td>
<td>4.5 – 5.5</td>
<td>0.05</td>
<td>0.4</td>
<td>0.2</td>
<td>0.000</td>
<td>0.44</td>
<td>0.16</td>
</tr>
<tr>
<td>Re-leached</td>
<td>Fe</td>
<td>C</td>
<td>Si</td>
<td>Cr</td>
<td>Ti</td>
<td>Al</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>FactSage®</td>
<td>97</td>
<td>0.9</td>
<td>0.46</td>
<td>0.86</td>
<td>0.05</td>
<td>0.004</td>
<td>0.43</td>
<td>0.21</td>
</tr>
<tr>
<td>Experiment</td>
<td>93.7</td>
<td>3.4 – 5.2</td>
<td>0.1 – 0.5</td>
<td>0.5</td>
<td>0.2 – 0.8</td>
<td>&lt; 0.006</td>
<td>0.42</td>
<td>0.05</td>
</tr>
<tr>
<td>Re-leached with lime</td>
<td>Fe</td>
<td>C</td>
<td>Si</td>
<td>Cr</td>
<td>Ti</td>
<td>Al</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>FactSage®</td>
<td>97</td>
<td>0.8</td>
<td>0.3</td>
<td>0.88</td>
<td>0.06</td>
<td>0.005</td>
<td>0.47</td>
<td>0.17</td>
</tr>
<tr>
<td>Experiment</td>
<td>94.1</td>
<td>3.8</td>
<td>0.34</td>
<td>0.15</td>
<td>0.27</td>
<td>0.012</td>
<td>0.44</td>
<td>0.04</td>
</tr>
</tbody>
</table>
tent opens applications to the slag for example for construction purposes but as a network former sodium lowers considerably the liquidus temperature of slag by forming a low melting and better soluble NaAlO2 compound.

The removal of sodium oxide leads to a raise of the liquidus temperature for all raw materials, which can be seen in Fig. 7. In case of red mud directly from the landfill the liquidus temperature shows an almost linear rise with decreasing sodium oxide content in the remaining slag. Due to the high alumina content, the corundum precipitation already starts at higher temperatures and raises the liquidus temperature of the slag. Moreover, the figure shows that depending on the slag composition and the activity of the components alumina and titania, either corundum or perovskite start to precipitate. The firstly decreasing liquidus temperature of the re-leached red mud slags can be related to the separation into two melts with lower liquidus temperatures. With decreasing sodium oxide content parts of the alumina form a second melt with high amounts of a titania, lowering the liquidus temperature of the entire slag system. During cooling perovskite is precipitated from this second melt. If a critical sodium oxide level is exceeded, the alumina concentration becomes dominant and instead of the formation of a second melt alumina is precipitated directly as corundum. As a consequence the liquidus temperature rises again with diminishing sodium oxide content.

The calculated viscosities show almost the same values for all raw materials. Red mud directly from the landfill has the lowest viscosity promising the best processability. Re-leached red mud is thicker and the viscosity can be lowered by the addition of lime as it is done and shown by re-leached red mud with CaO/SiO2 = 0.5. Unfortunately it was impossible to verify the viscosities by experimental measurements.

In Tab. 4 the compositions of the gained metal phases are shown. It is obvious that the carbon content in the experiments is always much higher as the predicted value. Surely this is the result of carburization from the graphite crucible the metal phase was continuously in contact with. Therefore, the calculations of the needed carbon amounts cannot be experimentally verified. The carbon absorption of the melt is kinetically determined and was controlled during the experiments by the holding time in the crucible. By keeping the holding time in the experiments short (10 min) the experimental proven carbon content in the metal phase is comparable to the results of Logomerac [12] and Ziegenbalg [13], shown in Tab. 2.

The silicon content is always lower as predicted and in the range between 0.1 and 0.5 wt %. It is the result from slower kinetics of the three-phase reaction concerning the volatile intermediate product SiO(g), which has a high vapor pressure at process temperature. Thus, SiO(g) rather evaporates than being reduced to metallic silicon in the pig iron phase. Also titania is partly reduced and detectable in the pig iron in concentrations of about 0.2 wt %. The chromium content is lower as predicted. While FactSage® transfers almost the entire chromium in the metal phase, experiments prove that only half of the Cr2O3 is reduced. It is probably difficult to obtain the predicted equilibrium since chromium is a rather ignoble element and the final slag contains only 0.15 – 0.25 wt % Cr2O3. The chance that chromium oxide gets in contact with carbon or a CO bubble for reduction is low, thus, it takes a lot of time to assure the equilibrium. Phosphor can be removed from the slag into the metal phase even to significant lower levels because it is nobler than chromium and possibly reduced chromium will be re-oxidized by P2O5. The pig iron phase will, therefore, end up with phosphor concentrations of 4200 – 4700 ppm.

### 6 Conclusions

The predicted compositions of slag and metal phase are in good agreement with experimental results. Moreover, the calculations and the experiments confirm the experiences reported from literature. After the carbothermic reduction of red mud, the hazardous residue from the Bayer process, a salable pig iron with about 4 wt % carbon and less than 0.5 wt % silicon and 0.2 wt % titanium can be obtained. The
slag is adjustable in its viscosity by addition of lime and the sodium content can be varied by the length of the reduction time. The slag viscosity plays an important role during the reduction process, since many reduction products like CO, Na and SiO are gaseous species and have to pass through the melt. At high viscosities the ascent of gas bubbles is hindered and leads to a foaming slag. The addition of lime during the prior leaching step affects the process handling in the smelting step positively by decreasing the slag viscosity which was obvious during the experiments. Unfortunately the calculation of the viscosity is not that easy because the high content of titanium in trivalent and tetravalent state is not exactly defined in any known model for slag viscosities. But FactSage® states the viscosities of all slags in the range of 0.27 – 0.36 Pa s with positive effect on lowering the viscosity by the addition of lime even though lime increases the liquidus temperature by 100 °C to 1500 °C.

The project upon which this publication is based is funded by the German Federal Ministry of Education and Research (BMBF) under project number 033R085A. This publication reflects the views of the authors only.

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