USAGE OF BORON COMPOUNDS IN COPPER PRODUCTION

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ΒY

AYDIN RÜŞEN

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Approval of the thesis:

USAGE OF BORON COMPOUNDS IN COPPER PRODUCTION

submitted by AYDIN RÜŞEN in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Metallurgical and Materials Engineering Department, Middle East Technical University by,

Prof. Dr. Canan Özgen	
Dean, Graduate School of Natural and Applied Sciences	
Prof. Dr. C. Hakan Gür	
Head of Department, Metallurgical and Materials Eng.	
Prof. Dr. Ahmet Geveci	
Supervisor, Metallurgical and Materials Eng. Dept., METU	
Prof. Dr. Yavuz A. Topkaya	
Co-Supervisor, Metallurgical and Materials Eng. Dept., METU	
Examining Committee Members:	
Prof. Dr. Abdullah Öztürk	
Metallurgical and Materials Eng. Dept., METU	
Prof. Dr. Ahmet Geveci	
Metallurgical and Materials Eng. Dept., METU	
Prof. Dr. Naci Sevinç	
Metallurgical and Materials Eng. Dept., METU	
Prof. Dr. Ali İhsan Arol	
Mining Eng. Dept., METU	
Assoc. Prof. Dr. C. Bora Derin	
Metallurgical and Materials Eng. Dept., İTU	

Date:

01.02.2013

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 : Aydın, RÜŞEN

Signature :

ABSTRACT

USAGE OF BORON COMPOUNDS IN COPPER PRODUCTION

Rüşen, Aydın Ph.D., Department of Metallurgical and Materials Engineering Supervisor : Prof. Dr. Ahmet Geveci Co-Supervisor : Prof. Dr. Yavuz A. Topkaya

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Copper losses to slag are generally between 0.7-2.3% during the copper matte smelting stage. In this study, the aim was to reduce these losses in the slag phase. For this purpose, usage of some additives (especially calcined colemanite labeled as CC, boric oxide-B₂O₃ and calcium oxide-CaO as well) as flux material was investigated.

The flash furnace matte-slag (FFM-FFS) obtained from Eti Copper Inc. and a master matte-slag (MM-MS) produced synthetically were used as starting materials. Additives were tested in various amounts under two different atmospheres (N_2 and low Po_2 obtained by mixture of CO₂/CO gases). Temperature and duration were also used as experimental variables.

Experimental results have indicated that 2 hours was sufficient to obtain a low copper content in slag about 0.3% and 0.4% for FFS and MS, respectively. It was also seen that the copper content in slag decreased with increasing CC addition at all oxygen partial pressures and at all temperatures. Furthermore, the addition of all additives up to 4% had great influence in lowering the copper content in the final slags (~0.3%Cu).

From FactSage calculations, it could be concluded that the colemanite addition decreased the liquidus temperature which led to early melting of slag and allowed enough

duration for settling of matte particles within the slag without substantial changing its viscosity, which resulted in less mechanical copper losses to the slag. By using colemanite in copper production, it was possible that a new application area for boron compounds which are produced in Turkey could be created.

Keywords: Pyrometallurgy, copper matte smelting, copper losses to slag, colemanite, viscosity of slag.

BAKIR ÜRETİMİNDE BOR BİLEŞİKLERİNİN KULLANILMASI

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Bakır matı izabesi aşamasında, curufa giden bakır kayıpları genellikle %0,7 ile %2,3 arasındadır. Bu çalışmada, curuf fazına giden bu kayıpların azaltılması hedeflenmiştir. Bu amaçla, flaks malzemesi olarak bazı katkı maddelerinin kullanımı (özellikle CC olarak adlandırılan kalsine kolemanit-2CaO.3B₂O₃.5H₂O, yanı sıra bor oksit-B₂O₃ ve kalsiyum oksit-CaO) araştırılmıştır.

Deneylerde, Eti Bakır İşletmelerinden temin edilen flaş fırın mat-curuf (FFM-FFS) ve sentetik olarak üretilen mastır mat-curuf (MM-MS) numuneleri başlangıç malzemeleri olarak kullanılmıştır. Çeşitli miktarlardaki katkı maddeleri iki farklı atmosfer altında (azot ve CO₂/CO gaz karışımı ile elde edilen düşük oksijen kısmi basınç atmosferleri) test edilmiştir. Bunların dışında, sıcaklık ve süre de deney değişkenleri olarak kullanılmıştır.

Deneysel sonuçlar, düşük bakır içerikli curuf (FFS ve MS için sırasıyla %0,3 ve %0,4) elde etmek için 2 saatlik sürenin yeterli olduğunu göstermiştir. Ayrıca, tüm oksijen kısmi basınçları altında ve tüm sıcaklıklarda curuftaki bakır içeriğinin CC ilavesinin artışı ile azaldığı görülmüştür. Bunun yanında, %4'e kadar tüm katkı maddeleri (CC, B₂O₃ ve CaO) ilavelerinin, nihai curuflar içindeki bakır miktarının yaklaşık %0,3 değerine azaltılmasında büyük bir etkiye sahip oldukları görülmüştür.

ÖΖ

FactSage hesaplamalarından, kolemanit ilavesinin curufun sıvılaşma sıcaklığını düşürdüğü, bunun curufun viskozitesi önemli ölçüde değişmeksizin curufun erken erimesine yol açtığı ve mat taneciklerinin çökelmesi için yeterli süreye imkân verdiği böylece daha az mekanik bakır kayıpları ile sonuçlandığı çıkarımı yapılabilmiştir. Kolemanitin bakır üretiminde kullanılması ile ülkemizde üretilen bor bileşikleri için yeni bir kullanım alanının oluşması mümkün kılınmıştır.

Anahtar Kelimeler: Pirometalurji, Bakır mat izabesi, curufa giden bakır kaybı, kolemanit, curuf viskozitesi.

to my wife Selmin and my daughter Elif Gökçe...

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TABLE OF CONTENTS

ABSTRACT	v
ÖZ	vii
ACKNOWLEDGEMENTS	х
TABLE OF CONTENTS	xi
LIST OF TABLES	xiv
LIST OF FIGURES	xvi
CHAPTERS	
1. INTRODUCTION	1
2. THEORETICAL BACKROUND OF COPPER METALLURGY	3
2.1 Introduction	3
2.2 History of Copper	3
2.3 Properties of Copper	4
2.4 Sources of Copper	5
2.5 Extraction of Copper	7
2.5.1 Pyrometallurgical Methods	8
2.5.1.1 Concentration of Copper Ores	8
2.5.1.2 Smelting of Copper Concentrates	10
2.5.1.3 Converting of Copper Mattes	18
2.5.1.4 Continuous Direct –To-Copper Smelting	18
2.5.1.5 Refining of Blister Copper	20
2.5.2 Hydrometallurgical Methods	20
2.6 Applications of Copper	21
2.7 Secondary Resources of Copper	22
2.8 Eti Copper Production Plant	23
3. COPPER SMELTING SLAG AND ITS VISCOSITY	27
3.1 Introduction	27
3.2 Physical Chemistry of Copper Smelting	27
3.3 Formation of Matte and Slag	28
3.3.1 Matte (Cu-Fe-S) System	29
3.3.2 Slag (FeO-Fe ₂ O ₃ -SiO ₂) System	31
3.4 Copper Losses to Slag	33
3.4.1 Control of Copper Losses to Slag	39

3.4.2 Recovering of Copper from Slag	40
3.5 Flux Usage in Copper Smelting	40
3.5.1 Usage of Boron Compounds as Fluxing Agent	41
3.6 Viscosity and Slag Structure	41
3.7 Viscosity Measurement	44
3.7.1 Experimental Methods	45
3.7.2 Estimation Models	46
4. EXPERIMENTAL	51
4.1 Introduction	51
4.2 Apparatus	51
4.2.1 Furnace	54
4.2.2 Gas Supplying System	54
4.2.3 Crucibles	55
4.3 Materials	56
4.3.1 Flash Furnace Matte-Slag (FFM-FFS)	56
4.3.2 Master Matte-Slag (MM-MS)	56
4.3.3 Fluxes (Colemanite, Boric Oxide and Calcium Oxide)	57
4.4 Characterization of the Matte and Slag Samples	58
4.4.1 Chemical Analyses	58
4.4.2 X-Ray Analysis	60
4.4.3 SEM Analysis	61
4.4.4 Thermal Analysis	64
4.5 Experimental Procedure	65
4.7 Modeling of Liquidus Temperature and Viscosity	66
5. RESULTS AND DISCUSSION	71
5.1 Introduction	71
5.2 Effect of Reaction Duration on Copper Losses to Slag with CC	
Addition	72
5.2.1 Experiments with EBİ Flash Furnace Slag-Matte (FFS-FFM)	72
5.2.2 Experiments with Synthetic (Master) Slag-Matte (MS-MM)	78
5.3 Effect of Oxygen Partial Pressure on Copper Losses to Slag with CC	
Addition	83
5.3.1 Experiments with EBİ Flash Furnace Slag-Matte (FFS-FFM)	83
5.3.2 Experiments with Synthetic (Master) Slag-Matte (MS-MM)	87
5.4 Effect of Temperature on Copper Losses to Slag with CC	
Addition	90

5.4.1 Experiments with EBI Flash Furnace Slag-Matte (FFS-FFM)	91
5.4.2 Experiments with Synthetic (Master) Slag-Matte (MS-MM)	95
5.5 Effect of CaO and B_2O_3 Additions on Copper Losses to Slag	97
5.6 Results of Liquidus Temperatures and Viscosity Calculations	104
5.7 Industrial Testing at EBİ	109
6. CONCLUSIONS AND RECOMMENDATIONS	111
REFERENCES	115
APPENDICES	
A: Vertical Furnace Temperature Profile and Temperature Calibration	121
B: CO-CO ₂ Gases Calibrations and Oxygen Partial Pressure Calculation	124
C: Calculation of Dissolved Copper in Slag	128
CURRICULUM VITAE	130

LIST OF TABLES

TABLES
Table 2.1 Properties of Copper 4
Table 2.2 Copper Mineral Types 5
Table 2.3 Copper Mine Reserves and Copper Mine Production in the World 7
Table 3.1 Calculated settling velocities for residence durations of different matte
droplets settling through molten slag
Table 4.1 Chemical analyses of all of the samples (FFM, FFS, MM and MS)
as wt.%
Table 5.1 Chemical analysis results of experiments with FFS and FFM with various
additions of CC and different reaction duration as wt.% (under nitrogen atmosphere
at 1250 °C)
Table 5.2 Chemical analysis results of experiments with MS and MM with various
additions of CC and different reaction duration as wt.% (under nitrogen atmosphere
at 1250 °C)
Table 5.3 Chemical analysis results of experiments with FFS and FFM with various
additions of CC and under different partial pressure of oxygen atmosphere as wt.%
(at 1250 °C for 2 hours)
Table 5.4 Chemical analysis results of experiments with MS and MM with various
additions of CC and under different partial pressure of oxygen atmosphere as wt.%
(at 1250 °C for 2 hours)
Table 5.5 Chemical analysis results of experiments with FFS and FFM with various
additions of CC at different temperatures as wt.% (at controlled $Po_2=10^{-9}$ atm. for 2
hours)
Table 5.6 Chemical analysis results of experiments with FFS and FFM with various
additions of CC at different temperatures as wt.% (under nitrogen atmosphere for 2
hours)
Table 5.7 Chemical analysis results of experiments with MS and MM with various
additions of CC at different temperatures as wt.% (at controlled $Po_2=10^{-9}$ atm. for 2
hours)

Table 5.8 Chemical analysis results of experiments with FFS and FFM with various	
additions of CaO and B_2O_3 as wt.% (under nitrogen atmosphere at 1250 °C for 2	
hours)	98
Table B.1 Po2 values corresponding to (Pco2/Pco) ratio	126

LIST OF FIGURES

FIGURES

Figure 2.1 Map of Copper Deposits in Turkey	6
Figure 2.2 Main processes for extracting copper from sulfide ores by	
pyrometallurgical route. Parallel lines indicate alternative processes. (*Principally	
Mitsubishi and Vanyukov smelting)	9
Figure 2.3 Typical Outokumpu flash smelting furnace	13
Figure 2.4 Noranda process reactor	15
Figure 2.5 Cutaway view of Isasmelt furnace (typically ~3.5 m diameter and 12	
m high, it smelts up to 3000 tons of new concentrate per day)	17
Figure 2.6 A schematic representation of Mitsubishi process	19
Figure 2.7 Industrial consumption of copper	22
Figure 2.8 Schematic flowsheet of Eti Copper Plant	24
Figure 3.1 Simplified partial phase diagram for the FeO-FeS-SiO2 system at	
1200 °C illustrating immiscibility resulted from SiO2 (equilibrated with metallic	
iron)	28
Figure 3.2 Simplified ternary phase diagram Cu-Fe-S at 1200 °C, showing paths	
for matte smelting; 40% Cu matte (A), reverberatory; 50% Cu matte (B),	
Outokumpu flash smelting; 65% Cu matte (C), Mitsubishi; 75% Cu matte (D),	
Noranda. Paths for converting; slag blow from A, B, C or D to E (white metal);	
Copper blow: E to F (high-sulfur copper)	30
Figure 3.3 Partial liquidus diagram for the system Cu ₂ S-FeO-FeS	30
Figure 3.4 The stability diagram of Fe-O-SiO ₂ at 1300 °C under 1 atm	31
Figure 3.5 Liquidus diagram and oxygen isobars for ternary system FeO-Fe ₂ O ₃ -	
SiO ₂	33
Figure 3.6 Laboratory studies on the effect of matte grade on copper losses	34
Figure 3.7 Effect of oxygen pressure on cuprous content of slag	35
Figure 3.8 Schematic representation of silica tetrahedron and structures of	
crystalline and liquid silica (White: Oxygen atoms, Black: Silicon atoms)	42

Figure 3.9 Stages in the breakdown of silica melt lattice brought about by the	
addition of an oxide of a divalent metal, such as CaO. Metal ions are	
represented by the shaded circles. The concentration of metal oxide increases	
from top to bottom	44
Figure 4.1 A schematic diagram of experimental set-up	52
Figure 4.2 A general view of experimental set-up	53
Figure 4.3 Saturation Magnetization Analyzer (SATMAGAN S135)	59
Figure 4.4 X-Ray diffraction patterns of EBİ flash furnace slag (FFS) and master	
slag (MS)	61
Figure 4.5 a, b, c) Backscattered electron images (BSE) of FFS, d) Secondary	
Electron (SE) image of FFS	62
Figure 4.6 EDS spectra taken from particles labeled on SE images in Figure 4.5	
with numbers 1 to 6	63
Figure 4.7 TGA-DTA curves of ground colemanite	64
Figure 5.1 Variations of the copper amount in FFS with the addition of CC and	
reaction duration (under nitrogen atmosphere at 1250 °C)	75
Figure 5.2 SE images of a representative sample of experiment S-12	76
Figure 5.3 EDS spectra taken from particles labeled on SE images in Figure 5.2	
with numbers 1 to 6	77
Figure 5.4 Variations of the copper content of MS slag with the addition of CC	
and reaction duration (under nitrogen atmosphere at 1250 °C)	80
Figure 5.5 Images of a representative sample of (F-11) under the same	
magnification for the same area a) SE, b) BSE	81
Figure 5.6 EDS spectra taken from particles labeled on SE and BSE images	
in Figure 5.5 with numbers 1 to 5 and general EDS spectra (6) taken from the	
complete SE image	82
Figure 5.7 Effect of partial pressure of oxygen and addition of calcined	
colemanite to FFS and FFM on copper losses to slag (at 1250 °C for 2 hours)	85
Figure 5.8 Color mapping of the representative slag sample (P-5)	87
Figure 5.9 Effect of partial pressure of oxygen and addition of calcined	
colemanite to MS and MM on copper losses to slag (at 1250 °C for 2 hours)	89
Figure 5.10 Color mapping of the representative slag sample (B-3)	90
Figure 5.11 Effect of temperature and addition of calcined colemanite to FFS	
and FFM on copper losses to slag (at controlled $Po_2= 10^{-9}$ atm. for 2 hours)	93
Figure 5.12 Effect of temperature and addition of calcined colemanite to FFS	
and FFM on copper losses to slag (under nitrogen atmosphere for 2 hours)	94

Figure 5.13 Effect of temperature and addition of calcined colemanite to MS and	
MM on copper losses to slag (at controlled Po ₂ = 10 ⁻⁹ atm. for 2 hours)	97
Figure 5.14 Effect of some additives (CaO, B ₂ O ₃ , CC) on copper losses to slag	
(under nitrogen atmosphere at 1250 °C for 2hours)	99
Figure 5.15 The separated matte-slag phases after experiments (at 1250 °C for	
2 hours under nitrogen atmosphere) with the addition of B_2O_3 a) 2%, b) 4%, c)	
6% and d) 10% (climbing of the slag including matte on the sides of the silica	
crucible). (*m.p: matte or metallic copper particles)	102
Figure 5.16 The separated matte-slag phases after experiments (at 1250 °C for	
2 hours under nitrogen atmosphere) with the addition of CaO a) 2%, b) 4%, c)	
6% and d) 10% (matte sticking to the slag)	103
Figure 5.17 The separated matte-slag phases after experiments (at 1250 °C for	
2 hours under nitrogen atmosphere) with the addition of CC a) 2%, b) 4%, c)	
6%, d) 10%, and e) without CC addition	104
Figure 5.18 Variations of the calculated liquidus temperature of the experimental	
slags with the addition of CC and reaction duration a) for S series, b) for F series	105
Figure 5.19 Change in liquid slag region with the addition of CC on phase	
diagram of FeO-Fe ₂ O ₃ -SiO ₂ calculated by "Phase Diagram" module of FactSage	
6.2	106
Figure 5.20 Variations of predicted viscosity of the resultant slags with the	
addition of CC and reaction duration	107
Figure 5.21 Change in liquid slag region with the 10% addition of CaO, B_2O_3 and	
CC on phase diagram of FeO-Fe ₂ O ₃ -SiO ₂ calculated by "Phase Diagram"	
module of FactSage 6.2	108
Figure A.1 Temperature profile in the hottest zone of the vertical tube furnace	122
Figure A.2 Temperature calibration of the vertical tube furnace	123
Figure B.1 Calibration curve of CO gas flow	124
Figure B.2 Calibration curve of CO ₂ gas flow	125

CHAPTER I

INTRODUCTION

Copper, history of which is dating back thousands of years is the most important nonferrous metal together with aluminum, nowadays. It is widely used in electrical industry (Communication, Electricity, Energy, Heating, Transport etc.) due to high electrical and heat conductivities. Copper is generally present as sulfides, oxides and carbonates in the earth's crust in forms of chalcopyrite, cuprite, azurite and bornite [1–3].

Pyrometallurgical route (concentration, smelting, converting and refining) is generally used to produce most of the primary copper from sulfidic ores [3]. In the smelting stage, two different liquid phases are formed; namely, a matte phase with high copper content and a slag phase including oxidized materials. Nearly 2.2 tons of slag containing 0.7-2.3% Cu is disposed to produce one ton of copper metal [3–5]. Iron oxide and silica are the main components of most copper smelting slags, while Al₂O₃, CaO, MgO etc. are present at concentration less than 10% apart from some copper and other valuable metals such as Co, Zn, Ni, etc.[3,6]. Not only the considerable amount of valuable metals in slag but also huge quantity of discarded slag resulted in very crucial economic as well as environmental problems for all copper plants [7–9].

Several investigations [10–12] have been carried out to recover these valuable metals, especially focusing on copper [13–15] from smelting slag by pyrometallurgical and/or hydrometallurgical methods. However, all of the results obtained have indicated that some part of the copper always remains in slag in the form of Cu₂O, Cu₂S or metallic phase. Copper losses to slag generally depend on matte grade, partial pressure of oxygen, slag composition (magnetite amount, silica saturation level and so its viscosity) and temperature [3,15].

In matte smelting, copper can be lost to slag both as mechanical and physicochemical losses [14–17]. The considerable parts of copper losses to slag arise from mechanically

entrained particles such as metallic copper or matte droplets which cannot settle to the matte phase by passing through the slag layer due to the high viscosity of slag or limited settling duration. The latter results from the solubility of copper in slag in the form of sulfide/oxide or in metallic form, meaning that the copper is present in slag melt as copper ions [6,13,18].

Silica (SiO₂) and limestone (CaCO₃) are the most common fluxing agents in copper smelting. Silica, the main fluxing agent, is used to facilitate the separation of matte and slag by generating fayalite (2FeO.SiO₂) phase which is formed with the reaction of SiO₂ with FeO from oxidation of iron sulfide in chalcopyrite. Although the best matte-slag separation occurs at saturation with silica, excessive amount of SiO₂ leads to increase in the viscosity of slag with the presence of magnetite and so more copper is lost in a more viscous layer which affects the settling rate of matte or copper inclusions [3,19]. It can be stated that these particles are kept in slag, which results in mechanical copper losses. On the other hand, the addition of calcium oxide (CaO) balances the basicity of slag, decreases the copper solubility in iron silicate slag and also decreases the melting point and viscosity of slag, but increases the density of slag [17,20,21]. As colemanite (2CaO.3B₂O₃.5H₂O) contains boric oxide (B₂O₃) which contributes to the decrease of liquidus temperature and density of slag [22,23], it should be possible to use it as flux to diminish copper losses in copper smelting. Besides, the studies conducted by some researchers [24-27] in the steel industry on colemanite usage as flux already proved that its addition decreases the viscosity and the melting temperature of the steelmaking slags.

The main goal of the present study was to minimize copper losses to slag, especially mechanical ones, by the addition of colemanite supplied by Eti Mine Works (Bigadiç-Turkey). Calcined colemanite (2CaO.3B₂O₃) was used on two different types of slag (a) as-received copper smelting slag obtained from Eti Copper Plant and (b) synthetically prepared copper smelting slag.

The synthetically prepared slag was a more oxidizing one and it was used to determine whether it would be possible to use colemanite also as flux in copper converting, besides silica. A computer software program named as FactSage, was used to estimate the changes in liquidus temperature and slag viscosity in this thesis study.

CHAPTER II

THEORETICAL BACKROUND OF COPPER METALLURGY

2.1. Introduction

In this chapter, the basic knowledge in copper history, properties, sources and application areas are given. In addition, the production methods of copper are presented in detail. Moreover, the secondary resources of copper in the world are summarized. Finally, the information about Eti Copper Plant is given.

2.2. History of Copper

History of copper starts about ten thousand years ago and continues until today. Initial copper objects such as weapon or jewelry produced by cold working of native copper about 9000 years ago have been found in Turkey. Technical breakthroughs, especially invention of smelting process and development of bronze, resulted in common usage of copper and start of the Bronze Age. The earliest copper smelting process is known to be realized in the Middle East around 4500 B.C. and it spread throughout to Asia and Africa in later centuries. Copper usage predominantly for weapon, tools and construction of machinery, decreased gradually at around 3000 B.C. by the invention of iron and aluminum and led to development of steel as well. After a few centuries, the demand for copper began to increase due to its usage as coinage originally developed in Turkey.

Copper has been used by mankind in early times as tools, jewelry, weapon and then coinage, roofing, plumbing etc. until discovery and widespread usage of electricity. Furthermore, after 19th Century, copper became a crucially important metal due to its high electrical conductivity in the world [1,3,28,29].

2.3. Properties of Copper

The chemical symbol for copper (Cu) comes from its Latin meaning "Cuprum" which means metal of Cyprus since copper was mainly mined on Cyprus, in the Roman era. Its atomic number is 29, its atomic weight is 63.546 g/mole, and its color is reddish-orange. Although there are 27 isotopes of copper, only two of them are stable with 63 and 65 atomic numbers. Copper as a transition metal is located with gold and silver in group 11 of the periodic table. Copper, having excellent electrical conductivity, is the best conducting material among all other elements next to silver. This feature makes it an indispensable metal in electrical and electronics industry. Copper with high thermal conductivity is also used in cooling systems. It is fairly resistant to atmospheric conditions, but sulfur and its compounds have corrosive effects on it. Due to being soft material (Mohs hardness scale value is 3), copper can be handled with ease (cold working) but casting and welding ability is not good. Other physical, atomic and miscellaneous properties of copper are given in Table 2.1 [1,3,28,30,31].

Solid Density (at RT)	8.96 g/cm ³	Ionization energies (1 st)	745.5 kJ/mole
Liquid Density (at MP)	8.02 g/cm ³	Ionization energies (2 nd)	1957.9 kJ/mole
Melting Point	1084.6 °C	Atomic radius	128 pm
Boiling Point	2562 °C	Magnetic ordering	Diamagnetic
Heat of fusion	13.26 kJ/mole	Electrical resistivity (20 °C)	16.78 n.Ώ.m
Heat of vaporization	300.4 kJ/mole	Thermal conductivity (20 °C)	401 W/m.ºK
Heat capacity (at 25°C)	24.44 J/mole.ºK	Thermal expansion (25 °C)	16.5 µm/ m.ºK
Crystal structure	FCC	Young's modulus	110-128 GPa
Oxidation States	(+1), (+2)	Shear modulus	48 GPa
Electronegativity	1.9 (Pauling S.)	Mohs hardness	3.0

Table 2.1: Properties of Copper [31]

2.4. Sources of Copper

Copper is widely dispersed in the Earth's crust in different forms; sulfides, carbonates, chlorides, silicates, oxides and sulfates. The most important minerals are sulfide type; chalcopyrite (CuFeS₂) and bornite (Cu₅FeS₄). All principle commercial copper minerals including secondary ones like chalcocite, covellite, malachite, azurite, etc. are listed in Table 2.2.

Mineral	Chemical Formula	
Chalcopyrite	CuFeS ₂	34.6
Bornite	Cu₅FeS₄	63.3
Chalcocite	Cu ₂ S	79.9
Covellite	CuS	66.5
Malachite	CuCO ₃ .Cu(OH) ₂	57.5
Azurite	2CuCO ₃ .Cu(OH) ₂	55.3
Chrysocolla	CuO.SiO ₂ .2H ₂ O	36.2
Atacamite	Cu ₂ Cl(OH) ₃	59.5
Cuprite	Cu ₂ O	88.8
Antlerite	CuSO ₄ .2Cu(OH) ₂	53.7

Table 2.2: Commercial Copper Milneral Types [3	Table 2	.2:	Commercial	Copper	Mineral	Types	[3]
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The average level of copper content in the Earth's crust is 68 g/t [31], but it does not usually exceed 2% value in any copper ore deposit. Copper ores can mainly be mined in two different ways depending on its concentration. They are generally mined in open pits when the average amount of copper found is between 0.5% and 1% or mined from underground if the percentage of copper is more than 1% on the average in ore deposits. However, cut-off grade for mining types is always dependent on operation costs and copper prices [3].

Although copper deposits are spread throughout of the world, the most important ones exist in Chile, Peru, USA, and China. Turkey is a relatively poor country in terms of copper minerals considering the fact that Turkey's copper reserves are 0.3% that of the world. Figure 2.1 shows map of Turkey's copper deposits (Küre, Ergani, Murgul, Çayeli, Madenköy, etc.). Today, there is only one integrated copper smelting plant with annually around 35000 ton blister copper production in Turkey located in Samsun to process the copper ores or concentrates obtained from Küre and Murgul deposits. Copper production and reserves data for leading countries in the world obtained from ICSG (International Copper Study Group) and USGS (United States Geology Survey) is given in Table 2.3 [3,32–35].



Figure 2.1: Map of Copper Deposits in Turkey [35]

COUNTRY	2008	2009	2010	2011°	Reserves
Chile	5360	5320	5420	5420	190000
United States	1220	1310	1110	1120	35000
Peru	1049	1260	1250	1220	90000
China	915	960	1190	1190	30000
Australia	875	960	870	940	86000
Indonesia	817	950	872	625	28000
Russia	675	750	703	710	30000
Zambia	502	655	690	715	20000
Turkey	83	100	105	97	2070
Other countries	3687	2965	3795	4160	181000
World total	15100	15130	15900	16100	690000

Table 2.3: Copper Mine Reserves and Copper Mine Production in the World (1000 tons) [31-33]

e: Estimated

2.5. Extraction of Copper

Metallic copper can be produced by hydrometallurgical or pyrometallurgical route depending on the ore type. In copper production, while pyrometallurgical route (concentration, smelting, converting and refining) is more suitable for sulfidic ores, hydrometallurgical method is mostly used for ores having oxidized minerals and rarely used for chalcocite (Cu₂S) mineral containing ores. Copper metal can also be obtained from recyclable objects such as scrap copper and copper alloys which are another major source of copper with approximately 20% of mine production [3,36,37].

2.5.1. Pyrometallurgical Methods

As stated above, different treatment techniques are available to produce blister copper or other end products. General tendency has been towards sulfidic copper ores since their abundance (more than 80% of the world's copper ores) and use are higher than oxidized ones. Therefore, the major part of pure copper metal is produced from sulfidic ores by pyrometallurgical route as shown in Figure 2.2. However, the pyrometallurgical processing of copper varies worldwide with respect to the charge materials, process, operating parameters, and the physical shape, size, as well as orientation of the vessel. Plant operations may be either batch, semi-continuous, or fully continuous to produce blister copper or other products.

All of these methods require a concentration stage since copper ores having too little copper (0.5-2% Cu) are not economical to be smelted directly. After this stage, concentrated copper ore is used as input material in one of the smelting processes (batch, semi-continuous, or fully continuous) to generate copper matte. Extraction proceeds with converting of mattes, fire-refining of blister copper and electro-refining of anode copper, respectively.

2.5.1.1. Concentration of Copper Ores

Copper ores, especially sulfidic ones, are not suitable for direct heating and melting due to the present less valuable grade (0.5-2% Cu) in them. Therefore, they need to be concentrated to obtain a concentrate containing up to or more than 20%Cu by physical processes before pyrometallurgical route. Fortunately, copper ores can be concentrated effectively by comminution (crushing and grinding) and then froth flotation stages in order to reach reasonable copper content.

A flotation reagent preferentially added to the system leads to the isolation of Cu minerals from gangue minerals by attachment of the Cu minerals on rising air bubbles and sinking of the other minerals. At the end of this process, a concentrate with more than 20% Cu is generally obtained to be used as input material in copper smelter plant [3,37].



Figure 2.2: Main processes for extracting copper from sulfide ores by pyrometallurgical route. Parallel lines indicate alternative processes. (*Principally Mitsubishi and Vanyukov smelting) [3]

2.5.1.2. Smelting of Copper Concentrates

Smelting is a metallurgical thermal process which is operated in a large hearth-type furnace at 1200 - 1300 °C under usually neutral atmosphere to separate the gangue (oxidized materials) from the sulfide minerals associated with the valuable metals.

In the smelting stage, by melting copper concentrates together with a suitable flux, mainly silica, two different liquid phases are formed: "matte" and "slag". The former is a copper rich phase including 40 to 70 %Cu and the latter is a less-dense silicate phase containing oxidized materials with as low copper content as possible. In addition to these molten phases, SO₂ gas is generated in this stage by oxidation of the S in the sulfide concentrates. Percentage of SO₂ among the off-gases coming from smelting and also converting stage plays an important role to able to produce sulfuric acid. Example reactions belonging to matte smelting can be written as;

2CuFeS ₂ + 13/4O ₂ =	Cu ₂ S.½FeS +	3/2 FeO + 5/2SO ₂	(Rx. 2.1)
in oxygen	molten matte		
enriched air	1220 °C	$\Delta H_{^{0}25^{0}C}$ =-450MJ/kg mole CuFeS ₂	

2FeO + SiO ₂ =	= 2FeO.SiO ₂		(Rx. 2.2)
silica flux	molten slag (fayalite)		
	1250 °C	$\Delta H_{^{o}25}o_{c}$ =-20MJ/kg mole FeO	

During smelting, apart from the matte and slag, magnetite (Fe₃O₄) can appear as a separate phase due to the oxidizing conditions in the furnace. It settles down to the bottom of the hearth which leads to an increase in copper losses and a decrease in operational volume of the furnace. Magnetite with higher melting point than that of slag also affects the slag viscosity adversely. Therefore, it should be reduced by adding carbon to form liquid FeO in the slag. As a result of this, a decrease in slag viscosity and an improvement in settling rate can be obtained [3].

All of the pyrometallurgical copper production methods are accompanied with copper losses to slag varying between 0.7-2.3% Cu. Therefore, the main purpose of the copper matte smelting is to generate a slag with the minimum Cu content. The subject of copper losses to slag is explained in detail in Chapter 3.

Copper mattes are mostly smelted in flash furnaces and top lance furnaces (at the start of 2010 there were 35 flash furnaces and 12 top lance furnaces), and less frequently in reverberatory, blast and electric furnaces [3,36].

Reverberatory Furnace Smelting

Reverberatory furnace was developed to be able to charge for smelting both copper sulfide concentrates and calcine in a molten bath with a processing capacity up to 1000 tons per day. As opposed to other methods, copper concentrate with 6-8%H₂O content can be charged to a reverberatory furnace. However, if the concentrate is charged to the furnace after roasting, it leads to lower energy consumption and achieves higher smelting rate.

In conventional reverberatory furnaces, several air-fuel burners are placed in one of the end walls to enable heating of the charged materials directly. Year after year, air-fuel burners have been replaced with oxy-fuel burners positioned at the furnace roof due to the following advantages: i) higher temperature resulting in faster heating and melting, ii) better focus of flame on the charge, iii) decreasing of heat loss owing to absence of nitrogen [3,36].

In this type of furnace, the oxidation of sulfides within the copper ores is limited and the main purpose is to yield/obtain a slag phase having the lowest copper content possible, and a matte phase with the highest grade of copper. Therefore, flue gases formed having 2-2.5%SO₂ is very poor to manufacture sulfuric acid, which is the main negative aspect for reverberatory type furnaces. These furnaces were widely used in the world in the past, but most of them were terminated with the invention of flash and new bath smelting methods since recent smelting processes require as much as half of the energy consumed by them [37].

• Blast Furnace Smelting

Blast furnace for copper matte smelting, designed after the iron blast furnace, was developed to smelt coarse high grade copper ores for both sulfidic and oxidic types. With a rectangular cross section, its shape is different from the iron blast furnace. In a characteristic blast furnace, there are three main regions for heating, reduction and smelting. Due to exhaustion of coarse high grade copper ores and improvements in new technologies, nowadays, these furnaces are mostly used as a secondary copper smelter [38].

Electric Furnace Smelting

Although electrical furnace shows similarities with reverberatory furnace in terms of copper smelting, only dry or roasted copper concentrate can be charged to this type of furnace. The furnace is heated to a desired temperature by applying electrical power on several graphite electrodes submerged into slag. By this way, molten slag and matte layers can be obtained separately. This method is thought to be environmentally better since the amount of off-gas, also SO₂ gas, is too little. Although the use of electric furnace leads to high electricity cost, it is widely operated in the world for smelting of scrap and recovering of copper from molten slags due to the low amount of off-gas output [36,37].

• Flash Furnace Smelting (Outokumpu and Inco)

Flash smelting was firstly installed in Finland by Outokumpu in early 1950's and a few years later a new designed autogenous flash smelting was developed in Canada by Inco in order to treat copper concentrates. Nowadays, flash smelting has become the standard technology in this field and more than half of copper smelting is performed by flash furnace process. When we consider industrial applications of flash smelting process, Outokumpu process (~ 30 plants) is more widespread in the world than Inco process (~ 5 plants) [3]. Basically, a trend in flash smelting is towards an autogenous process by supplying considerable oxygen enriched air blast and very fine copper concentrate. At the end of the process, a high grade matte with Cu-Fe sulfides is continuously tapped, and an iron silicate slag with little copper (1-2% Cu) is discharged in the opposite direction of the matte [3,36].

Outokumpu Flash Smelting

Outokumpu flash smelting process uses only air or oxygen enriched air to burn fuel as well as sulfur in dry and finely ground concentrates which are injected to the vertical reaction shaft using a jet burner and mixing with a suitable flux. In the furnace, the dry concentrate is oxidized and then smelted directly into the copper matte (50-70% Cu) and silicate slag (1-2% Cu). Combustion reaction between concentrate and oxygen-enriched air blast takes place as given in Rxs. 2.1 and 2.2.

Fine concentrate particles are already smelted when they arrive at the settler region of the furnace, during which hot gases exit from the furnace by means of an uptake. At the end of

process, copper matte is tapped continuously from the bottom of the furnace and transferred to converter. On the other hand, the slag formed is discharged regularly from the upper taphole to be transported the disposal area in order to recover metal values in it generally by flotation.

Typical Outokumpu flash smelting furnace, given in Figure 2.3, includes five main characteristics; i) at least one concentrate burner to integrate fine concentrate with oxygen blast and blow them into the furnace, ii) a reaction shaft to realize all reactions between oxygen and Cu-Fe-S particles, iii) a settler to gather matte and slag layers separately, iv) separate tapholes to remove molten matte and slag from the furnace, v) an uptake to dispose of off-gas containing SO₂ [3,36].



Figure 2.3: Typical Outokumpu flash smelting furnace [3]

In Outokumpu process, major part of the energy is supplied from the oxidation reactions of Fe and S; nevertheless, settler zone in the furnace needs to be heated in order to provide furnace's heat balance. High concentration of SO₂ in the off-gas allows manufacturing of sulfuric acid [37].

Eti Copper Company (called as EBİ located in Samsun) is the only plant in Turkey that produces Cu from primary ore. This facility has Outokumpu flash furnace smelting apart from converting and refining steps. Detailed information about EBİ will be given at the end of this chapter.

Inco Flash Smelting

Inco flash smelting principally is the same as Outokumpu process but it has some differences in its shape. In this process, uptake is located in the center of the furnace, and two concentrate burners are horizontally placed on both ends of the furnace. Inco process does not require extra/additional heat like Outokumpu; it is fully autogenous due to using highly oxygen enriched air blast. An important positive feature of Inco is to generate off-gasses with considerable amount of SO₂ (75-80% by volume), which is quenched with water, cleaned of dust and addressed to sulfuric acid plant. Matte (~60% Cu) is tapped and sent to the converter and slag (~1% Cu) is discharged to the disposal area without any Cu removal process [36,37].

Noranda Furnace Smelting

Noranda is a bath smelting process with a cylindrical shape (4-5 m diameter and 18-26 m long) and refractory lined furnace, shown in Figure 2.4, that can be applied to numerous materials such as complex concentrates, industrial waste, scrap and so on. In this process, oxygen-enriched air (sometimes with dried concentrate) is sent to the furnace through the submerged tuyeres (35-60 pcs. with 5-6 cm diameter), which leads to production of turbulence in bath and to the occurrence of high intensity smelting reactions. Simultaneously, moist concentrate, flux, scrap and coal are continuously fed to the furnace by means of "slinger"; a belt feed system located in the end-wall of the reactor on the bath. In order to obtain high SO₂ concentration in off-gases, operation conditions should be under control [3,36].

The Noranda process has some advantages; it a) does not require blending and/or drying facilities to feed the concentrate into the reactor, b) does not need the water cooling system, c) can make use of common siliceous flux, d) consume lower refractory compared to other methods.



Figure 2.4: Noranda process reactor [36]

Noranda reactor having a rotation mechanism and submerged tuyeres is similar in design to a copper matte converter like Peirce-Smith converter. For this reason, it was initially operated in the direct copper making mode (together with smelting and converting), but later it was modified and only used to matte smelting due to the lower production rate. Today, more than ten Noranda and El Teniente processes with a capacity ranging from 1000 to 3500 tons concentrate per day are operated throughout the world, mainly in Chile. The El Teniente reactor shape resembles very much to that of Noranda with respect to operating conditions and furnace design. Both reactors give super-high grade matte (70-72 %Cu) and a slag with 4-6 %Cu [36].

• Top Lance Furnace Smelting (Ausmelt and Isasmelt)

Top-lancing technology (TSL) was developed by the CSIRO in Australia in the early 1970s in order to get rid of some disadvantages of flash smelting such as generating high amount of dust, large size of vessel [39]. Nowadays, two different organizations (Ausmelt and Isasmelt) are commercially marketing this technology in the world for various applications; copper, lead and nickel smelting. Their operating conditions and furnace shapes are very similar to

each other [3]. A schematic view of Isasmelt furnace is given in Figure 2.5. TSL technology has made an important progress in recent years. Nowadays, several smelters are under construction in various countries (China, Russia, India and Peru) [40].

In Ausmelt/Isasmelt smelting, agglomerated moist charge, flux and coal are continuously charged into a refractory lined cylindrical furnace, and oxygen enriched air with fuel is injected to the furnace by means of a submerged lance to generate vigorously stirred bath. In order to protect the lance from physical and chemical damages and to extend its service life, it is covered with frozen slag. The mixture of the matte and slag is tapped regularly into a settling furnace heated electrically or fuel-fired so that they are separated from each other. After separation, the matte (~60% Cu) is transferred to converting furnace and the slag (~0.7% Cu) is discarded to waste area. The off-gas including 25%SO₂ is handled and sent firstly to waste heat boiler, then to gas cleaning stage and finally to sulfuric acid plant [39,41].



Figure 2.5: Cutaway view of Isasmelt furnace (typically ~3.5 m diameter and 12 m high, it smelts up to 3000 tons of new concentrate per day) [3]

2.5.1.3. Converting of Copper Mattes

Blister copper is obtained by converting Cu matte produced by one of the aforementioned processes. Metallic copper production takes place via a two-stage process:

Slag-forming stage;

Iron sulfide in the matte is preferentially oxidized by blowing of air or oxygen enriched air via submerged tuyeres and so iron oxides combine with silica flux to generate a slag containing about 25 % SiO₂ and 2 to 8 % Cu which is recycled to the matte smelting stage or treated separately for copper recovery. At the end of this stage, copper sulfide called white metal remains in the matte;

II) Copper making stage;

Cu₂S remaining at the end of first stage is further oxidized to form SO₂ and blister (metallic) copper which is subjected to refining operations.

Although there are three types of converters: Peirce-Smith, Hoboken and Top Blown Rotary in use or under construction, 90% of Cu matte converting is done in the cylindrical type Peirce-Smith converter; this is due to its high chemical efficiency and simplicity. By contrast to smelting, Peirce-Smith converting, a batch (discontinuous) process causes unsteady flow of SO₂ in off-gasses. In addition, the process allows leakage of SO₂ and air leaks into offgasses when converter's mouth opens during charging and pouring. Hoboken converter was developed to minimize air leakage by using a 'goose neck', which leads to an increase in SO₂ concentration in off-gas. However, in order to prevent accretion of splash and dust in the 'goose neck', considerable care should be taken. That's why, industrial usage of it is limited [3].

2.5.1.4. Continuous Direct –To-Copper Smelting (Mitsubishi Process)

For many years, researchers have investigated the production of blister copper at one step, i.e., combining smelting and converting stages. It is expected that combining of these two stages will lead to some advantages; such as steady flow of SO₂ gas, saving of energy and lowering of costs. However, studies showed that copper-making in one furnace is not possible due to the formation of a slag with approximately 15% Cu as copper oxide (about 25% of the Cu entering a direct copper smelting furnace ends up as dissolved copper in the
slag). In spite of the disadvantage of this Cu rich slag, due to advantages of the continuous processing, researchers tried to improve continuous copper-making from concentrates. Three industrial smelting/converting processes were individually developed by Mitsubishi, Outokumpu and Noranda. With known at least four facilities in use, Mitsubishi process is the most advanced and common process among them [3,36].

Mitsubishi process is operated continuously with three furnaces; smelting (S), electric slag cleaning (CL) and converting (C), which are connected to each other according to gravity flow of molten material. Figure 2.6 shows a schematic representation of Mitsubishi process. In smelting furnace, dried copper concentrate, flux, coal and oxygen-enriched air are injected to the furnace by means of vertical lances. After oxidation of Fe and S in the concentrate, the matte (65-70%Cu) and iron-silicate slag are formed, and they are continuously transferred to CL furnace. In this furnace, matte- slag separation takes place due to the density differences in the CL furnace. While the matte continuously flows to the C furnace to convert to metallic copper, the slag with 0.7-0.9%Cu is discarded to stockpile after water granulation. In C furnace, mixture of CaCO₃ flux and oxygen-enriched air blow into the matte layer by means of lances to oxidize Fe and S in matte and to obtain molten blister copper. Converter's slag with a high copper amount is disposed regularly to water granulation step, and then it is fed to smelting furnace for recycling of Cu [42,43].



Figure 2.6: A schematic representation of Mitsubishi process [42]

2.5.1.5. Refining of Blister Copper

All copper production methods after smelting and converting proceed with the fire refining and then electro-refining processes. The aim of the fire-refining stage is to remove most of the sulfur and oxygen in the blister copper. Typical blister copper includes nearly 0.01%S and 0.5%O after Peirce-Smith converting. It is possible that during solidification, combining of dissolved S and O forms SO₂ bubbles in newly cast anodes, which affects negatively their physical properties. According to the stoichiometric calculations, when 0.01 wt.% dissolved S combines with the equivalent dissolved oxygen, 2 cm³ of SO₂ is produced per cm³ of copper at 1083°C [3,36].

Sulfur and oxygen from molten blister copper are removed in two steps. In the first step, air is blown through the melt to remove sulfur by oxidizing as SO₂. By this way, the amount of remaining sulfur is decreased to desired level. In the second step, oxygen removal as CO and $H_2O_{(g)}$ is carried out by blowing hydrocarbon (e.g. natural gas, LPG, propane) into the copper melt [44].

Electrolytic treatment of cast anodes is the last step of the pyrometallurgical production of copper. This process is carried out by electro-chemically dissolving copper from impure copper anodes into CuSO₄-H₂SO₄-H₂O electrolyte and by selectively electroplating pure copper from this electrolyte without the anode impurities. In principle, when an electric potential are applied between copper anode and a metal cathode in the electrolyte, copper is electro-chemically dissolved from the anode into the electrolyte. Afterwards, copper cations (Cu⁺⁺) in the electrolyte move to the cathode by convection and diffusion. During the electrorefining, Au, Pt, Se, Te, Pb and Sn are not dissolved in the electrolyte and so they don't gather at the cathode. They can be obtained from anode slimes. So this process helps to produce copper without harmful impurities and to separate noble metals like Au and Ag from copper to recover as by-products [3].

2.5.2. Hydrometallurgical Methods

In the world, over 80% of copper production is from the primary sulfide ores by smeltingconverting-refining routes. Other parts of the copper production are realized by hydrometallurgical treatment of copper ores (oxidic and chalcocite). In this method, copper ores are initially leached with a convenient reagent (mostly H₂SO₄), and solvent extraction method is subsequently applied to selectively separate and to increase the concentration of copper in the pregnant leach solution. Depending on the copper concentration in the pregnant leach solution; Electrowinning, Cementation or Precipitation can be carried out as the last step to yield copper metal by hydrometallurgical method [3,45].

There are several leaching methods; in-situ, dump, heap, vat, agitation and pressure oxidation leaching. The choice of the leaching method for raw materials is mainly dependent on copper value in the ore, the topography of the mine deposit, climatic conditions and cost of the processing such as milling, roasting and so on [45]. Major part of oxidic copper ores is treated by heap leaching due to the environmental and economic reasons (the low capital and production costs). The most popular solvent for copper-bearing minerals is dilute sulfuric acid (H₂SO₄) since oxidized copper minerals are quickly dissolved in it by the following reactions;

$$CuO + H_2SO_4 \rightarrow Cu^{++} + (SO_4)^{--} + H_2O$$
 (Rx. 2.3)

To enable the dissolution of sulfide minerals in sulfuric acid, firstly oxidation step is needed. At this stage, bacterial actions significantly accelerate the dissolution of sulfide minerals by the reaction like;

$$Cu_2S + 5/2 O_2 + H_2SO_4 ------→ 2Cu^{++} + 2(SO_4)^{--} + H_2O$$
 (Rx. 2.4)
(bacteria enzyme catalyst)

More recently, the use of hydrometallurgical method is showing some increase, which can be explained by some advantages of this method; lower investment costs, less environmental pollution, capable to treat low-grade ores (<0.5%Cu), and easier control of the process [45].

2.6. Applications of Copper

As aforementioned, copper has some beneficial properties; excellent electrical conductor & heat transfer, malleable & ductile, machinable & formable and corrosion resistant. Therefore, it is an important base metal required for various applications in different areas such as electricity, energy, plumbing, transportation, architecture, communication, as shown in Figure 2.7. Copper is essential and also crucial metal for several highly technological applications due to the physical, chemical and aesthetic properties. Therefore, it makes contribution to sustaining and improvement of society for developed or developing country [32].



Figure 2.7: Industrial consumption of copper [46]

As seen from Figure 2.7, with the excellent conductivity, copper is indispensable material for all kind of electrical/electronic applications which accounts for about 1/3 of the worldwide copper use. Construction including plumbing, roofing, taps, valves etc. is another important application area for copper and its alloys due to their high ability to resist to corrosion. Copper is widely used in transport industry (automobiles, airplanes, trains, ships and so on) and industrial machinery and equipment thanks to its machinability and durability beside its thermal and electrical conductivity. Additionally, when copper combines with other metals like zinc, tin or aluminum makes an alloy such as brass, bronze etc., they exhibit different characteristics and can be used in numerous specific applications. Since copper is produced as ingot, cathode, slab, wire or rod, copper and its alloys are mostly used in applications after fabrication to a new form such as wire, sheet, plate or powder by extrusion, rolling, drawing, melting, electrolysis or atomization.

2.7. Secondary Resources of Copper

In the world, copper is generally produced from primary copper-bearing ores. However, increasing demand of copper metal with progressing technological improvements has necessitated recovering metals from secondary resources or extraction of metals from low-grade ores. That is, secondary resources have become a very important source for copper, like other metals, due to depletion of high grade ores and increasing the demand of this metal. Fortunately, copper can be recycled without losing physical or chemical properties.

From this aspect, it is classified as the most recycled one among all of the other metals. As noted before, nowadays, about 80% of copper is produced from copper mines and remaining is obtained from industrial wastes (scraps) called as secondary copper.

Taking into consideration that more than two tons of slag containing 0.5-2%Cu are formed to produce one ton copper, slags which are discarded annually, about 25 million tons from copper manufacturers in the world are thought as another main source to recover copper. However, it is not easy to recover the valuable metals from slags due the processing difficulties. Huge quantity of discarded slags containing considerable amount of valuable metals cause very important economic and environmental problems for all copper plants, therefore, they should be evaluated by appropriate processes like flotation, magnetic concentration, leaching, electrical slag cleaning furnace treatment (slag settling) [7–9,32,47,48].

2.8. Eti Copper Production Plant

Eti Copper Co. (formerly Black Sea Copper Works) is the only plant in Turkey that produces copper from primary ores with Outokumpu type flash furnace. It was constructed by the government in 1973 in Samsun/Turkey in order to process copper ores from the Black Sea region deposits such as Murgul and Küre. It was privatized with Murgul and Küre deposits in 2004. After this date, it has been operated by the private company processing ~200000 tons concentrates and yielding ~38000 tons blister copper per year.

Eti Copper Plant (called as EBİ) includes mainly smelting, converting, anode casting, electrorefining, slag flotation and sulfuric acid production facilities. Its flowsheet is given schematically in Figure 2.8.

Concentrates from Murgul and Küre (mainly composed of Chalcopyrite), flux (mainly silica sand from Ladik or moulding sand) and lignite from Russia/Ukraine are provided from stockpiles area having 50000 tons capacity (mostly for concentrate) and loaded to rubber conveyors to be transferred to the smelting furnace. Charge mixture is initially passed through a drying furnace (rotary kiln type with 30 m in length and 3 m in diameter) at the rate of 45t/h in order to decrease the moisture of charge from 9-10% to 0.2% by using hot furnace gases at 350-400 °C from the waste heat boiler. Moisture content of the mixture at the end of rotary kiln should be as low as possible because it affects the quality and efficiency of combustion in reaction shaft.

Main components of the flash furnace are concentrate burner, reaction shaft, settler zone, off-gas uptake and matte-slag tapholes. At the top of the reaction shaft of the flash furnace, there is a concentrate burner having capacity of 750-800 tons concentrates per day to feed the dried charges after mixing with air blast and recycle dust and to provide a homogenous distribution of the mixture in the combustion tower.



Figure 2.8: Schematic flowsheet of Eti Copper Plant

Outokumpu flash furnace has a rectangular shape and it is 18m in length, 8 m in width and 2.5 m in height. Its reaction shaft and off-gas uptake sizes are 6.5 m in height with 5.5 m in diameter and 10.6 m in height with 3.5 m in diameter, respectively. In reaction shaft, most of the combustion reactions occur between the concentrates (Cu-Fe-S minerals such as chalcopyrite) and oxygen, and so called also as combustion tower. Its interior is lined with magnesia-chromite refractory nearly 30 cm thick and backed up by water-cooled copper

jackets or steel sheet. Interior of settling zone is also lined with the same bricks but having different thickness; some part of the roof ~20 cm, others ~40 cm and sidewall thickness ~40 cm and also supported with water cooled system. Even though refractories of furnace sidewalls are considerably thick; they are rapidly worn out due to magnetite-rich slag generation near water cooled zone and smelting process continues without them.

After combustion of dried Cu-Fe-S minerals with air blast (700-800 m³/h for one ton of feeding) in the shaft zone at about 1250 °C, molten droplets fall down to settler zone where matte and slag separation takes place owing to the density difference. Densities of EBI matte and slag are 4.7 g/cm³ and 3.7 g/cm³, respectively. Meanwhile, SO₂ bearing (8-12 %) hot gasses at around 1200 °C are sent to cooling, dust removal and sulfuric acid production by passing throughout the uptake of the furnace. Molten matte (45-50%Cu) and slag (0.8-1.5%Cu) are tapped regularly through their tapholes, separately. While the matte is sent to converter to obtain blister copper, the slag is discarded to disposal area to recover copper sequentially by cooling, grinding and flotation process.

As mentioned previously, converting of copper matte is realized in two steps; slag formation stage and blister copper forming stage, which can be summarized by the following reactions;

First stage;

$$2FeS_{(in matte)} + 3O_{2(in blast)} + SiO_{2(flux)} \rightarrow 2FeO_{2(slag)} + 2SO_{2(off-gas)} + heat$$
(Rx. 2.5)

Second stage;

$$Cu_{2}S (\text{in matte}) + O_{2} (\text{in blast}) \rightarrow 2Cu^{\circ} (\text{molten copper}) + SO_{2} (\text{in off-gas}) + \text{heat}$$
(Rx. 2.6)

In ETİ plant, the Peirce-Smith type converter is used to obtain molten blister copper (99-99.5%Cu). It has a rotating system with three positions; charging, blowing and skimming. In the first position, molten matte is charged to the converter and then air blast is supplied into molten matte via submerged tuyeres. Finally, the molten iron silicate slag is discarded with high amount of copper (4-8%Cu). To provide continuity in case of a converter failure or refractory wear, there are two Peirce-Smith converters in ETİ plant; while one is in operation, the other is at stand-by.

Molten blister copper needs to be fire-refined in order to remove its sulfur (0.01%S) and oxygen (0.5%O). Fire refining employs a rotary furnace similar to Peirce-Smith converter with much less number of tuyeres through which air and then hydrocarbon gas is injected, successively at above 1200 °C. Refining of 250 tons charge of blister copper requires ~1

hour for sulfur removal and ~2 hours for oxygen removal, totally ~3 hours. After the firerefining, molten copper with ~0.002% S and ~0.15% O as well as other impurities (Ni, Co, Fe, Sn, Sb etc.) is casted as anodes of about 55-60 kg of each.

Anode ingots are sent to the electro-refining process to obtain pure copper by removing almost all impurities. In this process, copper is dissolved into CuSO₄-H₂SO₄-H₂O electrolyte from fire refined anodes and only copper cations are collected onto the starting cathode metal which is selected as thin pure copper sheet. Electro-refining of each cathode takes about 3 weeks and then it is removed from the cell. By this way, pure copper (> 99.99%Cu) is obtained as cathode ingots and then they are sent to stock area to be sold.

Slags from smelter and converter are initially cooled in the pits having 12x15 meter dimensions for 24 hours and then cooling is accelerated by spraying water onto the slag. Cooled slag is crushed, ground and screened to obtain a proper particle size and so it enables the treatment in flotation unit. In this process, the copper slag is concentrated to over 20%Cu, which makes it a suitable feed material for flash smelting furnace.

Handling of waste gases including high level of SO₂ is important not only to manufacture sulfuric acid but also to protect the environment from sulfur dioxide emissions. Since off-gases leave the furnace at temperatures above 1200 °C, their thermal energy is initially gained back via a waste heat boiler, and then, they are cleaned by electrostatic precipitator from dust particles prior to entering the sulfuric acid plant [34,38,44,49,50].

CHAPTER III

COPPER SMELTING SLAG AND ITS VISCOSITY

3.1. Introduction

This chapter covers the copper smelting fundamentals in terms of matte and slag and gives important information about copper losses to slag in detail. Also, some important recommendations on the control of copper losses are offered and the recovery methods of valuable metals from slag are presented. Furthermore, the relationship between viscosity and slag structure are summarized. Finally, the experimental viscosity measurement methods and estimation models for molten slag viscosities are explained.

3.2. Physical Chemistry of Copper Smelting

It is well known that the main objectives of copper matte smelting are to generate two immiscible molten phases (matte and slag) by means of exothermic reactions (oxidation of Fe and S in the concentrate) and to make sure that all of copper in the concentrates are collected in the matte phase after they are sulfidized. However, copper in the concentrate tends to form copper oxide under oxidizing atmosphere. Fortunately, FeS in the matte reacts with the non-sulfidic copper in accordance with following reaction;

$$FeS_{(in matte)} + Cu_2O_{(in slag)} \rightarrow FeO_{(in slag)} + Cu_2S_{(in matte)}$$
(Rx. 3.1)

The equilibrium constant for (Rx. 3.1) is;

$$K = (a_{Cu2S} * a_{FeO}) / (a_{Cu2O} * a_{FeS})$$
(Eq. 3.1)

In this reaction, the equilibrium constant (K) value at the smelting temperature of 1250 °C is nearly 10⁴. If a_{Cu2S}/a_{FeS} is equal to 1 and a_{FeO} is equal to 0.3, then a_{Cu2O} is approximately

3*10⁻⁵. Such a high K value demonstrates that FeS almost completely sulfidizes whole copper oxide at the smelting temperature, which agrees with industrial experience [3,18,51].

3.3. Formation of Matte and Slag

The FeO-FeS-SiO₂ ternary diagram, seen in Figure 3.1, well describes the formation of matte and slag phases from an oxysulfide liquid by adding silica without any copper component [3,52].



Figure 3.1: Simplified partial phase diagram for the FeO-FeS-SiO₂ system at 1200 °C illustrating immiscibility resulted from SiO₂ (equilibrated with metallic iron) [3]

According to Figure 3.1, in the absence of silica, FeS and FeO combine to form a single oxysulfide liquid for more than 31% FeS at 1200 °C. However, the sufficient presence of

silica encourages the development of two different liquids, one of which is oxide-rich while the other is sulfide-rich liquid. From this figure, it can also be concluded that more silica addition leads to fairly good separation since a, b, c and d lines show the equilibrium compositions of the two melts. When SiO₂ saturation is reached, two liquid phases, which correspond to FeS-lean melt (slag) and FeS-rich melt (matte), acquire the compositions given by points A and B, respectively [3,18,51,53].

On the basis of ternary systems mentioned above, immiscibility between matte and slag in the quaternary system Cu₂S-FeO-FeS-SiO₂ is studied by Yazawa [16]. It was noted that immiscibility behaviour resembles very much to that of FeO-FeS-SiO₂ ternary system. Separation between the matte and slag starts in the system containing over 5% SiO₂ and reaches to maximum differentiation at silica saturation.

3.3.1. Matte (Cu-Fe-S) System

As stated before, the typical copper smelting matte is composed of Cu, S and Fe as well as minor constituents (Zn, Pb, As etc.). Although there are small solubilities of oxygen and silica in the matte, they decrease dramatically to negligible values with its increasing Cu₂S ratio. When the minor constituents are ignored, the matte can be described with a ternary system Cu-Fe-S as seen in Figure 3.2 [3,18,53].

In order to clarify the phenomena of the copper smelting system regarding matte-slag equilibrium, a comprehensive study was carried out on quasi-ternary system Cu₂S-FeO-FeS in equilibrium with silica-saturated slags which is given in Figure 3.3. Considering the smelting temperature (at about 1250 °C), there is a wide range of a single liquid region from eutectic point, located at about 27% Cu₂S, 57%FeS and 16%FeO, to nearly 60%FeO corresponding to 1250 °C isotherm. However, mattes with such a composition (having high FeO content) are never encountered [16,52,54].

The most crucial matte characteristics are; i) their density (5.2 g/cm³ for pure Cu₂S - 3.9 g/cm³ for pure FeS) which is higher than that of slag (3-3.7 g/cm³), ii) their relatively low viscosities, about 10 centipoise. These lead to settling of the matte in the bottom of the furnace [3].



Figure 3.2: Simplified ternary phase diagram Cu-Fe-S at 1200 °C, showing paths for matte smelting; 40% Cu matte (A), reverberatory; 50% Cu matte (B), Outokumpu flash smelting; 65% Cu matte (C), Mitsubishi; 75% Cu matte (D), Noranda. Paths for converting; slag blow from A, B, C or D to E (white metal); Copper blow: E to F (high–sulfur copper) [55]



Figure 3.3: Partial liquidus diagram for the system Cu₂S-FeO-FeS [52]

3.3.2. Slag (FeO-Fe₂O₃-SiO₂) System

Industrial smelting slags frequently based on fayalite contain mainly iron oxide (as FeO and Fe₃O₄) and SiO₂ as well as low amount of CaO, Al₂O₃, ZnO, PbO, MgO and so on. When minor oxides such as CaO, Al₂O₃, ZnO are ignored, the smelting slags can be identified by the components of Fe-O-SiO₂. The stability diagram of Fe-O-SiO₂ at 1300 °C under 1 atm. can be seen in Figure 3.4. Since it is not possible for metallic iron to exist in the slag under highly oxidizing atmosphere, iron can be found as Fe⁺² and/or Fe⁺³. For this reason, iron-silicate slags without any metal or liquid matte can be represented by the ternary system FeO-Fe₂O₃-SiO₂, given in Figure 3.5.



Figure 3.4: The stability diagram of Fe-O-SiO2 at 1300 °C under 1 atm

As seen from Figures 3.4 and 3.5, the liquid slag phase (2FeO.SiO₂ or Fe₂SiO₄ called as fayalite) is bordered by γ -Fe, SiO₂, Fe₃O₄ and FeO. In addition, it is seen that the composition of the condensed phases is strongly dependent on the partial pressure of

oxygen of the gas phase. Furthermore, these figures verify that Fe_2O_3/FeO ratio increases with increasing partial pressure of oxygen from too low levels (for equilibrium with solid iron, ~10⁻¹² atm at 1250 °C) to relatively high values (for equilibrium with solid magnetite, ~10⁻⁷ atm at 1250 °C) [53].

The industrial flash smelting furnaces generally operate with slags near the silica saturation which corresponds to the vicinity of the liquidus line AD, whereas industrial converters run with slags very close to magnetite saturation, i.e. by the side of CD liquidus line in Figure 3.5.

The important properties of slags are; i) their relatively high viscosity (500-2000 centipoise) considering that of matte (~10 centipoise) and Cu metal (~3 centipoise), ii) their density in the range of 3 to 3.7 g/cm^3 depending on the composition [3].

Unlike the matte, liquid slags have ionic structures consisting of molten oxides such as SiO_2 , FeO_x , Al_2O_3 , CaO. Their structures with some physical properties will be explained in detail at the end of this chapter.



Figure 3.5: Liquidus diagram and oxygen isobars for ternary system FeO-Fe₂O₃-SiO₂

3.4. Copper Losses to Slag

In all new and conventional copper making techniques, copper loss to slag is encountered as a major problem. While copper losses to slag are between 0.7 and 2.3%Cu in smelting stage, they reach to 4-8%Cu in converter step. In matte smelting, copper losses to slag can arise from several factors; matte grade, temperature, partial pressure of oxygen, slag composition such as magnetite amount as well as silica saturation level, and slag properties such as its viscosity, density and melting point [3,15,52,56]. Depending on these factors, as stated earlier, copper losses to slag can occur in two forms; i) originated from mechanically entrainment of matte or/and metal components, ii) dissolved copper species in slag in both oxide and sulfide forms [6,13,18].

The ratio of mechanically entrained versus dissolved copper differs from plant to plant because factors (operating conditions) affecting copper losses to slag alter for each plant. However, general opinion is that at lower matte grades, most of the copper losses arise from mechanically entrained matte and metallic copper. As for the higher matte grades (>70%Cu), the majority of losses result from physico-chemical losses [15–17].

• Effect of Matte Grade on Copper Losses

Several researchers [6,18,57–60] have investigated the matte-slag equilibrium in their laboratory studies. They agree with that copper content in slag is directly dependent on matte grade, which is explicitly seen in Figure 3.6. Apart from A and B lines, it can be seen in Figure 3.6, the more copper amount exists in matte, the more copper will dissolve into the slag, and the richer copper matte droplets will be entrapped in slag.



Figure 3.6: Laboratory studies on the effect of matte grade on copper losses [6]

Researchers [61] proposed an empirical equation related to copper solubility in slag;

$$K = (%Cu(in slag))/(%Cu(in matte))$$
(Eq. 3.2)

where K, empirical constant, was defined as 0.01. After years, Biswas and Davenport [3] corrected this constant as 0.013 by adding mechanically entrapped inclusions. However, K value is not applicable universally; its value can be shifted depending on composition of slag and smelting furnace conditions.

• Effect of Oxygen Partial Pressure on Copper Losses

After a number of studies were realized by researchers [52,62–64] about the effect of oxygen partial pressure on copper losses to fayalite type slags, they agreed with that the solubility of copper in silicate-saturated slags is strongly dependent on the oxygen partial pressure. Since most of the copper dissolved in cuprous form (Cu₂O) in intermediate oxygen potentials, Figure 3.7 gives the copper content in slag as cuprous against oxygen pressure equilibrated by CO+CO₂ atmosphere at different temperatures.



Figure 3.7: Effect of oxygen pressure on cuprous content of slag [52]

Toguri and Santander [63] derived an empirical relation from their experimental results to estimate solubility of copper in fayalite slag in equilibrium with FeS-Cu₂S as seen in Eq. 3.3, and they also stated that there is a linear relationship between copper solubility and $(Po_2)^{1/4}$ at a constant copper activity.

Wt.%Cu_(in slag) = 27.59*(a_{Cu2O})^{1/2} (at 1250 °C) (Eq. 3.3)

Where a_{Cu2O} is activity of copper oxide which can be calculated by using Rx. 3.1. In Eq. 3.1 (equilibrium constant of Rx. 3.1), the matte was assumed as a first approximation to form ideal solution, and assuming that a_{FeO} =%FeO in slag (nearly 0.4 for fayalite slag). Therefore, one can find wt.%Cu in slag which corresponds to physicochemical losses as Cu₂O.

• Effect of Temperature on Copper Losses

Temperature is another factor affecting the copper losses to slag by two different ways. One of them is negative effect that copper solubility in silica-saturated fayalite slag increases with increasing temperature, i.e. higher physico-chemical losses [62,63,65]. However, in the second effect, an increase in temperature decreases viscosity of slag and this leads to a decrease in mechanical losses [54,56,66–68].

Effect of Slag Composition on Copper Losses

As stated, the principle components of fayalite slag are silica and iron oxide (FeO_x, magnetite) apart from minor amounts of CaO, Al₂O₃, and alkali oxides. Silica flux should be added to the system as much as possible to get well separation, however, higher silica increases slag viscosity and this ends up with the increase in mechanically entrapped copper losses. On the other hand, the solubility of copper decreases with increasing silica level in slag, i.e. lower physico-chemical losses. Yannopoulos [56] noted that the minimum copper losses arising from mechanical entrainment can be obtained with 35%SiO₂ content of the slag.

There seems to be an agreement in the literature [17,56,69-71] that as CaO content (up to 15%) of slag increases, the copper solubility in slag as well as viscosity and melting point of slag decreases, but Al₂O₃ has the reverse effect on copper loss, i.e. alumina increases the

viscosity of slag and so copper losses to slag increase. It was reported that the minimum copper losses to slag were obtained by 8% CaO addition to a slag containing 30% silica.

Magnetite is considered/accepted a common problem in copper metallurgy. Presence of considerable quantity of magnetite (including >7% Fe₂O₃) causes an increase in viscosity of slag and thus mechanical losses increase [72]. Magnetite is also held responsible for increasing copper losses to slag via SO₂ gas bubbles according to the following reaction [3];

$$3Fe_3O_4 + FeS \rightarrow 10FeO + SO_2$$
 (Rx. 3.2)

Furthermore, increasing settlement of magnetite in the furnace hearth leads to decreases in furnace volume and so production capacity.

• Effect of Physical Properties of Slag on Copper Losses

In smelting of copper, the physical properties (viscosity, density, surface tension and interface tension) of slag and matte are evidently excessively important to achieve good separation between matte and slag.

Viscosity plays a very crucial role in most of the metallurgical processing, especially in copper smelting and converting stages. It causes not only mechanically entrained copper losses to slag but also several operating problems related to skimming and tapping of slag.

Several researchers [3,19,54–56,73] are in good agreement that the matte particle droplets from several millimeters up to a few microns are floated into the slag by SO₂ bubbles according to Rx. 3.2. The settling rate (velocity) of these matte particles which are mechanically entrapped or floated in the slag can be theoretically calculated by the Stokes' law (Eq. 3.4):

$$v = [g_c^*(\rho_{matte} - \rho_{slag})^*(r_D)^2]/(18^*\mu_{slag})$$
(Eq. 3.4)

where v is the rate of settling (cm s⁻¹), ρ_{matte} and ρ_{slag} are the density of matte and slag (g/cm³) respectively, μ_{slag} is the viscosity of the slag (Poise), and r_D is the radius of the particle (cm). This equation gives the most accurate results when matte droplet diameter is below 1mm. By the assumption that the alteration of slag and matte densities by differentiation in composition is insignificantly low, it can be concluded that settling rate is

directly related to slag viscosity and matte particle diameter. For constant matte particle diameter, viscosity can be defined as the main factor to influence the settling velocity. On the other hand, for a constant slag viscosity, settling velocity explains how long the matte droplets in different sizes settle the furnace bottom. Table 3.1 summarizes that the settling duration gets shorter as the matte particle diameter increases.

Apart from the matte diameter, settling rate is also influenced by lots of other parameters, mainly temperature and slag composition due to their effects on viscosity. Detail information about viscosity and its effects will be given at the end of this section.

According to investigations [3,54,56,74] the surface tension of smelting slag is not strongly dependent on temperature. However, an increase in basicity of slag increases the surface tension of slag due to the fact that most of the basic oxides have a high surface tension value. On the other hand, B_2O_3 with the lowest surface tension among all possible oxides in the slag shows a tendency to be located at the slag surface layer [75].

Drop Diameter (mm)	Settling Velocity (m/s)	Duration to settle through one meter of slag (s)
10	0.55	2
3	0.049	20
1	0.0055	183
0.3	0.00049	2039 (0.57 h)
0.1	0.000055	18349 (5.1 h)

Table 3.1: Calculated settling velocities for residence durations of different matte droplets settling through molten slag (Assuming ρ_{matte} 4500 kg.m⁻³ and ρ_{slag} 3500 kg.m⁻³)

As for interfacial tension of copper matte and fayalite slag, there is a linear decrease with increasing FeO/SiO₂ ratio, but a non-linear behavior seems with the addition of CaO in slag. Interfacial tension between copper matte and slag slightly increases up to 4% CaO addition, after this point it falls gradually [76].

Density is another important physical property of slag affecting copper losses to slag since copper matte is separated from fayalite slag by difference of specific gravity. Density differences between matte and slag should be as high as possible. Matte density is mainly affected by its Cu₂S content (from 3.9 for pure FeS to 5.2 for pure Cu₂S), and a slight decrease occurs with increasing temperature [3]. Researchers [74,76] noted that density of fayalite slag decreases with increasing silica content and increasing temperature as well as by adding basic oxides.

3.4.1. Control of Copper Losses to Slag

Several recommendations were made by Davenport and co-workers to minimize copper losses to slag in smelting stage [3]. These are;

I) Minimizing slag generation;

This can be achieved by increasing concentrate grades or by adding less flux. The former leads to presence of less gangue in the concentrate and so less slag production. The latter causes decrease in slag viscosity and so easier settling of matte. However, this also leads to an increase in activity of FeO and so two undesirable facts occur; more dissolved Cu₂O and more magnetite formation.

II) Minimizing copper concentration in slag;

This can be succeeded by supplying enough silica to produce well separated matte and slag phases, by maximizing slag fluidity (avoidance of excessive magnetite formation) and avoiding an extremely thick slag layer as well as by keeping away from tapping of slag with matte.

III) Optimizing settling conditions;

Smelting conditions which favor mechanically entrapped inclusions to settle easily to the matte phase should be improved by decreasing slag viscosity, by increasing settling duration and by minimizing slag layer. However, it may not be possible to apply all these conditions at the same time to a smelting furnace. Therefore, a separate furnace, called cleaning furnace of electric type, has been operated in some plants for smelting slags.

3.4.2. Recovering of Copper from Slag

In order to recover valuable metals (especially copper due to mechanical losses) from slags, researchers have developed several pyrometallurgical and/or hydrometallurgical methods which are flotation, magnetic concentration, settling of the matte particles and centrifuging as well as leaching processes with sulfuric acid, oxygen peroxide and sodium chloride. All of the results obtained have shown that some part of copper always remains in slag in the forms of Cu₂O, Cu₂S or in metallic form [10–15,18,47,48,77,78].

Pyrometallurgical slag settling in electric furnace is widely used to recover copper from slags. This step is operated immediately after smelting of concentrate to obtain a long settling duration for suspended matte droplets and also to convert the dissolved Cu₂O in the slag to suspended Cu₂S particles [3].

Froth flotation is another method to remove copper from slags, which is operated after slow solidification, crushing and grinding to -100 μ m. This way is commonly used to float matte particles (sulfide minerals) and metallic copper. However, if valuable metals in slag are in the form of oxide, they could not be operated effectively to recover them [8].

Leaching is also important method to extract the copper from smelting/converting slags. Lots of leaching agents such as sulfuric acid, hydrochloric acid, ammonia, cyanide have been used by researchers [8,10,47,79] for recovering of copper as well as other valuable metals. Sulfuric acid is the most common leachant and nearly 90% recovery of Cu can be obtained by sulfuric acid leaching if previously roasted, which is considered an alternative to flotation. However, silica gel formation during leaching decreases the recovery of copper to about 60%. Slow or rapid cooling of slag also directly affects the recovery of valuable metals to obtain higher or lower degree, respectively [79].

3.5. Flux Usage in Copper Smelting

During pyrometallurgical copper extraction, as stated earlier, silica is being widely used as a fluxing agent to promote well separation of matte and slag. However, there exist some inherent inconveniences such as high viscosity and strong acidity, which causes the loss of valuable metals. For these reasons, beside silica, limestone (CaCO₃) is usually added to balance slag viscosity and basicity. Several authors [13,24,26,80,81] have investigated other fluxing agents aside from CaO such as colemanite or boric acid for certain metallurgical industries.

3.5.1. Usage of Boron Compounds as Fluxing Agent

In copper metallurgy, to investigate the effect of colemanite and boric acid addition on the Murgul reverberatory furnace slag, a number of trials were carried out by Geveci in 1975 [13]. In these experiments, crushed and ground matte and slag samples were heated to 1250 °C under argon atmosphere in iron crucibles. It was reported that the matte-slag equilibrium condition was obtained very rapidly by the addition of boric acid or colemanite. Furthermore, it was noticed that there was no need to add colemanite or boric acid after reaching to the equilibrium copper content of slag; these additions corresponded to 6% boric oxide by weight of slag.

In iron and steel industry, colemanite was tested to be used as flux instead of CaF₂ during production of steel in BOF and also it was used as an additive material in sintering stage [24–26,81]. In these studies, it has been reported that the use of colemanite as a flux in steel production has several advantages; it decreases melting point of the slag and increases slag fluidity. It also increases the solubility of lime and magnesia. Furthermore, no significant damage was noticed in refractory materials. However, it was emphasized that there was one disadvantage of using colemanite in steel production. It was possible that boron in the colemanite could be reduced and passed to metal phase. So, the negative aspect was that some boron dissolved in the steel and increased its hardness which would cause hot tearing in rolling or forging.

3.6. Viscosity and Slag Structure

Viscosity is generally defined as an indication of the resistance to shear within the fluid. Considering that viscosity of melt is directly related to structure, it is one of the important physicochemical properties affecting copper losses to slag. In order to understand the effect of this phenomenon on slag, its structure was investigated by several researchers and their results demonstrated that each oxide in the slag can behave as a glass former (network-forming), a glass modifier (network-breaking) or an amphoteric oxide (network intermediates) [75,82].

As commonly known, the copper smelting slags are mixtures of iron-silicate with small amount of other oxides, i.e. they are frequently based on silicate structure. Studies on glassy and molten silica have indicated that the building unit is (SiO₄)⁴⁻ tetrahedral where Si⁴⁺ is positioned in the center and O²⁻ atoms are in the corners. In silicate slags, these silica

tetrahedra can form a high order polymeric species such as $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$ or $Si_4O_{13}^{10-}$ owing to the polymerization of silicate anions. SiO_2 as a pure glass former oxide leads to high viscosity of slag with low electrical conductance which corresponds to the presence of covalent bonding. In addition, high viscosity shows that a three dimensional covalent network of the crystals is kept on fusion. Figure 3.8 schematically represents the solid and molten structures of silica.

In tetrahedron structure, seen in Figure 3.8, one silicon atom is bonded to four oxygen atoms with four covalent bonds. To illustrate this two-dimensionally (for the sake of clarity), one of the covalent bonds (one of the oxygen atoms illustrated) is omitted.



Figure 3.8: Schematic representation of silica tetrahedron and structures of crystalline and liquid silica. (White: Oxygen atoms, Black: Silicon atoms) [82]

Covalent structure in silica has some widely known properties in solid form. For example, it is noticeably stiff and not easily deformable, and the bonds maintain the powerful interaction in molten form, which results in high viscosity of liquid slag. However, by the addition of a

(basic) metallic oxide such as K₂O, Na₂O, Li₂O, MgO, CaO, PbO, ZnO to the glass former (i.e. silica), the oxygen bridges between silica groups breaks down as follows;

$$(:: Si - O - Si:) + MO = 2(:: Si - O) + M^{2+}$$
 (Rx. 3.3)

The reaction between silica and metal oxide allows the entrance of negative charges on the unshared corners in which already present covalent bonds between tetrahedras are ruptured, and the cations are collected around the positions of negative charges. Therefore, a metal-silicate component probably forms as an initial crystalline structure. In this manner, two different kinds of oxygen may appear as bridging oxygen (BO) and non-bridging oxygen (NBO). The former act as links between tetrahedral units, and the latter is described as oxygen bonded to a cation such as Na⁺, Ca²⁺, Mg²⁺ etc. which is not tetrahedrally coordinated. The ratio of BO to NBO gives a hint about the polymerization degree of the silica melt.

According to X-Ray studies on Si-O tetrahedral in molten silicate, further addition of basic oxides leads to continuous breakdown of silica structure, as seen in Figure 3.9. These changes in the structure result in less viscous melt by altering it into an ionic conductor.

Apart from the slag composition, viscosity also notably depends on temperature. When temperature is increased, chains of the silica structure tend to be broken and so the viscosity of slag decreases. Although there are a few equations between viscosity and temperature, the most common one (Eq. 3.5) is derived by Arrhenius to explain the effect of temperature on viscosity:

$$\mu = A_A^* \exp(E_\mu/RT) \tag{Eq. 3.5}$$

where A_A is a constant depending on the slag structure, E_{μ} is the activation energy for viscous flow (also depending on structure), T is the temperature in Kelvin and R is the Gas constant [75].



Figure 3.9: Stages in the breakdown of silica melt lattice brought about by the addition of an oxide of a divalent metal, such as CaO. Metal ions are represented by the shaded circles. The concentration of metal oxide increases from top to bottom. [82]

3.7. Viscosity Measurement

Viscosity can be determined experimentally with various viscometers (or rheometers) or its value can be predicted by several mathematical methods developed on the basis of composition and temperature.

3.7.1. Experimental Methods

While there are many experimental instruments/methods to accurately measure the viscosity for low temperatures (<100 °C), they are limited in number for viscosity measurements for high temperatures (>1000 °C) due to the difficulties of operational conditions and material selections [83]. Nevertheless, researchers [52,54,66,84–86] have carried out countless experimental investigations for various slag systems due to the significance of slag viscosity in metallurgical applications. The main viscometer types which can be used at high temperature are summarized below:

<u>Falling sphere viscometer</u>: This viscometer is principally based on the Stoke's Law. It contains a circular cylinder filled with a fluid and a smooth sphere /ball positioned in the melt. The time period for the ball to fall the length of the cylinder is used to calculate the viscosity of the melt by means of the Stoke's Law. Falling body viscometers with simple design have been commonly used to quantify high viscosities of melts like glass and slag, but the method is not suitable to measure low viscosities as it is yields inaccurate results.

<u>Capillary viscometer</u>: A melt droplet is poured through a capillary tube and the time that it takes to reach the receiver is recorded. Viscosity is calculated by using the recorded time, radius of capillary, volume of melt droplet, applied pressure and length of the tube in the Hagen Poiseuille equation. Capillary viscometers are not suitable to measure physical properties at high temperature (>1200 °C) owing to the difficulties in both capillary material and crucible selection.

<u>Concentric cylinder (rotational) viscometer:</u> Rotational viscometer is the most accepted one among all types because it yields more accurate results and it is easy to operate. It is widely used to measure the dynamic viscosity of materials with Newtonian behavior, such as glass, slag and mould powders. In this method, the dynamic viscosity is determined through measurement of the torque or the rotation speed of a rotor immersed in the molten sample. The viscometer contains a centrally adjusted bob (spindle) in the cylindrical crucible.

More detailed information about the design and operation conditions of these viscometers as well as other methods, such as Oscillating, Rod elongation or Squeeze film viscometers, can be found in the literature [75,83,87,88].

3.7.2. Estimation Models

Researchers [52,86,89–94] have developed lots of estimation models as a function of both temperature and composition to correlate physicochemical properties of slag based on the structural properties and the experimental results. Estimation models including a number of different approaches/equations can be classified as fully empirical, semi-empirical or fully mathematical equations in terms of temperature and composition. Indeed, a prediction model is composed of combining of two models; one of them is to correlate temperature effect e.g. Arrhenius, Weymann-Frenkel, Bockris-Reddy, Eyring, Quasi-structural, empirical, and the other is for compositional effect such as Urbain, Optical basicity, Quasi-structural, Thermodynamics as well as empirical models.

Fully empirical models are incomplex mathematical equations based on only experimental viscosity measurements/results depending on the slag components and operating temperature. Unfortunately, these type of models are valid for a narrow temperature and composition range studied by the authors [95]. An example for this model was noted by researchers [52] defining the term Kv (viscosity modulus) as follows;

$$Kv = wt.\%(FeO + CaO + MgO + Fe_3O_4) / wt.\%(SiO_2 + Al_2O_3)$$
(Eq. 3.6)

where Kv represents a simple base-to-acid ratio. In this equation, it was assumed that FeO, CaO, MgO and Fe₃O₄ as network breaking oxides have a similar effect on viscosity while SiO₂ and Al₂O₃ as network forming oxides have opposite effect.

Utigard-Warczok equation [75] is another well example for fully empirical models. They also proposed a simple viscosity ratio (Vr) depending on the slag constituents;

Vr= A/B;

(Eq. 3.7)

where A= SiO₂+1.5Cr₂O₃+1.2ZrO₂+1.8Al₂O₃;

B=1.2FeO+0.5(Fe2O3+PbO)+0.8MgO+0.7CaO+2.3(Na2O+K2O)+0.7Cu2O+1.6CaF2

This equation was modified in view of the activation energies of each item and temperature correlation, and so a new more sophisticated equation was obtained to calculate viscosity of multi-component slags as a function of composition and temperature;

$$Logn(Pas) = -0.49 - 5.1(Vr)^{0.5} + [-3660+12080(Vr)^{0.5}] / T(K)$$
 (Eq. 3.8)

McCauley-Apelian Equation is one of the semi-empirical models since a thermodynamic Clausius-Clapeyron equation is used to describe the temperature dependence of viscosity while slag constituents depend on the experimental data. Therefore, application of this equation is limited in terms of slag composition [95].

Urbain proposed a viscosity estimation model for slags based on Weymann-Frenkel equation in terms of temperature;

$$\eta = A^{*}T^{*}exp(10^{3*}B/T)$$
 (Eq. 3.9)

where A and B are related to the slag constituents (oxides) which are classified as 3 groups;

- glass formers (X_G= X_{SiO2}+X_{P2O5}),
- glass modifiers (X_M= X_{CaO}+X_{MgO}+X_{FeO}+X_{MnO}+X_{TiO2}+X_{Na2O}+X_{CaF2})
- amphoterics (X_A=X_{Al2O3}+X_{B2O3}+X_{Fe2O3}).

$$B = B_0 + B_1^* X_G + B_2^* (X_G)^2 + B_3^* (X_G)^3$$
(Eq. 3.10)

Riboud equation has the same formulation to that of Urbain. However, A and B values differs from that of Urbain, as seen in Eq. 3.12 and Eq. 3.13, and also slag components were divided into 5 groups instead of 3. These groups are;

- "SiO₂" = SiO₂ + P_2O_5 + TiO₂ + ZrO₂,
- "CaO" = CaO + MgO + FeO + B₂O₃,
- "Na₂O" = Na₂O + K₂O
- "CaF₂"
- "Al₂O₃"

$$InA = -19.81 + 1.73X_{CaO'} + 5.82X_{CaF2'} + 7.02X_{Na2O'} - 35.76X_{Al2O3''}$$
(Eq. 3.12)

$$B = 31,140 - 238,996X_{CaO'} - 46,356X_{CaF2'} - 39,159X_{Na2O'} + 68,833X_{Al2O3'}$$
(Eq. 3.13)

Initial lida model uses the Arrhenius equation in terms of temperature and uses basicity index to express viscosity as a function of slag components which are divided into two groups, namely basic and acidic, i.e. there is no any compositional effect for amphoteric oxides in this equation. Hence, the modified lida model has been developed by taking into consideration amphoteric oxides behavior separately for each slag system. Besides this, the model needs several physical properties, such as melting point, formula weight, molar volume, density etc., to calculate the viscosity of slag, which makes it more complicated [92].

Mill [75] proposed a new model (NPL: National Physical Laboratory, UK) based on optical basicity of slag (a measure of de-polymerisation) to predict viscosity of mould flux and slag. It is also based on Arrhenius equation (Eq. 3.14) with respect to temperature dependency. A corrected optical basicity (Λ_{cor}) is needed to adjust the composition considering amphoteric oxide (Al₂O₃). Therefore, A and B in Arrhenius equation can be determined as;

Inq(Pas)= InA + exp(B/T) (Eq. 3.14)
InA= -232.7 (
$$\Lambda_{cor}$$
)² +357.3 (Λ_{cor}) -144.2 (Eq. 3.15)

 $\ln(B/100) = -1.77 + 2.88/(\Lambda_{cor})$ (Eq. 3.16)

KTH model (commercial name is Thermoslag) developed in the Royal Technical Institute by Seetharaman et al [89] is based on Eyring equation which is proposed to predict viscosities of complex ionic liquids in terms of temperature. It is also based on Gibbs free energy of melt in the view of compositional dependence as follows;

$$\eta = h^* N_A^*(\rho/M)^* \exp(\Delta G_{\eta}/RT)$$
(Eq. 3.17)

$$\Delta G_{\eta} = \Sigma \Delta G_{\eta}^{(\text{oxides})} + \Delta G_{\eta}^{(\text{mix})}$$
(Eq. 3.18)

where $\Delta G_{\eta}^{(\text{oxides})}$ is Gibbs free energy of pure oxides and $\Delta G_{\eta}^{(\text{mix})}$ is Gibbs free energy for interactions of cations only. This method works well for fayalite based synthetic slags.

Kontratiev and Jak [94,96] proposed a new model to estimate the viscosity of molten slag by modifying Urbain model. Their modified model has been developed on the basis of a quasichemical thermodynamic model and Weymann-Frenkel equation. While in Urbain model, m and n are the experimental constants (Eq. 3.11), in modified Urbain model, m is described as a model parameter depending on the molar fractions of slag constituents. Another important modification is to use a continuous compositional dependence of B which was previously calculated separately for each modifier. After modifying, more accurate viscosity results could be obtained. B has a sophisticated mathematical expression including sets of parameters for each component. New m equation can be expressed for a quaternary system Al₂O₃-CaO-FeO-SiO₂ as follows;

$$m = m_A X_A + m_C X_C + m_F X_F + m_S X_S$$
(Eq. 3.19)

where X_A , X_C , X_F , and X_S represent the molar fractions of Al₂O₃-CaO-FeO-SiO₂ respectively, and m_A , m_C , m_F , m_S values are model parameters.

The results calculated by this model are in accordance with more than 3000 values obtained experimentally for various unary, binary and ternary systems. This model is integrated into FACT (Facility for the Analysis of Chemical Thermodynamics) software program which is widely used commercial program to estimate physical properties of slags.

In this study, Fact-Sage software program was used to estimate the viscosity of resultant slags as well as trends of liquidus temperature for final slags. More detailed information will be given in "Modeling of Liquidus Temperature and Viscosity" section in the next chapter.

CHAPTER IV

EXPERIMENTAL

4.1. Introduction

In this chapter, initially, the apparatus used during this study will be introduced. Then, the materials (matte-slag samples and colemanite) with their physical, chemical and mineralogical characterizations will be given. Procedure of these experiments will also be described. Finally, the modeling by FactSage software will be explained.

4.2. Apparatus

Experimental set-up mainly consisted of a high temperature vertical tube furnace and a gas supplying system including Argon (Ar), Nitrogen (N₂), Carbon monoxide (CO) and Carbon dioxide (CO₂) gases. In Figures 4.1 and 4.2 a schematic diagram and a general view of the experimental set-up used in this study are given, respectively.



Figure 4.1: A schematic diagram of the experimental set-up

52



Figure 4.2: A general view of the experimental set-up

4.2.1. Furnace

The vertical tube furnace consisted of a programmable temperature control unit and a recrystallized alumina reaction tube with 50mm inside diameter and 1000mm length enclosed by MoSi₂ heating elements which allowed up to 1700 °C maximum furnace temperature. The ends of the reaction tube were closed with silicon stoppers fitted with alumina rods for gas inlet and outlet.

Before the experiments, the hot zone of the tube furnace was determined, and a recrystallized alumina support rod with a plate was placed in this zone. Then, the radiation shields were placed at either end of the reaction tube to provide thermal insulation. After an empty silica crucible was inserted to the hottest region with the help of the support rod, the temperature profile of the furnace was obtained as given in Appendix A. According to the temperature profile of the furnace, the constant temperature zone was maintained in the range of ± 3 °C within the length of 80 mm which corresponded to silica crucibles' height. Furnace was heated to the desired temperature in exactly 5 hours. After being kept at that temperature for a certain period of time, it was cooled at a rate of ~4 °C/minutes in all experiments.

4.2.2. Gas Supplying System

Gas supplying system included four silica gel columns, two gas cleaning furnaces for CO and CO₂, four flow meters (two of them being capillary type for CO and CO₂), a gas mixing unit (to mix CO-CO₂ gases), a gas control unit (to change the type of gas needed in flushing and in the main experiments), and two bubble flasks filled with H_2SO_4 (gas washing column) at the entrance as well as at the exit of the furnace to check for any leakage in the furnace.

All gases were initially passed through the columns of silica gel to remove any trace of moisture that may be present. Then, Ar which was used only for flushing and N₂ gases were sent to DK-800S-4 model flowmeters to control their flow rates while CO and CO₂ were passed through the gas cleaning furnace to remove oxygen present in the gases. Gas cleaning furnaces including pure copper chips were heated to 500 °C and kept at that temperature during the experiments. Since the experiments were performed under different atmospheres (N₂ and controlled oxygen atmosphere) after argon flushing of the furnace, a gas control unit was used to obtain the planned atmosphere in the furnace.
To provide the required oxygen partial pressure of the system, carbon monoxide – carbon dioxide (CO–CO₂) gas mixture was sent into the furnace. The flow rates of CO–CO₂ gases were controlled by two capillary flow meters since they could be easily installed and calibrated for measurement of small flows. As seen in Figure 4.1, this system included two leveling bottles filled with CuSO₄ solution to adjust the height of the liquid (dibutly phtalate) in manometers. Hence, the CO–CO₂ flow rates were determined by means of these leveling bottles by adjusting the height of liquids in manometers.

Prior to the main experiments, the capillary flow meters were calibrated by soap bubble method which is commonly used to measure the volume flow rate of gases. Calibration measurements and results are given in Appendix B. Consequently, the calibrated CO–CO₂ gases were mixed in a glass bead mixer and sent into the furnace in order to assure predefined oxygen partial pressure of the system. The oxygen partial pressure of the system was checked by using a DS oxygen probe (supplied from Australian Oxytrol System Co.) during the required experiments. It was suitable for the measurement of oxygen partial pressures up down to 10⁻²⁰ atmosphere at a temperature range from 700 °C to 1700 °C, which covered the experimental conditions studied in this thesis (Po₂: 10⁻⁷–10⁻¹¹ atm., Temp.: 1200 – 1300 °C). Since the oxygen probe output was DC millivolt, a potentiometer was connected to its output. This millivolt signal was used to calculate the oxygen partial pressure in the furnace by means of Nernst equation. All calculations of Po₂ depending on the CO/CO₂ ratio and also oxygen probe measurements are given in Appendix B.

4.2.3. Crucibles

Smelting experiments were done in silica crucibles produced in the Metallurgical and Materials Engineering Department of METU by slip casting method. For this purpose, equal amounts of silica (extra pure sea sand-Merck quality) and kaolinite were mixed with half as much as water to a prepare slurry. This slurry was ground in a ceramic ball mill for 8 hours and then it was poured into a previously prepared plaster mold (slip casting method). Crucibles were left to dry overnight, heated to 1450 °C in 10 hours kept at this temperature for 2 hours in a muffle furnace, and then cooled down to room temperature (firing method). Cooling rate was very slow (~3°C/min.) to prevent formation of any cracks in the crucibles. After firing, all crucibles (more than one hundred) were observed to be glazy in appearance without any visible deformation. According to X-Ray Fluorescence (XRF) analysis, the silica crucible consisted of 73%SiO₂, 16% Al₂O₃, 7%K₂O and small amounts of other oxides (2% Fe₂O₃, 1% CaO, 0.8% P₂O₅). As a result, each silica crucible had the dimensions within the

limits of 30±1mm inside diameter, 38±1mm outside diameter, 80±2mm height and 7±1mm bottom thickness.

4.3. Materials

In this investigation, two different kinds of slag-matte couples were studied. The first slagmatte couple belonged to Eti Copper Co., the copper smelter plant in Samsun-Turkey, and this was labeled as the flash furnace slag (FFS) – flash furnace matte (FFM). The second slag-matte couple was produced synthetically in the laboratory, and labeled as the master slag (MS) - master matte (MM). Colemanite was also used as a starting flux material in this study.

4.3.1. Flash Furnace Matte-Slag (FFM-FFS)

Representative flash furnace slag and matte samples were supplied by Eti Copper Inc. in powder form (-100 micron) so they were ready to use in the experiments. In order to check homogeneity of the FFS and FFM five samples of both FFS and FFM were taken from different points of their 10-kg containers. The results showed that both of them were well mixed homogenous powder samples. Analysis of these starting materials will be given under the caption "Characterization of the Matte and Slag Samples".

4.3.2. Master Matte-Slag (MM-MS)

Synthetic matte and slag samples were prepared by using the foundry laboratory facilities in the Metallurgical and Materials Engineering Department of METU. Master slag (MS) was produced by melting certain amount of reagent grade chemicals, namely 750 g hematite, 600 g silica powder and 230 g metallic iron powder, in a SiC pot above 1300 °C in an induction furnace under an argon atmosphere. After melting, the resulting slag was cast and then ground to powder form (below 150 μ m) by a disc mill to be able to use in the experiments. Considering the FeO-Fe₂O₃-SiO₂ system given in Figure 3.5, a synthetic slag containing 37.6% SiO₂, 60.0% FeO and 2.4% Fe₂O₃ without any copper was obtained near silica saturation.

For the production of a master matte sample containing 50% Cu; copper (850 g), sulfur (535 g) and iron (405 g) in powder form were melted in a SiC pot under the same conditions as those of the slag production. In this production of master matte, about 20% excess sulfur above the stoichiometric requirement was used because some part of the sulfur was oxidized during melting in spite of the argon atmosphere. Master matte was also ground to - 150 µm before using. Both the master matte and master slag analysis will be given in detail in the characterization part.

4.3.3. Fluxes (Colemanite, Boric Oxide and Calcium Oxide)

Boron in elemental or compound form is widely used in several industries. However, it always occurs in nature as a mineral. There are many different types of boron minerals and one of them is colemanite with a chemical formula $2CaO.3B_2O_3.5H_2O$. Ground colemanite is produced by Eti Mine Works Bigadiç Plant, Balıkesir-Turkey. In this study, ground colemanite with -75 µm particle size was supplied by the producer (Eti Mine Works General Management). It consisted of mainly $40\pm0.5\%$ B₂O₃, $26\pm1.0\%$ CaO, $5\pm0.5\%$ SiO₂, and the rest being loss on ignition (~24%) as well as low amount of other oxides (Al₂O₃, MgO and SrO).

Investigations [97–99] on colemanite showed that the dehydration of colemanite starts at 60 °C with the removal of moisture and is finalized at 460 °C for the full removal of 5 mole combined water. Colemanite samples used in these studies might have been taken from different regions and at different times and so the dehydration results of these studies could show small differences from each other. Based on these studies and the thermal analysis of ground colemanite (given in Thermal Analyses part, Figure 4.7) used in this study, it was calcined at 400 °C for 24 hours in a muffle furnace by mixing occasionally in order to decompose and eliminate any chemically bonded water that was present. As needed, the calcined colemanite was obtained by this way and kept in a desiccator to prevent moisture pick up. Calcined colemanite labelled as CC which contained 51.7%B₂O₃, 27.7%CaO, 8.6%CaCO₃, 7.9% SiO₂ and 4.1% other oxides (Al₂O₃, MgO and SrO) was used in all of the experiments.

As for boric oxide (B_2O_3), it was obtained after the calcination of boric acid (H_3BO_3) provided by Merck Co. at 900 °C in a nickel crucible for 2 hours. By this way, water in boric acid was removed, and then, molten B_2O_3 was poured on to a stainless steel plate. After cooling, it was powdered and stored in a desiccator to protect it from hydration. Reagent grade CaO supplied by Sigma Aldrich with 1305-78-8 CAS number was used in the related experiments.

4.4. Characterization of the Matte and Slag Samples

Characterization of the matte and slag samples was realized by using several analysis devices or techniques in terms of chemical, mineralogical and thermal analysis. Initially, their chemical compositions were analyzed by using Inductively Coupled Plasma - Mass Spectrometer (ICP-MS), X-Ray Fluorescence (XRF) and wet chemical analysis. In addition, magnetite content of each sample was determined by SATMAGAN S135 (Saturation Magnetization Analyzer). Then, the mineralogical characterizations of FFS and MS samples were done by X-Ray Diffractometer (XRD) and Scanning Electron Microscopy (SEM). Finally, the thermal behavior of the samples was investigated by thermogravimetric and differential thermal analysis (TGA-DTA).

4.4.1. Chemical Analyses

Chemical analyses of all of the samples used in the experiments were carried out by different techniques; wet chemical, ICP-MS, SATMAGAN and XRF. By wet chemical analyses at EBİ Analysis Laboratory, the analysis of Cu, S, Fe in matte and Cu, S, Fe_{total} as well as SiO₂ in slag were obtained. Perkin Elmer DRC II model ICP-MS (at METU Central Laboratory) was especially used to analyze boron (B) apart from other elements (Cu, Fe, S, Si, Ca, Al, Zn, Pb) in the resultant slag samples after CC addition.

The magnetite content of each sample was determined by SATMAGAN S135 (as shown in Figure 4.3) with a maximum error of $\pm 0.2\%$ of the measured values. This device was calibrated initially with standards, supplied by Outokumpu Company. Using these standard samples with known compositions (3.75%, 17.75%, 30.95% and 44.75% Fe₃O₄), a calibration curve was drawn based on these measurements. This calibration curve was used to determine the percentage of magnetite in all of the experimentally obtained samples.



Figure 4.3: Saturation Magnetization Analyzer (SATMAGAN S135)

Besides the above mentioned methods, the full analyses of all of the samples were performed by XRF (Bruker S8 Tiger) available in the Department of Metallurgical and Materials Engineering of METU.

The chemical analysis results obtained by the three different techniques mentioned above were in accordance with each other especially in terms of the copper content of slag. Table 4.1 summarizes the chemical analyses of FFM, FFS, MM and MS samples, which were obtained by ICP-MS method.

As can be seen from Table 4.1, the master slag did not contain any copper due to the fact that it was prepared synthetically from the reagent grade chemicals such as iron, silica and hematite by melting in a SiC pot at about 1300 °C in an induction furnace under an argon atmosphere. On the other hand, the flash furnace slag had 0.88 %Cu which was a typical copper loss to the actual Eti Copper industrial smelting slag. This copper value belonged to the minimum copper content in FFS among the five parallel chemical analyses.

Table 4.1: Chemical analyses of all of the samples (FFM, FFS, MM and MS) as wt.%.

Constituent Sample	Cu**	SiO ₂	Fe _{Total}	S	Zn	Pb	Fe ₃ O ₄	FeO***	CaO	Al ₂ O ₃
Flash Furnace Matte (FFM)	50.18	-	27.4	19.8	2.0	0.6	_	_	_	-
Flash Furnace Slag (FFS)	0.88	36.1	36.7	0.8	3.3	0.1	5.3	43.9	0.6	2.2
Master Matte (MM)	51.56	-	24.4	24.0	-	-	-	-	-	-
Master Slag (MS)	*	37.6	49.2	-	-	-	3.5	60.0	-	-

*: Master slag was synthetically produced without copper.

**: These analyses were done using ICP-MS and the standard deviations of Cu analyses in the slag and in the matte were ± 0.02 and ± 0.8 , respectively.

***: Calculated from the total iron analyses.

4.4.2. X-Ray Analysis

In order to do the mineralogical characterization of slag samples, a Rigaku D/MAX2200/PC model XRD instrument available in the Metallurgical and Materials Eng. Dept. of METU was used. The peaks of diffraction were recorded and plotted against a horizontal scale between 5 and 95 in degrees of 20, which was the angle of the detector rotation using intervals of 0.02° with CuK α radiation. The X-ray patterns which belong to FFS and MS samples are given in Figure 4.4.

As noted in the previous investigations [4,12,13,100], fayalite and magnetite were identified as the main phases of copper smelting slags. XRD patterns of FFS and MS seen in Figure 4.4 show similar results with those of the previous researchers. There are three different peaks in the MS pattern from those in FFS, which belong to quartz and cristobalite. Although the presence of CaO, Al₂O₃ as well as Zn was determined by the chemical analysis of FFS and also detected by researchers [101] with Electron Micro Probe Analyzer (EPMA), they could not be identified in the XRD pattern.



Figure 4.4: X-Ray diffraction patterns of EBİ flash furnace slag (FFS) and master slag (MS).

4.4.3. SEM Analysis

Since only the major phases were identified by the XRD analysis of FFS, Scanning Electron Microscope (SEM) findings combined with those of XRD were used to identify the minor or trace phases. SEM analyses were carried out on gold coated FFS samples by using JEOL JSM-6400 model equipped with Energy Dispersive X-Ray Spectroscopy (EDS). The results of SEM studies on FFS at different magnifications and the EDS results for the selected points are shown in Figures 4.5 and 4.6, respectively.



Figure 4.5: a, b, c) Backscattered electron images (BSE) of FFS, d) Secondary Electron (SE) image of FFS, (1: metallic copper, 2: matte inclusion, 3: complex sulfides, 4: carbon rich particles, 5: Al₂O₃, 6: CaO).

Sample taken directly from the flash furnace slag tapping hole at EBİ was cooled in air and ground to about 1-2 cm before coating with gold to study with SEM. It is known from the XRD pattern and chemical analysis results that FFS mainly consisted of iron silicate matrix corresponding to most of the gray regions apart from the particles observed in SE image (Figure 4.5.d) and BSE images (Figures 4.5.a,b,c). EDS analysis results indicated that there were three kinds of particles having Cu; as labeled in above figures (#1): metallic copper particles, (#2): matte inclusions of different sizes with varying copper percentages, (#3): complex (Cu-Fe-Zn) sulfides. Carbon rich particles, labeled as (#4) in Figure 4.5.c probably originating from lignite which was added at EBİ for the reduction of magnetite and copper

oxide, were also detected [102]. As seen in Figure 4.5.d, the particle labeled as (#5) was present in a matte particle (#2) and was composed of mainly AI with small amounts of Cu and Fe indicating an inclusion in matte. Analysis of particles labeled as (#6) in Figure 4.5.d. showed that FFS included also some small CaO particles. SEM results of the FFS are in accordance with the results of earlier studies by Jalkanen et al. [15], Herreros et al. [47], and Mihailova & Mehandijev [100].



Figure 4.6: EDS spectra taken from the particles labeled on SE images in Figure 4.5 with numbers 1 to 6.

4.4.4. Thermal Analysis

TGA-DTA (Seteram Labysys) analysis of ground colemanite was carried out to investigate its thermal behavior from 30 °C to 980 °C in the Central Laboratory of METU. As seen in Figure 4.7, colemanite has two endothermic peaks at around 380 °C and 400 °C. About 17.5 wt.% loss is due to the chemically bonded water removal. Other endothermic effects which may belong to calcite decomposition appear from 650 °C to 750 °C. During this decomposition, there is nearly 3.5 wt.% loss, which indicates that small amount of CO_2 in the calcined colemanite will be released as a results of CC addition to the system during the experiments.



Figure 4.7: TGA-DTA curves of ground colemanite

TGA-DTA analysis of master slag was not done because the master slag was already produced synthetically and its melting point was defined by means of FeO-Fe₂O₃-SiO₂ phase diagram (Figure 3.5). When the master slag composition (as seen in Table 4.1) was placed into this phase diagram including liquidus lines, the melting temperature of slag can be determined as being between 1200 °C and 1250 °C which nearly corresponds to liquidus temperature of MS estimated by FactSage (as 1248 °C).

Thermal behavior of flash smelting slags have been studied by several researchers [4,103]. Gorai et al. [4] described in detail the thermal behavior of typical flash furnace slag. He noted that slag gained weight in the range of 374 °C to 989 °C due to the oxidation of fayalite (FeO in fayalite turns to Fe₂O₃), and its weight loss was low from 989 °C to 1040 °C due to the oxidation of minor amount of copper and iron sulfides present in the slag. Above that temperature, the slag started to melt with an endothermic peak. Although fayalite as a major phase of the flash furnace slag melts at 1205 °C, it is known that melting temperature of slag may decrease or increase due to other components which may be presents in the slag. Therefore, the melting point of slag may vary depending on the composition. To determine the melting point of FFS, the ground slag sample was put in an alumina crucible and heated to 1100 °C for 30 minutes under nitrogen atmosphere. After cooling to room temperature, it was observed that the slag sample was sintered rather than appearing as liquid. Then, after heating another sample to 1150 °C and cooling, the FFS appeared as completely molten. Therefore, the melting point of FFS was in between 1100-1150 °C under nitrogen atmosphere.

4.5. Experimental Procedure

Experiments were conducted under two different atmospheres: nitrogen and atmosphere with controlled partial pressure of oxygen using CO₂ and CO gas mixtures. Before each experiment, the reaction tube was flushed with purified argon. Initial experiments were performed under an inert atmosphere of nitrogen with 0.15 L/min gas flowrate to prevent oxidation of the samples. The subsequent experiments were carried out under a predefined partial pressure of oxygen atmosphere which was generated by a mixture of CO-CO₂ gases with the CO₂/CO ratio in the range of 0.5 to 50. After the gases passed through silica gel columns for removing moisture, their flow rates were adjusted and monitored by using the flowmeters. Then, the gases were sent through a gas control unit to change to the type of gas needed in flushing and in the main experiments. Finally, each gas went through a gas washing column before entering the furnace to dry the gas. Slag and matte were melted together in the silica crucibles as mentioned before.

In the initial melting experiments with master and flash furnace slag-matte pairs, the reaction duration and amount of CC addition were selected as variables in the ranges of 30 minutes - 4 hours and 0 - 6% CC of the total matte and slag weight, respectively. Temperature was selected as 1250 °C for the initial experiments since the industrial copper matte smelting

operations are generally performed at a temperature range of 1220-1300 °C depending on the composition of copper concentrate.

The experiments that followed were carried out with master and flash furnace slag-matte pairs by the addition of CC (from 0% to 6%) under various partial pressure of oxygen $(10^{-7}, 10^{-9}, 10^{-11} \text{ atm.})$ at different temperatures (1200, 1250 and 1300 °C) for 2 hours.

In order to observe CaO and B_2O_3 additions on copper losses to slag, further experiments were performed by separately adding various amounts of CaO and B_2O_3 (0% - 10%) to EBİ matte-slag samples at 1250 °C for 2 hours under inert (N₂) atmosphere.

All of the melting experiments were performed with equal amounts of matte and slag samples (each of them being 30 g) as well as a certain amount of additive. These powder materials were placed in a silica crucible after proper mixing, therefore resulting in a uniform distribution of particles. This may lead to the entrapment of the matte particles, but it is a more realistic approach considering the concentrate charging in copper smelting plants. Having been loaded, the crucible was placed in the hot zone of the vertical tube furnace. Then, the furnace was heated up to the experimentally planned temperature with constant heating rate (4 \circ C/min.). The time at which furnace temperature reached to desired value (1250 \circ C for most of the experiments) was determined as the beginning of the experimental duration, i.e. zero time. Then, the crucible was kept at that temperature for a certain period of time (depending on the duration: $\frac{1}{2}$, 1, 2 or 4 hours); finally, it was cooled to room temperature under a controlled cooling rate and atmosphere.

After cooling, the matte and slag phases were separated from each other and from the silica crucible. It was observed that the matte-slag separation became easier with the addition of CC, but the slag-crucible separation became more difficult. The matte and slag samples were ground to -150 µm by using a laboratory disc mill, and they were sent to EBİ and METU Central Laboratory for the analysis of Cu, Fe, SiO₂, B₂O₃ and S by ICP-MS and wet chemical analysis. In addition, the full analyses of all resultant slags were obtained by means of XRF. These analyses were also used to estimate the viscosity and liquidus temperature of slag samples using FactSage software program.

4.6. Modeling of Liquidus Temperature and Viscosity

Initially, the experimental viscosity measurements of MS, FFS and the resultant slag obtained by the addition of CC were planned in this study. A detailed search to find a high

temperature viscometer in Turkey indicated that there is only one rotational type viscometer suitable for the high temperature viscosity measurements in the Şişecam Ar-Ge laboratory. A representative sample of FFS was sent there to be tested. Unfortunately, it was reported by the mentioned company that this trial had failed due to the unsuitable composition of slag with its high iron content. Therefore, making of a high temperature viscometer was considered. After a literature search on this subject, it was understood that finding a suitable container and spindle for the high temperature viscosity measurements was very difficult because of the interactions between the container/spindle and sample. Viscosities of melts (coal ash, flux or various types of slag) were measured in the past by several researchers [75,83–85,104–107] using different containers and spindles such as Pt, Mo, pure Fe, and recrystallized Al etc., and they also encountered some problems which are summarized as follows;

I) Flash smelter slag containing Cu and S was extremely aggressive on the Pt/Pt-Rh crucible and spindle (bob), and also iron in the slag reacted with Pt at elevated temperatures,

II) Aluminum container led to contamination of slag with up to 10% Al₂O₃,

III) Silica crucible reacted partially with slag so it was inevitable to study under SiO₂ saturation,

IV) Iron/steel container resulted in a study with iron saturated slag,

V) Mo crucibles did not give accurate results due to Mo dissolution in slag.

In the light of the problems given above, it could be concluded that each viscosity measurement needed a new container - spindle made of recrystallized alumina, pure Fe and silica, and limited trials could be performed with container - spindle made of Pt and Mo. This made the measure of viscosity of slag at high temperature very expensive. Furthermore, the presence of boron in our system could create problems in the case of viscosity measurements, because the slag composition might vary with time during the measurements due to the evaporation of boron from the slag [107]. Another problem might arise from fluid type. Viscosity for homogenous molten slag (as a Newtonian fluid) at high temperature could be measured experimentally, and a relationship between the viscosity and temperature/slag composition could be modeled successfully such as in Utigard-Warczok equation. However, for a non-Newtonian fluid (slag), which may contain some undissolved (crystalized) particles; the empirical models did not yield reasonable results. [108].

To sum up, it was attempted to install a high temperature viscometer but it could not be realized due to the above mentioned drawbacks and the budgetary problems of the project. Then, it was decided to use one of the viscosity prediction methods since the theoretical calculation of viscosity of a slag system can be made relatively easily by using one of the developed models mentioned earlier [89–95].

In recent years, the researchers [90–92,109–111] focusing on the estimation models of slag viscosity have preferred to base their studies on the thermodynamic calculations rather than the empirical results. FactSage as a commercial software program is one them, which includes a number of database, calculation and manipulation modules. Especially, Degterov and Pelton [112] have prepared a thermodynamic database for copper production (smelting and converting stages) to integrate FactSage program considering the thermodynamic and phase equilibria information about slag, matte and blister copper in the Cu-Fe-S-O-Si-Ca system available in the literature. This database covers Po₂ values, Ps₂ values and temperatures in the ranges of 10⁻¹²-10⁻⁶, 10⁻⁷-10⁻² and 1150-1350 °C, respectively, and yields good results. Therefore, FactSage software program was selected to estimate the viscosity of resultant slags as well as trends in liquidus temperature for final slags.

In this study, FactSage [113,114] 6.2 - "Equilib" module [115] was used to estimate the liquidus temperatures of the initial and final slags. In the precipitate target phase calculation, the temperature was calculated when a second phase first starts to form (activity = 1, and zero mole) from the «precipitate target phase» using FACT-SLAG solution phase. In addition, "Phase Diagram" module of FactSage 6.2 using FACT-SLAG solution phase was used to calculate the FeO-Fe₂O₃-SiO₂ ternary phase diagram.

Viscosity estimations of the initial and final slags were also carried out with FactSage 6.2 - Viscosity module which uses a new model for the viscosity of single-phase liquid slags and glasses [116]. The slag compositions in the present study fall within the limits of the model which was previously checked against the experimental data available for Al₂O₃-B₂O₃-CaO-FeO-Fe₂O₃-K₂O-MgO-MnO-Na₂O-NiO-PbO-SiO₂-TiO₂-Ti₂O₃-ZnO-F melts.

As noted in the materials section, calcined colemanite mainly contained CaO and B_2O_3 . The behavior of CaO was very explicit in terms of slag viscosity, but there was a controversy about the behavior of B_2O_3 in slag. In some models, one of which was FactSage, it was assumed that B_2O_3 is a glass former oxide like SiO₂ [95]. In some other models e.g. Riboud, it was assumed as a modifier like CaO [93]. Furthermore, it was also assumed by some researchers [75,83] as an amphoteric oxide like Al₂O₃.

In this work, it was assumed that B_2O_3 behaved as a glass former oxide; the viscosities and liquidus temperatures of the resultant slags were calculated by FactSage computer package and are given in the following section.

CHAPTER V

RESULTS AND DISCUSSION

5.1. Introduction

In the present study, to reduce the copper losses to slag in copper production, several experiments were carried out. In the experiments, the effects of calcined colemanite additions to FFS and MS slags in terms of reaction duration, temperature and oxygen partial pressure were investigated. Furthermore, the effects of CaO and B₂O₃ additions to FFS were also studied. The results have been presented in the following sections. Each experiment series was referred to with different experimental code as given below sequentially:

S series: Experiments with FFS-FFM under nitrogen atmosphere at 1250 °C for different duration (30 minutes - 4 hours) and various CC additions (0 - 6% of the total charge).

F series: Experiments with MS-MM under the same conditions with S series.

P series: Experiments with FFS-FFM at 1250 °C under different controlled oxygen partial pressure (Po₂) in the range from 10⁻⁷ to 10⁻¹¹ atm. and various amount of CC (0 - 6% of the total charge) for 2 hours.

B series: Experiments with MS-MM under the same conditions with P series.

PT series: Experiments with FFS and FFM with various additions of CC (0 - 6% of the total charge) at different temperatures (1200, 1250, and 1300 °C) under controlled Po₂=10⁻⁹ atm. for 2 hours.

E series: Experiments with FFS and FFM with various CC additions (0 - 10% of the total charge) at different temperatures (1200, 1250, and 1300 °C) under nitrogen atmosphere for 2 hours.

T series: Experiments with MS-MM under the same conditions with PT series.

C series: Experiments with FFS and FFM with various additions of CaO and B_2O_3 (0 - 10% of the total charge) under nitrogen atmosphere at 1250 °C for 2 hours.

5.2. Effect of Reaction Duration on Copper Losses to Slag with CC Addition

The initial melting experiments were performed with FFS-FFM and MS-MS pairs under nitrogen atmosphere at 1250 °C. The reaction duration and amount of CC addition were chosen as variables in the ranges of 30 minutes - 4 hours and 0 - 6% of the total matte and slag weight, respectively.

5.2.1. Experiments with EBİ Flash Furnace Slag-Matte (FFS-FFM)

In order to determine the effect of colemanite addition and reaction duration on copper losses to slag in copper matte smelting, a series of experiments were done. In these experiments, the FFS and FFM mixed with various amounts of CC (0, 2, 4 and 6% of the total charge) were melted together at 1250 °C under nitrogen atmosphere in silica crucibles and at different durations (30 minutes, 1, 2 and 4 hours). Results of the experiments are given in Table 5.1 and Figure 5.1.

Balance values of the chemical analysis given in Table 5.1 for the resultant slags analyzed by X-ray fluorescence (XRF) included all of other oxides such as; ZnO (3.9-4.2%), Al₂O₃ (2.2-5.0%), CaO (0.6-4.3%), PbO (<0.2%), BaO (<0.6%), K₂O (<0.6%) and MgO (<0.3%) for the S series.

As expected and seen from Table 5.1, B_2O_3 levels in the slags increased with the increasing CC additions. Besides, the calculations showed that some B_2O_3 in colemanite was being lost as gaseous boric oxide during the experiments as reported elsewhere by Aydoğdu & Sevinç [117]. CaO amount in slag also increased as calcined colemanite was added.

Al₂O₃ and K₂O concentrations in slag gradually increased with the experimental duration since the crucibles were made of silica and kaolinite. Sulphur content in the resultant slags, as shown in Table 5.1, fluctuated with the addition of CC. On the other hand, the boron

content in matte samples analyzed with ICP-MS was not higher than 20 ppm since the detection limit of this method was 0.002%.

In this study, the chemical analysis of Cu, B, Si and Fe were done by ICP-MS, and the standard deviation values of these elements were calculated after three parallel measurements. The standard deviation values as weight% for;

- B analyses in the slags were ±0.06.
- Cu analyses in slag and in matte were ±0.02 and ±0.8, respectively.
- Si analyses in the slags were ±0.7.
- Fe analyses in the slag and in the matte were ±0.8 and ±0.6.

All of these standard deviation values are also valid for the subsequent chemical analysis results in the present study.

				Sla	Matte Analyses					
Exp. Code	t (h)	CC add. (%)	Cu	SiO ₂	Fe	S	B ₂ O ₃	Cu	Fe	S
S–1	1/2	0	0.68	38.6	35.3	1.3	-	48.6	21.6	20.7
S–2	1	0	0.57	36.7	36.5	1.2	-	49.0	21.2	20.1
S–3	2	0	0.55	39.3	33.9	1.0	-	48.4	21.9	20.7
S–4	4	0	0.53	42.7	32.2	1.1	-	48.7	21.5	20.5
S–5	1/2	2	0.62	37.4	35.7	0.9	1.67	49.3	21.1	20.6
S–6	1	2	0.44	35.6	34.7	1.0	1.65	49.2	20.9	20.5
S–7	2	2	0.30	38.4	32.3	0.8	1.56	49.1	20.9	20.3
S–8	4	2	0.30	42.5	30.5	1.2	1.52	49.3	20.0	20.5
S–9	1/2	4	0.42	37.5	34.6	0.9	3.15	49.6	20.5	20.5
S–10	1	4	0.31	37.8	33.4	1.3	3.17	50.0	20.9	20.1
S–11	2	4	0.28	37.1	32.0	1.1	3.02	49.5	21.4	19.5
S–12	4	4	0.29	39.2	30.7	0.9	2.91	49.8	20.0	19.2
S–13	1/2	6	0.39	35.7	33.1	0.8	4.71	50.4	21.0	19.6
S–14	1	6	0.28	36.0	32.4	0.8	4.53	50.2	20.5	19.7
S–15	2	6	0.29	37.4	30.8	1.0	4.41	49.6	20.7	20.8
S–16	4	6	0.28	39.6	29.8	0.9	4.14	48.6	20.8	21.0

Table 5.1: Chemical analysis results of experiments with FFS and FFM with various additions of CC and different reaction duration, as wt.%. (under nitrogen atmosphere at 1250 °C)

The results presented in Table 5.1 could be examined in terms of two different variables, which are the reaction duration and the amount of CC additions; their effects on the copper losses to slag will be explained. According to the results of the melting experiments, it can be seen from Figure 5.1 that the increase in the reaction duration up to 2 hours caused decreases in copper losses to slag. There was no significant decrease in copper losses to slag beyond 2 hours. When considering the average smelting duration which is about 4 hours in the industrial flash furnace system, it was clear that the colemanite addition to the system tended to shorten the duration for settling of matte particles in the slag.



Figure 5.1: Variations of the copper amount in FFS with the addition of CC and reaction duration (under nitrogen atmosphere at 1250 °C).

On the other hand, according to the chemical analyses given in Table 5.1, it was observed that with the increasing amount of CC additions the copper losses to slag were reduced. For example, the experimental results for 1 hour at 1250 °C with the additions of 2, 4 and 6% CC showed that the copper was present in the slag in amounts of 0.44, 0.31 and 0.28%, respectively. It was observed that under the same conditions in the experiment without the addition of CC, the slag contained 0.57% Cu.

Keeping in mind that the slag viscosity and liquidus temperature play a crucial role in copper smelting to minimize the copper losses to slag, the copper content was also affected by slag composition (mainly magnetite and other oxides) and the addition of CC during copper smelting stage might also assist in separation of the two phases, matte and slag. This is due to breaking of silica bonds with the presence of CaO [82,118] and formation of low melting point compounds as a result of combining of B₂O₃ with other oxides [23,119]. Furthermore, the addition of CC reduces the solubility of copper [17,56,69,72] in iron silicate slag due to the presence of CaO in it, and, lowers the density of slag [22] due to the presence of B₂O₃ in

it. All these effects result in a significant decrease in copper content of slag, that is, less mechanical and physicochemical copper losses to slag.

Secondary electron (SE) images and EDS analysis of a representative sample of the experiment coded (S-12) with 4% CC addition after 4 hours of experimental duration are presented in Figures 5.2 and 5.3, respectively. According to the EDS analysis, it could be stated that the phases labeled as (#1) (black holes), (#2) (gray areas), (#3) (large particle) and (#4) (small particles) in Figure 5.2.a predominantly corresponded to glassy silicate matrix, crystalline fayalite, matte particle and Fe-Zn sulphide, respectively. The irregularly shaped area labeled as (#6) in Figure 5.2.b was likely to be magnetite whereas that labeled as (#5) was a sulphide of Fe, Cu and Zn.



Figure 5.2: SE images of a representative sample of experiment S-12, (1: glassy silicate matrix, 2: crystalline fayalite, 3: matte particle, 4: Fe-Zn sulphide, 5: complex sulphide, 6: magnetite).

It was observed from the mentioned SE images that the diameters of spherical matte or complex sulphide particles were in the range of 1 to 150 µm although those of FFS included particles up to 1 mm. So, it can be stated that after the addition of CC, matte inclusions larger than 150 µm had settled to the matte region for S-12 sample. When comparing the SE images of FFS with those of S-12, it was noted that the structure of FFS was different from that of S-12 due to the differences in cooling conditions.



Figure 5.3: EDS spectra taken from particles labeled on SE images in Figure 5.2 with numbers 1 to 6.

It is known from the literature [63] that the soluble copper amount in fayalite slag at 1250 °C can be predicted by Eq. 3.3. When this equation was applied to representative sample S-12 (see Appendix C in detail), the result showed that the slag included 0.27 %Cu which was defined as soluble copper amount in the slag. This value was nearly equal to copper value obtained by chemical analysis of S-12 slag. To sum up, it can be said that the copper amount in slag could be lowered to the minimum value of copper (~0.3% Cu) which arises from mostly dissolved copper in the slag in its oxidic form, Cu₂O. However, according to SEM and EDS results of S-12 sample (Figures 5.2 and 5.3), this representative slag contained matte, complex sulphide (Zn-Fe-Cu sulphide) or metallic copper particles. This

may be explained by some reactions which occur during solidification. It is known that when smelting slag is cooled slowly, the soluble copper oxide may react with soluble iron sulphide in the slag to produce copper sulfide as seen in Rx. 4.1. Copper oxide may also react with iron oxide to form metallic copper when iron sulphide in the slag is not enough (see Rx. 4.2).

$$Cu_2O_{(slag)} + FeS_{(slag)} = Cu_2S_{(matte)} + FeO_{(slag)}$$
(Rx. 4.1)

$$Cu_2O_{(slag)} + 3FeO_{(slag)} = 2Cu + Fe_3O_{4(slag)}$$
(Rx. 4.2)

Among these S series experiments, three of them (S-3, S-15 and S-16) were repeated in order to check reproducibility of the results, especially in terms of the copper content in slag. After analysis of the repeated experiments, the copper contents in slag for Re-S-3, Re-S-15 and Re-S-16 were obtained as 0.61, 0.31, 0.32%Cu, respectively. When compared with the initial values given in Table 5.1, it could be concluded that the relative error limits of the results in terms of the copper content in slag was within nearly $\pm 10\%$.

5.2.2. Experiments with Synthetic (Master) Slag-Matte (MS-MM)

The main reason for the preparation and usage of synthetic matte and slag samples was investigation of copper losses to slag under more oxidizing slag and without the presence of other oxides like CaO, Al₂O₃, ZnO, etc. Equal amounts of master slag produced synthetically without copper and master matte were mixed with a certain amount of CC such as 0, 2, 4 and 6%. This mixture was heated to 1250 °C and kept at that temperature under nitrogen atmosphere in silica crucibles for various durations (30 minutes, 1, 2 and 4 hours). The chemical analyses of each matte and slag sample obtained are presented in Table 5.2 and plotted in Figure 5.4.

Balancing values of the chemical analyses for the resultant slags (for F series slags), included all of other oxides which were analyzed by X-ray fluorescence (XRF); Al_2O_3 (1.5-3.0%), CaO (0-3.8%), K₂O (<0.3%) and MgO (<0.2%). As noted earlier, CaO and B₂O₃ levels in the slags increased with the increasing CC additions, and Al_2O_3 and K₂O concentrations in slag gradually increased with the experimental duration since the crucibles were made of silica and kaolinite.

				Sla	ig Analy	Matte Analyses				
Exp. Cod	t (h)	CC add. (%)	Cu	SiO ₂	Fe	S	B ₂ O ₃	Cu	Fe	S
F–1	1/2	0	1.60	34.0	44.8	1.9	-	48.2	29.9	21.9
F–2	1	0	1.50	30.7	44.3	1.8	-	47.0	30.7	22.2
F–3	2	0	1.44	36.0	44.0	1.8	-	48.9	28.1	23.0
F–4	4	0	1.19	35.4	42.7	1.6	-	47.3	30.2	22.4
F–5	1/2	2	1.45	30.0	45.2	2.3	1.90	49.1	29.2	21.7
F–6	1	2	1.30	31.7	44.8	1.4	1.78	48.2	29.7	22.1
F–7	2	2	1.22	33.5	43.4	1.7	1.75	45.5	31.1	23.4
F–8	4	2	0.90	33.8	42.6	1.6	1.76	48.3	28.9	22.7
F–9	1/2	4	0.72	33.7	44.6	1.1	3.65	48.4	29.4	22.2
F–10	1	4	0.60	34.5	42.5	1.2	3.44	48.4	28.9	22.7
F–11	2	4	0.58	34.7	41.1	1.2	3.80	49.0	29.2	21.7
F–12	4	4	0.42	36.1	41.3	1.1	3.60	47.6	29.9	22.5
F–13	1/2	6	0.48	34.6	40.7	1.2	5.40	47.6	29.7	22.6
F–14	1	6	0.43	34.7	40.7	1.0	5.11	48.2	28.7	23.1
F–15	2	6	0.40	35.0	40.8	1.1	5.01	49.4	28.6	21.9
F–16	4	6	0.42	36.7	39.2	1.1	4.56	50.1	27.9	22.0

Table 5.2: Chemical analysis results of experiments with MS and MM with various additions of CC and different reaction duration, as wt.%. (under nitrogen atmosphere at 1250 °C)

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Figure 5.4: Variations of the copper content of MS slag with the addition of CC and reaction duration (under nitrogen atmosphere at 1250 °C).

Considering that the master slag did not include any copper initially, as seen in Table 5.2 and Figure 5.4, the copper losses to slag decreased slowly with the increasing duration, but when CC was gradually added to the system as 2, 4 and 6%, the copper losses decreased considerably. For instance, while at the end of the 1-hour experiment (F-2) the copper content in the slag was 1.50%, it decreased to 1.19% at the end of the 4-hour experiment (F-4) without any colemanite addition. On the other hand, it is seen that the addition of CC to the system led to a rapid decrease in the copper content in slag which was reduced to a level as low as 0.40%. As seen from Table 5.2, the sulphur content of resultant slags also decreased gradually with the addition of CC.

The main difference between the two slags (synthetic and industrial) was the presence of other oxides such as CaO, Al₂O₃, and ZnO in FFS, as well as Fe/SiO₂ ratio. As stated before, these oxides affected the slag structure and also slag viscosity even when present in small amounts in slag and lead to a decrease in entrapping of matte particles due to the lower slag viscosity and liquidus temperature. The effect of these oxides can be seen from a comparison of copper losses between the two slags (MS and FFS) with the same amount of CC addition and the same settling time. When the results of experiments with FFS and MS

slags (S-10 and F-10) for 1 hour and 4% CC addition were compared, it was seen that the copper content of FFS and MS slags were 0.31% and 0.60%, respectively.

After analyzing the resultant slags, it was found that F series slags contained only 2 to 6% magnetite and S series slags contained 2 to 5% magnetite. According to Viswanathan et al. [72] who did viscosity measurements on fayalite slags, Fe₂O₃ content in FeO-Fe₂O₃-SiO₂ ternary system did not have much effect on the slag viscosity up to 7%, but beyond this amount, the viscosity of slag increased very sharply. Therefore, considering the magnetite contents of slags in the present study which were below this limit, it can be said that its effect on slag viscosity was not significant.

The images shown in Figures 5.5.a and 5.5.b are the SE and BSE images, respectively, of the same area for a representative slag sample of the experiment coded as (F-11) under the same magnification.



Figure 5.5: Images of a representative sample of (F-11) under the same magnification for the same area a) SE, b) BSE, (1: magnetite, 2: fayalite, 3: silicate matrix, 4: matte particle, 5: iron sulphide).

These images with EDS analysis as presented in Figure 5.6, indicated similar structures with S-12. The huge black area in Figure 5.5.a which was labeled as (#1) was a magnetite phase. Considering the EDS graphs, gray areas and small black holes in Figure 5.5.b could be named as fayalite (#2) and silicate matrix (#3), respectively. After the scanning of whole area of SE image corresponding to the last EDS graph (#6), small K and Al peaks were noticed

surprisingly although the starting materials (MS and MM) did not contain such elements. These unexpected elements might have come from the silica crucible because a small amount of kaolinite which is a clay mineral including Al and K, was used as binder to obtain a silica crucible. Since CC was added to the original matte-slag mixture, the resultant slags contained substantial amounts of B₂O₃ and CaO. However, there were no observations of any particles or peaks related with boron because B₂O₃ always went to amorphous phase, and it needed extensive annealing to be crystallized. On the other hand, the spherical matte inclusions labeled as (#4) with various sizes could be seen very easily and clearly on BSE image. Unlike the experiment coded as S-12, the experiment coded as F-11 did not include any complex sulphides due to the lack of zinc in MS and MM. Instead, the iron sulphide particles labeled as (#5) were identified.



Figure 5.6: EDS spectra taken from particles labeled on SE and BSE images in Figure 5.5 with numbers 1 to 5 and general EDS spectra (6) taken from the complete SE image.

Taking into account all above experimental results performed with both FFS-FFM and MS-MM samples under nitrogen atmosphere, it was observed that within the first 2 hours the copper content in slag decreased gradually and, there were small differences in the amount of copper in resultant slags after this point. Therefore, the reaction duration was chosen as 2 hours for the following experiments. To sum up, the subsequent experiments were continued with constant duration of 2 hours to investigate the effect on copper losses to slag with CC addition at various oxygen partial pressures and at different temperatures.

5.3. Effect of Oxygen Partial Pressure on Copper Losses to Slag with CC Addition

The ternary diagram FeO-Fe₂O₃-SiO₂ (as seen in Figure 3.5) with isobars for oxygen shows that the oxygen partial pressure varies from 10^{-7} to 10^{-11} atm. on the line of silica saturation. Therefore, in the present study, the next series of tests were conducted with FFS-FFM and MS-MS pairs in order to investigate the effect of oxygen partial pressure (10^{-7} , 10^{-9} and 10^{-11} atm.) with the CC addition (0, 2, 4 and 6% of the total charge) on the copper losses to slag. During the experiments, the following parameters were kept constant: Reaction duration: 2 hours; temperature: 1250 °C.

5.3.1. Experiments with EBİ Flash Furnace Slag-Matte (FFS-FFM)

In these experiments, FFS-FFM samples were melted together with a certain amount of CC in silica crucibles at 1250 °C under CO-CO₂ atmospheres with oxygen partial pressure (Po₂) in the range from 10⁻⁷ to 10⁻¹¹ atm. for 2 hours. Experimental results are summarized in Table 5.3 and Figure 5.7.

Balancing values of the chemical analyses for the resultant slags included all of other oxides analyzed by X-ray fluorescence (XRF) such as; ZnO (3.9-4.2%), Al₂O₃ (3.2-5.0%), CaO (0.8-3.6%), PbO (<0.2%), BaO (<0.6%), K₂O (<0.6%) and MgO (<0.2%) for P series slags.

				Sla	g Analys	Matte Analyses				
Exp. Code	Po ₂ (atm.)	CC add. (%)	Cu	SiO ₂	Fe	S	B ₂ O ₃	Cu	Fe	S
P–1	10 ⁻⁷	0	1.36	38.7	36.9	1.5	-	44.1	20.6	15.4
P–2	10 ⁻⁷	2	0.49	38.7	35.3	1.0	1.22	46.0	19.8	15.9
P–3	10-7	4	0.39	38.5	33.5	0.8	2.67	45.5	19.4	16.2
P–4	10-7	6	0.34	39.4	31.9	0.7	3.80	45.7	19.2	16.5
P–5	10 ⁻⁹	0	0.61	40.0	36.6	1.1	-	44.9	20.1	16.0
P-6	10 ⁻⁹	2	0.49	39.0	35.4	1.1	1.26	45.5	19.9	16.5
P-7	10 ⁻⁹	4	0.43	38.5	33.9	0.9	2.67	45.5	19.8	15.9
P-8	10 ⁻⁹	6	0.34	39.2	31.8	0.8	3.90	46.2	19.2	16.1
P-9	10 -11	0	0.51	40.5	36.6	1.2	-	43.9	20.9	16.1
P-10	10-11	2	0.38	40.2	35.5	1.0	1.26	44.6	20.8	16.2
P–11	10-11	4	0.34	39.0	33.9	0.9	2.71	46.2	19.7	16.4
P-12	10 -11	6	0.32	39.8	32.3	0.8	3.83	46.6	19.8	16.8

Table 5.3: Chemical analysis results of experiments with FFS and FFM with various additions of CC and under different partial pressure of oxygen atmosphere, as wt.%. (at 1250 °C for 2 hours)

Figure 5.7 shows the effect of oxygen partial pressure and CC additions at 1250 °C for 2 hours. Results of these experiments should be evaluated separately, in terms of the effects of oxygen partial pressure and CC additions.

As mentioned before, when the oxygen partial pressure of the FeO-Fe₂O₃-SiO₂ system was lowered, the magnetite formation in the system decreased. Therefore, it was expected that the copper losses would also decrease depending on the magnetite level in the slag because magnetite directly affects the viscosity of slag. However, in this study, the results obtained from SATMAGAN showed that magnetite level of the slags remained nearly constant (1.8 - 3.4% Fe₃O₄) as Po₂ value decreased. This may arise from settlement of the magnetite to the bottom of crucible due to its higher density than that of matte. In every experiment of this series, there was a thin magnetite layer between the crucible and matte phase. Unfortunately, this magnetite layer could not be separated from the crucible to be added to the resultant slag.



Figure 5.7: Effect of partial pressure of oxygen and addition of calcined colemanite to FFS and FFM on copper losses to slag (at 1250 °C for 2 hours)

According to the earlier studies [52,62–64], the concentration of dissolved copper in the silica saturated iron silicate slag is affected by the oxygen partial pressure. That is, the copper solubility in slag increases with increasing oxygen potential. It could be seen also in this study that in the experiments without CC addition the amount of copper lost in slag decreased with the decreasing partial pressure of oxygen.

As for CC addition effect, it is seen from Figure 5.7 that the amount of copper in slag decreased significantly from 1.36% to 0.34% Cu for a constant $Po_2=10^{-7}$ atm., but the decrease was more gradual for both $Po_2=10^{-9}$ and 10^{-11} atm. Considering that a typical Pierce Smith converter is operated at nearly oxygen potential of $Po_2=10^{-6}$ atm., such a low copper content in slag at oxygen partial pressure atm. ($Po_2=10^{-7}$ atm.) encourages the CC usage in converter stage.

As seen from Table 5.3, the sulfur content of resultant slags also decreased with the increasing CC additions. Since the amounts of S and Cu in slag showed similar behaviour, it is considered that this decline in sulfur contents in slag was due to decreasing mechanically entrapped matte particles in the resultant slag.

Among these experiments, P-1, P-5 and P-9 were repeated to check the reproducilibity of this series Comparing the results of previous and the repeated experiments for P-1, P-5 and P-9, it was seen that there was a good agreement between the results in terms of Cu, Fe, S, SiO₂, Al₂O₃, CaO and ZnO analyses. So, the initial values obtained were given for these experiments.

Color mapping techniques (by SEM-EDX) are being commonly used by researchers to separate available phases or to determine distribution of the constituents in a sample. In this study, to observe the distribution of constituens (especially Cu) in the slag, the color mapping technique was also applied to a representative sample selected as P-5. The color map of the slag sample is shown in Figure 5.8. In color mapping, Cu was represented by light blue, S by dark blue, Fe by pink, Si by yellow and O by green. Pictures showed the distribution of each element in the slag structure: the dark regions in each picture indicated that the element did not exist or was present in trace amounts. In the light of this explanation, it could be concluded from Figure 5.8 that Cu was present in the slag in two forms: combined with S as a matte particle (from Cu and S picture) or dissolved in the slag. As can be seen in Figure 5.8, the regions rich in Cu and S corresponded to matte particles, and remaining areas represented the dissolved copper in slag.

As seen in XRD pattern of the FFS, fayalite (composed of Fe-Si-O) was the main phase in the slag. By comparing of Si and Fe pictures, it could be concluded that, apart from fayalite, SiO₂ (probably being trydimite) also existed in the slag.



Figure 5.8: Color mapping of the representative slag sample (P-5)

5.3.2. Experiments with Synthetic (Master) Slag-Matte (MS-MM)

Further experiments with the synthetic samples (MS-MM) were conducted under different oxygen partial pressures to observe the effect of colemanite addition on the copper losses to slag. For this purpose, 10⁻⁷, 10⁻⁹ and 10⁻¹¹ atm. oxygen partial pressures were applied to the system for 2 hours at 1250 °C with the addition of varying calcined colemanite (%0, %2, %4 and %6) to the matte-slag mixture. All of the results of 12 experiments done are given in Table 5.4 and plotted in Figure 5.9.

Balancing values of the chemical analyses for the resultant slags included all of the other oxides analyzed by X-ray fluorescence (XRF) such as; Al₂O₃ (2.1-3.1%), CaO (0-3.3%), K₂O (<0.3%) and MgO (<0.1%). Magnetite level in B series slags measured by SATMAGAN was between 1.9 and 4.8% (for B series slags).

				Matte Analyses						
Exp. Code	Po ₂ (atm.)	CC add. (%)	Cu	SiO ₂	Fe	S	B ₂ O ₃	Cu	Fe	S
B–1	10 ⁻⁷	0	1.80	34.9	42.1	1.7	-	45.5	27.1	20.0
B–2	10 ⁻⁷	2	0.80	34.1	42.5	1.8	1.80	45.4	26.4	18.9
B–3	10 ⁻⁷	4	0.56	35.3	41.8	1.8	3.29	45.2	26.3	20.4
B–4	10 ⁻⁷	6	0.38	35.9	43.5	1.6	4.61	46.0	26.6	18.9
B–5	10 ⁻⁹	0	1.72	33.4	42.0	2.1	-	47.1	25.1	21.9
B–6	10 ⁻⁹	2	0.81	32.8	41.9	1.6	1.77	45.2	27.4	19.9
B–7	10 ⁻⁹	4	0.63	33.5	40.8	1.8	3.38	45.6	26.6	19.1
B–8	10 ⁻⁹	6	0.43	34.8	38.8	1.5	4.54	46.9	26.8	20.4
B–9	10 -11	0	1.28	34.3	43.0	1.2	-	45.1	28.7	18.2
B–10	10 -11	2	0.68	33.9	42.7	1.1	1.77	46.5	27.4	18.5
B–11	10 -11	4	0.60	33.5	41.4	1.1	3.22	46.2	26.8	19.8
B–12	10 -11	6	0.47	33.6	41.0	1.0	4.48	45.9	26.3	19.0

Table 5.4: Chemical analysis results of experiments with MS and MM with various additions of CC and under different partial pressure of oxygen atmosphere, as wt.%. (at 1250 °C for 2 hours)



Figure 5.9: Effect of partial pressure of oxygen and addition of calcined colemanite to MS and MM on copper losses to slag (at 1250 °C for 2 hours)

Apart from the effect of other oxides (CaO, Al₂O₃, ZnO etc.) present in FFS slag, it was expected that the results obtained using MS-MM sample would resemble those obtained using FFS-FFM. In the present study, it is seen from Figure 5.9 that the copper contents in the slags without CC addition exhibited a decrease with decreasing oxygen partial pressure as reported in the previous studies [6,62]. However, this effect decreased with the increasing calcined colemanite addition. In any case, it could be concluded from the experimental results that the copper amount in the slag decreased with the increasing additions of CC under all oxidizing atmospheres.

The amount of copper in the resultant slags for B series was higher than that in the slag for P series where the experiments were done with FFS-FFM. With the addition of CC for 2 hours at 1250 °C, 0.32% Cu was obtained as the lowest copper content in slag for P series while the minimum copper content for B series was 0.38%Cu.

Color mapping characterization applied to B-3 in this series of experiments is given in Figure 5.10. In color mapping, Cu was represented by red, S by dark blue, Fe by light blue, Si by yellow and O by green. Since the dark regions in each picture indicated that the element did not exist or was present in trace amounts, it could be deduced from Figure 5.10 that the copper was present in the slag in sulfide (or metallic) form. Based on the pictures belonging to Fe, O and Si, it could be concluded that both SiO₂ and Fe₃O₄ phases existed in the representative slag.



Figure 5.10: Color mapping of representative sample (B-3)

5.4. Effect of Temperature on Copper Losses to Slag with CC Addition

In order to find out the variation of copper in slag with temperature at different colemanite additions (from 0% to 6 % of total charge) in copper matte smelting, a series of experiments were carried out with FFS-FFM and MS-MM samples at 1200 °C, 1250 °C and 1300 °C for 2 hours. The experiments with FFS-FFM samples were conducted both under nitrogen atmosphere and at controlled Po₂ (fixed at 10⁻⁹ atm.) while the experiments with MS-MM samples were only performed under a controlled Po₂ of 10⁻⁹ atm.
5.4.1. Experiments with EBİ Flash Furnace Slag-Matte (FFS-FFM)

Initial experiments were started with FFS-FFM samples under a controlled partial pressure of oxygen (10-9 atm.) with various CC additions (0, 2, 4, 6% of the total charge) for 2 hours at different temperatures (1200, 1250, 1300 °C). The chemical analyses of the resultant slags and mattes are given in Table 5.5, and changes in the copper content of slag with the increasing temperature and CC additions is plotted in Figure 5.11.

				Sla	g Analys	Matte Analyses				
Exp. Code	Temp. (∘C)	CC add. (%)	Cu	SiO ₂	Fe	S	B ₂ O ₃	Cu	Fe	S
PT-1	1200	0	0.78	38.3	38.8	1.4	-	44.6	21.0	15.7
PT-2	1200	2	0.61	38.4	37.4	1.2	1.29	45.7	20.2	15.9
PT-3	1200	4	0.35	37.9	36.0	0.9	2.80	45.7	19.9	16.4
PT-4	1200	6	0.29	37.7	34.8	0.9	4.19	46.1	19.6	16.4
PT-5	1250	0	0.61	40.1	36.6	1.1	-	44.9	20.1	16.0
PT-6	1250	2	0.49	39.0	35.4	1.1	1.26	45.5	19.9	16.5
PT-7	1250	4	0.43	38.6	33.9	0.9	2.67	45.5	19.8	15.9
PT-8	1250	6	0.34	39.2	31.8	0.9	3.90	46.2	19.2	16.1
PT-9	1300	0	0.47	42.6	35.8	0.9	-	44.7	21.1	16.1
PT-10	1300	2	0.38	43.3	35.3	0.9	1.22	45.6	20.1	16.6
PT-11	1300	4	0.35	41.8	33.5	0.8	2.58	46.4	20.1	16.1
PT-12	1300	6	0.34	41.4	32.1	0.8	3.48	45.4	20.4	16.8

Table 5.5: Chemical analysis results of experiments with FFS and FFM with various additions of CC at different temperatures, as wt.%. (at controlled Po₂=10⁻⁹ atm. for 2 hours)

Further experiments were conducted with FFS-FFM samples under nitrogen atmosphere. In these trials, CC was added up to 10% of the total charge at three different temperatures, namely 1200 °C, 1250 °C and 1300 °C for 2 hours. The chemical analysis results of these experiments and the effect of temperature on copper content in the resultant slags are given in Table 5.6 and in Figure 5.12, respectively.

Chemically balancing values for the resultant slags of PT and E series included all of other oxides analyzed by X-ray fluorescence (XRF) such as; ZnO (3.4-4.2%), Al₂O₃ (3.6-5.1%), CaO (0.8-3.7%), PbO (<0.2%), BaO (<0.6%), K₂O (<0.7%) and MgO (<0.2%). Magnetite content in this series was between 2.1% to 3.4%.

				Sla	g Analys	Matte Analyses				
Exp. Code	Temp. (ºC)	CC add. (%)	Cu	SiO ₂	Fe	S	B ₂ O ₃	Cu	Fe	S
E-1	1200	0	0.66	34.5	41.4	1.4	-	48.7	22.9	21.6
E-2	1200	2	0.57	34.7	40.0	1.2	1.41	49.5	22.1	20.8
E-3	1200	4	0.33	34.5	38.0	1.0	2.93	49.3	21.2	21.1
E-4	1200	6	0.28	34.9	36.1	0.8	4.42	49.6	21.4	21.5
E-5	1200	10	0.26	36.0	33.5	0.6	7.02	49.2	21.3	21.1
E-6	1250	0	0.55	37.3	39.3	1.1	-	48.4	21.9	20.7
E-7	1250	2	0.36	37.3	38.0	1.0	1.43	49.1	20.9	20.3
E-8	1250	4	0.30	36.9	36.6	0.7	2.84	50.0	20.9	20.1
E-9	1250	6	0.29	36.9	35.7	0.8	4.31	49.6	20.7	20.8
E-10	1250	10	0.30	37.1	31.2	1.3	6.47	49.5	21.4	21.4
E-11	1300	0	0.58	37.1	38.4	1.0	-	48.3	22.6	20.4
E-12	1300	2	0.48	37.3	36.9	1.0	1.33	49.8	22.0	21.1
E-13	1300	4	0.46	37.7	35.0	0.8	2.71	49.3	21.6	20.8
E-14	1300	6	0.34	37.5	33.7	1.0	4.16	48.3	20.4	20.1
E-15	1300	10	0.27	38.4	31.0	0.6	6.53	50.3	21.2	21.4

Table 5.6: Chemical analysis results of experiments with FFS and FFM with various additions of CC at different temperatures as wt.%. (under nitrogen atmosphere for 2 hours)



Figure 5.11: Effect of temperature and addition of calcined colemanite to FFS and FFM on copper losses to slag (at controlled $Po_2=10^{-9}$ atm. for 2 hours)

From the ternary diagram of FeO-Fe₂O₃-SiO₂ (Figure 3.5), it is known that as the temperature increases, the liquid region of slag widens and silica saturation level also increases. Considering that all of the experiments were carried out in silica crucibles, the silica content of slags increased up to the saturation level with the increasing temperature as expected.

It is well known from the literature that the increases in temperature leads to decreases in viscosity, i.e. increasing fluidity and resulting subsequently in decreasing mechanical copper losses. On the other hand, as the temperature increases, greater amounts of copper dissolve in the slag. Experimentally, the copper content in the resultant slags (conducted at controlled Po₂=10⁻⁹ atm.) decreased with the increasing temperature, as seen in Figure 5.11. For example, when compared with the experimental results obtained without CC addition, increasing the temperature from 1200 °C to 1300 °C resulted in a decrease of copper content in slag from 0.78% to 0.47%.



Figure 5.12: Effect of temperature and addition of calcined colemanite to FFS and FFM on copper losses to slag (under nitrogen atmosphere for 2 hours)

However, as seen in Table 5.6 and Figure 5.12, there was a variation in the experimental results carried out under nitrogen atmosphere. For instance, without the calcined colemanite addition, the copper content in slag at 1200 °C was 0.66%Cu, and then it decreased to 0.55%Cu with an increase in temperature to 1250 °C. However, when the temperature reached to 1300 °C, the copper content of slag again increased to 0.58%Cu. The copper content in slag could show such fluctuations with the variation of temperature since the mechanical copper losses to slag decreases with increasing temperature while the physico-chemical copper losses increase.

This means that the effect of increasing temperature in decreasing mechanical copper losses was stronger than increases in copper solubility. Eventually, these results indicated that increasing not only temperatures but also CC additions caused a decrease in copper content of slag down to 0.29%.

It is also seen from Figure 5.12 that the calcined colemanite addition prevented more copper losses to slag at all temperatures. This condition could be explained as follows; colemanite, besides boric oxide which contributes to decreasing liquidus temperature and density of slag, includes also calcium oxide which balances the basicity of slag and leads to decreases in the melting point of slag. As a result, the melting temperature of slag is gradually decreased so the slag can become liquid even at temperatures lower than 1200 °C. Thus, the temperature dependence of copper losses to slag could be reduced with the addition of colemanite. In other words, the addition of colemanite decreased the effect of equilibration temperature in controlling of these losses. According to the experimental results, it should be emphasized that the colemanite addition was very effective in decreasing the copper losses to slag at all temperatures.

5.4.2. Experiments with Synthetic (Master) Slag-Matte (MS-MM)

Several experiments with the synthetic samples were performed under a fixed partial pressure of oxygen ($Po_2=10^{-9}$ atm.) for 2 hours to examine the effect of temperature on the copper losses to slag by the addition of calcined colemanite. Results of the experiments are given in Table 5.7 and Figure 5.13.

Chemically balancing values for the resultant slags included all of the other oxides analyzed by X-ray fluorescence (XRF) such as; Al_2O_3 (2.3-3.8%), CaO (0-3.4%), K₂O (<0.3%) and MgO (<0.1%). Magnetite level in T series slags measured by SATMAGAN was between 1.8 and 4.8% (for T series slags).

			Slag Analyses						Matte Analyses		
Exp. Code	Temp. (∘C)	CC add. (%)	Cu	SiO ₂	Fe	S	B ₂ O ₃	Cu	Fe	S	
T–1	1200	0	1.21	32.2	43.7	1.9	-	44.8	28.4	20.5	
T–2	1200	2	0.63	33.1	43.9	1.6	1.90	45.5	26.9	20.4	
T–3	1200	4	0.64	34.3	43.4	1.7	3.42	47.0	22.7	19.7	
T–4	1200	6	0.42	34.1	40.9	1.5	5.03	45.5	26.8	20.7	
T–5	1250	0	1.28	33.3	42.0	1.7	-	47.1	25.1	21.9	
T–6	1250	2	0.81	32.8	41.8	1.5	1.77	45.2	27.4	19.9	
T–7	1250	4	0.63	33.6	40.8	1.3	3.38	45.6	26.6	19.2	
T–8	1250	6	0.43	34.8	38.8	1.2	4.54	46.9	26.8	20.5	
T–9	1300	0	1.75	37.0	41.1	1.4	-	45.1	28.0	22.0	
T–10	1300	2	0.75	36.6	42.1	1.3	1.77	45.8	27.4	21.6	
T–11	1300	4	0.68	37.3	40.0	1.5	3.16	45.8	27.1	20.9	
T–12	1300	6	0.43	37.9	37.6	1.2	4.48	46.1	26.8	21.3	

Table 5.7: Chemical analysis results of experiments with MS and MM with various additions of calcined colemanite at different temperatures as wt.%. (at controlled $Po_2=10^{-9}$ atm. for 2 hours)

According to the experimental results given in Table 5.7 and plotted in Figure 5.13, the effect of temperature at the fixed calcined colemanite additions could not be seen clearly. The results of T1-T12 experiments and E1-E12 experiments were very similar. As stated before, many researchers [3,63,72,120] agreed with finding that the increasing temperature in the system leads to decreases of slag viscosity and so mechanical copper losses to slag also decrease. However, some of them noted that the rising temperature of slag resulted in increasing solubility of copper, which resulted in increased physico-chemical copper losses. To sum up, the mechanical copper losses to slag decreased with increasing temperature while the physico-chemical copper losses increased. It seems, as an overall effect, that the copper losses increased somewhat with increasing temperature without the addition of colemanite. However, this effect became negligible as the colemanite addition increased.



Figure 5.13: Effect of temperature and addition of calcined colemanite to MS and MM on copper losses to slag (at controlled $Po_2=10^{-9}$ atm. for 2 hours)

5.5. Effect of CaO and B₂O₃ Additions on Copper Losses to Slag

In this part of the study, the effects of some additives such as CaO and B₂O₃ as flux on the copper losses to slag were studied, aiming to minimize the copper content in slag. For this purpose, flash furnace slag and matte (FFS-FFM) with the addition each of CaO and B₂O₃ up to 10% of the total charge were melted in a vertical tube furnace in silica crucibles at 1250 °C under nitrogen atmosphere for 2 hours. Since we already had the experimental results for CC additions (2, 4 and 6% of the total charge) at the same conditions, only one experiment was performed with 10% CC addition. Therefore, the results of S-7, S-11 and S-15 were the same as those of C-9, C-10 and C-11, respectively. The experimental findings are given in Table 5.8 and Figure 5.14.

				Matte Analyses						
Exp. Code	Additive	Add. (%)	Cu	SiO ₂	Fe	S	B ₂ O ₃	Cu	Fe	S
C-1	CaO	2	0.53	36.7	31.1	1.0	-	48.3	21.4	18.7
C-2	CaO	4	0.35	37.7	29.3	0.9	-	49.1	21.6	20.0
C-3	CaO	6	1.30	38.2	28.8	1.3	-	49.7	21.8	21.2
C-4	CaO	10	1.82	39.1	26.0	1.2	-	49.4	21.9	20.9
C-5	B ₂ O ₃	2	0.40	36.5	36.1	1.1	2.90	49.1	20.7	19.7
C-6	B ₂ O ₃	4	0.36	37.1	35.4	1.1	5.89	49.2	20.3	20.2
C-7	B ₂ O ₃	6	1.20	37.8	34.7	1.3	8.11	49.7	20.5	21.5
C-8	B ₂ O ₃	10	1.78	37.7	34.9	1.0	12.50	50.9	20.2	20.6
C–9	СС	2	0.30	38.4	32.3	0.8	1.56	49.1	20.9	20.3
C–10	СС	4	0.28	37.1	32.0	1.1	3.02	49.5	21.4	19.5
C–11	СС	6	0.29	37.4	30.8	1.0	4.41	49.6	20.7	20.8
C–12	СС	10	0.30	37.1	31.3	0.9	6.38	48.6	20.8	21.0

Table 5.8: Chemical analysis results of experiments with FFS and FFM with various additions of CaO and B_2O_3 as wt.%. (under nitrogen atmosphere at 1250 °C for 2 hours)



Figure 5.14: Effect of some additives (CaO, B₂O₃, CC) on copper losses to slag (under nitrogen atmosphere at 1250 °C for 2 hours)

In order to explain the results correctly, some important information about the behavior of B₂O₃ should be given. Although boric oxide (B₂O₃) was not extensively employed in metallurgical applications, it was widely used in glass industry due to significant/desirable properties. For example, the addition of B₂O₃ to alkali-silicate composition such as SiO₂-Al₂O₃-CaO yielded the very crucial group of alkali-borosilicate glasses with relatively easy melting and a good chemical durability especially to attack by acid [121,122]. As for viscosity, the effect of B₂O₃ was considerably different at high and low temperatures. Its structural change, and the associated property change, depended on temperature variations. While the building unit of boron structure at low temperatures as oxygen tetrahedron [BO4]⁵⁻ lead to an increase in the viscosity of melt, at higher temperatures major part of the tetrahedrons turning into [BO₃]³⁻ triangles caused to break up the chains of molten matrix and so decrease the viscosity. Moreover, B₂O₃ addition to the slag decreased the melting point. In other words, boric oxide tended to form a eutectic due to its very low melting point, which resulted in a more effective decrease in the slag viscosity [123,124]. Considering the copper smelting operation temperature which was above 1200 °C, the total effects of structure change and eutectic formation result in a decrease in the viscosity of molten slag. There was

a clear consensus among researchers [20,24–27] studying B_2O_3 (or colemanite) systems at high temperature that the addition of B_2O_3 (or colemanite) decreased the viscosity of the melt.

As mentioned previously, a good/clear separation of matte and slag depends also on their density differences apart from other factors. Therefore, the addition of B₂O₃ leads to lowering of slag density and a better separation of matte and slag as well.

Based on all the positive effects mentioned above, it was expected that the copper losses to slag should decrease with the addition of B_2O_3 . From the data given in Table 5.8 and also Figure 5.14, it can be seen that the addition of B_2O_3 (up to 4%) to slag decreases the copper content in slag to a relatively low value as expected. However, beyond this point, the copper content in slag increased as B_2O_3 addition increased. This might be attributed to the climbing of the slag including small amount of matte particles on the side walls of the crucible, which occurred after the excessive addition of B_2O_3 in this study. On the other hand, as seen in Figure 5.15.c, there are several holes on the slag surface observed for only 6% and 10% B_2O_3 additions, which may be attributed to the evaporation of boron. Figure 5.15.d shows an example of the slag climbing after an experiment with 10% B_2O_3 addition to the matte-slag system. Since B_2O_3 in the slag lowers the surface tension between slag and crucible by occupying the surface [75], addition of B_2O_3 above a certain value partially caused this climbing of slag up the sides of the crucible.

It was reported [17,56,69-71] that CaO addition decreased the copper solubility in slag since it could replace any oxidic copper in the slag associated with silica. In addition, the presence of CaO in slag decreased its viscosity by breaking complex long silicate chains (as seen in Figure 3.9), which allowed easy settling and promotes a decrease in the copper losses to slag. Interfacial energy/tension is also an important parameter in the copper losses to slag. When interfacial tension is high between matte inclusions and slag, a good separation encourages increasing rate of settling. On the contrary, as interfacial tension between them decreases, the separation of these two phases becomes more difficult. According to the literature, the effect of CaO on interfacial tension between matte and slag exhibits a nonlinear behavior and there is a peak at 4%CaO. After reaching the maximum value, the interfacial tension between copper matte and slag decreases gradually with increasing CaO addition [74,76,125]. This effect was explained by Li et al. [76] as follows: "This may be interpreted by a stronger interaction between S in matte and Ca²⁺ in slag. With increasing Ca²⁺ concentration in slag, the amounts of transition of S from the matte to the slag increases". As it can be seen from Figure 5.14, the effect of CaO on the copper losses to slag as well as sulfur concentration in slag indicated a similar behavior to this, i.e. when CaO

was added to the matte-slag system up to 4% CaO, the copper and sulfur contents of slag decrease. After this point, any further increase in CaO addition caused a decrease in interfacial tension and also an increase in both copper and sulfur contents in slag.

In Figure 5.14, the curve belonging to CC addition showed better results with regards to the copper losses to slag. Taking all of experimental results into account, this behavior could be explained by the double effect of CaO and B₂O₃. Since the calcined colemanite (CC) included both CaO and B₂O₃, it exhibited more effective results than each of them. In any case, the addition of CC exceeding 4% had not beneficial effects, i.e. a change in copper content in slag after 4%CC addition was insignificant. Considering the chemical analysis of CC (having 51.7%B₂O₃, 27.7%CaO and 8.6%CaCO₃), the addition of 4%CC of the total charge corresponded to nearly 2.1% B₂O₃ and 1.4%CaO addition of total charge. These values were within the positive effect limits for CaO and B₂O₃. Negative effects of CC addition are expected to start from 12% CC addition because only then it includes more than 4%CaO and 6% B₂O₃.

Experimental observations should also be stated in here to clearly understand the effect of CC, i.e. CaO and B_2O_3 additions to the system. As stated before, as more and more CC additions were done, the easier the matte-slag separation took place. So the matte was easily separated from the slag by fingers without using any apparatus in all of the experiments performed with CC addition (even with 2% CC addition). However, as CC additions increased, the slag-crucible separation became more difficult. In B_2O_3 addition experiments, the separation difficulties (matte-slag and slag-crucible) were very similar to those in CC addition experiments. On the other hand, the experiments with up to 4% CaO addition resulted in easily separating matte and slag as well as slag from the crucible, but further addition of CaO led to a stronger/hard slag, and matte-slag separation was quite difficult. Figures 5.15, 5.16 and 5.17 show the separated matte-slag phases after experiments with the addition of B_2O_3 , CaO and CC, respectively.



Figure 5.15: The separated matte-slag phases after experiments (at 1250 °C for 2 hours under nitrogen atmosphere) with the addition of B_2O_3 a) 2%, b) 4%, c) 6% and d)10% (climbing of the slag including matte on the sides of the silica crucible). (*m.p: matte or metallic copper particles)



Figure 5.16: The separated matte-slag phases after experiments (at 1250 °C for 2 hours under nitrogen atmosphere) with the addition of CaO a) 2%, b) 4%, c) 6% and d) 10% (matte sticking to the slag)



Figure 5.17: The separated matte-slag phases after experiments (at 1250 °C for 2 hours under nitrogen atmosphere) with the addition of CC a) 2%, b) 4%, c) 6%, d) 10%, and e) without CC addition

5.6. Results of Liquidus Temperature and Viscosity Calculations

To understand the melting behavior of slags FactSage model was used to calculate liquidus temperatures. The calculated liquidus temperatures of representative slags belonging to S (experiments with FFS-FFM) and F (experiments with MS-MM) series are shown in Figures 5.18.a and 5.18.b. According to FactSage model calculations, the first precipitates forming were determined to be tridymite (SiO₂) or fayalite.



Figure 5.18: Variations of the calculated liquidus temperature of the experimental slags with the addition of CC and reaction duration a) for S series, b) for F series

As seen in Figure 5.18, the liquidus temperatures of final slags decreased remarkably with the increasing CC addition probably due to combining of other oxides with B_2O_3 . By this way, the eutectics with low melting points could form, which resulted in the lowering of the melting temperature of slag. When Figure 5.18.a is compared with Figure 5.18.b, it can be concluded that the liquidus temperatures of S series were generally higher than those of F series slags

due to the lower Fe/SiO₂ ratio and the presence of some oxides such as ZnO, BaO, etc. in the S series slags leading to increase in liquidus temperature.

To explain the decrease in liquidus temperature with the addition of CC, change in the liquid slag region of fayalitic slag with the addition of CC is calculated by using FactSage database [112,114] and shown on the FeO-Fe₂O₃-SiO₂ phase diagram as in Figure 5.19. Here, other oxides present in FFS were neglected. The calculated results showed that when 6% CC was added to the system, the liquid slag region increased considerably. This corresponded to liquidus temperature decreasing. As seen in Figure 5.18, CC addition lowered the liquidus temperatures for both experimental series. These calculated results are in accordance with our experimental results.



Figure 5.19: Change in liquid slag region with the addition of CC on phase diagram of FeO-Fe₂O₃-SiO₂ calculated by "Phase Diagram" module of FactSage 6.2.

Although the performed experiments were time dependent, i.e. not in the equilibrium, the viscosity values shown in Figure 5.20 were calculated using FactSage software (version 6.2). Accuracy of calculated viscosities using FactSage can be determined by comparing the experimental results with the data published elsewhere [52,54,72,85,86,126]. During the last few decades, researchers had reported that the viscosities of synthetic slags at 1200 °C and 1300 °C were within the range of 1 to 4 poise, although the viscosities of industrial copper smelting slags at the same temperatures were reported to be 2 to 18 poise depending on mainly acid to base ratio. These measured viscosities are in general agreement with the results of FactSage modeling not only for the industrial copper matte smelting slags, but also for the synthetic slags.



Figure 5.20: Variations of predicted viscosity of the resultant slags for F and S series with the addition of CC and reaction duration.

As seen in Figure 5.20, CC addition resulted in negligible increase in viscosity of F series slags whereas it had an opposite effect on S series slag. Taking into account that the two slags (F and S series) had nearly the same magnetite content, this might be due to the differences in Fe/SiO₂ ratios (for S series 1-0.75, for F series 1.5-1) between the two slag

series. Several researchers [86,126] stated that the viscosity of slag decreased significantly with the increasing Fe/SiO₂ ratio. In S and F series, Fe/SiO₂ ratio varied mainly depending on the duration (long duration lead to more SiO₂ and less Fe contents in slag and resulted in a decrease in Fe/SiO₂ ratio) and so each line had a different slope.

Apart from 6% CC addition, the change in the liquid slag region of fayalitic slag with 10% addition of CaO, B₂O₃ and CC each was also calculated by FactSage "Phase diagram" module. Figure 5.21 gives effects of additives on the FeO-Fe₂O₃-SiO₂ phase diagram at 1250 °C. It should be noted that other oxides (Al₂O₃, ZnO, K₂O, BaO etc.) present in FFS were omitted.



Figure 5.21: Change in liquid slag region with the 10% addition of CaO, B₂O₃ and CC on phase diagram of FeO-Fe₂O₃-SiO₂ calculated by "Phase Diagram" module of FactSage 6.2.

The calculated results indicated that when 10% CaO was added to the fayalite slag, the liquid slag region became narrower and shifted up (toward SiO₂) probably due to need of more SiO₂ to reach the equilibrium. On the other hand, 10% addition of B₂O₃ with very low melting point led to extension of liquid region towards FeO. It was very clear that 10 %CC addition increased greatly the liquid slag region in every direction (toward SiO₂, FeO and Fe₂O₃ corners) by maintaining its initial shape.

5.7. Industrial Testing at EBİ

The colemanite addition was industrially tested by EBİ to lower the copper losses to their slag during matte smelting. Ground colemanite supplied from Eti Mining Company was mixed with lignite/coke in weight ratio 1:2 (3% coke and 1.5% colemanite of charge). This mixture was fed to a rotary kiln for drying by conveyor. Although the charge materials were dried by using hot gases at 350-400 °C, the maximum temperature of charge materials reached was around 100 °C in rotary kiln furnace. However, the dehydration of colemanite needed at least 400 °C. In brief, the temperature in drying furnace was not high enough to calcine the colemanite. For this reason, the chemically bonded water in colemanite could not be removed during drying; dehydration took place only in the combustion tower of flash furnace.

After the colemanite addition to flash smelting furnace (at the end of first week), observations of engineers and workers at EBİ were as follows:

It was claimed that after the addition of colemanite, the furnace temperature (as well as matte and slag temperatures) increased at least 70-80 °C while supplied fuel was of the same amount. Therefore, the temperature was decreased gradually to the operating value by lowering fuel-oil/gas addition to the system; this resulted in considerable amount of fuel saving after colemanite addition. So, they claimed that the resulting benefit was somewhat higher than the cost of colemanite used.

With the addition of colemanite, the fluidity of slag dramatically increased. However, the copper content of slag did not decrease significantly. The reason of this was explained as follows: In Outokumpu flash smelter in Samsun, too much concentrate dust went out with offgas by passing through the uptake of the furnace. Some part of the dust sticking to the sides of the uptake walls reacted and formed matte droplets. Since the slag taphole was just below the uptake of the smelting furnace, these matte droplets fell into slag during tapping, which increased the copper losses to slag in such a continuous smelting system.

Any structural difference in slag and also in matte before and after the colemanite addition was not observed. During the colemanite addition, no negative effect was encountered in the smelting stage. To see the effect of colemanite addition in the final product (cathode ingots), this industrial testing should be continued at least for 1 month.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

In this study, mainly the effect of calcined colemanite (CC) addition as a flux to Turkish industrial copper matte smelting slags (FFS) and also to some oxidized synthetic master slags (MS) were investigated to observe changes in the copper content of slag. Besides, the effects of CaO and B_2O_3 additions to FFS with regard to the copper losses to slag were studied.

Initially, the effect of reaction duration with 0 to 6% CC addition on the copper losses to slag was studied for ½, 1, 2 and 4 hours at 1250 °C under nitrogen atmosphere with FFS-FFM and MS-MM pairs. The results of the experiments have indicated that 2 hours was sufficient to obtain a low copper content in slag. It was concluded that the copper losses to the matte smelting slag decreased with the increasing addition of CC, and at the end of experiments the minimum copper contents in EBİ flash furnace slag (FFS) and synthetic slag (MS) were obtained as 0.28% and 0.40%, respectively. It should be noted that 0.3% copper content in FFS could be achieved even with 2% CC addition in 2 hours.

Second series of experiments were carried out with the same matte-slag samples to determine the effect of changes in partial pressure of oxygen, i.e., more oxidizing or reducing conditions provided by CO₂/CO gas mixture, to the copper losses in matte smelting slags. From the experimental results, it was found that the amount of copper in slag slowly decreased with increasing CC additions under all oxidizing atmospheres, and the lowest copper contents in FFS and MS obtained after 6% CC addition were 0.32% and 0.43%, respectively.

The study was continued further with again FFS-FFM and MS-MM couples under an oxidizing atmosphere and with only FFS-FFM samples under nitrogen atmosphere in order to examine the temperature effect on the copper losses to slag for various calcined colemanite additions. As a result of experiments performed at different temperatures (1200,

1250 and 1300 °C), it was concluded that the matte-slag separation took place well and the copper content in slag was low (~0.3% Cu) even at 1200 °C after 4% CC addition. Since there were no significant differences between the results at those temperatures, the selection of lower temperature was thought to be reasonable to satisfy the economics.

The objective of final experiments was to observe the effects of CaO and B_2O_3 additions on the copper losses to slag and to compare their results with those of CC addition. As a conclusion, the experimental results of matte-slag-flux mixture conducted at 1250 °C for 2 hours under nitrogen atmosphere showed that the addition of each additive such as CC, CaO and B_2O_3 up to 4% led to a gradual decrease in the copper content of final slags. After this point, the copper losses to slag increased markedly/steeply with the increasing CaO and B_2O_3 additions. On the other hand, the calcined colemanite (CC) additions of more than 4% had a small effect on the copper losses to slag and showed a plateau at about 0.3% Cu.

By using FactSage software, the viscosities of resultant slags as well as trends of liquidus temperature of final slags were estimated for S (experiments with FFS-FFM at 1250 °C) and F (experiments with MS-MM at 1250 °C) series slags, and also the phase diagrams after some additives were calculated to see the behavior of liquid slag region. Results of calculations showed that the liquidus temperatures of final slags decreased remarkably with increasing CC addition for both FFS and MS samples. However, a negligible increase in viscosity on F series slags and a negligible decrease in viscosity on S series slag were observed. The phase diagrams calculated by FactSage indicated that CC addition increased greatly the liquid slag region in every direction (toward SiO₂, FeO and Fe₂O₃ corners) by maintaining its initial shape.

From all literature review and experimental results, it could be summarized that only CaO addition as a basic oxide led to a decrease in slag viscosity and solubility of copper in slag, and only B₂O₃ addition as an acidic oxide led to a small decrease in slag viscosity and decrease in the melting point and density of slag. On the other hand, the addition of calcined colemanite resulted in lowering of melting point and density of slag without substantial changes in viscosity. Due to these positive effects of colemanite addition, more clear separation between matte and slag as observed in the experiments would be expected during copper smelting stage. From FactSage calculations, it could be said that the colemanite addition decreased the liquidus temperature which led to early melting of slag and allowed enough duration for settling of matte particles within the slag without changing its viscosity, which resulted in less mechanical copper losses to the slag. So in the present study, the copper percent in the resultant slag decreased from 0.88% down to 0.3% with increasing addition of calcined colemanite. Therefore, it may be possible to avoid slag

treatment (flotation or electric settling furnace) by lowering the copper content of the matte smelting slag to acceptable levels which will correspond to about 0.3%Cu for commercial plants.

Recommendations for further works;

For any further laboratory investigation or plant test, the following recommendations can be given;

On the basis of the obtained results one can conclude that the colemanite addition lowers the liquidus temperature but not affecting the viscosity of slag substantially. Therefore, if the furnace operating temperature is decreased gradually depending on the amount of colemanite addition by lowering fuel/gas consumption, this will not only result in fuel savings but also will reduce refractory wear.

It is well known that the liquidus temperature and fluidity of slag play an important role in the furnace refractory life. Although, there are many studies about refractory-slag interactions, none of them includes the effects of boric oxide. To clarify this point, it will be necessary to study experimentally at laboratory scale the reactions between refractory and slag having boron compounds.

On the other hand, the addition of colemanite does not affect negatively downstream units of operation, since CaO present in a low amount (max. 5% CaO in slag) does not form a compound having high melting point such as calcium silicate and volatilized boron can be recycled with dust collection system.

Apart from mixing to coke as in EBİ trial, colemanite can be fed to smelting furnace by mixing to the silica flux (through concentrate burner) or injected directly to the flash furnace settling region by means of lances or tuyeres.

As mentioned previously, in converter stage of Mitsubishi process CaCO₃ was used as flux, and copper losses reached to high value (12-16% Cu) in this step. Such a high copper losses can be lowered by adding certain amounts of colemanite instead of CaCO₃. Considering that converter slag was sent to smelting furnace after granulation with water, colemanite in converter slag can also decrease copper losses to slag in smelting furnace.

It is expected that when colemanite is added to a furnace with a settler but without an uptake system like in flash smelting furnace (being a continuous system), better results can be obtained in terms of copper losses to slag.

To see the effect of colemanite addition on copper losses to slag, more detailed studies should be performed on smelting slags (as well as converter slags separately) not only on batch scale but also on pilot scale.

According to the experimental results carried out under the controlled partial pressures of oxygen, colemanite addition lowers the copper losses to slag even at high Po₂ pressures (10⁻⁷ atm.). Therefore, a research on the possibilities of using in converter stage (with converter slags) and its effect on copper losses to slag can be undertaken.

Due to positive experimental results at 1250 °C, the effect of CaO and B_2O_3 additions at different temperatures (especially at lower temperatures) on copper losses to slag can be investigated.

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APPENDIX A

VERTICAL FURNACE TEMPERATURE PROFILE AND TEMPERATURE CALIBRATION

First of all, the hottest zone of the furnace was determined by measuring temperature for each centimeter, and recrystallized alumina support rod has fixed in place which had 40 cm above the bottom of reaction tube.

In order to determine temperature profile of the furnace before experiments, an empty crucible was inserted to the hottest region in the furnace, and temperature profile of the furnace was obtained for different set-temperatures as shown in Figure A.1. Depending on the amount of charge used, the top of the slag melt would be between 3-5 cm above the inside bottom of the crucible. As seen from the Figure A.1, the temperature variation of the furnace in the distance of 5 cm was $\pm 3^{\circ}$ C. However, it is also seen from the Figure A.1 that there is small differences between set-temperatures and measured temperatures (real temperature in the furnace). Figure A.2 shows the temperature of furnace calibration to determine the correlation between set and real temperatures. According to temperature calibration, furnace temperature was set to 1265 °C to enable 1250 °C in the furnace.



Figure A.1: Temperature profile in the hottest zone of the vertical tube furnace

122



Figure A.2: Temperature calibration of the vertical tube furnace

123

APPENDIX B

CO-CO2 GASES CALIBRATIONS AND OXYGEN PARTIAL PRESSURE CALCULATION

The required oxygen partial pressure of the system was supplied by using $CO-CO_2$ gas mixture. Firstly, flow rates of $CO-CO_2$ gases were calibrated depending on the height of the liquid in manometers. Calibration curves for CO and CO_2 are given in Figure B.1 and B.2, respectively.



Figure B.1: Calibration curve of CO gas flow



Figure B.2: Calibration curve of CO₂ gas flow

After calibration of the gases, Po₂ values were calculated by means of the reaction between CO and CO₂ as follows;

Where ΔG° values are the Gibbs free energy of the reactions [B1].

In equilibrium; △Go_{Toplam} = R*T*In K, and K (Eq. constant)= Pco₂/Pco*(Po₂)^{1/2}

System will only have three gasses (CO-CO₂-O₂). If the temperature (T) is chosen as 1250 $^{\circ}$ C (1523 $^{\circ}$ K), (Since most of the experiments were conducted at 1250 $^{\circ}$ C);

-282400 + 86.81*1523 = 8.314*1523*In[Pco₂/Pco*(Po₂)^{1/2}]

 $[Pco_2/Pco^*(Po_2)^{1/2}] = 1.416^*10^5$ is obtained.

By using (Pco₂/Pco) ratio which is equal to flow rate ratio (Vco₂/Vco), Po₂ values required to the system can be calculated. Table B.1 gives some examples of Po₂ values corresponding to (Pco₂/Pco) for 1250 °C. It should be noted that these values needed to be recalculated for different temperatures.

(Pco ₂ /Pco) ratio or (Vco ₂ /Vco) ratio	Po ₂ values, atm.
0.1	5. 10 ⁻¹³
0.5	1.2.10 ⁻¹¹
1	5. 10 ⁻¹¹
2	2. 10 ⁻¹⁰
5	1.2.10 ⁻⁹
10	5. 10 ⁻⁹
20	2. 10 ⁻⁸
30	4.5. 10 ⁻⁸
40	8. 10 ⁻⁸
50	1.2. 10 ⁻⁷

Table B.1: Po₂ values corresponding to (Pco₂/Pco) ratio

As a result, to obtain Po_2 values of 1.10^{-7} , 1.10^{-9} and 1.10^{-11} atm., (Vco₂/Vco) ratio was selected as 47, 4.7 and 0.47 respectively.

In order to check Po₂ values, DS oxygen probe (supplied from Australian Oxytrol System Co.) was used in some experiments. Oxygen probe output was DC millivolt, and the corresponding oxygen concentration for this millivolt signal was calculated according to Nernst equation. This equation defined the electromotive force developed when there were different concentrations of a reactant on each side of an electrolyte [B2]. When atmospheric air was used a reference, the equation simplified to;

Po₂ = 0.209*exp[-46.421*(E/T)]
Where T is temperature (Kelvin) and E is sensor electromotive force (mV). According to the experimental results, oxygen concentration measured by probe and then calculated by this equation was in well accordance with that of the gas supplying system. For example, Po₂ was aimed to be fixed at 10^{-9} atm. for P-5 experiment by using a mixture of CO/CO₂ gases. During this experiment, the oxygen concentration was measured to be between $6.2^{*}10^{-10}$ and $4.4^{*}10^{-9}$ atm. by means of oxygen probe. These values were also the minimum and the maximum measured values during the experiment, respectively.

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APPENDIX C

CALCULATION OF DISSOLVED COPPER IN SLAG

There are several experimental studies [14,19, 63] on the solubility of copper in iron silicate slag at different temperatures and oxygen partial pressures ranging from 10⁻¹⁰ to 10⁻⁷ atm. As an example, Toguri and Santander [63] derived an empirical relation (Eq. 3.3) by using their experimental results to predict copper content in slag as follows:

Wt.%Cu_(in slag) =
$$27.59^{*}(a_{Cu2O})^{1/2}$$
 (at 1250 °C) (Eq. 3.3)

Where a_{Cu20} is activity of copper oxide which can be calculated by using Rx. 3.1:

$$FeS_{(in matte)} + Cu_2O_{(in slag)} \rightarrow FeO_{(in slag)} + Cu_2S_{(in matte)}$$
(Rx. 3.1)

The equilibrium constant for (Rx. 3.1) is;

$$K = (a_{Cu2S} * a_{FeO}) / (a_{Cu2O} * a_{FeS})$$
(Eq. 3.1)

Gibbs free energy for (Rx. 3.1) at 1523 °K is;

$$\Delta G_{01523} = -25063 \text{ cal/mole}$$
 (Eq. C.1)

The equilibrium constant (K) value at the smelting temperature of 1250 °C (1523 °K) is 3947. Since the Cu₂S-FeS system is assumed to be ideal, i.e. a_{Cu_2S}/a_{FeS} ratio is 1, and assuming that $a_{FeO}=\%$ FeO in slag (nearly 0.4 for S-12 slag). Therefore, the value of $a_{Cu_{2O}}$ can be calculated as follows;

 $3947 = 0.4/a_{Cu2O}$, and $a_{Cu2O} = 1.1*10^{-4}$

The wt. percent of Cu in the slag can then be calculated from the above expression (Eq. 3.3).

 $Wt.\%Cu_{(in slag)} = 27.59^{*}(1.1^{*}10^{-4})^{1/2}$

Wt.%Cu_(in slag) = 0.27

This value varies with the matte grade, slag composition and also temperature. According to the above thermodynamic calculation, the experimental value of about 0.3% Cu determined in this work was nearly all dissolved copper in the slag. The copper contents of the slags which were higher than 0.3% were probably due to the copper existing in the slag as matte particles or metallic copper which did not find time to settle from the slag.

CURRICULUM VITAE

PERSONAL INFORMATION

Surname, Name	: RÜŞEN, Aydın
Nationality	: Turkish (T.C.)
Date and Place of Birth	1 : 1977, Erzurum, Turkey
Marital Status	: Married with one daughter
Employment	: Research Assistant in Metallurgical and Material Eng.
	Dept., Middle East Technical University
Contact Details	: Metallurgical and Material Eng. Dept., Room: E-311, METU, 06531,
	Ankara/TURKEY
Phone -	-90 312 2105931
Fax -	-90 312 2102518
E-Mail a	arusen@metu.edu.tr, arusen25@gmail.com, aydinrusen@hotmail.com

EDUCATION:

- Bachelor of Science: Chemical Engineering Department, Atatürk University, 1997-2001.
- Master of Science: Metallurgical and Materials Engineering Department, METU, Jan. 2005 – Aug. 2007.
 SUPPORT AREA: Hydrometallurgy
 - THESIS: Recovery of Lead and Zinc from Çinkur Leach Residue
- **Doctor of Philosophy** : Metallurgical and Materials Engineering Department, METU, Sept. 2007 Feb. 2013

SUPPORT AREA: Extractive Metallurgy

THESIS: Usage of Boron Compounds in Copper Production

RESEARCH INTERESTS:

Hydrometallurgy, Recovery of Valuable Metals, Extractive Metallurgy of Copper, Nonlienar Optical Materials (Metal Borates), Ferroelectric Polymers

ACADEMIC POSITIONS:

<u>Research Assistant</u>: Jan. 2002- Sept. 2002, Atatürk University, Metallurgical and Materials Eng. Dept.

<u>Research Assistant:</u> Sept. 2002- 2013, Middle East Technical University Metallurgical and Materials Eng. Dept.

<u>Visiting Researcher:</u> Jan. 2010 – Jan. 2011, Bremen University Geosciences Dept. Crystallography Group, Bremen, Germany

LIST OF PUBLICATIONS:

Article in International Journal; (SCI)

- 1. Rüşen, A., Sunkar, A.S., Topkaya, Y.A., "Zinc and lead extraction from Çinkur leach residues by using hydrometallurgical method", Hydrometallurgy 93 (2008) 45-50.
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- <u>*Rüşen, A.,</u> Topkaya, Y., Geveci, A., "Variation of Copper Content in Slag with Temperature at Different Colemanite Additions in Copper Matte Smelting", 16th. International Metallurgy and Materials Congress (IMMC 2012), 13-15 September 2012, İstanbul, Turkey.
- (*: Presented by Aydın RÜŞEN)

Projects;

- Oct. 2005 Sept. 2007: "Recovery of Zinc and Lead from Çinkur Leach Residues by Using Hydrometallurgical Techniques", BAP project (No: BAP2004-03-08-04), METU (M.Sc. Thesis Project).
- Dec. 2007 Dec. 2009: "Bakır Üretiminde Bor Bileşiklerinin Kullanılması", supported by BOREN (No: BOREN2007-Ç0141).
- Dec. 2009 Dec. 2012: "Usage of Boron Compounds in Copper Production", supported by the State Planning Agency (Devlet Planlama Teşkilatı, DPT). (Ph.D. Thesis Project).

Assisted Courses and Laboratories:

METE 206 Materials Laboratory METE 208 Chemical Principles of Material Productions METE 305 Transport Phenomena METE 416 Fuels and Furnaces METE 435 Foundry Laboratory-1 METE 516 Production of Ferroalloys METE 525 Extractive Metallurgy of Copper

Languages:

English (ÜDS-2003: 71.25), German (Elementary- A2)