Kinetic of Carbothermic Reduction of MnO from High-carbon Ferromanganese Slag by Graphite Materials

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The kinetics of MnO reduction from a synthetic ferromanganese slag by different graphite materials was investigated using sessile drop wettability technique. It was found that the graphite substrates are not wetted by the slag drop at 1450°C, 1500°C and 1600°C. On the other hand, processing the photos taken during the reduction revealed that the contact angle between the graphite substrates and the slag drop is not changing appreciably during slag reduction, while the changes in the slag drop volume are more significant. A new method was developed and applied to convert the changes in the slag drop volume to the MnO concentration and therefore the MnO reduction curves for different graphite substrates were extracted. The relationship between the density of slag and its MnO content was also studied. A new kinetic interpretation method was developed and a main differential equation for carbothermic MnO reduction from a slag drop in sessile drop method was obtained. This method was used to calculate the MnO reduction rate constants for different graphite materials considering the changes in the slag/carbon contact area. Multivariate analysis was also used to determine the possible relationships between the graphite properties and the MnO reduction rate.

KEY WORDS: ferromanganese slag; sessile drop; wettability; carbothermic reduction; kinetics.

1. Introduction

The interaction of solid carbon with liquid slag is an important reaction in many metallurgical processes. In a shaft electric furnace, which is commonly used for high-carbon ferromanganese production, manganese oxides such as MnO, Mn2O3, and Mn3O4 in the burden are reduced to MnO directly by CO gas. Subsequently, in the coke bed area of the furnace where the process heat is generated manganese metal is produced through the interaction of a high MnO containing silicate slag with carbon:

$$\text{MnO}_{(\text{liquid})} + C_{(\text{solid})} = \text{Mn}_{(\text{liquid})} + CO_{(\text{gas})} \quad (1)$$

The carbothermic MnO reduction from liquid slags and the effects of many parameters on its kinetics have been studied by several investigators.1-12 These studies have been mainly conducted in graphite crucibles with or without initial metal phase. It has been observed that stirring has no significant effect on the kinetics of MnO reduction, while the reduction rate is affected by the slag composition and temperature. Therefore, it has been suggested that the reaction kinetics is not controlled by the diffusion of the components in the bulk of the metal and slag phases, and it is controlled by the chemical reaction.1-10 It has been also observed that the kinetics of MnO reduction is affected by the gas phase composition, and different MnO reduction rates are observed when different inert gases are used. It has been proposed that the carbothermic reduction of MnO is a mixed-control reaction involving both chemical reaction and mass transfer of CO in the gas phase.11 The mechanism of MnO reduction from slags by dissolved carbon in liquid iron is well known.3,5,6,10 According to this mechanism, MnO is reduced by Fe at the slag/metal interface and Mn and FeO are produced. Subsequently, FeO is reduced by CO gas at the slag/gas bubble interface and Fe and CO2 gas are produced, this reaction is followed by the regeneration of CO gas via the Boudouard reaction with the dissolved carbon in the metal at the metal/gas bubble interface. Based on the ionic conductivity of the slags, it has been suggested that the reaction of MnO with solid carbon is an electrochemical reaction,12 involving the following two stages:

Anodic: $C_{(\text{solid})} - O^2- = CO_{(\text{gas})} + 2e^-$ ..............(2)

Cathodic: $\text{Mn}^{2+} + 2e^- = \text{Mn}_{(\text{liquid})}$ ..................(3)

A few studies have been carried out to find the effects of the carbonaceous material properties on the kinetics of MnO reduction. It has been observed that the reductant type influences the SiO2 reduction from a MnO containing silicate slag significantly, while it does not have a large effect on the MnO reduction.13,14 It has recently been observed that the rate of MnO reduction from silicate slags is affected by the type of carbon material.15 The objective of the present study is to investigate the possible relationships between the kinetics of the carbothermic reduction of MnO and the properties of carbon materials. In this case, the interaction of a synthetic ferromanganese slag with different graphites is studied using sessile drop wettability technique. New methods for calculating the MnO reduction curves and the rate constants are developed. Furthermore, multivariate analysis is applied to investigate the relationship between the graphite properties and the MnO reduction kinetics.
2. Experimental Procedures

2.1. Materials

The main focus of this study involves the interaction of a MnO containing silicate slag with different graphites using the sessile drop wettability technique. The preparation of graphite substrates, the applied methods for their characterisation and their comparison are described in Sec. 2.1.1. The master slag preparation and the extracted phase diagram for the slag are described in Sec. 2.1.2.

2.1.1. Graphite Substrates

Six different purified graphites with more than 99.9 wt% fixed carbon content (ash content less than 0.1 wt%) were used in this study. For the sessile drop experiment a substrate of carbon materials with a flat surface is needed to be in contact with the liquid slag drop. The graphite materials were in the form of blocks and appropriate flat surfaces of them were prepared by machining. They were cut into slices with 3 mm thickness using a diamond wheel with 2 mm thickness. Then, graphite discs with a diameter of 10 mm were cut with a core drill from the slices.

Studying the effect of graphite properties on the slag reduction kinetics is an important aim of this study, therefore a part of the study was dedicated to characterise the graphite substrates. In this case, the cumulative pore volume, porosity, bulk density and average pore size were measured by mercury porosimeter. The specific surface area of the graphites was measured by BET method using helium–nitrogen gas as the surface adsorbate agent. The structural parameters such as 002 plane spacing ($d_{002}$) and the average crystallite size ($L_{(002)}$) were determined using X-ray diffraction (XRD). The surface roughness of graphite samples was measured using a standard roughness instrument, which has a diamond-needle with very low physical contact force with the samples. Moreover, the CO2 reactivity for all graphites was measured by thermogravimetry at 1000°C in a 100% CO$_2$ atmosphere. All the mentioned techniques for graphite samples characterisation were previously described and the results are summarised in Table 1.

Due to a large number of properties for the graphite samples, a multivariate analysis was used to compare and evaluate them. In this case, the ‘principle component analysis (PCA)’ model was applied. The score plot which can be used to study the differences among the graphites is shown by open symbols (○) in Fig. 1. The score plot shows that graphites have different properties, because they are not very close to each other. However, graphites A, B, and D are more similar than the other samples, and the highest differences are between graphites C and F. The loading plot, solid symbols (●) in Fig. 1, shows the differences and similarities between the property variables of the graphites.

The loading plot indicates that the cumulative pore volume is completely the same parameter as the porosity due to the overlapping of their points. However, bulk density is a completely different parameter and it has an inverse relationship with the porosity, because they are located in different areas and on a line through the origin. The surface roughness is close to the porosity, and it may indicate that the surface roughness is very dependent on the porosity. The loading plot also illustrates that the CO2 reactivity and the specific surface area are close parameters, and it may indicate that CO2 reactivity is mainly dependent on the surface area.

2.1.2. Master Slag

For preparing the master slag, high purity (+99.99%) fine powders of CaO, MgO, SiO$_2$ and Al$_2$O$_3$ were mixed in a ratio of CaO/MgO=2, CaO/Al$_2$O$_3$=1.34 and Al$_2$O$_3$/SiO$_2$=0.4. The powders were mixed in a ball mill containing stainless steel balls 6 mm in diameter for 6 h. The mixture was then melted in a graphite crucible in air at high temperatures using an induction furnace. The obtained slag was crushed in a tungsten carbide disc mill to a very fine powder and was then mixed with appropriate amounts of high purity MnO (+99.95%) fine powder by hand in plastic containers. The obtained mixture was melted in platinum crucible in air at 1550°C. The master slag compositions was measured by Electron Probe Micro-Analysis (EPMA) and the average composition in weight percent was 45%MnO–3.4%MgO–25%SiO$_2$–10%Al$_2$O$_3$–6.6%MgO. It is worth mentioning that this slag was upgraded to higher MnO contents for a few experiments for slag density measurements (Sec. 3.2).

The pseudo-ternary phase diagram for MnO–SiO$_2$–(CaO+MgO+Al$_2$O$_3$) slag system (CaO/MgO=2, CaO/

![Fig. 1. The score and loading plots for the graphite materials and their properties. Score plot: open symbols, loading plot: solid symbols (calculated by Unscrambler).](image)

| Graphite no. | Cumulative pore volume (×10$^3$ cm$^3$) | Average pore diameter (μm) | Porosity (%) | Bulk density (g/cm$^3$) | Surface area (cm$^2$) | Interplanar distance ($d_{002}$) (Å) | Crystallite size ($L_{(002)}$) (μm) | Surface roughness ($R_s$) (μm) | CO$_2$ Reactivity ($10^{-3}$/min) |
|-------------|------------------------------------------|-----------------------------|--------------|-------------------------|----------------------|---------------------------------|---------------------------------|--------------------------------|-------------------------------|
| A           | 10.5                                     | 2.5                         | 18.3         | 1.742                   | 4000                 | 3.364                           | 553.35                          | 1.27                           | 0.7                           |
| B           | 8.6                                      | 2.3                         | 15.3         | 1.779                   | 4000                 | 3.366                           | 503.19                          | 0.99                           | 0.3                           |
| C           | 13.8                                     | 2.58                        | 22.9         | 1.659                   | 7000                 | 3.358                           | 578.78                          | 3.41                           | 1                             |
| D           | 7.2                                      | 2.72                        | 13.4         | 1.858                   | 3000                 | 3.370                           | 425.30                          | 1.32                           | 0.4                           |
| E           | 8.8                                      | 2.06                        | 15.8         | 1.779                   | 6000                 | 3.377                           | 227.26                          | 1.02                           | 1.1                           |
| F           | 6.4                                      | 0.66                        | 12.1         | 1.885                   | 5000                 | 3.373                           | 442.79                          | 0.53                           | 0.6                           |
Al$_2$O$_3$=1.34) at different temperatures between 1180°C and 1680°C was calculated using FactSage thermodynamics software as illustrated in Fig. 2. In which the MnO content of slag during reduction changes along a straight line. The phase diagram shows that the MnO reduction from slag is taking place only in one phase region and it does not cross the liquidus surface at the experimental temperatures (1450 to 1600°C). This means that the MnO activity decreases continuously with decreasing the MnO content.8,9,16)

2.2. Furnace Construction and the Experimental Setup

A horizontal tube furnace was used in order to study the wetting properties in the sessile drop method. A schematic diagram of the experimental set up is shown in Fig. 3. The graphite substrate was located in the graphite sample holder and a 40±1 mg slag particle was put on the graphite surface. The furnace chamber was evacuated initially, and then the furnace was heated up slowly in a pure argon (99.9999% Ar) with 0.5 NL/min flowrate. The furnace was heated to 950°C in approximately 10 min, followed with a rapid heating rate of 120°C/min to the experiment temperature. In the present study, the isothermal reduction of the slag was investigated at 1450°C, 1500°C and 1600°C for 60, 60 and 30 min, respectively. The temperature was controlled using a two colour pyrometer having sensitivity from 900 to 2400°C and focused on the edge of the graphite sample holder (Fig. 3). A digital video camera with a telecentric lens was used to record images from the sample at 960×1280 pixels. In the experiments, drop images were captured every second and then they were processed by software to measure some parameters such as contact angle, slag/graphite contact area, and drop volume and so on. After completion of the wettability experiments, the samples were quenched. The weight of the solidified slag drops were measured, as there was no sticking between graphite and slag after the experiments. The slag drops were then mounted in epoxy and prepared for EPMA with wavelength dispersive spectrometers.

In addition to the slag reduction experiments, some experiments were carried out using sessile drop wettability approach to study the manganese evaporation kinetics. In this case, electrolytic manganese (+99.5% Mn) was evaporated on flat alumina substrate at 1450°C, 1500°C and 1600°C for 16, 13 and 6 min, respectively.

3. Results and Discussion

The obtained photos from the wettability experiments for slag were analysed using a locally developed software measuring different parameters such as drop height, drop diameter, drop volume ($V_d$), drop/substrate contact area ($A_c$), contact angle ($\theta$) and slag surface tension ($\sigma_s$). With regard to a large number of photos for each experiment, a few photos were selected for the analysis; for the experiments at 1450°C and 1500°C one photo per every 2 min after reaching the temperature were selected, while for ex-
periments at 1 600°C one photo per minute was selected.

3.1. Extraction of MnO Reduction Curves

In this study, the changes in the contact angle were firstly used to evaluate the rate of the MnO reduction. The contact angle, \( \theta \), for reduction by different graphite substrates were measured at all reduction temperatures as typically shown for 1 500°C in Fig. 4. As we see, graphite substrates are not wetted by the slag and the contact angle at the starting point is relatively high and more than \( \theta = 150° \). On the other hand, significant change in the wetting angle during slag reduction is not observed, indicating that the surface tension of the slag is not very dependent on the MnO content. The small changes in the slag surface tension with large MnO content changes is in agreement with the studies of Keke- lidze et al.\(^{17} \) and Yaser Lone et al.\(^{18} \) Figure 4 shows also that there are a lot of small fluctuations in the wetting angle changes and it becomes complicated to evaluate the rate of MnO reduction by calculating the changes in \( \theta \).

It was found that the changes in the slag drop volume are much larger than the contact angle changes for a certain MnO reduction extent. For example, the total change in the contact angle during slag reduction at 1 500°C by graphite F substrate is only 3.5% from 150.5° to 145.2°, while the total change in the drop volume is 20.2% from 13.54 to 10.80 mm\(^2 \). Thus, a good alternative option to study the kinetics of MnO reduction from a slag drop is measuring the changes in the drop volume during the reduction. The measured drop volume during reduction, \( V_s \), were normalized considering the initial drop volume, \( V_{s,i} \), and by calculating the \( V_s/V_{s,i} \) ratio. The typical changes in \( V_s/V_{s,i} \) during the slag reduction by all graphite substrates at 1 500°C are plotted as shown in Fig. 5. It is worth mentioning that the volume of the graphite substrate which is consumed by the reaction is very small in comparison with the measured drop volume and it has no significant effect on the calculations. Moreover, the graphite bulk densities (Table 1) are in a narrow range and all graphites are equally consumed until a certain \( V_s/V_{s,i} \) ratio. On the other hand, no bubbling was observed during the slag reduction, depicting that the produced CO gas through reaction (1) does not enter into the slag. Therefore, the changes in the \( V_s/V_{s,i} \) parameter can be used successfully to compare the slag reduction rates of different graphites.

Although the changes in \( V_s/V_{s,i} \) parameter can be qualitatively used to evaluate the MnO reduction rate, it is not a reliable quantification of the reduction rate. A method for studying the concentration changes inside the liquid droplet in sessile drop method have not been proposed yet. Attempts were made to plot a kind of “calibration curve” to find a direct relationship between the \( V_s/V_{s,i} \) parameter and the MnO concentration of slag droplet. It was found that there is a good linear relationship between the \( V_s/V_{s,i} \) parameter and the MnO concentration of slag droplet as the following.\(^{19} \)

\[
C_{\text{MnO}}(\text{wt}%) = 78.39 \left( \frac{V_s}{V_{s,i}} \right) - 33.98 \quad \text{at 1 450°C} \quad \ldots (4)
\]

\[
C_{\text{MnO}}(\text{wt}%) = 76.67 \left( \frac{V_s}{V_{s,i}} \right) - 32.56 \quad \text{at 1 500°C} \quad \ldots (5)
\]

\[
C_{\text{MnO}}(\text{wt}%) = 68.63 \left( \frac{V_s}{V_{s,i}} \right) - 22.77 \quad \text{at 1 600°C} \quad \ldots (6)
\]

Considering the curves of Fig. 5 and using Eqs. (4) to (6), the MnO reduction curves were calculated at all reduction temperatures as shown in Fig. 6. The calculated final MnO contents by the above method are confirmed considering EPMA analysis of the slag droplets after reduction (Table 2). The ratios between the amounts of slag components in Table 2 are approximately the same as the initial slag composition, indicating that only MnO reduction is taking place by graphite in the experimental conditions. It is also proved through the mass balance that there is no SiO\(_2\) reduction in the system. The total weight losses during slag reduction, which were measured by drop weighing after reduction were used to calculate the remaining MnO content in the slag by mass balance. The calculated MnO contents are close to the other results for final MnO contents and it confirms the applied method for slag MnO content calculations. Figure 6 indicates that the kinetics of MnO reduction from slag is affected by the type of graphite. The order of the curves for graphites A, B, D and C is always the same at all temperatures and only the positions of graphites E and F are changed with changing temperature (curve E is always above curve F). Obtaining approximately the same order for the curves at different temperatures suggests that the kinetics of MnO reduction at different temperatures is affected by the same graphite properties.

3.2. Slag Density

With respect to the initial and final mass of slag drop and the corresponding measured drop volume in wettablility experiment, the density of the slag for different MnO contents (measured by EPMA) were determined. Moreover, some additional experiments were carried out to study the slag
density in a wide range of MnO concentrations. In this case the master slag was upgraded in MnO content to higher concentrations (52 wt% and 65.4 wt%) by MnO powder addition to the slag powder and melting the mixture in a platinum crucible. Similar to the master slag, the reduction of these slags for different times at 1450°C, 1500°C and 1600°C were carried out in a wettability furnace. Then, the slag densities were calculated similar to the master slag. Figure 7 represents the obtained results and a fairly linear relationship between the density of slag and the MnO content is observed:

\[ \rho_s = 0.0149C_{\text{MnO}} + 2.3732 \text{ (g/cm}^3) \text{ at } 1450°C \]  
\[ \rho_s = 0.014C_{\text{MnO}} + 2.3977 \text{ (g/cm}^3) \text{ at } 1500°C \]  
\[ \rho_s = 0.0135C_{\text{MnO}} + 2.4359 \text{ (g/cm}^3) \text{ at } 1600°C \]  

The above equations indicate that the density of slag increases minimally with increasing the MnO content of slag. But, the slag density is not affected significantly by temperature and for a given MnO content very close densities are obtained at different temperatures. The difference between the densities at different temperatures is small at low MnO contents and it increases with increasing the MnO content. Comparing the reported densities for MnO containing silicate slags\(^{17,19}\) with the present study at 1500°C (Fig. 7(b)), it is observed that the density of slag is approximately 0.2 g/cm\(^3\) lower than slag densities in the literature. This difference is expected regarding the existence of Al\(_2\)O\(_3\) and MgO in the prepared master slag. Because, these compounds decrease the density of MnO containing silicate slags.\(^{17}\)

### 3.3. Manganese Evaporation

With regard to the high vapour pressure of manganese which is 1459, 2314 and 5365 Pa at 1450°C, 1500°C and 1600°C, respectively, the evaporation of produced manganese occurs during the slag reduction. In order to determine the manganese evaporation rates at experimental temperatures, the changes in the manganese metal droplet volume \((V_{\text{Mn}})\), measured in the wettability tests, was converted to the slag droplet mass \((m_{\text{Mn}})\) using the pure manganese densities at the reduction temperatures. The relationship be-

### Table 2. The EPMA results for slag chemical compositions after reduction, the final calculated MnO contents by the developed method in this study, and the calculated MnO contents from slag mass measurements.

| Graphite substrate type | Reduction temperature (°C) | EPMA analysis | \(\text{wt\% MnO Calculated by new method}\) | \(\text{wt\% MnO slag mass measurement}\) |
|------------------------|-----------------------------|---------------|------------------------------------------|-----------------------------|
| A                      | 1450                        | 15.2          | 6.8                                      | 11.9                       | 39.3                      | 36.8                      | 36.3                      | 36.0                      |
| B                      | 1450                        | 15.7          | 7.1                                      | 12.3                       | 30.5                      | 34.4                      | 35.3                      | 33.9                      |
| C                      | 1450                        | 17.0          | 7.9                                      | 13.9                       | 32.8                      | 28.4                      | 28.6                      | 26.3                      |
| D                      | 1450                        | 16.7          | 7.7                                      | 12.6                       | 31.4                      | 31.6                      | 31.8                      | 29.2                      |
| E                      | 1450                        | 15.4          | 7.1                                      | 12.7                       | 29.3                      | 35.5                      | 36.8                      | 36.5                      |
| F                      | 1450                        | 15.8          | 7.3                                      | 12.6                       | 30.2                      | 34.2                      | 34.0                      | 33.8                      |
| A                      | 1500                        | 16.6          | 7.3                                      | 12.9                       | 32.3                      | 30.9                      | 31.9                      | 30.1                      |
| B                      | 1500                        | 16.5          | 7.6                                      | 13.2                       | 32.1                      | 30.7                      | 31.5                      | 28.9                      |
| C                      | 1500                        | 16.9          | 7.9                                      | 13.2                       | 34.9                      | 27.1                      | 26.8                      | 26.3                      |
| D                      | 1500                        | 17.2          | 8.1                                      | 12.9                       | 34.4                      | 27.4                      | 28.8                      | 27.1                      |
| E                      | 1500                        | 16.7          | 7.8                                      | 12.5                       | 33.7                      | 29.3                      | 30.2                      | 28.6                      |
| F                      | 1500                        | 16.8          | 7.7                                      | 12.6                       | 33.9                      | 28.9                      | 29.3                      | 27.8                      |
| A                      | 1600                        | 15.8          | 7.6                                      | 12.5                       | 30.4                      | 33.7                      | 33.9                      | 33.7                      |
| B                      | 1600                        | 15.6          | 7.7                                      | 12.4                       | 31.2                      | 33.1                      | 33.2                      | 30.7                      |
| C                      | 1600                        | 16.2          | 7.9                                      | 12.7                       | 32.5                      | 30.7                      | 29.9                      | 28.7                      |
| D                      | 1600                        | 16.1          | 8.0                                      | 12.7                       | 32.3                      | 30.9                      | 30.3                      | 29.1                      |
| E                      | 1600                        | 16.2          | 7.9                                      | 12.4                       | 32.0                      | 31.5                      | 30.9                      | 27.8                      |
| F                      | 1600                        | 16.4          | 8.0                                      | 12.5                       | 32.0                      | 31.1                      | 30.4                      | 28.4                      |
The density of pure Mn, \( \rho_m \), and temperature \( T \) is:

\[
\rho = \rho_m + \lambda_{Mn}(T-T_m) \quad \text{(10)}
\]

where \( \rho_m \) (=5.76 g/cm\(^3\)) is the pure manganese density at melting point \( T_m = 1246°C \) and \( \lambda_{Mn} \) is a temperature dependent factor, \( \lambda_{Mn} = -0.00092 \text{ g/cm}^3\text{K} \) reported by Iida and Guthrie.\(^{20} \)

Using Eq. (10), the pure manganese metal densities at 1450°C, 1500°C and 1600°C were calculated as 5.57, 5.53 and 5.43, respectively.

Figure 8 shows the changes in the mass of the manganese drop at the experimental temperatures (calculated by \( m_{Mn} = V_{Mn} \rho \)), and it indicates that the manganese evaporation rates are 1.26, 3.02 and 5.01 mg/min at 1450°C, 1500°C and 1600°C, respectively.

The rate of manganese evaporation from pure manganese and carbon saturated manganese at different temperatures was studied by Gee and Rosenquist\(^{21} \) and Skjervheim,\(^7 \) respectively. Their results and the results in the present study are shown in Fig. 9. As we see the measurements in this study are a little higher than the measurements of Gee and Rosenquist; this may be related to the experimental procedures. In fact, evaporation is a surface phenomenon and it might be faster from a melt drop (this study) than a melt in crucible (Gee and Rosenquist) due to the higher surface to volume ratio of the melt. Figure 9 shows that carbon saturated manganese evaporates slower than pure manganese. This may be related to the lower activity of manganese in Mn–C\(_{sat}\) alloy.

The highest rates of Mn production in the slag reduction experiments were obtained for graphite C substrate. These rates were calculated by mass balance and they are maximum 0.173, 0.204 and 0.374 mg/min at 1450°C, 1500°C and 1600°C, respectively. Comparing these manganese production rates with the manganese evaporation rates indicates that the rate of manganese evaporation is always much higher than the rate of manganese production. The microstructural studies by EPMA also indicated that there is no metal phase at the slag/graphite reaction interface. As an important conclusion, there is no metal phase present in the slag/graphite interface during reduction, and MnO is reduced only by the solid carbon and not by the dissolved carbon in liquid manganese.

### 3.4. Kinetic Study of MnO Reduction

#### 3.4.1. Mathematical Formulation

As mentioned the MnO reduction from slag is taking place in the one-phase region and the MnO activity starts to decrease after starting to react with carbon (reaching the experimental temperature). Therefore, the rate of the forward MnO reduction (1) can be expressed by the following equation:

\[
\text{Rate} = k_A C_{\text{MnO}}^{\alpha} \quad \text{(11)}
\]

where \( C_{\text{MnO}} \) is the concentration of MnO in weight percent, and \( \alpha \) is the order of reaction with respect to MnO, \( A_c \) is the reaction interfacial area (slag/graphite contact area) and \( k \) is a proportionality factor referred to as the rate constant. The latter parameter is a function of temperature \( T \) according to the Arrhenius equation:

\[
k = k_0 \exp \left( -\frac{Q_{\text{app}}}{RT} \right) \quad \text{(12)}
\]

where \( k_0 \) is a constant called frequency factor, \( Q_{\text{app}} \) is the...
apparent activation energy for the chemical reaction (1), and \( R \) is the universal gas constant. The rate of MnO reduction can also be expressed by the rate of the consumption of MnO in the slag:

\[
\text{Rate} = -\frac{m_s}{100} \frac{dC_{\text{MnO}}}{dt} \tag{13}
\]

where \( m_s \) denotes the slag mass at reduction time \( t \) and it is a function of the slag volume, \( V_s \), and the slag density \( \rho_s \):

\[
m_s = \rho_s V_s \tag{14}
\]

By combining Eqs. (11), (13) and (14) we get:

\[
-\rho_s \frac{dC_{\text{MnO}}}{C^0_{\text{MnO}}} = 100k \frac{A_s}{V_s} dt \tag{15}
\]

For a given temperature, the slag density is a linear function of the MnO content of the slag as described in Sec. 3.2. Thus we can write:

\[
\rho_s = aC_{\text{MnO}} + b_1 \tag{16}
\]

where \( a \) and \( b_1 \) are constants at a given temperature.

It was found in the wetting experiments that \( A_s/V_s \) ratio is always changing linearly during the MnO reduction at a given temperature. Figure 10 shows \( A_s/V_s \) changes during MnO reduction by graphite C substrate at 1 450°C, 1 500°C and 1 600°C. This figure indicates that the \( A_s/V_s \) increases during MnO reduction, and this increase is larger at higher temperatures. Generally the changes in \( A_s/V_s \) during MnO reduction at the reduction temperatures can be written as follow:

\[
\frac{A_s}{V_s} = a_2t + b_2, \quad T = \text{const.} \tag{17}
\]

where \( a_2 \) and \( b_2 \) are constants and they are dependent on the both type of graphite substrate and the reduction temperature.

Combining Eqs. (15), (16) and (17), we obtain:

\[
-(aC_{\text{MnO}} + b_1) \frac{dC_{\text{MnO}}}{C^0_{\text{MnO}}} = 100k(a_2t + b_2)dt \tag{18}
\]

Equation (18) is a main differential equation describing the carbothemic MnO reduction from a slag drop by carbon substrate at a given temperature. Under isothermal conditions the left-hand side of Eq. (18) is only dependent on the MnO concentration, while the right-hand side of this equation is a function of the reduction time. Considering \( C^0_{\text{MnO}} \) as the initial MnO content and \( C^0_{\text{C(MnO)}} \) as the equilibrium concentration of MnO in the system, integration between the limits \( C^0_{\text{MnO}} - C^0_{\text{MnO}} < t = 0 \) and \( C^0_{\text{MnO}} - C^0_{\text{MnO}} < t = \text{at an arbitrary time} \ t \) then gives:

\[
a_1(C^0_{\text{MnO}} - C_{\text{MnO}}) + b_1 \ln \left( \frac{C^0_{\text{MnO}} - C^0_{\text{MnO}}}{C^0_{\text{MnO}} - C_{\text{MnO}}} \right) = k(50a_2t^2 + 100b_2t) \quad \text{for} \ \alpha = 1 \tag{19}
\]

\[
a_1 \ln \left( \frac{C^0_{\text{MnO}} - C^0_{\text{MnO}}}{C^0_{\text{MnO}} - C_{\text{MnO}}} \right) + \frac{b_1}{1-\alpha} \left( (C^0_{\text{MnO}} - C^0_{\text{MnO}})^{1-\alpha} - (C^0_{\text{MnO}} - C^0_{\text{MnO}})^{1-\alpha} \right) = k(50a_2t^2 + 100b_2t) \quad \text{for} \ \alpha \neq 1, 2 \tag{20}
\]

The left-hand side of Eqs. (19) to (21) is only a function of MnO content, \( F(C_{\text{MnO}}) \), and the expression in the parenthesis in the right-hand side is a time function \( G(t) \). Thus, a general equation can be re-written for different reaction orders as the following:

\[
F(C_{\text{MnO}}) = kG(t) \tag{22}
\]

Regarding the constant value for the rate constant \( k \) at a given reduction temperature, a plot of \( F(C_{\text{MnO}}) \) against \( G(t) \) must be a straight line passing origin where the slope is the rate constant. Based on the calculated MnO reduction curves (Fig. 6) and the corresponding slag density changes presented in Sec. 3.2, the changes in \( F(C_{\text{MnO}}) \) for the reduction of slag with all graphite types at all reduction temperatures were calculated. Using the \( A_s/V_s \) ratio changes for reduction by all graphite types at the reduction temperatures, the changes in \( G(t) \) were also calculated.

Figure 11 shows the calculated \( F(C_{\text{MnO}}) \) values against \( G(t) \) for \( \alpha = 1 \) for reduction by graphite C at different temperatures. It is worth mentioning that the calculations for other reaction orders give similar \( F-G \) plots as the first order reaction, however, the \( F(C_{\text{MnO}}) \) values are different for different reaction orders. Figure 11 indicates that there is a good linear correlation between \( F(C_{\text{MnO}}) \) and \( G(t) \) at

![Fig. 10](image1.png)  
*Fig. 10.* The changes in the \( A_s/V_s \) ratio during MnO reduction by graphite C at 1 450°C, 1 500°C and 1 600°C.

![Fig. 11](image2.png)  
*Fig. 11.* The plots of \( F(C_{\text{MnO}}) - G(t) \) for graphite C substrate at 1 450°C, 1 500°C and 1 600°C (calculated for \( \alpha = 1 \)).
1450°C and we can draw a fairly straight line through the calculated points. The linear relationship between $F(C_{\text{MnO}})$ and $G(t)$ indicates that a constant $k$ in Eq. (22) is obtained and it is not changed during MnO reduction. This may indicate that the mechanism of MnO reduction from slag at this temperature is not changed during MnO reduction from initial MnO content (45 wt%) to around 28 wt% which is the highest reduction extent for the case of graphite C. Figure 11 indicates also that there is an initial linear relationship between $F(C_{\text{MnO}})$ and $G(t)$ at 1500°C and 1600°C and then it deviates from linearity. This may indicate that the mechanism of MnO reduction at these temperatures is the same as 1450°C to some extent and then it is changed to another mechanism. Figure 11 illustrates that this change occurs approximately at $F(C_{\text{MnO}})=0.8$ and $F(C_{\text{MnO}})=0.6$ at 1500°C and 1600°C, respectively. The same deviation point of $F(C_{\text{MnO}})=0.8$ for all types of graphites are obtained, and it may indicate that the change in the mechanism is not related to the carbon material properties and it is more dependent on the slag and temperature.

3.4.2. The Rate Constant and the Activation Energy

According to the Eq. (22), the slope of the plot of $F(C_{\text{MnO}})$ against $G(t)$ is the rate constant $k$. In the present study the linear part of the $F–G$ plots at different temperatures was considered to calculate the rate constant, because the mechanism of MnO reduction is assumed to be the same in this part at different temperatures. The rate constants for different reaction orders ($x=1, 1.3, 1.6, 2$) were calculated at 1450°C, 1500°C and 1600°C and the results are summarised in the Table 3. Although the rate constant values are not the same for different reaction orders, there are approximately the same ratios between the rate constant values for all reaction orders at different temperatures. Thus, it is expected to obtain close activation energies for different reaction orders for each type of graphite.

Taking natural logarithm on both sides of Eq. (12) gives:

$$\ln k = \ln k_0 - \frac{Q_{\text{app}}}{RT} \quad \text{(23)}$$

Equation (23) indicates that from a graph of $\ln k$ against $1/T$, the $k_0$ value and the apparent activation energy $Q_{\text{app}}$ for each type of graphite can be extracted. The plot of $\ln k$ vs. $1/T$ for all graphite materials and for the first reaction order is shown in Fig. 12. Moreover, the calculated $k_0$ and $Q_{\text{app}}$ for all graphite materials and for different reaction orders are summarised in Table 4. This table shows that $Q_{\text{app}}$ is not dependent on the order of reaction and very similar activation energies are obtained for different reaction orders. This table indicates that the apparent activation energy of the carbothermic MnO reduction is in the range of 148 to 254 kJ/mol. These calculated activation energies are smaller than the reported activation energies for MnO reduction from various slags by solid carbon materials, which are in the range of 332–407 kJ/mol. The difference between the obtained activation energy in this study and the literature is probably related to the applied methods. In this study we used sessile drop method to interact a small slag droplet with the carbon substrate. But, in the other studies much larger amounts of slag were reduced in graphite crucibles. One advantage of the present study is making use of the changes in the slag/carbon contact area in the rate constant calculations, which has not been considered in other studies. It is worth mentioning that the reported activation energies might be “apparent” and not “absolute” values due to the unknown real reaction area between slag and carbon.

3.4.3. Some Aspects of the MnO Reduction Kinetics

In principle, the rate of a chemical reaction is proportional to the reaction rate constant, reaction area and the driving force of the reaction. Therefore, in the case of carbothermic MnO reduction through reaction (1) we can write:

$$\text{Rate} = k_0 \exp\left(\frac{\Delta G_{\text{app}}}{RT}\right) \cdot \frac{A_{\text{reaction}}}{A_{\text{eq}}} \cdot \frac{\alpha_{\text{MnO}}}{K_{\text{eq}}}$$

$\text{(24)}$

$$\ln k = \ln \frac{k_0}{\alpha_{\text{MnO}} K_{\text{eq}}} - \frac{Q_{\text{app}}}{RT} \quad \text{(25)}$$

Fig. 12. Arrhenius plot for different graphite materials ($x=1$).

Table 3. The calculated rate constants for different reaction orders.

| Graphite type | Temperature (°C) | $k$ for $x=1$ mol m$^{-2}$ s$^{-1}$ | $k$ for $x=1.3$ mol m$^{-2}$ s$^{-1}$ | $k$ for $x=1.6$ mol m$^{-2}$ s$^{-1}$ | $k$ for $x=2$ mol m$^{-2}$ s$^{-1}$ |
|--------------|----------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| A            | 1450           | 0.00427                         | 0.00143                         | 0.00047                         | 0.0001                          |
|              | 1500           | 0.00690                         | 0.00227                         | 0.00075                         | 0.0016                          |
|              | 1600           | 0.00279                         | 0.00086                         | 0.00033                         | 0.0006                          |
| B            | 1450           | 0.00342                         | 0.00115                         | 0.00037                         | 0.0008                          |
|              | 1500           | 0.01063                         | 0.00349                         | 0.00115                         | 0.0026                          |
|              | 1600           | 0.00099                         | 0.00136                         | 0.00047                         | 0.0011                          |
| C            | 1450           | 0.00507                         | 0.00169                         | 0.00057                         | 0.0013                          |
|              | 1500           | 0.00960                         | 0.00317                         | 0.00103                         | 0.0024                          |
|              | 1600           | 0.00335                         | 0.00112                         | 0.00037                         | 0.0009                          |
| D            | 1450           | 0.00436                         | 0.00145                         | 0.00049                         | 0.0011                          |
|              | 1500           | 0.00840                         | 0.00277                         | 0.00091                         | 0.0020                          |
|              | 1600           | 0.00223                         | 0.00073                         | 0.00023                         | 0.0005                          |
| E            | 1450           | 0.00422                         | 0.00141                         | 0.00049                         | 0.0010                          |
|              | 1500           | 0.00755                         | 0.00349                         | 0.00082                         | 0.0019                          |
|              | 1600           | 0.00298                         | 0.000986                        | 0.00032                         | 0.0007                          |
| F            | 1450           | 0.00392                         | 0.00131                         | 0.00044                         | 0.0010                          |
|              | 1500           | 0.00798                         | 0.00263                         | 0.00087                         | 0.0019                          |
|              | 1600           | 0.00627                         | 0.00143                         | 0.00047                         | 0.0011                          |
where $K_{eq}$ is the reaction constant, $p_{CO}$ is the CO partial pressure in the system and $a_{Mn}$ is the produced manganese activity (activity of carbon assumed to be unity).

The term of $a_{Mn}p_{CO}/K_{eq}$ in Eq. (24), which is the MnO activity at equilibrium is negligible. Because $K_{eq}$ is larger than 1 at the experimental temperatures and Ar atmosphere ($p_{CO}=0$) is used. As we know the rate of MnO reduction by all graphite samples increases with increasing the temperature. This increase is not related to the MnO activity in slag (driving force), because for a given MnO content the MnO activity decreases with increasing temperature due to the positive deviation from the raultian behaviour. The initial MnO activity at 1450°C is higher than 1600°C, however the rate of MnO reduction in one phase region of slag is not very dependent on the MnO activity, and it is mainly dependent on the activation energy and the reaction area.

### 3.5. Multivariate Data Analysis

In order to determine the relationship between the kinetics of MnO reduction and the graphite properties, a multivariate data analysis was carried out. In this case the ‘Partial Least Squares (PLS) regression method’ was applied to study the relationships between $X$ and $Y$ variables:

**X-variables:** The measured graphite properties in Table 1 and temperature were considered as the $X$-variables for multivariate analysis. For simplicity, only one property of the parallel graphite properties was selected for this analysis. Hence, they were consisted of average pore diameter, porosity, crystallite size, surface area, CO$_2$ reactivity, and the surface roughness.

**Y-variables:** Rate constant, activation energy and graphite–slag reactivity were considered as the $Y$-variables in multivariate analysis. The calculated rate constants and activation energies in Tables 3 and 4 for $a_{/H11001}$ were used. Although some experimental techniques have been developed to study the propensity of carbon to react with gases (like CO$_2$ reactivity test), no experimental technique has been suggested to measure the propensity of carbonaceous materials to react with liquid slags. A method, which is measuring the slope of the MnO reduction curve, $-d(^{wt%MnO})/dt$, until reaching a fixed MnO content of slag is used as the graphite–slag reactivity parameter as described in the previous publications. In this case the slope of the reduction curves in Fig. 7 between 45 wt% MnO and 35 wt% MnO were calculated as summarised in Table 5.

**PLS Analysis**

PLS analysis indicated that there is good correlation between the measured and predicted graphite–slag reactivities, rate constants and activation energies. The suggested relationship between the $X$-variables and the $Y$-variables are illustrated in Fig. 13. Figure 13(a) indicates that the graphite–slag reactivity is affected extensively by temperature and the surface roughness. As we see higher reactivities are obtained at higher temperatures and for graphites with larger surface roughnesses. The other physical properties, which are in relation to the surface roughness (pore size and porosity), are the next in order of importance. The rate constant of the MnO reduction by carbon is mainly dependent on the temperature and then surface roughness (Fig. 13(b)). As we see the rate constant is not very dependent on the surface roughness of graphite as observed for graphite–slag reactivity. Different dependence of graphite–
slag reactivity and the rate constant on X-variables may indicate that there is a difference between the essences of these parameters. As we expect the rate constant is more dependent on the temperature (Eq. (12)), while graphite–slag reactivity is more material dependent. These results can suggest that the rate constant calculation cannot be used to show the graphite–slag reactivity of carbon materials. Figure 13(c) illustrates that the activation energy is not used to show the graphite–slag reactivity of carbon materials. This kinetic method allows considering the changes in this ratio are also greater at higher temperatures.

4. Conclusions

Kinetic of MnO reduction from slag by various graphite substrates was studied using sessile drop wettability technique. New kinetic mathematical formulation was developed and applied to study the interaction of slag drop with carbon substrates. This kinetic method allows considering the changes in the slag/carbon contact area during the reaction for rate constant calculations. The apparent activation energy for MnO reduction by graphite substrates was obtained in the range of 149–255 kJ/mol. The important results of this study are summarised as below:

(1) Carbon materials are not wetted by high MnO containing slags and a contact angle above 150° is observed between the carbon substrate and slag drop.

(2) The changes in the volume of slag drop during reduction are more significant than the changes in the contact angle, and these changes can successfully be used to evaluate the rate of slag reduction.

(3) The density of MnO containing silicate slags decreases linearly with decreasing the MnO content. The density changes are more dependent on the MnO content variations than the temperature variations in the range of 1 450–1 600°C.

(4) The evaporation rate of produced manganese through the slag reduction is very high in wettability experiment so that it provides the situation of having only slag–carbon reactions in the system and no reaction takes place between the slag and the liquid metal phase (dissolved carbon). The manganese evaporation rate is 1.26, 3.02 and 5.01 mg/min at 1 450°C, 1 500°C and 1 600°C, respectively.

(5) The ratio of slag/carbon contact area over the slag drop volume changes linearly during MnO reduction. The changes in this ratio are also greater at higher temperatures.

(6) The rate of MnO reduction by graphite materials is mainly dependent on temperature, and then the carbon properties.

(7) Multivariate analysis indicates that the MnO reduction rate increases with increasing the surface roughness. Graphite surface area improves the reaction kinetics significantly, while an increase in porosity and pore size of graphite will decrease the rate of slag reduction. The rate of slag reduction decreases with increasing the crystallite size in graphite.

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