



# Electrochemical effects of direct current on the reduction of manganese oxide from molten $\text{MnO-SiO}_2\text{-CaO-Al}_2\text{O}_3$ slag

by X.W. Pan\*

## Synopsis

*It has been found that the MnO content of a slag decreases sharply when direct current is applied to a metal-slag system consisting of liquid Mn-Si-C<sub>sat</sub> metals and MnO-SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> slag in graphite crucibles.*

*This paper reports a preliminary investigation into the electrochemical effects of direct current on the metal-slag system, the silicon content of the metals, and the MnO content of the slag. The results show that, when a direct current of 7 A is maintained, the MnO content of a metal containing 10 to 11 per cent silicon by weight is reduced rapidly from 26,5 to 17,2 per cent by weight. This reduction seems to proceed further when the process is continued. When the direct current and the voltage are kept constant at 7 A and 4 V respectively, the MnO content of a metal containing 1 to 2 per cent silicon by weight is reduced to 1 from 25 per cent by weight, which results in a manganese yield of 96 per cent.*

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## Introduction

Manganese is a valuable and widely used alloying material. The recovery of manganese as a strategic and critical material in both melting and refining processes is therefore very important. The melting efficiency depends, in part, on the distribution of manganese among the metal, slag, and gas phases. Therefore, attention has been drawn to the thermodynamic properties of the metals and slag<sup>1-7</sup>, such as multi-component equilibria among metal, slag, and gas; the activities of components in the metal and slag phases; the effects of reaction temperature and pressure on multi-component equilibrium; the effects of different components on the activities of MnO and SiO<sub>2</sub> in slag such as those containing CaO, Al<sub>2</sub>O<sub>3</sub>, and MgO from the production of manganese and ferromanganese alloy; and the effects of carbon, iron, and silicon on the activities of manganese. Workers<sup>8,9</sup> have also investigated other factors that are involved in the production processes, such as the viscosity, liquidus temperature, and electrical conductivity of slags, in order to maximize the efficiency of the processes.

The electrochemical effects of direct current in the ferromanganese processes, however, have received little attention because direct current is not normally used in processes involved in the recovery of manganese. However, in the use of the direct-current arc furnace in the steel industry<sup>10,11</sup>, it is important that the electrochemical effects of direct current on the reduction of manganese from slag to metal should be investigated. This paper reports on the preliminary phase in such an investigation.

## Experimental aspects

The apparatus used in the work described here is shown in Figure 1. Briefly, the equipment consists of an electric furnace with a graphite heating element, a direct-current source of 60 V and 20 A, and a current recorder. The temperature inside the furnace was measured by a Pt/10% Rh-Pt thermocouple, which was protected by an Al<sub>2</sub>O<sub>3</sub> tube and was placed just below the graphite crucible. The graphite crucible was 42 mm in outside diameter and 36 mm in inside diameter, and was led to the electrical connection out of the furnace by molybdenum wire of 1,0 mm diameter. A graphite electrode of 10 mm diameter with a plate 20 mm in diameter was placed at the top of the furnace. The cross-section of the crucible is shown in Figure 2.

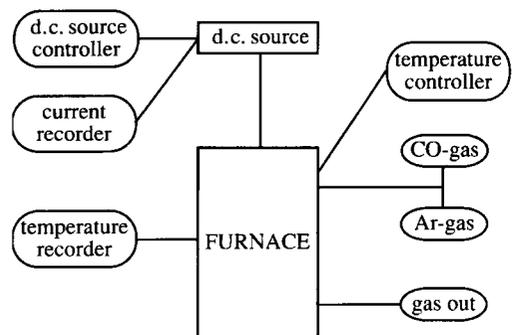


Figure 1—The experimental apparatus

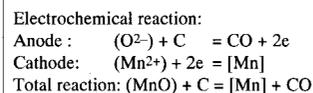
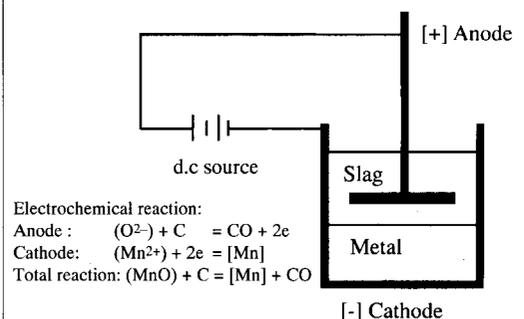


Figure 2—Cross-section of the crucible

# Reduction of manganese oxide

*The increase in the silicon content of the metal is largely dependent on the voltage, a low voltage resulting in a low silicon level.*

*The primary results show that the direct-current method could give a more efficient recovery of manganese from slag to metal.*

## Acknowledgements

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The master slag was pre-melted in a graphite crucible by the use of analytically pure oxides such as MnO, CaO, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>, and was crushed after it had cooled. Small amounts of oxides were added to the pre-melted master slag according to the experimental requirement.

The metals were prepared from analytically pure manganese and silicon. The argon and carbon monoxide gases were of chemically pure grade.

The experimental runs were made in the following manner. After the graphite crucible charged with metal and slag had been put into the furnace, the furnace was flushed with argon gas for 20 minutes before it was heated, in order to minimize oxidation inside the furnace. The argon was changed to carbon monoxide when the temperature reached 1400°C, and was kept for 20 minutes to eliminate the argon and homogenize the temperature of the charge. The metal and slag were then heated rapidly from 1400 to 1500°C. Zero time occurred when the top graphite electrode was put into the slag with a distance of 5 to 7 mm between the electrode and the slag-metal interface. In some cases, zero time started after the MnO had been charged into the crucible with molten slag 5 minutes later. A period of 2 to 3 minutes was sufficient to melt the charged 20 g of MnO in the slag. The slag composition used in the experiments was as follows in percentages by weight: 50 SiO<sub>2</sub>, 25 to 30 MnO, 15 to 20 CaO, and 0 to 10 Al<sub>2</sub>O<sub>3</sub>. The metal consisted of the following, also in percentages by weight: 0 to 15 Si, 85 to 100 Mn, and C picked up from the graphite crucibles. The direct current was kept constant at 5 A and 7 A, and the voltage varied in the range 4 to 26 V.

The molten slag was sampled by use of copper wire of 2 mm diameter. The samples of slag were analysed in an electron microprobe with a wavelength dispersion spectrometer. The composition of the metals was determined from the composition of the slag and from mass balances, which were in very good agreement with the chemical analyses.

## Results and discussions

### Electrode processes

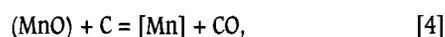
The electrode processes in these experiments can be summarized as follows. On the top graphite anode, the oxygen ions (free or linked to silicon or aluminium in the silicate or aluminate ions) were first oxidized electrochemically to oxygen, and then the oxygen was reacted with carbon from the anode to produce carbon monoxide gas by pure chemical reaction on the surface of the graphite anode:



At the cathode of the slag-metal interface, manganese ions were reduced to metal by an electrochemical reaction:



By summation of these partial reactions, the process ends in the electrochemical reduction of MnO by carbon from the graphite anode according to reaction [4]:



where the round and the square brackets refer to the slag and the metal phases respectively.

The advantage over pure chemical reduction in the thermocarbon production process is that the metal obtained at the slag-metal interface, without touching the reductant carbon of the top graphite anode, could be used in the production of carbon-free manganese, instead of the strongly carburized metal that is produced by the conventional electro-reduction furnace. In the vicinity of the anode, the evolution of carbon monoxide from the slag was observed visually as soon as the current was passed through the system. The resulting bubbles caused a slight but observable fluctuation in the voltage of the direct-current source because of polarization. Figures 3 and 4 show clearly that the applied direct current at a constant 7 A dramatically increased the rate of MnO reduction, which quickly resulted in increasing the metal and decreasing the slag. When the direct current ceased, the reduction of MnO also stopped.

### Electrochemical equilibrium

The application of direct current can break the chemical equilibrium established in the system consisting of MnO-SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> slag, Mn-Si-C<sub>sat</sub> metals, and CO gas, and can help the carbon to ultimately reduce the MnO, which means that the application of direct current will help to decrease the MnO in the slag and to increase the manganese yield. Figure 3 shows that the MnO in the slag was hardly reduced without the use of direct current and, after the application of a constant direct current at 7A, the MnO content was reduced very quickly and this tendency of rapid reduction seemed to be maintained.

Figure 5 demonstrates that, when the direct current and the voltage were kept constant at 7 A and 4 V respectively, the MnO content of the slag was reduced to 1 per cent by weight from 25 per cent by weight, and the silicon content of the metal was maintained at 1 to 2 per cent by weight, which resulted in a manganese yield of 96 per cent.

# Reduction of manganese oxide

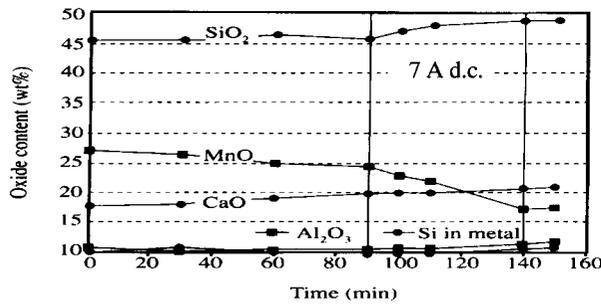


Figure 3—Effect of a direct current of 7 A on the composition of the slag and the metal at 1500°C and 1 atm. CO

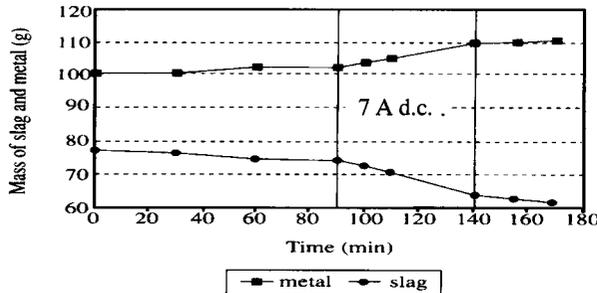


Figure 4—Effect of a direct current of 7 A on the reduction of MnO from slag to metal at 1500°C and 1 atm. CO

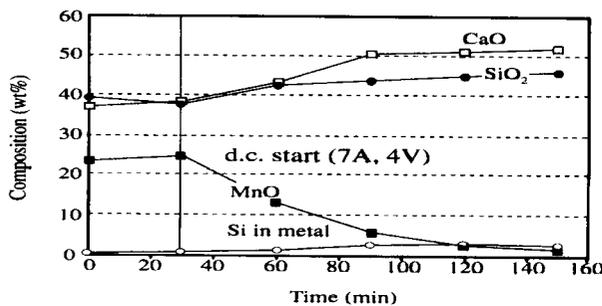


Figure 5—Effect of a constant direct current of 7 A and 4 V on the composition of the slag and the metal at 1500°C and 1 atm. CO

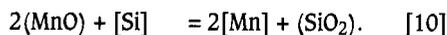
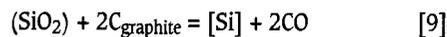
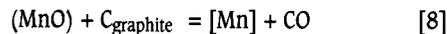
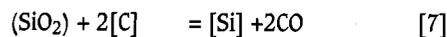
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From the well-known second law of thermodynamics for a process that takes place at constant temperature and pressure in the presence only of volume work, we have

$$\Delta G \leq 0. \quad [5]$$

When  $\Delta G = 0$ , the chemical reaction is in equilibrium.

The process consists of several chemical reactions, such as the following:



When all the chemical reactions involved in the process are in equilibrium among the slag, metal, gas, and graphite phases within all the components, the state is known as simultaneous equilibrium.

If a direct current with electric potential  $E(V)$  is applied to the system,

$$\Delta G \leq -W' \quad [11]$$

$$W' = NFE, \quad [12]$$

where  $\Delta G$  is the change in Gibbs energy,  $W'$  is the electrical work,  $N$  is the number of electrons transferred, and  $F$  is Faraday's number. The equality sign refers to a reversible process, and the inequality sign to an irreversible process.

When the reaction  $(\text{MnO}) + \text{C} = [\text{Mn}] + \text{CO}$  has reached chemical equilibrium, it can continue in the right direction if a direct current with  $E(V)$  is applied. When the reaction has reached equilibrium,

$$NFE = NFE^\circ - RT \ln (K)_e \quad [13]$$

$$(K)_e = (a_{[\text{Mn}]}P_{\text{CO}})/(a_{(\text{MnO})}a_{\text{C}}), \quad [14]$$

where  $(K)_e$  is the electrochemical equilibrium constant.

Figure 6 shows the relation between the applied  $E(V)$  and the activities of Mn and MnO under electrochemical equilibrium. When the CO pressure is 1 atm. and the activity of the carbon is unity, a very small  $E(V)$  can increase  $(K)_e$  considerably. When the activity of the manganese in Mn-Si-C<sub>sat</sub> metals is 0,17 and 0,5, the activity of the MnO in the slag equilibrated with the metals will decrease sharply from 0,12 and 0,34 respectively to almost zero with a voltage of only 0,35 V, which shows that the electrochemical effect of direct current on the reduction of manganese is very efficient, giving a much higher manganese yield than in the pure chemical process.

# Reduction of manganese oxide

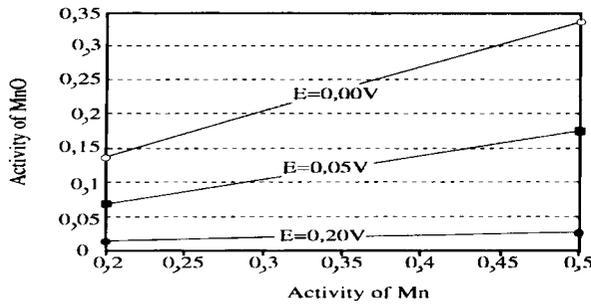


Figure 6—Relation between the activities of MnO and Mn with electric voltage at 1500°C

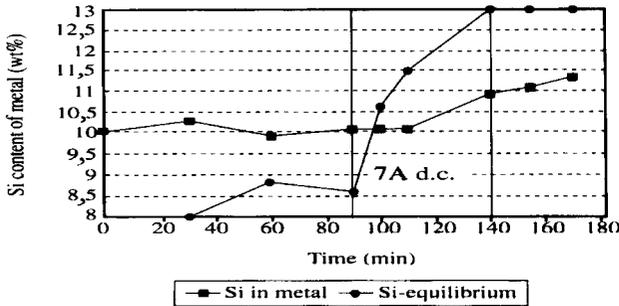


Figure 7—The effect of a direct current of 7 A on the composition of the slag at 1500°C and 1 atm. CO (the graph for silicon equilibrium is after Ding and Olsen<sup>6</sup>)

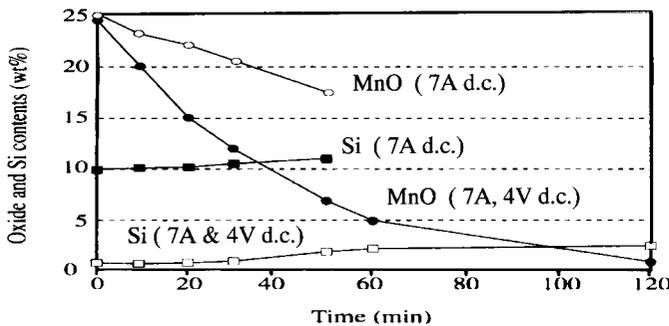


Figure 8—The effect of a direct current on the MnO content of the slag and on the silicon content of the metal at 1500°C and 1 atm. CO

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## Silicon content of the metal

It is well known that a low MnO content in the slag phase is a major goal in the production of ferromanganese of low silicon content<sup>12,13</sup>. In the chemical reaction, the MnO content of a slag is reversely proportional to the silicon content of the metal. In the electrochemical reaction, the MnO content depends mostly on the carbon monoxide pressure and the voltage applied. As discussed earlier, a very low voltage will considerably reduce MnO. The silicon content of the metal is controlled largely by the voltage, current density, slag composition, temperature, and carbon monoxide pressure.

Figures 7 and 8 show that the silicon content of the metal is much affected by the supplied voltage. The silicon can be kept constant until the voltage is higher than the critical voltage. The results show that a low silicon content (1 to 2 per cent by weight) in the metal and a low MnO content (1 per cent by weight) in the slag can be obtained in the same metallurgical vessel.

The voltage must be strictly controlled to keep a low silicon content in the metal, which is also related to other factors, such as polarity, current density, distance between anode and cathode, section-area ratio of anode to cathode, temperature, and carbon monoxide pressure. Further investigations are necessary to show the electrochemical effects of direct current on the reduction of MnO from slag to metal.

## Conclusions

The results given in this paper represent the preliminary phase of an investigation on the electrochemical reduction of MnO from slag to metal by the application of direct current. The major results of the experiments described here are as follows.

- The application of direct current can break the chemical equilibrium among the Mn-Si-C<sub>sat</sub> metal, MnO-SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> slag, carbon monoxide gas, and graphite phases, and can cause the reaction to favour the reduction of MnO from slag to metal.
- When the direct current and voltage are maintained constant at 7 A and 4 V respectively, the MnO in the slag can be reduced to 1 per cent by weight from 25 per cent by weight, and the silicon in the metal can be maintained at 1 to 2 per cent by weight, which produces a manganese yield of 96 per cent in the one-step reduction process.
- The direct-current method could have potential in keeping the MnO in the slag at a low level so that the slag can be disposed of without requiring re-treatment in another metallurgical vessel and, in a one-step process, for producing refined ferromanganese and a low-silicon Si-Mn alloy. ♦