

## Production of high carbon ferromanganese from a manganese ore located in Erzincan

İsmail Seçkin ÇARDAKLI\*, Naci SEVİNÇ, Tayfur ÖZTÜRK

*Department of Metallurgical and Materials Engineering, Middle East Technical University,  
Ankara-TURKEY*

*e-mail: cardakli@metu.edu.tr*

Received: 02.09.2010

### Abstract

Ferromanganese is an important additive used in the production of steel. Turkey produces more than 25 million tons of steel a year and the quantity produced is steadily increasing. Ferromanganese is not produced in Turkey, therefore, the country's entire supply is imported. Studies related to ferromanganese production would be beneficial for future investments in ferromanganese production facilities. The production of high carbon ferromanganese from a manganese ore deposit located in Erzincan was examined in this study. The ore was smelted using carbon as the reducing agent. Time, weight ratio of graphite to ore, fluorspar addition, and charge basicity were used as the experimental variables and the resulting alloy and slag phases were subjected to chemical analysis. The objective of this study was to investigate the possibility of high carbon ferromanganese production from manganese ore in Erzincan.

**Key Words:** Smelting, high carbon ferromanganese, pyrometallurgy

### 1. Introduction

Manganese plays a crucial role in the iron and steel industry. As an alloying element, it improves the strength, toughness, hardenability, workability, and abrasion resistance of steel. About 90%-95% of all the manganese produced in the world is used in iron and steel production in the form of alloys such as ferromanganese, silicomanganese, and ferrosilicomanganese. Manganese has two important properties in steelmaking: its ability to combine with sulfur to form MnS and its deoxidation capacity (İmer, 1997). About 30% of the manganese utilized in steel industry is used for its properties as a sulphide former and deoxidant. The other 70% of the manganese is used purely as an alloying element. Turkey produced 25.3 million tons of crude steel in 2009 (Steel Statistical Yearbook, 2010) and production continues to increase. The demand for ferromanganese in the Turkish iron and steel industry is increasing continuously parallel to the growth in steel production. Because ferromanganese is not produced in Turkey, its supply must be imported. Turkish manganese ore reserves are around 4.6 million tons (Manganez Özel İhtisas Komisyon Raporu, 2001) and the largest manganese ore beds are located in the Denizli-Tavas region.

---

\*Corresponding author

Metallurgical grade manganese ores (>40% Mn) are usually processed into suitable metallic alloy forms by pyrometallurgical processes, which are very similar to iron pyrometallurgical processes. In its production process, a mixture of manganese ore, reductant (a form of carbon), and flux (CaO) are smelted at temperatures above 1200 °C to enable carbothermal reduction reactions and alloy formation. Standard grade ferromanganese can be produced either in a blast or electric furnace. High carbon ferromanganese can be produced by 3 different processes: blast furnace, discard slag electric furnace, and high manganese slag electric furnace. During high carbon ferromanganese production, parameters such as temperature, time and, charge basicity affect the manganese recovery. Generally, an increase in these parameters increases the extent of carbothermal reduction reactions, thus increasing the manganese recovery from charge. In this study, holding time, basicity of charge, fluorspar content, and weight ratio of graphite to ore were used as the experimental parameters. Experiments were conducted at 1600 °C as this was the maximum temperature of operation of the furnace used. During the experiments, the temperature was constant at 1600 °C, as high as possible to obtain enough energy for highly endothermic reduction reactions.

## 2. Materials and methods

The experiments in this study were conducted using a conical graphite crucible, into which a mixture of 100 g of uncalcined manganese ore and carefully weighed amounts of graphite powder, lime, and fluorspar were added. The chemical analysis of calcined and uncalcined ore, graphite powder, lime, and fluorspar is given in the Table. Time, basicity of charge, fluorspar content, and weight ratio of graphite to ore were used as the experimental parameters. A reductant must have a low ash content so it does not affect the slag basicity during experiments. For this reason, low-ash graphite was used as a reductant in the experiments in this study. The graphite crucible and its contents were covered with a graphite lid and placed into an electronically controlled muffle furnace. The furnace was heated to 1200 °C at a rate of 10 °C/min and then the temperature was raised to 1600 °C at a rate of 5 °C/min. The temperature was held at 1600 °C for a predetermined amount of time, then switched off and cooled to room temperature. The crucible was then taken out of the furnace and broken to remove the metal and slag phases, which were carefully weighed and subjected to chemical analysis.

## 3. Results and discussion

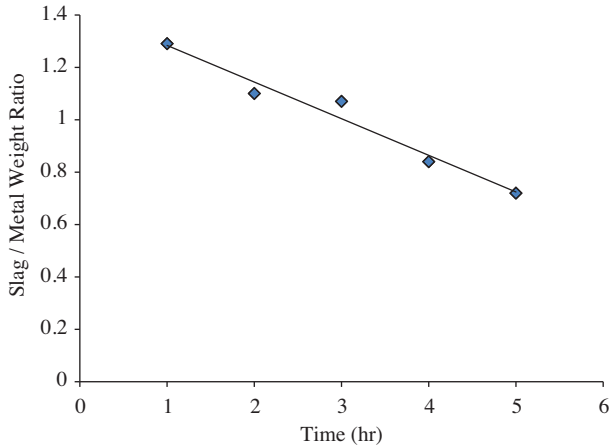
Carbothermal reduction of MnO and SiO<sub>2</sub> from the slag by carbon is governed by the following reactions:



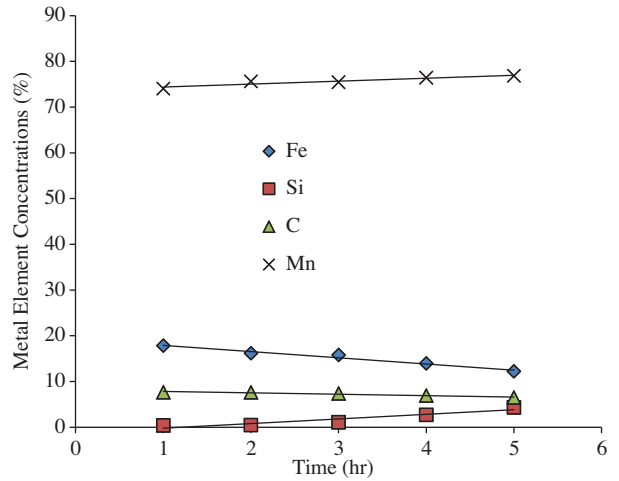
As the extent of the reduction increases over time, the weight of the metal phase increases, whereas the weight of the slag phase decreases. This trend is shown in Figure 1, where the weight ratio of slag to metal is seen to decrease over time. The weight variations of the Fe, Mn, Si and, C concentrations of the metal phase are shown in Figure 2 and the variations of MnO and SiO<sub>2</sub> concentrations in the slag phase are shown in Figure 3. The variation of recoveries of Mn and Si, defined as weight of Mn in metal/weight of Mn in charge and weight of Si in metal/weight of Si in charge, respectively, are shown in Figure 4.

**Table.** Chemical analysis of calcined and uncalcined ore, graphite powder, lime, and fluorspar.

| Elements                       | Calcined ore (wt. %) | Uncalcined ore (wt. %) | Graphite (wt. %) | Lime (wt. %) | Fluorspar (wt. %) |
|--------------------------------|----------------------|------------------------|------------------|--------------|-------------------|
| C                              | 0.05                 | 0.93                   | 95.32            | 0.29         | 0.05              |
| S                              | 0.01                 | 0.01                   | 0.03             | 0.01         | 0.02              |
| MnO <sub>2</sub>               | 70.87                | 70.48                  | -                | -            | -                 |
| MgO                            | 1.89                 | 1.85                   | -                | 0.84         | 0.15              |
| Al <sub>2</sub> O <sub>3</sub> | 3.42                 | 3.19                   | -                | 0.16         | 0.73              |
| SiO <sub>2</sub>               | 11.30                | 10.97                  | -                | 0.61         | 6.26              |
| CaO                            | 8.51                 | 8.09                   | -                | 98.00        | 0.19              |
| Fe <sub>2</sub> O <sub>3</sub> | 2.45                 | 2.61                   | -                | 0.04         | -                 |
| Na <sub>2</sub> O              | 0.34                 | 0.33                   | -                | -            | -                 |
| K <sub>2</sub> O               | 0.50                 | 0.47                   | -                | -            | -                 |
| TiO <sub>2</sub>               | 0.12                 | 0.11                   | -                | -            | -                 |
| BaO                            | 0.10                 | 0.08                   | -                | -            | -                 |
| P <sub>2</sub> O <sub>5</sub>  | 0.29                 | 0.20                   | -                | -            | -                 |
| SrO                            | 0.15                 | 0.18                   | -                | -            | -                 |
| CaF <sub>2</sub>               | -                    | -                      | -                | -            | 92.30             |
| Ash                            | -                    | -                      | 0.80             | -            | -                 |
| Moisture                       | -                    | -                      | 0.32             | 0.05         | 0.30              |
| Volatile matter                | -                    | -                      | 3.53             | -            | -                 |



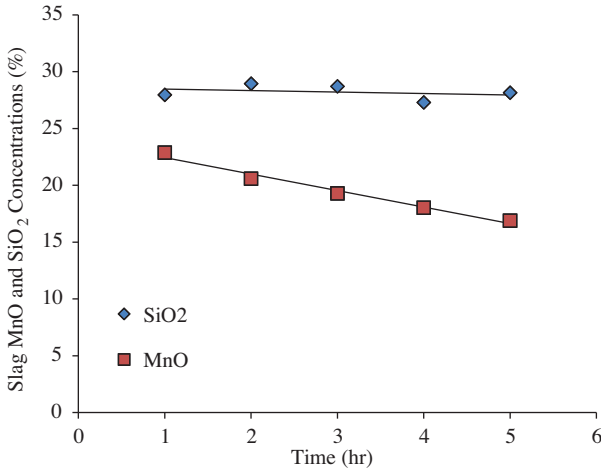
**Figure 1.** Effect of time on the weight ratio of slag/metal.



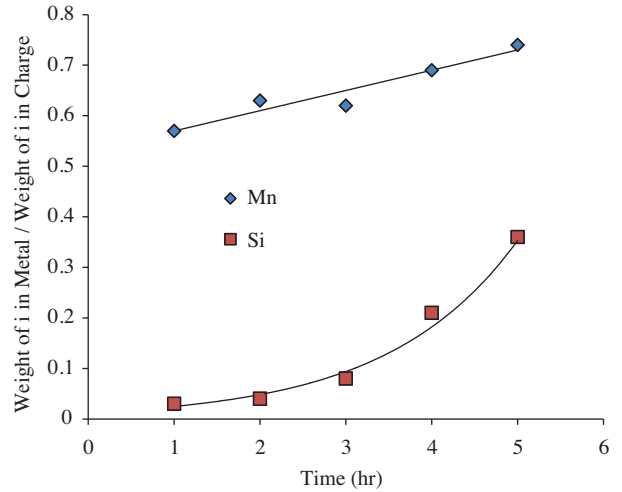
**Figure 2.** Variation of metal Fe, Mn, Si, and, C concentrations with smelting time.

The concentration of Fe in the metal is seen to decrease slightly over time during a 1-5 h period (Figure 2). However, there is almost no change in the weight of Fe in the metal during this period. Iron oxide is less stable than MnO and SiO<sub>2</sub> and is almost completely reduced in less than 1 h. Therefore, there is almost no change in the weight of Fe in the metal phase beyond 1 h. The decrease in the concentration of Fe in the alloy is due to the increase in the weight of the metal over time. The concentration of Mn in the metal and the weight of Mn in the metal are seen to increase over time (Figure 2). It can be seen in Figure 3 that the concentration of MnO and the weight of MnO in the slag decrease continuously within a time range of 0-5 h.

Thus, it can be concluded that the reduction of MnO is a slow process, taking longer than 5 h to complete. Both the concentration and weight of Si in the metal increase over time as is seen in Figure 2. Figure 3 shows that the concentration of SiO<sub>2</sub> in the slag remains steady, while the weight of the SiO<sub>2</sub> decreases with time. The decrease in the total the weight of the slag is the reason why the concentration of SiO<sub>2</sub> essentially remains constant, in spite of the decreased weight of the SiO<sub>2</sub>. Figure 4 shows that the reduction of SiO<sub>2</sub> is not complete and would continue after the 5 h period. Türkdoğan et al. (1980) also noted that the reduction of SiO<sub>2</sub> from the slag into the metal by carbon is slow process. The decrease in the carbon content of the metal is shown in Figure 2. The metal is contained in a graphite crucible. Therefore, the system is expected to become saturated with carbon as time passes. The solubility of carbon in the Fe-Mn-Si system decreases with an increase of the Si content in the metal. Therefore, the carbon content of the metal decreases over time due to the increase in the Si content (Figure 2).

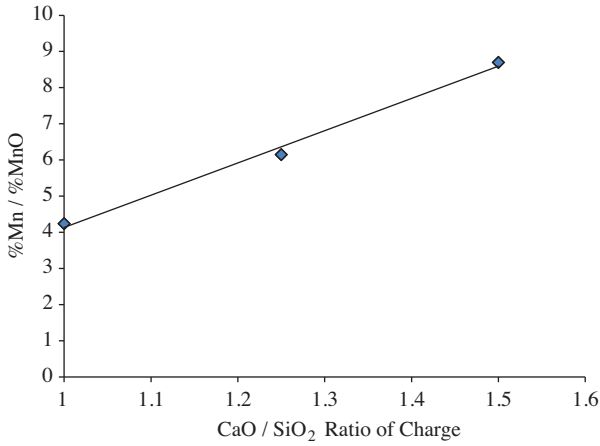


**Figure 3.** Variation of slag MnO and SiO<sub>2</sub> concentrations with smelting time.

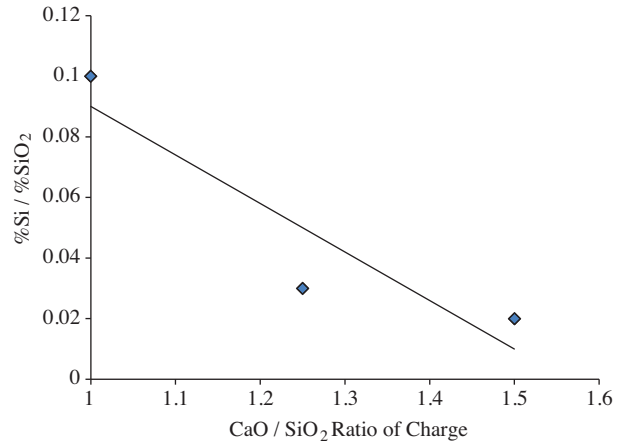


**Figure 4.** Variations of Mn and Si recoveries with smelting time.

In the present study, the charge basicity was defined as the ratio of the total weight of CaO to the total weight of SiO<sub>2</sub> in the charge. Charge basicity and accordingly, slag basicity were increased by adding lime to the charge. The effect of charge basicity on the reduction reactions at a temperature of 1600 °C are shown in Figures 5 and 6, where the Mn distribution ratio; Mn%/MnO% and Si distribution ratio; Si%/SiO<sub>2</sub>%, are plotted against the total weight ratio of CaO to the total weight of SiO<sub>2</sub> in the charge. Change in basicity of the slag affects the activity coefficients of the oxides (Türkdoğan et al., 1956; Mehta et al., 1960). MnO is a basic oxide and SiO<sub>2</sub> is an acidic oxide. An increase in the basicity of the slag increases the activity coefficient of MnO and the extent of the reduction, whereas an increase in the basicity of the slag decreases the activity coefficient of SiO<sub>2</sub> and decreases the extent of the reduction. In other words, more MnO and less SiO<sub>2</sub> are reduced with increasing basicity of the slag. Therefore, the manganese distribution ratio increases and the silicon distribution ratio decreases with the increase in basicity as illustrated in Figures 5 and 6, respectively. Manganese recovery; defined as the ratio of the weight of manganese in the metal to the weight of manganese in the charge, is seen to increase with increasing basicity, whereas silicon recovery; defined as the ratio of the weight of silicon in the metal to the weight of silicon in the charge, is seen to decrease with increasing basicity as shown in Figure 7.

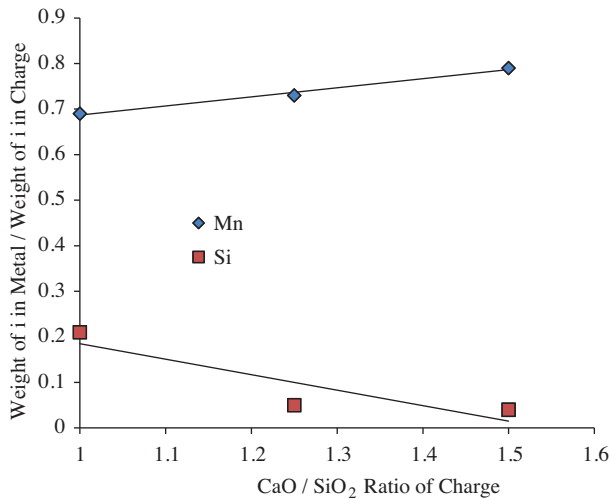


**Figure 5.** Variation of the manganese metal-slag distribution ratio with basicity of charge.

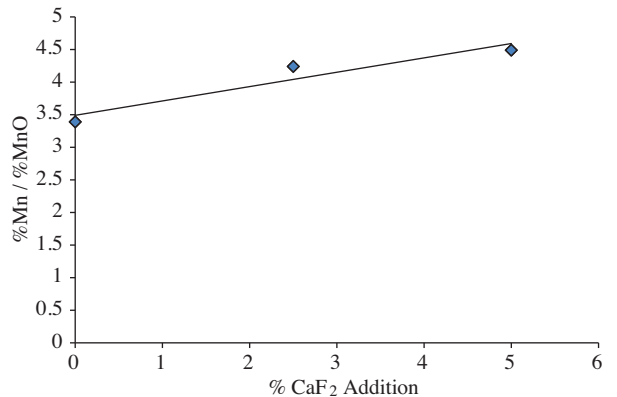


**Figure 6.** Variation of the silicon metal-slag distribution ratio with basicity of charge.

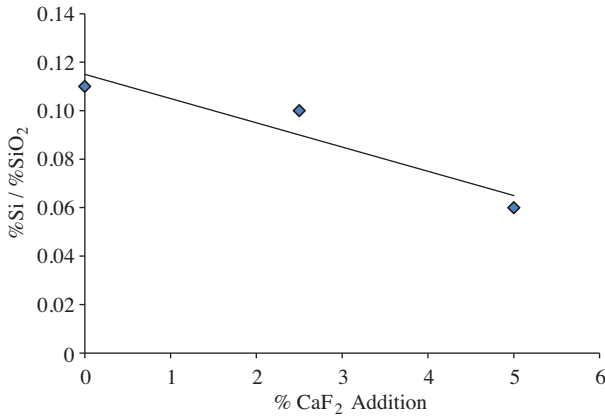
Fluorspar is a substance which increases the fluidity of slag and increases the rate of the solution of the lime in the slag. There have been experimental studies on the effect of the addition of  $\text{CaF}_2$  on slag viscosity proving this fact (Kor et al., 1979; Emeksiz, 1991). Because of increase in fluidity with the addition of  $\text{CaF}_2$ , metal-slag separation in the system is improved. In the present study, the best result for slag-metal separation was observed with an addition of  $\text{CaF}_2$  at 2.5% of the total weight of the  $\text{CaF}_2$  free charge. Therefore, all of the experiments in which the  $\text{CaF}_2$  content was not a variable were conducted with 2.5%  $\text{CaF}_2$ . Experiments were conducted with 0%, 2.5%, and 5%  $\text{CaF}_2$  additions to study its effect on the smelting of Erzincan manganese ore at 1600 °C. The manganese distribution ratio  $\text{Mn}\%/\text{MnO}\%$ , silicon distribution ratio  $\text{Si}\%/\text{SiO}_2\%$ , and manganese and silicon recoveries with the quantities of  $\text{CaF}_2$  added are shown in Figures 8, 9, and 10, respectively. The Mn distribution ratio is seen in Figure 8 to increase with the addition of  $\text{CaF}_2$ , whereas the Si distribution ratio is seen to decrease in Figure 9. The variations of Mn and Si recoveries are similar to Mn and Si distribution ratios as seen in Figure 10.



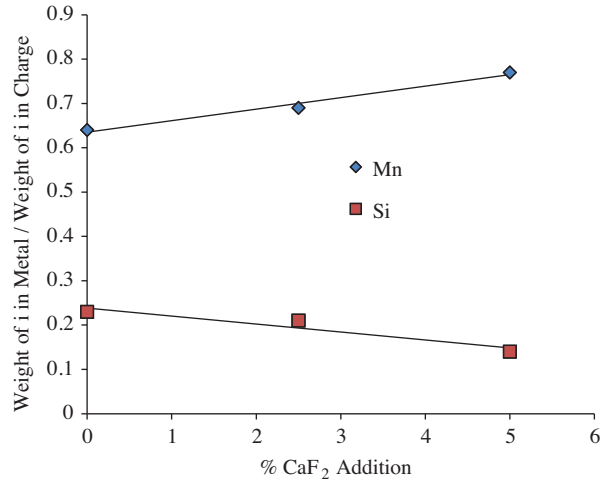
**Figure 7.** Variation of Mn and Si recoveries with basicity of charge.



**Figure 8.** Effect of the addition of fluorspar on the manganese metal-slag distribution ratio.

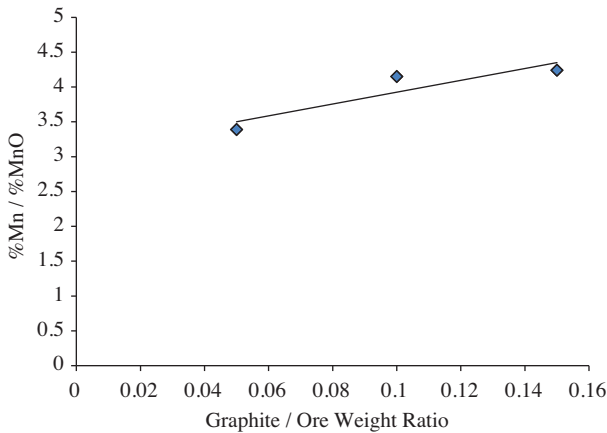


**Figure 9.** Effect of the addition of fluorspar on the silicon metal-slag distribution ratio.

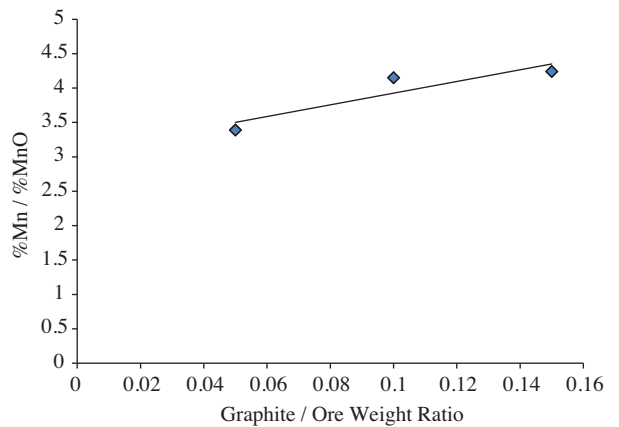


**Figure 10.** Effect of the addition of fluorspar on manganese and silicon recoveries.

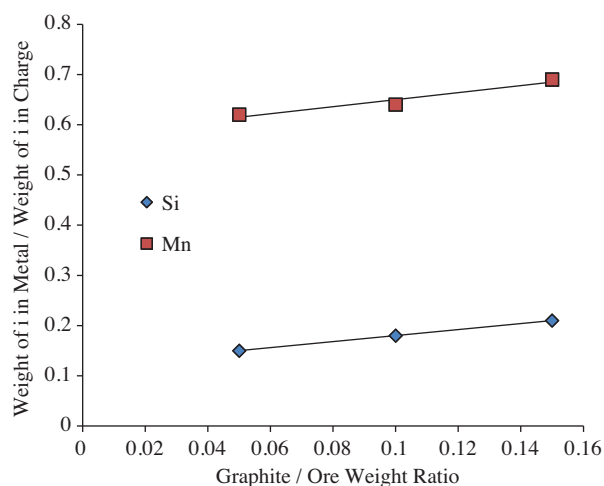
In the experiments aiming to examine the effect of the quantity of graphite in the charge during smelting at 1600 °C, the ratio of graphite to ore was taken as 0.05, 0.10, and 0.15. In all the other runs, the ratio of graphite to ore was constant at 0.15. It can be seen in Figures 11 and 12 that the manganese distribution ratio and the silicon distribution ratio increase with an increase in the weight ratio of graphite/ore. Since the reduction reactions of MnO and SiO<sub>2</sub> take place by carbon, increasing the quantity of graphite in the system is seen to increase the extent of the reduction of these oxides from the slag. The manganese and silicon recoveries also increase with the addition of more graphite into the system as is seen in Figure 13.



**Figure 11.** Effect of the weight ratio of graphite/ore on the manganese metal-slag distribution ratio.



**Figure 12.** Effect of the weight ratio of graphite/ore on the silicon metal-slag distribution ratio.



**Figure 13.** Effect of the weight ratio of graphite/ore on manganese and silicon recoveries.

#### 4. Conclusion

Smelting of Erzincan manganese ore with carbon at a temperature of 1600 °C was studied. It was found that almost all of the iron oxides in the charge were reduced into metal in less than 1 h, whereas the carbothermal reduction of MnO and SiO<sub>2</sub> was still not complete at the end of 5 h. Results indicated that metal Mn and Si content, and Mn and Si recoveries from the charge increase over time. Slag SiO<sub>2</sub> content remains almost constant over time, whereas slag MnO content decreases as time passes. Erzincan manganese ore has a CaO%/SiO<sub>2</sub>% ratio less than 1. Charge basicity was changed by the addition of lime into the charge. The experiments were conducted with charge basicities of 1, 1.25, and 1.5. Results showed that the Mn metal-slag distribution ratio increases and the Si metal-slag distribution ratio decreases with increasing charge basicity. Mn recovery increases with increasing charge basicity, whereas Si recovery from charge decreases with an increase in charge basicity. Fluorspar was used to obtain a good slag-metal separation. The Mn metal-slag distribution ratio and Mn recovery from the charge increased, while the Si metal-slag distribution ratio and Si recovery from the charge decreased with an increase of CaF<sub>2</sub>. The effect of the weight ratio of graphite to ore was investigated by conducting experiments with graphite to ore weight ratios of 0.05, 0.10, and 0.15. It was concluded that an increase in the weight ratio of graphite to ore increased both the Mn and the Si metal-slag distribution ratios and increased Mn and Si recoveries. Experimental results show that it is possible to produce high carbon ferromanganese with Mn content above 75% (close to the chemical composition specified by ASTM standards) by smelting Erzincan manganese ore. Mn recovery during the smelting experiments was about 60%-80%.

#### Acknowledgements

We would like to thank Asil Steel Works for performing all chemical analyses for this study at their laboratories. We are grateful to board member Necdet Utkanlar, plant manager Hüseyin Keçeci, and Hikmet Yazgan, who conducted the chemical analyses carefully.

### References

- Emeksiz, F., “Smelting of High Carbon Ferromanganese from Denizli-Tavas Manganese Ore”, MSc Thesis, Middle East Technical University, Ankara, 1991.
- İmer, S.T., “Smelting of High Carbon Ferromanganese from Denizli-Tavas Manganese Ore.”, MSc Thesis, Middle East Technical University, Ankara, 1997.
- Kor, G.J.W., “Equilibria Between Liquid Mn-Si Alloys and MnO-SiO<sub>2</sub>-CaO-MgO Slags”, Metallurgical Transaction B, Vol. 10B, 367-374, 1979.
- “Manganez Özel İhtisas Komisyon Raporu”, VIII. Beş Yıllık Kalkınma Planı, Devlet Planlama Teşkilatı, Ankara, 2001.
- Mehta, S.R. and Richardson, F.D., “Activities of Manganese Oxide and Mixing Relationships in Silicate and Aluminate Melts.” Journal of the Iron and Steel Institute, Vol. 203, 524-528, 1965.
- “Steel Statistical Yearbook 2010”, World Steel Association, Belgium, 2010
- Türkdoğan, E.T., “Silicon and Manganese Reactions in Ferromanganese Blast Furnace Processes”, Journal of the Iron and Steel Institute, 74-79, 1956.
- Türkdoğan, E.T., Kor, G.J. and Fruchan, R.J., “Studies of Blast Furnace Reactions”, Ironmaking and Steelmaking, No. 66, 268-280, 1980.