ABSTRACT

Low chromium losses to slag are one of important issues in HCFeCr production. This will decrease the production cost per ton of alloy and contribute to a more efficient use of natural resources. Chromium content in slags from HCFeCr production at Ferbasa in Brazil has been investigated. The tapped slag contains normally around 8% Cr₂O₃ and is a mixture of oxides that were liquid during tapping and remnants of solid chromite grains. Tapped slags with higher % Cr₂O₃ contained more undissolved chromite ore. Chromium content in the liquid slag phase was nearly constant independent of total chromium content in the slag and accounted for around 30 to 70 % of Cr₂O₃ in the slags. Higher chromium contents in the tapped slags are due to higher amount of undissolved chromite ore.

The main chromium sources at Ferbasa are lump ores and concentrates from the local chromite ores, Jaccurici and Comisa. Comisa ore has a higher Fe-content than Jaccurici ore, and contains higher amount of and other types of gangue minerals. The chromite in Comisa is zoned with an outer Fe-rich rim while chromite in Jaccurici is homogenous. Comisa ore has lower melting temperatures than Jaccurici ores. Industrial experience at Ferbasa is that Comisa ore gives lower chromium content in the slag while Jaccurici ore must be used when high Si-content in the alloy is needed.

Melting properties of the ores are expected to affect temperature in the coke bed where the reduction takes place. The temperature here is together with ore composition, mineralogy and slag chemistry, the main factors determining chromium losses to slag. The observed higher Si-content in the alloy with increased amount of Jaccurici ore in the charge mixture, shows that higher melting temperatures of the ore will give higher temperature in the coke bed. Lower chromium contents in the slag with use of Comisa ores shows that other factors as mineralogy and texture are more important for chromium losses than the temperature in the coke bed.

KEYWORDS: Chromium ores, slags, carbothermic reduction.

1. INTRODUCTION

High Carbon Ferrochromium, HCFeCr, is mainly produced by reduction of chromite ores by carbon in Submerged Arc Furnaces (SAF). The produced alloys contain 45-75 % Cr depending on ore composition and around 0-10 % Si depending on customer specification. Chromium yield depend on chromium content in the slag and amount of slag. They will both vary with ore type [1]. A reduction of chromium losses to the slag, will increase chromium yield and by this reduce energy consumption and production cost per ton of tapped alloy.

In this work the possibilities for reducing chromium losses to slags at the Ferbasa plant in Brazil has been investigated. Ferbasa produces HCFeCr in 5 furnaces with a size from 18.5 to 24 MVA. The chromium sources are two local ores, Comisa and Jaccurici. Both lump ores and concentrates are used. The concentrates are sintered before they are fed to the furnaces. Coke is used as reductant.
Different types of chromite ores are available and used by different producers. The chromium source in all these are chromite spinels with the simplified formulae \((\text{Fe,Mg})(\text{Cr,Al})_2\text{O}_4\). In addition the ores contain varying amounts and types of gangue minerals. The main differences between the ores are their Cr/Fe ratio that determines the Cr content in the alloy. Another important characteristic is the Mg/Al ratio of the spinel that affects both slag composition and how easily the ores are reduced. Chemical composition of the ore will also affect the need for fluxes and amount and composition of tapped slag.

Chromium can as illustrated in figure 1, be found in tapped slag both as small metal prills, as undissolved remnants of chromite ore and as chromium dissolved in the liquid slag phase. The liquid slag phase in HCFeCr production is most often a mixture of \(\text{MgO, CaO, Al}_2\text{O}_3\) and \(\text{SiO}_2\) in addition to some \(\text{CrO}_x\) dissolved in the slag, where \(x\) can have a value between 1 and 1.5. At the strongly reducing condition in the final stage of HCFeCr production, \(x\) is close to 1. Amount of \(\text{CaO}\) and amount of dissolved \(\text{CrO}_x\) in slags from Ferbasu discussed in this paper, are low and the slag can be presented by the \(\text{MgO, Al}_2\text{O}_3, \text{SiO}_2\) phase diagram in figure 2. The green area represents slag compositions that are liquid at 1500°C. Outside this area the slag is either solid or a mixture of solid and liquid. Amount of solid depend on slag composition and temperature. In HCFeCr production, the slag temperature is normally assumed to be between 1600 °C and 1800 °C, depending on operational procedure and ore type.

![Diagram of phases in tapped slag from HCFeCr production](image1)

**Figure 1**: Phases in tapped slag from HCFeCr production [1]

During reduction of chromite ores, chromium diffuses out from the solid chromite spinel, dissolves in the liquid slag before it is reduced to alloy [1]. Chromium losses to slag are in addition to temperature, affected by properties of the chromite spinel, properties of the slag and the interaction between these phases during dissolution of chromite grains. By using a slag composition, e.g. flux type and amount, suited to the actual ore or ore mixture, it might be possible to reduce the Cr losses to the slag.
2. ORE PROPERTIES

The main chromium sources at Ferbasa are the local ores, Comisa and Jaccurici. Lump and concentrate of these two ores have been investigated. Jaccurici lump and Jaccurici concentrate are taken from different layers in the mine with different structure and this is expected to give differences in properties.

Chemical composition, mineralogy and melting properties of the ores have been investigated. Compositions of the ores were determined by Ferbasa. Samples for the other investigations were taken out by first crushing the lumps down to about -5 mm in a jaw crusher. Each of the ores was then split down to about 50 gram. One sample of each was used for mineralogical investigations. From one sample of each, about 5 pieces were hand-picked from the split material and used for measurement of melting properties in the sessile drop furnace.

2.1. Chemical composition

Chemical composition of the investigated ores, are shown in table 1. These can be compared with chemical composition of selected chromite ores from other countries shown in table 2. The most important differences between the ores from Ferbasa are the lower silica content in Jaccurici concentrate. The investigated sample of Comisa concentrate is not representative and has lower
chromium content than typical for this ore type. When compared with other commercial chromite ores, shown in table 2, the ores from Ferbasa are most similar to ore from Finland and Turkey.

**Table 1: Chemical analysis of investigated chromite ores**

<table>
<thead>
<tr>
<th>Ore</th>
<th>Cr$_2$O$_3$,%</th>
<th>FeO,%</th>
<th>Al$_2$O$_3$,%</th>
<th>MgO,%</th>
<th>SiO$_2$,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jacurici lump</td>
<td>37.20</td>
<td>15.89</td>
<td>14.24</td>
<td>19.96</td>
<td>10.04</td>
</tr>
<tr>
<td>Jacurici concentrate</td>
<td>43.53</td>
<td>18.01</td>
<td>18.06</td>
<td>14.52</td>
<td>3.74</td>
</tr>
<tr>
<td>Comisa lump</td>
<td>36.37</td>
<td>18.05</td>
<td>11.22</td>
<td>20.54</td>
<td>11.80</td>
</tr>
<tr>
<td>Comisa concentrate</td>
<td>31.67</td>
<td>24.89</td>
<td>6.20</td>
<td>19.85</td>
<td>14.32</td>
</tr>
</tbody>
</table>

**Table 2: Typical composition of chromite ores from different Countries [2]**

<table>
<thead>
<tr>
<th>Country</th>
<th>Cr$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>FeO</th>
<th>Al$_2$O$_3$</th>
<th>MgO</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Cr/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brazil</td>
<td>41.0</td>
<td>14.92</td>
<td>17.0</td>
<td>16.0</td>
<td>1.5</td>
<td>9.0</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>Finland</td>
<td>35.5</td>
<td>18.3</td>
<td>12.4</td>
<td>15.0</td>
<td>1.4</td>
<td>11.3</td>
<td>1.76</td>
<td></td>
</tr>
<tr>
<td>India</td>
<td>51.5</td>
<td>12.5</td>
<td>6.0</td>
<td>16-26</td>
<td>0.5-1</td>
<td>11.0</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>Iran</td>
<td>40-52</td>
<td>12.41</td>
<td>9.92</td>
<td>14.92</td>
<td>0.7</td>
<td>5.02</td>
<td>2.8-3.5</td>
<td></td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>54-91</td>
<td>13-16</td>
<td>14.7</td>
<td>3.6</td>
<td>12-14</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Madagascar</td>
<td>42</td>
<td>13-16</td>
<td>15.9</td>
<td>17-20</td>
<td>0.3</td>
<td>4.6</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Ruaaia</td>
<td>39</td>
<td>18.8</td>
<td>15.1</td>
<td>13.2</td>
<td>0.6</td>
<td>12-15</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>South Africa</td>
<td>44.4</td>
<td>19.8</td>
<td>15.1</td>
<td>13.2</td>
<td>0.6</td>
<td>12-15</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>Turkey</td>
<td>34-42</td>
<td>14</td>
<td>8.0</td>
<td>21.0</td>
<td>0.6</td>
<td>12-15</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>Zimbabwe</td>
<td>49.2</td>
<td>18.27</td>
<td>11.57</td>
<td>12.35</td>
<td>0.48</td>
<td>6.58</td>
<td>2.4</td>
<td></td>
</tr>
</tbody>
</table>

2.2. Mineralogy

The occurrences of the various minerals in each ore were determined by a combination of optical microscopy and XRD. The chemical composition of the chromite's and their variation were determined by EPMA. The XRD measurements were performed with BRUKER D8 Advance XRD. DIFFRACT$^+$ SEARCH software in combination with database PDF 2.

The textures of the ores are shown in figure 2. Comisa lump and concentrate and Jacurici lump have approximately the same grain size, while the grains in Jacurici concentrate are considerably smaller. The difference in grain size between Jacurici lump and Jacurici concentrate is not a result of the concentration process, but a property of the original ore. The Jacurici ores are from the same mine, but from different layers. The difference in original grain size is expected to affect melting and reduction properties. The observed difference illustrates that ores should not automatically be categorized according to mine name.

The main mineral in both ores are chromite spinels. Comisa and Jacurici contain as shown in coupled to measured temperatures. Contain more gangue minerals, more different types of gangue minerals and more of gangue minerals with high OH-content than Jacurici. These differences are expected to affect melting properties. The main mineralogical difference between Comisa and Jacurici are related to differences in their chromite spinels. The chromite in Jacurici has a very homogenous composition, containing around 16 % FeO, while the chromites in Comisa have an outer Fe-rich rim with around 41 % FeO, and an inner core with around 23 % FeO. This zoning can
be seen in figure 2. Comisa ores have a higher Cr\textsubscript{2}O\textsubscript{3} and FeO content and lower Al\textsubscript{2}O\textsubscript{3} and MgO content than Jaccurici ores. Composition of the chromite's are shown in table 4.

![Figure 2: Texture of Comisa and Jaccurici ores](image)

**Table 3:** Mineralogy of Comisa and Jaccurici chromite ores

<table>
<thead>
<tr>
<th>Ore type</th>
<th>Comisa, lump</th>
<th>Comisa, conc.</th>
<th>Jaccurici, lump</th>
<th>Jaccurici, conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clinoclore</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromite, Fe-low</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromite, Fe-high</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Mg-chromite</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tale</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetite</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dolomite</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mica</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amphibole</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyroxene</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 4:** Composition of chromite grains in Comisa and Ferbasa ores

<table>
<thead>
<tr>
<th>Ore</th>
<th>% Cr\textsubscript{2}O\textsubscript{3}</th>
<th>% FeO</th>
<th>% Al\textsubscript{2}O\textsubscript{3}</th>
<th>% MgO</th>
<th>% gangue*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jacurici conc</td>
<td>48,45</td>
<td>17,98</td>
<td>19,59</td>
<td>15,00</td>
<td>4-6</td>
</tr>
<tr>
<td>Jacurici lump</td>
<td>48,88</td>
<td>15,86</td>
<td>19,89</td>
<td>16,42</td>
<td></td>
</tr>
<tr>
<td>Comisa conc</td>
<td>49,88</td>
<td>32,06</td>
<td>7,96</td>
<td>8,74</td>
<td></td>
</tr>
<tr>
<td>Comisa lump core</td>
<td>53,72</td>
<td>27,20</td>
<td>9,19</td>
<td>10,27</td>
<td>20-25</td>
</tr>
<tr>
<td>Comisa lump outer rim</td>
<td>49,29</td>
<td>41,25</td>
<td>1,95</td>
<td>5,77</td>
<td></td>
</tr>
</tbody>
</table>

* % gangue estimated by Cyro Takano: University of Sao Pauz

2.3. Melting properties

Chromite spinels, FeCr\textsubscript{2}O\textsubscript{4} will first melt at temperatures above 2100°C. Mixing in solid solutions with MgCr\textsubscript{2}O\textsubscript{4} and MgAl\textsubscript{2}O\textsubscript{4} will increase the melting temperatures while increased Fe-content lower the melting temperatures. Chromite ores contain gangue minerals that melt at lower temperature. The chromite spinels are dissolved in this primary slag. When the slag is in contact with solid carbon, Cr and Fe oxides in the slag are reduced to alloy. In industrial production of HCFerCr, partly dissolved chromite grains are not in equilibrium with the surrounding slag [1]. Reduction of chromite will then depend on kinetics of dissolution of the chromite grains in the surrounding slag [1]. Melting and reduction will happen simultaneously and melting and reduction
properties cannot be investigated separately. When talking about the melting behaviour, one is actually talking about the reduction and melting behaviour.

Melting properties of the Comisa and Jaccurici ores were investigated in a sessile drop furnace. The sessile drop furnace was designed to measure the contact angle of a liquid drop on a 10 mm diameter substrate. In this furnace it is possible to measure the wetting angle of a sessile drop, observe the melting point of substances and investigate the reactivity between different materials. The furnace is typically heated at 5 to 100°C/min, although up to 1000°C/min is feasible. The maximum temperature is 2400°C. Changes of sample shape is recorded by video and coupled to measured temperatures.

In the current investigation, samples of chromite ore powder were pressed into small cylinders, 3 mm in diameter and 2-4 mm high. The sample was placed on a graphite substrate and heated in CO-atmosphere with 20°C/min to 1350 °C and further with 5 °C/min until complete melting. In investigations of inhomogeneous materials as minerals with such small samples, large scattering is expected and melting of two parallels of each ore was studied. The melting properties were determined by visual analysis of the recorded data. The melting properties of the investigated chromite ores are shown in table 5 Pictures from melting experiments with these ores are shown in Figure 3.

Comisa ores has marked lower melting temperatures than Jaccurici ores. Comisa start to melt around 1500°C while Jaccurici start to melt between 1550°C and 1700°C. The lowest melting temperature for Jaccurici might not be representative. Comisa ores are completely melted at around 1700°C while Jaccurici ores are not completely molten until between 1730°C and >1800°C. There are no clear differences between lump and concentrate, but the results for Jaccurici indicate slightly lower melting temperatures for lump than for concentrate. For all ores gas evolution starts before the ore start to melt. Gas evolution is normally taken as an indication of start of reduction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Start melting, °C</th>
<th>Start reduction, °C</th>
<th>Finish melt., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comisa lump</td>
<td>1492</td>
<td>1665</td>
<td>1706</td>
</tr>
<tr>
<td>Comisa lump</td>
<td>1561</td>
<td>1661</td>
<td>1696</td>
</tr>
<tr>
<td>Comisa Conc.</td>
<td>1511</td>
<td>1591</td>
<td>1679</td>
</tr>
<tr>
<td>Comisa Conc.</td>
<td>1506</td>
<td>1592</td>
<td>1675</td>
</tr>
<tr>
<td>Jaccurici lump</td>
<td>1551</td>
<td>1689</td>
<td>1732</td>
</tr>
<tr>
<td>Jaccurici lump</td>
<td>1659</td>
<td>1682</td>
<td>1733</td>
</tr>
<tr>
<td>Jaccurici Conc.</td>
<td>1670</td>
<td>1708</td>
<td>&gt;1770</td>
</tr>
<tr>
<td>Jaccurici Conc.</td>
<td>1695</td>
<td>1707</td>
<td>&gt;1800</td>
</tr>
</tbody>
</table>

The difference between Comisa and Jaccurici might be a result of the considerably higher amount of gangue minerals in Comisa. Gangue minerals start to melt at lower temperature than chromite, and the chromite dissolves in the melted gangue minerals. The Fe-rich outer rim around the chromite from Comisa can also contribute to its lower melting temperatures

3. INDUSTRIAL SLAGS

Five samples of industrial slags from Ferbasa were investigated with the objective to see if chromium losses to slag were a result of undissolved chromite grains or of high chromium content in the liquid slag phase.
Slags with especially high chromium content were produced for this investigation. The slags were from production with charge mixtures with different ores, and it is therefore not possible to relate the results to characteristics of the different ores.

<table>
<thead>
<tr>
<th></th>
<th>Initial melting</th>
<th>Start reduction</th>
<th>Completely molten</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comisa lump</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jaccurici lump</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1561 °C</td>
<td>1661 °C</td>
<td>1696 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1659 °C</td>
<td>1682 °C</td>
<td>1733 °C</td>
</tr>
</tbody>
</table>

Figure 3: Pictures from sessile drop experiments

3.1. Chemical composition of the slags

Chemical analysis of the slag samples provided by Ferbasa, are shown in table 6. Compared to analysis of typical slags from other producers shown in table 8, the slags from Ferbasa have a low to medium Cr content. The total chromium losses to slag depend in addition to chromium content in slag also on the slag volume. This is not known for the cases in table 6 and table 7.

3.2. Cr-content of different phases in the slags

The slag samples were crushed in a jaw crusher to −5 mm, then 5 pieces of each slag was selected randomly for microprobe investigations. In microprobe typical areas of each sample were selected for further investigations. Pictures were taken of these areas and representative grains of each of the phases were analysed by EPMA.

Table 6: Chromium content in investigated slags

<table>
<thead>
<tr>
<th></th>
<th>Cr₂O₃, %</th>
<th>SiO₂, %</th>
<th>FeO, %</th>
<th>Al₂O₃, %</th>
<th>MgO, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag A</td>
<td>10,63</td>
<td>31,40</td>
<td>3,95</td>
<td>20,15</td>
<td>31,13</td>
</tr>
<tr>
<td>Slag B</td>
<td>6,95</td>
<td>36,40</td>
<td>1,65</td>
<td>20,80</td>
<td>31,50</td>
</tr>
<tr>
<td>Slag C</td>
<td>14,10</td>
<td>28,8</td>
<td>4,9</td>
<td>21,4</td>
<td>28,02</td>
</tr>
<tr>
<td>Slag D</td>
<td>7,36</td>
<td>37,20</td>
<td>1,90</td>
<td>21,35</td>
<td>29,38</td>
</tr>
<tr>
<td>Slag E</td>
<td>7,36</td>
<td>37,38</td>
<td>1,81</td>
<td>20,97</td>
<td>29,25</td>
</tr>
</tbody>
</table>

The microprobe analyses showed that all the slag samples were a mixture of partly reduced chromite ores that were solid during production and oxide phases that were liquid during production. In addition the slags contained some metal prills. During tapping and cooling, the liquid slag phases had solidified as several phases with different chromium contents. Average analysis for
the bulk slags were calculated by estimating area fraction of each phase from the microprobe pictures and assuming that this represent percentage of the phase. The slags from Ferbasas were too complex to give reliable analysis with this method, but indicate the differences between the samples. Phases and texture in Slag C with highest and slag B with lowest chromium contents are shown in figure 4. A slag sample from Elkem Rana is shown for comparison. This has similar texture to the slags from Ferbasas, but lower chromium content in the liquid slag phase. A more detailed examination of chromite particles, as included in figure 5 show that a separate slag surrounds the chromite grain. This rim has a high concentration of spinel MgAl₂O₄, and is believed [1] to retard the dissolution rate of chromite grains.

![Microprobe pictures of industrial slag B and C from Ferbasas. 40x magnification, and slag from Elkem Rana. White is metal, Light grey id undissolved chromite grains. Darker phases is solidified liquid slag phase](image)

Slag sample B with highest % Cr₂O₃ contained as shown in table 6 most undissolved chromite grains; 20 %. Slag C with lowest chromium content contained only 4.5 % chromite grains. Cr content in the liquid slag phase were around 5 % in all the slags, and nearly independent of their total chromium content in the slag.

<table>
<thead>
<tr>
<th>Table 7: Distribution of chromium between phases in slags</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Cr₂O₃ in sample</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>Slag C</td>
</tr>
<tr>
<td>Slag A</td>
</tr>
<tr>
<td>Slag D</td>
</tr>
<tr>
<td>Slag E</td>
</tr>
<tr>
<td>Slag B</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 8: Chromium content in slag from Elkem Rana [1] and from Outokumpu [3]</th>
</tr>
</thead>
<tbody>
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Increased Cr content was in all the investigated samples a result of increased amount of undissolved chromite grains while there were only minor changes in Cr content of the liquid slag phase. In the investigated industrial slags from Ferbasa, between 33 and 72 % of Cr₂O₃ occur in chromite grains. The rest (28 -67%, calculated as Cr₂O₃) is dissolved in liquid slag phase as CrOₓ where x is between 1 and 1.5. Earlier investigated slag from Elkem Rana [1] also contained undissolved chromite grains. This slag had a lower Cr content in the liquid slag phase and contained more undissolved chromite grains.

Lower chromium losses to the slag can thus be achieved either by increased rate for dissolution of chromite grains to the liquid slag phase or by increased rate for reduction of chromium oxide from slag to alloy. The variation in content of chromite grains between the investigated slags from Ferbasa, and the difference between chromium content in liquid Ferbasa and in liquid Elkem Rana slag show that both these approaches are possible.

4. INDUSTRIAL EXPERIENCE

In most industrial operation the charge does not consists of one ore alone but is a mixture of several different ores and fluxes and quartz. Correlation between furnace performance and raw material properties are thus often difficult to obtain. At Ferbasa systematic use of Jaccurici and Comisa ores over several years has made it possible to identify clear differences between these two ore types. Comisa has its advantage in producing a slag with lower chromium content. Amount of slag is not measured, so it is not known how much of this that can be attributed to higher slag volume due to higher amount of gangue minerals in Comisa ore. But the overall experience is that increased percentage of Comisa ore in the charge mixture will reduce the chromium losses. Jaccurici ore has its advantage in making to possible to produce an alloy with a higher Si-content. So when an alloy with higher Si is produced, Jaccurici ore is used and a higher chromium loss to the slag is accepted.

5. DISCUSSION

To achieve low chromium losses to slag and a high yield in HIICFeCr production, the produced slag must contain a low amount of undissolved chromite grains and have a low content of dissolved chromium in the liquid slag. Slag-metal separation must in addition be good enough to avoid mixing of alloy with the tapped slag. The two first subjects were investigated.

At Ferbasa HIICFeCr is produced in SAF furnaces. The final reduction of chromite to ferrochromium alloy takes place in a coke bed, below the electrode tip. In this reaction zone chromium oxide from the chromite spinel is first dissolved in the slag surrounding it, and then chromium oxide in the slag is reduced to chromium alloy. To be able to drain into the coke bed, the charge mixture must have a low enough viscosity to flow between the coke particles. It must then be partly molten and reduced. At the top of the coke bed, the charge is heated until it reaches the temperature between start melting and final molten where its viscosity is low enough. This melting temperature varies between the ores. The temperature in the coke bed is affected by the temperature at the top of the coke bed. Thus use of ores with higher melting temperatures is expected to give higher temperatures in the coke bed. Based on the melting experiments with ores from Ferbasa, the temperature in the coke bed is expected be higher with use of Jaccurici ores than with use of Comisa ores.

The higher temperature in the coke bed with Jaccurici ore is confirmed by the higher Si-content in alloy experienced when Jaccurici ore is used. This knowledge about correlation between
ore melting properties and Si-content in alloy, presents a possible method to better control alloy quality.

In earlier investigations of ores from Elkem Rana [1], it was found that partly reduced chromite grains in the slag were not in equilibrium with the slag. The reduction rate was determined by the dissolution rate of the chromite grains while reduction from the slag was determined by mass transfer in the slag phase. The driving force for the dissolution depends on the composition both of the chromite grains and the slag where they dissolves. Higher temperature will increase the dissolution rate.

Increase chromium content in the slags from Ferbasa investigated in this work, was a result of increased amount of undissolved chromite grains. Operation or charge mixtures that increases dissolution rate for chromite ore will thus reduce chromium losses to the slag. The final reduction of chromite ores takes place in the coke bed. A higher temperature in the coke bed is under otherwise equal conditions expected to give better reduction of chromium. If this is the main factor controlling chromium losses, a charge mixture with Jaccurici ore would give lower losses than a charge mixture with Comisa ore. The industrial experience at Ferbasa is opposite, increased amount of Comisa ore in the charge mixture, and reduces chromium content in the slags. Thus chromium loss must be governed by other parameters in addition to temperature. Composition of the chromite grains will affect diffusion of chromium out of the grains and dissolution of chromite in the slag. Higher Fe content and lower MgO and Al₂O₃ content, as well as higher content of gangue minerals in Comisa compared to Jaccurici can be factors that contributes to lower amount of undissolved chromite grains when Comisa ore is used. Another characteristic with Comisa ores is the more porous Fe-rich rim surrounding the grains. Both the cracks and the high content of easily reduced iron oxides will most likely contribute to faster dissolution of the chromite. Their effect has not been studied here and should be investigated further to clarify the effect of ore characteristics on dissolution rate.

The driving force for the dissolution depends in addition the composition of the chromite grains also of the slag where they dissolve. Total slag composition and composition of the liquid slag will therefore be of importance. Content not only of chromium but of all compounds in these phases have an effect. This is illustrated by the detailed picture of Slag B in figure 5. The undissolved chromite grain has an outer rim of MgAl₂O₄ that does not dissolve in the surrounding slag. This prevents further dissolution of chromium.

Chromium content in liquid phase of slags from Ferbasa varies little and it contain only 4-5 % % Cr₂O₃. They have a much higher Cr content in the liquid slag phase than what was found in industrial slags from Elkem Rana where it was from 3% and down to lower than 1%[1]. Although the percentage of chromium in the liquid slag phase is low, it accounts for up to 65 % of the chromium losses to the slag. A reduction of this percentage down to the levels observed at Elkem Rana, would give a considerable decrease in chromium losses to slag. How low levels that can be reached, depend on equilibrium composition of the actual slags and the temperature in the reduction zone. This is not known for the investigated slags from Ferbasa. Composition of the liquid slag will also affect mass transfer of chromium from the chromite grains to the coke particles where it can be reduced. Changes in slag composition might, based on this, be one of the possible methods to reduce chromium losses to slag.

6. CONCLUSION

Tapped slags from HCFeCr production at Ferbasa contain chromium both as undissolved chromite grains and as chromium dissolved in the liquid slag phase. Slags with higher chromium content have increased amount of undissolved chromite grains. The liquid slag phase has a stable
chromium content of around 5%, and accounts for 28-67% of the total chromium loss. Slag composition is believed to affect both these chromium sources. Jaccurici ore has higher melting temperatures than Comisa ores. Industrial experience at Ferbas where Si-content in the alloy increases with increasing amount of Jaccurici ore in the charge mixture, shows that higher melting temperatures of the ore will give higher temperature in the coke bed. Reduction rate for SiO₂ to Si increases with increasing temperature.

Comisa ore will in spite of its lower melting temperatures give lower chromium losses to the slag. The main reasons for this are believed to be both the higher amount of gangue minerals in Comisa and differences in composition of the chromites. Especially the Fe-rich rim surrounding the chromite grains is believed to contribute to a faster dissolution rate of chromite and lower chromium losses to slag with use of Comisa ore. Further investigations are needed to confirm this and reveal the mechanisms.

7. REFERENCES
