

Kinetics of Gaseous Reduction of Manganese Ore

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0. ABSTRACT

The reduction of Mn_3O_4 to MnO has been investigated in a thermo balance apparatus. The charge was composed of Mn_3O_4 and coke, in about the same proportion as in an industrial scale reduction furnace. Except Argon supplied at the start before heating to reaction temperature, no extra gas was furnished. The reaction between the two solids proceeded through CO and CO_2 as gaseous intermediates. The reaction can be described by the shrinking core reaction model for the manganese oxide, and seems to be rate-controlled by chemical reaction at the reaction front or a mixed resistance of chemical reaction and gaseous diffusion through the product layer.

1. INTRODUCTION

The research group at SINTEF/NTNU working on Manganese processes is conducting research both on the solid state pre-reduction and the smelting process.

When a manganese ore lump descends through the shaft in the furnace, the ore often with an inlet composition corresponding to MnO_2 , it decomposes or is reduced by the countercurrent CO -containing gas first to Mn_2O_3 and then to Mn_3O_4 . The reaction mechanisms for these two steps depend on the mineralogical phases present and are usually explained by the shrinking unreacted core model, Berg and Olsen^{1,2}. After the ore has been exposed to temperatures up to $1000\text{ }^\circ\text{C}$ we might have a core of Mn_2O_3 surrounded by a layer of Mn_3O_4 and an outer layer of MnO . When the temperature increases above $1000\text{ }^\circ\text{C}$ the oxide will be reduced to MnO . These reactions seem to be controlled by pore diffusion through the product layer. The size of the pores, and the CO diffusivity, increases with temperature up to a certain point, where it starts to decline rapidly due to heavy sintering, Berg and Olsen^{1,2}.

The present paper is based on results obtained by Stalheim³. In this work we wanted to study only the last

gaseous reduction step from Mn_3O_4 to MnO . Furthermore we did not want to have an outer layer of MnO at

start. To accomplish this it was decided to produce Mn_3O_4 by decomposing manganese ore.

2. EXPERIMENTAL

2.1 RAW MATERIALS

Chemical analyses of the ores and coke that were used are shown in Table 1 and Table 2. The ores and the coke were taken from samples we received from Norwegian producers.

	COMILOG	BHP
Component	Wt %	Wt %
Mn	62.7	55
Fe	1.5	1.5
SiO_2	2.2	5
Al_2O_3	4.7	5
K_2O	1.0	2

Table 1. Chemical analysis of ores, after calcination at $1100\text{ }^\circ\text{C}$

		Wt%		
Fix-C		86.9		
Volatiles		2.0		
Ash		11.1		
-In ash:				
SiO_2	43.9%		MnO	5.9%
Al_2O_3	27.9%		K_2O	3.8%
FeO	6.2%		CaO	2.6%

Table 2. Chemical analysis of coke

We have not, however investigated if the samples were representative for the ores they used.

2.2 EQUIPMENT

The equipment used for the experiments was a thermobalance apparatus, with which it was possible to

weigh a crucible with weight up to 1.2 kg. The crucible was made of Kanthal APM, an FeCrAl alloy.

The crucible can be placed in a furnace, which can be moved up and down by a pulley system. Figure 1 shows the crucible and Figure 2 the experimental setup.

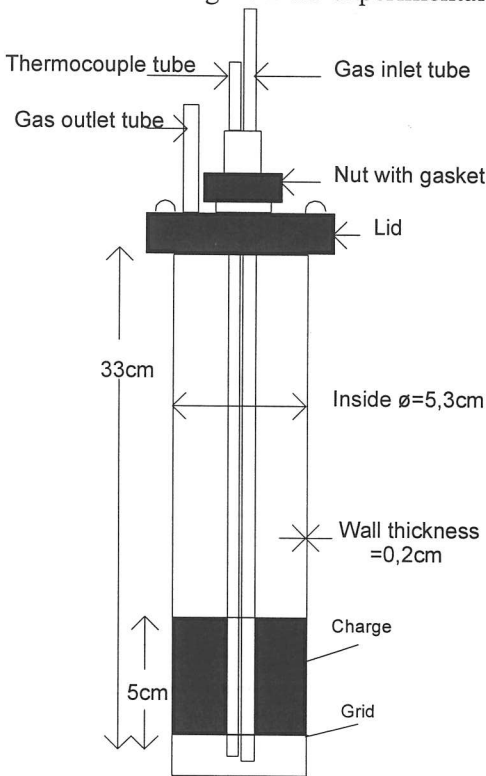


Figure 1 Crucible

2.3 CHARGE COMPOSITION

To prepare the charge, the ore was heated in the furnace in an argon atmosphere at 1100 °C. The coke was similarly calcined, and we observed a weight loss of 1,8 %, which is equal to the content of volatiles.

The charge for each experiment was mixed of 100 g of calcined ore and 20 g of coke. For the experiments with Comilog ore this gives a molar ratio of 0.25 mol Mn_3O_4 /mole C, which is a typical ratio for a FeM process.

2.4 EXPERIMENTAL PROCEDURE

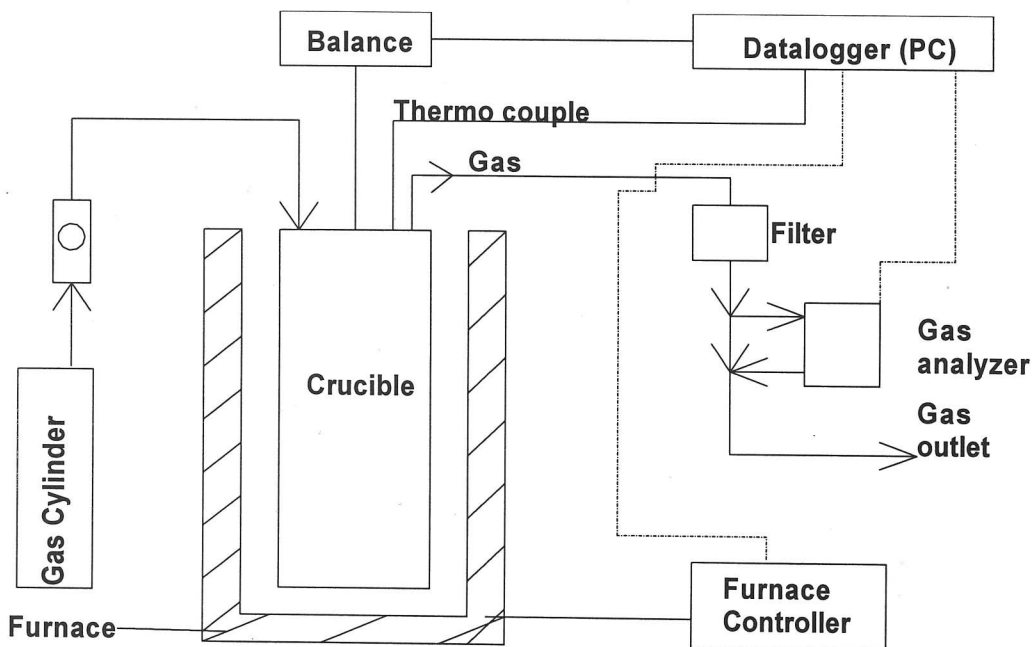
The furnace is heated to the set temperature for the experiment (1000 to 1100 °C). The mixed charge of ore and coke is poured into the crucible. The gas tubes and thermocouples are set in place and the crucible is hung in the wire attached to the weight. Argon gas is blown through the crucible for 5 minutes before the furnace is elevated to the position where the lid is in height with the furnace top. The argon gas is switched off. When the temperature in the crucible has reached 850 °C, the weight is tared.

The gas produced during the experiment leaves the crucible through a tube and goes through a silicon tube to an IR gas analyzer measuring the content of CO and CO_2 .

After the reduction experiment has run the wanted time (in the present experiments preferably to the time when further weight loss is negligible), argon is again blown through and the furnace is lowered. After the crucible is cooled, the resulting charge is weighed, and also split manually in a reduced ore fraction and a coke fraction which are separately weighed.

3. EXPERIMENTAL RESULTS

3.1 CALCULATIONS



The experimentally measured values of weight loss represent the total weight loss, W_{tot} of both ore and coke. The weight losses of ore W_m are calculated by help of the analyses of the outgoing gas, and the calculated values are also checked with the results of weighing the manually separated ore fractions.

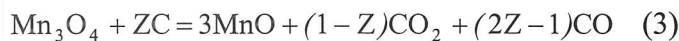
Ore reduction:



Boudouard reaction:



Adding these two equations we obtain:



Coke consumption per mole of removed oxygen is calculated by :

$$Z = 1 / (1 + \% \text{CO}_2 / 100) \quad (4)$$

The relation between the derivatives of W_{tot} and W_m at any time is calculated by:

$$k = \frac{dW_{tot} / dt}{dW_m / dt} = \frac{3Z + 1}{4} \quad (5)$$

The reaction rate (mole Mn_3O_4 per unit time) is given by the equation:

$$\frac{dn_{\text{Mn}_3\text{O}_4}}{dt} = \frac{1}{16k(t)} \cdot \frac{dW_{tot}}{dt} \quad (6)$$

The weight loss of ore is given by:

$$W_m(t) = 16 \cdot \int_0^t \frac{dn_{\text{Mn}_3\text{O}_4}}{dt} \cdot dt = \int_0^t \frac{1}{k(t)} \cdot \frac{dW_{tot}}{dt} \cdot dt \quad (7)$$

The weight losses are measured as discrete points. The integral is calculated by the trapezoid method:

$$W_m(t_N) = \int_0^{t_N} f(t) dt = \frac{\Delta t}{2} [f(0) + f(t_N)] + \Delta t \cdot \sum_{i=1}^{N-1} f(t_i) \quad (8)$$

where:

$$f(t) = \frac{1}{k(t)} \cdot \frac{dW_{tot}(t)}{dt} \quad (9)$$

and

$$t_N = \Delta t \cdot N \quad (10)$$

The coke consumption is calculated by:

$$\frac{dn_C}{dt} = Z \cdot \frac{dn_{\text{Mn}_3\text{O}_4}}{dt} = \frac{4}{3} \cdot (k - 1) \cdot \frac{dn_{\text{Mn}_3\text{O}_4}}{dt} \quad (11)$$

4. RESULTS AND DISCUSSION

4.1 DATA REGISTERED

Figure 3 shows temperature, total weight loss, % CO and % CO_2 as function of time for Experiment No. 3, which was conducted with 2-4 mm Comilog at 1100 °C.

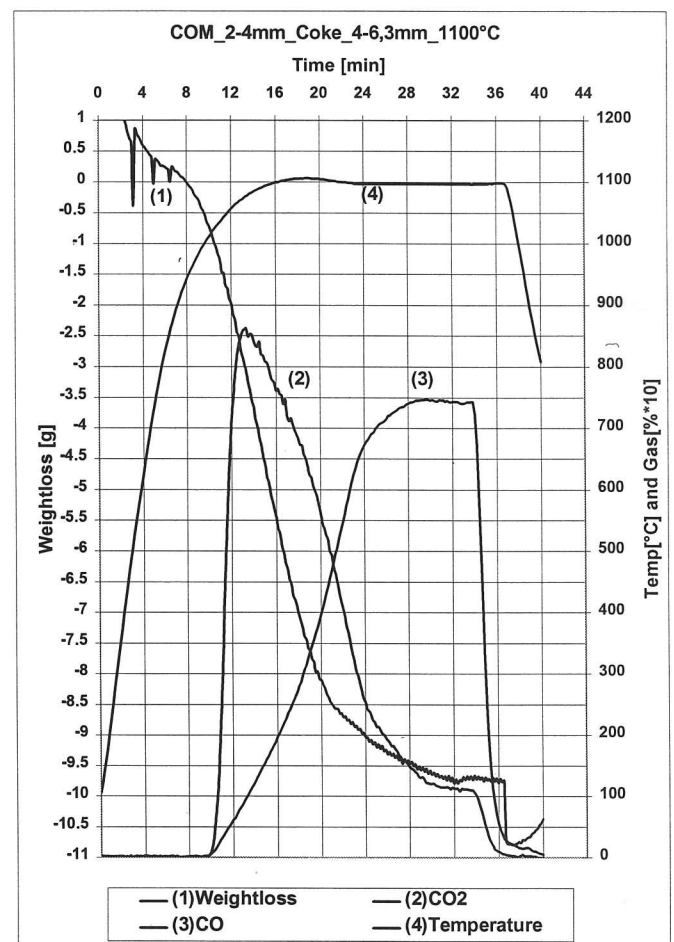


Figure 3. Registered data in exp. No. 1

4.2 WEIGHT LOSS OF ORE

With the COMILOG ore a weight loss of 6.7% corresponds to 100% conversion from Mn_3O_4 to MnO . With the BPH ore a weight loss of 6.0% corresponds to 100% conversion.

Figure 4 shows the weight loss for Comilog ore, 2-mm, reduced with two different size ranges of coke; 2- and 4-6.3 mm at temperatures 1000 and 1100 °C. We observe that the size of coke has no effect at 1000 °C. At 1100 °C the reduction actually has gone faster with the greater coke size, but the difference is small. This is not unexpected; as long as we have a big surplus of C, the coke size does not matter.

The temperature has a great effect. When the temperature is increased from 1000 to 1100 °C, the time needed for 90% conversion decreases 65%.

In Figure 5 the weight losses with Comilog ore are compared to weight losses with BHP ore. We observe that the times needed for a conversion of 80% or more are approximately the same for the two different ores (80% conversion is equivalent to 5.4% weight loss for the COMILOG ore and 4.8% for the BHP ore).

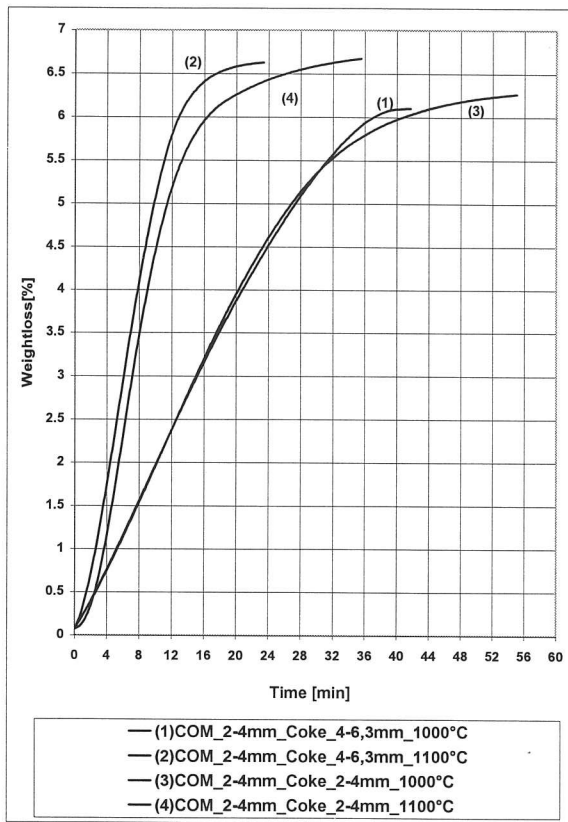


Figure 4. Weight loss of COMILOG ore 2-4 mm and two coke sizes

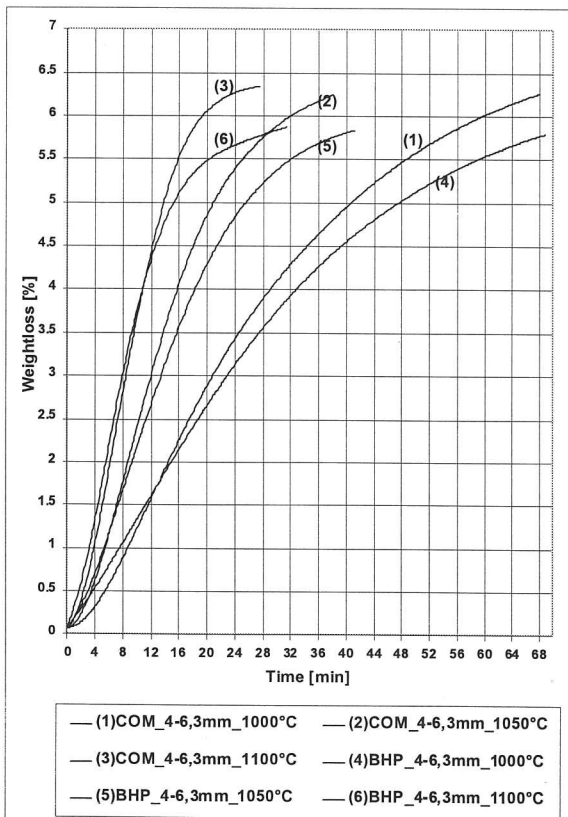


Figure 5. Weight loss of COMILOG and BHP ore; Coke size = 4-6,3 mm

4.3 REACTION RATE

Figure 6 shows reaction rate as function of time for 4-6.3 mm Comilog ore at temperatures 1000-1100 °C.

Figure 7 shows reaction rates calculated at 40% and 80% conversion as functions of temperature for different ore sizes (Comilog). We observe that:

- Reaction rate increases with increasing temperature
- Reaction rate decreases with increasing ore particle size.

4.4 REACTION MECHANISM

The total system consists of two solid phases and a gas phase. To analyze such a system, we can use the model presented by Szekely, Evans and Sohn⁴. As a first approximation, we have in the present paper analyzed separately the reactions in the ore and in the coke.

The fraction of unconverted ore ($1-X_m$) is traced as a function of reaction time in Figure 8. Assuming the shrinking-core model, Figure 9 shows the dimensionless radius of the unreacted core (r_c/R) as function of reaction

time. Comparing these curves, with the theoretical curves, given by Szekely, Evans and Sohn⁴ or by Levenspiel⁵ it seems that several mechanisms are determining the rate of the reduction reaction. The results given as fraction of unconverted ore indicate that either chemical reaction control or diffusion through product layer or both is rate controlling. When the results are plotted as dimensionless radius of the unreacted core, they indicate chemical reaction control or mixed control.

Figure 10 shows the reaction rate ($\ln[r]$) as function of $1/T$, calculated from the results given in Figure 7. From these results, Table 3 gives the activation energies calculated for the temperature ranges 1000-1050 °C and 1050-1100 °C

	COM 2-4	COM 2-4	COM 6,3-9,5
Temp. range	X=0,4	X=0,8	X=0,4
°C	kJ/mole		
1000-1050	207	209	194
1050-1100	121	125	111

Table 3 Activation energy

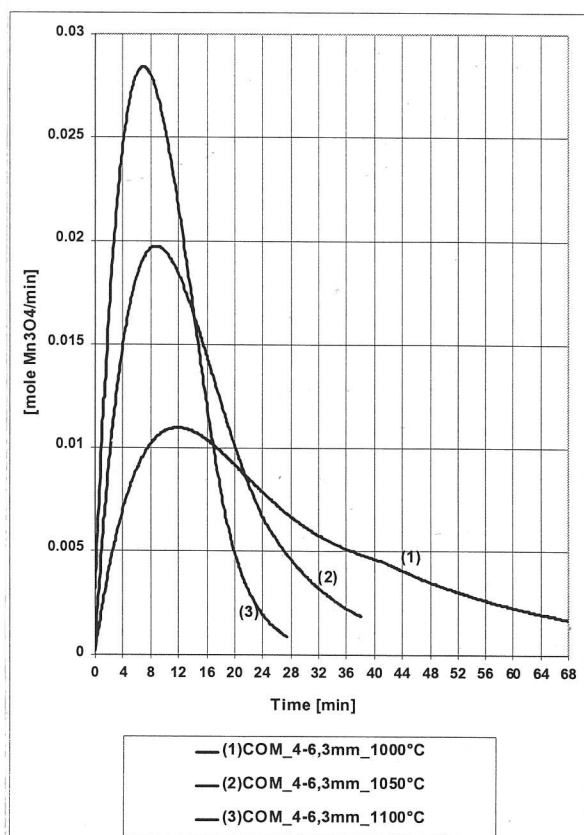


Figure 6. Reaction rate as function of time;Coke size = 4-6,3 mm

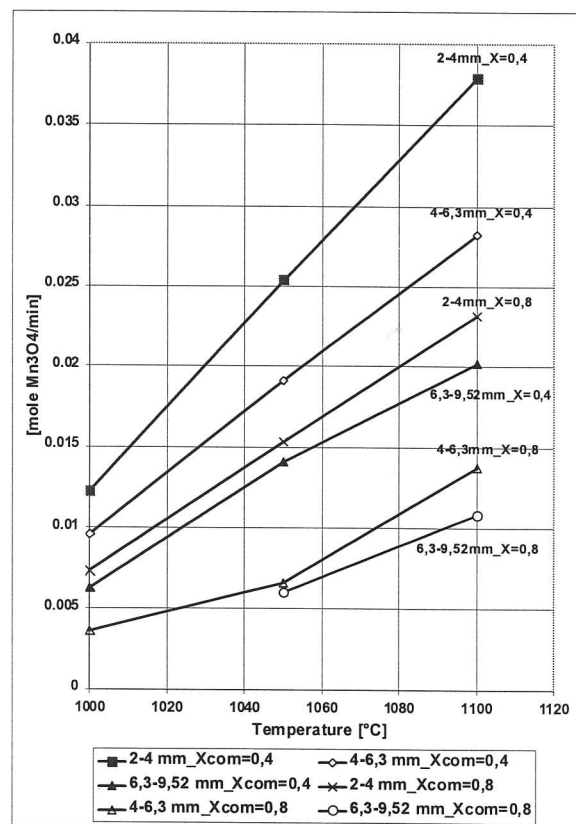


Figure 7. Reaction rate as function of temperature; X=0,4 and 0,8; Coke size = 4-6,3 mm

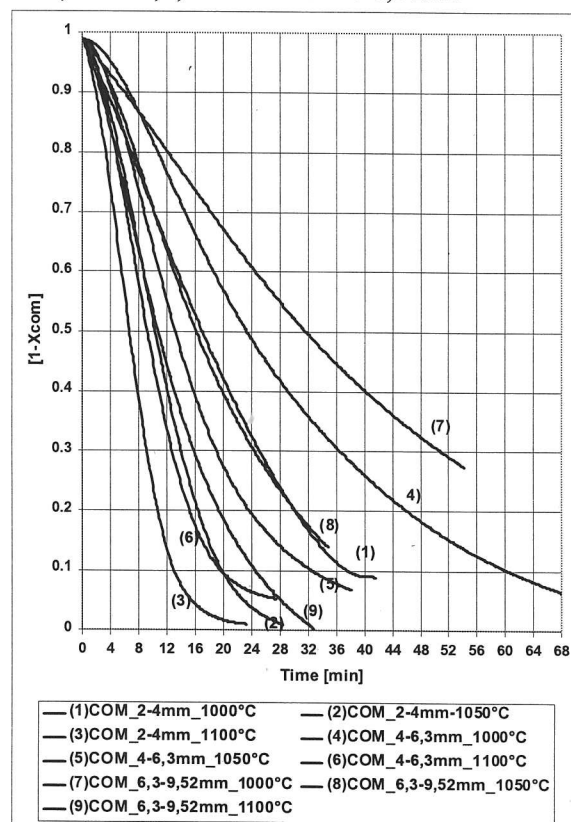


Figure 8. Conversion of Mn_3O_4 as function of reaction time, coke = 4-6,3 mm

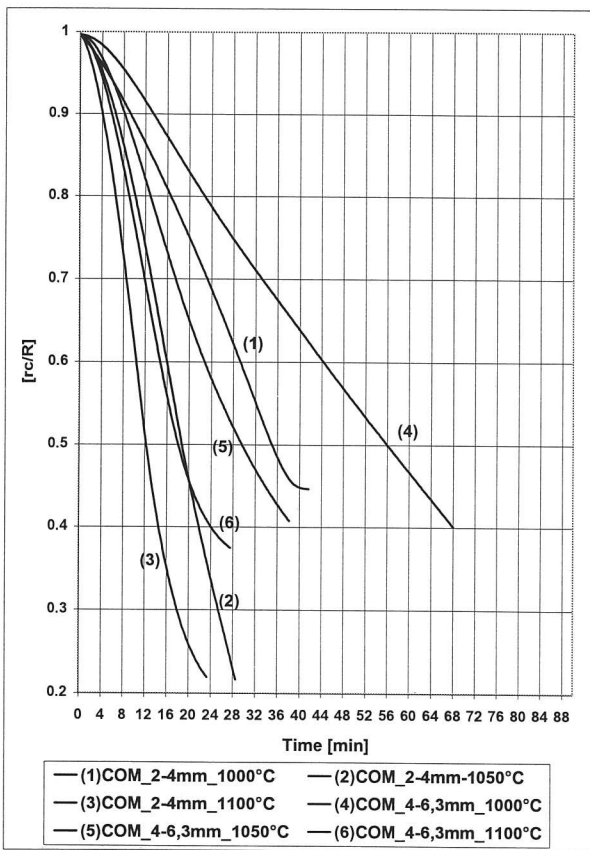


Figure 9. Progress of reaction; Mn_3O_4 reduction

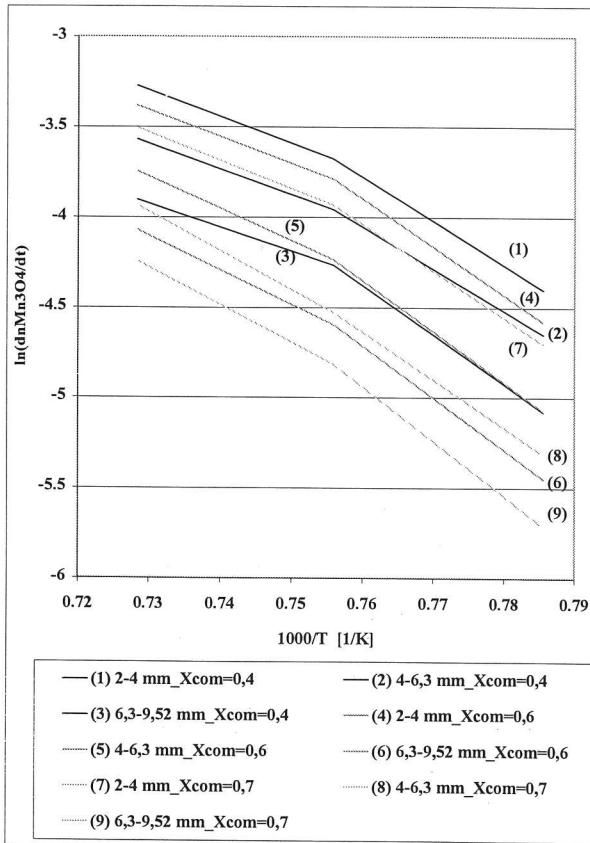


Figure 10. Logarithmic reaction rate as function of $1/T$

The activation energy is about 200 kJ/mole in the 100-1050 °C range, which clearly indicates chemical reaction control, and the difference between the finest and the largest fractions is small. But the activation energy is substantially lower in the 1050-1100 °C range, indicating perhaps a change in mechanism for high temperatures.

The fraction of unreacted coke ($1-X_c$) is plotted as a function of reaction time in Figure 11. Analyzing these curves we must bear in mind that there is a large surplus of coke, as in the industrial process. 100 % conversion of ore corresponds to consumption of about 20 % of the coke. Actually the curves in Figure 11 show the same trends for the individual experiments as Fig. 8 do. This shows that for these experimental conditions, and with the type of coke used, the Boudouard reaction seems to have little influence.

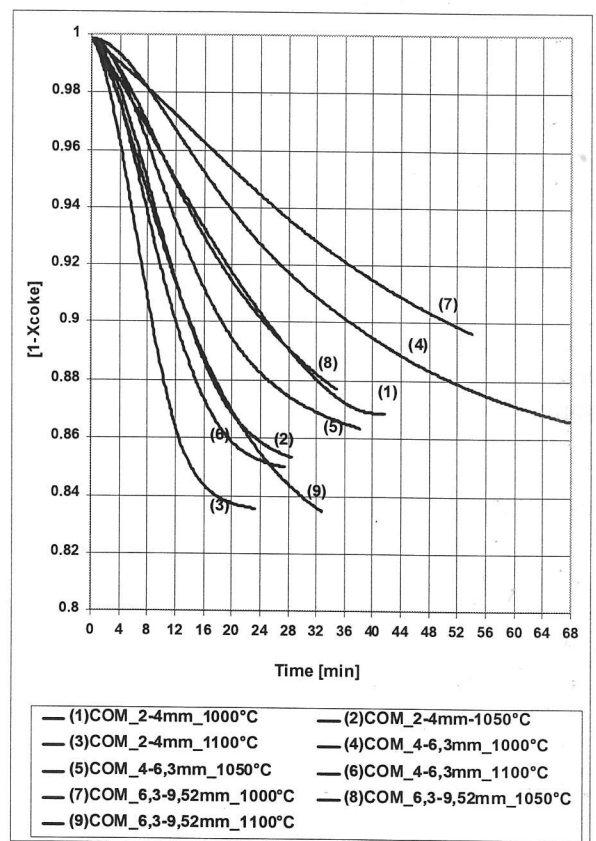


Figure 11. Consumption of coke; Coke size = 4-6,3 mm

5. CONCLUSION

It has been an aim for the present work, to analyze the reaction system in a FeMn process at the last gas-solid reduction (to FeO). It was chosen not to feed CO gas to the reactor. These experiments can not be directly

ompared with the industrial process. But by performing reduction experiments in laboratory scale at different conditions; with and without feed gas, with different ores and cokes, varying coke/ore ratios, size ranges and temperatures, we hope to obtain more general reduction rate parameters. So far the present results show that the chemical reaction in the ore to a great extent controls the total reaction rate for the reduction of Mn_3O_4 to MnO . To evaluate the Boudouard reaction, and thus coke consumption in an industrial process, experiments where we also feed CO-gas to the reactor shall be conducted.

X_C Fractional conversion of C
 Z Moles coke consumed per mole of removed oxygen

ACKNOWLEDGMENTS

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NOTATION

$k=k(t)$ Ratio between the derivatives of W_{tot} and W_m
 n_A Moles of substance A ($A=Mn_3O_4, C, \dots$)
 R Radius of ore particle, [cm]
 r Reaction rate, [mol/s]
 r_c Radius of unreacted core, [cm]
 T Temperature, [K]
 t Time, [s]
 $W=W_m$ Weight loss of ore, [g]
 W_{tot} Total weight loss, [g]
 $X=X_m$ Fractional conversion of Mn_3O_4 to MnO