INTERFACIAL PHENOMENA AND REACTION KINETICS BETWEEN CARBON AND SLAG CONTAINING MnO

M. Yaser Lone, Haiping Sun, Samir Ganguly[1] and Oleg Ostrovski

School of Material Science and Engineering
The University of New South Wales, Sydney, 2052 Australia
[1]Tasmanian Electrometallurgical Company, Bell Bay, TAS 7253 Australia
E-mail: h.sun@unsw.edu.au

ABSTRACT

Wettability of graphite by synthetic SiO_2-Al_2O_3-CaO-MnO slags with varied MnO content and by industrial slags was studied at 1350-1600 °C using sessile drop method under argon atmosphere. Initial contact angle was the lowest (110-115°) for the MnO-free slag. For slags with 10-40 wt% MnO, the initial contact angle was in the range 125-135°. The contact angle decreased with the contact time. The change in the contact angle with slag mass was found insignificant. The surface tension of slags obtained from the drop shape analyses was 500-800 mN/m and varied in a narrow range with temperature and MnO concentration. The reduction rate increased with increasing MnO content in the synthetic slag from 20 wt% to 40wt% and temperature. Increasing temperature also increased the rate of reduction. No correlation was observed between the reduction rate and MnO content in the synthetic slags in the range 0-20 wt% and in the industrial slags. The rate of SiO_2 reduction from the molten slag was close to the rate of MnO reduction. The MnO-free slag had the largest contact area with graphite substrate.

Keywords: *reduction, wettability, graphite, slag, manganese, surface tension.*

1. INTRODUCTION

In the production of manganese alloys, manganese and other oxides are reduced by carbon from molten slag. In the kinetic studies by Ranking and Van Danverter, [1] and Rankin and Wynnyckyj [2] two possible mechanisms for the reduction of manganese oxide were suggested; indirect reduction via gas phase and direct reduction at the interfaces of slag-coke or slag-reduced alloy. These studies showed that the rate of the overall MnO reduction is limited by the Boudouard reaction [1], or by transport of CO_2 from the gas-slag interface to the gas-carbon [2]. Ostrovski and Webb [3] investigated the reduction of high siliceous manganese ore by graphite at 900 - 1400ºC. The reduction of manganese oxide was predominantly observed at the graphite/slag interface, which was considered to be evidence of direct reduction. Sun *et al*. [4] investigated the reduction rate of FeO in slag by coke; the rate of reduction was found most likely to be jointly dominated by the mass transfer of FeO in slag and the reduction reaction at slag-coke, slag-gas or slag-metal interfaces.

Interfacial properties have strong influence on the reduction kinetics affecting carbon-slag contact area and CO gas bubbles formation at the reaction sites. At present, data on the interfacial properties of carbon – MnO-slag systems are very limited. The reduction proceeds with the formation of a CO bubble which nucleates in pores and roughness of a coke particle or char. Penetration of molten slag into the pore depends on the wetting of the coke by slag. Wettability and contact angles between the molten slag and coke have a strong effect on the growth of CO gas bubble and reduction rate.

This work studies interfacial and kinetic phenomena in the process of reaction of graphite with slag containing MnO.

2. EXPERIMENTS

Carbon substrates were manufactured by cutting, grinding and polishing graphite plates. Slag samples were prepared by melting a mixture of SiO_2, CaO and Al_2O_3 in a muffle furnace; they were then quenched, crushed,

ground, and mixed with MnO. Afterwards the slag samples were sintered in an induction furnace with graphite susceptor under argon gas. The synthetic slag composition is shown in Table 1.Three industrial slags were also studied; their composition is given in Table 2. Mass of slag was varied between 0.1- 0.6 grams.

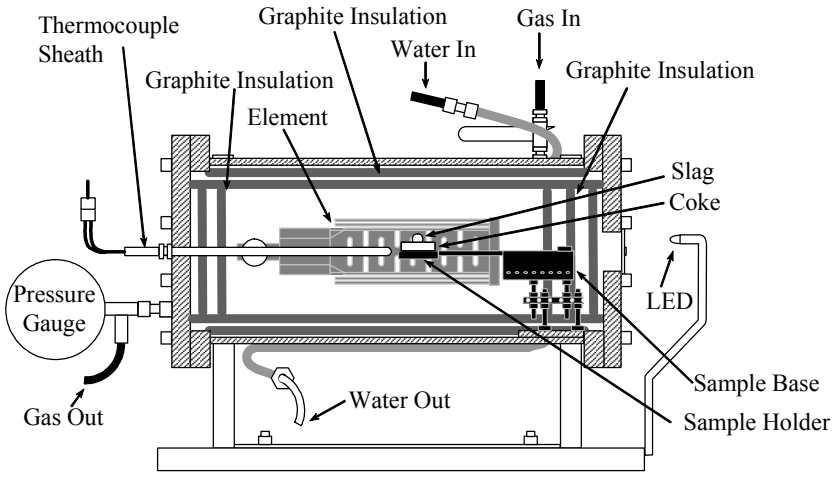
Table 1: Composition of synthetic slag, wt%

	MnO	Al_2O_3	SiO_2	CaO
L0	0	15	55	30
L5	5	14.25	52.25	28.5
L10	10	12.75	46.75	25.50
L20	20	12	44	24
L40	40	9	33	18

Table 2: Composition of industrial slag, wt%

	Mn	Fe	SiO_2	Al_2O_3	Na_2O	MgO	CaO
I1	35.75	0.60	23.45	10.4	0.54	2.23	13.0
I2	33.64	0.49	27.0	11.7	0.49	1.58	11.9
I3	11.85	0.28	43.85	13.18	0.44	8.06	15.4

Experimental set-up used to study reaction between graphite and SiO_2-Al_2O_3-CaO-MnO slag is shown in Fig. 1. A slag sample was mounted on the substrate and placed in the high temperature zone of a horizontal furnace with carbon heating element. The furnace was heated at the rate of 500°C/minute to the predetermined



Furnace Cross-section View

Figure 1: Experimental set-up to study graphite-slag reaction

temperature. A video-camera was used to observe slag shape, contact angle and contact area between slag and substrate during the reaction. Experiments were conducted at 1350-1600°C in argon atmosphere. Oxygen from argon was removed by passing gas through copper turnings at 500°C. Extent and rate of reduction process were monitored by analyzing CO and CO2 content in the off-gas using IR sensor. Blank experiments were conducted, in which only graphite was heated.

3. RESULTS AND DISCUSSION

3.1 Interfacial Phenomena

Figures 2 and 3 present images of the slag drop containing 0% (Slag L0, Fig. 2) and 40 wt% MnO (Slag L40, Fig. 3) on graphite substrate, at 1500°C for different reaction times. Figures 2(f) and 3(f) show the measurement of contact angle, contact area and coordinate system for measuring droplet shape. The gas bubbles were

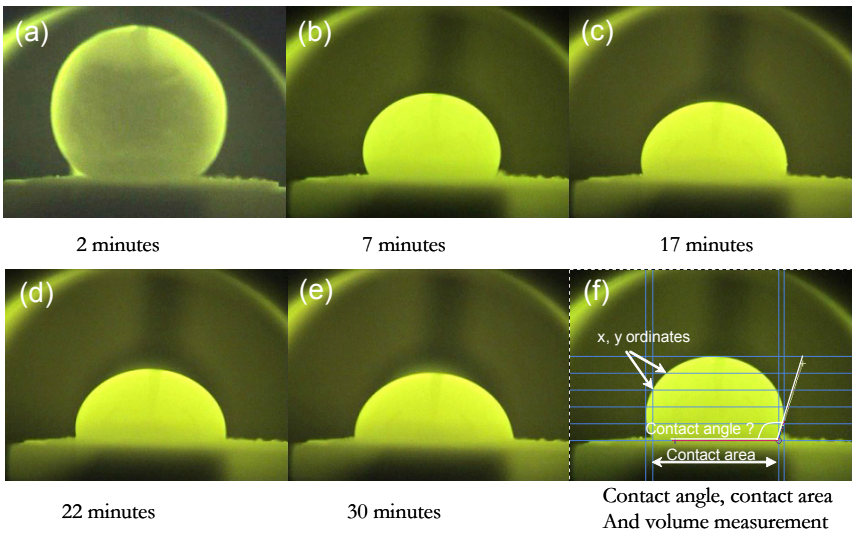


Figure 2: Images of MnO-free slag droplet on a graphite substrate at 1500°C for the reaction times of 2 (a), 7 (b), 17 (c), 22 (d) and 30 (e) minutes; f: Contact angle, contact area and shape measurement

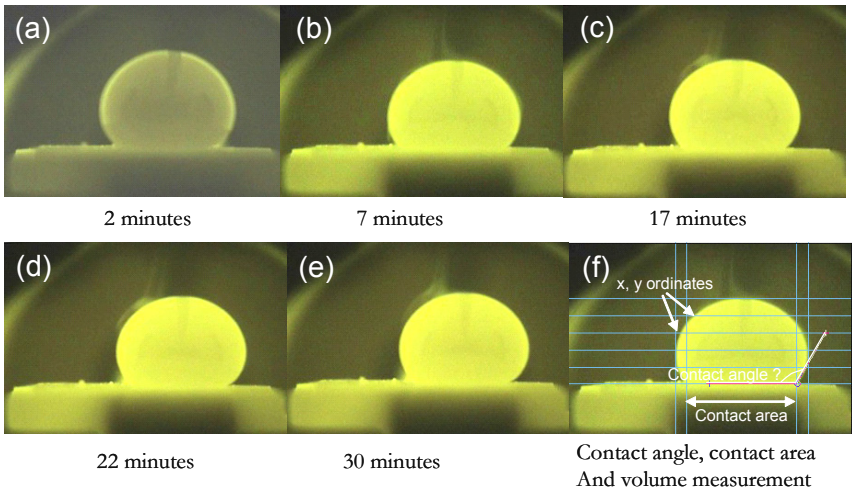


Figure 3: Images of a droplet of slag with 40% MnO on a graphite substrate at 1500°C for the reaction times of 2 (a), 7 (b), 17 (c), 22 (d) and 30 (e) minutes; f: Contact angle, contact area and shape measurement

observed generated at the graphite-slag interface, then spread throughout the droplet and broke at the droplet top; the slag droplet swelled by the trapped gas bubbles in the slag as seen in Figure 2(a). This phenomenon is known as foaming. After this, gas bubbles left the slag from its top. Dynamic contact angle between slag and graphite slightly decreased with the reaction time. When slag contained 40%MnO, as seen in Figure 3, the foaming was less intensive and the contact angle was larger as compared with the slag without MnO.

3.2 Contact angle

Contact angles between slags and graphite substrate are presented in Figure 4. Change in the contact angle with time for synthetic slags containing different concentrations MnO is shown in Fig. 4(a). Initial contact angle was the lowest (110-115^o) for the MnO-free slag. For slags with 10-40 wt% MnO, the initial contact angle was in the range 125-135^o. The contact angle decreased with the contact time. This decrease was steeper for the slag containing less MnO. The contact angle between graphite and industrial slags (Fig. 4(b)) did not follow this tendency; the contact angle for the industrial slag with 35.8% MnO decreased more than for slags containing 11.9 and 33.6 % MnO during 30 min contact time. The temperature and slag mass, as seen in Figures 4 (c) and 4 (d), did not show a visible effect on the contact angle. It can be concluded that the slag chemistry is a major factor affecting the contact angle between graphite and slag.

SiO_2 is known as the surface active oxide in the silicate slag, which reduces slag surface tension and slag-carbon interfacial tension as well. Therefore, it can be expected that replacing MnO with SiO_2 in slag reduces the contact angle. This explains the trend in change in the contact angle for synthetic slags with different MnO content.

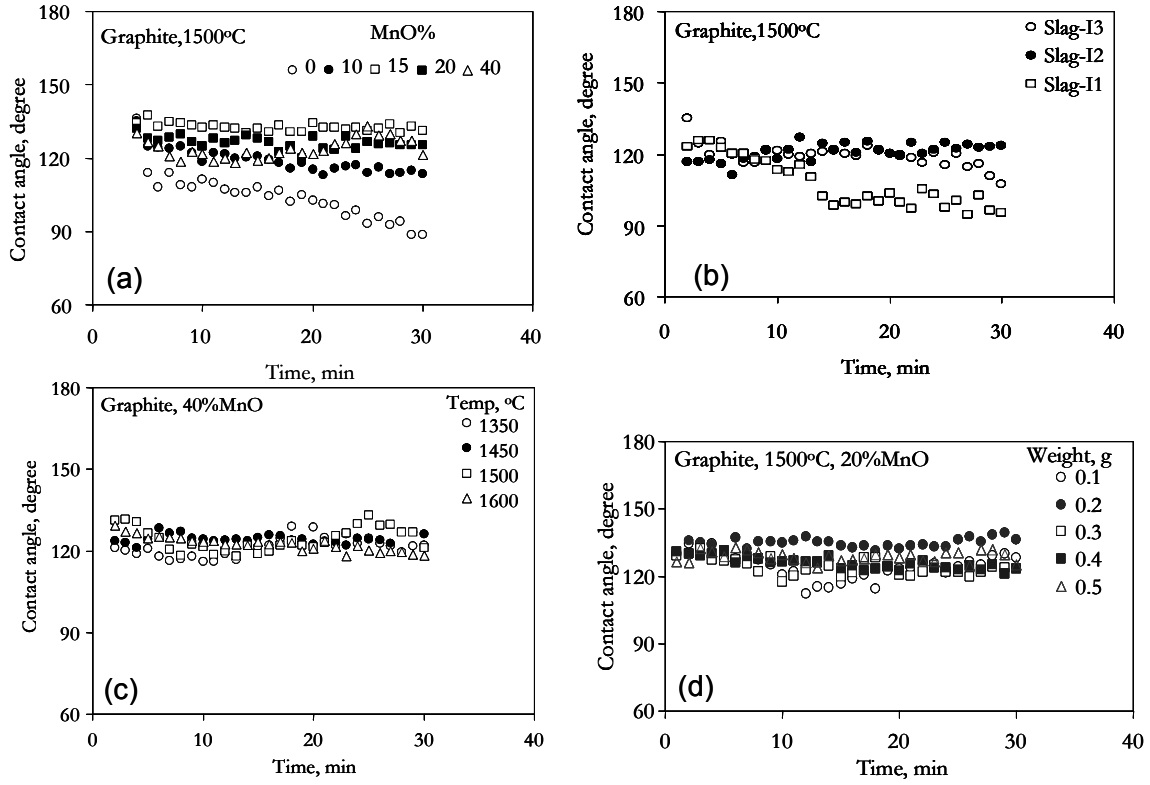


Figure 4a & b: Change in the contact angle with time for the synthetic (a) and industrial slags (b); c & d: Change in the contact angle at different reaction temperatures (c) and different slag mass (d)

3.3 Slag Volume

The change in the slag droplet volume during 30 minutes of reaction is shown in Fig. 5. The slag volume change was due to the formation of gases as a result of slag-carbon reaction. At the initial stage, the gas was released from the droplet top. A significant decrease in slag volume was observed during initial few minutes of the reaction (Fig. 5(a)), particularly for the MnO-free slag. After this the droplet volume was relatively stable. There was no direct correlation observed between the slag volume and CO generation rate (Fig 5 (b)).

Slag foaming depends on the slag viscosity, density and the surface tension. The density and surface tension are reduced, and the viscosity is increased, when MnO in the slag is replaced with SiO_2.

Figure 5(c) shows a decrease in the maximum volume of a slag droplet as a function of the MnO content of the slag. The volume of the MnO-free slag droplet is significantly higher than volume of slags containing MnO. It can be explained by suppression of the foaming by replacing SiO_2 with MnO and the increased slag density. Temperature had no visible effect on the slag volume (Fig. 5 (d)).

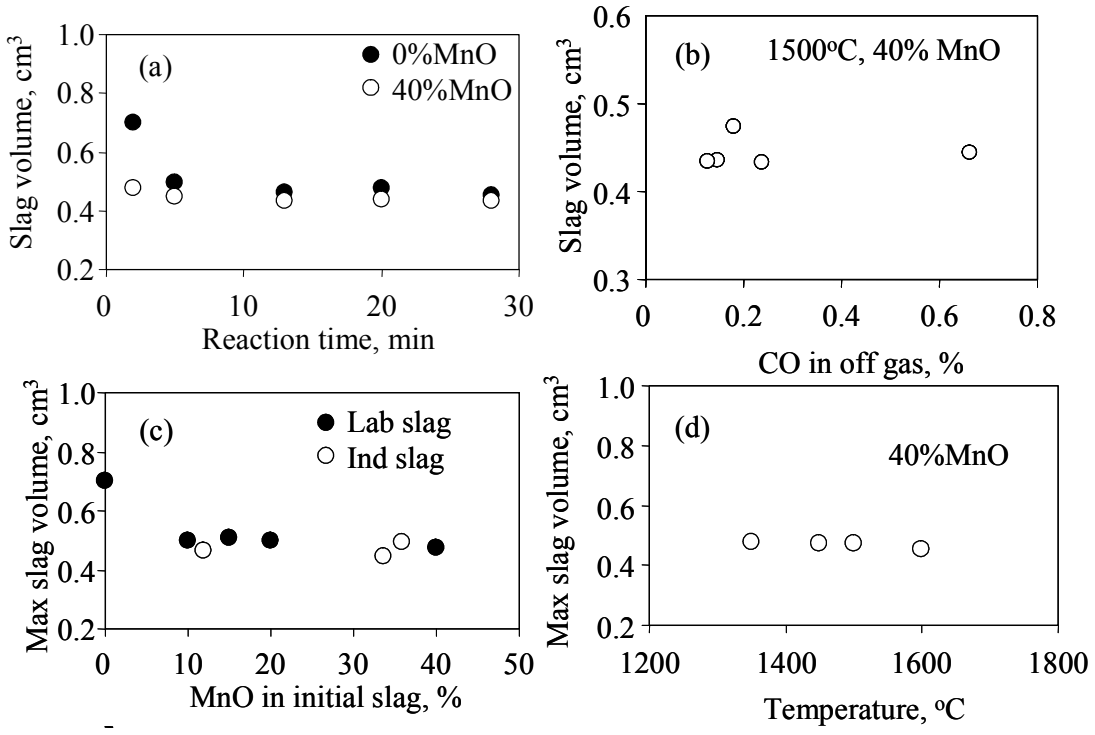


Figure 5a: Change in the slag droplet volume with time for synthetic slags containing 0 and 40 % MnO; b: Change in the droplet volume vs. CO content in off gas during the reaction of 40% MnO slag with graphite at 1500°C; c: Max volume vs. MnO content for the laboratory and industrial slags; d: Max volume of slag with 40 wt% MnO vs. reaction temperatures. 0.6 grams of slag was reacted with graphite for 30 minutes in each case

3.4 Surface tension

The surface tension of liquid slag was determined from the droplet's image analysis using Laplace equation as described in work [5]. The change in surface tension of synthetic and industrial slags with time is shown in Figure 7. The surface tension practically did not change with time as seen from the plot for the slag with 40 wt% MnO in Fig. 7(a). Figs. 7(b) and 7(c) show that the surface tension had a tendency to increase with increasing MnO content, although the effect of MnO content on the surface tension was weak, particularly

for the synthetic slag. In a CaO-MnO- SiO_2 system studied by Kekelidze *et al.* [6], the increase of the surface tension was observed with decreasing CaO or increasing MnO in the slag. It is also known [7], that the surface tension of CaO-SiO_2 and MnO-SiO_2 binary systems decreases with increasing silica concentration. The results shown in Figs. 7(b) and (c) are in agreement with these literature data; with increasing MnO and corresponding decreasing CaO and SiO_2 contents, the surface tension of the slag tends to increase.

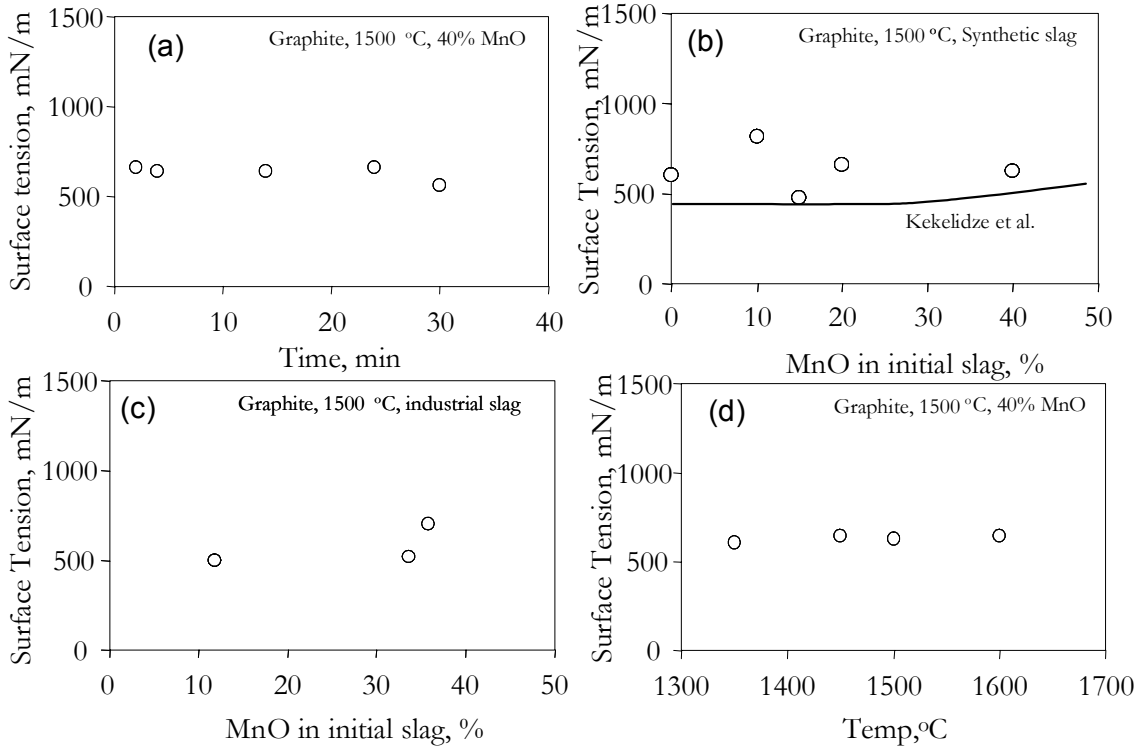


Figure 7 a: Change in surface tension with time of slag containing 40 wt% MnO; b and c: Average surface tension vs. MnO content for synthetic (b) and industrial (c) slags; d: Average surface tension vs. reaction temperature

3.5 Slag-graphite contact area

Slag-graphite contact (reaction) area is plotted in Figure 8. Contact area increased with reaction time for synthetic slags with 0 and 10 wt% MnO and industrial slags I1 and I2, and did not change with time for other slags. Increase in the MnO content in the slag reduced the contact area (Figs. 8 (a) and 8 (b)). The temperature had a minor effect on the reaction area (Fig. 8 (c)). Figure 8 (d) shows the correlation between the contact area and the contact angle: the contact angle decreased with increase in contact angle.

3.6 Reaction kinetics

The reduction of MnO and SiO_2 occurs at the slag-graphite interface at high temperatures through reactions MnO+C=Mn+CO or/and 7MnO+10C=Mn_7C_3 + 7CO, SiO_2+C=SiO+CO or/and SiO_2+2C=Si+2CO. Rate of the reduction was determined by measuring contents of CO and CO_2 gases in off gas by the infrared sensor. As CO_2 in the off gas was negligible compared to CO, only CO gas was taken into account. The CO contents in the off-gas detected in the blank run where only substrate was heated and in the experiment with slag containing 40 wt% MnO are shown in Figure 9 (a). The CO observed in the blank run where slag was absent is attributed to oxygen adsorbed on graphite substrate and furnace interior. The CO generated by the slag-graphite reaction was obtained by deduction of CO measured in the blank run from the CO content recorded in the

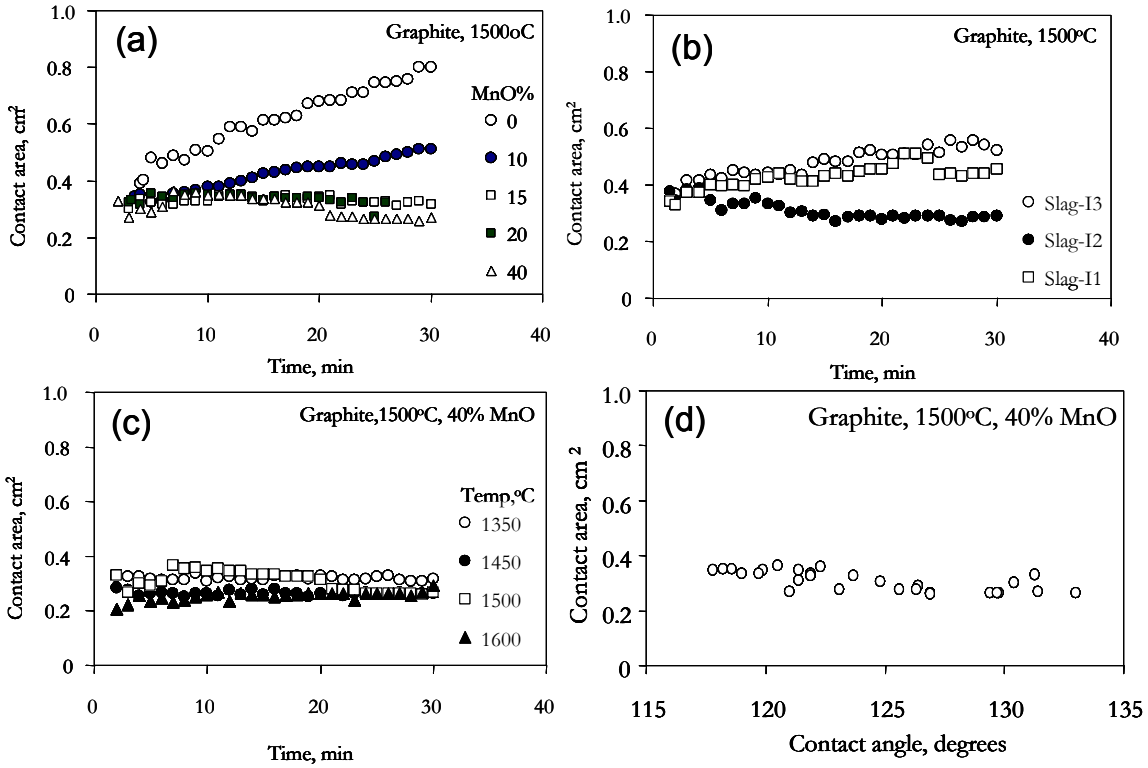


Figure 8 a & b: Graphite-slag contact area for synthetic (a) and industrial (b) slags; c: Contact area for the slag with 40 wt% MnO at different reaction temperatures; d: Contact area vs. contact angle for the slag with 40 wt% MnO

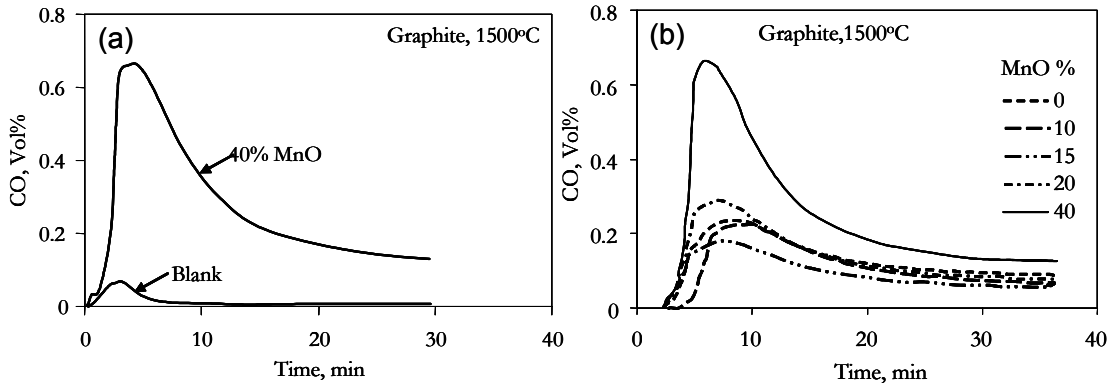


Figure 9 a: CO content in the off gas in the blank run and experiment with 0.6g of 40 wt% MnO; b: CO evolution in reduction of 0.6 g of slags with different MnO contents

reduction experiment. Figure 9 (b) shows CO content in the off gas in reduction of synthetic slags with different MnO contents at 1500°C.

Amount of CO gas produced in the course of reaction was obtained by integrating CO content in the Ar-CO gas (flow rate 1Nl/min) over the time period. Figure 10 shows the amount of CO gas produced during the reduction of synthetic slags (Fig 10(a)) and industrial slags (Fig. 10(b)). Effect of temperature on CO generation in the process of reduction of the slag containing 40 wt% MnO is shown in Fig. 10(c).

The rate and amount of CO evolution increased significantly with an increase of MnO in the synthetic slag from 20 wt% to 40 wt%, while no correlation was observed between the CO content in the off gas and MnO content in the synthetic slag in the range 0-20 wt% MnO. CO concentration in the off-gas in experiments with industrial slags was about the same for all three slags, although initial MnO concentration in these slags was quite different.

Temperature had a strong effect on the rate and amount of CO generated in the reaction (Fig. 10(c)). Thermodynamically, reduction reactions in argon in the experimental temperature range can be completed. Increasing temperature increased reduction kinetics and, as a result, rate and amount of CO production. There is no correlation between the effect of temperature on CO generation (Fig. 10(c)) and slag droplet volume (Fig. 5(d)). This can be interpreted as an indication that CO gas is not bubbled through the molten slag in the course of reduction.

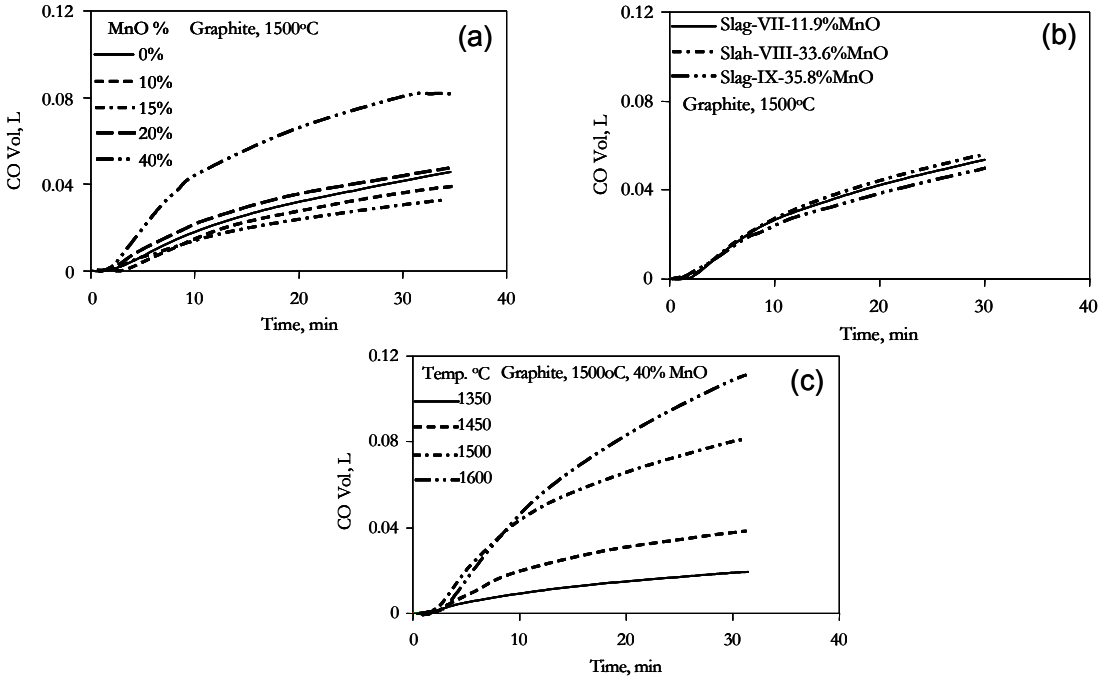


Figure 10 a & b: CO produced during the reduction of synthetic (a) and industrial (b) slags; c: CO generated in the reduction of the synthetic slag with 40 wt% MnO at different temperatures

Figure 11 shows a relationship between a number of moles of MnO in the synthetic slag and a number of moles of oxygen removed as CO gas during 30 minutes reduction at 1500°C. The number of moles of oxygen removed was in excess relative to the number of moles of MnO in slags with 0 – 40 wt% MnO (Fig. 11 (b)). This difference can be attributed to the SiO_2 reduction. Higher degree of reduction of SiO_2 was observed from the slag with lower MnO content. Moreover, the rate of SiO_2 reduction from the MnO-free slag was close to the rate of MnO reduction from the slag with 10-20 wt% MnO. As mentioned above, SiO_2 is a surface active component. The graphite-contact angle for the MnO-free slag was the lowest and the contact area the largest among investigated slags under experimental conditions in this study. The contact area is a significant factor affecting the rate and extent of reduction.

4. CONCLUSIONS

Reaction of graphite substrate with synthetic and industrial slags containing MnO was studied at 1350-1600°C. Contact angle, droplet parameters and CO evolution rate were measured in the course of reaction.

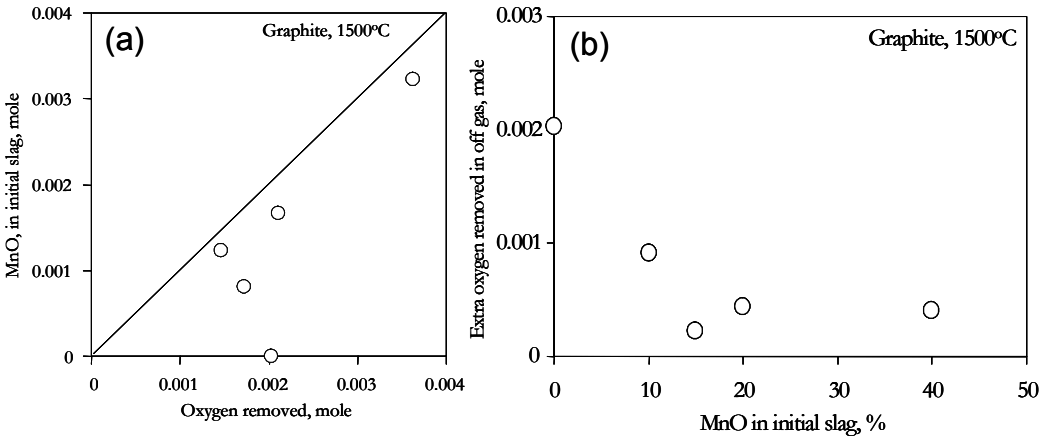


Figure 11 a: Correlation between MnO content in the synthetic slag and oxygen removed to the gas phase; b: Excess oxygen removed to the gas relative to MnO initial content in the slag

These data were used to calculate droplet volume, graphite-slag contact area, slag surface tension, rate and extent of CO evolution in the reduction process. Contact angle between molten slag and graphite substrate was dynamic; it slightly decreased with the reaction time. The contact angle was the smallest and contact area the largest for the MnO-free slag. The MnO-free slag also exhibited the largest volume and volume change in the initial reaction stage.

Effect of MnO content in the synthetic slag in the range 10-40 wt% and effect of temperature on the droplet volume was minor. Volume of industrial slag was also insensitive to the slag chemistry and temperature.

Surface tension of the slag was found in a range of 600-800 mN/m. The graphite-slag contact area decreased with increasing MnO content in the slag. Effect of temperature on the contact area was insignificant.

CO evolution and reduction rate of the synthetic slag by graphite increased with increasing MnO content from 20 to 40 wt%, while it changed in a narrow range for slags with 0-20 wt% MnO.The reduction rate of different industrial slags was about the same. The reduction rate increased with increasing temperature. In the course of slag-graphite reaction, MnO and SiO_2 were reduced. The rate of SiO_2 reduction from the MnO-free slag was close to the rate of MnO reduction from slags with 10-30 wt% MnO.

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