Production of Ferromanganese and Silicomanganese from Tavas Ore, Turkey
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Abstract
In this work, ferromanganese and silicomanganese were produced by carbothermic methods from the Denizli-Tavas manganese ores containing 43.4 % Mn. Reduction smelting experiments were carried out in laboratory scale electric arc furnace of 270 kVA. Ferromanganese containing 85.1 % Mn, 1.2 % Si was produced by 82.1 % manganese recovery with 20 % coke and 7.9 % CaO addition. Silicomanganese alloys containing 69.7–78 % Mn, 12.8–18.2 % Si were obtained by using charge having ore and silica or ore, ferromanganese slag and silica with 30 % coke addition by 70 % manganese recovery.

Introduction
Manganese is an element which is added to molten steel in the form of ferromanganese and silicomanganese for alloying and/or deoxidizing and desulfurizing. 95 % of world manganese production is consumed as ferromanganese and silicomanganese in iron and steel production [1,2,3]. Although Turkey's total steel production is beyond 12 million tons, these ferroalloys have not been produced from domestic sources. Turkey has imported 33950 tons ferromanganese and 93910 tons silicomanganese in 1996 [4].

Total amount of manganese metal in Turkish manganese ores is estimated as over 1.5 million tons [5]. Leading manganese ore with the 43.4 % Mn concentration is located in Denizli, Tavas area.

In this study, parameters for ferromanganese and silicomanganese production by carbothermic reduction smelting from Denizli Tavas manganese ore has been investigated in a laboratory scale electric arc furnace. Effects of reducing material and flux that is added to the charge in varying amounts on manganese and impurity concentrations in ferroalloy and manganese recovery were examined.

Experimental Procedure
Raw Materials
Manganese in the ore was in the form of MnO2 and MnCO3. This ore contains 43.42 % Mn, 12.70 % Si, 4.21 % Ca, 3.21 % Fe, 3.04 % C, 60.79 % Al, 0.67 % Mg, 0.021 % S, 0.04 % P.

Reductant coke had a composition of 82.19 % fixed carbon, 4.12 % volatile matter, 13.68 % ash. In experiments for the production of low silicon ferromanganese, CaO with 99.5 % purity was used as the fluxing agent. For the production of silicomanganese, SiO2 with 99.5 % purity was used.

Experimental Apparatus
A Laboratory scale, mono phase, submerged electric arc furnace lined with magnesia, powered with a 270 kVA DC transformer was used in this study [6,7]. Heart of the furnace crucible has a diameter of 10 cm and height of 40 cm. While graphite bottom electrode is fixed in the refractory material of the furnace, top graphite electrode has the ability to move in vertical axis (Figure 1).

Fig.1. The details of the laboratory scale arc furnace.

Experimental Procedure
Depending on the aimed production, 1 kg manganese ore mixed with coke and CaO or SiO2 made up the charge, and directly transferred to the arc furnace after a homogeneous mixing. After every 30 minutes smelting period, upper electrode was lifted up to stop the arc and temperature of the slag was measured by using a submerged Pt-PtRh10 thermocouple. When the furnace cooled down, metal and slag were separated, weighted and analysed.
Results and Discussion

Effect of Coke Addition

Upper graphite electrodes, with diameters of 3.5, 4 and 5 cm were used in experiments, for the production of ferromanganese. But, in experiments carried out with electrodes of 5 cm diameter, refractory erosion had been noticed as a result of high temperature. This also caused the smelting regime to behave in an irregular manner. This is why only 3.5 and 4 cm diameter electrodes were used during rest of the experiments.

For obtaining highest manganese recovery and concentration in ferroalloy amount of the coke content of the charge was changed.

Increasing the fixed carbon amount in the charge increased the recovery and the concentration of manganese in the metal by using 3.5 and 4 cm diameter electrodes (Figure 2). However in these conditions, silicon concentration in the metal had been exceeded the limits given in DIN 17564 (1.5%).

![Figure 2](image)

**Fig.2.** Changes of manganese and silicon concentration in metal, and manganese recovery as a function of added fixed carbon in charge. (△: 4 cm diameter electrodes, ▲: 3.5 cm diameter electrodes.)

When the charge containing 15.4 % fixed carbon was smelted with a 3.5 cm diameter electrode, manganese concentration in ferromanganese and its recovery were 79.3 % and 75.8 % respectively. But silicon concentration in this alloy was determined as 5.5 %.

It was found that, in the experiment carried out with 4 cm diameter electrode and 13.7 % fixed carbon in charge, stability of smelting regime becomes irregular after 25 minutes. The results given in Figure 2 were obtained from experiments that were carried out for 20 minutes. In these experiments manganese and silicon concentration in ferroalloy and manganese recovery were 79.5 %, 2.83 % and 78.7 % respectively.

Increasing the reductant amount in the charge caused iron concentration in the ferroalloy to decreased up to 6.5 %, but had no effect on the carbon concentration (5-6 %). The phosphor content of the alloys varied between 0.08-0.15 %.

![Figure 3](image)

**Figure 3** represents the change in manganese concentration in the slag as a function of the slag temperature which was measured with a submerged Pt-PtRh10 thermocouple, in the experiments carried out with electrodes of 3.5 cm in diameter. It is clear that increase in slag temperature caused to increase the manganese concentration in slag. It was also previously shown that electrode diameter and smelting time has a direct effect on the slag temperature [8].

**Effect of CaO Addition**

Although recovery of manganese and manganese concentration in ferromanganese were quite acceptable, flux addition was necessary in order to decrease the silicon concentration in the ferroalloy to given standard limits. Experiments of researching the flux effects had been done with 4 cm diameter electrodes with the charge having fixed carbon 13.7 %, CaO was chosen as the flux and it has been added to the charge in different amounts to investigate the effect on silicon and manganese concentration in metal, and manganese recovery.

Changes in the silicon concentration in the metal and manganese concentration in the slag as a function of the added CaO to the charge are shown in Figure 4. It was observed that silicon in alloy and manganese in slag decreased down to 0.84 % and 1.89 % respectively by adding 9.5 % CaO to the charge. But when excess amount of CaO added to the charge, silicon in metal and manganese in the slag increased dramatically.

Maximum manganese concentration has been obtained as 85.1 % in ferromanganese by using the charge having 7.7 % CaO and under these conditions the manganese recovery was 82.1 %, as shown in Figure 5.

Manganese in metal reached high concentrations when CaO amount in the charge was below 9.5 %. Manganese concentration in metal decreased down to 77.7 % when CaO concentration increased up to 14.3 %. It is found out that increase in the CaO concentration increases the slag temperature, which in turn, increases the manganese concentration in the slag. This also causes manganese recovery to decrease to 61.5 %.
It is also determined that any amount of CaO addition had no serious effect on iron, carbon, and phosphor concentrations of ferromanganese and their values were 7%, 6%, and 0.08-0.15% respectively.

Table 1. Analyses of prepared charge types which are used in silicomanganese production experiments (weight%).

<table>
<thead>
<tr>
<th>Charge Composition, weight %</th>
<th>Mn (%)</th>
<th>Si (%)</th>
<th>Fe (%)</th>
</tr>
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<tbody>
<tr>
<td>Ore (% 78.1) + SiO₂ Sand (% 21.9)</td>
<td>33.9</td>
<td>31.2</td>
<td>2.5</td>
</tr>
<tr>
<td>Ore (% 43.5) + Slag (% 43.5) + SiO₂ Sand (% 13)</td>
<td>31.9</td>
<td>31.2</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Figure 6 represents the variation of the manganese and silicon concentration in the metal as a function of the fixed carbon amount in the charge. The highest manganese concentration, from the charge mixture of ore and silica sand was 69.7% when fixed carbon in charge was 15.6%. However in silicomanganese produced from charge containing ore, silica sand and slag, the manganese concentration was 78.0% when fixed carbon was 17.0%.

In experiments where manganese ore and silica sand mixture were used as the charging material, increase in reductant material caused to increase silicon concentration in metal, and was found out to be 18.5% when the fixed carbon was 18.0%. Moreover, in experiments where manganese ore, slag and silica sand were used as the charging material, increase in reductant material caused to increase silicon concentration in metal to up to 22.1%

Silicomanganese

Denizli, Tavas manganese ore, silica sand of 98.5% purity and slag of the unfluxed ferromanganese production experiment with 29.3 Mn, 26.3% SiO₂, 8.5% Ca, 7% Mg, 0.6% Fe and 0.2% S concentration were used in silicomanganese production experiments. Same quality coke as in ferromanganese production was used as a reductant material. Aimed composition was 65-75% Mn and 15-25% Si and different charges were prepared by mixing the ore with silica sand or ore, slag and silica sand. At the beginning, the manganese and silicon concentration in the charge was fixed (Table 1). Smelting experiments were carried out for 30 minutes in the same DC arc furnace with a 4 cm diameter top electrode.
Optimum production parameters are described as conditions where maximum concentration and recovery is obtained in experiments of ferromanganese and silicomanganese production. Distribution of manganese, iron and silicon among metal, slag and lost material are given in bar graphs (Figure 8, 9 and 10). Elements reacting with furnace refractory and escaping from the system as volatile gases are accepted and calculated as the lost material.

Fig. 8. Distribution of manganese, iron and silicon between metal (ferromanganese) and slag after reduction smelting of the charge having no CaO addition (Metal contains 79.5 % Mn, 11.65 % Fe, 2.83 % Si and 5.85 % C).

Fig. 9. Distribution of manganese, iron and silicon between metal (ferromanganese) and slag after reduction smelting of the charge containing 7 % CaO (Metal contains 85.1 % Mn, 7.01 % Fe and 1.28 % Si, 6.50 % C).

Conclusion

Ferromanganese containing 85.1 % Mn and 1.3 % Si was obtained with 82.1 % manganese recovery when 13.7 % fixed carbon and 7.7 % CaO was added to the charge, and smelted for 30 minutes.

Silicomanganese containing 69.7 % Mn and 18.2 % Si was produced with 70.7 % manganese recovery when 15.6 % fixed carbon was added to the charge mixture of ore and silica sand, and smelted for 30 minutes.

References


