MELTING AND REDUCTION OF MANGANESE SINTER AND PELLETS

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ABSTRACT

Manganese ore fines cannot be added to the submerged arc furnace directly as they will prevent even gas flow through the burden. Low gas permeability in the burden will lower the degree of pre-reduction of ore and subsequently increase the carbon and energy consumption of the process. In addition, it is a potential hazard In order to utilize manganese ore fines in the furnace they are agglomerated into sinter, pellet or briquettes. In this work the melting and reduction properties of sinter and pellets have been investigated. The effect of adding fluxes such as dolomite and quartz has also been investigated. Results show that an increased content of acid oxides will lower the melting point and subsequently increase the reduction rate.

KEYWORDS: *Manganese, agglomerates, sinter, smelting, reduction, fluxes.*

1. INTRODUCTION

Manganese alloy is produced in a submerged electric arc furnace or in blast furnaces. The reduction of manganese oxide in blast furnace has in the recent years become more unusual due to the high consumption of carbon materials [4]. During mining, transportation and handling a large fraction the manganese ore is broken up into different size fractions. The fine ore can disrupt the flow of CO- and CO_2-gas through the burden, subsequently reducing the degree of pre-reduction. The fine fractions must therefore be agglomerated into larger lumps, in order to promote even gas flow. This can be achieved through a number of different processes. The agglomerates used in this work has been sintered and pelletized, which means that is has been partly molten and reduced, in order to create bigger lumps.

The raw materials consist of MnO_2, Mn_2O_3, Mn_3O_4 and MnO in combination with SiO_2, Al_2O_3, CaO and MgO. In ferromanganese production CaO and MgO are considered basic oxides. Similarly SiO_2 and Al_2O_3 are acid oxides. The term *basicity* is used to describe the ratio between basic oxides and acid oxides. Manganese ores mainly contain MnO_2 or Mn_2O_3, whereas the sinter and pellets are pre-reduced to Mn_3O_4 and MnO. During the prereduction with CO gas in the industrial furnace all higher manganese oxides are reduced to MnO before the melting starts. Even though green ore and heat treated sinter contains the same oxides species the mineralogy differs. In green Gabonese ore Si is found in quartz, but in sinter made from the same ore it is found in tephroite(Mn_2SiO_4) [6]. In figure 1 the ternary phase diagram for the MnO-SiO_2-Al_2O_3-system is shown. It can be seen that the melting temperatures for tephroite, rhodonite and spessartite are considerably lower than the liquidus for the pure oxides, and studies shows that there is a clear relation between slag composition and the liquidus temperature [12]. Hence, there is also a relation between basicity and liquidus composition, given by the MnO content of the slag, at a given temperature [13]. An increased amount of acidic oxides will decrease the liquidus temperature, or the liquidus MnO content at a given temperature. In this work the reduction of heat treated raw materials, such as sinters and pellets, and the effect of low melting phases is studied. The melting and reduction of manganese ore, sinter and pellets is a study of the MnO-SiO_2-Al_2O_3-CaO-MgO-slag system and the establishment of the first liquid slag. The sample will contain two phases at temperatures required for reduction, a solid MnO phase and a liquid slag containing all the oxide

species. As the liquid slag is reduced by solid carbon the composition of both phases stays the same but the amount of solid MnO decreases. MnO is reduced from the liquid part of the slag, and solid MnO will dissolve into the slag to replace the reduced MnO. This reduction will take place on the top of coke bed found in the lower part of the furnace [11]. When all the solid MnO is dissolved into the liquid slag, the viscosity is at the lowest, and it will flow into the coke bed before it is tapped from the furnace [1].

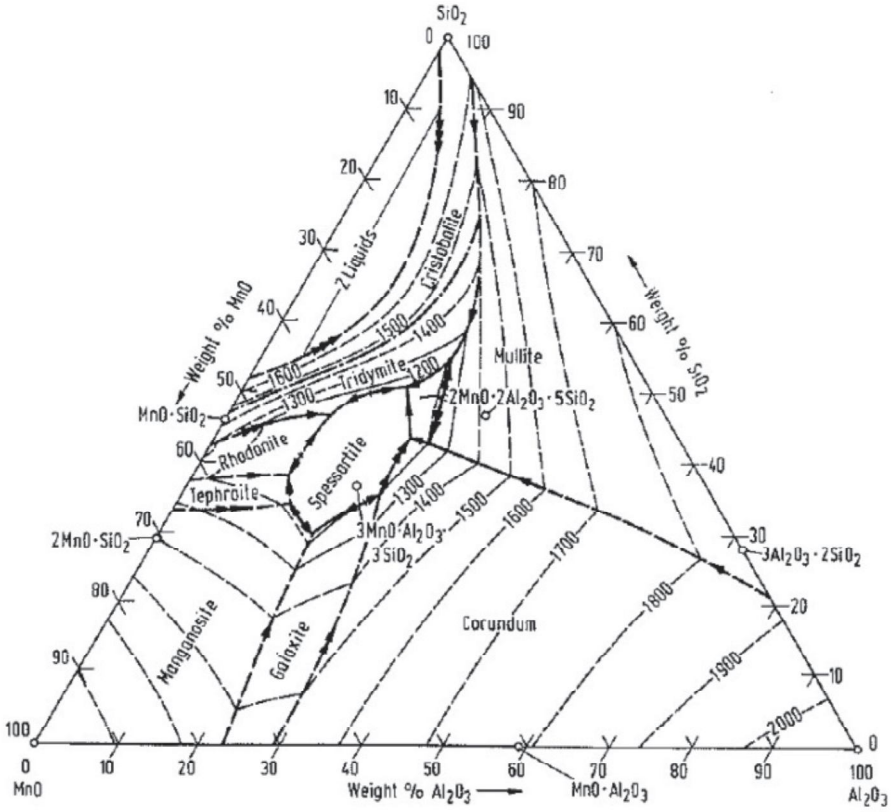

Figure 1: Liquidus lines in MnO-SiO_2-Al_2O_3- slag system [3]

2. EXPERIMENTS

During these experiments several agglomerated raw materials were used. Pellets were made from Gabonese ore, CVRD ore called MF15, and Assmang ore. The pellets were made by crushing and grinding green ore to a powder, and then adding powder and water to a rotating drum. 0.5% of bentonite was used a binder. The pellets were heat treated at 1200 °C for 30 minutes. Industrial sinters from CVRD and Gabonese ore were also studied. The composition of the sinters and the ores before pelletizing is given in table 1. To investigate the melting and reduction of manganese raw materials under more industrial like conditions a 50 kW induction furnace was used. A carbon crucible was used to contain the sample mix. The carbon crucible also acts as a heating element in the induction furnace. The experimental setup is arranged to give a temperature gradient, simulating the top of the cokebed.

A 10 cm coke layer in the bottom of the crucible will work as the coke-bed in the industrial furnace. A 10 cm layer of charge mixture was placed on top of the coke layer. The charge mixture itself is a mixture of manganese raw material, dolomite/quartz and coke. A 10 cm coke layer on the top works as insulation, and ensures that the charge is not re-oxidized. An s-type thermocouple was placed inside a carbon tube which rested on top of the coke bed. Another thermocouple was placed

on top of the charge mix. The thermocouple on top of the coke bed was used as a reference when controlling the temperature of the furnace.

Table 1: Chemical composition of raw materials

Ore	Vale sinter	MF 15 ore	Gabonese sinter	Gabonese ore	Assmang ore
Mn	43.2	44.3	60.3	50.2	38.1
Fe	5.2	6.0	2.7	4.9	5.1
SiO_2	14.6	5.0	6.9	3.6	5.9
Al_2O_3	10.5	8.2	5.7	4.9	0.32
CaO	3.9	0.22	0.19	0.13	13.7
MgO	0.98	0.33	0.11	0.08	3.8
TiO_2	0.5	0.4	0.16	0.12	0.01
K_2O	1.4	1.2	0.79	0.87	0.01
BaO	0.6	0.49	0.39	0.25	0.13

The composition of the charge mixture is given in table 2. In each experiment around 1 kg of charge mixture were used.

Table 2: Relative charge composition and final temperature of induction furnace experiments

Sample	Mn - sourse	Coke*	Quartz*	Dolomite*	Temperature
D 1	Gabonese sinter	25	0	25	1369
D 2	Gabonese sinter	25	0	25	1448
D 3	Gabonese sinter	25	0	25	1509
D 4	Gabonese sinter	25	0	25	1568
Q 1	Gabonese sinter	25	35	0	1303
Q 2	Gabonese sinter	25	35	0	1385
Q 3	Gabonese sinter	25	35	0	1455
Q 4	Gabonese sinter	25	35	0	1494
CP 1	Gabonese pellets	25	0	0	1315
CP 2	Gabonese pellets	25	0	0	1375
CP 3	Gabonese pellets	25	0	0	1420
CP 4	Gabonese pellets	25	0	0	1475
MF 151	MF 151pellets	25	0	0	1330
MF 152	MF 151pellets	25	0	0	1410
MF 153	MF 151pellets	25	0	0	1520
VS 1	Vale sinter	25	0	0	1175
VS 2	Vale sinter	25	0	0	1220
VS 3	Vale sinter	25	0	0	1330
VS 4	Vale sinter	25	0	0	1380
AS 1	Assmang pellets	25	0	0	1405
AS 2	Assmang pellets	25	0	0	1500
AS 3	Assmang pellets	25	0	0	1590

*Per 100 g of sinter

The size of the coke particles was 5-10 mm and the sinter and flux particles were sieved to 8-18 mm. The crucible was heated up to 1200°C where it was held for 30 minutes. This was done to ensure that the ore was completely pre-reduced before the last heating step. After the pre-reduction step the crucible temperature was increased 20°C per minute until the target temperature was reached. The furnace is then shut down and the melting and reduction reaction stops instantly due to the endothermic nature of the reaction. The experiments were repeated with different target temperatures in order to investigate the temperature dependence of the reduction and melting. After cooling the crucibles were filled with epoxy. A two cm thick vertical slice was cut out from the middle of crucible. These slices were used as a basis to determine the fraction of melted and reduced sinter.

3. RESULTS

The experiments conducted with the induction furnace are listed in table 2. When the temperature was increased above 1200°C the raw materials started to soften and melt. The melted and reduced sinter drained down into the coke bed. Three different categories were used to characterize the melting behaviour of the sinter/pellets; sinter/pellets with original shape, partially reduced sinter/pellets and melted and reduced sinter/pellets. By visual inspection the area fraction of ore that appeared unchanged after the experiment was classified as unreduced ore. The area fraction that had clearly changed shape or color was classified as partly molten or softened, and the area fraction that had flowed into the coke bed at the bottom was classified as reduced. The visual apperance of these three classifications is shown in figure 2.

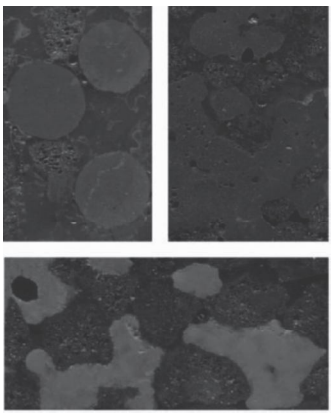

Figure 2: Assmang pellets with original shape(top left), partially molten pellets(top right) and completely reduced slag found in the coke bed (bottom)

The area fraction of the reduced sinter, partially molten sinter/pellets and sinter/pellets with original shape versus max temperature is given in figure 3.

Slizovkiy et al. [2] investigated the reduction of different manganese ores and sinters using the same S.C.I.C.E. technique used in this work. When the Gabonese sinter is mixed with quartz the temperature needed for melting and reduction is lower compared to a charge without quartz. At 1450°C, without quartz, they found only around 40% of reduced ore compared to 90% found in these experiments. The decrease in melting and reduction temperatures, with quartz, is expected from the phase diagram in figure 1 due to the increased amount of SiO_2 in the charge. The Vale sinter, high in acid oxides such as SiO_2 and Al_2O_3, also has a low meltingpoint and a high reduction rate. The decrease in melting temperature is expected from the phase diagram in figure 1. Low melting point for Vale sinter was also found by Ringdalen et al. [7].

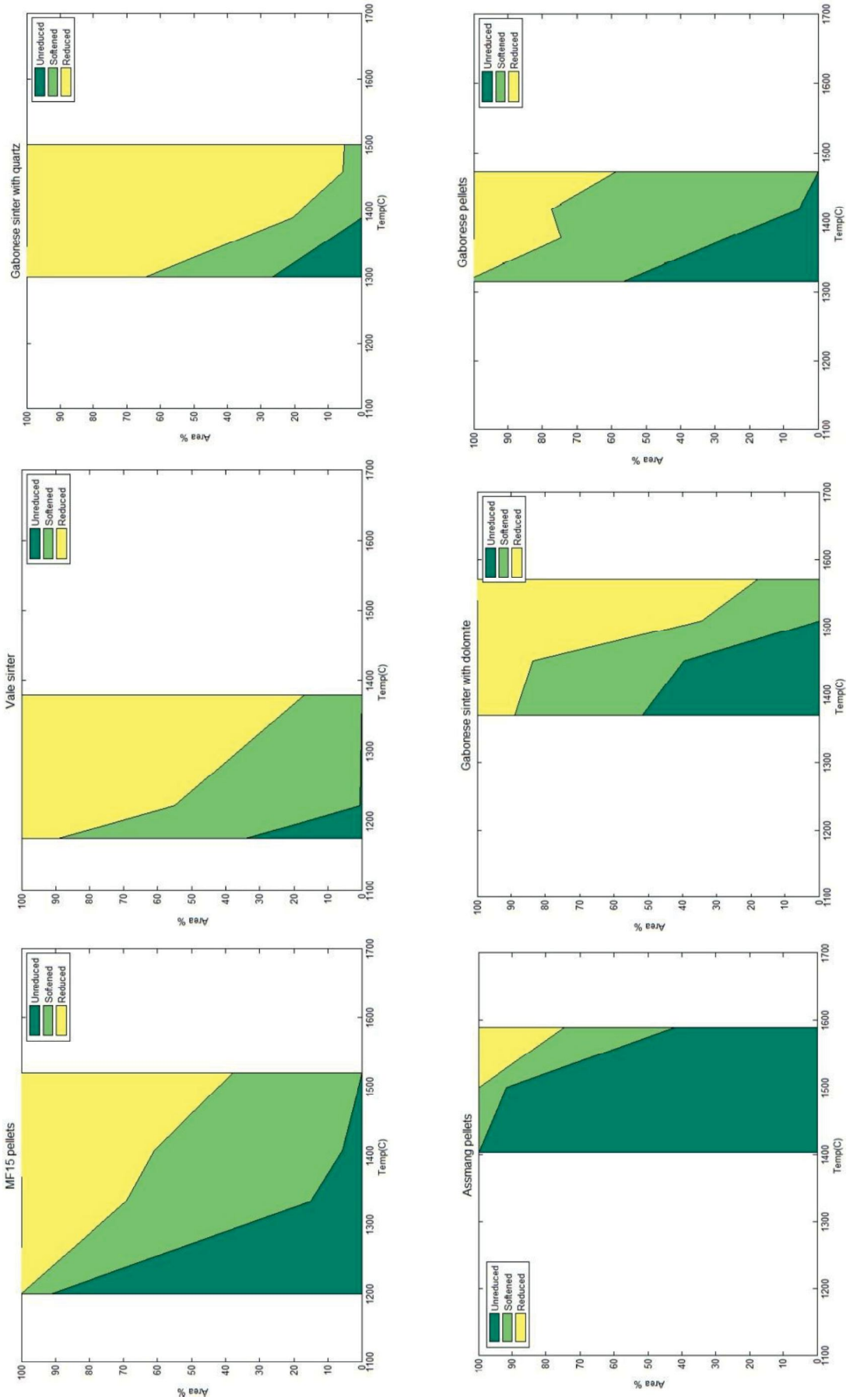

Figure 3: Area fraction of unmelted, melted and reduced sinter/pellets as a function of temperature for the different raw materials

Fluxing the Gabonese sinter with dolomite gave the opposite effect of quartz. The melting and reduction temperature seems to be around 150°C higher than the temperature observed in the quartz experiments. Xakalashe [1] has found the same temperature effect of dolomite and quartz using Gabonese ore instead of sinter. The Assmang pellets, also low in acid oxides and high in basic oxides, had a high melting point and a low reduction rate. The increased liquidus temperature will lower the amount of liquid slag at a given temperature and therefore decrease the contact area between sinter and coke, subsequently decreasing the reduction rate. The highly basic Assmang pellets also have a low melting/reduction rate.

Figure 4 shows the reduction path for all the charge mixtures in a ternary phase diagram. For all the charge mixtures except Assmang pellets and Gabonese sinter with dolomite, the liquid phase should contain between 65 wt% and 75 wt% MnO. EPMA analysis shows that slag from these samples from the top of the cokebed at around 1400°C contain 60 wt% to 65 wt% MnO. Slag from the Assmang pellet experiment contain only 9 wt% MnO. Low MnO content in this experiment was expected from the phase diagram. The sinter and dolomite experiment should also produce a slag with low MnO content, but the analysis revealed that the content was 58 wt%. This indicates the the mixing between the dolomite and sinter is not complete at the top of the cokebed. Completely reduced slag from the bottom of cokebed in this experiment had a MnO of 3.5 wt%, which is low compared to the other experiments. This means that the dolomite is only dissolved completely into slag after the reduction on top of the cokebed.

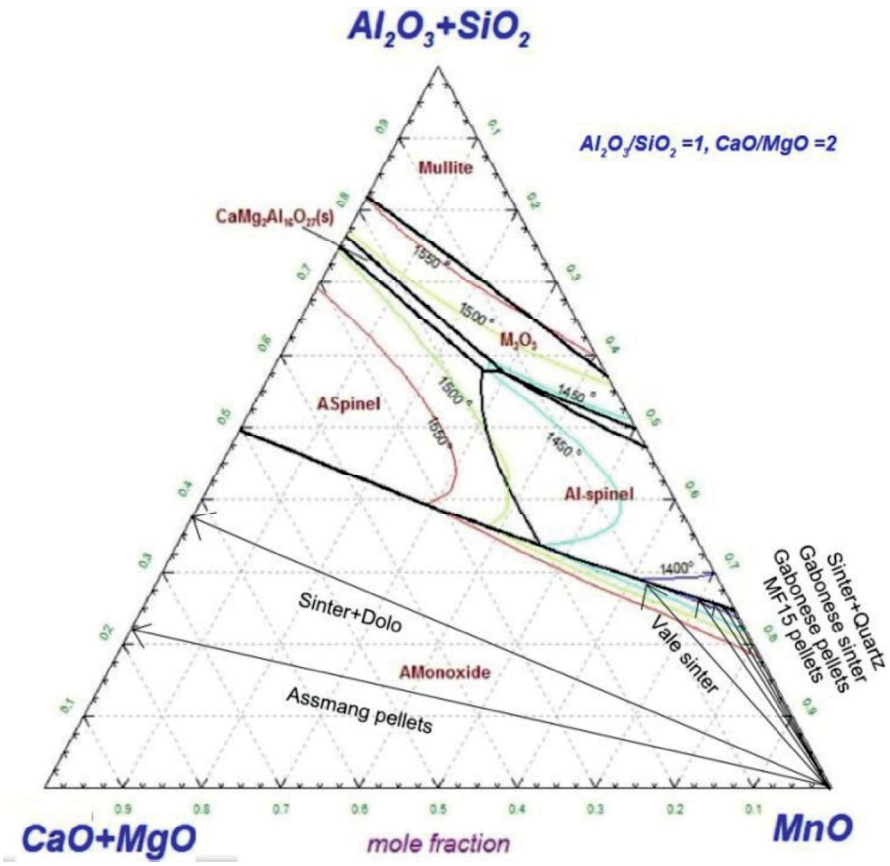

Figure 4: Reduction paths of the manganese raw materials plotted in a ternary liquidus phase diagram from Factsage

A SEM image from the interface between quartz and sinter in one of the quartz and sinter experiments is shown in figure 5. The phase closes to the quartz has the chemical composition of

rhodonite ((Mn,Fe,Mg,Ca)SiO_3) with mainly Mn. Between the rhodonite and MnO-SiO_2 slag, two phases can be seen; a dark phase with composition close to that of spessartine ($MnAl_2Si_3O_{18}$), and a light dendrittic phase with the composition of tephroite.

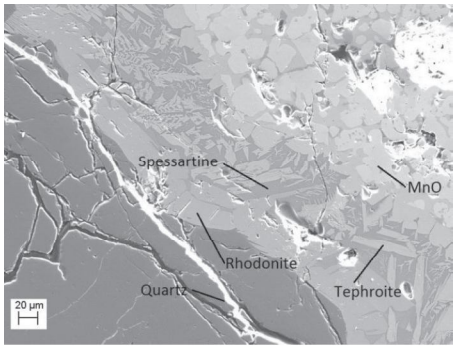

Figure 5: Inteface between sinter and Quartz at 1200°C

The dendrittic structure indicates that parts interface zone was liquid at high temperatures, and solidified into rhodonite and tephroite. Spessartine has a lower melting point than tephroite which is needed in order for the dendrittic growth of tephroite to be possible. The spessartine is enriched in aluminium, subsequently leaving the slag close to the MnO phase low in aluminium. The development of a tephroite phase in ore containing SiO_2 upon heating and reduction has also been observed by Kononov et al [9]. EPMA showed that both green sinters used in this work had manganese phases containing silicon and aluminium, with composition close to tephroite and spessartine. From figure 1 it is clear that these phases has a low liquidus temperature and will be the first phases in these sinters that melts upon heating. This could explain the fact that these sinters start to melt and reduce at a lower temperature than the ores studied by Slizovskiy et al.

4. MODELLING

The softening and reduction of manganese ore has been modelled by Slizovskiy et al [2]. determining the rate constants for softening and reduction of ore. The time dependent reduction can be expressed by the rate constant, the area of reduction, the activity of MnO in the slag, and the calculated temperature dependent equilibrium activity of MnO in the slag [4]:

$$\frac{\delta w_{red}}{\delta t} = k_{1,red} A(t)(a_{MnO} - a_{MnO(eq)}) \tag{1}$$

The rate constant is estimated from an Arrhenius equation:

$$k_{1,red} = k_{0,red} \exp(\frac{-E_1}{RT}) \tag{2}$$

where $k_{0,red}$ is a constant dependent on the ore, E_1 is the activation energy for the reduction, R is the gas constant and T the temperature. It is assumed that the reduction will only occur when there is a liquid slag phase present, that is, when the ore is melted to a solid MnO phase and a liquid slag phase. Hence, the area of reduction can be estimated by the amount of partly molten ore, since the contact area between solid particles are small. The amount of partly molten ore can also be expressed:

$$\frac{\delta w_{soft}}{\delta t} = k_{1,soft} W_0 \tag{3}$$

where the rate constant of softening ore can be estimated from an Arrhenius equation:

$$k_{1,soft} = k_{0,soft} \exp(\frac{-E_2}{RT}) \tag{4}$$

Using the amount of softened ore found from equation (3) the area of reduction can be estimated:

$$A(t) = \frac{l}{\rho_{ore}} \frac{S_P}{V_P} \int \frac{\delta w_{soft}}{\delta t} dt \tag{5}$$

where ρ_{ore} is the density of the ore, V_P is the volume of one ore particle and S_P is the surface area of one ore particle. l is the reacting coefficient which is assumed to 0,33 in these calculations, that is one-third of the melted ore has a boundary towards a coke particle If equation (3) is inserted into equation (5) the resulting equation can be expressed as:

$$A(t) = \frac{l}{\rho_{ore}} \frac{6 w_0}{D_P} \int k_{0,soft} \exp(\frac{-E_2}{RT}) dt \tag{6}$$

where D_P is the diameter of an ore particle. Some assumption has to be made in order to use this model:

- The density of slag and ore is equal and constant during softening and reduction.
- The ore particles are all spherical with the same diameter (15 mm).
- The contact area between softened ore and coke is one third of the total surface area of the ore(l=0,33).
- There is always solid MnO present in the slag and the activity of MnO in the slag is unity.
- The equilibrium activity of MnO in the slag is calculated from the equilibrium constant.

The values $k_{0,\,red}$, $k_{0,\,soft}$ E_1 and E_2 were found by comparing the model to the experimental results. The values where fitted by minimizing the squares of the difference between the model and experimental results. The values found for $k_{0,\,red}$, $k_{0,\,soft}$ E_1 and E_2 is given in table 3.

Table 3: Parametr for modeling softening and reduction

Sample	$k_{0,soft}$	E_2	$k_{0,red}$	E_1
Gabonese sinter and quartz	$7.00 \cdot 10^{11}$	379	$4.26 \cdot 10^{10}$	350
Gabonese sinter and dolomite	$2.50 \cdot 10^{12}$	418	$2.03 \cdot 10^{11}$	390
Gabonese sinter*	$1.28 \cdot 10^{11}$	375	$7.99 \cdot 10^{10}$	370
Gabonese pellets	$2.50 \cdot 10^{11}$	374	$2.68 \cdot 10^{10}$	370
Assmang pellets	$2.50 \cdot 10^{12}$	471	$5.38 \cdot 10^{11}$	441
Vale sinter	$2.46 \cdot 10^{11}$	330	$2.77 \cdot 10^{11}$	355
Gabonese ore*	$1.00 \cdot 10^{11}$	346	$3.41 \cdot 10^{10}$	370
MF 15 pellets	$1.24 \cdot 10^{11}$	375	$7.99 \cdot 10^{10}$	370

*From Slizovsiy [2]

Comparing the parameters for the modelling with those obtained by Slizovskiy et al. it is clear that adding dolomite will change the parameters $k_{o,soft}$ and E_2 closer to that of Assmang ore, which is higher in CaO, than Gabonese sinter. The values $k_{o,soft}$ and E_2 for the experiment with quartz is close to those for sinter alone found by Slizovskiy et al. The values found for $k_{0,red}$ varies more from those found by Slizovskiy, but this could be due to the fact that they had a fixed value of 370 kJ/mole for E_1. The $k_{0,red}$ for Assmang pellets is high compare to the others, but the reduction is slow. According to other authors [5, 8] an increase of basic oxides can increase the reduction rate in homogenous slag, but when there is still solid MnO present in the slag, a higher content of basic oxides can slow down the reduction [10].

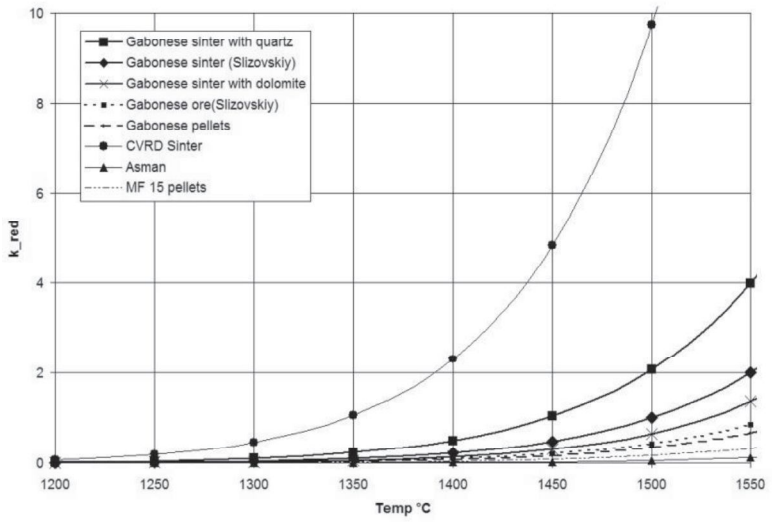

Figure 6: Reduction rate as a function temperature

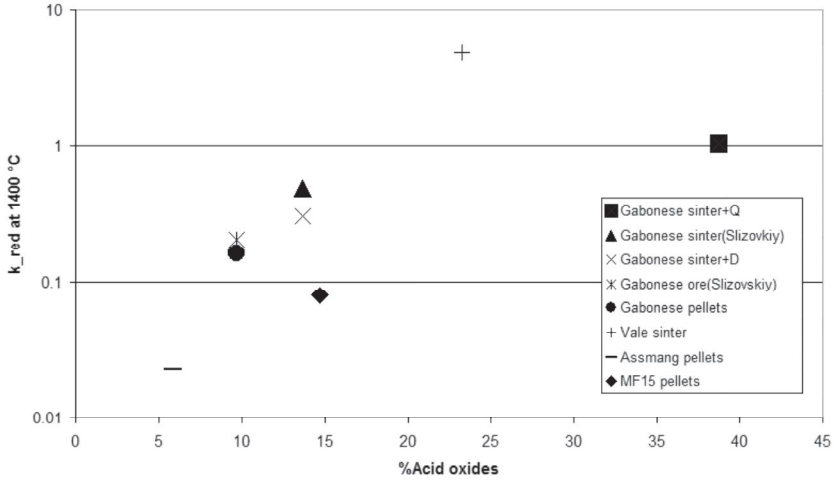

Figure 7: Reduction rate as a function total acid oxide content

The slow reduction of highly basic raw materials can therefore be expected. The k_{red} as a function of acid content is plotted in figure 7. The reduction rate is plotted as a function of acid oxide content since the basicity value is not very useful when describing the chemistry of the sample when the amount of basic oxide is very low, as it is in some of the materials used. The reduction rate increases when the amount of acid oxide increases. In the case where quartz is added

to the charge the reduction rate does not increase as much as one would expect from this figure. This indicates that the reduction rate increases more when the acid oxides are properly incorporated into the material compared to when they are added as lumps. Comparing the parameters for the modelling with those obtained by Slizovski et al. it is clear that adding dolomite will change the parameters $k_{o,soft}$ and E_2 closer to that of Assmang ore, which is high in CaO, than Gabonese sinter. The values $k_{o,soft}$ and E_2 for the experiment with quartz is close to those for sinter alone found by Slizovskiy et al. As figure 7 shows there is a close relation between reduction rate and amount of acid oxides. As the addition of acid oxides probably decreases the melting point of the material, the reduction rate is increased indirectly.

5. CONCLUSIONS

- Addition of quartz lowers the melting temperature, due to forming low melting manganese silicates. Several distinct phases are observed in the quartz sinter interface, indication that it has been completely liquid. High quartz content also lead to lower activation energy for melting and reduction.
- Dolomite has the opposite effect, rising the melting temperature. The activation energy for both softening and reduction will increase with increasing dolomite content, which leads to slower reduction. The Assmang pellets that are naturally high in CaO and MgO also have a low melting/reduction rate.
- The Vale sinter, which is high in SiO_2 has the highest melting and reduction rate of all the raw materials.
- High content of acid oxide will decrease the melting point and increase the amount of liquid phase available for reduction. This increases the reduction rate at a given temperature.
- Presence of low melting silicate- and aluminate-phases in the raw materials will lower the melting temperature, and increase the reduction rate, more than SiO_2 added as lumps to the charge.

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