FACTORS AFFECTING THE REDUCIBILITY OF SINTERED CHROMITE PELLETS AND CHROMITE LUMPY ORE

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ABSTRACT

The energy consumption and recovery of chromium are important economic factors in ferrochrome production. Outokumpu has a lot of experience of the reduction behavior of the sintered pellets in industrial-scale furnaces and also on the grounds of numerous laboratory and pilot-scale investigations.

Sintered pellets have shown a superiority over lumpy ore and briquettes made of the same chromite grade. The good performance of the pellets has also resulted in investigations on the reasons for such a performance. In this study, the factors affecting pellet behavior in smelting furnace were investigated. This study is divided into two sections, i.e. the investigations were on the factors affecting solid state reduction and on the factors affecting reduction under melting. These tests were performed by means of thermo gravimetry and by smelting tests.

The correlation between the pellet characteristics and reduction behavior was shown and its influence on industrial-scale furnaces was discussed. Factors worth of consideration are for instance, the extent of oxidation during sintering, slag formation and chemistry in respect of molten state reduction, and the grain size of the chromite mineral in the raw material in respect of kinetic reasons (retention time in smelting).

1. INTRODUCTION

Outokumpu Oy has developed a steel belt sintering process for sintering pellets from fine chromite concentrate. Smelting of these pellets results in excellent efficiency and smelting key figures. The recovery of chromium depends on the grade of chromite, the method of chromite pre-treatment and the smelting process (e.g. temperatures).

This study is divided into two sections. Firstly, it considers the factors which affect solid state reduction, i.e. the effect on the reducibility of the pellets above the melting zone of the submerged electric arc furnace. The tests were performed by means of thermo gravimetry. Secondly, the study considers reduction under melting, i.e. at higher temperatures with or without flux (quartzite). These tests were performed by means of smelting tests in an induction furnace at different temperatures with coke and quartzite. However, the results on the non-fluxed charges will not be presented in this context.

The test series included both laboratory and pilot plant sintered pellets. These were pelletized out of Finnish, South African, Indian and Kazakh concentrates. The series also included process pellets from Finland and South Africa and ores from Finland, South Africa, India, Russia and Madagascar.

The majority of the tests were made on samples which were pelletized and sintered from Finnish concentrate at the Outokumpu Research Oy. The factors studied were as follows: sintering temperature, compressive strength, degree of oxidation (e.g. sesqui oxide content), porosity (e.g. wood dust), coke powder addition and dolomite addition.
Several additional tests were executed on foreign chromite grades in order to broaden the knowledge of the effects of Cr/Fe, purity, chromite grain size (ores vs. pellets), grinding method (ball mill grinding vs. pressure grinding) and oxidation degree (weathered ore) of chromite raw materials on reducibility.

2. EXPERIMENTAL WORK

The chromite reduction test project started with the development of the reduction test methods. Several methods were compared. The test facility included the Netzsch STA 409 C thermal analyzer, the Cahn TG 2171 gravimetric analyzer as well as induction smelting procedures in SiC or Al\textsubscript{2}O\textsubscript{3} crucibles. The methods were carefully compared and their usability considered [1]. The Cahn TG 2171 analyzer was selected for the solid state reduction test method because it allowed for a larger sample amount. The smelting tests were first executed in SiC crucibles which enabled a much faster heating rate than the Al\textsubscript{2}O\textsubscript{3} crucibles. In the course of the project, proper quality SiC crucibles were no longer available (they contained too much free graphite). The Al\textsubscript{2}O\textsubscript{3} crucibles substituted for the SiC crucibles.

The next phase of the study concerned the reducing agent. The metallurgical coke, char coke and gas coke were compared [2] and [3]. Correspondingly, metallurgical coke was compared with graphite [1]. Comparative reduction tests were performed both on argon and carbon monoxide. The metallurgical coke with a considerably low reactivity was selected as the reducing agents. Almost all tests were performed with the same lot of the metallurgical coke.

2.1 Chromite sample preparation

The chromite cases came from the laboratory and from the batch sintering tests. Some process pellets were included in the test series.

In the TG tests, the laboratory pellet grades based on the same batch of Finnish concentrate, which was ground to a fineness of 80 % -74 µm and was then carefully homogenized.

The factors studied were as follows: sintering temperature, compressive strength, degree of oxidation (e.g. sesqui oxide content), porosity (e.g. wood dust), coke powder addition and dolomite addition. The test series included six pelletizing mixture cases which were as follows (Kemi concentrate and 1.0 % bentonite as binder) [4]:

- No additions, 1.5 % \( C_{\text{fix}} \)
- 20 vol.% wood dust (2.2 wt.%), 1.5 % \( C_{\text{fix}} \)
- 5 wt.% dolomite, 1.5 % \( C_{\text{fix}} \)
- 20 vol.% wood dust (2.2 wt.%), 5 wt.% dolomite, 1.5 % \( C_{\text{fix}} \)
- No additions, 0 % \( C_{\text{fix}} \)
- 20 vol.% wood dust (2.2 wt.%), 5 wt.% dolomite, 0 % \( C_{\text{fix}} \)

The sintering tests included four tests on every mixture. These were “100 kp” / normal oxidation, “200 kp” / normal oxidation, “100 kp” / prolonged oxidation and “200 kp” / prolonged oxidation. The heating of the pellets in the sintering tests followed that of the pellets in steel belt sintering. The prolonged oxidation was executed by stopping the pellet cooling at 1100°C for 60 minutes. The temperatures needed for a compressive strength of 100 kp respectively of 200 kp varied depending on the pelletizing mixture. This also affected the oxidation of chromite iron [4].

This phase of the study included 24 sintering cases. Some differences in the pellet characteristics are worthy of mention. In the case of large concurrent additions of wood dust and dolomite, the sintering temperature had to be increased by 120-150°C in order to achieve the strength target. Porosity of the pellets principally depends on the material characteristics and on the pelletizability of the mixture. The maximum temperature and thus the compressive strength as well as the oxidation have a minor effect on porosity. A simultaneous addition of dolomite and wood dust increased the porosity by 7.9 % points in the case of 1.5 % \( C_{\text{fix}} \). The effect of
carbon addition on the porosity was 2.3 % points /4/. An addition of wood dust or dolomite increased the softening point of the sintered pellet. When simultaneously added, the softening temperature increased by 62°C.

The oxidation degree of chromite was determined by two means, i.e. by analyzing chemically the $\text{Fe}^{2+}$ content and by determining the sesqui oxide content by means of quantitative XRD. The sesqui oxide content reflects the extent of deformation of the chromite lattice. The sesqui oxide content was 32.9 % on average when normal oxidation was used and 42.0 % when prolonged oxidation was used. A carbon addition of 1.5 % $C_{\text{fix}}$ decreased the sesqui oxide content by 8.5 % points. Two examples of the chemical composition of the pellets are presented in Table 1 [4].

Table 1: Chemical composition of the sintered pellets of the laboratory test series

<table>
<thead>
<tr>
<th>Pelletizing and sintering case</th>
<th>$\text{Cr}_2\text{O}_3$</th>
<th>$\text{SiO}_2$</th>
<th>$\text{Al}_2\text{O}_3$</th>
<th>$\text{MgO}$</th>
<th>$\text{CaO}$</th>
<th>$\text{Cr}/\text{Fe}$</th>
<th>$\text{Fe}^{2+}$ / $\text{Fe}_{\text{tot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No additions, 1.5 % $C_{\text{fix}}$ normal oxidation</td>
<td>43.1</td>
<td>4.2</td>
<td>12.7</td>
<td>10.7</td>
<td>0.4</td>
<td>1.52</td>
<td>0.228</td>
</tr>
<tr>
<td>5 wt.% dolomite, 1.5 % $C_{\text{fix}}$ prolonged oxidation</td>
<td>42.9</td>
<td>4.4</td>
<td>12.3</td>
<td>10.6</td>
<td>1.5</td>
<td>1.55</td>
<td>0.042</td>
</tr>
</tbody>
</table>

The smelting tests included several sintered pellet grades prepared in the batch sintering test series. The composition of these pellets as well as the composition of two process pellet grades and five chromite lumpy ore samples are presented in Table 2 [4-8]. The size of the pellets was 12 mm. The ore was crushed to a size of 10-25 mm.

The coke for the TG tests was crushed and screened to a size of 0.074-0.149 mm and the coke for the smelting tests to a grain size of 2.5-5.0 mm. Quartzite was crushed and screened to a grain size of 2.5-5.0 mm.

Table 2: Chemical composition of the batch sintering and process pellets and the ore

<table>
<thead>
<tr>
<th>Chromite</th>
<th>$\text{Cr}_2\text{O}_3$</th>
<th>$\text{SiO}_2$</th>
<th>$\text{Al}_2\text{O}_3$</th>
<th>$\text{MgO}$</th>
<th>$\text{CaO}$</th>
<th>$\text{Cr}/\text{Fe}$</th>
<th>$\text{Fe}^{2+}$ / $\text{Fe}_{\text{tot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>South African process pellets</td>
<td>43.1</td>
<td>4.8</td>
<td>12.8</td>
<td>9.7</td>
<td>0.46</td>
<td>1.49</td>
<td>0.24</td>
</tr>
<tr>
<td>Tornio process pellets, P04</td>
<td>45.6</td>
<td>3.7</td>
<td>12.0</td>
<td>10.2</td>
<td>0.37</td>
<td>1.62</td>
<td>0.30</td>
</tr>
<tr>
<td>South African UG2a, batch</td>
<td>41.6</td>
<td>2.6</td>
<td>14.7</td>
<td>9.0</td>
<td>0.17</td>
<td>1.31</td>
<td>0.21</td>
</tr>
<tr>
<td>South African UG2b, batch</td>
<td>41.0</td>
<td>2.3</td>
<td>16.2</td>
<td>9.1</td>
<td>0.12</td>
<td>1.32</td>
<td>0.09</td>
</tr>
<tr>
<td>South African UG2c, batch</td>
<td>41.1</td>
<td>3.0</td>
<td>15.3</td>
<td>9.6</td>
<td>0.35</td>
<td>1.34</td>
<td>0.18</td>
</tr>
<tr>
<td>Kemi concentrate, batch</td>
<td>43.8</td>
<td>3.9</td>
<td>13.1</td>
<td>8.9</td>
<td>0.43</td>
<td>1.47</td>
<td>0.14</td>
</tr>
<tr>
<td>Indian conc.A, pressure gr., fluxed, batch</td>
<td>51.0</td>
<td>4.4</td>
<td>13.1</td>
<td>10.5</td>
<td>0.4</td>
<td>2.55</td>
<td>0.23</td>
</tr>
<tr>
<td>Indian conc.B, ball mill gr., un-fluxed, batch</td>
<td>54.8</td>
<td>1.6</td>
<td>10.5</td>
<td>12.0</td>
<td>0.1</td>
<td>2.72</td>
<td>0.14</td>
</tr>
<tr>
<td>Indian conc.C, ball mill gr., fluxed, batch</td>
<td>52.5</td>
<td>6.2</td>
<td>11.2</td>
<td>10.4</td>
<td>0.5</td>
<td>2.87</td>
<td>0.24</td>
</tr>
<tr>
<td>Kazakh concentrate, batch</td>
<td>52.9</td>
<td>6.9</td>
<td>7.0</td>
<td>19.1</td>
<td>0.1</td>
<td>3.76</td>
<td>0.24</td>
</tr>
<tr>
<td>South African chromite ore</td>
<td>40.2</td>
<td>6.1</td>
<td>17.3</td>
<td>9.3</td>
<td>1.0</td>
<td>1.45</td>
<td>0.78</td>
</tr>
<tr>
<td>Kemi chromite lumpy ore</td>
<td>36.3</td>
<td>11.6</td>
<td>10.2</td>
<td>14.8</td>
<td>0.9</td>
<td>1.67</td>
<td>0.72</td>
</tr>
<tr>
<td>Indian lumpy ore A</td>
<td>42.7</td>
<td>7.8</td>
<td>13.5</td>
<td>8.7</td>
<td>0.02</td>
<td>1.84</td>
<td>0.04</td>
</tr>
<tr>
<td>Russian ore</td>
<td>41.7</td>
<td>11.5</td>
<td>6.5</td>
<td>22.3</td>
<td>0.02</td>
<td>3.22</td>
<td>0.77</td>
</tr>
<tr>
<td>Madagascar ore</td>
<td>50.9</td>
<td>4.1</td>
<td>11.3</td>
<td>13.7</td>
<td>1.8</td>
<td>3.78</td>
<td>0.87</td>
</tr>
</tbody>
</table>
2.2 Test Procedures

2.2.1 TG Tests

The reduction tests were carried out with a Cahn TG-2171 thermo balance. The test was implemented with a single pellet to ensure a constant temperature across the pellet and good contact between coke and pellet.

The inner diameter of the furnace tube is 32 mm. The size of the test crucible is $\Phi 15.6/19.9$ mm * h 27.5/29.3 mm. This enables the study of one pellet (usually 2.5-3.0 g, $\Phi 12$ mm) or a lump of ore in a coke powder batch of 2.4 g. The tests were carried out either in pure Ar (99.97 %) or in pure CO (99.7 %). The maximum temperature was 1600°C and in some tests 1500°C (CO).

In each test, one chromite pellet was embedded in coke powder (0.074-0.149 mm in grain size). The coke was carefully homogenized before the tests. The pellet + coke batch with the crucible was put in the furnace. The furnace chamber was flushed with pure argon for 20 minutes. Then, the sample was heated in pure argon to 1000°C at a heating rate of 10°C/min and then to the maximum temperature at a rate of 5°C/min. The retention time at the maximum temperature was 180 min, still in pure argon. The maximum temperature was 1600°C. In the case of CO, CO was substituted for Ar at 1000°C. CO flow continued till the end of the retention time (i.e. 180 min) at 1600°C.

The sample was cooled to 800°C at a rate of 5°C/min and further to 25°C at a slightly slower rate (the capacity of the cooling fan was limited) in pure Ar. After cooling, the sample with the crucible was weighed. The coke and the pellet were also weighed separately. The pellets were also photographed. In addition, samples were prepared for chemical analyses.

The need for “background” tests was proved in the previous test series [1-3]. In the background tests (with aluminium oxide) preceding the reduction tests, the weight loss of the cokes exceeded to a great extent the loss of ignition determined in the chemical analyses of the cokes (1000°C). The reason for high ignition losses is the reaction of coke carbon with the ash components of coke. In order to study the reasons, equilibrium composition calculations with HSC Chemistry 5.11, X-ray analysis of the coke samples and a brief EDS analysis of a sample were performed. The investigation proved the formation of SiC, Al$_2$CO, SiO(g), silicides, and carbides, the formation of which also results in the formation of CO(g) and in a decrease in weight. Chemical analyses of the cokes showed an increase in the carbon content; by 1.9 %-points in the case of metallurgical coke and 6.2-7.2 %-points in the case of the char and gas cokes. This large an increase means that the ash content of the coke has been reduced considerably, and also that coke remains effective towards the end of reduction (the reduction rate, i.e. dm/dt decreased only slowly towards the end of the test).

With the implementation of the background tests, the weight loss of these reactions could be calculated apart from the total weight loss, the remaining weight loss corresponding to the losses due to chromite reduction. In the background test, an amount of 2.4 g of crushed Al$_2$O$_3$ was heated in a coke powder bed of 2.4 g using the normal reduction test procedure. A separate background test was carried out for each maximum temperature case.

2.2.2 Smelting Tests

The smelting tests were executed with the presence of quartzite. No other fluxes were used. The charges were calculated with the following assumptions: chromium, iron and nickel recoveries 100 %, metal composition: 7 % C, 3 % Si, trace elements 1 %, slag melting point 1650°C, coke carbon efficiency 95 %.

In the reduction test, the pellets, coke and quartzite were mixed well and put into the induction furnace in an Al$_2$O$_3$ crucible. The crucible was covered with a lid made of brick. The charge was heated during 120 minutes to the maximum temperature (1650°C) at which the retention time was 30 min. After cooling, the sample with the crucible was weighed and the loss of ignition of the charge was calculated. After the tests, samples of slag were taken for chemical analyses (Cr$_{tot}$, Fe$_{tot}$, Cr$_{met}$, Fe$_{met}$) and SEM/EDS. Samples of metal were taken for the analyses of Cr, Fe, C, Si, S. With the presence of quartzite, the reduction resulted in the formation
of a larger metal lump and some metal droplets in the slag. Both were weighed and the recovery of metal was calculated.

2.3 Definition of the Reduction Degree

2.3.1 TG Tests

The reduction degree was calculated as a degree of metallization and as oxygen removal. The degree of metallization was calculated as a ratio of \((\text{Cr}_{\text{met}} + \text{Fe}_{\text{met}}) / (\text{Cr}_{\text{tot}} + \text{Fe}_{\text{tot}})\). Oxygen removal means the ratio of the corrected weight loss in the test relative to the total oxygen content of chromium and iron oxides. The weight loss was corrected taking into consideration the decompositions in ore and the reaction of coke carbon with the coke ash (according to the background tests). The oxygen removal may exceed 100% due to heavy \(\text{SiO}(g)\) and \(\text{Mg}(g)\) reduction (reduction of the gangue minerals), the amount of which could not be studied by background tests. In most of the ore cases, the samples melted in the course of reduction at 1600°C resulting in an increase in \(\text{SiO}(g)\) formation.

2.3.2 Smelting tests

The reduction degree was defined as metal recovery relative to the theoretical maximum content of chromium and iron. The large metal lump and the metal droplets separated from the slag were weighed and analyzed. The metal amount was corrected to a metal composition of 7 % C and 3 % Si, which was the composition assumption of the charge calculations.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric Analyses

The research work started with the investigation of the factors affecting the reduction of sintered pellets. First, the effects of pellet characteristics were studied. Only Kemi concentrate was used as the raw material of the pellets in order to exclude the effect of chemical composition (except that of a dolomite addition). Most of the tests were carried out in an Ar atmosphere with a maximum temperature of 1600°C. In some cases, the surface of the pellet deactivated with the result of a delayed or totally suspended reduction. In these cases, tests were also performed in CO at 1600°C or in CO at 1500°C.

The thermogravimetric analysis gives the weight loss of the test sample in the course of heating (or cooling). This data was presented as a rate of weight loss, which is a more informative way of presentation.

The chromite pellet reduction starts as a reaction of \(\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}\) about at 890°C. The presence of CO has no significant effect on the starting temperature, because the reaction \(\text{C} + \text{CO}_2 \rightarrow 2 \text{CO}\) is not very fast at this stage. The \(\text{dm}/\text{dt}\) peak temperature is about 1010°C. Since the ferric iron is reduced, \(\text{dm}/\text{dt}\) slows down to nil. In the case of pellets, the ferrous iron reduction restarts approximately at 1195°C in Ar and at 1125°C in CO. In the case of ores, reduction restarts at higher temperatures, i.e. approximately at 1270°C in Ar and 1225°C in CO. The principal reduction achieves the maximum (peak III) just before or as the maximum temperature 1600°C is reached. Figure 1 presents three typical pellet cases. The reduction of a pellet may proceed quickly to a high degree of metallization without the formation of a passive surface layer (Figure 1a). The reduction may also be delayed for a while and restart later (Figure 1b). The passivation of the surface may also be final at this maximum temperature (Figure 1c). The passivation is due to the formation of a dense layer on the surface of the pellet. This layer may consist of metal carbides or of a high melting slag rich in spinel. In most of the cases, substituting CO for Ar does not prevent surface passivation.

The tests on six pelletizing mixtures and 24 sintering cases gave several interesting findings. An addition of wood dust increases the carbon content and the \(\text{Fe}^{2+}/\text{Fe}_{\text{tot}}\) ratio of the sintered pellets. Wood dust increased RD when no dolomite was used [4].

Prolonged oxidation decreased the reduction degree (RD) considerably in the case of weak pellets, but seems to have less effect in the case of strong pellets. As an average of the cases of strong and weak pellets,
Figure 1: Three different types of rate reduction (dm/dt) curves
prolonged oxidation decreased RD of non-fluxed pellets by 7 % points and that of dolomite-fluxed pellet 16 % points.

Dolomite addition decreased RD by 13 % points / normal oxidation and 22 % points / prolonged oxidation.

Omission of the carbon addition increased the sesqui oxide content. In the reduction tests, omission of carbon in sintering decreased RD by 5.8 % points when no dolomite was used and by 22.1 % points with the addition of dolomite. Leaving out the carbon addition has disastrous effects on reducibility in the case of dolomite-fluxed pellets. If dolomite is being used to increase the basicity of the chromite pellets, the addition of carbon should be considerably larger than in the case with no dolomite.

Dolomite impairs the RD, but the effect may be different at higher temperatures due to the higher softening temperature (T-5%) of the dolomite-containing pellets. In the case of dolomite-fluxed pellets, the high softening temperature results in poor metal nucleation onto the surface of the pellet.

The tests showed that porosity does not have as large an effect on the RD of chromite pellets as is supposed. The softening point of the sintered pellets may have effect on the RD by changing the reduction mechanism, i.e. a decrease in the softening point possibly increases reduction via the liquid state. If so, the maximum temperature applied, i.e. 1600°C may give too poor an impression of the effects of dolomite on the reducibility of chromite.

One important characteristic of the chromite raw material is the refractoriness of the material. The raw material should stay unmelted to high temperatures close to the electrode tips where the reduction is fast and mainly via the liquid state. If the softening temperature of the raw material is too high a level in the burden, where the temperature is too low for reduction. If in addition, there is no contact with coke carbon, the partly molten chromite forms large dense aggregates (crusts) in the burden resulting in poor gas permeability in the burden, in irregular electrical loads at various electrodes, possibly even in gas explosions, in electrode breakages and in poor FeCr production.

A comparison of the six mixtures as an average of four strength/oxidation cases gave the reduction degrees (RD / TG) as follows [4]:

- wood dust / 1.5 % Cfix 75.6 %
- no additions / 1.5 % Cfix 73.0 %
- no additions / 0 % Cfix 67.2 %
- dolomite / 1.5 % Cfix 64.2 %
- dolomite + wood dust / 1.5 % Cfix 59.4 %
- dolomite + wood dust / 0 % Cfix 37.3 %

In the case of the unfluxed laboratory pellets, substituting CO for Ar had practically no effect on the reduction degree (RD), whereas in the case of dolomite fluxed pellets, the RD increased considerably [5]. The maximum temperature of reduction was decreased by 100°C to 1500°C and tests were repeated in CO in the case of two laboratory pellets, of which one was the grade with no flux (normal oxidation; SK3) and the other the grade included dolomite fluxing (prolonged oxidation; SK25). The tests showed that the dolomite-fluxed pellet was reduced much better than the un-fluxed pellet. Both of the tests were repeated. The RD of SK3 decreased from 85.9 % to 37.6 % and the RD of SK25 from 65.8 % to 52.4 %. The existence of dolomite in the pellet changes the temperature level at which the deactivation of the pellets surface takes place. Dolomite fluxing also retards the metal nucleation onto the pellet surface (Figure 2). The temperature at which deactivation may occur, depends on silicate chemistry but depends very little on the softening temperature of the pellet (T-5%). A high T-5% as in the case of Tornio process pellets (no dolomite) resulted in a high reduction degree [5].
3.2 Smelting Tests

The first part of the smelting tests concentrated on the proportion of chromite lumpy ore in the smelting charge. Two series of charge mixtures were studied and these were Tornio process pellets with Kemi upgraded lumpy ore and batch sintered pellets made of South African UG2c concentrate with South African chromite ore. Both of the series included tests on pellet proportions of 100 %, 65 % and 0 %. Coke was used as a reductant and quartzite as a flux. The charges were heated over 120 minutes to a maximum temperature of 1650°C, at which the retention time was 30 minutes. The maximum temperature of the thermocouple outside the crucible was 1770°C in order to prevent the damaging the thermoelement. The temperature difference between this thermocouple and that in the charge mixture gave a lot of information about the state of reduction and melting (a sort of a differential thermal analysis !).

The Finnish and the South African chromites behaved similarly in reduction. ?The South African chromites resulted in a slightly higher metal recovery than the Kemi chromites. The principal reason is the lower Cr/Fe of South African concentrates and ores (pellets 1.32, ore 1.45) compared to the Finnish ones (pellets 1.62, ore 1.67).

An increase in the proportion of ore in the mixture impaired the metal recovery. The findings were similar in both of the cases (South African vs. Finnish chromites). A proportion of 30 % of ore decreased the metal recovery by 2.9 % points and a proportion of 100 % by 9.7 % points [6]. The principal reasons are the larger size of the chromite grains in the ore and the deformed chromite lattice in the sintered pellets (favorable for reduction). The effect of the ore proportion can be presented by the following formulas:

\[
RD(\%) = -0.097 \times ore\ proportion\ (\%) + 79.67 \quad (South\ African\ chromites) \quad (1)
\]

\[
RD(\%) = -0.096 \times ore\ proportion\ (\%) + 78.41 \quad (Finnish\ chromites) \quad (2)
\]

As presented previously, the Finnish pellets came from the Tornio SBS plant and the South African pellets from the batch sintering tests carried out at ORC. In the beginning of 2006, a sample of a South African SBS plant was received at ORC. Smelting test on these pellets resulted in a RD of 79.1, which is almost the same as found with the batch pellets [8].

Next, several additional tests were executed on foreign chromite grades in order to extend the knowledge of the effects of Cr/Fe, purity, chromite grain size (ores vs. pellets), grinding method (ball mill grinding vs. pressure grinding) and oxidation degree (weathered ore) of chromite raw materials on reducibility.
The pellet grades were batch sintered out of Indian concentrate C (ball mill ground, fluxed, 6.2 % SiO₂, Cr/Fe 2.87), Indian concentrate B (ball mill ground, no flux, only 1.6 % SiO₂, Cr/Fe 2.72), Indian concentrate A (pressure ground, 4.4 % SiO₂, 2.55) and out of Kazakh concentrate (ball mill ground, 6.9 % SiO₂, Cr/Fe 3.76). The data from the previous tests on Finnish and South African concentrates were included.

The chromite ore grades were from Madagascar (only 4.1 % SiO₂, Cr/Fe 3.78), India (7.8 % SiO₂, Cr/Fe 1.84) and from Russia (11.5 % SiO₂, Cr/Fe 3.22).

The chromite materials could be categorized into six groups according to their behavior in heating. Smelting and reduction retards heating. These phenomena may take place in a different order or simultaneously. When simultaneous, the effect on heating is the greatest. A late surge of energy consumption usually indicates to difficult slag formation due to a low gangue mineral content or due to the refractoriness of the gangue mineral and may also indicate slow reduction. The preceding groups ranked from fast to slow slag formation/reduction were as follows: 1. Finnish and South African ores, 2. Russian and Madagascar ores, 3. Finnish and South African pellets, 4. Indian C and Kazakh concentrate pellets, 5. Indian ore and 6. Indian B (very pure) and Indian A (pressure ground) concentrate pellets. These groups are compared in Figure 3. The difference between the first and last group in regard to the maximum temperature difference range was more than 30 min! However, please note that the industrial process temperatures vary from case to case enabling good smelting results also in the case of chromite with a high Cr/Fe and MgO content [7].

The reduction tests showed that a reasonable reduction degree can also be achieved in the case of high Cr/Fe chromite raw materials at 1650°C if the gangue mineral type is chemically favorable for slag formation. A combination of a high Cr/Fe and a very low SiO₂ content is most often disadvantageous for reduction at too low temperatures. Sintering of the chromite concentrate seems to improve reducibility also in the case of high Cr/Fe chromite concentrates. Pressure grinding (a larger grain size) seems to be unfavorable for reduction in the case of a high Cr/Fe chromite.

Regardless of high reduction degrees in some ore cases, the large grain size of ores also affects the amount of residual primary chromite grains in the FeCr slag. The surface of the large chromite grains is totally reduced but the core of the same grains is practically unaltered and unreduced. This results in decreased chromium recovery in the industrial smelting process.

Figure 3: Time of the maximum $T_{outside} - T_{charge}$ (i.e. the time of max. energy consumption). Comparison of chromite types
4. CONCLUSIONS

The recovery of chromium depends on the grade of chromite, the method of chromite pre-treatment and the smelting process (e.g. temperatures). An extensive study on the factors affecting chromite reduction was executed. The first section of the study considered the factors which affect solid state reduction, i.e. the effect on the reducibility of the pellets above the melting zone of the submerged electric arc furnace. The second section of the study considered reduction under melting, i.e. at higher temperatures with flux (quartzite).

Pellet characteristics have quite a significant effect on the reducibility of chromite pellets. The following conclusions were drawn from the observations of solid state reduction tests:

- The porosity does not have as large an effect on the reduction degree (RD) of chromite pellets as supposed. However, a large addition of wood dust increased porosity and RD but also increased the amount of carbon added as well as lowering the oxidation degree of iron.
- Leaving out the carbon addition in the pelletizing mixture impairs reduction. The effects on reducibility are particularly bad in the case of dolomite-fluxed pellets.
- Oxidizing sintering of chromite pellets improves reducibility, but over-oxidation may have disadvantageous effects.
- Dolomite fluxing of the chromite pellets affects reduction variably, i.e. depending on the reduction temperature. At a certain temperature, a deactivating layer forms on the surface of the pellets resulting in a halt in reduction.
- A combination of dolomite / weak pellets / over-oxidation (high sesqui oxide proportion) was found very undesirable from a reducibility point of view.
- The chromite characteristics, e.g. chemical composition, chromite mineral grain size and pre-oxidation of chromite (i.e. sintering) also affect the reduction under melting. The following conclusions were drawn from the smelting test observations:
- The Finnish and the South African chromites behaved similarly in reduction. An increase in the proportion of ore in the mixture impaired the metal recovery. The difference in the metal recovery between a 100 % of pellets and a 100 % of ore charge was close to 10 % units.
- The reduction tests showed that a reasonable reduction degree can also be achieved in the case of high Cr/Fe chromite raw materials even at 1650°C if the gangue mineral type is chemically favorable for slag formation. A combination of a high Cr/Fe and a very low silica content is most often disadvantageous for reduction at too low temperatures.
- Sintering of chromite concentrate seems to improve reducibility also in the case of high Cr/Fe chromite concentrates.

REFERENCES