PRODUCTION OF HIGH CARBON FERROMANGANESE FROM A
MANGANESE ORE LOCATED IN ERZİNCAN

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

İSMAİL SEÇKİN ÇARDAKLI

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
METALLURGICAL AND MATERIALS ENGINEERING

SEPTEMBER 2010

Approval of the thesis:

PRODUCTION OF HIGH CARBON FERROMANGANESE FROM A MANGANESE ORE LOCATED IN ERZİNCAN

submitted by **İSMAİL SEÇKİN ÇARDAKLI** in partial fulfillment of the requirements for the degree of **Master of Science in Metallurgical and Materials Engineering Department, Middle East Technical Univesity** by,

Prof. Dr. Canan Özgen
Dean, Graduate School of **Natural and Applied Sciences** ⎯⎯⎯

Prof. Dr. Tayfur Öztürk
Head of Department, **Metallurgical and Materials Engineering** ⎯⎯⎯

Prof. Dr. Naci Sevinç
Supervisor, **Metallurgical and Materials Engineering Dept., METU** ⎯⎯⎯

Prof. Dr. Tayfur Öztürk
Co-Supervisor**, Metallurgical and Materials Engineering Dept., METU** ⎯⎯⎯

Examining Committee Members:

Prof. Dr. Haluk Atala
Metallurgical and Materials Engineering Dept., METU ⎯⎯⎯⎯⎯⎯

Prof. Dr. Naci Sevinç
Metallurgical and Materials Engineering Dept., METU ⎯⎯⎯⎯⎯⎯

Prof. Dr. Tayfur Öztürk
Metallurgical and Materials Engineering Dept., METU ⎯⎯⎯⎯⎯⎯

Prof. Dr. İshak Karakaya
Metallurgical and Materials Engineering Dept., METU ⎯⎯⎯⎯⎯⎯

Dr. Abdi Aydoğdu
General Directorate of Mineral Research and Exploration ⎯⎯⎯⎯⎯⎯

Date: ⎯⎯⎯⎯⎯⎯

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : İsmail Seçkin ÇARDAKLI

Signature   :

ABSTRACT

PRODUCTION OF HIGH CARBON FERROMANGANESE FROM A MANGANESE ORE LOCATED IN ERZİNCAN

Çardaklı, İsmail Seçkin

M.S., in Department of Metallurgical and Materials Engineering
Supervisor: Prof. Dr. Naci Sevinç
Co-Supervisor: Prof. Dr. Tayfur Öztürk

September 2010, 66 pages

Main purpose of this study was to investigate the production of high carbon ferromanganese by smelting a manganese ore located in Erzincan. Time, charge basicity, fluorspar addition and coke to ore weight ratio were used as experimental variables.

After characterization of the ore, a mixture of 100 grams of uncalcined manganese ore and carefully weighed amounts of coke powder, lime, fluorspar and scrap iron were put into a conical graphite crucible. The graphite crucible with its contents was covered with a graphite lid and placed in an electronically controlled muffle furnace. The furnace was heated to 1600 ^{o}C and held at this temperature for a predetermined time and cooled to room temperature. The crucible was taken out of the furnace and the metal and slag phases formed were removed from the crucible by

breaking the crucible and carefully weighed. Finally, the metal and slag phase were subjected to chemical analysis.

The experimental results show that Erzincan manganese ore can be used in the production of high carbon ferromanganese.

Keywords: High carbon ferromanganese, pyrometallurgy

ÖZ

ERZİNCANDA BULUNAN BİR MANGANEZ CEVHERİNDEN YÜKSEK KARBONLU FERROMANGANEZ ÜRETİMİ

Çardaklı, İsmail Seçkin

Bu çalışmanın temel amacı Erzincan'da bulunan bir manganez cevherinden ergitme yolu ile yüksek karbonlu ferromanganez eldesinin incelenmesidir. Zaman, şarj bazikliği, eklenen fluşpat miktarı ve kok / cevher ağırlık oranı deney parametreleri olarak kullanılmıştır.

Cevherin karakterizasyonundan sonra, 100 gram kalsine edilmemiş cevher ve dikkatlice tartılan kok tozu, kireç taşı, fluşpat ve hurda demir karışımı konik grafit pota içerisine konmuştur. İçeriğiyle birlikte bir grafit kapakla kapatılan grafit pota elektronik kontrollü fırına yerleştirilmiştir. Fırın 1600 ^{o}C'ye kadar ısıtılmış ve önceden belirlenen süre kadar beklenmiş ve oda sıcaklığına soğutulmuştur. Pota fırından çıkarılmış ve oluşan metal ve curuf fazları pota kırılarak potadan alınmış ve dikkatlice tartılmıştır. Son olarak metal ve curuf fazları kimyasal analize tabi tutulmuştur.

Deneysel sonuçlar Erzincan manganez cevherinin yüksek karbonlu ferromanganez üretiminde kullanılabileceğini göstermiştir.

Anahtar Kelimeler: Yüksek karbonlu ferromanganez, pirometalurji

To My Parents;

Adil and Sevinç Çardaklı

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

CHAPTER 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 the ferrous products, especially 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 and silicomanganese.

Manganese has two important properties in steelmaking: its ability to combine with sulphur to form MnS and its deoxidation capacity. Today about 30% of the manganese used 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.

Ferromanganese demand of Turkish iron and steel industry is increasing continuously with respect to the growth in the steel production. Today, Turkey produces 25.3 million tons of crude steel and production increases. Since there is no ferromanganese production plant in Turkey all this demand is supplied by importing. On the other hand, Manganese ore reserves in Turkey are around 4.6 million tons and the largest manganese ore beds are located in the Denizli-Tavas region. The ore used in this study is located in Erzincan around Kemaliye region. The ore is obtained from Alya Mining. The ore is hydrothermal based and the ore grade is about 42%. The main manganese mineral of ore is pyrolusite.

In this study, production possibility of high carbon ferromanganese from ore located in Erzincan by smelting process with carbon was investigated. After characterization, the ore was dried and then used in smelting experiments. In the experiments, uncalcined ore was smelted with lime, scrap iron, fluorspar, carbon in

the form of graphite powder. In the study the effect of time, charge basicity, fluorspar addition and graphite to ore weight ratio on the smelting process were investigated.

CHAPTER 2

LITERATURE REVIEW

2.1. Properties of Manganese

Manganese, 7th group element of the periodic table, is the twelfth most abundant element in the earth's crust. The most common isotopes of manganese are ^{51}Mn, ^{52}Mn, ^{54}Mn, ^{55}Mn, and ^{56}Mn. But only ^{55}Mn is stable in nature. Its valances in nature are +2, +3, +4, and +7. For the formation of manganese in oxide form in mines, a high oxidation potential is required. Some physicochemical properties of manganese are listed in Table 2.1.

Table 2.1 Physicochemical properties of manganese [1]

Atomic number	25
Atomic weight	54.9380
Density at 20 ^{o}C	7.43 g/cm^3
Atomic volume	1.39 cm^3/mol
Melting point	1244 ^{o}C
Boiling point	2060 ^{o}C
Specific heat at 25.2 ^{o}C	0.48 J/g
Latent heat of fusion	244 J/g
Hardness, Mohs' scale	5.0
Compressibility	8.4 x 10^{-7}
Solidification shrinkage, %	1.7
Latent heat of vaporization at b.p.	4020 J/g
Standard electrode potential	1.134 V
Magnetic susceptibility	1.21 x 10^{-7} m^3/kg

Chemically pure manganese is obtained by reduction of manganese oxides with calcium and magnesium or with alkaline metals. In addition there is an electrolytic method of producing pure manganese. When manganese oxides are reduced by hybrids of alkaline-earth metals, it is possible to obtain metal manganese containing 99.999% Mn [2].

2.2. Manganese Minerals

Manganese occurs widely in crystalline rocks deposited as the oxide. Major ores of manganese are generally with manganese contents above 35%. There are more than 300 kinds of minerals known in nature. Most of these are in the form of oxides in hydrated or dehydrated form, carbonates and silicates. In Table 2.2, the chemical compositions and physical properties of most common manganese minerals can be found.

Table 2.2 Manganese minerals [3]

Mineral	Formula	% Mn	Density, g/cm^3
Bementite	$Mn_8Si_6O_{15}(OH)_{10}$	43.2	3.5
Rhodonite	$MnSiO_3$	42	3.5
Rhodochrosite	$MnCO_3$	47.8	3.3 – 3.6
Psilomelane	$BaMn_9O_{16}(OH)_4$	45 – 60	4.4 – 4.7
Pyrolusite	MnO_2	63.2	5
Manganite	$Mn_2O_3H_2O$	62.5	4.3
Braunite	$Mn_2Mn_6SiO_{12}$	66.6	4.8
Hausmannite	Mn_3O_4	72	4.7 – 5.0
Cryptomelane	KMn_8O_{16}	60	4.3
Jacobsite	Fe_2MnO_4	23.8	4.8
Bixbyite	$Mn_2Fe_2O_3$	30 – 40	5

Rhodonite: Rhodonite is a member of the pyroxene group of minerals. It has prismatic cleavage at right angles. It often occurs with rhodocrosite.

Rhodochrosite: It is the most famous carbonate mineral of manganese. Its color is pink and has glassy brightness.

Psilomelane: The amount of manganese present corresponds to 70-80% of manganous oxide with 10-15% of available oxygen. It is dark gray to black amorphous material and relatively hard.

Pyrolusite: It contains 60-63% manganese and sometimes contains various amounts of chemically bound water. Pyrolusite is extensively used for the manufacture of spiegeleisen (20% manganese iron-alloy), of ferro-manganese and of various alloys such as manganese-bronze.

Manganite: It is steel grey in color and has metallic brightness with medium hardness.

Braunite: It contains about 69% Mn and up to 10% SiO_2, corresponds by its composition to anhydrous manganese sesquioxide. This mineral is dark gray to black, with medium hardness.

Hausmannite: It is a hard brownish black opaque mineral.

Jacopsite: Jacopsite is a manganese iron oxide mineral. It is a magnetite and spinel.

Bixbyite; contains 30-40% Mn. It is a metallic dark black rare mineral sought after by collectors.

There are also some other minerals of manganese such as *Kryptomelane* which contains 45-60% Mn and *Wad* which is a hydrous mixture of manganese oxides and iron oxides of variable manganese content.[3]

2.3. Manganese Ores.

Manganese ores are classified according to their contents of manganese. In general ores containing at least 35% manganese are classified as manganese ores. Ores having 10–35% Mn are known as ferruginous manganese ores, and ores containing 5–10% manganese are known as manganiferrous ores. Ores containing less than 5% manganese with the balance mostly iron are classified as iron ores. Manganese ores are also classified as metallurgical, battery and chemical quality ores. Metallurgical ore is used in ferromanganese or special manganese alloy production or as chemicals. Battery ores are natural or artificial. They are manganese

oxide with various purities. Chemical quality manganese ores are classified as group A or group B depending on their manganese, iron and silica contents

Table 2.3 gives a breakdown of the world's total estimated manganese ore reserves that account for 98–99% of the known world reserves of economic significance. [4].

World manganese ore production was an estimated 11.9 million tons (contained manganese) in 2006, up 8% from that in 2005. The bulk (98%) of manganese ore was produced in 10 countries. On a manganese-content basis, the leading producer countries of manganese ore were, in decreasing order, South Africa (19%), Australia (18%), China (13%), Brazil (12%), and Gabon (11%). Table 2.4 shows the production of manganese ores in the world by countries. [5]

Table 2.3 World Manganese Reserves and Reserves Base [4]

Countries	Reserves (million tons)	Reserve base (million tons)	% in total
Australia	68	160	13.6
Brazil	35	57	7
China	40	100	8
Gabon	52	90	10.4
India	56	150	11.2
Mexico	4	8	0.8
South Africa	95	4000	19
Ukraine	140	520	28
Other Countries	10	115	2
Total(rounded)	500	5200	100

Table 2.4 World Production of Manganese Ore [5]

Countries	Mn content (percentage)	2002	2003	2004	2005	2006
Australia	37 - 53	2189	2564	3431	3136	4556
Brazil	37 - 51	2529	2544	3143	3200	3128
China	20 - 30	4500	4600	5500	7500	8000
Gabon	45 - 53	1856	2000	2460	2859	3000
Ghana	32 - 34	1136	1509	1597	1715	1700
India	10 - 54	1553	1650	1776	2389	2003
Kazakhstan	20 - 30	1792	2361	2318	2208	2250
Mexico	36 - 37	245	320	377	369	370
South Africa	30 - 48	3322	3501	4282	4612	5213
Ukraine	30 - 35	2470	2591	2362	2260	2400
Other	-	526	529	696	829	750
Total	-	22100	24200	27900	31100	33400
	Units in thousand metric tons					

A potentially important future source of manganese is the deep-sea nodules found over wide areas of ocean bottom. At depths of 4–6 km, billions of metric tons of nodules are scattered over the ocean floor in concentrations of up to 100,000 t/km^2. Metal content varies widely. Higher grade nodules are found in the North Pacific Ocean. Although the prime interests in deep-sea nodules are the nickel, copper, and cobalt values, the large quantities of manganese could also be of future importance.

2.3.1. Manganese in Turkey

There are no global quantities of manganese ore beds in Turkey. MTA Institute has conducted several studies about locating manganese ore reserves. Studies have shown that most of the reserves are ferrogeneous manganese ores with a capacity of about 4.6 million tons.

The main manganese reserves in Turkey are; Denizli-Tavas, Zonguldak-Ereğli, Gaziantep-Musabeyli, Artvin-Borçka, Erzincan-Kemaliye as shown table 2.5. Among these beds Denizli-Tavas region has the largest manganese ore beds with a proven reserve of 4.000.000 tons and production from this bed is roughly 20.000 tons per year. This is a carbonate type ore body with a relatively low content of manganese (30-31% Mn). There have been many studies conducted by different organizations and institutes to use this ore body in Turkish iron and steel industry [6].

Table 2.5 Turkey Manganese Ore Reserves [6]

Province	Reserve (thousand tons)
Adana	76.5
Artvin	135.8
Denizli	4014.2
Erzincan	24
Gaziantep	194.9
Muğla	28
Rize	9.5
Trabzon	54.85
Zonguldak	24
Total	4561.75

2.4. Ferromanganese

2.4.1. Types of Ferromanganese

According to the specification given in the ASTM standards, ferromanganese can be designated as four main groups in ten grades as shown in Table 2.6.

Another classification is also given for types of ferromanganese as below.

1. Low-Carbon Ferromanganese: It is used for steels with critical carbon content. In this type, carbon content is ranging from 0.07 to 0.75%. Low carbon ferromanganese is suitable for use in the production of 18-8 Cr-Ni stainless steels in which a carbon-content well below 0.10% is required.

2. Medium-Carbon Ferromanganese: This alloy contains 80-85 % Mn, 1.25-1.50% C and 1.50% Si (max.). It is commonly used in making low carbon manganese steels. It is also used in the production of Hadfield manganese steel, when large amounts of return scrap are being melted.

3. High-Carbon Ferromanganese: This alloy contains 80-75% Mn, 7.5% C and 1.2% Si. It is commonly used iron and steel industry as deoxidizer, sulphur fixer and alloying agent.

4. Low-Fe Ferromanganese: It is used for several purposes in the Ni, Al, and Cu industries where high Mn and low Fe are required and where low-carbon content of pure manganese metal is not necessary. It contains 85-90 % Mn, 2 % Fe, 3 % Si, and 7 % C.

5. MS (Machining Screw) Ferromanganese: It contains 80-85 % Mn, 0.35 % Si, and 1.25-1.50% C. This low-silicon alloy is developed to add during production of free machining screw steels.

6. DQ (Drawing Quality) Ferromanganese: It contains 86 % Mn, 0.45 % C, 0.40 % Si, and 0.17 % P. This is refined manganese product which is used as additive to steels for drawing quality steel sheets where both low-silicon and low-carbon contents are desirable. This alloy is also used as addition agent for stainless and constructional alloy steels.

7. Exothermic Ferromanganese: Several grades of Fe-Mn briquettes are sold, containing constituents that cause an exothermic reaction when added to a steel bath, e.g. barium salts. This special material is used for ladle additions of Mn to prevent chilling of the ladle contents. [7]

Table 2.6 ASTM Standards of Ferromanganese [8]

	Standard Ferromanganese			Medium Carbon Ferromanganese				Nitrided Medium Carbon Ferromanganese	Low Carbon Ferromanganese	
Grade	A	B	C	A	B	C	D		A	B
Mn%	78.0 - 82.0	76.0 - 78.0	74.0 - 76.0	80.0 - 85.0	80.0 - 85.0	80.0 - 85.0	80.0 - 85.0	75.0 - 80.0	85.0 - 90.0	80.0 - 85.0
C% max.	7.5	7.5	7.5	1.5	1.5	1.5	1.5	1.5	0.75 0.5 0.1	0.75
Si% max.	1.2	1.2	1.2	1.5	1.0	0.70	0.35	1.5	2.0	5.0 - 7.0
P% max.	0.35	0.35	0.35	0.30	0.30	0.30	0.30	0.30	0.20	0.30
S% max.	0.05	0.05	0.05	0.02	0.02	0.02	0.02	0.02	0.02	0.02
N%	-	-	-	-	-	-	-	4% min	-	-

2.5. Production of Ferromanganese

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 above 1200 °C to enable reduction reactions and alloy formation. Standard grade

ferromanganese can be produced either in a blast furnace or in an electric furnace. High carbon ferromanganese can be made by three different practices: blast furnace, discard slag electric furnace, and high manganese slag electric furnace. Medium carbon ferromanganese can be produced by a de-carbonation process or through a redox reaction between silicon in the silicomanganese alloy and manganese ores. Low carbon ferro-manganese is produced by the reaction of manganese ore and low carbon silico-manganese. Table 2.3 gives the world production of ferromanganese by country. There is no production of ferromanganese in Turkey. All need is imported. [9].

Table 2.7 Ferromanganese World Production by Country [10]

Country	2005		2006		2007	
	Blast Furnace	Electric Furnace	Blast Furnace	Electric Furnace	Blast Furnace	Electric Furnace
Australia	-	120000	-	125000	-	125000
Brazil	-	480000	-	573000	-	575000
China	500000	1150000	600000	1400000	620000	1500000
France	-	109000	-	140000	-	140000
India	-	170000	-	180000	-	180000
Italy	-	32000	-	13000	-	15000
Japan	-	448616	-	406489	-	431000
Korea	-	124434	-	169202	-	209321
Mexico	-	89641	-	62000	-	62000
Norway	-	250000	-	245000	-	245000
Russia	108000	145000	125000	170000	120000	180000
South Africa	-	570574	-	656235	-	750000
Ukraine	30000	359000	30000	373000	30000	368000
Total	638000	4048265	755000	4512926	770000	4780321
	Units in metric tons					

2.5.1. Production of High Carbon Ferromanganese

2.5.1.1. Blast Furnace Production

High carbon ferromanganese is produced in blast furnaces in a process similar to the production of pig iron in blast furnaces. But there are some important differences between two processes. The iron oxides are reduced by CO in the shaft region of the furnace according to the reactions given below:

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \qquad (1)$$

$$Fe_3O_4 + CO = 3FeO + CO_2 \qquad (2)$$

$$FeO + CO = Fe + CO_2 \qquad (3)$$
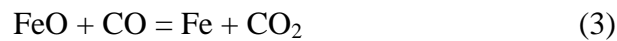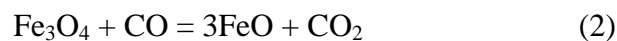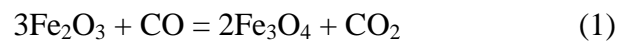
Manganous oxides are reduced by solid carbon in the bosh and heart regions of blast furnace because of higher temperatures according to reactions given below:

$$Mn_3O_4 + 4C = 3Mn + 4C \qquad (4)$$

$$MnO + C = Mn + CO \qquad (5)$$
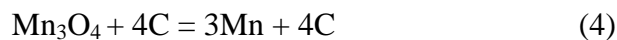
Thus, ferromanganese production in blast furnace needs larger amounts of coke than pig iron production in a blast furnace. Preheating the blast and oxygen enrichment are used to reduce coke requirement. Dolomite or limestone added to the charge raises the activity of MnO for reduction. Small slag volume, basic slag and high blast temperature are required for high manganese recovery. By careful control and a more uniform charge mixture in the shaft, manganese recoveries of over 90% and coke rates of 1530 kg/t are reported [11].

2.5.1.2. Electric Furnace Production.

In the case of the blast furnace, the thermal energy required for the smelting process is supplied by the combustion of additional coke, which in most countries is a more expensive form of energy than electricity. Capital requirements for a new facility generally favor the electric furnace process. Important furnace design

parameters for high carbon ferromanganese production are electrode diameter and spacing, hearth diameter, crucible depth, voltage range, and KVA capacity of the transformer. Because the resistivity of the burden in the electric furnace production of ferromanganese is low, low voltages between the electrodes are necessary to maintain satisfactory penetration of the electrodes in the charge. To obtain the proper power loading for the furnace, higher currents are required. Therefore, to operate within the current carrying capacities of carbon electrodes, the diameter of the electrodes for ferromanganese furnaces is larger than for other ferroalloy furnaces.

Most electric furnaces have sealed covers. The sealed cover is generally preferred because it allows better fume control at lower capital cost and lower energy requirement. The crucibles are steel shells lined with refractory oxide brick and an inner lining of carbon blocks. The hearth is similar, but has a thicker carbon lining. Electric energy is supplied to the smelting reaction through three carbon electrodes, of the Søderberg, i.e., self-baking, type. An important consideration for a successful smelting operation is the slag composition. The composition of the slag has pronounced effects on furnace resistivity, smelting temperature, recovery of manganese, and the amount of silicon in the ferromanganese. Blending of ores or the addition of fluxing reagents is often necessary to produce the desired slag composition

Two processes are employed in production of ferromanganese in electric furnace; high manganese slag process and low manganese slag process [12].

2.5.1.2.1. High Manganese Slag Practice.

The high manganese slag practice is used by most plants where high grade manganese ores are smelted and silicomanganese is also produced. Manganese content of this slag ranges from 30–42%. Typical slag analyses for the other compounds are 2 to 5% MgO, 10 to 30% Al_2O_3, 15% CaO and 27% SiO_2. These slags are usually used in silicomanganese production, increasing the overall manganese recovery. Small amounts of fluxes may be used, such as dolomite or limestone, depending on the manganese concentration desired in the slag [13].

2.5.1.2.2. Discard Slag Practice.

The discard slag practice is followed when the ore is of such low quality that a high degree of manganese extraction is required to achieve the alloy grade, or the ore contains base oxides, e.g., CaO and MgO, which if smelted alone, leads naturally to low manganese slags. Manganese content of the slag from this practice ranges from 10 to 20% and manganese recovery in alloy ranges between 85 and 90%. The components of the slag are 2 to 8 % MgO, 4 to 10% Al_2O_3, 35% CaO and 31% SiO_2. If the ores contain little CaO or MgO, the charge is made up of manganese ores, coke, and a basic flux such as limestone or dolomite. Better results are obtained when the required basic oxides (CaO or MgO) are contained in the manganese ores. Power consumption is higher than that for the high manganese slag practice because of the additional energy required to calcine dolomite or limestone in the charge and the greater amount of manganese extracted from the slag which results in higher CO content in the off-gas than in that of the high manganese practice [19].

2.5.2. Production of Medium-Carbon Ferromanganese

Medium-carbon ferromanganese contains $1 - 1.5\%$ carbon and has a manganese content of $75 - 85\%$. Medium-carbon ferromanganese can be produced either by refining high-carbon ferromanganese with oxygen or by the silicothermic route, whereby the silicon in silicomanganese is used to reduce additional MnO added as ore or slag.

2.5.2.1. Silicothermic Production of Medium-Carbon Ferromanganese

In the silicothermic production of medium carbon ferromanganese, a high-grade slag or a melt containing manganese ore and lime is contacted with silicomanganese containing $16 - 30\%$ silicon. The silicon in the alloy acts as the reducing agent in the process, which reduces the manganese oxide in the melt according to reaction given below:

$$Si + 2MnO = SiO_2 + 2Mn \qquad (6)$$

The purpose of the lime is to reduce the activity of the SiO_2 in the melt, thus forcing the above reaction as far to the right as possible. The ratio of CaO to SiO_2 in the slag should be greater than 1.4 for a sufficient reduction in the activity of SiO_2. The carbon entering the process in the silicomanganese remains entirely in the metal phase and is therefore found in the product. Thus, to produce a medium-carbon ferromanganese containing 1%C, a silicomanganese containing 20% Si is necessary.

The heat produced by the silicothermic reduction is not sufficient to sustain the process; hence it is usually carried out in an electric arc furnace. These furnaces are lined with magnesite bricks, which are fairly resistant to the highly basic slag. These furnaces can be tilted so that the slag can be separated from the metal.

Although the silicothermic reduction process is more energy intensive than the decarburization of high-carbon ferromanganese, it has the advantage that the final carbon content is limited only by the carbon content of the initial silicomanganese. The silicothermic process can therefore be used to produce low-carbon ferromanganese and industrial manganese metal [15].

2.5.2.2. Production of Medium-Carbon Ferromanganese by Oxygen Refining of High-Carbon Ferromanganese

In the MOR (manganese oxygen refining) process patented by Union Carbide, high-carbon ferromanganese is decarburized in a similar manner to the steelmaking process in the basic oxygen furnace. However, there are several distinctive differences in the case of ferromanganese:

1) A final temperature of 1750 ^{o}C compared to 1550 ^{o}C
2) Refractory attack is more severe
3) Difficult casting of the final alloy
4) The higher vapor pressure of manganese
5) The higher volume and temperature of the off-gas

In the MOR process, oxygen is blown into the molten high-carbon ferromanganese and the temperature is increased from its tapping value of 1300 to 1750 ^{o}C. The heat required is supplied by the oxidation of manganese to manganese oxide and carbon to carbon monoxide. In the early part of the blowing process, most of the oxygen is consumed by oxidation of manganese, and the temperature of the

melt increases from 1300 to 1550 ^{o}C. Here after, carbon is rapidly oxidized and the temperature rises to 1650 ^{o}C. Above this temperature, the rate of carbon removal decreases and manganese is once again oxidized. The process is stopped at 1750 ^{o}C, which corresponds to a carbon content of 1.3 %. Further reductions in carbon content result in unacceptably high losses of manganese. In the MOR process, the recovery of manganese is about 80% and the distribution of manganese can be broken down as follows:

Alloy MC FeMn 80%

Fume formed by vaporization 13%

Slag formed by oxidation of Mn 5%

Other losses, splashing 2%

The successful operation of this process depends on the design of the blowing vessel and oxygen lance as well as giving careful attention to operational procedures. The MOR process has many advantages over the silicothermic process: lower energy consumption, lower capital investment, lower production cost, and greater flexibility. The main disadvantage of the process is that its use is limited to production of medium carbon ferromanganese because the carbon content cannot be reduced to below 1.3 %. [16].

2.5.3. Production of Low-Carbon Ferromanganese

Low-carbon ferromanganese contains 76 – 92% Mn and 0.5 – 0.75% C. The production of low-carbon silicomanganese is not possible by the decarburization of high carbon ferromanganese without extremely high losses of manganese. It must accordingly be made of a silicothermic reduction process.

The process is similar to that used in the silicothermic production of medium-carbon ferromanganese. High-purity ores are used and in particular ores containing iron and phosphorus should be avoided. An artificial manganese ore produced as a high-grade slag is particularly suitable because of its low impurity level and because all the manganese is present as MnO. The reduction of the higher oxides of manganese is therefore unnecessary. The operating figures for 1 t of ferromanganese containing 85 – 92% Mn, 0.1% C, and 1% Si with a manganese recovery of 75% are:

Calcined manganese ore 1250 – 1350 kg
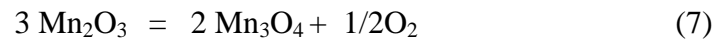
Silicomanganese (32 – 33% Si) 800 – 850 kg

Quicklime 1000 – 1100 kg

Electrodes 10 – 12 kg

Electricity 1800 – 2500 kWh [16].

2.6. Thermodynamics of Reduction of Manganese Oxides

Mn_2O_3, Mn_3O_4, MnO_2 and MnO are known oxide forms of manganese in nature. The higher manganese oxides dissociate at high temperatures according to reactions given below.

$$2\ MnO_2 \ = \ Mn_2O_3 \ + \ 1/2O_2 \qquad\qquad (6)$$

$$3\ Mn_2O_3 \ = \ 2\ Mn_3O_4 + \ 1/2O_2 \qquad\qquad (7)$$

$$Mn_3O_4 \ = \ 3\ MnO + \ 1/2O_2 \qquad\qquad (8)$$

Since the oxide phases transform from one into another due to the temperature and partial pressure of oxygen. Hahn and Muan [17] have studied the Mn_2O_3 - Mn_3O_4 - MnO system. According to their research reaction (7) occurs between 845 °C to 1029 °C and reaction (8) occurs between 1248 °C and 1562 °C. Dressel and Kenworthy [18] found different dissociation temperatures for the oxides since it depends on the oxygen partial pressure of the system as shown in figure 2.1 and chemical composition of the minerals.

16
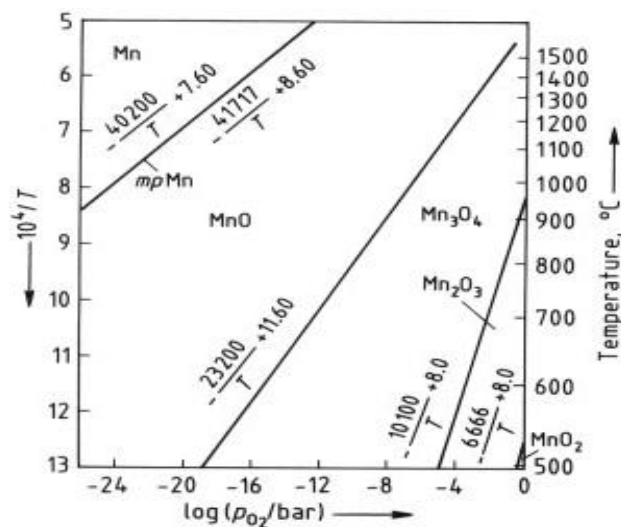
Figure 2.1 Variation of oxygen partial pressure in the Mn–O system with temperature [16]

According to all these researches [18-20] the gaseous reduction of higher manganese oxides starts with the dissociation of MnO_2 into manganic oxide at about 425 °C After that, the reduction of the oxides Mn_2O_3 and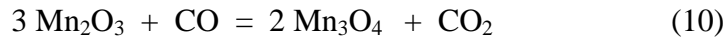 Mn_3O_4 occurs in the Mn – C – O system by the aid of reducing agents like carbon and carbon monoxide with the reactions given below:

$$3\ Mn_2O_3\ +\ C\ =\ 2\ Mn_3O_4\ +\ CO \qquad\qquad (9)$$

ΔG^o, kJ/mol = -0.25 – 0.17T $\qquad$ (25-1100 °C)

$$3\ Mn_2O_3\ +\ CO\ =\ 2\ Mn_3O_4\ +\ CO_2 \qquad\qquad (10)$$
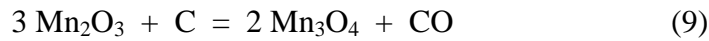
ΔG^o, kJ/mol = -170.71 – 0.004T $\qquad$ (25-1100 °C)

$$Mn_3O_4\ +\ C\ =\ 3MnO\ +\ CO \qquad\qquad (11)$$

ΔG^o, kJ/mol = 110.96 – 0.21T $\qquad$ (25-1244 °C)

ΔG^o, kJ/mol = 84.35 – 0.20T $\qquad$ (1244-1700 °C)

$$Mn_3O_4\ +\ CO\ =\ 3MnO\ +\ CO_2 \qquad\qquad (12)$$
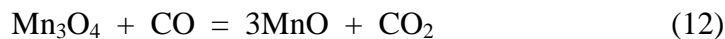
ΔG^o, kJ/mol = 110.96 – 0.21T $\qquad$ (25-1244 °C)

ΔG^o, kJ/mol = 84.35 – 0.20T $\qquad$ (1244-1700 °C)

After the reduction of high manganese oxides to MnO, very high pressures of CO is required to continue the reduction reactions with CO. The reduction of MnO can be presented with the below given reactions;
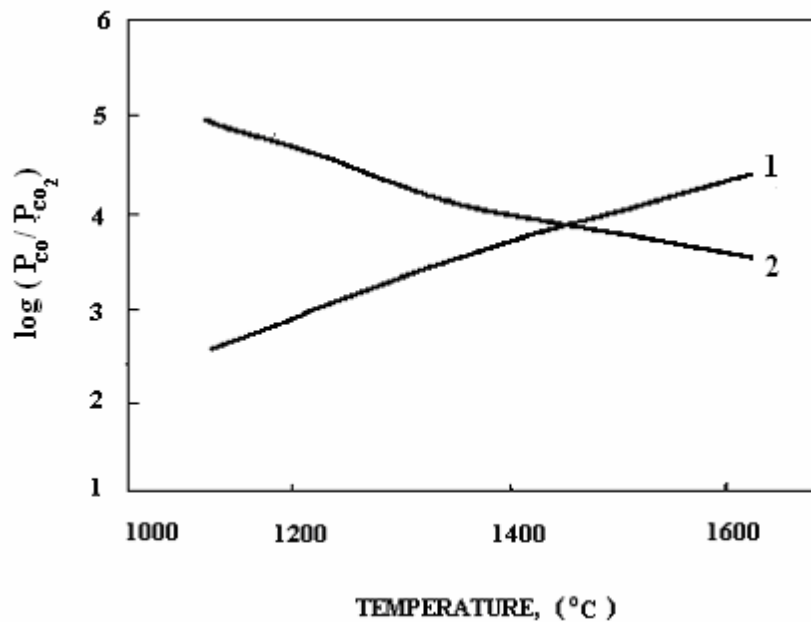
$$MnO + CO = Mn + CO_2 \qquad\qquad (13)$$

$$\Delta G^o, \text{kJ/mol} = 102.29 - 0.01T \qquad (25\text{-}1227\ ^\circ C)$$

$$\Delta G^o, \text{kJ/mol} = 116.73 - 0.01T \qquad (1227\text{-}1777\ ^\circ C)$$

$$CO_2 + C = 2CO \qquad\qquad\qquad (14)$$

In Figure 2.2, variations of the equilibrium constants of reactions (13) and (14) with temperature are given. It can be deduced from this figure that by assuming that the activities of Mn and MnO of the reaction (13) are unity at temperatures above 1420 $^\circ$C and at P_{CO}/P_{CO_2} ratios greater than 6600, MnO can be reduced by CO in the presence of carbon. However, even small amounts of CO_2 may inhibit the reaction. Because of high partial pressure requirement of carbon monoxide, the reduction of MnO by carbon monoxide does not occur.

Figure 2.2 Plots of log (P_{CO}/P_{CO_2}) against temperature for equations (13) and (14) 1) $MnO + CO = Mn + CO_2$, 2) $CO_2 + C = 2CO$ [21]

The reduction of MnO by solid carbon or iron carbide occurs with the following reactions:

$$MnO + 10/7C = 1/7\ Mn_7C_3 + CO \qquad\qquad (15)$$
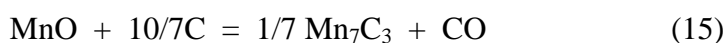
ΔG^o, kJ/mol = 284.22 – 0.18T (717-1087 °C)

ΔG^o, kJ/mol = 282.01 – 0.18T (1087-1137 °C)

ΔG^o, kJ/mol = 280.22 – 0.18T (1137-1244 °C)

ΔG^o, kJ/mol = 280.35 – 0.18T (1244-1700 °C)

$MnO + 10/7Fe_3C = 1/7\,Mn_7C_3 + 30/7Fe + CO$ (16)

ΔG^o, kJ/mol = 246.09 – 0.15T (717-840 °C)

ΔG^o, kJ/mol = 269.42 – 0.17T (840-1087 °C)

ΔG^o, kJ/mol = 267.21 – 0.17T (1087-1137 °C)

ΔG^o, kJ/mol = 265.42 – 0.17T (1137-1244 °C)

ΔG^o, kJ/mol = 271.15 – 0.17T (1244-1537 °C)

The standard free energy changes for reduction of MnO by carbon or Fe_3C to metal or carbide are almost identical in the range from 800 °C to 1300 °C and the most likely product is Mn_7C_3. In figure 2.3 the Pourbaix diagram for Mn – O – C system, drawn by Downing is shown. It shows the stability regions of manganese oxides at specified temperatures and oxygen partial pressures. The gaseous phase is composed of CO, CO_2 and manganese vapour, and the total pressure at any point on this figure is the sum of the partial pressures of the above gas constituents. Lines of constant total pressure are given in the figure for values of 1, 10^{-2}, 10^{-4}, 10^{-6} atm. It can be seen from the diagram that in the presence of carbon the higher oxides of manganese, Mn_2O_3 and Mn_3O_4, are unstable at all temperatures and for all total pressure and they are reduced to MnO. The reduction sequence of MnO by carbon at 1 atm. total pressure is shown by the curve AB. The reduction of MnO starts at about 1267 °C to form Mn_7C_3 and this reacts with excess MnO to form liquid manganese metal at about 1727 °C.
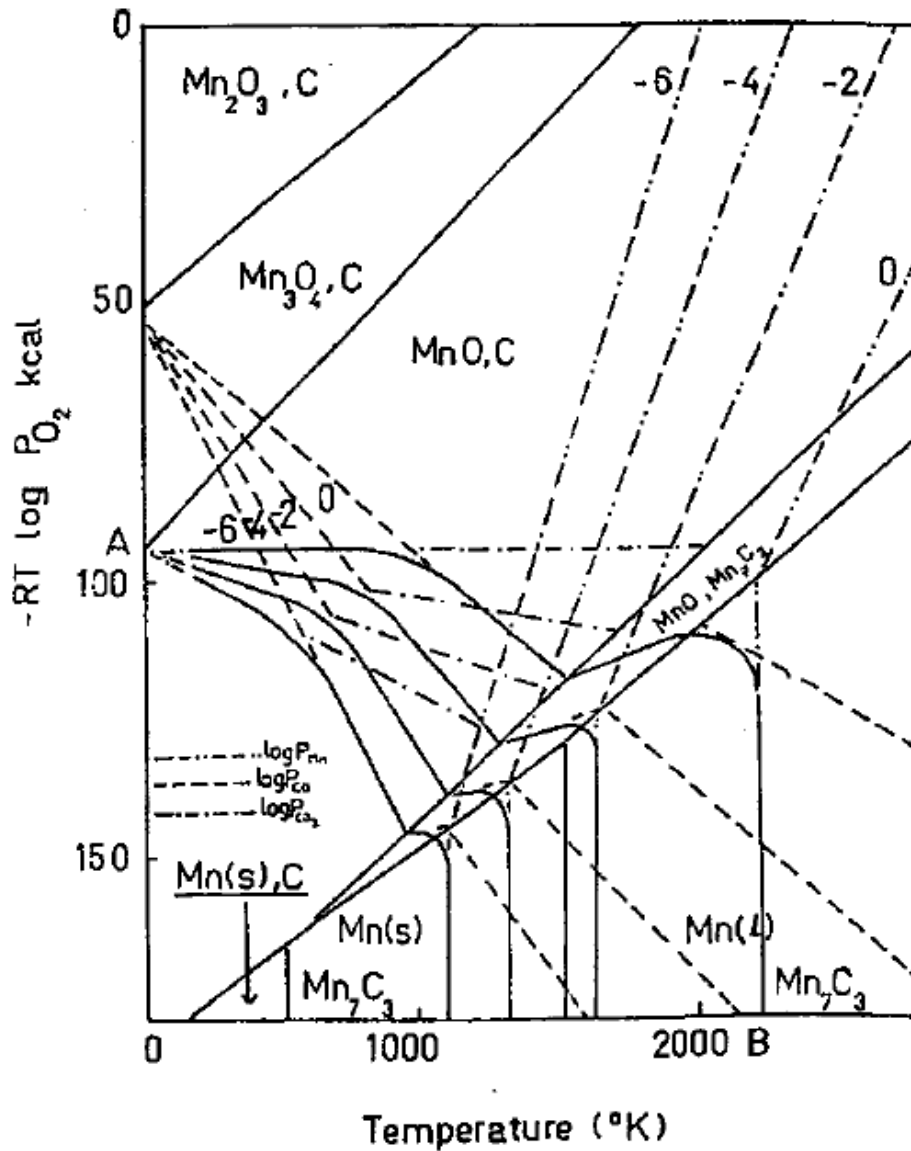
Figure 2.3 Oxygen Potential Temperature Diagram for The Mn-O-C system [22]

2.7. High Carbon Ferromanganese Slags

The main elements in high carbon ferromanganese are iron, manganese, silicon and carbon. Oxides of iron, silicon, and manganese are present in the slag phase during the production and are reduced into metal phase by the aid of carbon through reduction reactions. Among them, SiO_2 is the most stable oxide. That means the reduction of silica into metallic phase is difficult. The stability of MnO is less than that of SiO_2 and more than that of FeO, which is the least stable oxide.

Apart from FeO, SiO_2 and MnO, slag also contains oxides such as MgO, CaO and Al_2O_3. The slag properties such as viscosity, liquidus temperature, and basicity

and the reduction rate and reduction extent of the oxides are affected by each constituent in the slag. Therefore, chemical composition of the slag is very important since it determines the final grade and the quality of ferromanganese produced.

Although MnO and SiO_2 decrease the liquidus temperature of slag, CaO results in higher liquidus temperatures. When MgO is substituted by CaO in small amount in basic slags, liquidus temperature decreases. Also, slag viscosity is affected by each constituent of the slag and mostly by SiO_2. SiO_2 increases the slag viscosity especially in less basic slags. MnO and MgO both have a lowering effect in slag viscosity [23].

CaO – MnO – SiO_2 ternary system was studied by Glasser [24]. Figure 2.4 and 2.5 give CaO-MnO-SiO_2 liquidus surface showing primary phase fields and CaO-MnO-SiO_2 liquidus surface showing isotherms respectively. In general, the liquidus temperatures decrease rapidly from the melting point of relatively refractory phases such as SiO_2, Ca_2SiO_4, CaO, and MnO to a series of ternary liquidus minima. An extensive range of compositions adjacent to these minima also have relatively low liquidus temperatures. These three ternary liquidus minima have been located at the following temperatures and compositions (in weight percent) ; 1265 ^{o}C 5% CaO, 48.4% MnO, 46.6% SiO_2; 1195 ^{o}C, 17.5% CaO, 45%MnO, 37.5%SiO_2 ; 1204 ^{o}C, 15% CaO, 53% MnO, 32%SiO_2
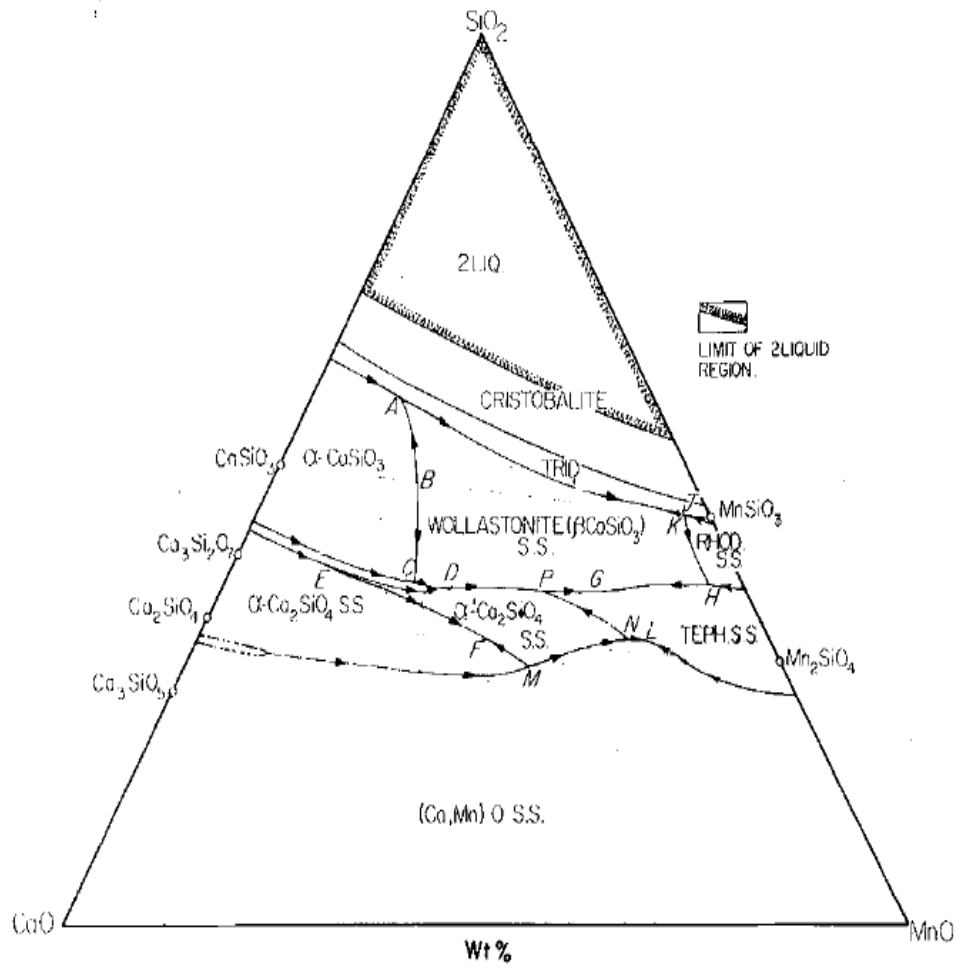
Figure 2.4 CaO-MnO-SiO$_2$ liquidus surface showing primary phase fields [24]
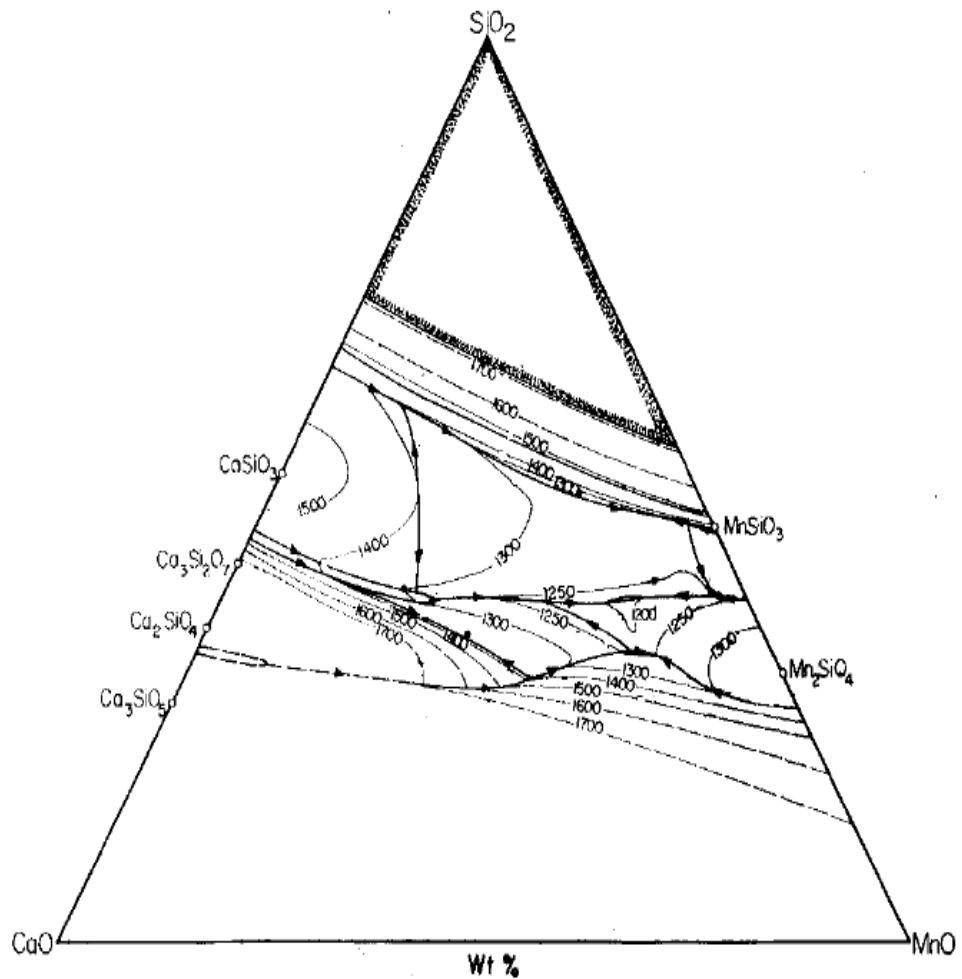
Figure 2.5 CaO-MnO-SiO$_2$ liquidus surface showing isotherms [24]

Zhao et al [25, 26] studied MnO – (CaO + MgO) – (SiO$_2$ + Al$_2$O$_3$) system with a fixed Al$_2$O$_3$/SiO$_2$ weight ratio of 0.17 and MgO/CaO weight ratio of 0.17 for temperatures in the range 1473 – 1673 K and studied MnO – (CaO + MgO) – (SiO$_2$ + Al$_2$O$_3$) system with a fixed Al$_2$O$_3$/SiO$_2$ weight ratio of 0.17 and MgO/CaO weight ratio of 0.25 for temperatures in the range 1393 – 1673 K. Their results showed that the liquidus temperatures and primary phase fields in the quinary system are markedly different from the system MnO – CaO – SiO$_2$ under reducing conditions as shown in figures 2.6 and 2.8. The liquidus temperature is principally dependent on the modified basicity weight ratio (CaO + MgO) / (SiO$_2$ + Al$_2$O$_3$) at low MnO concentrations, and dependent on mole ratio (CaO + MgO) / (SiO$_2$ + Al$_2$O$_3$) at higher MnO concentrations as shown in figures 2.7 and 2.9.
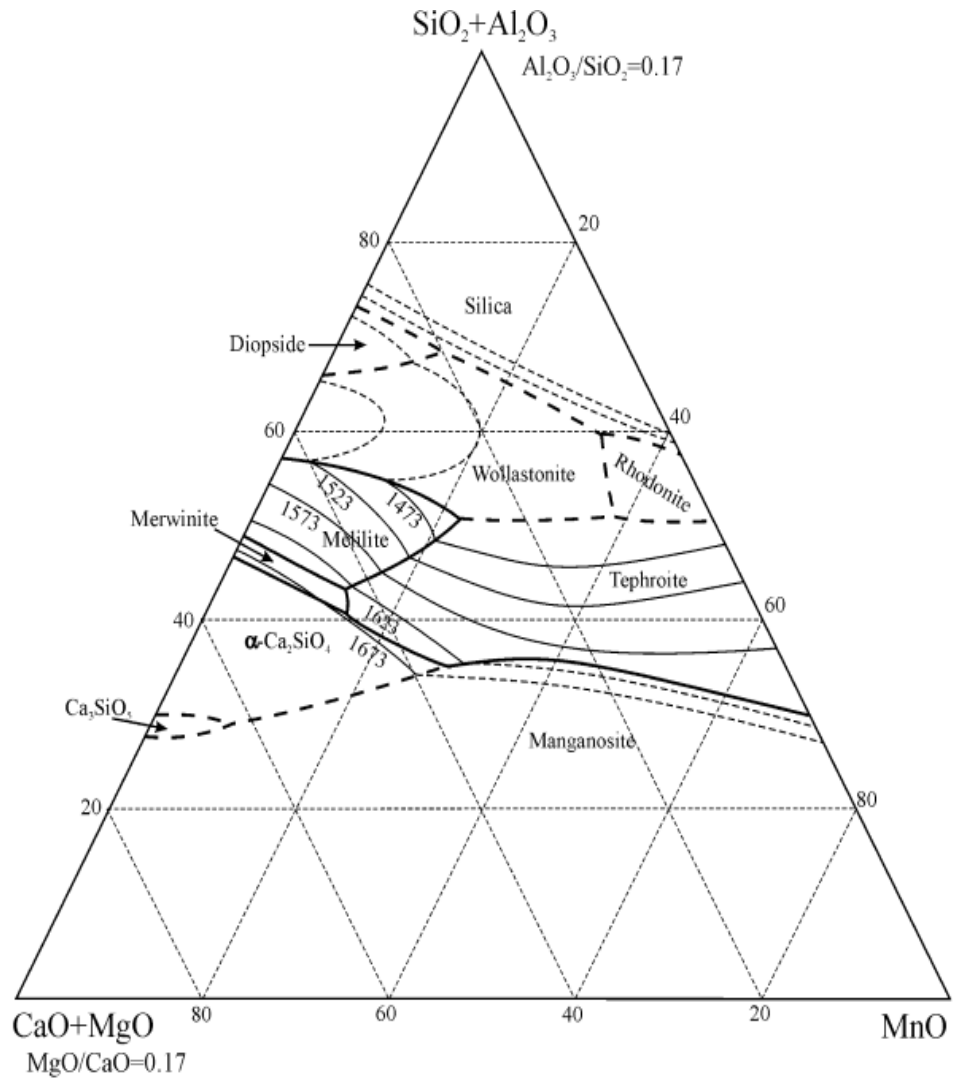
Figure 2.6 Liquidus of the system "MnO – CaO – MgO – SiO$_2$ – Al$_2$O$_3$ with weight ratios of Al$_2$O$_3$/SiO$_2$=0.17 and MgO/CaO=0.17 in equilibrium with Mn–Si alloy, compositions in wt%, temperatures in K [25].
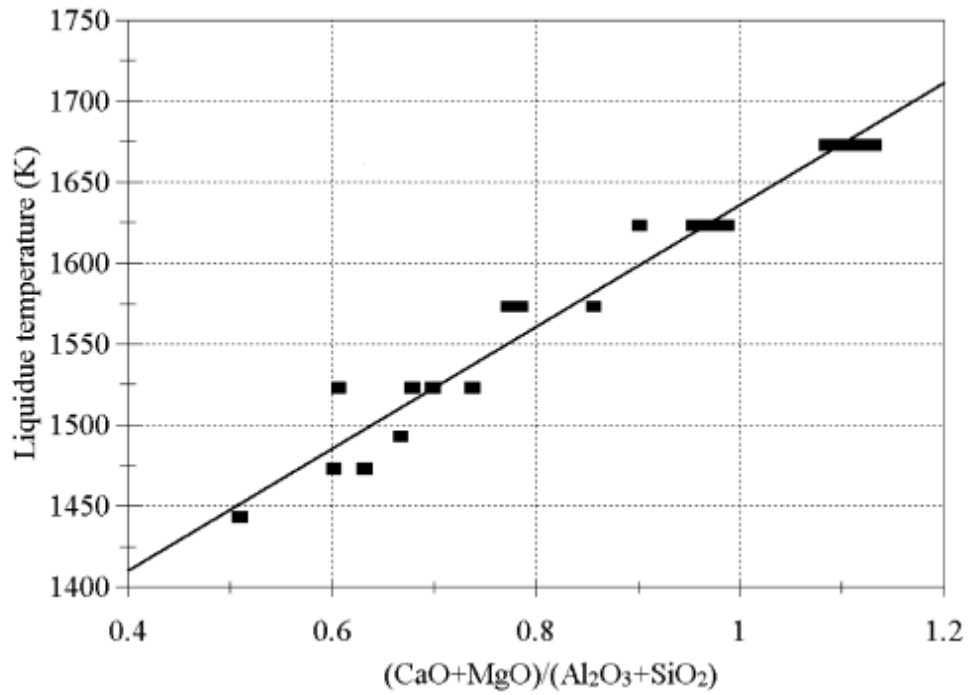
Figure 2.7 Relationship between liquidus temperatures and modified basicity $(CaO+MgO)/(Al_2O_3+SiO_2)$ of the liquid phase at 0–30 wt% "MnO" with Al_2O_3/SiO_2 weight ratios of 0.15–0.19 and MgO/CaO weight ratios of 0.15–0.19 [25].

Figure 2.8 Liquidus of the system "MnO – CaO – MgO – SiO₂ – Al₂O₃ with weight ratios of Al₂O₃/SiO₂=0.17 and MgO/CaO=0.25 in equilibrium with Mn–Si alloy, compositions in wt%, temperatures in K [26].
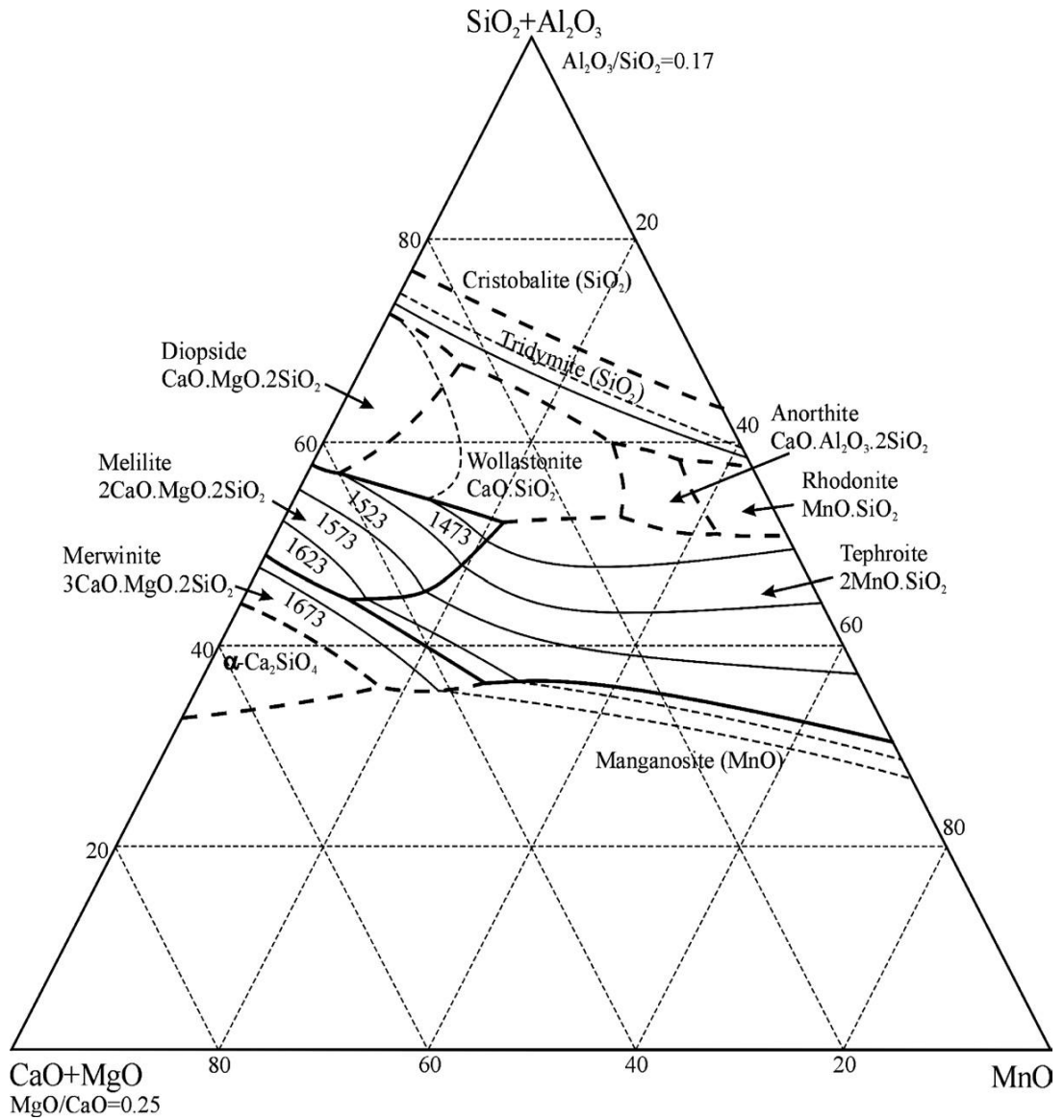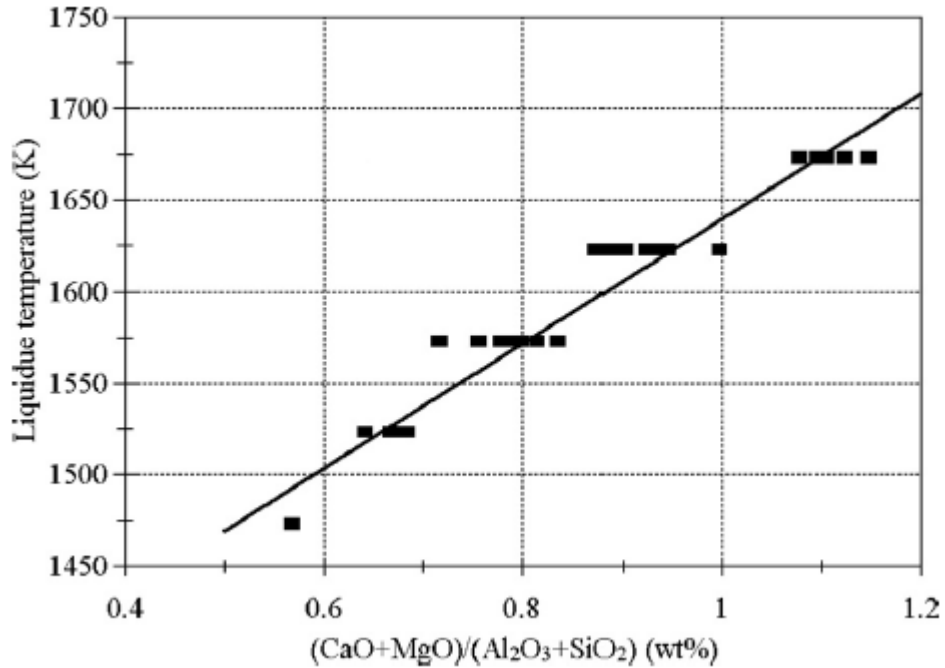
Figure 2.9 Relationship between liquidus temperatures and modified basicity $(CaO+MgO)/(Al_2O_3+SiO_2)$ of the liquid phase at 0–30 wt% "MnO" with Al_2O_3/SiO_2 weight ratios of 0.16–0.20 and MgO/CaO weight ratios of 0.20–0.26 [26].

Another important factor affecting the ferromanganese production is the slag viscosity. Slag viscosity decreases with increasing temperature. Slag viscosity is influenced mostly by SiO_2 which increases viscosity in basic slags. CaF_2, MnO and MgO lower the viscosity of slag with increasing contents. Xuegong Bi [27] et al studied the effects of CaO/SiO_2 ratio, MgO content and CaF_2 content of CaO – MgO – SiO_2 – Al_2O_3 – MnO – CaF_2 slags and found that increased basicity, and increased MgO and CaF_2 contents decreased the viscosity of slag in the temperature range of $1300 - 1500\,^{o}C$.

The effect of CaF_2 addition on slag viscosity in the system CaO – MgO – SiO_2 – Al_2O_3 – CaF_2 at temperatures up to $1500\,^{o}C$ was investigated by Bills [28]. In the experiments, 2% and 9% CaF_2 were added into a slag with CaO/SiO_2 ratio of 40:40 and 5% and 15% CaF_2 were added into the slag with CaO/SiO_2 ratio of 35:50. The results of experiments showed that addition of CaF_2 decreased the slag viscosity considerably and this effect was much greater at temperatures around $1250\,^{o}C$ and $1300\,^{o}C$.

2.8. Previous Studies on Manganese in Department

Emeksiz [29] studied the production of high carbon ferromanganese from Denizli-Tavas manganese ore. In his study a high-grade manganese ore (41%) was smelted with coke, lime, scrap iron and fluorspar in graphite crucibles at 1600 °C. Time, lime addition, fluorspar addition and coke/ore weight ratio were used as experimental parameters. Two hours duration time and coke / ore weight ratio less than 0.2 were found as the optimum parameters for production. The experimental results showed that Denizli-Tavas manganese ore may be used in the production of high carbon ferromanganese.

İmer [30] studied the same ore with a lower Mn grade (31%Mn). He smelted calcined ore with coke, lime, fluorspar and scrap iron in conical shaped graphite crucibles at 1600 °C. He concluded that manganese concentration and weight of the metal increased with time in the experiments conducted for 1, 2 and 4 hours. The manganese content of the metal increased with increasing basicity in the experiments conducted with CaO / SiO$_2$ ratios of 1, 1.5 and 2.0. CaF$_2$ addition was found to obtain good metal – slag separation with CaF$_2$ additions of 5% and 10% of the weight of the (ore + coke + lime + scrap iron) mixture. He produced a high carbon ferromanganese product which was close to the standard ferromanganese composition defined by ASTM [8].

The smelting of silicomanganese from Denizli-Tavas manganese ore was investigated by Keskinkılıç [31]. The mixtures of calcined manganese ore, active carbon, calcium oxide and quartz were smelted in graphite crucibles with an electronically controlled muffle furnace. Experiments were done at 1600, 1650, 1700 °C and for 1, 1.5 and 3 hours. He concluded that as the temperature of the system increased, the reduction extents of both MnO and SiO$_2$ increased. 1.5 hour smelting time and 1700 °C was determined to be the optimum conditions for production. Also the highest recoveries were obtained when the charge basicity was 0.58 and active carbon/ore wt. ratio value was 0.219.

Kalfaoğlu [32] investigated the solid state reduction of Denizli-Tavas manganese ore to produce ferromanganese by using graphite. Experiments were conducted at 1100, 1150, 1200, 1250, 1300 °C and with constant amount of carbon and calcined manganese ore. Experiments were conducted under argon atmosphere

to prevent oxidation inside the furnace. Experimental results showed that approximately 60% reduction of the manganese ore took place at and below 1200 °C. At and above 1250 °C it was observed that this reduction efficiency increased to approximately 90%. Results showed that it was possible to produce Fe-Mn alloy from the Denizli-Tavas manganese ore by solid state reduction with carbon.

Akıl [33] investigated optimization of conditions to produce manganese and iron carbides from Denizli – Tavas manganese ore by solid state reduction. The effects of temperature, time, amount of active carbon addition and CaO addition were used as experimental variables on reduction. Experiments were performed in a horizontal tube furnace. From the experimental results, the optimum conditions found for reduction of Denizli-Tavas manganese ore were 1250 °C, 4 hours, 100% of stoichiometric amount of active carbon and 5% CaO addition. Under the optimum conditions 83.85% reduction of calcined ore was obtained

CHAPTER 3

EXPERIMENTAL

3.1. Preparation for the Experiments

The main materials used in the experiments were Erzincan manganese ore, graphite powder, lime, fluorspar and scrap iron which were analyzed and prepared carefully for the experiments.

3.1.1. Ore Preparation

Erzincan manganese ore was obtained from Alya Mining in bags in the form of big pieces. The big pieces were reduced to -8 mm size by means of a jaw crusher. The product size was then reduced to -1 mm by using roll crusher. The product of roll crusher was put into a disc grinder and ore size was obtained to -1 mm. This ore powder was separated out and put together and mixed a lot of times for homogeneous distribution. After that, quatering was done. Firstly, the heap of ground ore was split into four quarters by means of a device called Jones Riffle. And then, the heaps in the opposite quarters were mixed together. This process was repeated several times in order to obtain a good distribution. This ore powder was dried at 150 ^{o}C for 4 hours in a muffle furnace and 4% weight loss was observed. A representative sample was taken from the ground ore powder and screen analysis was done. The results of screen analysis are given at table 3.1.

Table 3.1 Screen Analysis of Ore

Tyler Mesh	Weight (%)
+ 28	0.45
-28 +35	1.28
-35 +48	8.74
-48 +65	32.83
-65 +100	39.84
-100 +200	7.61
-200	9.25

3.1.2. Chemical Composition of Ore

The ore was firstly calcined at 900° C for 5 hours in a muffle furnace. Both the calcined and uncalcined ore samples were sent to chemical laboratories of Asil Steel Works and analyzed. The results are given in table 3.2. After calcination, about 13% weight loss of total sample was observed. It is seen that there is not important composition change of ore after calcination. That's why, the uncalcined ore was used in the experiments.

Table 3.2 Chemical Composition of Calcined and Uncalcined Ore

Elements	Calcined (wt. %)	Uncalcined (wt. %)
C	0.05	0.93
S	0.005	0.01
MnO_2	70.87	70.48
MgO	1.89	1.85
Al_2O_3	3.42	3.19
SiO_2	11.30	10.97
CaO	8.51	8.09
Fe_2O_3	2.45	2.61
Na_2O	0.34	0.33
K_2O	0.50	0.47
TiO_2	0.12	0.11
BaO	0.10	0.08
P_2O_5	0.29	0.20
SrO	0.16	0.18

3.1.3. Graphite Powder

The analysis of graphite powder used in the experiment was done by Asil Steel Works is given in table 3.3.

Table 3.3 Chemical Analysis of Graphite Powder

Element	Weight (%)
Sulphur	0.03
Ash	0.80
Moisture	0.32
Volatile Matter	3.53
Fixed Carbon	95.32

3.1.4. Lime

Limestone used in the experiments was obtained from Heda Medical Health Industry Trade Co. Ltd. The chemical analysis of lime was done at Asil Steel Works laboratories and the results are given in table 3.4.

Table 3.4 Chemical Analysis of Limestone

Elements	Weight (%)
C	0.29
S	0.01
CaO	98.00
Al_2O_3	0.16
SiO_2	0.61
Fe_2O_3	0.04
MgO	0.84
Moisture	0.05

3.1.5. Fluorspar

Fluorspar was obtained from Asil Steel Work in the form of pebbles. Its analysis done by Asil Steel Work is given table 3.5. Fluorspar was ground in a grinding mill before use.

Table 3.5 Chemical Analysis of Fluorspar

Element	Weight (%)
C	0.05
S	0.024
CaF_2	92.30
Al_2O_3	0.73
SiO_2	6.26
Fe_2O_3	0.19
MgO	0.15
Moisture	0.30

3.2. Experiments

In the experiments predetermined amounts of uncalcined manganese ore, graphite powder, lime, fluorspar and scrap iron were carefully weighed, mixed together, charged into a graphite crucible and heated up to $1600^{o}C$. The crucible was held at that temperature for a predetermined period and cooled down to room temperature. Time, basicity of charge, fluorspar content and graphite to ore weight ratio were used as the experimental parameters. The total weight of charge was 126.17 grams.

One parameter was changed and the other three parameters were constant in a given run. Holding times used in the experiments were 1 hour, 2 hours, 3 hours, 4 hours and 5 hours. Holding time was 4 hours in the experiments in which time was not a variable.

Charge basicity was defined as the ratio of the total weight of CaO in the charge to the total weight of SiO_2 in the charge. Charge basicities used in the experiments were 1, 1.25, 1.5. Charge basicity was taken as 1 in the experiments in which basicity was not a variable.

The quantity of fluorspar used in the experiments was expressed as the percentage by weight of the fluorspar free charge. In the experiments fluorspar quantity was taken as 0%, 2.5% and 5% of the fluorspar free charge. In the experiments where the fluorspar addition was not a variable, this value was 2.5%.

Graphite to ore weight ratio was defined as the ratio of the weight of the graphite to that of the ore in the charge. In the experiments, graphite to ore weight

ratio was taken as 0.05, 0.10, 0.15. In the experiments where graphite to ore ratio was not a variable, the value used was 0.15

The crucible to be used in slag - metal reaction experiments should withstand the severe conditions and it should be possible to contain the two liquid phases in the crucible without leakage of either phase through the crucible walls. There should be minimum interaction between the crucible and the liquid metal and slag phases. İmer [30] conducted some experiments with SiO_2 and Al_2O_3 crucibles for smelting Denizli Tavas manganese ore. In these experiments, he was concluded that there was the leakage of slag phase through the crucible walls. When the experiments were conducted with graphite crucibles, there was no leakage of slag phase through the crucible walls. That's why, in the experiments, conical shaped graphite crucible as shown in figure 3.1 was used for obtaining enough metal depth for chemical analyses. Then, the crucibles were broken to extract metal and slag phases obtained during smelting.

Before experiments, some preliminary experiments were conducted to obtain slag and metal phases. In these experiments, there was excess amount of graphite powder and fluorspar. After smelting experiments, the excess amount of graphite powder and fluorspar remained as a layer above slag phase. Therefore, to obtain meaningful results from studies on slag – metal reactions, the amount of graphite powder and fluorspar was decreased until there was only metal and slag phase in the system. Additionally, for obtaining good smelting results, the ratio of Fe weight in charge / Mn weight in charge must be equal to about 1 / 8 [7]. That's why, 4.67 g scrap iron is added into the charge mixture during experiments.

The experiments reported in this study were conducted by use of the conical graphite crucible in which a mixture of 100 grams of uncalcined manganese ore and carefully weighed amounts of graphite powder, lime, fluorspar and scrap iron put into. The graphite crucible with its contents was covered with a graphite lid and then placed in an electronically controlled muffle furnace. The furnace was then heated first to 1200^oC at the rate of 10^oC/minute and then to 1600^oC at the rate of 5^oC/minute. The furnace was held at 1600^oC for predetermined time and then switched off and cooled to room temperature. The crucible was then taken out of the furnace and the metal and slag phases were removed from the crucible by breaking

the crucible. The metal and slag phases were carefully weighed and subjected to chemical analysis in the laboratories of Asil Steel Works. The chemical analyses of metal and slag phases were conducted by use of Thermo Arl XRF 9900 XP spectrometer and leco CS 600 carbon and sulphur analyzer.
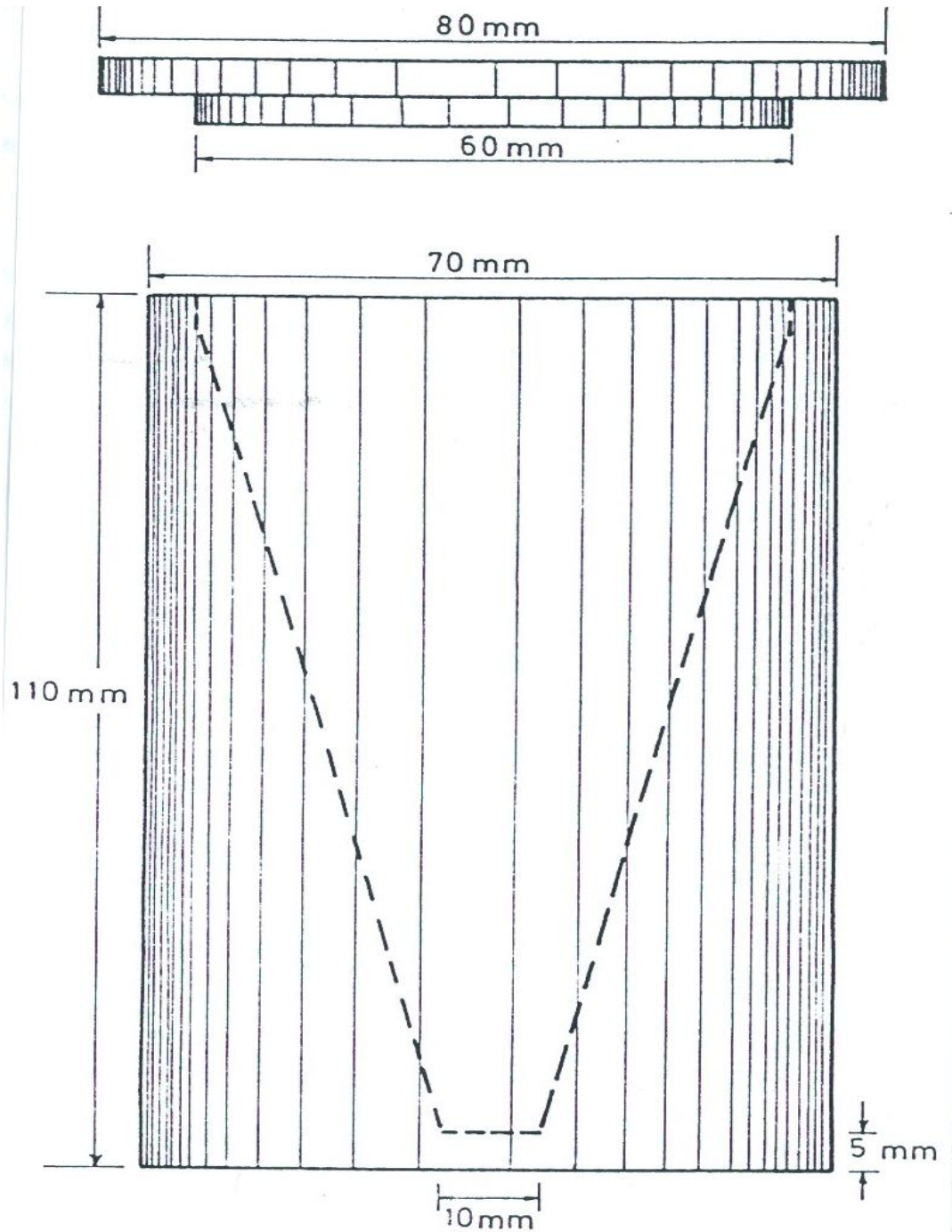
Figure 3.1 Schematic drawing of graphite crucible

35

CHAPTER 4

RESULTS and DISCUSSION

4.1. Presentation of Results

The experimental results are presented in table 4.1 where the experimental parameters; basicity, graphite to ore ratio, amount of CaF_2 addition and holding time at $1600^{o}C$, and, the weights and compositions of the resulting slag and metal phases are given.

Table 4.1 Experimental Results of Metal and Slag

Exp. No	Ti. (hr)	Char Bas.	Graphit /Ore	%CaF$_2$ Add.	Metal Weight (gr)	Slag Weight (gr)	Alloy Composition (%)						Slag Composition (%)						
							Mn	Fe	Si	C	S	P	CaO	MnO	SiO$_2$	Fe$_2$O$_3$	Al$_2$O$_3$	MgO	CaF$_2$
1	1	1	0.15	2.5	34.15	44.08	74.03	17.83	0.41	7.65	0.001	0.20	35.22	22.87	27.95	0.28	5.88	2.83	5.25
2	2	1	0.15	2.5	36.44	40.00	75.61	16.17	0.49	7.64	0.002	0.22	36.20	20.58	28.94	0.53	6.06	2.97	5.25
3	3	1	0.15	2.5	36.22	38.68	75.45	15.79	1.10	7.39	0.001	0.21	37.47	19.28	28.70	0.34	5.71	2.93	5.64
4	4	1	0.15	2.5	40.06	33.46	76.43	13.94	2.69	6.93	0.003	0.17	38.87	18.02	27.28	0.71	5.86	3.28	5.77
5	5	1	0.15	2.5	42.42	30.61	76.85	12.21	4.35	6.51	0.003	0.15	40.07	16.89	28.14	0.32	6.14	3.42	4.89
6	4	1.25	0.15	2.5	41.39	37.00	77.36	14.02	0.67	7.66	0.001	0.20	39.05	12.57	31.13	0.39	7.20	3.85	5.81
7	4	1.5	0.15	2.5	44.34	40.54	78.52	13.25	0.43	7.92	0.001	0.20	46.12	9.03	26.98	0.20	5.57	3.05	8.94
8	4	1	0.05	2.5	36.90	30.76	74.18	16.09	2.03	7.45	0.001	0.26	34.75	21.87	28.15	0.43	6.15	3.04	5.60
9	4	1	0.1	2.5	38.25	27.03	73.66	16.34	2.36	7.40	0.002	0.25	37.03	17.74	29.87	0.35	6.39	3.45	5.17
10	4	1	0.15	0	38.30	32.14	74.15	15.00	3.12	7.63	0.001	0.20	40.01	21.86	27.78	0.20	5.88	3.17	0.00
11	4	1	0.15	5	43.06	32.63	78.76	13.37	1.70	6.40	0.002	0.20	37.40	17.55	27.86	0.14	5.44	3.12	8.56

4.2. Discussion of Results

4.2.1. Effect of Time

Time was used as a variable in runs 1,2,3,4 and 5. During the reduction reactions of iron, manganese and silicon oxides with carbon, there is CO formation in the system which leaves the system. As a result, there is weight loss in the system. The weight loss of the charge as a percentage of the original weight plotted against time is given in figure 4.1. It is noticeable that there is a serious weight loss in the first hour. When the crucible was put into the furnace, the temperature of furnace was equal to 25 ^{o}C. Until the temperature reached 1600 ^{o}C, the crucible was held at the furnace for 3.5 hours. During this period, calcination of ore, the reduction of all iron oxides and burning of all volatile matter in the charge take place. Also the reduction reactions of MnO and SiO_2 are fast during the first hour. All of that causes this serious weight loss of charge. Because, MnO and SiO_2 are stable oxides, the reduction of them continue beyond five hours but more slowly than that of the first hour. In other words, there is no complete reduction of MnO and SiO_2 in the system after five hours.

As a result of the reduction reactions with carbon a metallic phase containing Fe, Mn, Si, C, S and P forms in the system. As the extent of the reduction increases with time the weight of the metal phase increases whereas the weight of the slag phase decreases. This trend is shown in figures 4.2 and 4.3. It is seen from figure 4.4 that the slag to metal weight ratio decreases with time

Variation of the Fe, Mn, Si and C concentrations of the metal phase with time is shown in figure 4.5 and the variation of MnO and SiO_2 concentrations of the slag phase with time is shown in figure 4.6. Variations of the weights of Fe, Mn, and Si in the metal phase and the weights of MnO and SiO_2 in the slag phase with time are shown in figure 4.7 and 4.8, respectively. 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, with time is shown in figure 4.9.

From figure 4.5 it is obvious that the Fe concentration of the metal slightly decreases from 1 to 5 hours whereas there is almost no change in the weight of Fe in the range of 1 to 5 hours as shown in figure 4.7. This result indicates that almost all

of the iron oxides are reduced to metallic Fe in less than one hour. Hence, there is almost no change in the weight of Fe in the metal phase beyond one hour. The decrease of the concentration of Fe in the alloy is due to increase in the metal weight with time.

Manganese concentration of the metal and weight of Mn in the metal are seen to increase with time from figures 4.5 and 4.7, respectively. It is seen from figures 4.6 and 4.8, respectively, that MnO concentration of the slag and MnO weight in the slag decreases continuously with time in the range of 0 to 5 hours. It can be concluded that the reduction MnO is a slow process and takes some time. It is not complete even at the end of 5 hours. This is obviously seen by analysing figure 4.9 where the quantity of manganese reduced into the metal expressed as a ratio of the quantity of the total manganese in the charge is plotted against time. It is seen from the figure that 57, 63, 62, 69 and 74% of the manganese in the charge is reduced into the metal at the end of 1, 2, 3, 4 and 5 hours, respectively.

Silicon concentration of the metal and weight of silicon in the metal increase with time as seen from figures 4.3 and 4.5, respectively. It is seen from 4.4 and 4.6, respectively, that SiO_2 concentration of the slag remains steady while weight of SiO_2 in the slag decreases with time. The reason for the SiO_2 concentration of the slag to essentially remain constant in spite of decreased weight of SiO_2 in the slag is decrease in total weight of the slag. In figure 4.8 it is noticeable that the slope of the curve for MnO is slightly bigger than the slope of the curve for SiO_2. This fact indicates that the reduction of SiO_2 is relatively slower than the reduction of MnO. From figure 4.9 it is also seen that the reduction of SiO_2 is not completed and reduction would continue after the 5 hour period. This is due to the fact that SiO_2 is the most stable oxide in the system and the reduction of SiO_2 from the slag into the metal by carbon is a very slow process which is also verified by a study done by Türkdoğan, et al [34].

The carbon content of the metal is seen to decrease with time from figure 4.5. The metal is contained in a graphite crucible. Therefore, the system is expected to be saturated with carbon after a while. The solubility of carbon in the Fe – Mn – Si system decreases with increase in metal silicon content [35]. The carbon content of

the metal therefore decreases with time since the silicon content of the metal increases with time as seen from figure 4.5
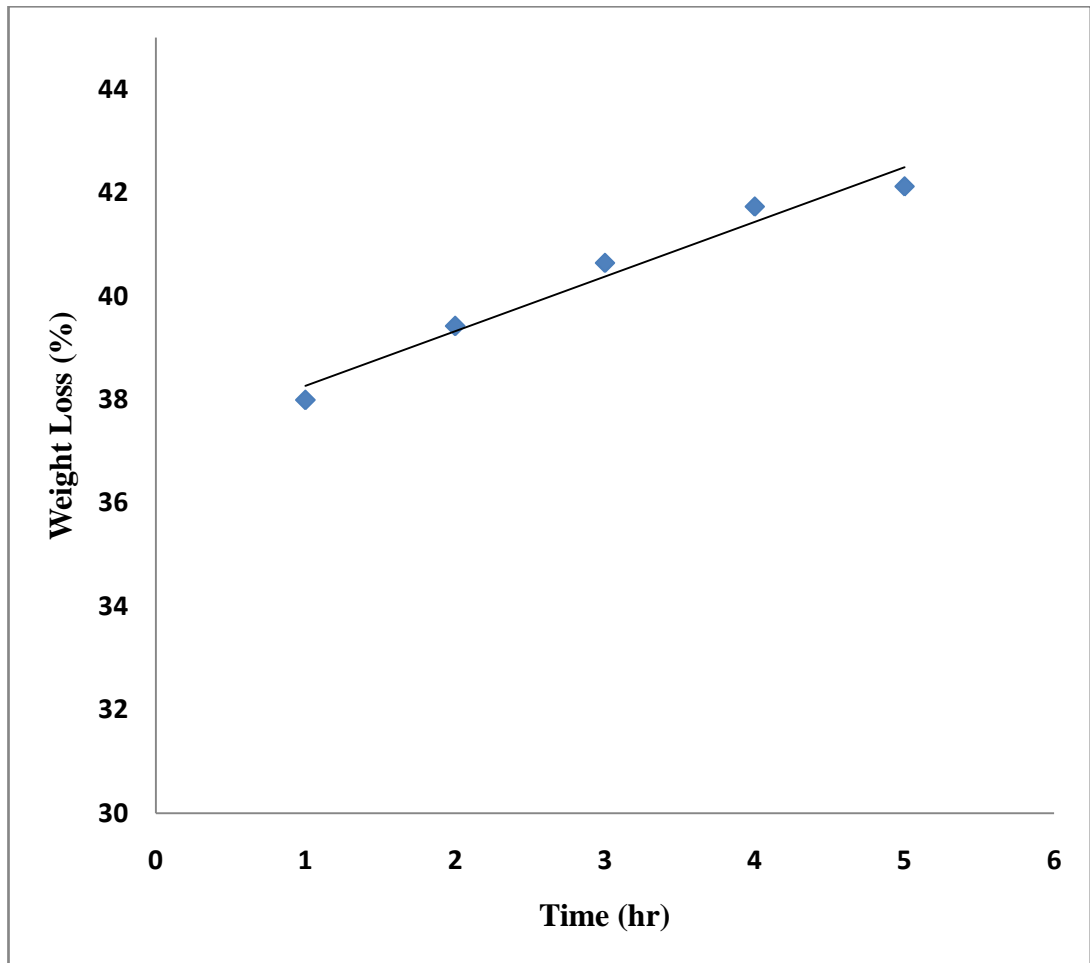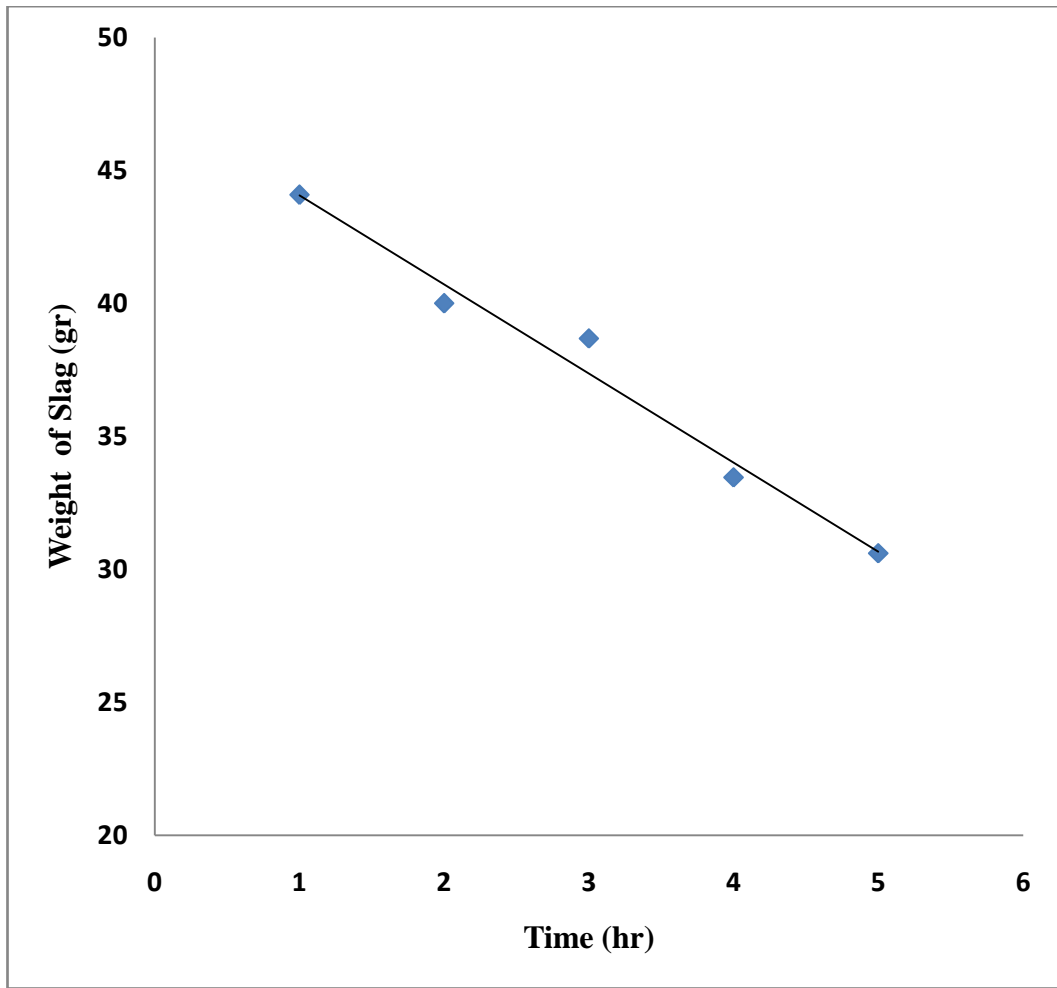

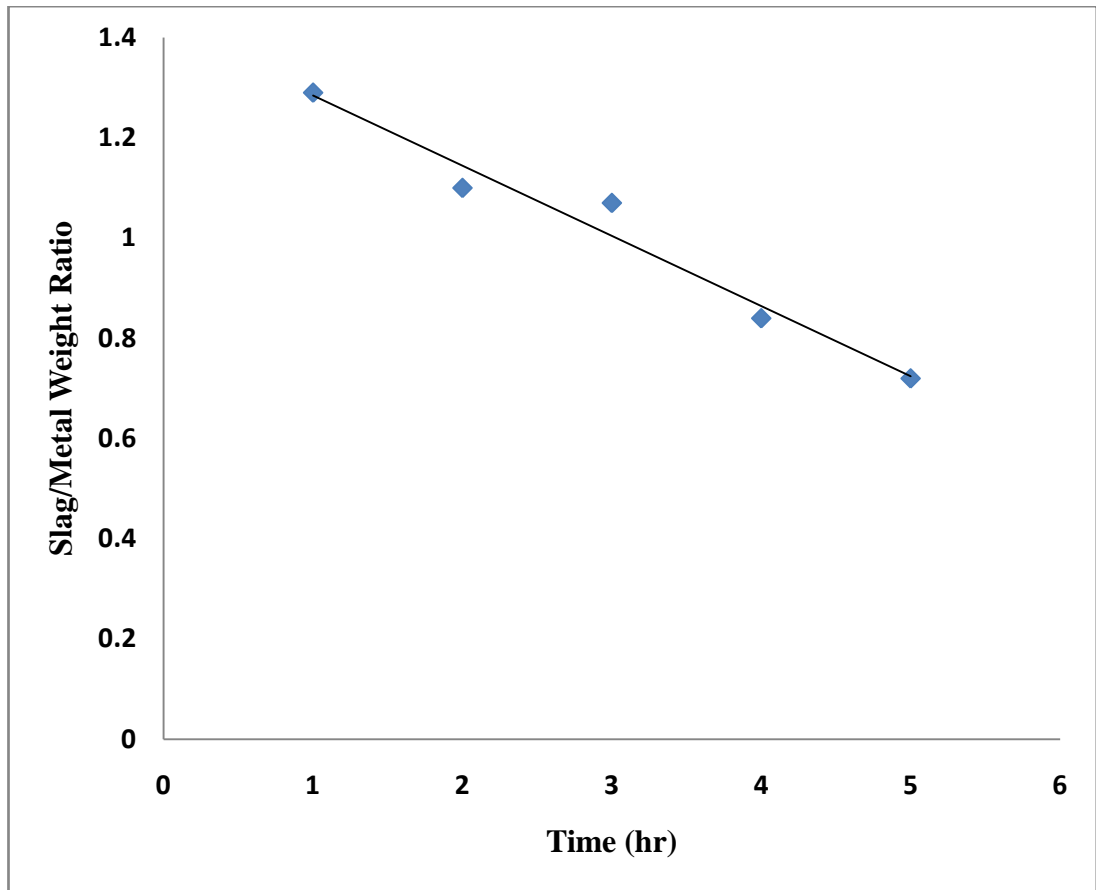**Figure 4.1** Variation of Weight Loss of Charge with Smelting Time
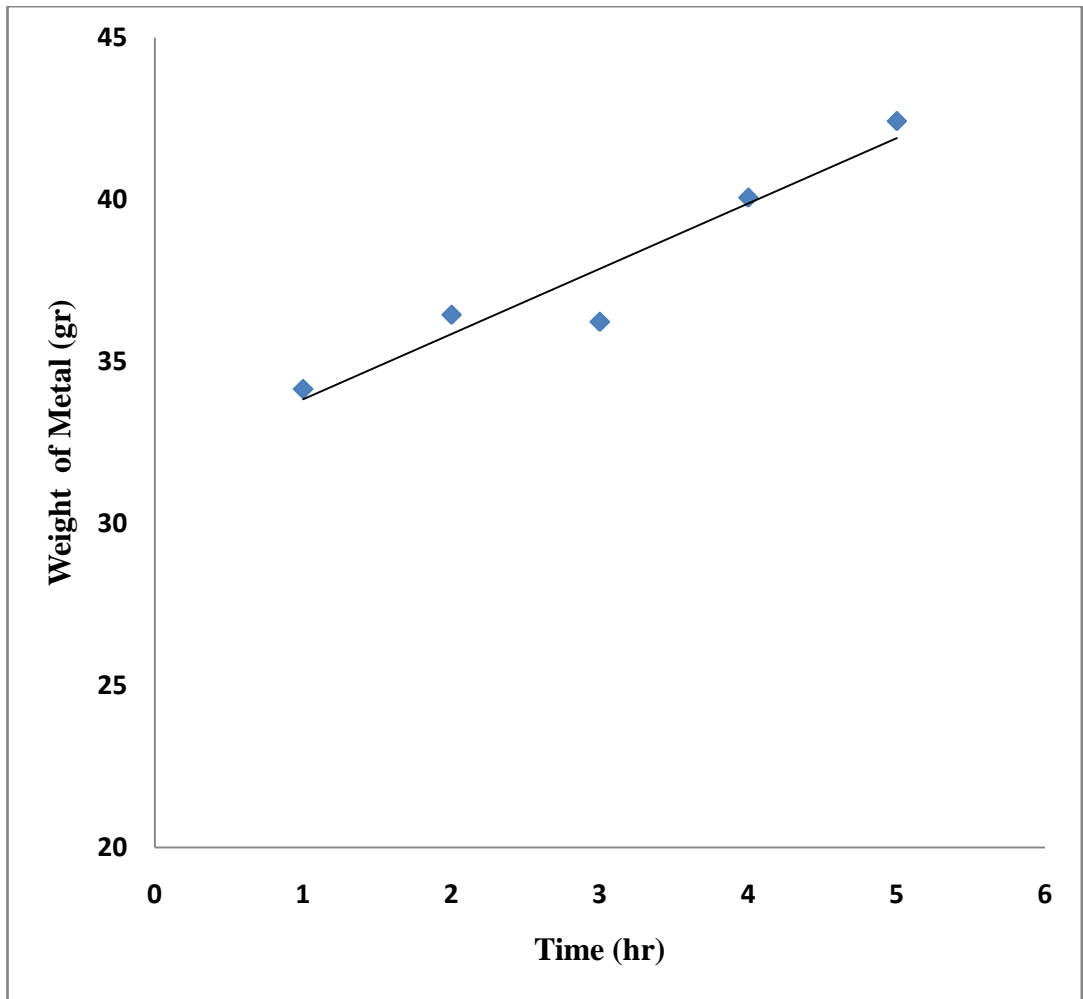
Figure 4.2 Variation of Weight of Metal with Smelting Time
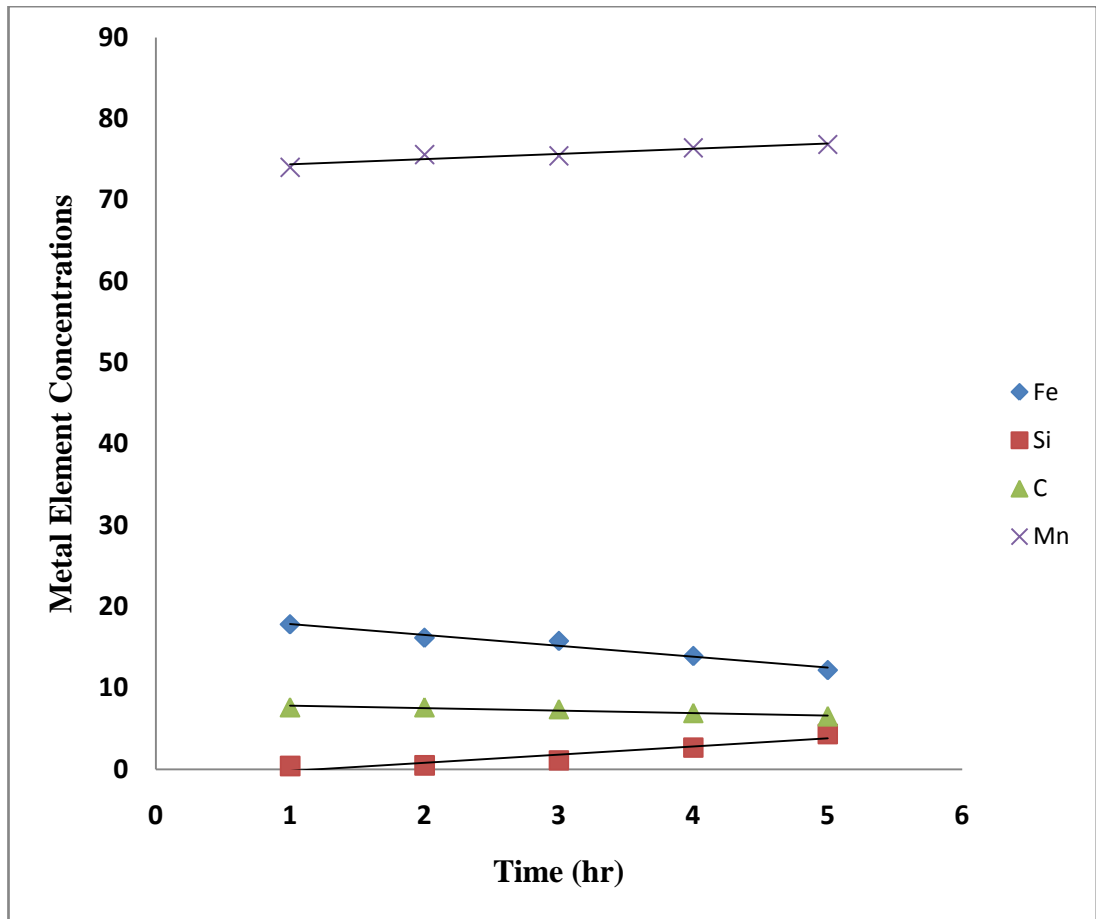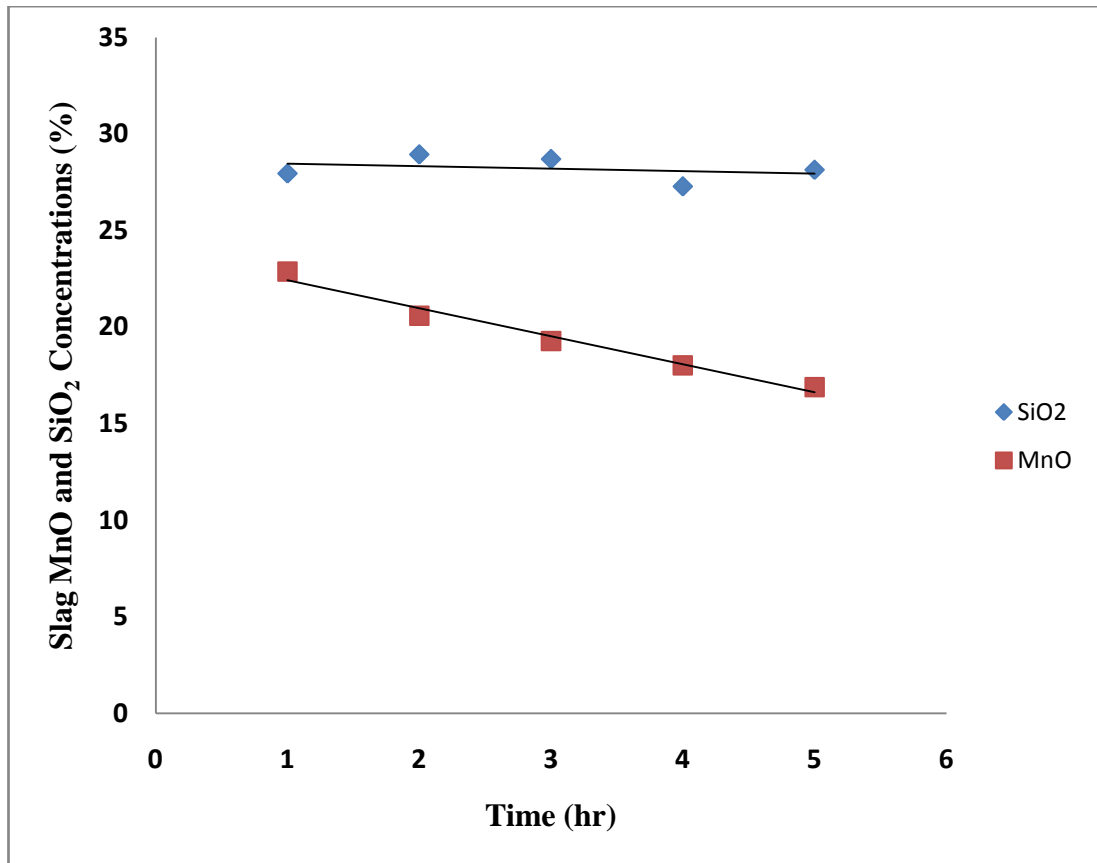
Figure 4.3 Variation of Weight of Slag with Smelting Time

Figure 4.4 Effect of Time on Slag/Metal Weight Ratio

Figure 4.5 Variation of Metal Fe, Mn, Si, and C Concentrations with Smelting Time

Figure 4.6 Variation of Slag MnO and SiO$_2$ Concentrations with Smelting Time
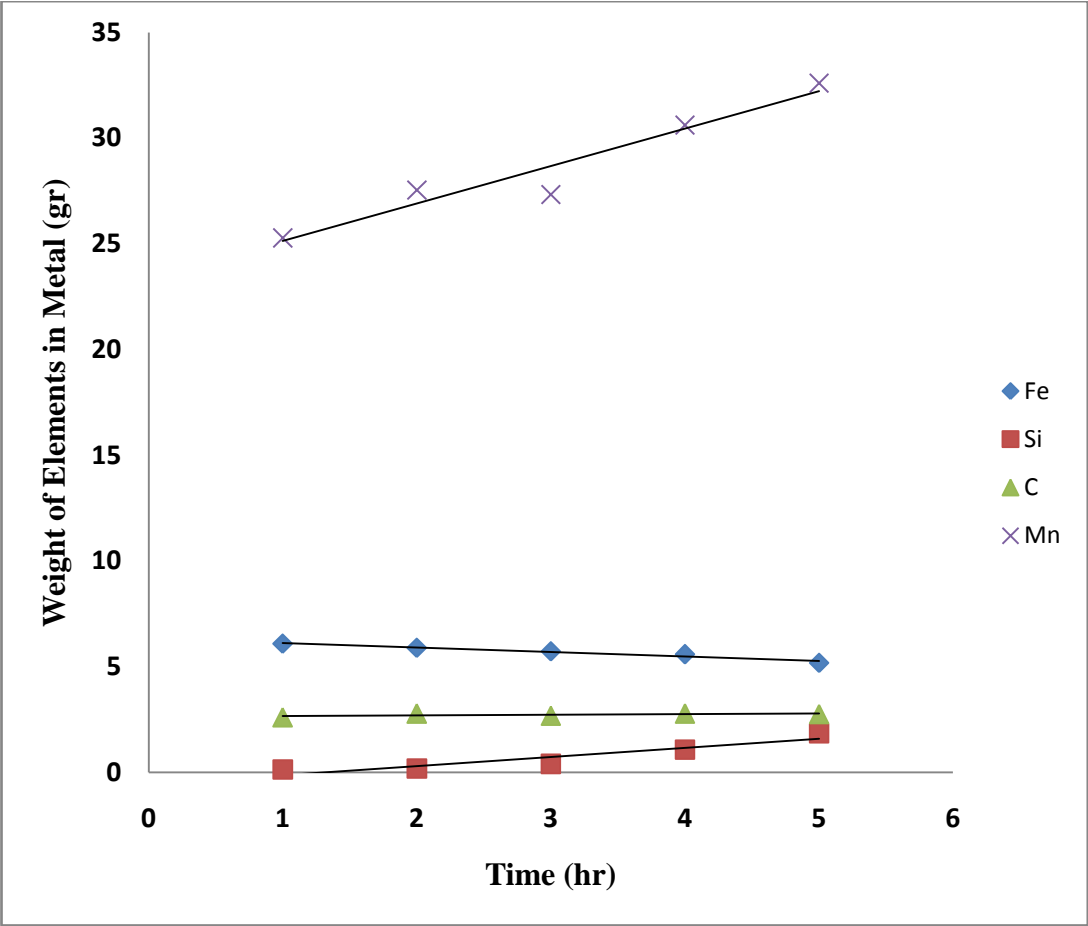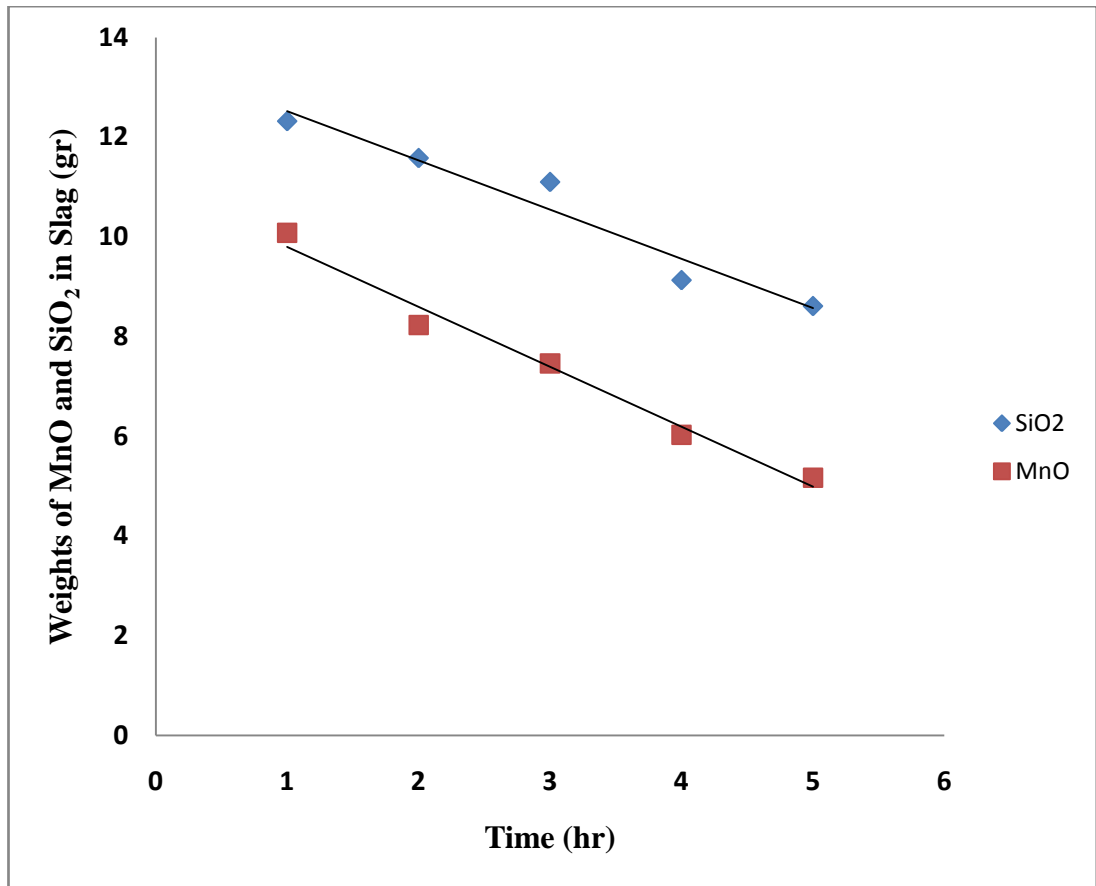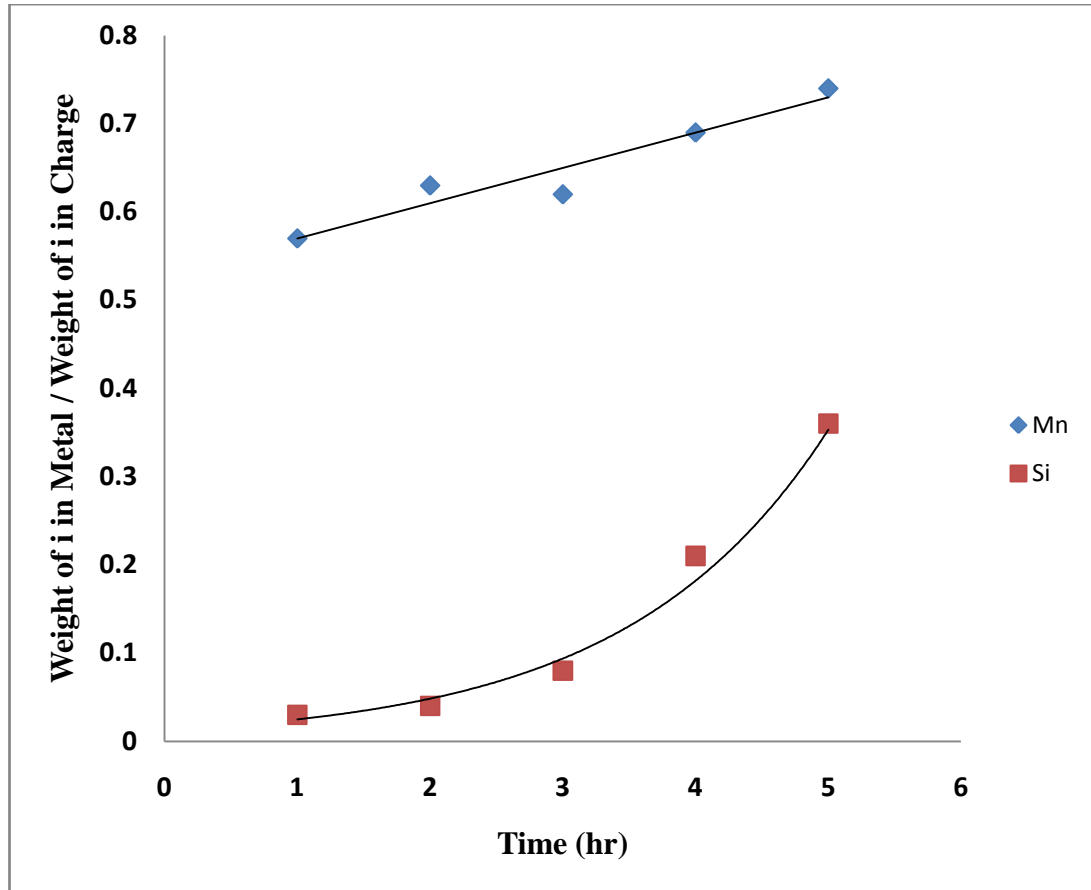
Figure 4.7 Variations of Metal Mn, Si, Fe and C Weights with Smelting Time

**Figure 4.8** Variations of Slag MnO and SiO$_2$ Weights with Smelting Time

Figure 4.9 Variations of Mn and Si Recoveries with Smelting Time

4.2.2. Effect of Basicity

In the present study the charge basicity was defined as the ratio of total weight of CaO to the total weight of SiO_2 in the charge. Charge basicity, and accordingly slag basicity was increased by adding lime into the charge. The effect of charge basicity on the reduction reactions are shown in figures 4.10 and figure 4.11 where manganese distribution ratio, %Mn / (%MnO) and silicon distribution ratio, %Si / (%SiO_2), are plotted against the ratio of total weight of CaO to the total weight of SiO_2 in the charge.

Reduction of the primary oxides from the slag by carbon is governed by the following reactions:

$$MnO + C_{(s)} = Mn + CO_{(g)} \qquad (17)$$

$$SiO_2 + 2C_{(s)} = Si + 2CO_{(g)} \qquad (18)$$
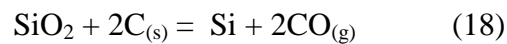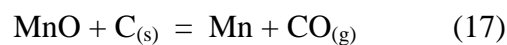
Change in basicity of the slag affects the activity coefficients of the oxides [36, 37]. MnO is a basic oxide and SiO_2 is an acidic oxide. An increase in the basicity of the slag increases the activity coefficient of MnO and the extent of the reduction in reaction (17); whereas an increase in the basicity of the slag decreases the activity coefficient of SiO_2 which decreases the extent of the reduction in reaction (18). In other words, more MnO and less SiO_2 are reduced with increasing basicity of slag. Hence, manganese distribution ratio increases and silicon distribution ratio decreases with the increase in basicity as illustrated in figures 4.10 and 4.11, respectively where the basicity ratio is defined as the ratio of total weight of CaO to the total weight of SiO_2 in the charge.

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 which is an expected result as shown in figure 4.12.
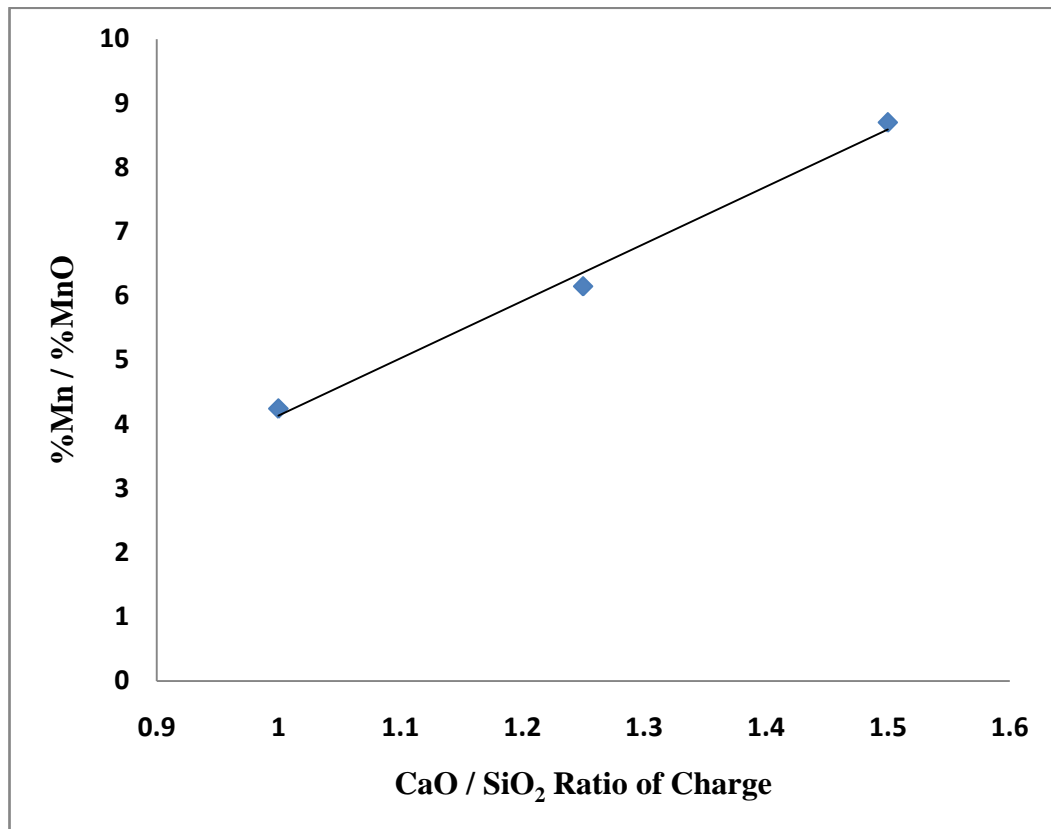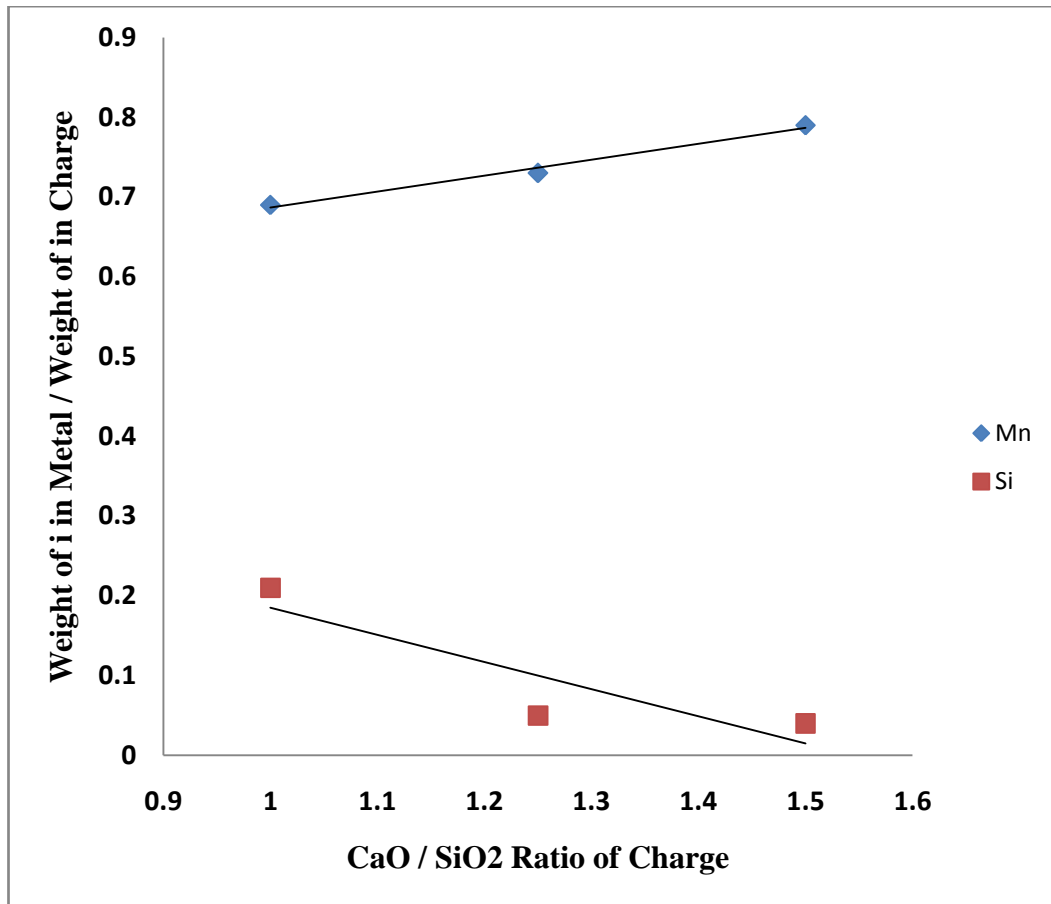

Figure 4.10 Variation of Manganese Metal – Slag Distribution Ratio with Basicity of Charge
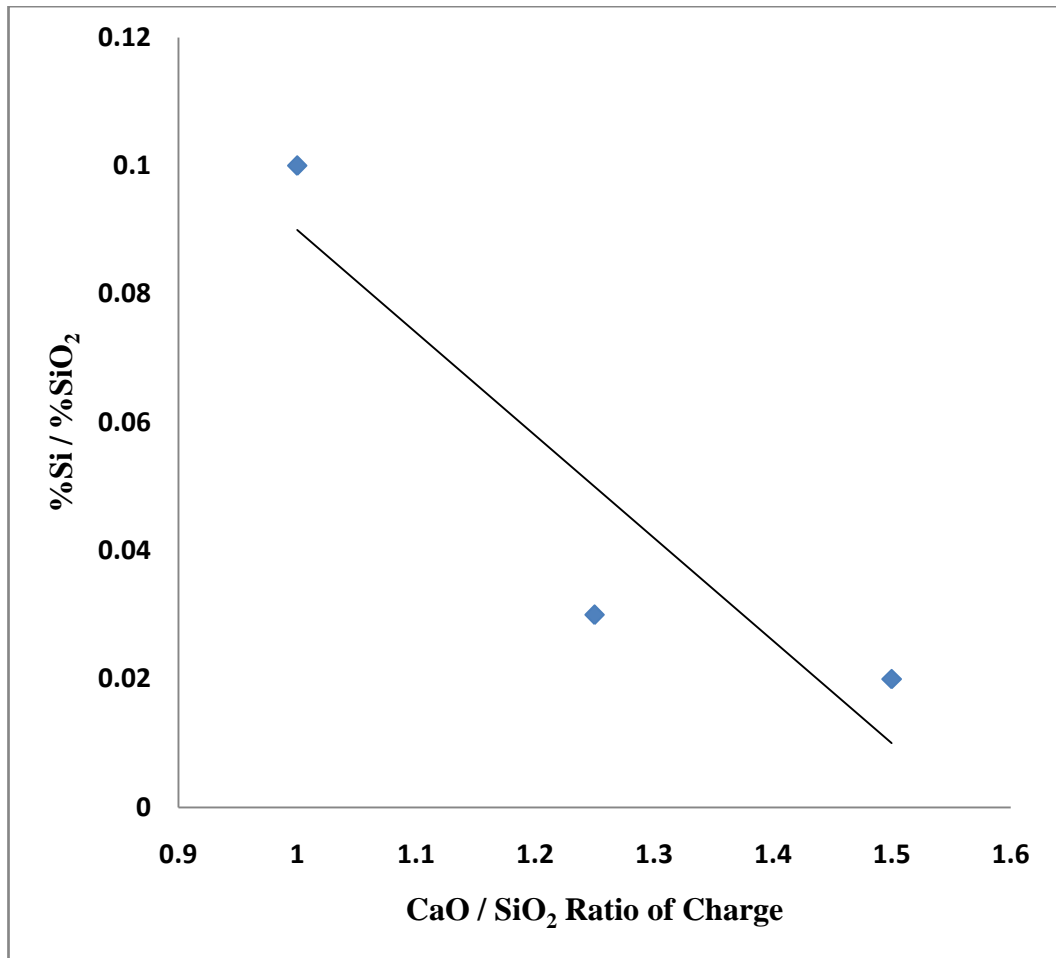
Figure 4.11 Variation of Silicon Metal - Slag Distribution Ratio with Basicity of Charge

**Figure 4.12** Variation of Mn and Si Recoveries with Basicity of Charge

4.2.3 Effect of Fluorspar Addition

Fluorspar is a substance, which increases the fluidity of slag and increases the rate of the solution of lime in the slag. In the literature there are experimental studies on the effect of CaF_2 addition on slag viscosity proving this fact. Because of increase in fluidity with the CaF_2 addition, metal – slag separation in the system is improved. Experiments were conducted by use of CaF_2 free charge and with CaF_2 addition of 2.5% and 5% of the weight of the CaF_2 free charge. Best results for slag – metal separation was observed at 2.5% CaF_2 addition. Therefore, all of the experiments in which CaF_2 content was not variable were conducted with 2.5% CaF_2 addition.

The variation of manganese concentration of the metal, silicon concentration of the metal, manganese distribution ratio %Mn/%MnO, silicon distribution ratio %Si / %SiO$_2$, and manganese and silicon recoveries with the quantities of CaF_2 added are shown in figures 4.13, 4.14, 4.15, 4.16 and 4.17 respectively.

51

The experimental points in figure 4.13 show that Mn concentration of the metal increase with the CaF_2 addition. Si concentration is seen to decrease with the CaF_2 addition from figure 4.14. From the experimental points Mn distribution ratio is seen from figure 4.15 to increase with the CaF_2 addition. Si distribution ratio decreases when the CaF_2 addition is increased to 5% as seen from the experimental points in figure 4.16. The variation of Mn recovery and variation of Si recovery are similar to the variation of Mn distribution ratio and variation of Si distribution ratio respectively, with CaF_2 addition as seen from figure 4.17.

Two of the studies that have been found in the literature on the effect of CaF_2 on the smelting of manganese ores are study of Kor [38] and that of Emeksiz [29]. Kor reported that due the addition of CaF_2 into the system silica reacts with fluorspar according to the reaction

$$SiO_2 + 2CaF_2 = SiF_{4(g)} + 2CaO \qquad (19),$$
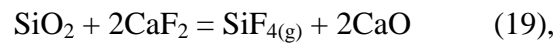
and metal silicon content decreases. Emeksiz found the Mn distribution ratio to slightly increase and the Si distribution ratio to slightly decrease with CaF_2 addition. The result of Emeksiz shows that Mn recovery is not affected by CaF_2 addition.
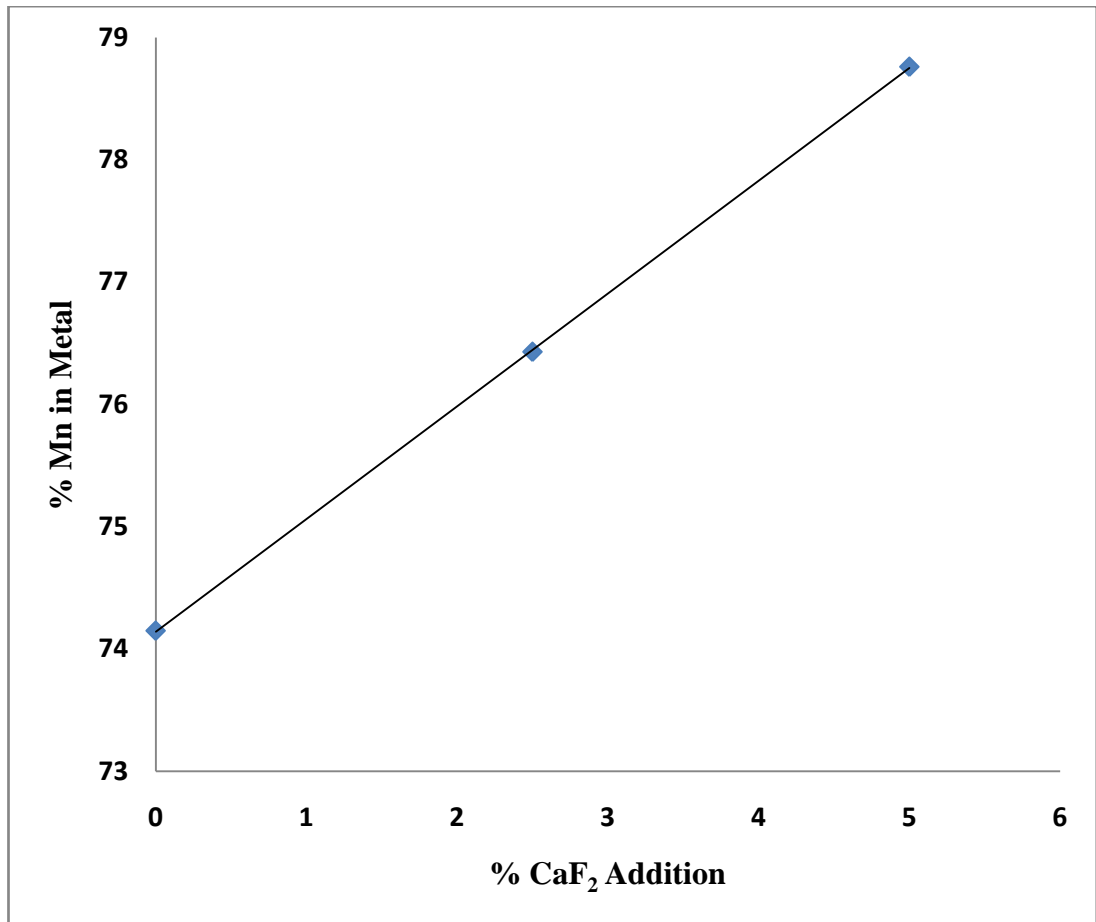
Figure 4.13 Effect of Fluorspar Addition on Metal Mn Concentration
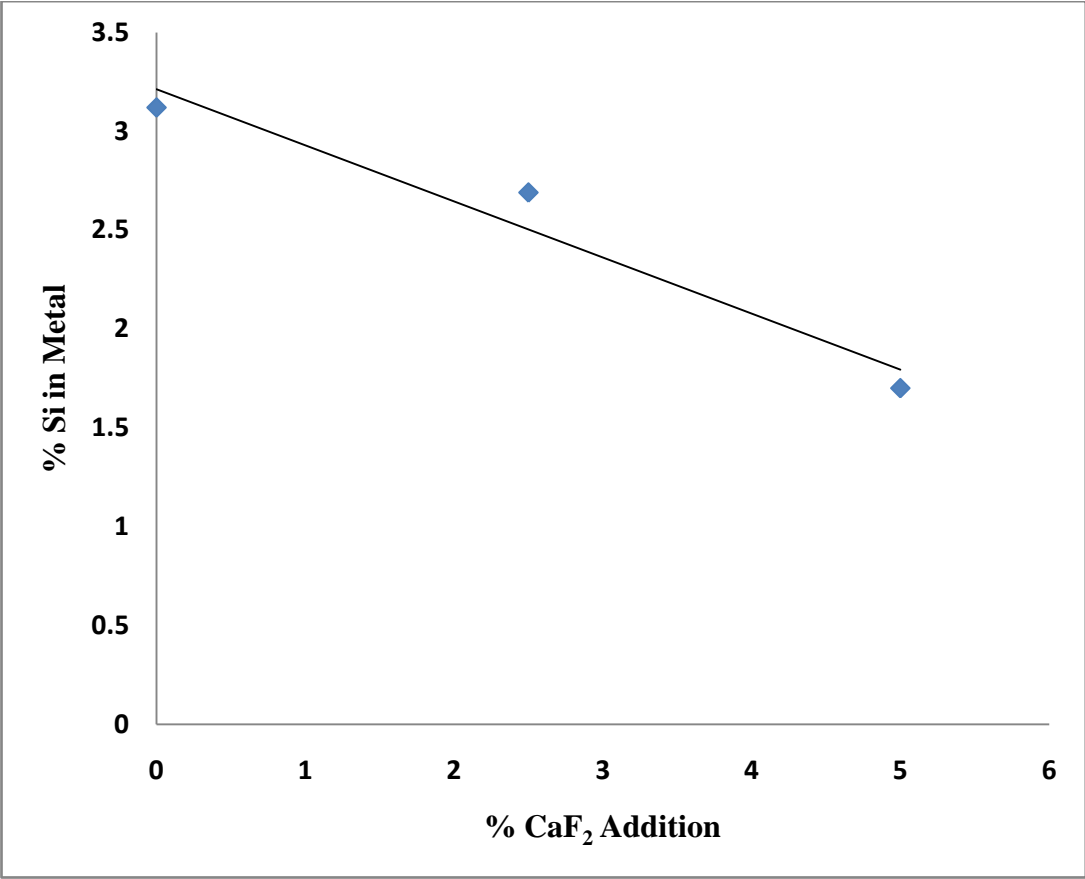
Figure 4.14 Effect of Fluorspar Addition on Metal Si Concentration
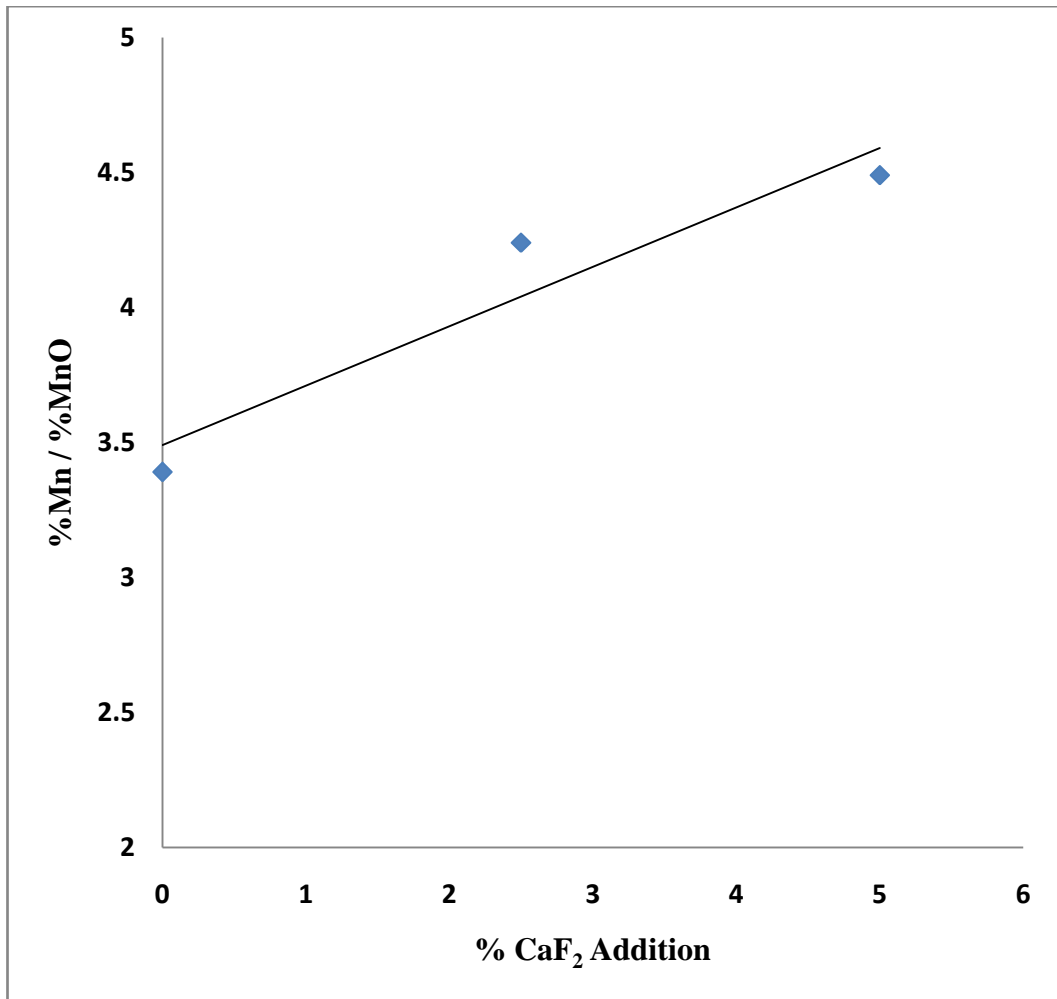
Figure 4.15 Effect of Fluorspar Addition on Manganese Metal – Slag Distribution Ratio

Figure 4.16 Effect of Fluorspar Addition on Silicon Metal - Slag Distribution Ratio

Figure 4.17 Effect of Fluorspar Addition Manganese and Silicon Recoveries

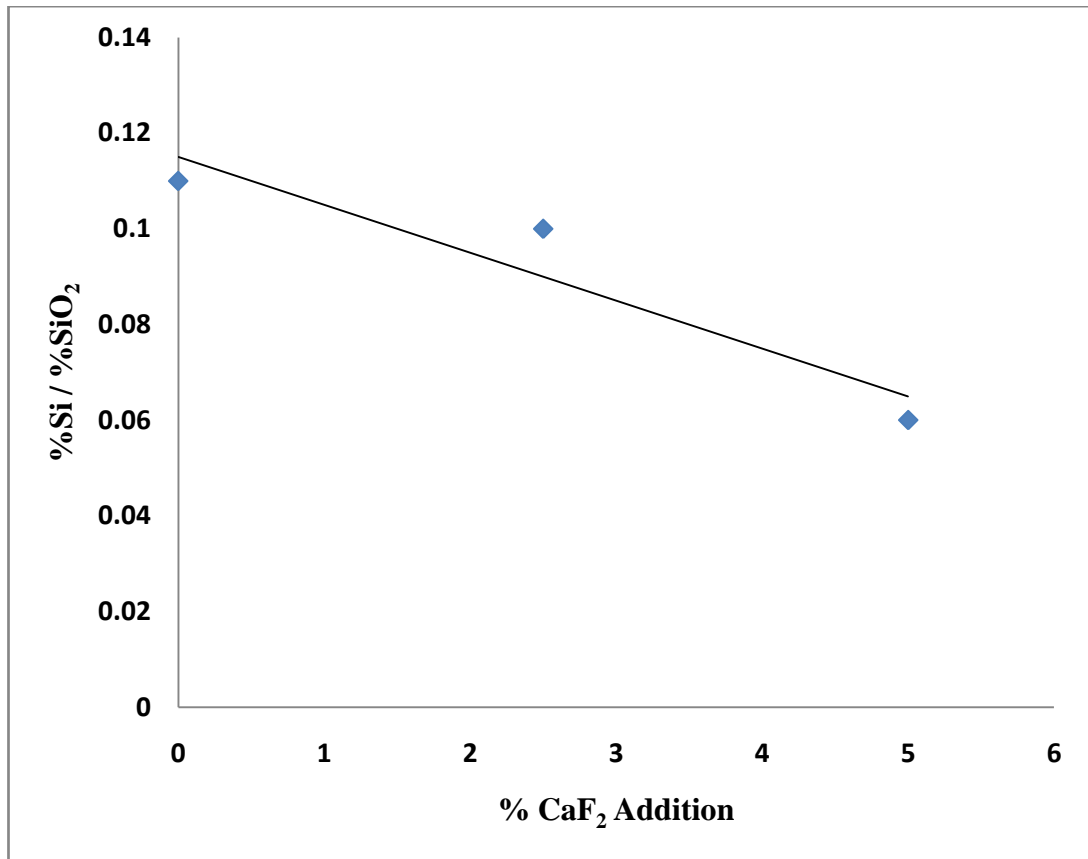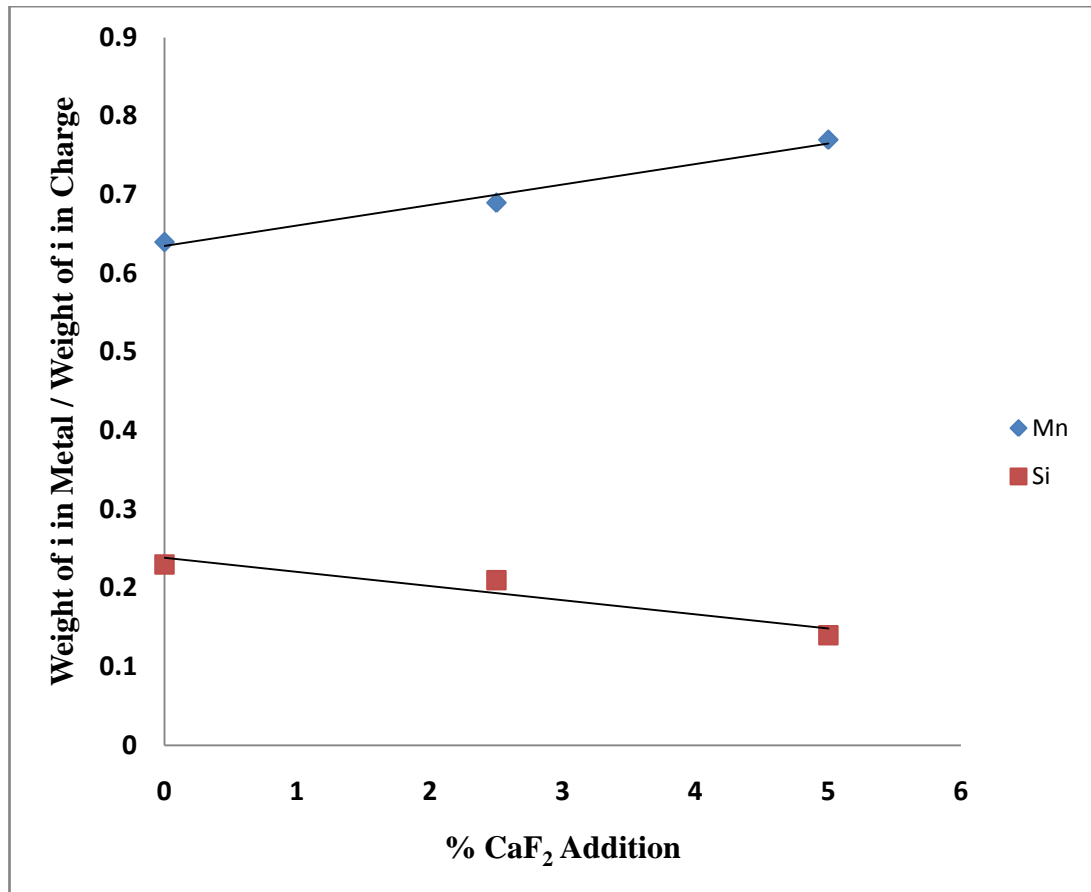### 4.2.3 Effect of Graphite to Ore Ratio

In the experiments graphite powder was used as the reducing agent. The amount of graphite necessary to reduce all of manganese oxides, iron oxides and 30% of the silicon oxides into elemental iron, manganese and silicon was calculated from the known analysis of the ore and graphite powder. This graphite powder amount was found to be 21.36 gr. During the experiments in which 21.36 grams of graphite powder was used a layer of unreacted graphite powder was observed above the slag at the end of the experiments. This layer was also observed to contain significant amounts of metal and slag beads which were not settled down into the slag and metal phase lying below. Because the experiments were done in graphite crucibles, the carbon supplied into the system came not only from graphite powder but also from graphite crucible itself. Before and after each experiment the crucible was weighed in order to see the weight loss during the production. After each experiment the walls of the graphite crucible was seen to be thinned. The weight loss

of the crucible was about 50%. For this reason, the graphite amount had to be lower than the stoichiometric quantity calculated above.

During the experiments in which 15.00 grams of graphite was used a layer of unreacted graphite powder was not observed above the slag. This amount of graphite was divided by the weight of ore and graphite to ore ratio of 0.15 was found. In the experiments with aim of examining the effect of the quantity of graphite in the charge during smelting experiments, graphite to ore ratio was taken as 0.05, 0.10 and 0.15. In all the other runs graphite to ore ratio was constant at 0.15.

It is seen from figures 4.18 and 4.19 that the manganese distribution ratio and the silicon distribution ratio increase with an increase in the graphite / ore weight ratio. Since the reduction reactions of MnO and SiO_2;

$$MnO + C_{(s)} = Mn + CO_{(g)} \qquad (20)$$

$$SiO_2 + 2C_{(s)} = Si + 2CO_{(g)} \qquad (21)$$
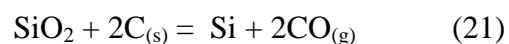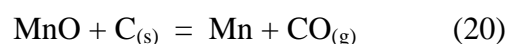
take place by carbon it is an expected result that increasing the quantity of graphite in the system increases the extent of the reduction of these oxides from the slag. The manganese and silicon recovery also increases with the addition of more graphite into the system as seen from figure 4.20.

Figure 4.18 Effect of Graphite / Ore Weight Ratio on Manganese Metal – Slag Distribution Ratio
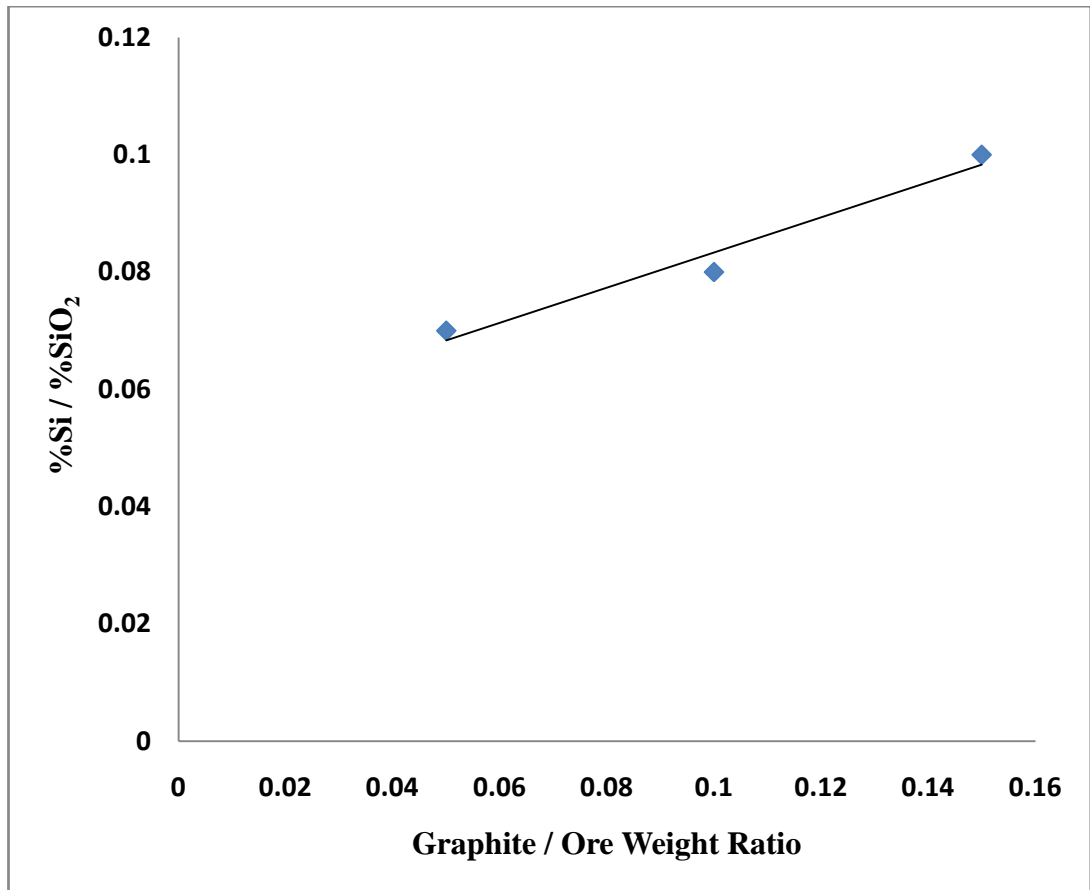
Figure 4.19 Effect of Graphite / Ore Weight Ratio on Silicon Metal - Slag Distribution Ratio
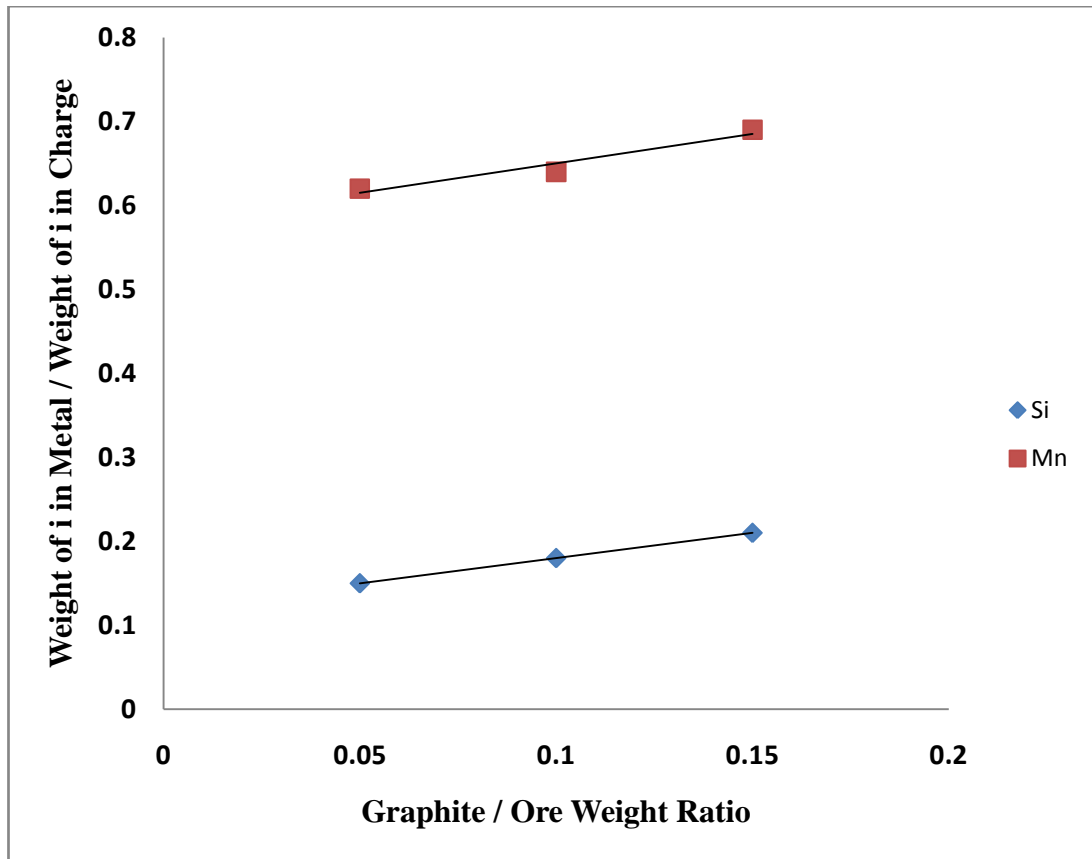
Figure 4.20 Effect of Graphite / Ore Weight Ratio on Manganese and Silicon Recoveries
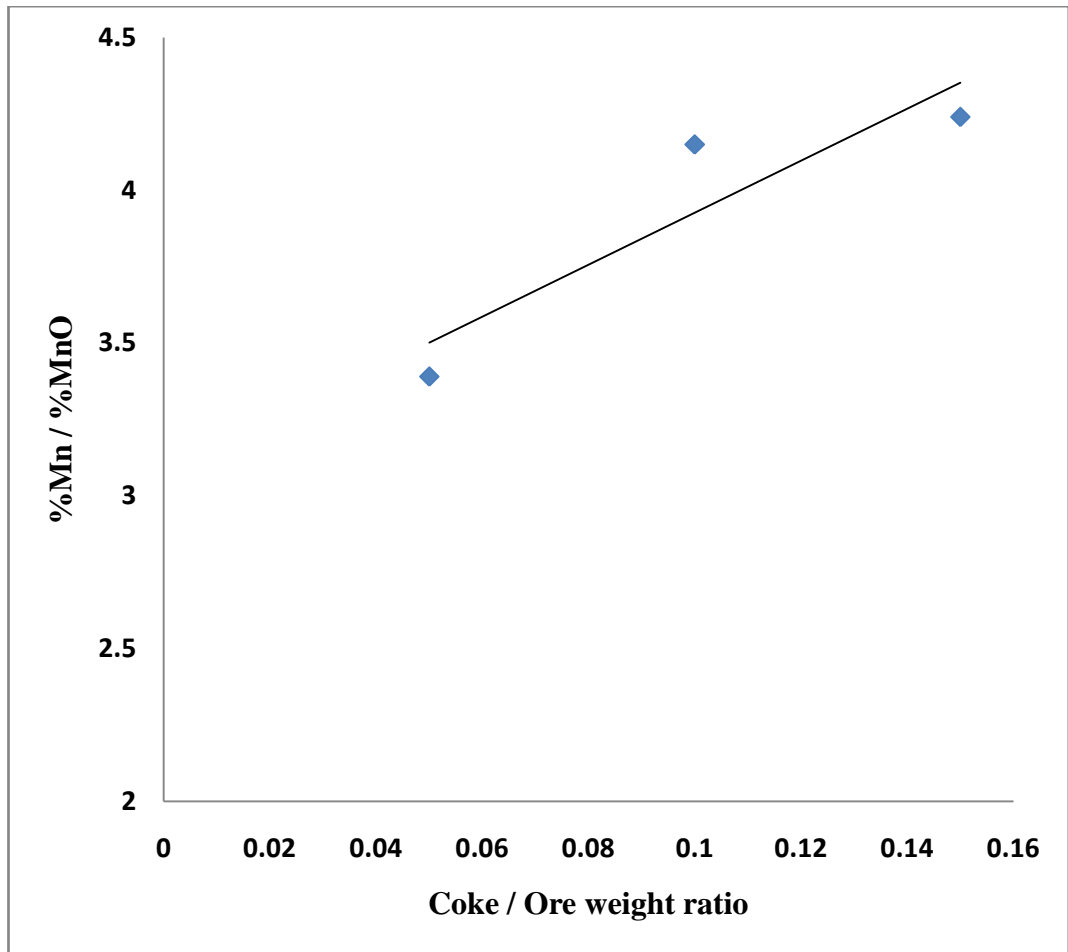
CHAPTER 5

CONCLUSIONS

In this study the production possibilities of high carbon ferromanganese by smelting Erzincan manganese ore with graphite powder in graphite crucibles has been investigated. The variation of smelting time, charge basicity, *graphite* to ore weight ratio and fluorspar addition has been used as experimental parameters. Experiments were conducted at 1600 ^{o}C in an electronically controlled muffle furnace.

Effect of time on experiments was investigated in the range 1 to 5 hours. It was found that almost all of the iron oxides in the charge were reduced into metal in less than 1 hour whereas reductions of MnO and SiO_2 were still not complete at the end of 5 hours. The results indicated that metal Mn and Si contents and Mn and Si recoveries from the charge increased with time. Slag SiO_2 content was found to remain almost constant whereas slag MnO content was found to decrease with time.

Erzincan manganese ore is not a self − fluxing ore, %CaO / %SiO_2 < 1. CaO was added to the charge to study the effect of basicity on smelting. Experiments were conducted with charge basicities of 1, 1.25 and 1.5. Results showed that manganese metal − slag distribution ratio increased and silicon metal − slag distribution ratio decreased with increasing charge basicity. Mn recovery was found to increase with increasing charge basicity whereas Si recovery decreased with increase in the charge basicity.

Fluorspar was added into the charge in amounts of 2.5% and 5% of the weight of CaF_2 free charge. Fluorspar addition resulted in good slag − metal separation. Manganese metal − slag distribution ratio increased and silicon metal - slag distribution ratio decreased with increase in CaF_2 addition. Mn recovery from

the charge increased whereas Si recovery from the charge decreased with the addition of fluorspar into charge.

Effect of graphite to ore weight ratio was investigated by conducting experiments with graphite to ore weight ratios of 0.05, 0.10 and 0.15. It was concluded that increase in graphite to ore weight ratio increased manganese and silicon metal – slag distribution ratios and manganese and silicon recoveries from the charge.

Experimental results show that it is possible to produce high carbon ferromanganese with above 75% manganese content close to chemical composition specified by ASTM standards by smelting Erzincan manganese ore. Manganese recovery during the smelting experiments was about 60 – 80 percent.

REFERENCES

1. Christie T., "Mineral Commodity Report 7 - Manganese", New Zealand, Institute of Geological and Nuclear Sciences Ltd., 2007

2. Akarca Ş.S., "Beneficiation of Denizli-Tavas Region Manganese Ores", Master of Science Thesis in Metallurgical and Materials Engineering Department, Middle East Technical University, Ankara, August 2000

3. Elyutin V.P., Pavlov Y.A., Levin B.E. and Alekseev E.M., "Ferroalaşımların İstihsali Elektrometalurji", İstanbul Teknik Üniversitesi Kütüphanesi, pp. 104 – 175, 1968

4. "Mineral Commodity Summaries 2009", U.S. Department of the Interior and U.S. Geological Survey, Washington, 2009

5. Corathers L. A., "2006 Minerals Yearbook", U.S. Department of Interior and U.S. Geological Survey, 2008

6. "Manganez Özel İhtisas Komisyon Raporu", VIII. Beş Yıllık Kalkınma Planı, Devlet Planlama Teşkilatı, Ankara, 2001

7. Geveci A., "METE 516 Production of Ferroalloys Lecture Notes", Middle East Technical University, Ankara, 1998

8. American Society for Testing and Materials (ASTM), "Annual Book of ASTM Standards", Volume 01.02, "Ferrous Castings; Ferroalloys", pp. 59 - 61, 1993.

9. Zhang W and Cheng C. Y. "Manganese Metallurgy Review. Part I: Leaching of Ores/Secondary Materials and Recovery of Electrolytic / Chemical Manganese Dioxide", Hydrometallurgy 89, pp.137 – 159, 2007

10. Corathers L. A., "2007 Minerals Yearbook Manganese [Advance Release]", U.S. Department of Interior and U.S. Geological Survey, 2009

11. Mulko G. N., Bondar A. A., Zaitsev V. A. Nitskii E. A. And Cherkasov E. G." Making Ferromanganese in Blast Furnaces", Metallurgist, vol.44, nos. 1 – 2, pp. 51 – 55, 2000

12. Akıl C., "Optimization of Conditions to Produce Manganese and Iron Carbides from Denizli-Tavas Manganese Ore by Solid State Reduction", Master Of Science Thesis in Metallurgical and Materials Engineering Department, Middle East Technical University, Ankara, 2007

13. Holappa L. And Xiao Y., "Slags in Ferroalloys Production – Review of Present Knowledge", The Journal of the South African Institute of Mining and Metallurgy, pp. 429 – 437, 2004

14. Matricardi, L. R., Downing, J. and Updated by Staff "Manganese and Manganese Alloys" Kirk-Othmer Encyclopedia of Chemical Technology, 2005.

15. Olsen S.E., Tangstad M. and Lindstad T., "Production of Manganese Ferroalloys", Tapir Academic Press, pp. 205 – 213, 2007

16. Wellbeloved D. B., Craven P. M. and Waudby, J. W., "Manganese and Manganese Alloys" Ullmann's Encyclopedia of Industrial Chemistry, 2000

17. Hahn, Jr., W. C. and Muan, A., "Studies in the System Mn - O", Am. Jour. of Sci., vol. 258, pp. 66 – 78, 1960.

18. Dressel, W. M. And Kenworthy, H., "Thermal Behaviour of Manganese Minerals in Controlled Atmospheres", U. S. B. M.. Rep., no. 576, p.35, 1961.

19. Tereyama, K. and Masao, I., "Study on Thermal Decomposition of MnO_2 and Mn_2O_3 by Thermal Analysis", Trans. Japan. Inst. Metals, vol.24, no.11, pp. 754 – 758, 1983.

20. Kor, G. J. W., "Thermal Decomposition of Mn_2O_3 and the reduction of Mn_3O_4 by C and CO", Metallurgical Transaction B., vol.9B, pp. 307 – 311, 1978

21. Akdoğan, G., "Kinetics and Mechanisms of the Solid State Carbothermic Reduction of Wessel Type Ferromanganese Ore", PhD Thesis, University of Witwatersrand, Johannesburg, 1992

22. Rankin, W. J. And Van Deventer, J. S. J., "The Kinetics of the Reduction of Manganous Oxide by Graphite", South African Inst. of Min. and Metallurgy, pp. 239 – 247, 1980.

23. Urquhart, R. C., "The Physico – Chemical Properties of Slags Associated with the Production of High Carbon Ferromanganese", Canadian Metallurgical Quarterly, vol. 19, pp. 323 – 327, 1980

24. Glasser F. P., "The Ternary System CaO – MnO – SiO_2", Journal of American Ceramic Society, Vol.45, No.5, pp. 242 – 249, 1962

25. Zhao B., Jak E. and Hayes P.C., "Phase Equilibria in High MgO Ferromanganese and Silicomanganese Smelting Slags", ISIJ International, Vol.45, No.7, pp. 1019 – 1026, 2005

26. Zhao B., Jak E. and Hayes P.C., "Phase Equilibria in the System "MnO" – CaO – MgO – SiO_2 – Al_2O_3 with Al_2O_3/SiO_2 Weight Ratio of 0.17 and MgO/CaO Weight Ratio of 0.25 at Mn – Si Alloy Saturation", ISIJ International, Vol.46, No.11, pp. 1594 – 1602, 2006

27. Xuegong Bi et al., "Slag Compositions for Ferromanganese Making Blast Furnaces", Ironmaking and Steelmaking, vol.20, no.6, pp. 476 – 481, 1993

28. Bills, P. M., "Viscosities in Silicate Slag System", Journal of the Iron and Steel Institute, pp. 133 – 140, 1963

29. Emeksiz F., "Smelting of High Carbon Ferromanganese from Denizli-Tavas Manganese Ore", Master of Science Thesis in Metallurgical and Materials Engineering Department, Middle East Technical University, Ankara, September 1991

30. İmer S.T., "Smelting of High Carbon Ferromanganese from Denizli-Tavas Manganese Ore", Master Of Science Thesis in Metallurgical and Materials Engineering Department, Middle East Technical University, Ankara, September 1997

31. Keskinkılıç E., "Smelting of Silicomanganese from Denizli-Tavas Manganese Ore", Master Of Science Thesis in Metallurgical and Materials Engineering Department, Middle East Technical University, Ankara, 2001

32. Kalfaoğlu F., "Solid state carbothermic reduction of Denizli-Tavas manganese ore", Master Of Science Thesis in Metallurgical and Materials Engineering Department, Middle East Technical University, Ankara, 1997

33. Akıl C., "Optimization of Conditions to Produce Manganese and Iron Carbides from Denizli-Tavas Manganese Ore by Solid State Reduction", Master Of Science Thesis in Metallurgical and Materials Engineering Department, Middle East Technical University, Ankara, 2007

34. Türkdoğan, E.T., Kor, G.J. and Fruchan, R.J., "Studies of Blast Furnace Reactions", Ironmaking and Steelmaking, No.66, pp.268 – 280, 1980

35. Türkdoğan, E.T., and Hancock, R. A., "Equilibrium Measurements between Carbon Saturated $Mn – Fe – Si$ Melts and $CaO – Al_2O_3 – MnO – SiO_2$ Slags", Trans. Inst. Min and Met., Vol.67, pp 573 – 600, 1957

36. 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, pp. 524–528, 1965

37. Türkdoğan, E.T., "Silicon and Manganese Reactions in Ferromanganese Blast Furnace Processes", Journal of the Iron and Steel Institute, pp.74 – 79, 1956

38. Kor, G. J. W., "Equilibria Between Liquid $Mn – Si$ Alloys and $MnO – SiO_2 – CaO – MgO$ Slags", Metallurgical Transaction B., vol 10B, pp. 367 – 374, 1979