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THE RATE AND MECHANISM FOR REDUCTION OF MANGANESE OXIDE FROM SILICATE SLAGS

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ABSTRACT

The reduction of manganese oxide in synthetic SiO_2-MnO-CaO-Al_2O_3 slags and multicomponent ferromanganese slag was investigated, using solid carbon and carbon saturated manganese melts as reducing agents. The temperature range was from 1450 to 1600°C and the ambient atmosphere normally carbon monoxide at atmospheric pressure. A thermobalance was used to monitor the weight loss during the reaction. It is concluded that the reduction takes place in two stages and that both stages are controlled by chemical reactions. The first stage is probably controlled by the MnO reduction and the slower second stage by the simultaneous reduction of SiO_2. Industrial ferromanganese slag is reduced much faster than synthetic slags possibly due to its content of minor components such as sulfur and alkalies. Among experimental variables which have been studied are slag and metal composition, reaction temperature, stirring rate and melt geometry. A mathematic model has been developed and compared with experimental data.

INTRODUCTION

Manganese ferroalloys are either produced in blast furnaces or in submerged arc furnaces. The alloys are classified as high carbon ferromanganese and silicomanganese. Simultaneous reduction of MnO and SiO_2 takes place, especially in the silicomanganese process. Most published research on kinetics and mechanism of the reduction process is related to the iron blast furnace where the slag contains less than 4% MnO.

Tarby and Philbrook [1] studied the rates of MnO and FeO reduction in silicate slags by carbon saturated iron. The reduction of MnO was shown to occur in two distinct stages: an initial fast stage characterized by rapid gas evolution, and a second slower stage. The apparent order of reaction for the first stage was greater than unity (between 1,1 and 2,9), whereas the second stage behaved as a pseudo first-order reaction with respect to the concentration of MnO in the slag. A two stage reduction of MnO was later confirmed by Pomfret and Grieveson [2]. The initial fast stage was found to proceed to some critical ratio of MnO activity in the slag and of Mn activity in the metal - still far from equilibrium.

Upadhya, Sommerville and Grieveson [3] studied the reduction rate of FeO in slag by carbon in iron. This reaction also takes place in two stages. The fast stage proceeds only partially towards equilibrium and is then followed by a slow second stage. They found that increased silica content in the slag slowed down the rate of FeO reduction and suggested that the silica reduction interferes with the second stage of the FeO reduction by some form of a coupling mechanism, and that this leads to an extremely slow approach towards final equilibrium. According to Pomfret and Grieveson [4], the rate of silica reduction seems to control the ultimate rate of approach to final equilibrium for most slag/metal/carbon reactions.

In general the reduction of silica is much slower than that of manganese oxide. Pomfret and Grieveson [5] examined the rate of silica reduction from a silica saturated slag, [CaO-6%MgO-SiO_2], by carbon saturated iron in CO-gas atmosphere at 1460°C. They concluded that the rate of this reaction is controlled by an interfacial reaction with an apparent activation energy of + 385 kJ $mole^{-1}$ of silica. This value is in agreement with slag/metal reactions where the silica reduction is interpreted as the breaking of Si-O bonds. Grieveson [6] suggested that one possible reason for the change from a fast initial stage to a slow second stage could be a complete consumption of all free oxygen ions (O^{2-}) in the slag during the first stage. In the second stage, therefore, the oxygen must be taken from a silicate anion, a process whose rate is expected to be consistent with that for silica reduction.

Upadhya [7] studied the reduction of MnO in [CaO-Al_2O_3-SiO_2] slag by carbon in iron. He suggested that the fast initial stage takes place as a combination of two separate reactions occurring at two different interfaces. MnO is first reduced by an exchange reaction with iron at the slag/metal interface producing FeO which is next reduced indirectly by carbon via a gaseous phase mechanism. He found that the overall rate of MnO reduction is controlled by the intrinsic rate of a chemical reaction at the gas/metal interface.

EQUILIBRIUM RELATIONS AND STOICHIOMETRY

Comprehensive measurements have been made during the last years to provide the necessary equilibrium data for the slag/metal/gas system in question [8,9]. These data formed the necessary basis for the subsequent kinetic investigation [10] where the intention was to study the rate and mechanism of MnO reduction in silicate slags. Under strongly reducing conditions and in the temperature range of the industrial process, all iron will be present in the metal phase. Calcium, aluminum and magnesium exist in the form of oxides and their presence in the metal phase may be neglected. Only manganese and silicon are distributed between the two condensed phases. The following reactions are considered:

$$(MnO) + \underline{C} = \underline{Mn} + CO_{(g)} \qquad (1)$$

$$(SiO_2) + 2\underline{C} = \underline{Si} + 2CO_{(g)} \qquad (2)$$

$$2(MnO) + \underline{Si} = (SiO_2) + 2\underline{Mn} \qquad (3)$$

$$(SiO_2) + \underline{Si} = 2SiO_{(g)} \qquad (4)$$

$$\underline{Mn} = Mn_{(g)} \qquad (5)$$

where parentheses denote the slag phase and underscored the metal phase.

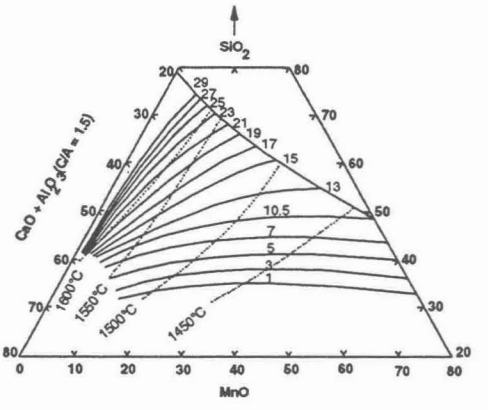

FIG. 1. Isoconcentration lines (solid) for Si in [Mn-Si-C_{sat}] alloys in equilibrium with [SiO_2-MnO-CaO-Al_2O_3] slags at 1550°C. Dotted lines represent slag compositions at complete slag/metal/gas equilibrium at given temperatures and P_{CO}=1 atm. Ref. [8].

Ternary [SiO_2-MnO-CaO] and quaternary [SiO_2-MnO-CaO-Al_2O_3] slags were equilibrated with [Mn-Si-C_{sat}] alloys in CO gas atmosphere [8]. Equilibrium studies have also been carried out with multicomponent industrial FeMn slag and Fe-containing metal [9]. As an example, equilibrium relations for quaternary [SiO_2-MnO-CaO-Al_2O_3] slags with fixed CaO/Al_2O_3 ratio=1.5 and [Mn-Si-C_{sat}] alloys are presented in Figure 1. The solid lines represent partial slag/metal equilibrium, giving compositions of slags in equilibrium with different alloys at 1550°C. Each line corresponds to a certain alloy with a fixed silicon content as shown. Dotted lines show slag compositions at slag/metal/gas equilibrium. Each line is for a fixed CO-pressure (p_{CO}=1atm) and a certain temperature as shown. For example, knowing the CO-pressure, the temperature and the alloy composition, the equilibrium slag composition will be

located at the intersection point between the actual solid and dotted lines.

Some silica will be reduced parallel to the MnO reduction. An increasing amount of silicon in the metal is required to maintain slag/metal equilibrium with decreasing content of MnO in the slag. Corresponding chemical analysis of slag and metal have shown that partial slag/metal equilibrium is established during the course of reduction. This is because the two-phase reaction (3) is much faster than the three phase reactions (1) and (2).

Examples of reduction 'paths' are shown in Figure 2. They represent two different slag/metal ratios. Since slag/metal equilibrium is established, each path is determined by equilibrium relations and stoichiometry. The solid circle marks the initial slag composition and the squares mark the two different end points. Run I represents the lowest slag/metal ratio and Run II the highest.

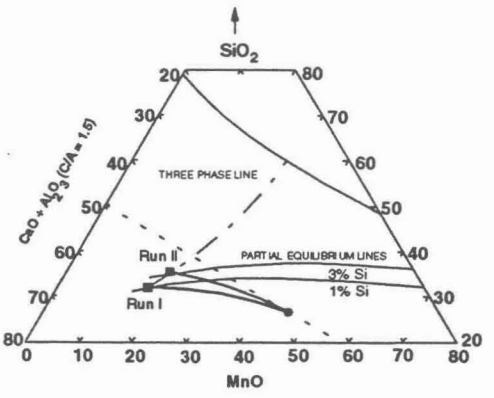

FIG. 2. The effect of different slag/metal weight ratios on the reaction path. Run I represents the lowest slag/metal ratio and run II the highest.

EXPERIMENTAL

Most experiments were carried out with synthetic ternary [SiO_2-MnO-CaO] slags and quaternary [SiO_2-MnO-CaO-Al_2O_3] slags, the latter with a fixed CaO/Al_2O_3 ratio equal to 1.5. Experiments were also carried out with a multicomponent industrial ferromanganese slag. Its composition was [25%SiO_2-34.7%MnO-16.7%CaO-9.6%Al_2O_3-7.7%MgO-1.6%BaO-0.4%TiO_2-2.5%K_2O-0.7%S]. This slag was upgraded as required to higher manganese oxide contents by addition of MnO.

The initial MnO content was usually chosen to be 45% which is quite high compared with earlier published research dealing with slags containing only about 4% MnO and less. The temperature range was from 1450 to 1600°C. A majority of the experiments were performed at 1500°C. Graphite crucibles of two different sizes were used, one 60 mm high and I.D. 43.5 mm and the other 40 mm high and 30 mm I.D. The ambient gas atmosphere for experiments reported here was carbon monoxide at atmospheric pressure, except for one experiment with argon injection into the melt.

A thermobalance was used to measure the reduction rate. The weight loss due to escaping CO-gas is an indirect measure of the MnO reduction. At elevated temperatures reactions (2), (4) and (5) will also cause some weight change in the system. Reaction (4) can be neglected at these temperatures, but it is impossible to prevent some effect of the reactions (2) and (5). Action has been taken to correct for their effect.

All experiments were carried out in a resistance-heated graphite-tube furnace. The furnace was evacuated and flushed with argon gas and the temperature was slowly increased. At 1400°C the flushing gas was changed from argon to carbon monoxide. 'Zero time' was chosen to be 3 min after the reaction temperature was reached. The weight change was recorded during 24 hours and continuous wt% MnO in the slag was calculated as explained by Skjervheim [10].

Parallel slag sampling experiments were carried out to calibrate the results obtained using the thermobalance. Sampling was also the only way to follow experiments with gas bubbling and stirring of slag and metal. Copper coated iron rods were used for sampling. The slag samples, less than 0.2 gram each, were analyzed in an electron probe microanalyzer (EPMA). The percentage MnO was measured along with the concentration of the other components in the slag. Finally, at ended runs, the metal was analyzed for silicon by a wet chemical method.

RESULTS AND DISCUSSION

Results obtained at 1500°C with two typical slags, marked A and B, are shown in Figure 3. The initial weight of the slags was 50g and of carbon saturated manganese metal 110g. Wt% MnO in slag, calculated from recorded weight losses, is shown versus time in minutes. Both slags are synthetic, slag A with initial composition [27,5%SiO_2-45%MnO-27,5%CaO] and slag B having the same content of MnO and SiO_2 but some CaO is replaced by Al_2O_3: [27.5%SiO_2-45%MnO-16.5%CaO-11%Al_2O_3]. The equilibrium content of MnO in both slags is about 20%. It appears that equilibrium is not attained even after 1400 minutes.

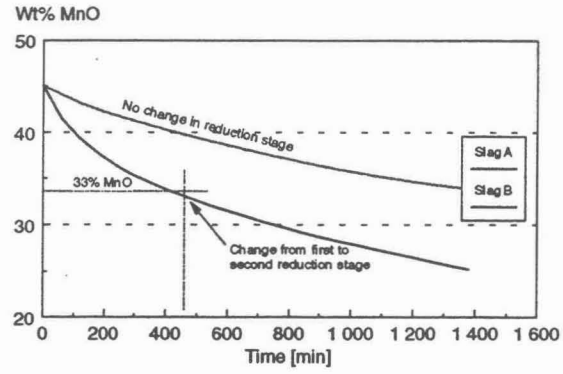

FIG. 3. Weight percent MnO in slag versus time for two different slag compositions. Slag A 27.5% CaO, slag B 16.5% CaO. Slag A is reduced in two stages whereas the first stage is missing for the more acid slag B. The equilibrium content of MnO is about 20% for both slags.

The more basic slag A is reduced in two stages, which is in accordance with previous investigations [1,2,3]. The first stage is relatively fast with vigorous CO formation whereas the second stage is much slower . This is illustrated in Figure 4 where $\ln(C_t-C_{eq})$ is plotted against time. C_t is the MnO concentration at a given time and C_{eq} is the equilibrium MnO concentration. The plot changes from a curved to a straight line after about 450 minutes. It is assumed that this reflects a change in reduction mechanism.

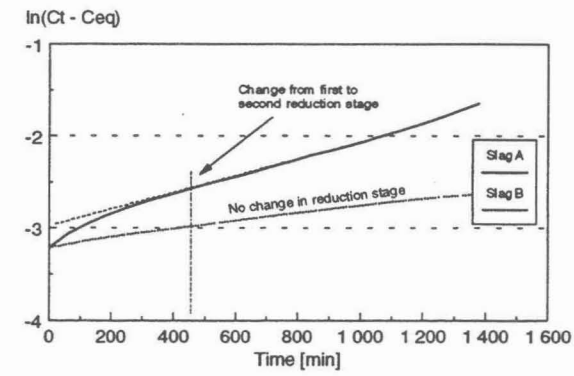

FIG. 4. $\ln(C_t - C_{eq})$ is plotted vs. time for the same experiment (fig.3). A change in reaction order seems to take place after about 450 minutes.

The faster initial stage is missing when the more acid slag B is reduced - Figures 3 and 4. In other experiments, not shown here, CaO was partly replaced by additional SiO_2. Again the fast initial stage was missing. As for alumina, the retarding effect of silica is obvious.

The basicity ratio is calculated according to the formula:

$$B = \frac{\Sigma n_{basic}}{\Sigma n_{acid}} = \frac{n_{MnO}+n_{CaO}}{n_{SiO2}+n_{Al2O3}}$$

The basicity, defined as the mole ratio of basic oxides over acid oxides, changes value continously as MnO is reduced. Grieveson [6] suggested a change from a fast stage to a slow second stage after complete consumption of all free oxygen ions, O^{2-}. This is expected to be the case when the orthosilicate composition (B=2) is reached for a [SiO_2-MnO-CaO] slag. Thus, if any other complex net forming agents are disregarded, the first stage should take place as long as B>2 and the second stage should be dominant for B<2.

The basicity ratio is shown for the two slags A and B in Figure 5, and the reduction path of slag A is shown in Figure 6. The orthosilicate line, connecting $2CaO{\cdot}SiO_2$ and $2MnO{\cdot}SiO_2$, represents slag compositions where B=2. The change from stage 1 to stage 2 takes place, as shown, where the reduction path crosses the orthosilicate line.

Experiments were carried out with and without stirring of the slag and metal phases. The stirrer was a 8 mm graphite rod immersed into the liquid slag and metal, rotating at 100 r.p.m. No effect was observed on the reduction rate. The obvious conclusion is that diffusion is not controlling the rate of reduction.

When graphite crucibles are used as here, two sources of carbon are available for slag reduction. That is solid carbon in the crucible wall and carbon dissolved in the liquid manganese metal. Some effort was made to distinguish between these two carbon sources. A molybdenum sheet was inserted between the slag and the crucible wall to avoid contact with solid graphite. Hence, the only reaction site was at the slag/metal interface. The rate of MnO reduction per unit area was calculated and compared with an identical experiment without the molybdenum sheet. The average rate of MnO reduction during the slow second stage was found to be 2.3 times larger at the slag/graphite interface than at the slag/metal interface[1]. Two other experiments were carried out with crucibles of different geometry, and therefore with different slag/metal to slag/graphite interface ratios. Again the higher rate was observed at the slag/graphite interface.

In one experiment a graphite tube was immersed and CO-gas blown directly to the slag/metal interface at a rate of 2 l/h for 20 hours. In a parallel experiment the gas was shifted from CO to Ar. The results of these experiments are illustrated in Figure 7. The rate of reduction is not significantly influenced by CO-bubbling whereas the injection of Ar-gas considerably increased the overall reduction rate. Due to the CO-gas formed during the reduction, the average partial pressure of CO in the 'Ar-experiment' has been about 0.6 atm.

The effect of the reduction temperature is of special interest. Results obtained for one and the same slag at three different temperatures 1450°C, 1500°C and 1600°C are given in Figure 8. Wt% MnO is calculated based on observed weight losses, and plotted vs. time in the figure. The rate of reduction is very

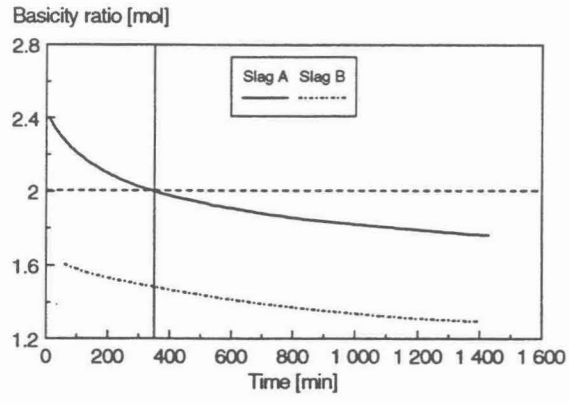

FIG. 5. Basicity ratios for slag A and B (fig.3) plotted vs. time. Slag A reaches B=2 after about 330 min which fits reasonable well with the change from stage 1 to stage 2 (shown above). Slag B is in the acid range all the time, and the reduction takes place as a second stage reduction.

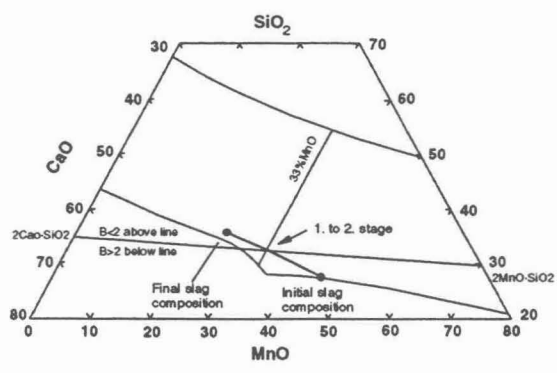

FIG. 6. The reduction path of Slag A is shown. The 'horizontal' stipulated line indicates the boundary between the orthosilicate below (B>2) and the non-orthosilicate state above the line (B<2).

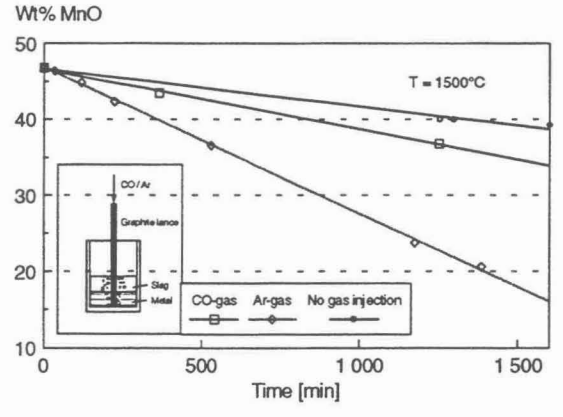

FIG. 7. Weight percent MnO in slag versus time. Effect of CO and Ar-bubbling. 130g slag [36.67%SiO_2-45%MnO-18.33%CaO] and 110g metal.

[1] In previous publication [11] erroneous reported to be equal .

sensitive to the temperature, which confirms that the rate is controlled by chemical reactions and not by diffusion.

Calculation of activation energy is not relevant because the reaction proceeds at two interfaces and in two reaction stages. Thus, if the concept of activation energy is introduced, four different activation energies should be calculated. An overall temperature dependence factor, **E**, may however be calculated. **ln k** was plotted versus the inverse of reaction temperature for three different experiments at 1450, 1500 and 1550°C. **k** is the rate constant, here defined as the slope of each curve, recalculated to mole CO/hour. In such a way an apparent activation energy was calculated to 407 kJ mole^{-1} CO for the second stage.

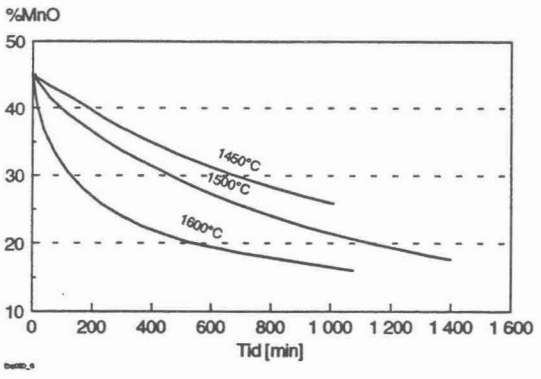

FIG. 8. Weight percent MnO in slag versus time. Effect of reaction temperature. 100g slag [27.5%SiO_2-45%MnO-27.5%CaO]. Exp. at 1450 and 1500°C without initial metal. Exp. at 1600°C with 110g metal.

Most of these experiments were carried out with carbon saturated manganese metal. In the ferromanganese and silicomanganese processes, iron will also be present. When 10% iron was added to the metal, the rate of MnO reduction increased in the first stage. If we disregard any catalytic effect of iron on the MnO reduction, we can assume that iron acts as a diluent to the manganese and is hence lowering the Mn activity of the metal phase and therefore increasing the MnO reduction potential. Another explanation may be a coupled reaction mechanism where iron takes part in the initial reduction of MnO as reported by Uphadya [7]: (MnO) + Fe = Mn + (FeO).

Industrial slag

The result obtained with industrial slag upgraded to 45%MnO is compared with a parallel experiment with synthetic slag [27.5%SiO_2-45%MnO-27.5%CaO], shown in Figure 9. Both experiments were carried out without initial metal and with 100g of slag. 1450°C was chosen as reaction temperature to prevent too vigorous CO evolution. This is also close to a realistic temperature for the ferromanganese process.

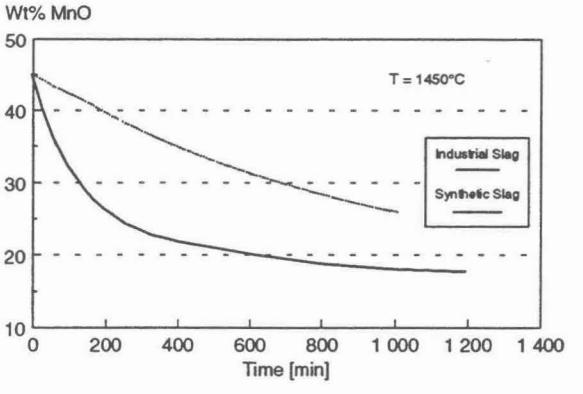

FIG. 9. Weight percent MnO in slag versus time. Multicomponent industrial slag [45%MnO] is compared with synthetic slag A [27.5%SiO_2-45%MnO-27.5%CaO]. 100g slag without initial metal. Final composition of industrial slag close to equilibrium.

As seen in the figure, industrial slag is reduced much faster than synthetic slag and reaches approximately 18% MnO which is close to equilibrium. Efforts were made to find a reasonable explanation. Different oxide additions were made to synthetic slags to try to copy the composition of industrial slag, but similar high reduction rates were not obtained.

Certain elements or compounds tend to accumulate preferentially at the slag/metal interface. In one experiment 0.2% S was added to the Mn-C_{sat} alloy to investigate its influence on the overall MnO reduction from [27.5%SiO_2-45%MnO-27.5%CaO] slag. As shown in Figure 10 the rate was onsiderably increased. Sulfur seems to play an active role in the reaction mechanism. Some sulfur is always present in industrial slag and this could be the reason for its higher reduction rate.

At present we have no further explanation as to how sulfur affects the rate and mechanism.

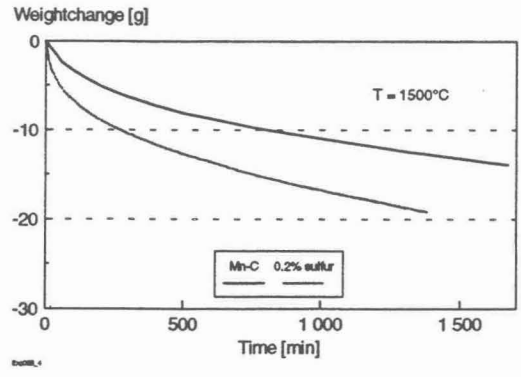

FIG. 10. Weight change versus time. Effect of sulfur addition to metal. 100g slag A and 110g metal.

Mathematic model

A mathematic model can predict future results before the actual experiment is carried out and thereby optimize experimental planning. Further it is a useful tool to calculate and extrapolate to conditions which are not directly covered by laboratory experiments, e.g. different initial MnO concentrations, higher or lower temperatures, different reaction areas etc. The model can also be used to scale kinetic results from laboratory work to a full scale industrial processes. The following expression has been derived to describe the kinetics of carbon reduction of MnO in various silicate slags:

$$C_t = \left((1 - x(1-\alpha)\, e^{y})^{\frac{1}{1-\alpha}} \right) (C_i - C_{eq}) + C_{eq}$$

where x and y are defined as follows

$$x = k\, t\, \frac{A(t)}{V_s(t)} \quad , \quad y = -\frac{E}{R}\left(\frac{1}{1773} - \frac{1}{T} \right)$$

C_t	: MnO concentration with respect to time
C_i	: MnO concentration at start
C_{eq}	: MnO concentration at equilibrium
t	: time in minutes
T	: temperature [°K]

A(t)	: reaction area with respect to time [cm^2]
$V_s(t)$	: volume of slag with respect to time [cm^3]
E	: apparent activation energy
R	: gas constant

The two unknowns in the equation are the proportionality factor **k** and the 'reaction order' α. The model gives good fit for a constant value of the reaction order, $\alpha = 2$. The proportionality factor, k, is optimized until the best fit is obtained. Its value is very dependent on the slag properties and it can be used to characterize the different types of slag as shown in Table 1.

Table 1:

Slag type	Slag composition	k
Industrial slag	Multicomponent	0.01
Basic synthetic slag	27.5%SiO_2-45%MnO-27.5%CaO	0.0012
Acid synthetic slag	36.7%SiO_2-45%MnO-16.3%CaO	0.00028

The model has proved to be valid for various slag compositions, slag amounts, reaction temperatures, reaction areas and reaction times.

An example on how to use the model is shown in Figure 11. A coke bed is considered in which the void fraction is filled with a stagnant volume of slag. The coke particles are supposed to be

spherical and to have an average diameter of 0,5 cm and particle density 1g cm^{-3}. The reaction temperature is 1360°C and the equilibrium content of MnO in the slag is 30%. We wish to estimate the necessary size of a coke bed to reduce the MnO content in a ferromanganese slag from 70 to 35 wt% in two hours. The value of the proportionality factor is chosen, k = 0,01, since this is an industrial ferromanganese slag, see Table 1. Wt% MnO is shown in the figure for different slag/coke weight ratios. It can be seen that the required ratio is approximately 0.5. The necessary coke bed is then 2 tons per 1 ton of slag. If the temperature is raised with 50°C to 1410°C, the slag/coke weight ratio is increased to about 1.0 (not shown in the figure), and the necessary coke bed is reduced to 1ton. The calculated coke bed sizes fit well with experience from the full scale industrial process.

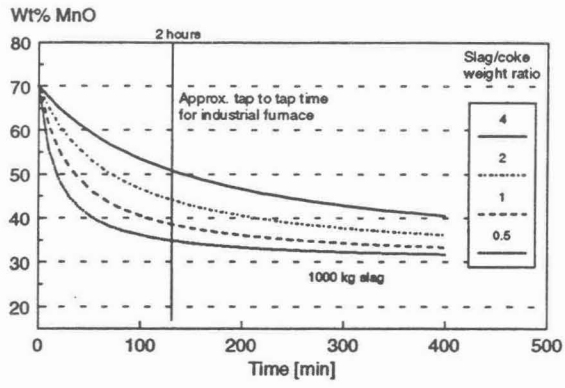

FIG. 11. Calculations based on the equation above to show how different slag/coke weight ratios affects the MnO reduction. Industrial slag k=0.01. The average coke size is assumed constant during reduction and equal to 0.5 cm.

CONCLUSIONS

The results are in good agreement with previous investigations. Reduction of MnO from basic slags takes place in two stages, an initial fast stage and a second slower stage. The change in rate and mechanism seems to take place at a certain slag basicity when the free O^{2-} ions have been consumed. In the second stage oxygen must be obtained from a silicate anion (SiO^{4-}_4), a process whose rate is expected to be consistent with that for silica reduction. The fast stage is completely missing when sufficiently acid slags are reduced.

The importance of the temperature in both stages, and lack of stirring effect, leads to the conclusion that both stages are controlled by chemical reactions and not by any transport mechanism. An apparent activation energy has been calculated to 407 kJ $mole^{-1}$ CO for the second stage.

The source of carbon is of importance. The average rate of MnO reduction during the slow second stage was found to be 2.3 times larger per unit area at the slag/graphite interface than at the slag/metal interface.

The rate of reduction was not significantly influenced by CO-bubbling whereas injection of Ar-gas considerably increased the overall reduction rate.

Industrial slag is reduced much faster than synthetic slags. Efforts were made to find a reasonable explanation. Different oxide additions were made to synthetic slags to try to copy the composition of industrial slag, but similar high reduction rates were not obtained. The rate of reduction is, however, considerably increased by addition of sulfur to the system. Some sulfur is always present in industrial slags and it is good reason to believe that this is one reason for its higher reduction rate.

A mathematical model has been developed which gives very good consistency between calculated and experimental data. The model also gives results which fit well with experience from the full scale industrial process.

ACKNOWLEDGEMENT

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