

BEHAVIOR OF AGGLOMERATES IN FERROMANGANESE PRODUCTION

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ABSTRACT

Agglomerates like sinter and briquettes are often used as raw materials in the Submerged Arc Furnace producing ferromanganese. In this paper the effect of agglomerates on furnace operation will be discussed. While the positive effect of sinters as cooling agents as well as its positive effect on the flow pattern of the gas is well known, other effects like CO reactivity, strength and melting temperature are studied and presented here for two ores. It is shown that heat treated material, like sinter and pellets, will give a lower CO reactivity, a higher strength and lower melting temperature compared to lumpy ores and briquettes. One of the contributing factors is the porosity.

1 INTRODUCTION

In the production of ferromanganese alloys, one of the major costs is the cost of manganese raw materials, mainly manganese ore. Both from an economic point of view, as well as an environmental point of view, full optimization of the raw materials is desired. However, the small sized material – fines - can not be added directly to the furnace as operational instability may arise. The detrimental effect of fines is dependent on chemical composition, size of fines and also on the process itself; silicomanganese versus ferromanganese, open versus closed furnace, and the size of furnace. The fines will hence be agglomerated to gain a better size. Although the by far most used agglomeration technique for manganese ores are sintering, also pelletizing and briquetting are possible agglomeration techniques. In this paper the properties of lump material versus sinter, pellets and briquettes will be discussed.

When discussing the use of agglomerates in the furnace, e.g. lumpy ore versus sinter from the same ore, the chemical composition of the materials will mainly be the same as it reaches the high temperature zone in the furnace. After the raw materials are melted into a liquid slag, there will be small differences between the slag from an ore versus a sinter. The differences between these two raw materials will thus only be of interest in the prereduction zone, where the raw materials are still solid, as well as in the area on top of the cokebed where the Mn-source is melting. Some properties and their effect on the furnace operation are well known. Typical properties within this group are:

- ~ Oxygen content affecting power consumption, off gas temperature, CO/CO₂ off gas ratio and furnace stability.
- ~ CO reactivity affecting power consumption and C-consumption
- ~ Warm strength is believed to affect the stability
- ~ Cold strength which affect the fines generation, which again affects the stability
- ~ Porosity which affect the degree of prereduction, water content and cold strength
- ~ Shape factor and sizing affecting segregation and gas permeability in charge

In addition there are other properties, which are less familiar, both regarding basic measurements and their effect on furnace operation. In these groups we have:

- ~ Melting temperature, which may affect the temperature in the cokebed zone and the reduction temperature.
- ~ Sintering properties which should be very related to the melting temperature and the exothermic reactions in the particles
- ~ Thermal conductivity, which affects all the chemical reactions, as all are temperature dependent.
- ~ There is a big question if the electrical resistivity of solid ore particles has any interest in the operation, as one may argue that the electrical current will run through the cokebed with liquid slag and not the solid charge.

In this paper the CO reactivity and warm strength is compared between lumpy ore and pellets, sinter and briquettes from two ores. The agglomerates are all made in the laboratory, and may hence not be directly comparable with industrial agglomerates. In addition, a review on the melting temperature is done.

2 EXPERIMENTAL

Sinter, pellets and briquettes was produced in small scale apparatus from the same ore as used for reference. Lumpy ore, briquette and sinter was crushed and sieved to 10-14mm particles. Pellets and lumpy ore A at this size was not obtained, and + 6.3 mm pellets and + 4.5mm lumpy ore A was used. The chemical analyses of the material used in the CO reactivity tests are shown in Table 1.

Sinter was produced of the ore, coke breeze and returns in a pilot scale sintering plant. As the sintering of ore B was not successful, only previous results will be used for strength discussion. It is believed that the temperature was not high enough during the sintering.

Table 1: Chemical analyses of materials in wt%.

	Ore A				Ore B			
	Lump	Sinter	Pellet	Briquette	Lump	Pellet	Briquette	Sinter
Mn	52.5	53.1	54.0	39.1	52.3	57.8	39.9	55.4
MnO ₂	77.9	18.1	29.3	57.7	78.0	29.1	60.1	23.8
Fe	2.8	5.85	5.7	4.6	2.7	2.9	2.6	3.5
SiO ₂	2.6	6.41	5.6	5.9	3.1	6.6	8.4	8.6
Al ₂ O ₃	4.3	7.42	7.3	6.1	5.1	6.2	5.5	6.8
CaO	0.18	0.35	0.23	5.7	0.07	0.09	5.8	0.22
MgO	0.03	0.30	0.19	0.42	<0.01	0.11	0.31	0.05
BaO	0.34	0.32	0.33	0.23	0.16	0.21	0.15	0.21
K ₂ O	1.44	1.19	1.26	0.95	0.69	0.91	0.78	0.94
TiO ₂	0.21	0.35	0.39	0.31	0.11	0.14	0.14	0.16
P	0.10	0.10	0.11	0.08	0.12	0.13	0.10	0.14
S	0.01	0.01	<0.01	0.12	0.02	<0.01	0.13	0.01
CO ₂	0.1		0.1	0.2	0.2	0.1	0.2	
H ₂ O	4.5	<0.1	<0.1	11.6	4.9	<0.1	10.9	

The pellets were produced by grinding the raw materials to a d50 around 20µm. The pellets are made in a drum pelletizer with 0.5% of bentonite as binder and water. The green pellet moisture is about 14 to 15%. The green pellets are then burnt in a Muffle furnace to 1200°C in about 3 hours and then kept at this temperature for 30 minutes. The green pellets shrink about 10% when indurated.

In the production of briquettes, the raw material was <6 mm and was pressed in a 5 cm diameter cylinder with 10% cement as binder. The briquettes were cured for 2 weeks to obtain strength.

The furnace used for the heat treatment of the material under reductive atmosphere is shown in Figure 1 and Figure 2. 270-280g material is required for each experiment. During the experiment, the material will be heated under reducing atmosphere with a blend of CO and CO₂ gas flow. The heating rate is 1°/min up to 1100°C, the gas flow is 70% CO + 30% CO₂ at 1 atm 4 NI/min. When the

temperature in the steel-crucible reaches 1100°C, the sample is quenched under Ar. The temperature in the crucible, the weight loss and the off-gas composition in CO and CO₂ are measured during the experiment.

The abrasion strength of the agglomerate is measured after cooling with a Hannover drum. Procedure for the abrasion test was to sieve the sample at 14.0 – 10.0 – 6.3 – 4.5 – 3.15 – 1.6 mm for 15 minutes and weight each fraction, put everything in the Hannover drum and tumble it 30 minutes at a speed of 40rpm. After tumbling, the sample is sieved and weighted again.

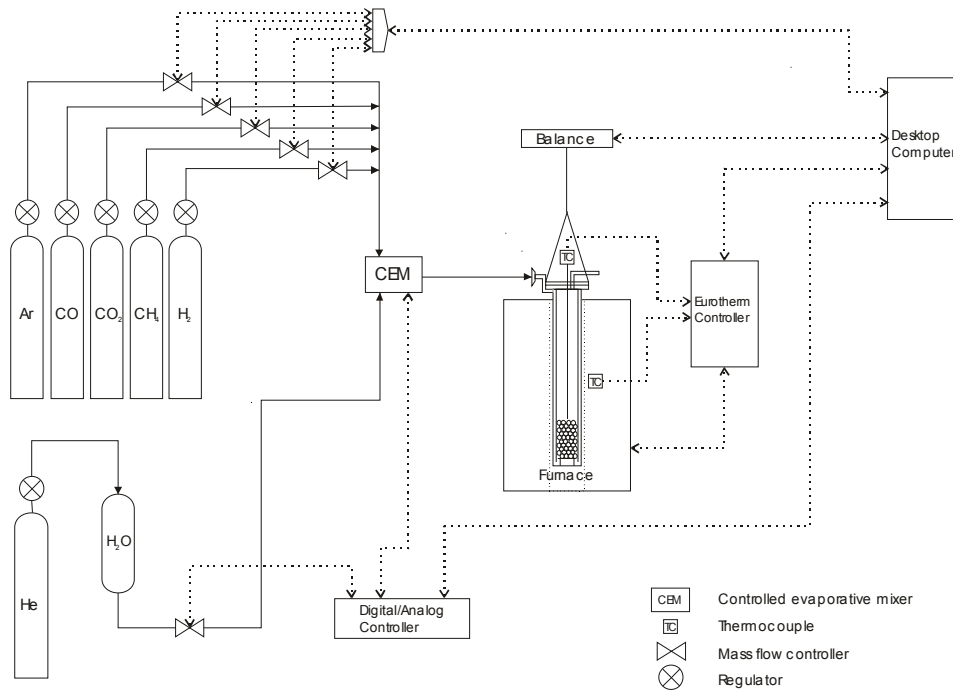


Figure 1: Piping and instrumentation diagram of the DisVaDri furnace.

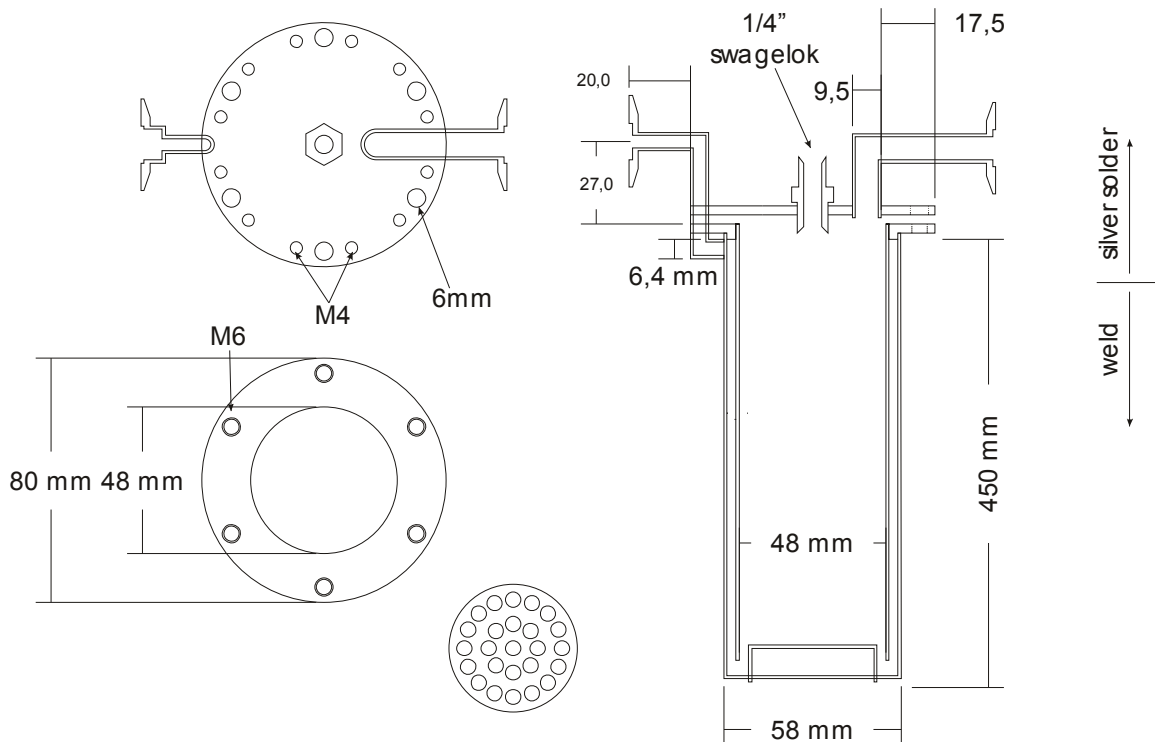


Figure 2: Side view of crucible and top views of flange components

Two parameters are calculated: the Cohesion index CI and the Thermal stability index TI which are defined this way:

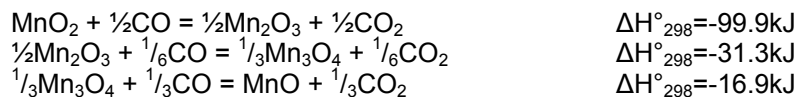
C.I.= quantity of material in the same original size range, meaning >10mm for most of the materials except for the pellets (>6,3mm) and ore A (>4,5mm).

T.I.= quantity of material >1,6mm after tumbling

One should note that previous papers studying mechanical strength of raw material might have calculated slightly different indices.

3 RESULTS AND DISCUSSION

When the high oxygen ores, Ore A and Ore B, is heated in CO gas at increasing temperature, the following reactions occur:



As these reactions occur, the temperature rises in the ore as all of these reactions are exothermic. The CO is consumed and CO₂ produced, and the weight of the sample will simultaneously decrease. This is clearly shown in Figure 3, where Ore B is heated to 1100°C. As the MnO₂ is reduced to Mn₂O₃ (=MnO_{1.5}), Mn₃O₄ (=MnO_{1.33}) and then finally to MnO, the molar ratio O/Mn is reduced from 2 to 1. By recalculating the weight loss (or off gas composition) to O/Mn level, the O/Mn level can be shown as a function of temperature as shown in Figure 4. In the figure it is assumed that all the manganese oxides are reduced to MnO at 1100°C. This is a valid assumption, as seen in Table 2. All of the materials investigated have more than 93% divalent manganese and less than 7% trivalent manganese. In the lower temperatures (<500°C) this graph will not be accurate as also bound water and some oxygen connected to the iron will be reduced.

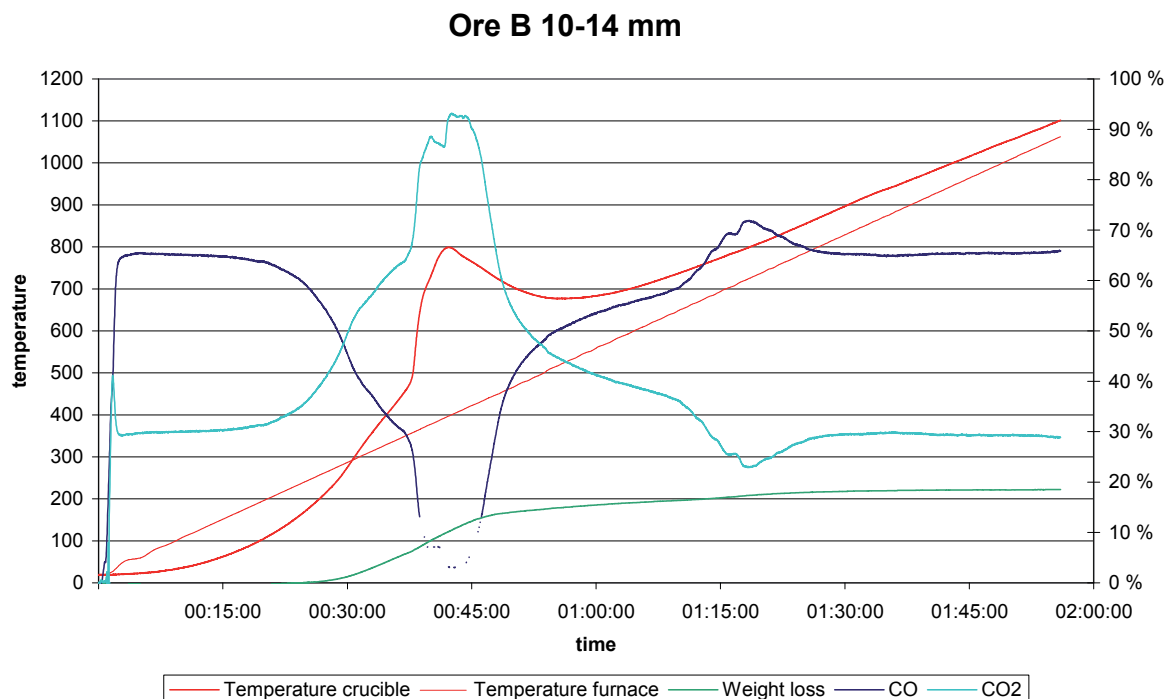


Figure 3: Ore B heated up to 1100°C in reducing atmosphere with measurement of weight loss and off-gas composition versus temperature.

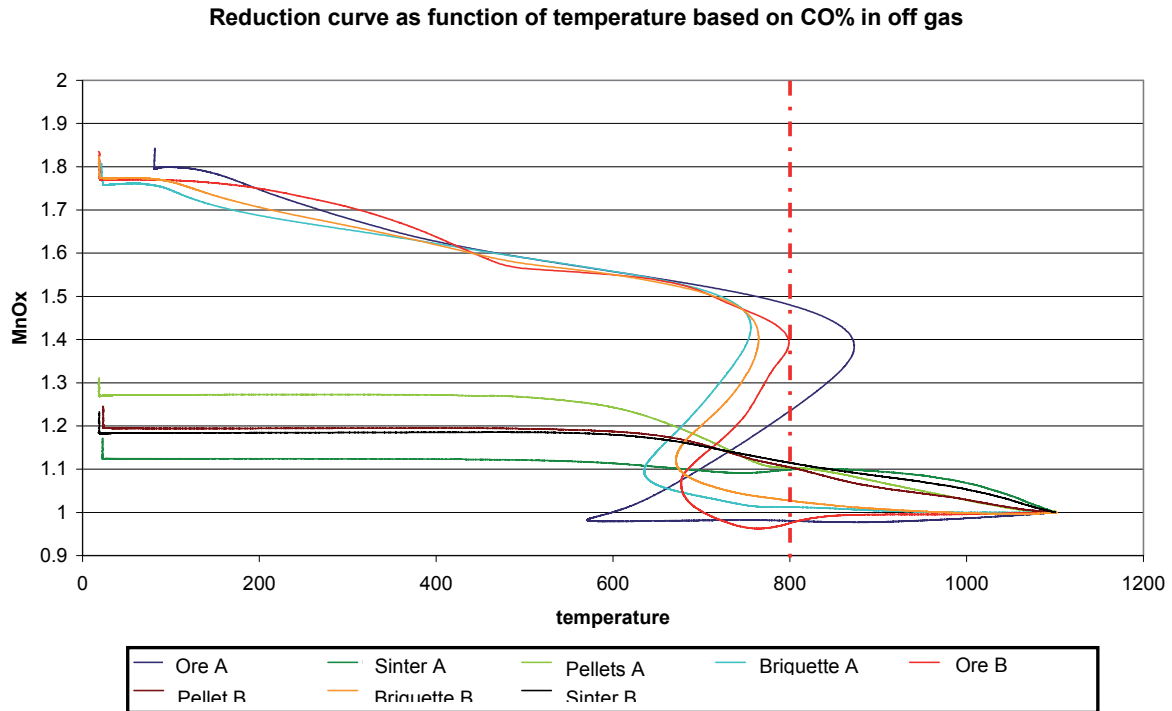
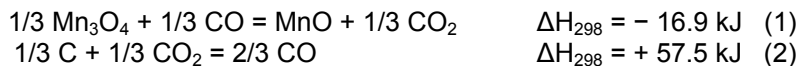


Figure 4: Reduction curves as function of temperature for various manganese ores and agglomerates. Start and finish point given by chemical analysis, the rest of the curve is calculated from the weight loss

Figure 4 shows the content of oxygen left in the ore as a function of temperature. At 800°C it is seen that ore and the briquettes have a lower oxygen content compared to the sinter, which will be slightly lower than the pellets. It is very clear that the agglomeration technique will determine the CO reactivity more than the difference between the two ores. This is also in accordance with previous publications[1,4]. Comparing the sinters and the ores especially [1], Temco sinter has a lower reactivity compared to Groothe Eylandt ore. In Ishak and Tangstad (2007), [4] it is shown that sinter from Gabon has a lower reactivity compared to Gabonese ore, and Mamatwan sinter has a lower reactivity compared to Mamatwan ore. In these reviews the sinter shows a generally lower CO reactivity compared to the lump ore. However, this comparison has not been the main issue in these investigations, and hence the sinter and ore may not be from the same original source.

When the ore is heated to 800°C the manganese oxides will be somewhere between MnO and Mn₃O₄. In the industrial furnace at this temperature, the reaction at the surface of the coke is sufficiently rapid to make the ore reduction reaction (1) and the ‘Boudouard reaction’ (2) run simultaneously. As a result the CO₂ gas formed by reduction of Mn₃O₄ may in turn react with carbon to give the overall reaction (3):



Assuming that the all of the oxygen above MnO at 800°C will react with carbon, the increase in carbon consumption and power consumption is calculated and shown in Table 2. While the high oxygen materials, the briquettes and the lumpy ore, will be totally prereduced, the sinter and pellets will give about 100 kWh higher power consumption due to the difference in degree of prereduction. There will of course be an uncertainty in these numbers as, first of all the temperature of 800°C is an assumption, and next, the heating rate and gas composition is not 100% the same as in an industrial furnace.

Table 2: Oxygen left as MnO_x at 800°C for each manganese ore and agglomerate which will lead to extra coke consumption

	Oxygen as MnO _x before experiment (analysis)	Oxygen left as MnO _x at 800°C Calculations based on CO in off-gas / weight loss	Oxygen left as MnO _x at 1100°C (analysis)	Theoretical extra consumption of coke (kg) per tonne of FeMn	Theoretical extra power consumption kWh per tonne of FeMn
Ore A	1.94	1.00 / 1.00	1.0	0	0
sinter	1.22	1.14 / 1.10	1.0	18 – 25	72 – 100
pellet	1.34	1.15 / 1.10	1.0	18 – 26	72 – 104
briquettes	1.93	1.00 / 1.01	1.0	0 – 2	0 – 8
Ore B	1.94	1.04 / 1.00	1.02	0 – 7	0 – 28
pellets	1.31	1.22 / 1.10	1.03	18 – 38	72 – 152
briquettes	1.95	1.00 / 1.01	1.0	0 – 2	0 – 8
sinter	1,27	1,11	1,03	19	76

The thermal decomposition during heating and reduction (CI) as well as the abrasion strength (TI) is shown in Table 3. In each end of the scale are the pellets, with the highest strength of the materials, and briquettes, with the lowest strength. The briquettes give around 70% -1.6mm after the reduction and tumbling. For Ore A the sinter gives a somewhat higher strength during tumbling than the ore. This is in agreement with previous publications [2], where the sinter from Gabon has a higher tumbling strength compared to Gabonese ore.

Table 3: Cohesion index and thermal stability index for the various ore and agglomerates

	Cohesion index	Thermal index
Ore A	29	61
sinter	35	80
pellet	94	96
briquettes	0	30
Ore B	14	64
pellets	96	92
briquettes	0	31

For these two ores, which is very similar in many respects, the porosity, as shown in Table 4, may explain some of the difference in CO reactivity and strength. Where the ores and briquettes show the highest porosity, they also have the highest reactivity and the lowest strength. As the porosity is lower in the sinter, the CO reactivity is higher and the strength is lower. The lowest porosity is definitely in the pellets, where the strength are highest and CO reactivity lowest.

Table 4: Absolute density and porosity for the manganese ores and agglomerates

Sample	Absolute density (g/cm ³)	Porosity (%)
Ore B	4.6	18.5
briquette	3.25	22.19
sinter	3.84	11.13
pellet	4.12	4.68
Ore A	4.15	22.58
briquette	3.28	24.34
sinter	4.18	17.70
pellet	4.33	11.85

Table 5: Melting characteristics of the materials compared to melting temperature of ore (no replicas)

Material	Start melting	Start reduction	Finish melting
Ore B	Ref	21	146
briquette	-44	-36	146
sinter	-81	29	263
pellet	-4	13	221
Ore A	Ref.	47	165
briquette	-203	-184	50
sinter	-94	-85	97
pellet	-159	-133	65

The melting temperature of the ore may be an important factor affecting the temperature in the high temperature area of the furnace. The melting temperature is affected by the chemical composition, the mineralogy and the grain size of the minerals. When considering the concept of a melting temperature, both the liquidus composition as well as the reduction rate is of importance. A few introductory melting experiments were performed in a sessile drop furnace, Table 5. Although there are no conclusive data due to any replicas, all the agglomerates melts at a lower temperature compared to the ore. Both sinters melt at about 100K lower temperature. This is in accordance with previous publications; Gaal et al. [6] found that comparing CVRD sinter and CVRD ore, the sinter starts to melt and reduce at lower temperatures. The reduction of the sinter starts about 100°C lower temperature compared to the ore. Also experiments with industrial sized particles show that the sinter is melted and reduced at a lower temperature [7]. The difference in melting temperature, and hence the reduction temperature, was about 100°C between the ore and sinter.

The effect of the melting temperature may affect the temperature in the coke bed zone. However, whether a high melting temperature is beneficial or detrimental to the operation may be discussed. Although one may believe that a high melting temperature will give a high temperature in the coke bed, and hence good reducing conditions, several SiMn furnaces operate with high quantities of low melting HC FeMn slag. Thus, these matters need to be further clarified.

In addition to CO reactivity, strength and melting temperature, also oxygen content, shape factor, thermal conductivity and electrical resistivity may be important parameters when discussing the effect agglomerates versus lumpy ore has on the furnace operation.

The oxygen level of the ore is one of the main contributors to the power consumption and is also the biggest difference between the lump and the sinter. As the CO reduction of MnO₂ to Mn₂O₃, Mn₂O₃ to Mn₃O₄, and Mn₃O₄ to MnO, are all exothermic, they develop a lot of energy. Hence, assuming a constant off-gas temperature;

- an MnO₂ ore will decrease the power consumption by a little less than 650 kWh/t compared to an Mn₃O₄ sinter
- an Mn₂O₃ ore will decrease the power consumption by about 150 kWh/t compared to a Mn₃O₄ sinter

Although, a high oxygen ore may lower the power consumption, it also requires a more stable operation, as higher oxygen contents will bring both a higher amount of energy and gas into the furnace.

There is always a discussion if the electrical current will flow through the solid charge to a great extent. The latest results regarding electrical resistivity on charge materials are from Miyauchi et al [9, 10] are shown in Figure 5. These are from two different articles and hence, there may be no consistency between the ores and the sinter. From this figure, no distinct difference is seen between the ores and the sinters, neither in electrical resistivity nor in melting temperatures.

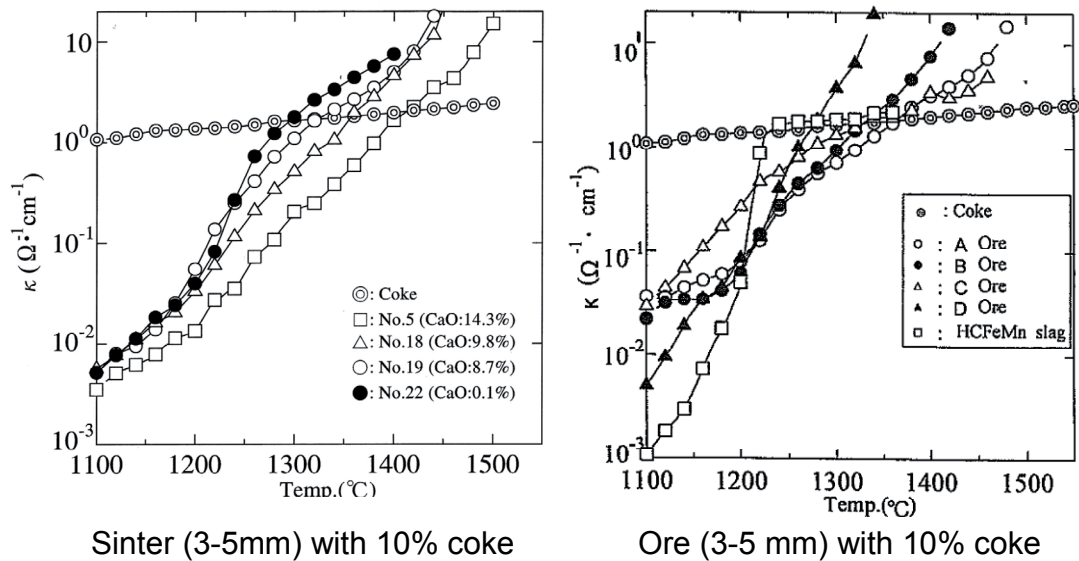


Figure 5: Electrical resistivities of sinter and ore mixtures with 10% coke from Miyauchi et al. 2001, 2004.

4 CONCLUSION

The two high oxygen ores, Ore A and Ore B, has been briquetted, sintered and pelletized in laboratory scale equipment. The CO reactivity, warm strength and melting point have subsequently been tested. It is shown that the CO reactivity is lower for heat treated materials like sinter and pellets, versus lumpy ore and briquettes. This may partly be due to the lower porosity in the sinter and pellets. The porosity may also contribute to the higher strength in the sinter and, especially, the pellets. The melting temperature of the ore will decrease when the grain size is smaller, and sinter will melt at about 100K lower temperature compared to the lumpy ore. Although uncertainties in the results due to unhomogeneity in materials, it is a trend for both types of ores.

5 ACKNOWLEDGEMENT

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