Kinetics of the Prereduction of Manganese Ores

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ABSTRACT

In the ferromanganese production a high reactivity of the higher manganese oxides will give a low carbon and energy consumption. By reviewing 6 laboratory investigations, it was found that Comilog and BHP ore had a higher reactivity than Asman, Mamatwan and Wessel. This may be because the minerals in the Comilog and BHP (pyrolusite (MnO_2) and kryptomelane ($K_2Mn_8O_{18}\cdot xH2O$)) are forming bixbyite ($(Mn,Fe)_2O_3$) which is reduced faster than braunite ($3(Mn,Fe)_2O_3\cdot MnSiO_3$, $7(Mn,Fe)_2O_3\cdot CaSiO_3$), which are the main minerals in Asman, Mamatwan and Wessel. Comilog has a higher porosity than BHP and has therefore in industrial practice given a better result regarding the reactivity. It is also found that the Mn_3O_4 reactivity is very dependent on the pre-treatment of the ore. A high precalcining temperature gives a low reactivity, while a low temperature will give a high reactivity.

1 INTRODUCTION

Several manganese-containing ferroalloys are produced. The most commonly used is high-carbon ferromanganese (HC FeMn). This alloy is either produced in blast furnaces or in electric furnaces. The electric furnace process, however, is more flexible than the blast furnace process, in that slags can be further processed to silicomanganese and refined ferromanganese. The choice of process is also dependent on the relative price of electricity and coke.

The raw materials, manganese ores, coke and fluxes, are heated, and the manganese oxides prereduced by hot CO gas from the reaction zones deeper in the furnace. The exothermic reactions contribute favourably to the heat required. Efficient production of HC FeMn depends on the degree of prereduction that occurs in the upper region of the furnace. Ores with a high reactivity will decrease the carbon and energy consumption. In this paper a comparison of the reactivity of various manganese ores are made.

2 PROCESS CHEMISTRY

The higher manganese oxides which predominate in manganese ores (MnO_2, Mn_2O_3 and Mn_3O_4) are relatively unstable and are easily reduced in solid state in the presence of CO.

$$MnO_2 + {}^1/_2CO = {}^1/_2Mn_2O_3 + {}^1/_2CO_2 \qquad (1)$$

$${}^1/_2Mn_2O_3 + {}^1/_6CO = {}^1/_3Mn_3O_4 + {}^1/_6CO_2 \qquad (2)$$

$${}^1/_3Mn_3O_4 + {}^1/_3CO = MnO + {}^1/_3CO_2 \qquad (3)$$

Gas reduction of the higher Mn-oxides are exothermic reactions, and a considerable amount of heat is produced, thereby preheating the charge materials in the furnace. The extent of gas reduction is reflected by the furnace off-gas CO_2/CO-ratio.

Solid Mn_3O_4 converts easily to MnO in the presence of CO according to reaction (3). The equilibrium CO/CO_2-ratio is $8\cdot 10^{-5}$ at 1000°C. The CO-gas reduction of Mn_3O_4 is thus a question of kinetics rather than thermodynamics.

After the temperature has increased to 700-1000°C the reaction on the coke surface is sufficiently rapid to make the ore reduction (3) and the Boudouard reaction (4) to run simultaneously. Thus, CO_2 formed by the reduction of Mn_3O_4 may react with carbon to give the overall reaction (5):

$$^{1}/_{3}Mn_3O_4 + ^{1}/_{3}CO = MnO + ^{1}/_{3}CO_2 \quad (3)$$

$$\underline{^{1}/_{3}C + ^{1}/_{3}CO_2 = ^{2}/_{3}CO \quad (4)}$$

$$^{1}/_{3}Mn_3O_4 + ^{1}/_{3}C = MnO + ^{1}/_{3}CO \quad (5)$$

If the Mn_3O_4 reactivity of the ore is low, most of the Mn_3O_4 will be present in the high temperature area in the furnace. The CO_2 produced from the reduction of Mn_3O_4 (3) will react according to the Boudouard reaction (4). The Boudouard reaction (4) is strongly endothermic, and as a result, the "direct reduction" of Mn_3O_4 (5) is also endothermic.

There is a close connection between carbon consumption, energy consumption and off gas analyses as shown in Figure 1. The maximum and minimum amounts of carbon are given by the extent of the Boudouard reaction (4). Maximum carbon consumption occurs when no gas reduction takes place, that is when all the Mn_3O_4 is reduced with carbon. Minimum carbon consumption occurs when the ore is completely reduced to MnO in the gas reduction zone. Then the off gas will not contain any CO.

Iron is always present in manganese ores. Reduction of the iron oxides runs parallel to the reduction of manganese oxides. Complete reduction in solid state to sponge iron is possible.

$$^{1}/_{3}Fe_3O_4 + ^{4}/_{3}CO = Fe + ^{4}/_{3}CO_2 \quad (6)$$

$$^{1}/_{3}Fe_3O_4 + ^{4}/_{3}C = Fe + ^{4}/_{3}CO \quad (7)$$

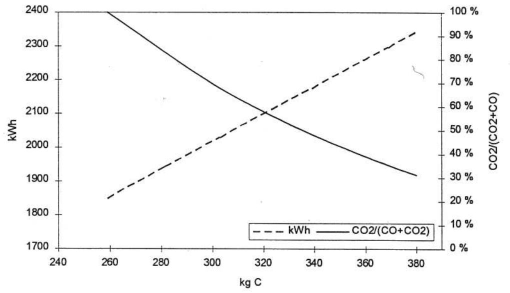


Figure 1. An example of energy consumption and off gas analyses versus carbon consumption (Tangstad, 1996).

3 RESULTS

Sørsdal (1986) investigated the prereduction of 6 ores as lumps and pellets. The chemical analyses are shown in Table 1. The ores were reduced by CO gas during heating, 10 degrees/min., up to 1200°C. The reactivity of the ores was found by measuring the CO_2 content in the off gas. The coke consumption and the power consumption per ton of metal produced in an industrial furnace are, as previously described, dependent on the CO_2 production in the high temperature area. Aderbigbe and Szekely (1981) found that the kinetics of the Boudouard reaction will be significant for a metallurgical coke from about 1000°C, but when alkalis are present this temperature will decrease by 100 to 200 degrees (Forsberg, 1988). Sørsdal's results are therefore rearranged so we can compare the CO_2 formation above 825°C per ton Mn and Fe in the various ores. This is shown in Figure 2 and Figure 3.

For both types of materials BHP ore have the highest reactivity, followed by Comilog, Wessel and Mamatwan. The highest reactivity will give the least amount of oxygen released above 825°C. Temco sinter and Ghana carbonate differ in order between lump and pellets, but for both materials they have a lower reactivity compared to BHP ore. There are some discrepancies in this study, as the measured amount of CO_2 developed are only in agreement with the amount expected from the analyses within 50%. This may be due to inaccuracy in analyses (where the sum varies from 89 to 102%), variations in gas flow into the furnace, and, of course, the inhomogeneity of the ore.

Table 1 Analyses of ores investigated by Sørsdal (1986)

	BHP	Mamatwan	Ghana carb.	Temco sinter	Comilog	Wessel
MnO_2	64.4	32.5			76.2	35.1
Mn_3O_4				75.2		
MnO	0.1	18.4	40.3		2.7	25.3
Fe_2O_3	5.7	6.0	1.7	10.0	8.0	13.9
SiO_2	18.6	6.2	15.4	8.3	5.3	5.4
Al_2O_3	2.4	0.5	1.9	4.3	2.3	1.9
CaO	0.7	13	3.9	1	6	4.9
MgO	0.3	4.2	5.6	0.5	1.4	0.6
CO2	0.2	14.7	31		0.3	2.2
K2O	2.3	0.1	0.5		0.5	0.3

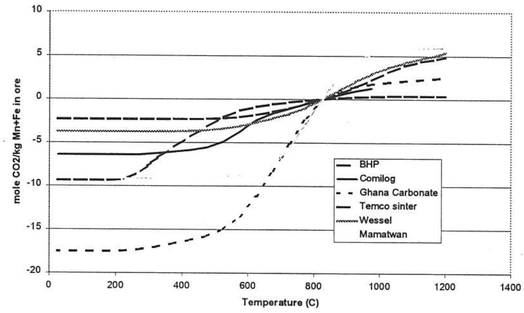


Figure 2. The reactivity of 6 ores using lump material (after Sørsdal, 1986)

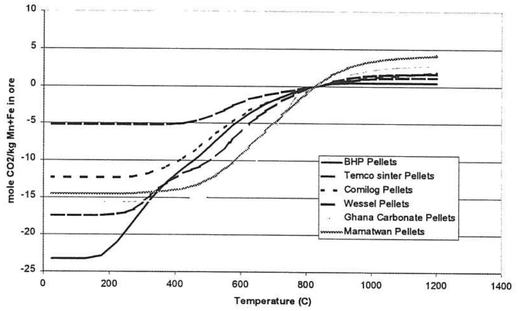


Figure 3. The reactivity of 6 ores using pellets (after Sørsdal, 1986)

Table 2. Ore data used by Todd et al. (1979)

	%Mn	%Fe	Av. Ox	x (MnOx)	Porosity	Density g/cc
A1	45	5.1	9.6	1.74	36	2.66
A2	56.5	3.4	15.3	1.95	12	3.97
A38-1	44.9	14.1	7.3	1.56	1	4.26
A46-1	53.7	6.1	9.5	1.62	0	4.45
A50-1	55.7	6.8	9.6	1.6	0	4.57
C-5	47.3	2.3	12.6	1.93	53	2.07
G-2	48.4	3.4	9.4	1.68	7	3.83
G-3	52.2	0.9	13	1.97	5	3.96
W-3	26.1	39	5.4	1.72	6	4.52
W-4	49.6	12.5	8	1.56	2	4.63
W-5	46.8	6.7	6.1	1.46	9	4.06

Todd et al. (1979) tested the reactivity of ores by heating the samples 3 degrees/min in a $33\%CO_2 - 67\%CO$ atmosphere. The ore data given are shown in Table 2. Based on the Mn and Fe content, the weight loss (which is mainly oxygen) per ton Mn+Fe is calculated and shown in Figure 4. Point zero is set to the weight loss at 800°C, as it is assumed that the oxygen released above this temperature will consume coke and thereby increase the power consumption. The smallest oxygen loss above this temperature is Comilog, followed by Amapa, Asman and Wessel. One of the BHP samples also show a very low oxygen release, and the other of the BHP samples gives a somewhat higher release. It can be concluded that the BHP ore is one of the better ores.

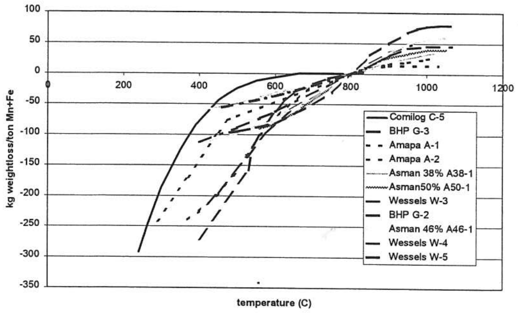


Figure 4. Reactivity found by Todd et al. (1979)

Table 3. Oxidation level of ores used by Beck (1998)

	BHP	Comilog
% MnO_2	48.9	64.27
% Mn_2O_3	28.16	5
% Fe_2O_3	1.89	4.61

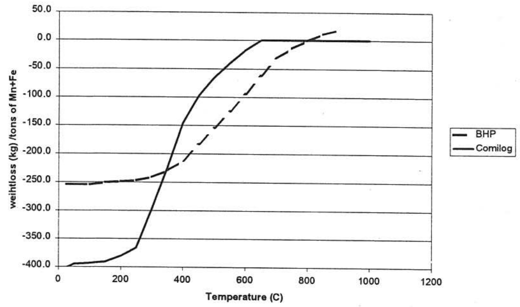


Figure 5. Reactivity of a Comilog and BHP sample after Beck (1998)

Beck (1998) investigated the reactivity of BHP and Comilog with CO gas at a heating rate of 8°C/min. The oxidation level is given in Table 3. Beck found that Comilog has a lower oxygen release above 800°C, compared to BHP (Figure 5). Beck also studied the reactivity of Comilog, BHP and Asman ore with H_2 at increasing temperature. As was shown in the previous studies, Comilog reacted fastest, followed by BHP and Asman. Asman had a much lower rate compared to Comilog and BHP.

Table 4. Comparison of the Mn_3O_4 reactivity given by the time it takes to react 50% and 75% of the ore Stalheim (1998).

Temp. (C)	Comilog	Comilog	BHP	BHP
	$\tau_{0.5}$	$\tau_{0.75}$	$\tau_{0.5}$	$\tau_{0.75}$
1000	23.3	41.3	23	39.2
1050	13.1	21.3	13.5	21.5
1100	9.2	13.8	8	12.8

Table 5. Comparison of the Mn_3O_4 reactivity found by Ruud (1994)

Ore	Weight loss (g/min per kg Mn+Fe)
Asman 48	8.4
Asman 48	8.2
Asman 48	7.4
BHP	11.2
Gloria	10.4
Comilog	9.9

Stalheim (1998) and Ruud (1994) investigated the Mn_3O_4 reactivity at high temperatures by precalcining the samples. Stalheim (1998) found that BHP and Comilog differed very little in reactivity (Table 4). The results from Ruud (1994) (Table 5) show that BHP had the highest reactivity followed by Gloria, Comilog and Asman. But as in the previous studies, we can see that the statistical significance is small, as there is a great difference within the same ore.

In the dr. thesis of Berg (1998) both Asman and BHP were studied. The results can be summarised as follows: The bixbyite particles in the BHP were reduced faster than the braunite particles in the Asman ore. As the BHP ore is composed mostly of pyrolusite, and Asman mainly of braunite, it is assumed that BHP will be reduced faster than Asman on average.

This is not what was found in investigating the prereduction rate of Comilog, BHP and Asman ore at CRT (Wasbø, 2001). The ores were heated at 2 degrees/minute in a 60%CO/40%CO2 mixture. The calculated amount of oxygen developed above 800°C is shown in Table 6. While Comilog is best, Asman is here rated faster than BHP. An inconsistency within the data is the fact that large BHP particles reduce faster than small BHP particles.

Table 6. Mass oxygen released from the ore above 800°C (Wasbø, 2001) per tons of Mn and Fe.

	2-5mm	10-15mm
Comilog	0 kg	48 kg
Asman	28 kg	39 kg
BHP	87 kg	69 kg

The most relevant test when investigating how good the different ores are, is using an industrial furnace. In spring –98 frnc. no. 11 at Eramet Norway Porsgrunn changed from BHP ore to Comilog ore. The charge mixture during the change is shown in Figure 6. In the MOR pellets, the sinter and the Samapa sinter the manganese is present as Mn_3O_4 and Gloria is a carbonate ore. As can be seen in Figure 7, the gas mixture changed steadily with increasing amounts of Comilog ore. The carbon consumption decreased accordingly (Figure 8). It must be emphasized that the furnace was in good condition before and during the change. In late May, the furnace had a planned stop, and in late June there was a water leakage in the furnace. The results regarding the off gas analyses and carbon consumption are therefore not as significant in this period as earlier in the run.

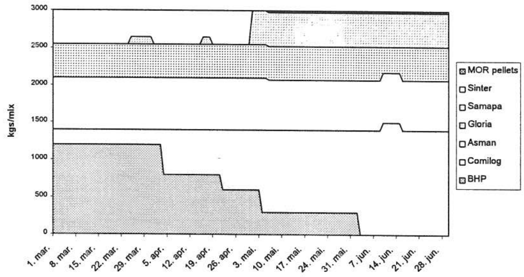


Figure 6. Manganese sources during transfer from BHP to Comilog.

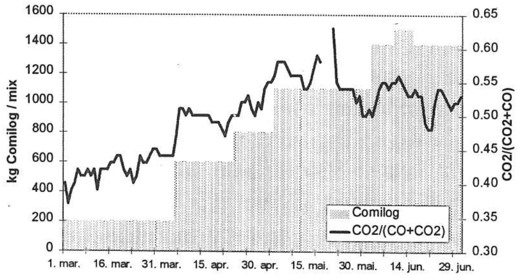


Figure 7. Off gas analyses with increasing amount of Comilog ore.

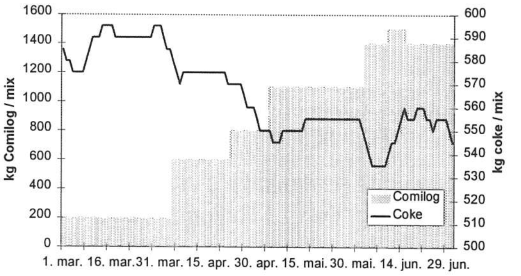


Figure 8. Coke consumption during increase of Comilog ore.

4 DISCUSSION

In the industrial manganese process, the consumption of energy and carbon is determined by the reactivity of the ore, that is, how much of the oxygen will be released at high temperatures. Seven laboratory investigations were reviewed to determine which ores would give the lowest consumption of carbon and energy. The results are summarised in Table 7. In all the studies BHP and Comilog are found as the most reactive ores. BHP is best in some, Comilog in others. There are however, major uncertainties in these studies. The largest one is the inhomogeneity of the ore. Each type of ore have different qualities, and even within one quality two different lumps may have a difference in reactivity. Despite this, BHP and Comilog stand out as the most reactive ores in all the studies. This can be explained by the fact that the reduction of bixbyite, which both Comilog and BHP will be reduced to, is faster than the reduction of braunite ores Asman, Wessel and Mamatwan as shown by Berg (1998).

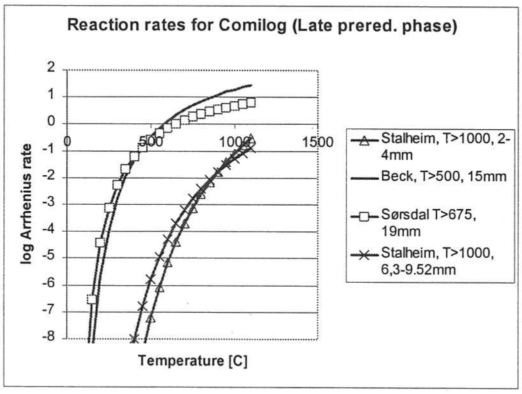
Table 7. A summery which gives the order of reactivity from the different publications.

Sørsdal lump	Sørsdal pellet	Todd et al.	Beck	Stalh	Ruud	Berg	Wasbø
BHP	BHP	Com	Com	Com BHP	BHP	BHP (?)	Com
Com	Tem.S.	BHP(?)	BHP		Glo	Asm	Asm
Gh.C.	Com	Am	(Asm)		Com		BHP
Tem. S.	Wes	Asm			Asm		
Wes	Gh.C.	Wes					
Mam	Mam						

Com-Comilog, Gh.C.-Ghana Carbonate, Tem.S.-Temco Sinter, Wes-Wessel, Mam- Mamatwan, Am-Amapa, Asm-Asman, Glo-Gloria

In the industrial furnace it was found that the Comilog ore would give a large economic benefit on the operation compared to the BHP ore, as the Comilog ore gave a much better prereduction and therefore a lower power and carbon consumption. This may be explained by the higher porosity in the Comilog ore as shown in Table 2. This is in accordance with Wasbø (2001) who also measured the porosity of Comilog and BHP ores. While the porosity of Comilog varied between 11 and 49% (7 samples), BHP ore varied between 5 and 7% (4 measurements).

In addition to the comparison of the different ores, one may also investigate further and find the reaction rates of the reduction of the higher manganese oxides. It is then of great importance that the reaction mechanism is known. By investigating the semi-reduced BHP particles, it is found that the Mn_3O_4 phase is only present in minor amounts (Berg, 1998). Between the Mn_2O_3 and MnO, the Mn_3O_4 phase will only be present as a thin rim around the Mn_2O_3 core. This means that the Mn_3O_4 reduction is as fast as the Mn_2O_3 reduction. This is verified by excavations of pilot scale furnaces (Tangstad, 1996) and industrial furnaces (Tangstad, 1999). By investigating the BHP semi-reduced ore samples by XRD, only Mn_2O_3 and MnO are found. It is found that the Mn_3O_4 reduction rate of a precalcined sample, which is calcined at high temperatures (Ruud, 1994, Stalheim, 1998), is much lower than the Mn_3O_4 reduction rate found from the reduction of a green ore. This is shown in Figure 9, where the Mn_3O_4 reaction rate versus temperature for the two different cases is shown. The reduction rate for BHP ore particles are found to be controlled by the diffusion through the product layer (Berg, 1998). The structure of the product layer is however, dependent on the conditions under which is it formed: When the Mn_3O_4 phase is formed under Ar gas at 900-1000°C, it will probably be denser compared to the formation at 600°C in CO gas. When investigating the reactivity of ores, one should therefore not precalcine the samples at high temperatures. It is the high temperature reactivity that should be compared, and the best way of doing this is to set point zero at about 800°C and see how much of the oxygen is released above this temperature.



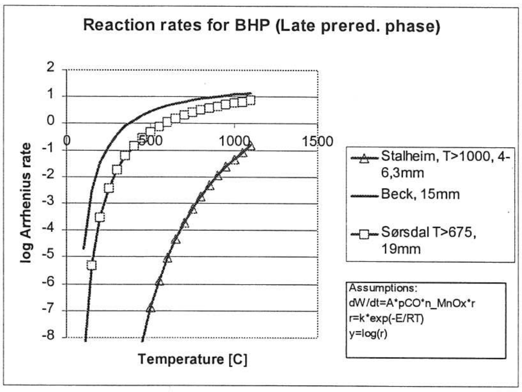


Figure 9. Reduction rates of Comilog and BHP ore under different heating rates.

5 CONCLUSION

In order to establish how the different ores affects the profitability of the FeMn production, a review of the prereduction reactivity was done. It was found that the ores which produced bixbyite were reduced faster than braunite ores. This means that BHP and Comilog ore will give a better prereduction, compared to Mamatwan, Wessel and Asman. Due to the high porosity in Comilog ore it reacted faster than BHP ore. In an electric furnace it was found that the carbon consumption went down 7% by substituting 40% of the mix from BHP ore to Comilog ore.

It was discovered that the Mn_3O_4 reactivity for BHP ore would change dramatically with the treatment before the Mn_3O_4 reduction. If the ore had been precalcined to Mn_3O_4 at high temperatures, the Mn_3O_4 reduction would be slow. If the green ore was reduced with CO gas at increasing temperatures, the Mn_3O_4 reduction was fast. The reactivity is determined by diffusion of gas through the product layer. If the Mn_3O_4 phase was formed at high temperatures the product layer would be denser and the reduction would therefore be slower.

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