MATERIAL AND HEAT BALANCE CALCULATIONS OF ETI-BAKIR PLANT BY COMPUTER

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MATERIAL AND HEAT BALANCE CALCULATIONS OF ETI-BAKIR PLANT BY COMPUTER

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ABSTRACT

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In this study the data taken from Outokumpu type Flash smelter of Eti-Bakır Plant (Samsun, Turkey) was used to write a computer program in Visual Basic with interface to Excel. Flash smelting is the pyrometallurgical process for smelting metal sulfide concentrates, used in Eti-Bakır plant. In this plant, copper flash smelting consists of blowing fine, dried copper sulfide concentrate mixtures, silica flux, lignite with air into the furnace and natural gas as main fuel. The molten matte is the principal product of the furnace and slag contains 0.5-2% Cu. It is sent to a slag treatment (flotation) process for Cu recovery. This flash furnace off-gas contains from 8-12 volume % SO_2 which is fixed as H_2SO_4. Written program was used to optimize the consumption of oxygen enriched air, fuel and lignite in this Flash Smelter by making material and heat balance of the plant.

Keywords: Flash Smelter, Copper, Computer Optimization of Parameters, Oxygen Enrichment.

ÖZ

ETİ-BAKIR TESİSİNİN MALZEME VE ISI DENGELERİNİN BİLGİSAYAR İLE HESAPLANMASI

Argyn, Aidar

Yüksek Lisans, Metalurji ve Malzeme Mühendisliği Bölümü

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Bu çalışmada, Samsun'daki Eti-Bakır Tesisinin Outokumpu tip flaş izabesinden alınan data, Visual Basic bilgisayar programı uygulaması ile Excel bağlantısı kullanıldı. Eti-Bakır tesisinde kullanılan flaş izabe, metalik sülfür konsantrelerin ergitilmesi için kullanılan pirometallurjik yöntemdir. Fabrikada, bakır flaş izabesi için hava ile üflenen ince ve kuru bakır sülfür konsantre karışımları, silika flaks ve linyit ana yakıt olan doğal gaz ile birlikte kullanılmaktadır. Fırının temel ürünü ergimiş mat ve 0.5-2% civarında bakır içeren curuftur. Bakırın geri kazanımı için curuf, flotasyon işlemine tabi tutulur. Flaş fırınından çıkan 8-12% hacmindeki SO_2 gazı H_2SO_4'e dönüştürülür. Fabrikanın malzeme ve ısı dengesini kullanılarak yazılan program, flaş fırınındaki tüketilen oksijenle zenginleştirilmiş hava, yakıt ve linyitin optimizasyonu için kullanıldı.

Anahtar Kelimeler: Flaş İzabe, Bakır, Bilgisayarla Parametrelerin Optimizasyonu, Oksijenle Zenginleştirme.

To My Family

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INTRODUCTION

Most of the big world corporations that deal with copper smelting employ flash smelting technology. However, there is no general agreement which smelting mode is better and optimum for different flash furnaces around the world. Each mode of furnace for different plants should be optimized not only with consideration of used furnace in that plant but also with consideration of many criteria as location of plant as well as properties of feed, etc.

The main purpose of present work is to develop a way by which optimization of flash smelter can be done. Of course, in the past, methods to optimize copper smelters were also developed (e.g. Davenport and Partelpoeg, 1987). However, in this work to calculate material and heat balances of smelting process more industrial way of looking is used rather than linear equations.

In present work as an optimization object Outokumpu type flash smelter which exists in Eti-Bakır plant, is chosen. Data which are used for calculations and writing a computer program to calculate material and heat balances were taken from the actual smelting plant.

In Chapters 2 and 3 of present work theoretical information about copper, copper smelting, Outokumpu type flash smelter and also Eti-Bakır plant are given. Technological calculations, assumptions that were made during the calculations and specifications are presented in Chapter 4. The results are discussed in Chapter 5 where also limitations of the optimized model and recommendation to the plant operators are presented.

CHAPTER 2

LITERATURE REVIEW

2.1 General information about copper

2.1.1 Copper and society

Within all of the materials used by human beings, copper has had one of the most profound effects on the development of civilization. From the dawn of civilization until today, copper has made, and continues to make, a vital contribution to sustaining and improving society. What makes copper and copper-based products so valuable to us, and why do societies depend on them? Copper's chemical, physical and aesthetic properties make it a material of choice in a wide range of domestic, industrial and high technology applications. Copper is ductile, corrosion resistant, malleable and an excellent conductor of heat and electricity. Alloyed with other metals, such as zinc (to form brass), aluminum or tin (to form bronzes), or nickel, for example, it can acquire new characteristics for use in highly specialized applications. In fact, society's infrastructure is based, in part, on copper (www.copper.org). For instance, copper is used for:

- conducting electricity and heat;
- communications;
- transporting water and gas;
- roofing, gutters and downspouts;
- protecting plants and crops, and as a feed supplement; and
- making statues and other forms of art.

Copper has been in use for at least 10,000 years, yet, it is still a high technology material, as evidenced by the development of the copper chip by the semi-conductors industry.

2.1.2 Properties of copper

Copper has Atomic Number 29, that is, an atom of copper has 29 protons. Copper is in column IB of the Periodic Table of the Elements, above Silver (Ag) and Gold (Au). Elements in the same column have some similar properties. Like silver and gold, copper is soft (with a Moh's hardness of 2.5 to 3, that is, harder than a fingernail, but softer than a steel pocketknife). The surface has a metallic luster. With a specific gravity of 8.2 (that is density as 8.2 g/cm^3), it is far denser than water with a specific gravity of 1, or sulfur, with a specific gravity of just over 2, or carbon in the mineral graphite (2.23). Silver, however, is below copper in column IB, and so it is denser (10.5) and gold, even lower, is far denser at 19. When copper combines with other elements, it has a charge of either +1 (called "cuprous") or +2 (called "cupric") (www.en.wikipedia.org/wiki/Copper).

Like gold and silver, copper is malleable. That is, it can be bent and shaped without cracking, when either hot or cold. It can be rolled into sheets as thin as 1/500 of an inch. Copper is also ductile, that is, it can be drawn out into thin wire. A copper bar 4 inches thick can be heated, rolled, then drawn into a round wire so thin that it is thinner than a human hair. This wire is 20 million times longer than the original bar. Copper is second only to silver in its ability to conduct electricity, but silver is too expensive for this sort of use. Bronze and brass, however, do not conduct electricity as well as pure copper. Besides electricity, copper also is an excellent conductor of heat, making it an important metal in cookware, refrigerators, and radiators. Copper is resistant to corrosion, that is, it will not rust. If the air around it often is damp, it will change from its usual reddish orange color to reddish-brown. Eventually, it is coated with a green film called a "patina" that stops all further corrosion. Other properties of copper are shown in Table 2.1 and designated in Figure 2.1 (www.en.wikipedia.org/wiki/Copper).

Table 2.1. Properties of copper

Chemical Symbol	Cu
Atomic number	29
Atomic weight	63.54
Density	8960 kg m^{-3}
Melting point	1356 K
Specific Heat C_p (at 293 K)	0.383 kJ kg^{-1} K^{-1}
Thermal conductivity	394 W m^{-1} K^{-1}
Coefficient of linear expansion	16.5 x 10^{-6} K^{-1}
Young's Modulus of Elasticity	110 x 10^{9} N m^{-2}
Electrical Conductivity (% IACS)	100 %
Electrical Resistivity	1.673 x 10^{-8} ohm-m
Crystal Structure	Face-Centered Cubic

2.1.3 Industrial usage of copper

Copper was the first metal that man extracted from the earth and along with tin gave rise to the Bronze Age. As the ages and technology progressed the uses for copper increased. With the increased demand, exploration for the metal was extended throughout the world laying down the foundations for the industry as we know it today. As mentioned above, copper is an excellent conductor of electricity, as such one of its main industrial usage is for the production of cable, wire and electrical products for both the electrical and building industries. The construction industry also accounts for copper's second largest usage in such areas as pipes for plumbing, heating and ventilating as well as building wire and sheet metal facings (www.lme.co.uk).

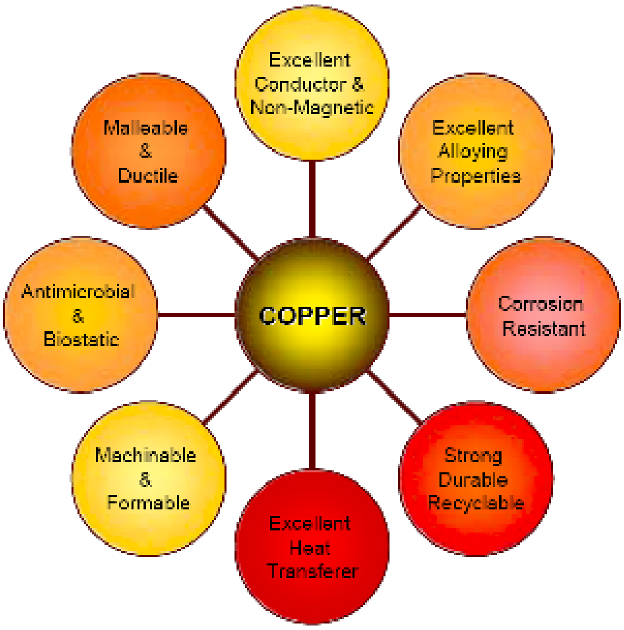


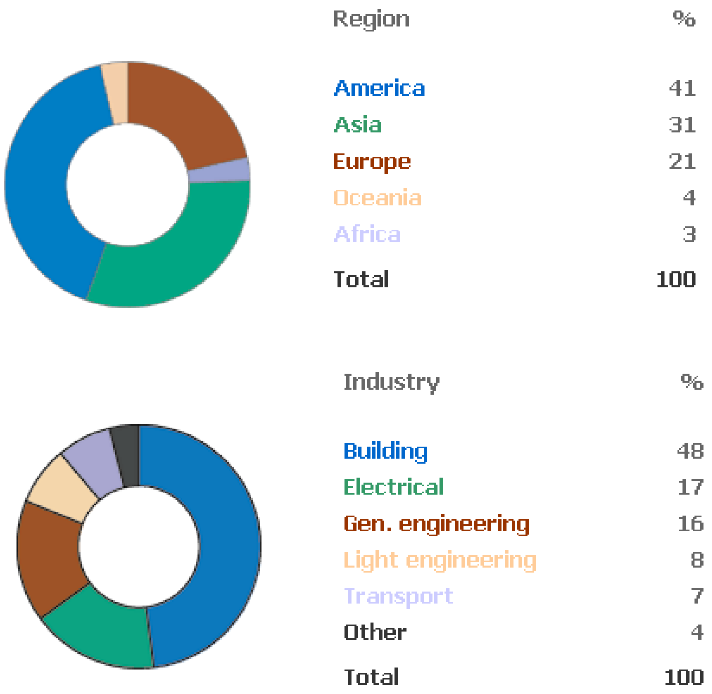
Figure 2.1. Properties of copper

In Figure 2.2 World copper production and industrial consumption of copper in the year of 2007 are indicated by diagrams according to London Metal Exchange (LME) (www.lme.co.uk).

2.1.4 Forecast 2008-2009 for copper production

As indicated in Forecast 2008-2009 of International Copper Study Group (ICSG) data (www.icsg.org), the copper market was essentially balanced in 2007 with a calculated deficit of around 40,000 t. Stronger growth in Chinese apparent usage and anticipated growth in supply that did not materialize shifted the market from an anticipated surplus. Projections for 2008 indicate a small surplus of around 85,000 t (0.5% of usage), and projections for 2009 indicate a larger surplus of around 430,000 t. (2.2% of usage).

World copper mine production in 2007 rose by 3% to 15.5 million tonnes, an increase of 465,000 t compared with that in 2006. Lower head grades, technical production problems and labor unrest resulted in a lower capacity utilization rate. Mine production is expected to increase by 955,000 t (+6%) to 16.4 Mt in 2008, and a further increase of 1.5 Mt (9%) to 17.9 Mt in 2009 is expected owing to new mine developments and increased capacity utilization. For both years, higher growth rates are expected for solvent extraction/electrowinning (SX-EW) production than for concentrate production (www.icsg.org).



Region	%
America	41
Asia	31
Europe	21
Oceania	4
Africa	3
Total	100

Industry	%
Building	48
Electrical	17
Gen. engineering	16
Light engineering	8
Transport	7
Other	4
Total	100

Figure 2.2. World copper production and Industrial consumption of copper (%), 2007 (www.lme.co.uk)

World production of refined copper (adjusted for both feed shortages and production disruptions) is projected to reach 18.6 Mt in 2008, an increase of about 490,000 t (+2.7%) compared with that of 2007. Refined production in 2009 is projected to increase by 7% to 19.9 Mt, an increase of about 1.3 Mt compared with that of 2008.

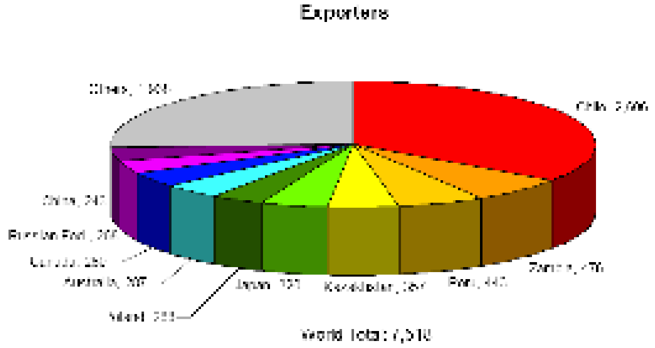
Electrolytic refinery production increases in China, India and Japan, and SX-EW production growth in Chile, Africa and the United States, are expected to account for most of the growth. Concentrates production in 2008 and 2009 is expected to restrain the growth of refined production, with surplus inventories of copper concentrates having been largely depleted during 2006/2007.

World refined copper usage increased by 6.4% in 2007 to 18.1 Mt driven by China, where apparent usage grew by 36% as net imports of refined copper rose by 134% to about 1.4 Mt. World usage outside of China decreased by around 1.5% with usage in the other three major markets (United States, EU-15 countries and Japan) decreasing by around 3.3%. In 2008, significantly lower growth in apparent refined usage in China and a decrease in the United States are expected to result in a lower world usage growth of around 2%. In 2009, world copper use is expected to grow by 5% to reach 19.5 MT. In Table 2.2 Forecast up to 2009 by regions and productions, and in Figure 2.3 Leading Exporters and Importers of refined copper of 2007 are indicated according to ICSG (The World Copper Factbook, 2007).

Production of copper at present time is one of the profitable deals, because situation on markets is stabilized and price for one ton of copper, as indicated on Figure 2.4 according to LME, is really high. Therefore, more developed countries can be restarting their old system of production of copper and decrease world deficit (www.lme.co.uk).

Table 2.2. Forecast to 2009 (www.icsg.org)

REGIONS	MINE PRODUCTION				REFINED PRODUCTION				COPPER USAGE			
('000T)	2006	2007	2008	2009	2006	2007	2008	2009	2006	2007	2008	2009
Africa	739	844	1,161	1,571	553	637	868	1,175	237	267	340	427
N.America	2,159	2,126	2,408	2,654	2,117	2,151	2,282	2,437	2,758	2,663	2,622	2,692
Latin America	6,735	7,129	7,311	7,615	3,565	3,595	3,940	4,211	548	535	557	579
Asean-10	919	898	850	998	504	522	520	550	764	769	780	794
Asia ex Asean/CIS	1,300	1,398	1,461	1,545	5,979	6,664	7,161	7,557	7,194	8,467	8,693	9,269
Asia-CIS	544	516	532	562	520	496	525	545	116	121	125	129
EU-27	806	748	776	827	2,499	2,445	2,602	2,758	4,218	4,070	4,128	4,266
Europe Others	733	755	788	820	1,158	1,139	1,150	1,176	1,050	1,087	1,099	1,141
Oceania	1,053	1,039	1,123	1,328	429	441	534	562	143	146	148	152
TOTAL	14,988	15,454	16,409	17,919	17,323	18,089	19,582	20,971	17,028	18,126	18,493	19,449
Adjustment for Primary Feed Shortage 1/							-397	-304				
Allowance for Disruptions 2/							-607	-788				
World	14,988	15,454	16,409	17,919	17,323	18,089	18,578	19,878	17,028	18,126	18,493	19,449



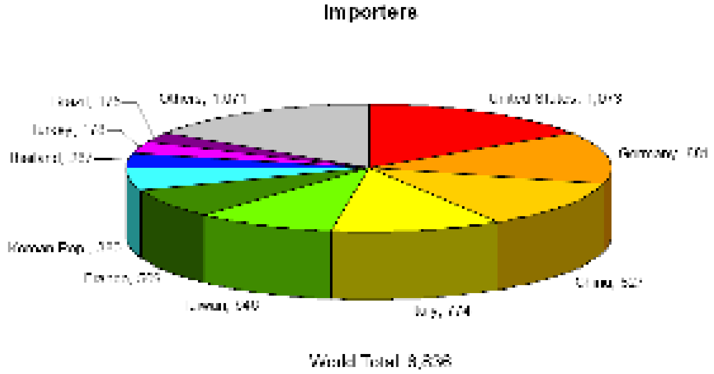


Figure 2.3. Leading Exporters and Importers of refined copper of 2007 (The World Copper Factbook, 2007)

2.2 Smelting overview

One requires many process steps to obtain 99.99 percent copper metal from sulfide ores that contain copper at levels most often below 1 percent. Although chalcopyrite ($CuFeS_2$) is the predominant copper sulfide ore mineral processed, other important copper sulfide ore minerals include bornite (Cu_5FeS_4), chalcocite (Cu_2S), covellite (CuS), and enargite (Cu_3AsS_4). Natural ores undergo comminution and separation by flotation at copper mining facilities to produce copper concentrate. Concentrate can contain from 25 to 35 percent copper; similar levels of iron and sulfur; minor percentages of oxides of aluminum, calcium, and silicon; and a small balance of trace metals that depend on the ore source (Goonan, 2004).

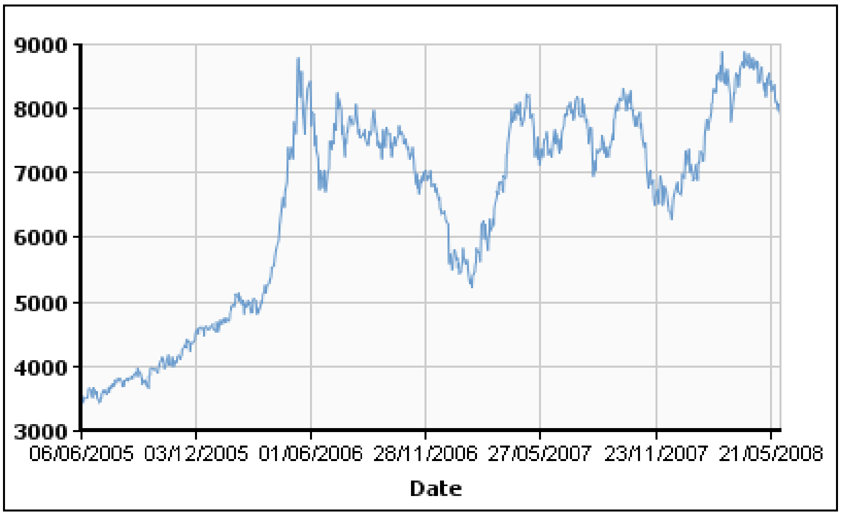


Figure 2.4. Copper Grade A price graph (US$/ton), (www.lme.co.uk)

Smelters may be integrated with a specific mine or company and process concentrates produced from the ores of that particular mine or from the company's multiple mine holdings. The Chuquicamata smelter in Chile, for example, is solely supplied by the Chuquicamata Mine, which is the world's second largest copper mine. The Miami smelter in Arizona takes concentrates supplied from mines and mills operated by Phelps Dodge Corporation in North America and South America. Other smelters process concentrates from multiple mines located in many countries. For example, the Saganoseki smelter in Japan, which has few copper resources but many of the world's largest smelters, takes and blends concentrates from such countries as Chile, Indonesia, and the Philippines. The charge (concentrate plus other items) to a given smelter is not chemically constant (Goonan, 2004).

Regardless of how many different flotation concentrates a smelting facility may process, the material supplied to a smelting furnace is generally a blend of materials, which includes concentrates, recycle dusts, and products of slag-cleaning operations (mattes).

Technically, smelting means to melt and fuse. With regard to copper smelting, it means to melt and fuse copper-bearing materials, which include concentrates, dust (circulating load), fluxes (slagmaking materials), and revert (circulating load) in a furnace. Heat is required for the melting and fusing and can be generated by several means, such as electric current, fuel combustion, or mineral oxidation. The oxidation of iron and sulfur in copper concentrate generates heat, which aids the melting of the charge. Air and industrial oxygen are important inputs to the modern primary smelting furnace.

In a flash furnace, finely ground copper-bearing materials (mainly concentrates) are injected with air or industrial oxygen enriched air into the furnace. The oxygen in air reacts with some of the iron, sulfur and fuel to produce sufficient heat to melt and fuse the remaining unreacted mass. The liquefied mass has two immiscible components - matte, which is a mixture of copper and iron sulfides, and slag, which is a mixture of aluminum trioxide, calcium oxide, iron oxide (the product of iron oxidation), and silicon dioxide. Slag is removed from the molten mass, and the remaining matte is moved to the next processing step. Any sulfur that has reacted with the oxygen forms a hot sulfur dioxide (SO_2) gas, which the gas-handling system collects and channels to an acid plant to recover the sulfur as sulfuric acid (H_2SO_4), or to another sulfur fixing plant, to recover the sulfur in a useful product, such as gypsum, oleum ($H_2SO_4 \cdot xSO_3$), or sulfur. During the generation of useful sulfur-bearing products from the collected SO_2, a small amount of the total sulfur load in treated gas goes into sludge. The result is that the H_2SO_4 production numbers are very slightly overstated. Other trace-metal impurities, such as arsenic (converted to arsenic trioxide) and mercury, distribute between matte, gas and slag. Part of the gas treatment is the removal of fine particulate (dust), which is continually recycled. The matte product of the primary furnace contains from 45 to 70 percent copper, the remaining major elements being iron and sulfur and small percentages of residual metals and oxygen.

In a batch process, matte is transferred to a converter vessel, which is another brick-lined container where a fluxing agent, either silica or limestone, is added, and the melt is oxidized with air. Furthermore, this processing step is where high-purity copper scrap is added. A two-step process occurs within the converting vessel. Step one is to oxidize the melt until the iron is completely eliminated. This is called the slag-forming step because the oxidized iron reacts with the flux to form an iron silicate slag. The slag, which contains a high percentage of copper, is recycled to either the smelting vessel or a slag-treating step to recover entrained or oxidized copper. The second step in the converting process is to eliminate the remaining sulfur from the Cu_2S by continuing the injection of oxygen (in air) after the iron-bearing slag has been removed. The SO_2, generated during both steps is collected and processed to acid. Coincident dust is collected and recycled. The product of the converting process is blister copper, which contains about 99.5 percent copper (Goonan, 2004).

The greater part of blister production is not cooled, but rather transferred hot to a fire refining (anode) furnace. The product of the anode furnace is a copper casting that performs as an anode in an electrolytic cell. The electrolytic refining step usually occurs at a different facility. In the anode furnace, the liquid copper, which contains high levels of dissolved gases, is treated with a reducing agent – pulverized coal, natural gas, or wooden poles. The reductant reacts with the dissolved oxygen, and the resulting metal can cool without the blistering effect and be cast into a mold where the cooled surface will be flat, which is a desired characteristic for electrolytic processing. The casting process involves pouring hot copper into molds, which are shaped as anodes; each mold is on the circumference of a wheel that turns to present an empty mold as the previously cast mold moves on and cools.

2.3 Chemistry of copper smelting

Copper is produced from copper sulfide concentrates by heating the concentrates in a furnace at temperatures of 1200-1250^{0}C and subjecting them to oxidation with air or oxygen-enriched air. Under these conditions, the concentrate particles are simultaneously oxidized and, as mentioned above, melt into two phases, a copper-iron sulfide solution which is called matte and an iron silicate slag. There are two basic types of copper smelting processes: flash smelting, where the exothermic reactions occur between air, or oxygen enriched air, and concentrate particles dispersed therein; and bath-smelting where the concentrate is enveloped and reacted in a turbulent bath of matte, slag and gas (Davenport et al., 2002). The principal reactions occurring in flash smelting furnace during the smelting of chalcopyrite concentrate can be represented as follows:

$$2CuFeS_2 + O_2 = Cu_2S + 2FeS + SO_2, \tag{2.1}$$

$$\Delta H^0_{298^0C} = -22475 \text{ kcal/kg-mol } CuFeS_2,$$

$$FeS_2 + 5/2O_2 = FeO + 2SO_2, \tag{2.2}$$

$$\Delta H^0_{298^0C} = -163100 \text{ kcal/kg-mol } FeS_2.$$

Written reactions provide much of the thermal energy required to heat, melt and superheat the flash smelting products.

Cu_2S and FeS are completely miscible above 1100^0C. They form a liquid sulfide matte phase which settles in the hearth of the flash furnace. FeO formed in the flash furnace by Reaction 2.2 is fluxed with silica to form a liquid slag phase which is immiscible with the matte and which, being less dense, floats on top of the matte. Flash furnace slags typically contain 26-36 wt. % SiO_2 depending upon desired slag characteristics. Silica content is generally minimized in situations where the copper is recovered from the slag by slow-cooling and processing in slag flotation facilities. Higher silica contents are required to produce slags with copper low enough to justify direct discard of the slag.

Flash furnace off-gases consist of SO_2 produced by Reactions 2.1 and 2.2, and N_2 from the oxidant. If supplementary fuel is burnt, the combustion products of the fuel (CO_2 and H_2O) are also constituents of the off-gas. Off-gas SO_2 concentration is determined by the extent of oxygen enrichment of the oxidant and by the amount of hydrocarbon fuel combusted in the furnace. Industrial SO_2 concentrations range from 8-80 volume %.

The temperature of flash smelting product gas is usually around 1250^0C. The slag is typically 50^0C cooler than the off-gas and the matte is typically $30\text{-}50^0$C cooler than the slag.

The operating parameter most significant to flash furnace operators is matte grade (i.e. mass % Cu in the matte). This parameter quantifies the extent of concentrate oxidation. The industrial range of matte grade produced by flash smelting furnace is 45-70% Cu with recent trends being toward higher matte grade.

2.3.1 The Cu-Fe-S system

Descriptions of the Cu-Fe-S system are available (Figure 2.5) from the works of Reuleaux, 1927 and Krivsky and Schuhmann, 1957. The notable feature of this system is that as liquid matte becomes increasingly sulphur deficient, a second, metal rich phase separates out. This is true over the entire range of Cu/Fe ratio including the Cu_2S and FeS ends (Biswas and Davenport, 1980).

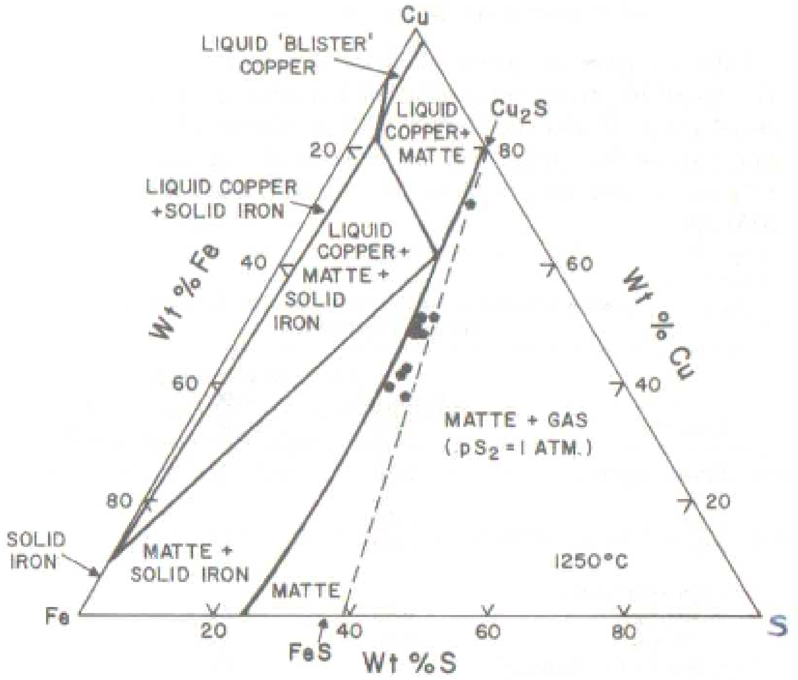


Figure 2.5. Copper-Iron-Sulphur equilibrium diagram, 1250^0C (Krivsky and Schuhmann, 1957)

A second important feature of the Cu-Fe-S system is that at smelting temperatures and pressures (1200^0C, 1 atm), any sulphur in excess of the Cu_2S-FeS pseudo-binary will be vaporized. Thus, mattes can only exist in a narrow composition range between the immiscibility region and the Cu_2S-FeS pseudo-binary. This position is shown on the 1250^0C isothermal section of the phase diagram (Figure 2.5) which also shows the compositions of a number of industrial mattes. As Figure 2.5 shows, industrial matter contains somewhat less sulphur than is required to form stoichiometric Cu_2S and FeS, i.e. the compositions are to the left of the Cu_2S-FeS line. This is due to the slightly oxidizing conditions in matte smelting furnaces (Biswas and Davenport, 1980).

2.3.2 The FeO-Fe_2O_3-SiO_2 system

The slags produced in industrial matte smelting consist primarily of FeO, Fe_2O_3 and SiO_2, with small amounts of Al_2O_3, CaO and MgO. Figure 2.6 shows the composition limits for the liquid region in the FeO-Fe_2O_3-SiO_2 system at 1200^0C and 1250^0C. Along the top line, the slag is saturated with solid silica. Along the bottom boundary line, the slag is saturated with solid FeO. The boundary at right marks the compositions at which dissolved FeO and Fe_2O_3 react to form solid magnetite:

$$FeO + Fe_2O_3 \rightarrow Fe_3O_4(s)\,. \tag{2.3}$$

Extensive oxidation and lower smelting temperatures encourage the formation of Fe_2O_3 in the slag. Avoiding these conditions minimizes magnetite precipitation. Along the left-hand boundary, the slag is saturated either with metallic iron or solid fayalite (Fe_2SiO_4) (Davenport et al., 2002).

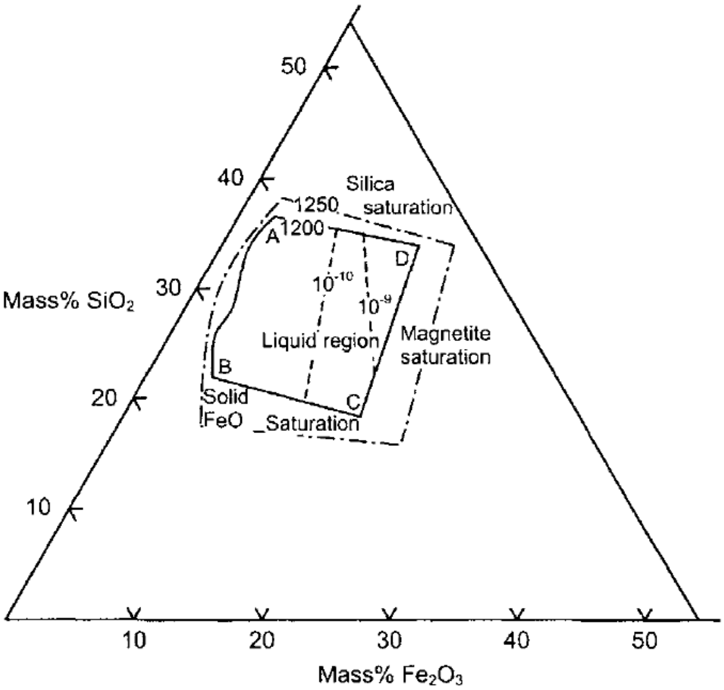


Figure 2.6. Liquidus surface in the FeO-Fe_2O_3-SiO_2 system at 1200^{0}C and 1250^{0}C (Muan, 1955)

2.4 Process description

Copper is mined from a variety of ores, often containing less than one percent copper. This copper is typically in the form of mineral compounds with sulfur, iron, arsenic, and tin. To facilitate transportation to smelters, concentration to about 30 percent copper content is accomplished at the mine sites via crushing, grinding, and flotation. The resulting concentrate is processed in a reverberatory furnace, an electric furnace, or one of several relatively oxygen enriched flash smelting furnaces to yield matte of as much as 65 percent copper content. The iron in this matte is oxidized in a converter to produce blister copper of 97 to 99.5 percent purity, which can then be further refined pyrometallurgically or hydrometallurgically (Background Report, 1992).

The traditional *reverberatory* smelting process as it exists involves the charging of fine concentrate and a siliceous flux to an internally fired smelting furnace maintained at a temperature as high as 1400^0C. Impurities in the charge oxidize with the flux to form a layer of slag, which floats on top of the molten matte, and much of the sulfur in the charge is released as 0.5-3% sulfur dioxide (SO_2) in furnace gas. Since this SO_2 content of gas is low, it cannot be used to make sulfuric acid; it is directly vented to atmosphere or collected as sulfates in environmental sensitive areas. The slag is frequently skimmed, and the matte is periodically tapped. It is very versatile furnace since it can melt any type of charge materials, fine or lumpy, dry or wet. Heat required for the melting process comes mainly from burning of fuel as well as the partial oxidation (limited) of the sulfide charge. Since it is mainly a melting furnace much fossil fuel is used. Therefore, it lost its popularity after 1973 energy crisis.

Electric arc smelting furnaces generate heat with carbon electrodes that are lowered through the furnace roof and submerged in the slag layer of the molten bath. The feed consists of dried concentrates or calcine. The chemical and physical changes occurring in the molten bath are similar to those occurring in the molten bath of a reverberatory furnace. The matte tapping and slag skimming practices are also similar. Only, the furnace gas contains higher SO_2; 4-8%. Since it uses much electric energy, it is economic in regions where electricity is cheap and plentiful.

Flash furnace smelting consists of blowing fine, dried copper sulfide concentrates and silica flux with air, oxygen enriched air, or oxygen blast into a hearth-type furnace maintained at approximately 1300^0C. Entry of these materials into the hot furnace causes the sulfide minerals of the concentrate to react rapidly with the oxygen of the blast. This leads to the controlled oxidation of the iron and sulfur in the concentrate, a large evolution of thermal energy, and the melting of the solids. The products of flash furnaces are matte of 45 to 65 percent copper, molten slag containing iron oxides plus gangue and flux oxides, and off-gas. The slag typically contains as much as two percent copper. This slag can be cooled slowly and a concentrate can be produced to feed to flash furnace or its copper content can be recovered in an electric slag cleaning furnace, if electricity is cheap. The flash furnace off-gas contains anywhere from 10 to 80 percent by volume sulfur dioxide (SO_2). In all copper smelting facilities utilizing flash smelting technology, the valuable thermal energy in this gas is recovered in a waste heat boiler, and the SO_2 is converted into sulfuric acid. One facility in Canada compresses the SO_2 into liquid form, while a facility in Eastern Europe reduces the SO_2 to elemental sulfur. Approximately 3 to 15 percent of the furnace charge exits the furnace as dust in the off-gas, primarily in the form of oxidized concentrate which has not settled out earlier. This dust is captured in a gas cleaning train, usually consisting of electrostatic precipitators, and is recycled to the furnace for copper recovery (Background Report, 1992).

The two types of flash furnaces currently in operation through the worldwide are Outokumpu furnaces and INCO furnaces. Both furnaces are constructed mainly of chrome-magnesia bricks (MgO and Cr_2O_3-MgO) surrounded by a steel shell. Because the concentrate feed to these flash furnaces must be dry for reasons that will be discussed below, rotary, flash, fluidized-bed, and spray dryers are used in conjunction with these furnaces to obtain a feed containing no more than 0.2 percent water by weight.

The *Outokumpu* flash smelting furnace is characterized by five major components:

- concentrate burners, which combine dry particulate feed with oxygen-bearing blast and direct the mixture in suspension form downward into the furnace;
- a reaction shaft where most of the reaction between oxygen and sulfide feed particles takes place;

- a settler where molten matte and slag droplets collect and form separate layers;
- an off-take for removing SO_2-bearing gases from the furnace; and
- tapholes near the bottom of the furnace for removing matte and slag.

INCO flash smelting consists of blowing industrial oxygen and dry concentrate horizontally into a hearth-type furnace. The principal advantage of INCO furnaces over Outokumpu furnaces is compactness, which enable them to be used to replace existing reverberatory furnaces, if there is space limitation. The reactions taking place are similar to those in an Outokumpu furnace, but without the benefit of fossil fuel combustion. This type of furnace is characterized by three major components:

- concentrate burners, two at each end of the furnace, through which ambient temperature oxygen, concentrate, and flux are blown into the furnace;
- a central gas off-take through which the off-gas is withdrawn for delivery to the cooling, dust removal, and SO_2 fixation systems; and
- matte and slag tapholes through which the liquid products are periodically removed from the furnace.

As with Outokumpu furnaces, maintenance of good gas/particle suspension and steady flow into the furnace are essential to efficient operation of these units. The primary differences in operating conditions derive from the exclusive use of industrial oxygen and the reliance on sulfur and iron oxidation for thermal energy input. The volume of off-gas is very small relative to Outokumpu furnaces, and SO_2 concentrations are much higher (approximately 75 percent).

External fuel combustion is required at INCO furnaces only during start-up periods, to bring the furnace chamber to its operating temperature. Slag produced at INCO flash furnaces typically contains no more than one percent copper, thereby eliminating the cost of slag cleaning equipment necessary to attain similar copper recovery efficiencies with Outokumpu furnaces. The off-gases from INCO furnaces are typically not routed through waste heat boilers, but rather proceed to dust settling chambers and gas cleaning systems. Dust recovery of 99.99 percent is achieved with various combinations of scrubbers, cyclones, and both wet and dry electrostatic precipitators. The INCO flash smelting furnace operated by Chino Mines Co. is able to maintain a consistent flow of constant strength gaseous SO_2 into its sulfuric acid plant by condensing some of the SO_2 in the off-gas when the flow rate of this gas stream is higher than usual, and evaporating this stored liquid SO_2 when the flow rate is low (Background Report, 1992).

The *Noranda* process allowed the continuous production of blister copper in a single vessel by effectively combining roasting, smelting and converting into one operation. Metallurgical problems, however, have led to the operation of these reactors for the production of copper matte. The Noranda process uses heat generated by the exothermic oxidation of sulfidic concentrates. Additional heat is supplied by oil burners or by coal mixed with the ore concentrates (Background Report, 1992).

The *Vanyukov* bath smelting furnaces for annually processing over two million tonnes of copper, Cu/Ni, Cu/Zn, and antimony sulphide have been in use for many years in a large number of enterprises within the Russian Federation and Kazakhstan. The process was commercialized in 1977. Feed material is injected by means of tuyeres into the molten upper slag layer which is about 1.5 m thick. The difference in this operation is that the gaseous oxidizing medium is injected directly into the foaming upper slag layer rather than into the matte layer as employed within other systems. The turbulent agitation caused by the continuous addition of feedstock mixed with oxygen and carbonaceous fuel creates rapid interaction and exothermic conditions. The heavier matte phase settles into the lower molten layer. Both molten matte and slag are continuously removed from the furnace (Bystrov, 2003). To date, technology transfer to western countries has been very sparse. It was predicted that the Vanyukov's attributes of high productivity coupled with efficiency and flexibility eventually may compete with the Outokumpu system in the next decade to process in excess of 5000 tonnes daily (Demetrio et al., 1999).

The *Isasmelt* process was originally developed for primary lead smelting, the development occurring in collaboration with CSIRO, the Australian Government research organization, via laboratory testwork at CSIRO and pilot plant and demonstration scale plants at Mount Isa Mines. Isasmelt copper smelting entails dropping moist solid feed into a tall cylindrical furnace while blowing oxygen-enriched air through a vertical lance into the furnace's matte/slag bath (Pritchard and Hollis, 1994). The products of the process are a matte/slag mixture and strong SO_2 off-gas. The matte/slag mixture is tapped periodically into a fuel-fired or electric settling furnace for separation. The settled matte (60% Cu) is sent to conventional converting. The slag (0.7% Cu) is discarded. The off-gas (25% SO_2) is drawn from the top of the smelting furnace through a vertical flue. It is passed through a waste heat boiler, gas cleaning and on to a sulfuric acid plant. A small amount of oxygen is blown through the side of the smelting furnace or lance (about halfway up) to ensure that sulfur leaves the furnace as SO_2 rather than S_2. This prevents sulfur condensation in the gas cleaning system. Most of the energy for smelting comes from oxidizing the concentrate charge. Additional energy is provided by combusting oil, gas, or coal fines blown through the vertical lance and coal fines in the solid charge. The main advantages of the process:

- its small "footprint", which makes it easy to retrofit into existing smelter;
- its small evolution of dust.

The 1990's and early 2000's saw Isasmelt smelting adopted around the world. It should soon account for 5% of world copper smelting. The future may see dry concentrate injection through the lance. This will improve the thermal efficiency of the process.

2.5 Historical development of the Outokumpu flash smelting process

The conventional process of smelting copper concentrates in a reverberatory furnace followed by converting in a Pierce-Smith converter has the inherent disadvantage of environmental pollution and high energy consumption. Flash smelting, as applied in the INCO (INCO staff, 1955a; INCO staff, 1955b) and Outokumpu (Bryk et al., 1958) flash smelting processes, has provided an attractive alternative to reverberatory smelting.

Since its development in 1946-48 and commission in 1949 (Bryk et al., 1958), the Outokumpu flash smelting furnace (Figure 2.7) has been developed along a path of improved productivity and energy conservation, longer campaigns between maintenance shutdowns and improved environmental control.

The success of the Outokumpu process is evident in its wide adoption in copper smelters around the world. Table 2.3 shows, in chronological order, locations of Outokumpu type flash smelters built in both hemispheres and that some of furnaces are under construction. Most of them are smelting copper concentrates, while some of furnaces smelt nickel or copper/nickel concentrates. One more development by Outokumpu is the adaptation of the process for lead smelting (Nernes and Talonen, 1982).

The smelting reactions in the shaft are highly exothermic and provide most of the heat required for heating the feed materials to the temperature of the reaction shaft

(1300-1350^{0}C) and for compensating for the heat losses through the wall of the reaction shaft. For a typical chalcopyrite concentrate and oxygen enrichment of about 40% O_2 in the air stream to the furnace, flash smelting is autogenous when producing a matte grade of about 60% Cu, i.e., no additional fuel is required. Enrichment to a higher level of oxygen would necessitate the addition of large quantities of non-sulfuric, or "inert" materials to the furnace, or somehow increasing the heat losses through the wall of the reaction shaft.

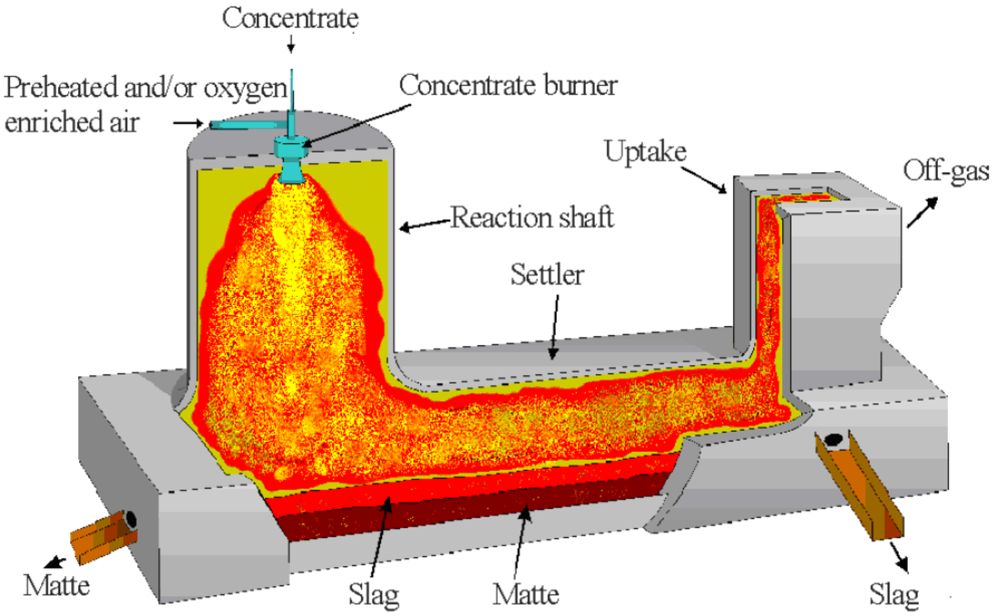


Figure 2.7. Flash smelting furnace with its main sections and material flows (Vaarno et al., 2003)

Pilot plant operations commenced at Harjavalta in February, 1947 (Bryk et al., 1958) and the first industrial plant was placed in operation in 1949. In 1956, the Ashio Smelter of Furukawa Mining in Japan became the first licensee of the process and this was followed by an installation of the process in Romania.

Table 2.3. Locations of Outokumpu type Flash Smelters (www.outotec.com)

Location	**Type**	**Year**[*]
Konkola Copper Mines Plc. Zambia	**Direct to Blister**	
Jiangxi Copper Corporation Guixi, China	**Cu Smelting**	
KGHM Polska Miedz S.A. Glogow, Poland	**Direct to Blister**	
Yanggu Xiangguang Copper Co. China	**Cu Smelting**	
Yanggu Xiangguang Copper Co. China	**Cu Smelting**	
National Iranian Copper Industries Khatoon Abad, Iran	**Cu Smelting**	**2004**
(Southern Peru Copper Corporation) (Ilo, Peru)	**Cu Smelting**	
(Southern Peru Copper Corporation) (Ilo, Peru)	**Cu Smelting**	
Boliden Mineral Rönnskär, Sweden	**Cu Smelting**	**2000**
WMC Olympic Dam, Australia	**Cu Smelting**	**1999**
Mineração Serra da Fortaleza Fortaleza, Brazil	**Ni Smelting**	**1998**
Indo-Gulf Fertilisers & Chemical Gujarat, India	**Cu Smelting**	**1998**
Jinlong Copper Tongling, China	**Cu Smelting**	**1997**
Kennecott Utah Copper Salt Lake City, USA	**Cu Converting**	**1995**
Kennecott Utah Copper Salt Lake City, USA	**Cu Smelting**	**1995**
Cia Minera Disputada de las Condes Chagres, Chile	**Cu Smelting**	**1995**
Jinchuan Non-ferrous Metals Jinchang, China	**Ni Smelting**	**1992**
WMC Olympic Dam, Australia	**Cu Smelting**	**1988**
BHP Billiton San Manuel, USA	**Cu Smelting**	**1988**
Codelco Chuquicamata, Chile	**Cu Smelting**	**1988**

Table 2.3. (continued)

Umicore Srednogorie, Bulgaria	**Cu Smelting**	**1987**
Mexicana de Cobre El Tajo, Mexico	**Cu Smelting**	**1986**
Jiangxi Copper Guixi, China	**Cu Smelting**	**1985**
Philippine Associated Smelting & Refining Isabel, the Philippines	**Cu Smelting**	**1983**
Caraíba Metais Camacari, Brazil	**Cu Smelting**	**1982**
Norilsk Mining & Metallurgical Co Norilsk, Russia	**Cu Smelting**	**1981**
Norilsk Mining & Metallurgical Co Norilsk, Russia	**Ni Smelting**	**1981**
LG-Nikko Onsan, South Korea	**Cu Smelting**	**1979**
Kombinat Górniczo-Hutniczy Miedz Glogow, Poland	**Cu Smelting**	**1978**
Gécamines Luilu, Zaire	**Cu Smelting**	
Phelps Dodge Playas, USA	**Cu Smelting**	**1976**
Atlantic Copper Huelva, Spain	**Cu Smelting**	**1975**
Hindustan Copper Khetri, India	**Cu Smelting**	**1974**
BCL Selebi-Phikwe, Botswana	**Ni Smelting**	**1973**
Peko Wallsend Metals Tennant Creek, Australia	**Cu Smelting**	**1973**
Black Sea Copper Works (Eti-Bakır) **(Karadeniz Bakır İşletmeleri)** Samsun, Turkey	**Cu Smelting**	**1973**
Nippon Mining Saganoseki, Japan	**Cu Smelting**	**1972**
WMC Kalgoorlie, Australia	**Ni Smelting**	**1972**
Nippon Mining Hitachi, Japan	**Cu Smelting**	**1972**
Norddeutsche Affinerie Hamburg, Germany	**Cu Smelting**	**1972**

Table 2.3. (continued)

Hibi Kyodo Smelting Tamano, Japan	**Cu Smelting**	**1972**
Peko Wallsend Metals Mount Morgan, Australia	**Cu Smelting**	**1972**
Hindustan Copper Ghatsila, India	**Cu smelting**	**1971**
Sumitomo Metal Mining Toyo, Japan	**Cu Smelting**	**1971**
Nippon Mining Saganoseki, Japan	**Cu Smelting**	**1970**
Dowa Mining Kosaka, Japan	**Cu Smelting**	**1967**
Combinatul Chimico Metalurgic Baia Mare, Romania	**Cu Smelting**	**1966**
Boliden Kokkola Kokkola, Finland	**Pyrite Smelting**	**1962**
Furukawa Ashio, Japan	**Cu Smelting**	**1956**
Boliden Harjavalta Harjavalta, Finland	**Ni Smelting**	**1959**
Boliden Harjavalta Harjavalta, Finland	**Cu Smelting**	**1949**

*Years refer to start-up times

Although the process was originally developed for treating copper concentrates, it has been applied successfully in the smelting of nickel concentrates since 1959 (Toivanen and Gronqvist, 1964; Niemela and Harkki, 1972). Also, from 1962 to 1975, Outokumpu operated a pyrite flash smelter (Anon., 1964), which treated 500000 t/year of pyrites and produced 350000 t/year of sulfuric acid. The plant was shut down in 1975 due to the high price of fuel and the low price of elemental sulfur. A more recent development has been the lead flash smelter (Nernes and Talonen, 1982), where different kinds of lead concentrates can be processed in a combined flash smelting/electric furnace system to produce directly lead bullion and waste slag.

In 1971, oxygen enrichment of the process air was adopted at Harjavalta (Anderson et al.; Harkki et al., 1976) smelter and the autogenous mode of operation was verified. Meanwhile in Japan, the Saganoseki Smelter (Yasuda et al., 1982) of Nippon Mining Company adopted high preheat temperature and moderate oxygen enrichment of process air in 1970.

Blister copper was first produced in pilot furnace of the Outokumpu Metallurgical Research Centre at Pori in 1969 and the first commercial plant for direct blister production using chalcocite concentrates (Yasuda, 1974; Juusela and Makinen, 1977) commenced in Poland in 1978. Concentrates low in iron (3-7%) and in impurities were found to be amenable to the direct production of blister. This feature results in a reduction in the amount of recycled slag and consequently copper. Such low-iron concentrates normally require high oxygen enrichment (Yazawa, 1974; Yazawa, 1977, Yazawa, 1979) and considerable amount of additional fuel.

2.6 The Outokumpu type flash smelting process

Outokumpu flash smelting consists of injecting dry concentrate and a combination of preheated air or oxygen-enriched air downwards into a furnace. Feed enters through the top of a reaction shaft located at one end of the Outokumpu furnace (Figure 2.7). Here it combusts with the blast oxygen. Off-gases leave via a vertical uptake shaft at the other end of the furnace.

The Outokumpu flash smelting furnace has undergone intensive development over the year (Elliot et al., 1983). The reaction shaft, the height of which is such that the reactions are nearly complete while the particles are in flight, is considered to be the most important section of the furnace. It is within this shaft that important process variables such as matte grade and smelting temperature are controlled.

During the 1950's when there were only two flash smelters in the world, namely the Harjavalta and Ashio smelters, there was relatively little control over the shaft temperature. In order to alleviate this problem, a concentrate burner was designed in 1959 (Fugii and Shima, 1971) to burn concentrate and heavy oil in the advent of any heat deficiency resulting from varying concentrate composition. In recent years, there have been further improvements in injecting and dispersing the concentrate in the reaction shaft. One type of concentrate burner used in the Outokumpu furnace (Figure 2.8a) (Lilja and Makitalo, 1979) consists of an inner nozzle system which serves to disperse the concentrate in part of the air stream (distribution air) and of a much larger concentric tube, which introduces the bulk of the air flow into the reaction shaft. As illustrated in Figure 2.8b and 2.8c (Lilja and Makitalo, 1979), the flared end of the distribution air tube serves to create an "umbrella" of concentrate particles which can be jettisoned as far as the walls of the reaction shaft.

A very significant development in flash smelting came about a few years before the world prices of fuel oil increased and when the cost of bulk oxygen became comparatively low (Juusela et al., 1974). This was the use of oxygen to enrich the air stream which was found to be more effective and economic than preheating. It served to reduce the amount of fuel requirement in the reaction shaft and resulted in a smaller amount of process gas and also in increasing the smelting capacity of the furnace.

The beneficial effects of oxygen enrichment led to the shortening of the height of the reaction shaft as in the case of Ashio, Japan, smelting furnace (Fugii and Shima, 1971). This reduction in the height of the shaft also represents a very effective way to reduce energy consumption in flash smelting because a significant amount of heat is lost from the walls of the reaction shaft.

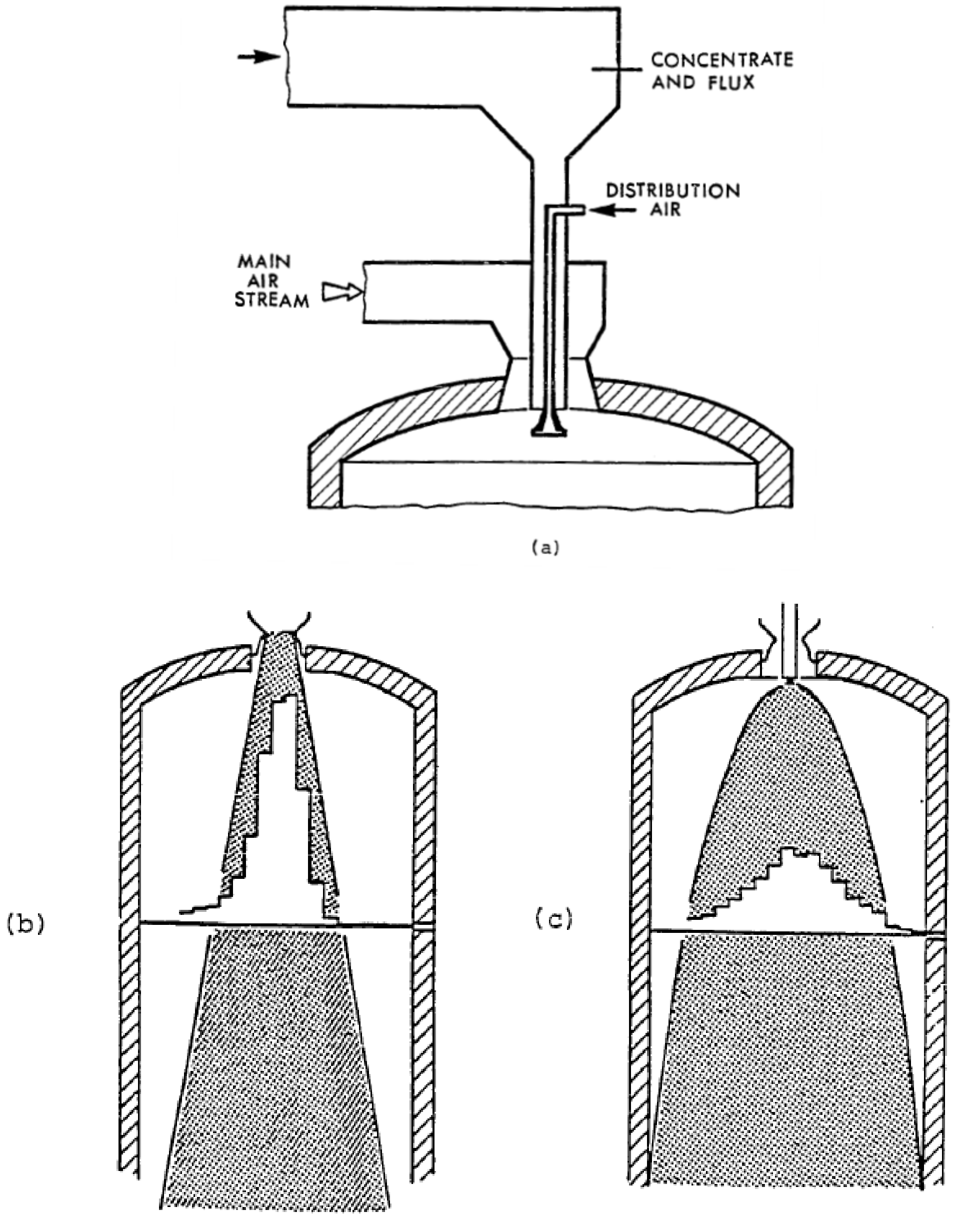


Figure 2.8. (a) Concentrate burner configuration, (b) dispersion cone without central jet distributor, (c) and with central jet distributor (Lilja and Makitalo, 1979)

Despite the beneficial effects of utilizing tonnage oxygen in flash smelting, its usage has resulted in a reduction of the air speed at the throat of the concentrate burner due to the reduced bulk air flow. This causes a decrease of the mixing energy per unit weight of the furnace charge. In order to overcome this condition, a modified burner has been developed where the velocity of the air passing through the throat can be controlled. As shown in Figure 2.9 (Kemori et al., 1985), the modification consists of a regulator which is adjustable vertically along the concentrate-chute by two rods. This permits a reduction of the cross-sectional area at the throat of the burner so that the appropriate air speed for efficient mixing can be obtained.

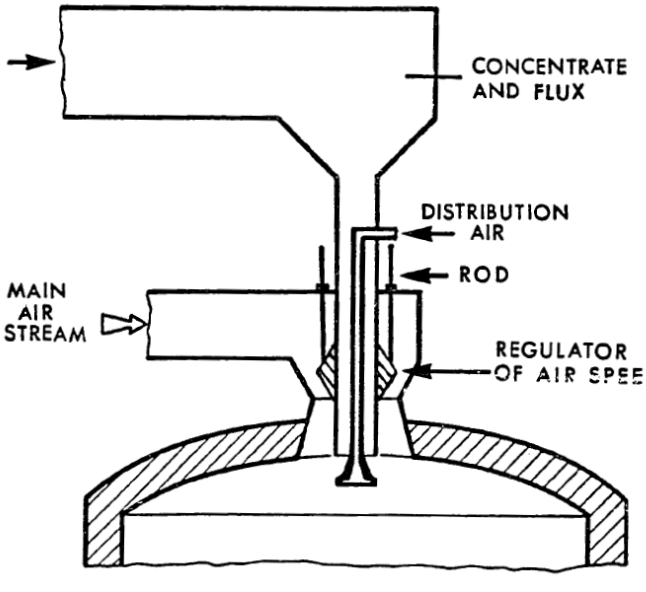


Figure 2.9. New type of concentrate burner with the regulator of air speed (Kemori et al., 1985)

2.7 Flash smelting as a significant process

Three-quarters of new copper smelting capacity commissioned in the 1970s employed flash smelting technology (Biswas and Davenport, 1980). This was the result of increasing concerns with energy costs and the environment.

2.7.1 Energy consumption in flash smelting

Flash furnaces require very little energy input. In fact, under certain conditions, flash furnaces can operate autogenously, i.e. without hydrocarbon fuel addition. This can be a big advantage over traditional reverberatory furnace smelting where hydrocarbon fuel must be provided for the bulk of the energy requirements.

The reason for this difference is that flash furnaces make extensive use of the heat generated by partially oxidizing their concentrate feed. Reverberatory smelting makes little use of the concentrate oxidation heat so that its fossil fuel requirements for smelting are large.

2.7.2 SO_2 generation in flash smelting

Government legislation and industry concern for the environment has imposed strict limits regarding sulfur dioxide emission. As a consequence, the SO_2 generated in smelters must be collected and fixed. Sulfur dioxide is fixed mainly as sulfuric acid, with minor amounts being fixed as elemental sulfur, liquid SO_2, and gypsum. Regardless of the fixation process, overall cost of sulfur fixation is minimized if smelters generate steady, concentrated streams of SO_2.

Flash furnaces inherently produce such steady streams of gas due to the following reasons.

1. Fuel consumption is low. Because little or no hydrocarbon fuel is consumed in flash smelting, the consequent dilution of the off-gas by hydrocarbon combustion products is minimized or eliminated;
2. Oxygen enrichment is used extensively. This leads to a more concentrated stream of SO_2 in off-gases because this is less dilution by nitrogen;
3. Flash furnace is designed as a sealed smelting unit. SO_2 generated in the furnace can be delivered to the sulfur fixation plant with little or no air dilution.

2.7.3 Process control

The campaign life and availability of a furnace not only depend on the furnace construction, but process controllability to obtain stable operation and to avoid process conditions that would influence furnace integrity. Here, the two key equipment pieces are the concentrate feeding system and the concentrate burner (Kojo et al., 2000).

Stable and controlled feed is currently obtained by using a system that controls the weight of the material fed into the furnace; several loss-in-weight (LIW) feeding systems have been delivered since 1994. The gravimetric feed system consists of a dosing valve and a dosing bin provided with an underneath screw conveyor. The material is fed by the screw conveyor into a charge drag conveyor, which transfers the material further via a concentrate chute into the concentrate burner. This arrangement secures good accuracy and a constant feed rate of the material to the burner. The complete package of the Outokumpu feed system includes the dosing bin with valves; the underneath screw conveyor with the local controls; and the central jet distribution-type concentrate burner with a ready assembled valve train and a local control panel for automatic and manual control of air/oxygen, distribution air, cooling air, and cooling water flow to the burner.

Before LIW, a volumetric concentrate feed system was normally used. The system was associated with inherent problems, such as an inability to react to the physical changes in the concentrate quality. Inaccurate measurement of the actual weight of the feed with, in extreme cases, uncontrolled concentrate exposure to the furnace was the subsequent result.

The Outokumpu concentrate burners are specifically designed for high oxygen enrichment, a wide turndown ratio, and high-control requirements. This burner arrangement has the capability to accommodate both the changing concentrate-feed quality and the feed rate, securing an even distribution of the feed material and process air in the furnace. It is designed to operate with optimum air/oxygen velocities at three selected working ranges, thus providing the flexibility to operate efficiently at a large range of material feeds according to process requirements. This burner includes the oxygen/concentrate control and distribution air adjustment as well as a middle lance for oxygen. The middle lance enables the control of the oxygen potential in the middle of the reaction shaft and the temperature profile in the furnace.

2.7.4 Developments of Outokumpu flash furnace

Process development is the elimination of process steps and a decrease in investment and operation costs. The best example of this is the direct-to-blister process, which is in operation in the Glogow smelter in Poland and in the Olympic Dam smelter in Australia. The limitations for the feasibility of direct-to-blister smelting have been high copper circulation via slag and the elimination of impurities (Kojo et al., 2000).

Compared with the times not so long ago, we are facing a different business environment today: flash converting has established itself as a commercially viable process, concentrates with a higher copper content are increasingly produced, and high-grade matte is an interesting market product. The prerequisites for economical direct-to-blister production (high copper content, sufficient Cu/Fe ratio in concentrate, and a flash furnace especially designed for blister copper production), are all available. The improvements made in furnace design and operation assure long campaign life and high on-line availability of the process. Further, the capital expenses for a direct-to-blister smelter have been lowered considerably over the years as the same size flash furnaces today are able to produce 3–4 times more than was possible only 20 years ago due to the adoption of the latest improvements and development work. Thus, the relative investment costs of the process have been decreasing, and investment in slag treatment, which has been limiting the feasibility of direct blister smelting, is possible. As a result, the feasibility threshold of the direct-to-blister process has become lower (Figure 2.10).

The progress shown in Figure 2.10 has been possible due to developments in flash-furnace equipment for high oxygen enrichment and the high utilization of oxygen as well as heat-balance control in low-reaction heats. Further developments in concentrate feeding and burning and in the flash-smelting process itself have reduced the copper content reporting to the slag. This again has reduced copper circulation through the slag cleaning and, hence, lowered the Cu/Fe ratio necessary for an economically feasible process. It may be appropriate to note that the original Cu/Fe ratio of the concentrate utilized at the Olympic Dam direct-to-blister smelter was 6:2; with the developments and the confidence gained with the process, the Olympic Dam expansion was based on a concentrate having a Cu/Fe ratio of 2:3 (Kojo et al., 2000).

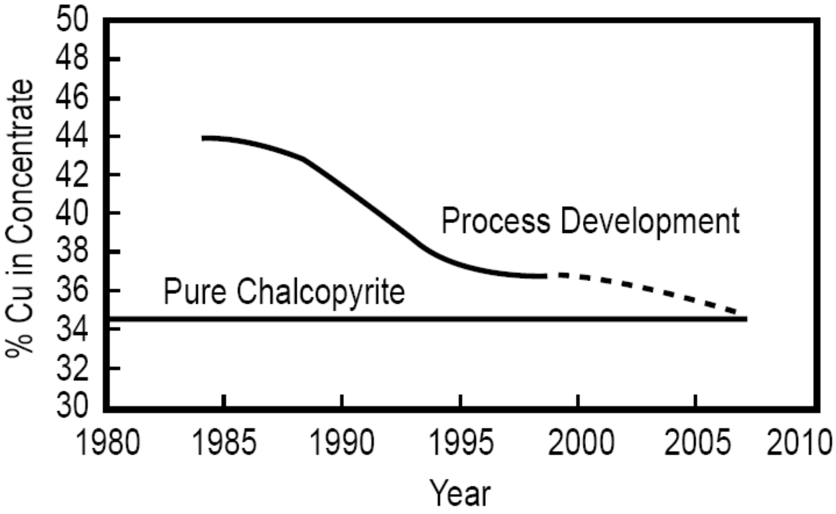


Figure 2.10. The feasibility of the direct-to-blister flash smelting process for Cu, Fe, S – concentrates (Kojo et al., 2000)

The elimination of impurities in the direct-to-blister process has also been improved by the development of furnace integrity; the latest furnace construction allows operation at higher temperatures, especially in the reaction shaft, where the impurities are effectively eliminated because of volatilization. This elimination allows the utilization of concentrates from which the direct-to-blister production would have earlier led to too high impurity contents of the blister.

A smelter with a flash furnace available for direct-to-blister production or flash converting would always have the potential to mix its own or foreign high-grade matte and concentrate and, in this way, produce profitable blister copper directly from lower grade concentrates. This is foreseen as a major step in the direction of direct-to-blister production, especially in older smelters seeking to reduce emissions and production costs (Kojo et al., 2000).

2.8. Previous material and heat balance calculations of flash smelter

One of the important contributions to the material and heat balance calculations is made by Davenport and Partelpoeg, 1987. Main objectives of "Mathematical Descriptions of Flash Smelting" part of mentioned work are:

- to demonstrate the many ways a flash furnace can be operated to achieve a prescribed set of goals;
- to determine the fuel, oxygen and blast preheat requirements of each such operation method;
- to indicate how a flash furnace can be controlled so as to consistently give desired products at prescribed temperatures;
- to show how the flash furnace can be optimized so as to achieve its objections with a minimum expenditure of resources.

In the mentioned work also the basic mass and heat balance equations for steady-state flash smelting are developed. It then adapts the equations to the feed materials and products of industrial flash smelting and shows how the equations can be used to determine the amounts of oxygen and flux which are required to smelt chalcopyrite concentrate in flash smelter.

The general mass balance equation which must be obeyed during all steady-state operations in Davenport and Partelpoeg, 1987 is:

$$\begin{matrix}\text{Mass of element i}\\ \text{entering the furnace}\end{matrix} = \begin{matrix}\text{Mass of element i}\\ \text{leaving the furnace}\end{matrix} \qquad (2.4)$$

In mathematical terms the enthalpy balance equation of steady-state operation of a furnace is:

$$\sum H_{\text{Reactants}} = \sum H_{\text{Products}} + \begin{array}{l}\text{conductive, convective}\\ \text{plus radiative}\\ \text{heat loss from the furnace}\end{array} \qquad (2.5)$$

$\sum H_{\text{Reactants}}$ represents the sum of the enthalpies of all feed materials entering the furnace. Its numerical value depends upon the quantity and temperature of each feed materials. $\sum H_{\text{Products}}$ represents the furnace products in the same way. Conductive, convective plus radiative heat loss from the furnace represents the amount of heat lost from the furnace by:

1) conduction through the furnace walls and eventual convection and radiation of this heat away from the furnace;
2) direct radiation of heat from the furnace through opening in the furnace walls and roof.

Biswas and Davenport, 1980 presented heat balance for matte smelting as given in Table 2.4 where comparison between reverberatory, Outokumpu flash and INCO flash smelting furnaces was done.

As seen from Table 2.4, the INCO oxygen process is autogenous whereas the Outokumpu process is not autogenous with air. It requires about half the fuel of an equivalent reverberatory smelting process.

Table 2.4. Simplified heat balances for reverberatory, Outokumpu flash and INCO oxygen flash smelting, basis 1 ton dry charge (Biswas and Davenport, 1980)

Item	Reverberatory furnace	Outokumpu flash furnace (air at 550^0C, no oxygen enrichment)	INCO oxygen (95% O_2) flash
Input heat	10^5 kcal	10^5 kcal	10^5 kcal
Sensible heat in converter slag	1.7	-	-
Sensible heat in air for sulfide oxidation	0.2 (220^0C)	1.0 (550^0C)	-
Heat of matte and SO_2 production	1.8	5.3	5.3
TOTAL:	3.7	6.3	5.3
Output heat	10^5 kcal	10^5 kcal	10^5 kcal
Sensible heat in matte (1150^0C)	1.9 (40% Cu)	1.5 (50% Cu)	1.5 (50% Cu)
Sensible heat in slag (1200^0C)	1.9	1.3	1.3
Sensible heat in SO_2 (1250^0C)	0.4	0.7	0.7
Sensible heat in N_2 from the air used for sulphide and iron oxidation	1.0	2.5	0.1
Heat losses (convection, radiation)	2.3	2.1	1.7
TOTAL	7.5	8.1	5.3
Net deficit to be made up by external energy	3.8	1.8	0.0
Fuel energy required	8.1×10^5 kcal (at 47% efficiency)	4.5×10^5 kcal (at 40% efficiency)	

CHAPTER 3

ETI-BAKIR SAMSUN PLANT

3.1 Introduction to Eti-Bakır Samsun plant

Eti-Bakır plant is situated 16 km to the East of Samsun city, near Tekkeköy village. It is located on 3.1 km^2 area. Plant produces blister copper from almost all of the resources of Black Sea region, but the main concentrate supply for the Samsun plant comes from Murgul Damar and Küre Bakibaba – Aşıköy ore deposits. Most of the gases produced during smelting are converted to H_2SO_4. Also, there is a flotation plant for processing and enrichment of the slag coming out from the flash furnace. In Figure 3.1 flowsheet of Eti-Bakır Copper Plant is given. Eti-Bakır copper plant uses 250000 ton per year of copper concentrate and produces about 40000 tons of blister copper per year.

Construction of Samsun plant was started on 28 May 1968 and on March 1973 first blister copper was produced. In August 1987 Japan specialists from Furukawa Limited Company made some modifications to the plant. The most noteworthy change was the installation of side-take system. But, due to blockage problems, this was changed to up-take again in November 2007 and it has been functioning well since then.

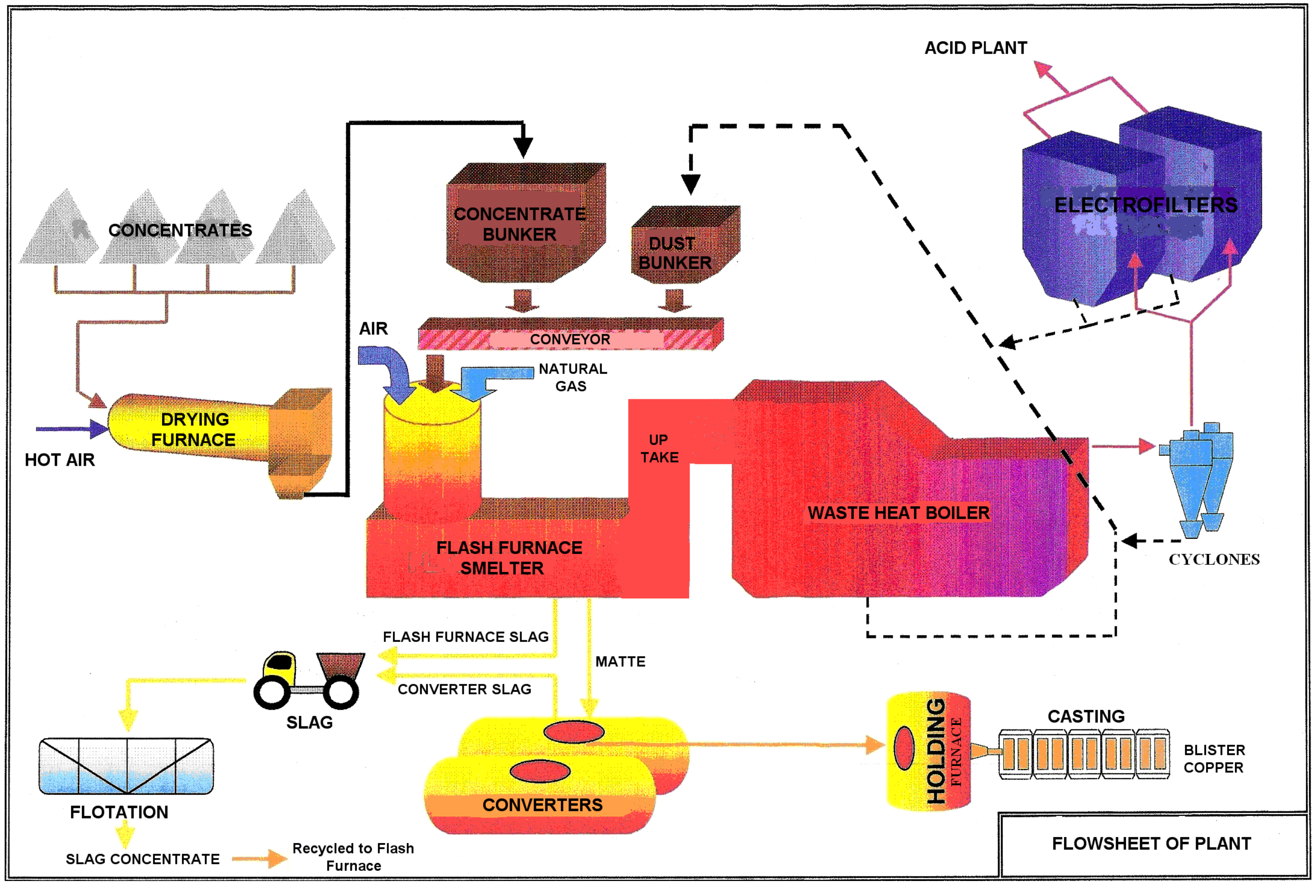


Figure 3.1. Flowsheet of Eti-Bakır Copper Plant

3.2 Main smelting units

The purpose of building this smelting unit was to produce blister copper from copper concentrates coming from inside and outside of Turkey. There are three main parts of smelting unit: Drying furnace, Flash furnace and Converter.

Concentrates coming to Eti-Bakır plant are stockpiled in 17 independent stockyards each of capacity to hold 3000 t and totally there is an area of 50000 t stocking capacity. For processing the copper concentrates, flux containing 87-90% SiO_2 is used. Flux and lignite for system are supplied from 5 bunkers, capacity of each is nearly 40 ton, by use of rubber conveyors. For loading concentrates on conveyor there are some loaders present. Mixture that contains moisture of 9-12% passes through 3 conveyors and is fed to rotary kiln type drying furnace at nearly 45 t/h. It is necessary to dry the raw materials for better production quality level and higher efficiency of reaction of feed material in combustion tower of flash furnace.

3.2.1 Rotary kiln type drying furnace

Materials supplied to drying furnace are dried by means of hot gases at 300-350^{0}C, coming from superheater system without any extra fuel requirement. All materials coming out from dryer are treated by cyclones with special air carrying system. Some larger particles of powder are taken away by separator and after crushing and grinding again supplied to the system. Moisture of the mixture is decreased in the drying furnace from 9-12% to 0.2-0.25% (weight percentage) and taken to a bunker with a capacity of 250 t. Automatic devices control all the temperatures of gases coming in and out of the dryer system (Kitap, 2006).

Technical data for drying furnace:

Diameter – 3 m, length – 30 m, rotation speed – 2 rev/min, process time in normal condition – 45 min, gas stream speed – 20 m/sec, incoming gas amount – 35000-40000 m^3/h, slope – 2^0.

3.2.2 Flash furnace

Figures 3.2 and 3.3 show Eti-Bakır plant design of Outokumpu flash furnace. It is 18.7 m long, 8 m wide and 2.44 m high (inside dimensions). It has a 6.44 m high reaction shaft with 5.5 m diameter and 10.6 m high off-gas up-take with 3.5 m diameter. It has one concentrate burner and smelts about 750-800 tonnes of concentrate per day, also furnace has 4 matte tapholes and 2 slag tapholes. In general flash furnace has the following five main features:

1. Concentrate burner which combines dry particular feed with air blast and blow them downward into the furnace;
2. A reaction shaft where most of the reaction between oxygen and Cu-Fe-S feed particles takes place;
3. A settler where molten matte and slag droplets collect and form separate layers;
4. Water-cooled copper block tapholes for removing molten matte and slag;
5. An up-take removing hot SO_2-bearing off-gas.

The interior of this flash furnace is lined with high-purity direct-bonded magnesia-chrome bricks. The bricks are backed by water-cooled copper cooling jackets on the walls and by sheet steel elsewhere. Reaction shaft and up-take refractory is backed by water-cooled copper cooling jackets or by sheet steel, cooled with water on the outside. Inner sides of furnace and reaction shaft are covered with chrome-magnetite bricks. The top of reaction shaft is covered with the same bricks with thickness of 400 mm, sidewalls – 290 mm, upper part of settler – 400 mm, sidewalls: on the bottom – 460 mm, upper side – 230 mm.

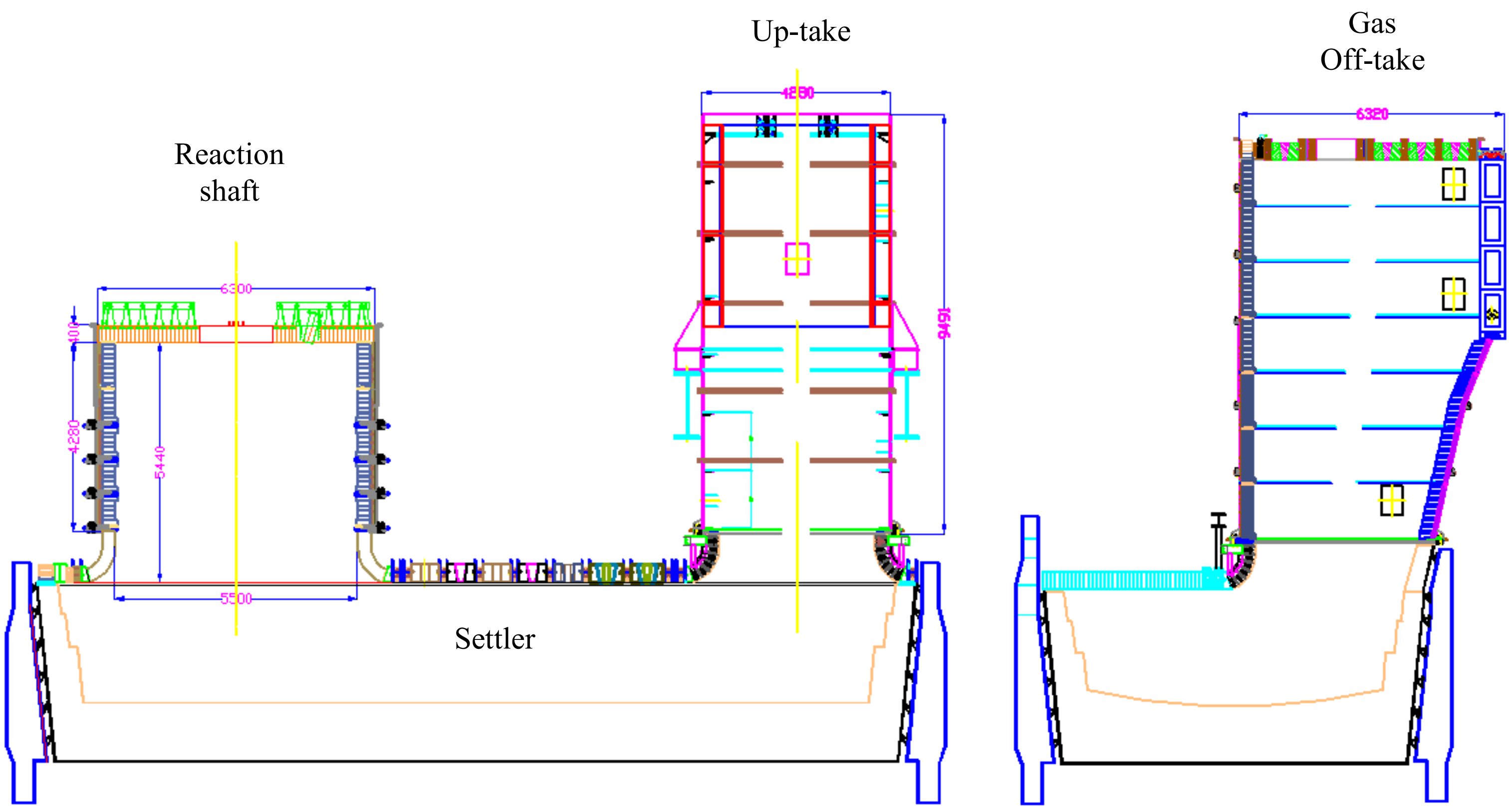


Figure 3.2. Outokumpu type flash smelter of Eti-Bakır plant (side view)

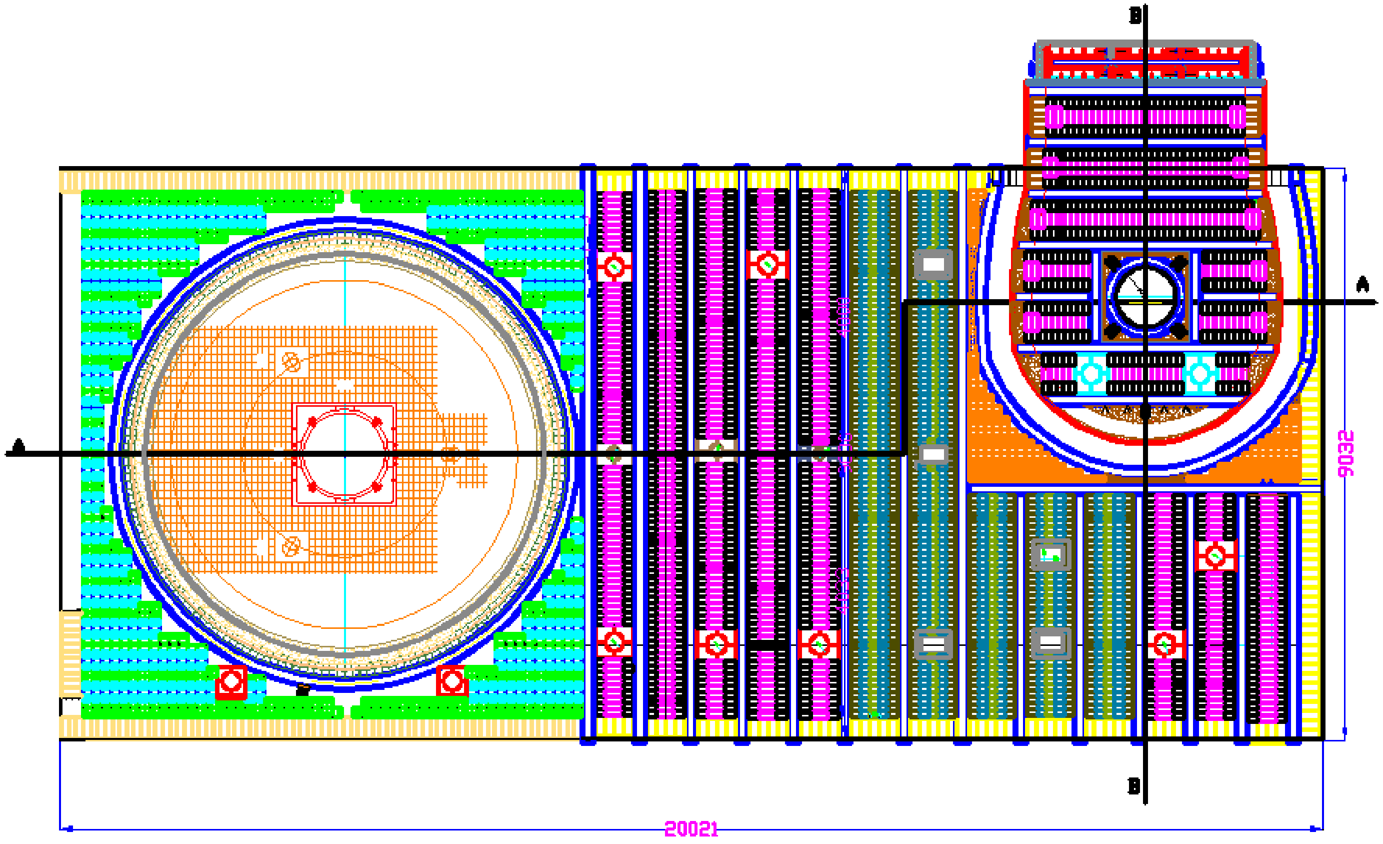


Figure 3.3. Outokumpu type flash smelter of Eti-Bakır plant (view from top)

The furnace rests on a 2-cm thick steel plate on steel-reinforced concrete pillars. The bottom of the furnace is air cooled by natural convection. Much of the furnace structure is in operating condition after 8 years of use. Slag line bricks may have eroded but the furnace can usually continue to operate without them. This is due to formation of magnetite-rich slag deposit on water-cooled regions of the furnace walls.

Dry concentrate and air blast are combined in the furnace reaction shaft by blowing them through a concentrate burner (Figure 3.4). Dry flux, recycle dust and lignite are also added through the burner. Concentrate burner consists of:

1. An annulus through which air blast is blown into the reaction shaft;
2. A central pipe through which concentrate falls into reaction shaft;
3. A distributor cone at the burner tip, which blows air horizontally through the descending solid feed.

The main goal of the burner is to create a uniform-blast suspension 360^0 around the burner. This type of burner can smelt up to 200 tonnes of feed per hour.

Matte and slag are tapped through single-hole water-cooled copper “chill blocks” imbedded in the furnace walls. The holes are typically 50-60 mm in diameter. They are plugged with moist fireclay which is solidified by the heat of the furnace when the clay is pushed into the hole. They are opened by chipping out the clay and by melting it out with steel oxygen lances.

One disadvantage of this technology is that too much dust goes out with gas which needs separation of that dust from gas and returns it to the process again. About 70% of this dust drops out in the waste heat boiler and cyclones. The remainder is caught in electrostatic precipitator where the particles are charged in a high voltage electrical field, caught on a charged wire or plate and periodically collected as dust "clumps" by rapping the wires and plates. Electrostatic precipitator exit gas contains about 0.1 gram of dust per Nm^3 of gas. The collected dust contains about 20-25% Cu.

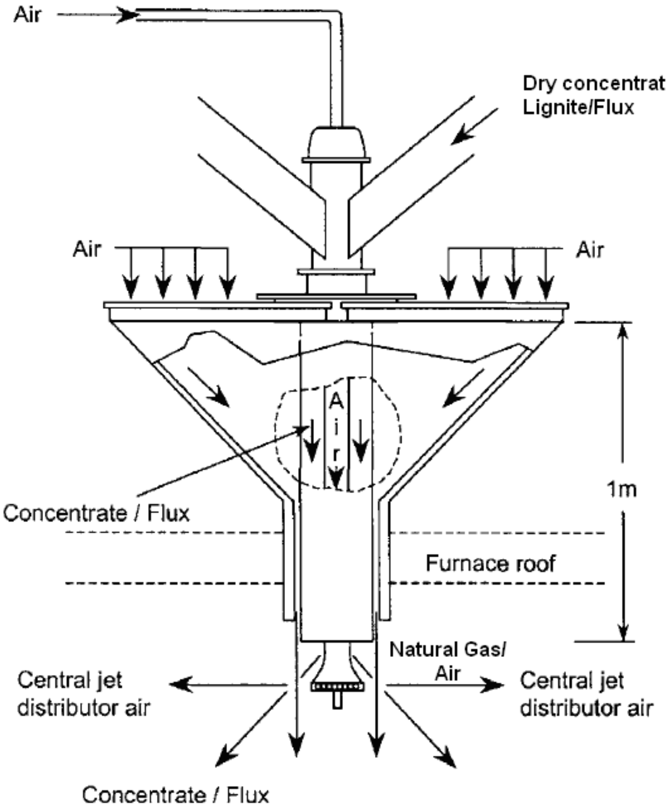


Figure 3.4. Central jet distributor Outokumpu concentrate burner

Dust is almost always recycled to the flash furnace for copper recovery. It is removed from the boilers and precipitators by drag and screw conveyors, transported pneumatically to a dust bin above the flash furnace and combined with the dried feed before it enters the concentrate burner.

The slag also contains recoverable amount of copper in it and that is why it is sent to flotation plant to be enriched up to 30-35% of copper. Two closed system conveyors with pallets supply dried concentrate to concentrate burner through four independent entrance holes. At the same time natural gas with pressured air is supplied from the same holes to make better separation of concentrate powder and ignition. Additional air is given through burners from the same points at 350-400^{0}C for burning.

Copper concentrate and flux pass through different reactions inside the reaction shaft at 650-1000^{0}C and fall down to settler area on the slag surface. In the settler part of the furnace slag and matte are separated due to density difference. Density of magnetite is higher than that of matte and slag; as a result, it goes down. If magnetite is not reduced to FeO and reacted with SiO_2 to turn into slag state, it accumulates on the bottom surface of furnace and may cause problems. The slag is tapped and filled into 35-ton ladles and sent to the flotation process. In the flash furnace there are also several thermometers to measure temperature at same critical point and devices to measure velocity of air stream. All collected data goes directly to process control room for checking. Some parameters of furnace are given in Table 3.1.

Table 3.1. Parameters of flash furnace of Eti-Bakır plant

Reaction air temperature	350-400^{0}C
Amount of reaction air for 1 ton of feeding	650-800 m^3/h
Feeding	35-40 tons/h
Concentration of SO_2 in off-gases of the flash furnace	8-12%
Density of matte	4.7 g/cm^3
Density of slag	3.7 g/cm^3
Matte grade	45-50%
Copper in furnace slag	0.8-2%

3.2.3 Converter

Converting is oxidation of molten Cu-Fe-S matte to form molten blister copper (99.5% Cu). It entails oxidizing Fe and S from the matte with oxygen-enriched air or air blast. In Eti-Bakır plant it is done in the Peirce-Smith converter, which blows the air blast into molten matte through submerged tuyeres (Figure 3.5).

The blast supply, rotating seal and bustle pipe are connected to the tuyeres. Flux and Cu-bearing revert are added from bins above the off-gas up-take. The converter rotates around its long axis in order to lift its tuyeres out of the liquids when it is not blowing and submerge them correctly in the matte during blowing.

The main raw material for converting is molten Cu-Fe-S matte from smelting. Other raw materials include silica flux and air. Several Cu-bearing materials are recycled to the converter- mainly solidified Cu-bearing reverts and copper scrap. The products of converting are:

1. Molten blister copper which is cast;
2. Molten iron-silicate slag which is sent to Cu recovery, then discard;
3. SO_2-bearing off-gas which is sent to cooling, dust removal and H_2SO_4 production.

The heat for converting is supplied entirely by Fe and S oxidation, i.e. the process is autothermal.

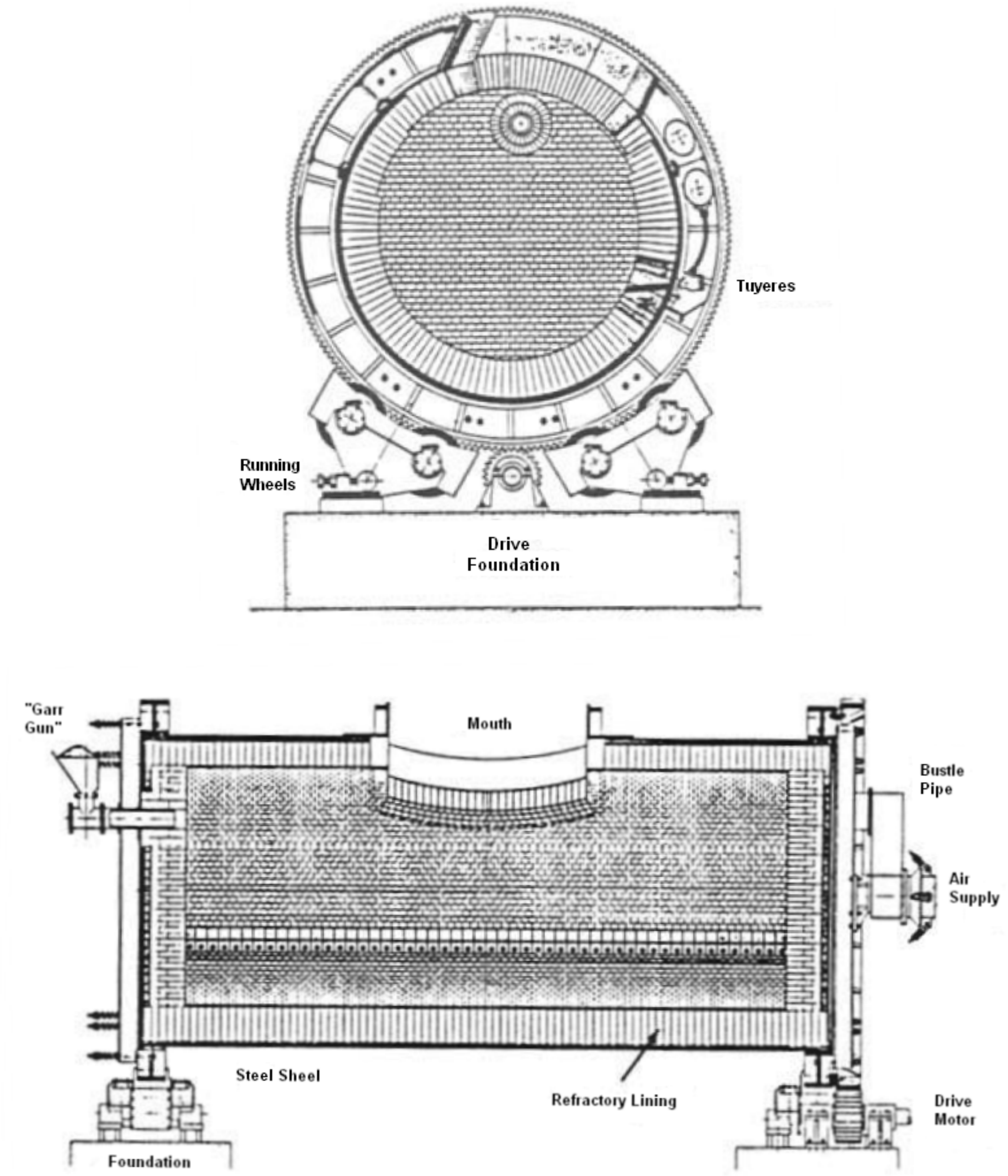


Figure 3.5. Pierce-Smith converter

Matte taken from flash furnace is supplied to one of two converters by crane. Normally both converters are working and charged 3 times in a day. In case of any refractory or blower failure, that converter will be taken to repair while the other still works. There are 40 tuyeres in each converter and when tuyeres are blocked they are opened by half automated system using a steel rod. Flux is added to converter in necessary amounts and air is also blown. As a result, two different periods take place in the converter: slag period and copper-making period. Technical and process data of converters which are used in Eti-Bakır plant are given in Table 3.2.

Table 3.2. Technical and process data of converters which are used in Eti-Bakır Plant

Diameter	4 m
Height	7.3 m
Tuyeres diameter	55 mm
Feeding mouth	2.5x2 m
Blowing capacity	25000 m^3/h
Slag blowing time	170 min
Copper blowing time	175 min
Matte feeding temperature	1150^0C
Blister copper temperature	1200^0C
Amount of matte	105 tons per period
Slag produces	50 tons per period
Blister copper produced	55 tons per period
Composition of Blister copper	99.5% Cu
Copper in converter slag	5-6%

Molten blister copper goes into hot holding furnace the capacity of which is 250 t. After that copper is poured into 50-60 kg ingots and prepared for sale. During converter processing copper absorbs some amount of SO_2 gas and when copper is cooling down in forms, SO_2 gas starts to go out and leaves bubbles in copper forms. Because of that reason cooled copper forms are called blister copper. There are also some impurities in blister copper such as: Ni, Co, Fe, Sn, Sb, As, Pb, Au, Ag and others.

CHAPTER 4

MASS AND HEAT BALANCE CALCULATIONS OF FLASH SMELTING

4.1 Calculation of mineralogical composition of input and output materials

In order to do calculations of material and heat balances, the compositions of ore concentrate, slag concentrate, flux, input dust, lignite, natural gas, matte, furnace slag and output dust were taken from ETI-BAKIR plant which uses Outokumpu type flash smelter to produce matte with a grade of 40-50% Cu. The data obtained are given in Table 4.1 and line flowsheet of the plant is shown in Figure 4.1. For heat balance calculations, the diagram of temperatures of input and output materials of this flash furnace is given in Figure 4.2; the reactions relevant to this process are also given on the same figures.

Basis: 1 ton of copper concentrate (mixture of Küre concentrate, Murgul concentrate, Murgul ore and slag concentrate).

MW – molecular weight;
AW – atomic weight.

4.1.1 Matte quantity

It is assumed that 97% of copper in copper concentrate forms matte. Rest is taken as loss in slag (Davenport et al., 2001):

$$Matte = 1000 \times \frac{Cu\ in\ conc. \times 97/100}{Cu\ in\ matte} = 1000 \times \frac{19.62 \times 97/100}{45} = 423\ \text{kg.}$$

From the analysis assume that 90% of matte in weight is a compound made up of Cu, Fe and S and the rest 10% contains oxides of metals such as Pb, Zn, Fe and etc. Also, Silica-to-Iron ratio in slag in flash smelting with production of low grade matte is taken as 0.7 (Davenport et al., 2002).

Table 4.1. Compositions of ore concentrate, slag concentrate, flux, input dust, lignite, natural gas, matte, furnace slag and output dust, %

Materials	Cu	Pb	Zn	Fe	S	SiO_2	Fe_3O_4	Others
Input:								
Cu concentrate	19.62	0.26	2.26	29.95	33.31	3.22	3.62	7.76
Kure conc.(44%)	17.7	0.02	1.1	34.1	37.2	1.6	-	-
Murgul conc.(35%)	23	0.6	3.4	31.9	32.8	2.1	-	-
Murgul ore (10.5%)	8	0.17	2	18	38	6	23.4	-
Slag conc (10.5%)	28	0.27	3.6	18	14	11	11.1	-
Flux	-	-	-	-	-	87	-	13
Input Dust	20	5	10	25	7	3	-	30
Lignite	53 (C)	6 (H)	23.4 (O)	-	1	-	-	-
Natural Gas, (mol.%)	85 (CH_4)	8 (C_2H_6)	3 (C_3H_8)	1 (C_4H_{10})	1 (CO_2)	0.5 (O_2)	1 (N_2)	0.5 (S)
Blast (vol.%)	-	-	21 (O)	79 (N)	-	-	-	-
Output:								
Matte	45	0.6	1.8	22	23	-	7.4 5.4(Fe)+ 2(O)	0.2
Furnace Slag	1.5	0.1	3	41	2	30	6.5 4.7(Fe)+ 1.8(O)	15.9
Dust (collected from Off-gas)	20	5	10	25	7	3	-	30
Off-gas	Will be defined by calculation							

Fe: AW=56 kg-atom;

FeS: MW=88 kg-mol;

Cu: AW=64 kg-atom;

Cu_2S: MW=160 kg-mol;

S: AW=32 kg-atom;

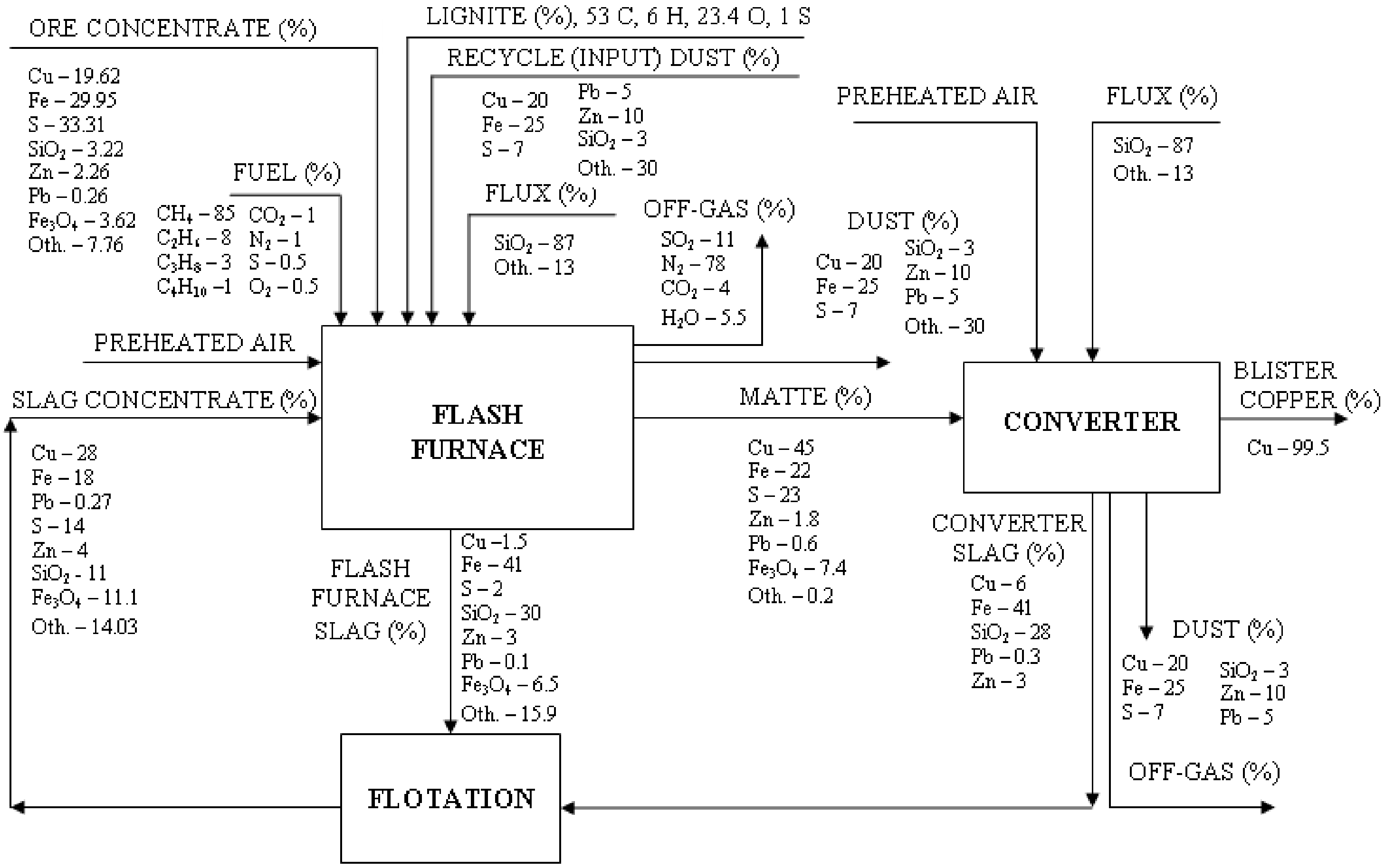


Figure 4.1. Flowsheet of plant with composition of all input and output materials

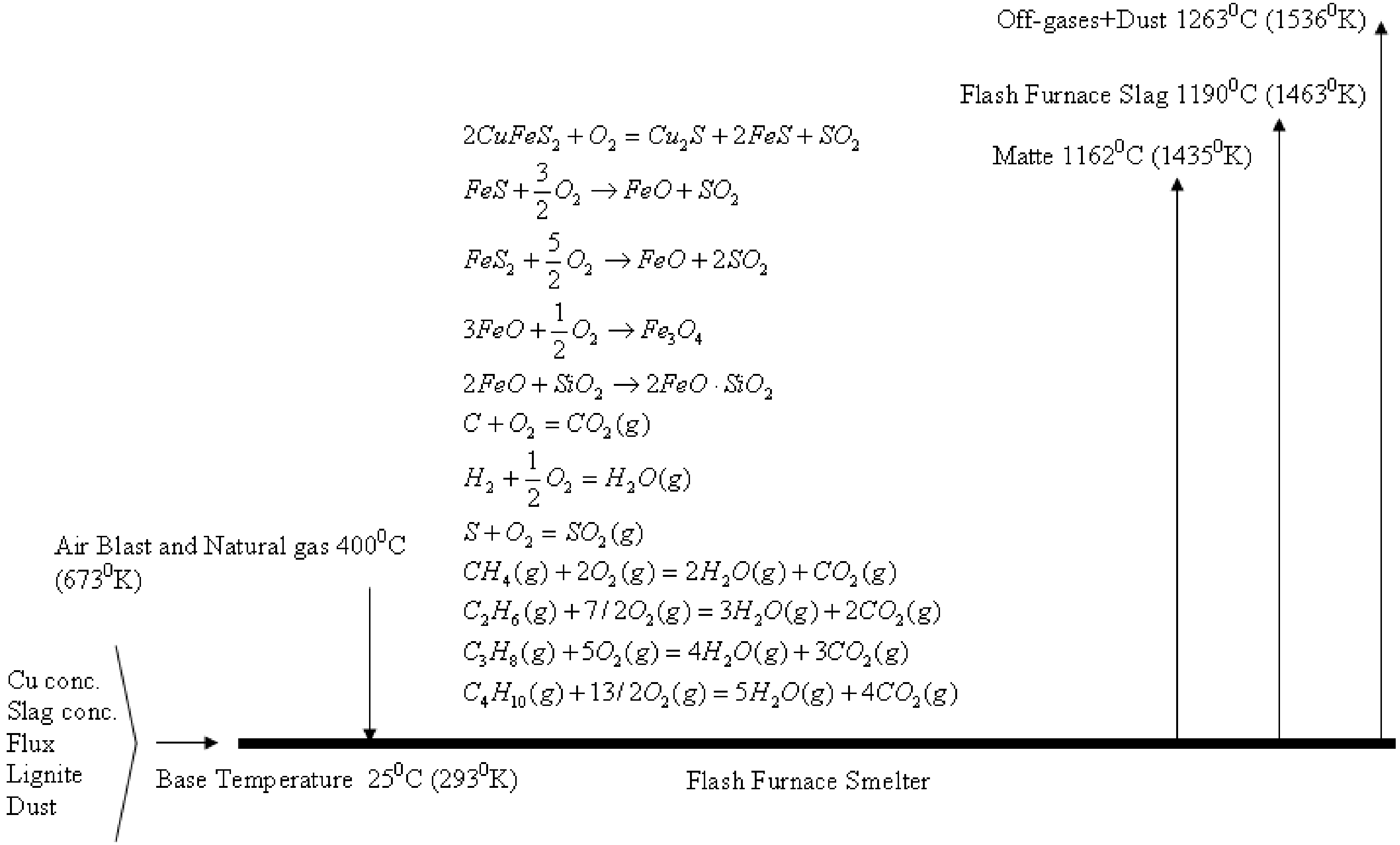


Figure 4.2. Diagram of heat balance of Flash Furnace

$$\text{Fe in matte as sulfide} = \{\text{matte} \times 90\% - \text{Cu}_2\text{S in matte}\} \times \frac{\text{AW of Fe}}{\text{MW of FeS}}$$

$$= \left\{\text{matte} \times \frac{90}{100} - 1000 \times \frac{\text{Cu in conc.} \times 97/100}{100} \times \frac{160}{128}\right\} \times \frac{56}{88}$$

$$= \left\{423 \times 0.9 - 10 \times 19.62 \times 0.97 \times \frac{160}{128}\right\} \times \frac{56}{88} = 90.88 \text{ kg};$$

$$\text{S in matte} = \left\{\text{matte} \times 90\% - 1000 \times \frac{\text{Cu in conc.} \times 97/100}{100} - \text{Fe in matte}\right\}$$

$$= 423 \times 0.9 - 10 \times 19.62 \times 0.97 - 90.88 = 99.51 \text{ kg};$$

$$\text{Fe in slag} = 1000 \times \frac{\text{Fe in conc.}}{100} - \text{Fe in matte as sulfide} - \text{Fe in matte as Fe}_3\text{O}_4$$

$$= 10 \times 29.95 - 90.88 - 423 \times \frac{5.4}{100} = 185.78 \text{ kg}.$$

4.1.2 Silica flux quantity

As mentioned above, $\frac{SiO_2}{Fe} = 0.7$,

$$SiO_2 \ in \ slag = Fe \ in \ slag \times 0.7 = 185.78 \times 0.7 = 130.05 \text{ kg/t.conc.}$$

SiO_2 to be supplied from silica flux,

$$\text{SiO}_2 \text{ from flux} = \text{SiO}_2 \text{ in slag} - \text{SiO}_2 \text{ in conc.} = 130.05 - 10 \times 3.22$$

$$= 97.85 \text{ kg/t.conc.}$$

Silica flux to be required,

$$Silica \ flux = SiO_2 \ from \ flux \times \frac{100}{SiO_2 \ in \ flux} = 97.85 \times \frac{100}{87} = 112.47 \text{ kg/t.conc.}$$

4.1.3 Flash furnace slag quantity

S in gas, is the amount of Sulfur generating SO_2 gas in the reaction, which can be calculated as the remaining Sulfur after some of Sulfur forms matte.

$$S\ in\ gas = S\ in\ conc. - S\ in\ matte = 1000 \times \frac{33.31}{100} - 99.51 = 233.59 \text{ kg/t.conc.}$$

Slag quantity means a product generated from copper concentrate and silica flux. Furnace slag is assumed to be mainly containing $FeO\text{-}SiO_2$ compound.

$$Slag\ quantity = Cu\ conc. - matte - S\ in\ gas + O\ of\ (FeO\ and\ Fe_3O_4) + silica\ \ flux;$$

41% of slag is Fe as FeO and 4.7% is Fe as Fe_3O_4. Therefore:

Fe as FeO of total Fe in slag $= \frac{41}{41+4.7} \times 100\% = 90\%$;

Fe as Fe_3O_4 of total Fe in slag $= 100 - 90 = 10\%$.

$$\text{O of (FeO and Fe}_3\text{O}_4) = \text{Fe as FeO} \times \frac{\text{AW of O}}{\text{AW of Fe}} + \text{Fe as Fe}_3\text{O}_4 \times \frac{4 \times \text{AW of O}}{3 \times \text{AW of Fe}}$$

$$= 185.78 \times \frac{90}{100} \times \frac{16}{56} + 185.78 \times \frac{10}{100} \times \frac{4 \times 16}{3 \times 56} = 47.77 + 7.08 = 54.85 \text{ kg/t.conc.};$$

$$Slag\ quantity = 1000 - 423 - 233.59 + 54.85 + 112.47 = 510.73 \text{ kg/t.conc.}$$

4.1.4 Full load of furnace

Full load of furnace is 38 t/h, but only 80% of feed is copper concentrate:

$$38 \times \frac{80}{100} = 30.4 \text{ t/h.}$$

4.1.5 Lignite quantity

Lignite which should be added to feed materials is about 2.5% of the total feed materials except dust and lignite:

$$\text{Lignite quantity} = \{\text{Copper conc.} + \text{silica flux}\} \times \frac{2.5}{97.5}$$

$$= \{1000 + 112.47\} \times \frac{2.5}{97.5} = 28.52 \text{ kg / t.conc.}$$

4.1.6 Input dust quantity

Dust quantity is about 6% of feed materials except dust:

$$\text{Input Dust quantity} = (\text{Copper conc.} + \text{Lignite} + \text{Silica flux}) \times \frac{6}{94}$$

$$= (1000 + 28.52 + 112.47) \times 6 / 94 = 72.83 \text{ kg/t.conc.}$$

Because indicated dust rate is given for only air blast without oxygen enrichment, dust rate should be indicated as a variable of off-gas volume throughout all calculations. In order to find that variable, dust quantity at a given rate should be divided by total output gas volume from furnace. Therefore, real dust rate as a variable will be indicated after the total volume of off-gas is defined.

4.1.7 Total of feed quantity

Total feed quantity is sum of copper concentrate, silica flux, lignite quantity and input dust amount.

$$Total\ \ feed\ quantity = 1000 + 112.47 + 28.52 + 72.83 = 1213.82\ kg / t.conc.$$

4.1.8 Output Dust quantity

According to data that was taken from Eti-Bakır plant, ratio between output and input dust can be assumed as 1.15.

$$Output\ Dust\ quantity = 1.15 \times Input\ Dust\ quantity = 1.15 \times 72.83 = 83.75\ kg / t.conc.$$

4.1.9 Magnetite balance

Balance equation:

$$Fe_3O_4 \text{ of copper conc.} = Fe_3O_4 \text{ of matte} + Fe_3O_4 \text{ of furnace slag;}$$

$$1000\times\frac{3.62}{100} = 423\times\frac{7.4}{100} + 510.73\times\frac{6.5}{100};$$

$$36.2 \text{ kg} = 31.3 \text{ kg} + 33.2 \text{ kg};$$

$$36.2 \text{ kg} \neq 64.5 \text{ kg}.$$

As seen from magnetite balance Fe_3O_4 deficiency is 64.5 kg – 36.2 kg = 28.3 kg. That amount of magnetite should be formed by oxidation of FeO to Fe_3O_4.

4.1.10 Volume of process air

O_2 in process air that is required to oxidize some of Sulfur and Iron in copper concentrate, which generates heat. Excess process air is 5%. Related reaction formulas are as follows:

$$\underset{32kg-atom}{S} + \underset{22.4Nm^3/kg-mole}{O_2} = \underset{22.4Nm^3/kg-mole}{SO_2}, \tag{4.1}$$

$$\underset{56kg-atom}{Fe} + \frac{1}{2}\underset{11.2Nm^3/kg-mole}{O_2} = \underset{72kg-mole}{FeO}, \tag{4.2}$$

$$\underset{168kg-atom}{3Fe} + \underset{44.8Nm^3/kg-mole}{2O_2} = \underset{232kg-mole}{Fe_3O_4}. \tag{4.3}$$

$$\text{Volume of process air} = \left\{\text{S in gas}\times\frac{22.4}{32} + \text{Fe as FeO in slag}\times\frac{11.2}{56}\right.$$

$$\left. + \text{formed } Fe_3O_4\times\frac{44.8}{232}\right\}\times 1.05\times\frac{100}{21} = \left\{233.59\times\frac{22.4}{32}\right.$$

$$\left. + 185.78\times\frac{90}{100}\times\frac{11.2}{56} + 28.3\times\frac{44.8}{232}\right\}\times 1.05\times\frac{100}{21} = 1012\ Nm^3/t.conc.$$

4.1.11 Volume of off-gas

Volume of off-gas at the outlet of reaction shaft:

$$SO_2 = S\ in\ gas \times \frac{22.4}{32} = 233.59 \times \frac{22.4}{32} = 163.51\ Nm^3 / t.conc.$$

Oxygen in excess air:

$$\mathrm{O_2} = \left\{ \text{Volume of process air} - \frac{\text{Volume of process air}}{1.05} \right\} \times 0.21$$

$$= \left\{ 1012 - \frac{1012}{1.05} \right\} \times 0.21 = 10.12\ Nm^3 / t.conc.;$$

$$N_2 = Volume\ of\ process\ air \times 0.79 = 1012 \times 0.79 = 799.5\ Nm^3 / t.conc.$$

Average water content in the feed is about 0.2%:

$$H_2O = total\ amount\ of\ feed \times \frac{0.2}{100} \times \frac{22.4}{18} = 1213.82 \times \frac{0.2}{100} \times \frac{22.4}{18} = 3.02\ Nm^3 / t.conc.$$

Total volume of off-gas $= 976.15 \dfrac{Nm^3}{t.conc.}$.

Dust rate as a variable = $\dfrac{Input\ Dust}{Total\ volume\ of\ off-gas} = \dfrac{72.83}{976.15} = 0.075$ kg dust per Nm^3 of off-gas.

4.2 Calculation of Heat Balance

Sources for all thermodynamic data for copper extraction system which is used in present calculations:

1. High temperature heat contents, heat capacities and enthalpy increment equations:
    - Kelley K.K., Bulletin 584, U.S. Bureau of Mines, 1960;
2. Standard enthalpies of formation at 298 K:

- King E.G., Mah A.D and Pankratz L.B. Thermodynamic properties of copper and inorganic compounds, International Copper Research Association, Inc., New York, 1973;

-Stull D.R, Prophet H et al. JANAF Thermochemical tables, Second edition, United States Department of Commerce, Document NSRDS-NBS 37, Washington, 1970.

Through the heat balance calculations assumptions about mineralogical compositions of copper concentrate, matte, furnace slag and output dust were done. According to analyses (APPENDIX B) that were proceeded on XRD in Metallurgical and Materials Engineering of Middle East Technical University average composition of copper concentrate, matte and furnace slag were chosen as follows:

Copper concentrate – $CuFeS_2$-FeS_2;
Matte – Cu_2S-FeS-Fe_3O_4-ZnO-PbO;
Furnace slag – FeO-Cu_2S-Fe_3O_4-SiO_2-ZnO-PbO.

Also, composition of output dust according to Davenport and Partelpoeg, 1987 and Gößling, 2001 was chosen as $CuSO_4$-CuO-Fe_3O_4-ZnO-PbO-SiO_2.

4.2.1 Inlet Heat

4.2.1.1 Reaction heat.

As mentioned at the beginning of calculations, copper concentrate consists of Küre concentrate, Murgul concentrate, Murgul ore and Slag concentrate. Copper which is in slag concentrate ($\approx 15\%$) is in matte form and 5% of all input iron is in oxide forms. It means that they will not react with oxygen.

The following reactions are assumed to take place.

$$2CuFeS_2 + O_2 = Cu_2S + 2FeS + SO_2; \tag{4.4}$$

$$\Delta H^0_{298} = -22475 \text{ kcal/kg-mol } CuFeS_2;$$

$$FeS + \frac{3}{2}O_2 \rightarrow FeO + SO_2; \tag{4.5}$$

$$\Delta H^0_{298} = -111750 \text{ kcal/kg-mol } FeS;$$

$$FeS_2 + \frac{5}{2}O_2 \rightarrow FeO + 2SO_2; \tag{4.6}$$

$$\Delta H^0_{298} = -163100 \text{ kcal/kg-mol } FeS_2;$$

$$3FeO + \frac{1}{2}O_2 \rightarrow Fe_3O_4; \tag{4.7}$$

$$\Delta H^0_{298} = -25700 \text{ kcal/kg-mol } FeO;$$

$$2FeO + SiO_2 \rightarrow 2FeO \cdot SiO_2; \tag{4.8}$$

$$\Delta H^0_{298} = -10000 \text{ kcal/kg-mol } SiO_2.$$

Cu in conc. $-19.62\% = 196.2$ kg;

CuFeS$_2$ in conc. $= \left(196.2 - 196.2 \times \frac{15}{100}\right) \times \frac{184}{64} = 479.46$ kg;

Fe in conc. $-29.95\% = 299.5$ kg;

Fe as oxide in copper conc. $= 299.5 \times \frac{5}{100} = 14.98$ kg;

Fe in CuFeS$_2$ $= 479.46 \times \frac{56}{184} = 145.78$ kg;

other Fe is present as FeS$_2$, Fe in FeS$_2$ $= 299.5 - 14.98 - 145.78 = 138.74$ kg;

FeS$_2$ $= 138.74 \times \frac{120}{56} = 297.3$ kg;

Fe as sulfide in matte – 22% $\Rightarrow 423 \times \frac{22}{100} = 93.06$ kg, as FeS: $93.06\times\frac{88}{56}=146.24$ kg.

According to Reaction 4.4:

$$\mathrm{FeS}=\mathrm{CuFeS_2}\text{ in Cu conc.}\times\frac{88}{184}=479.46\times\frac{176}{368}=229.3\text{ kg.}$$

It means that the amount of FeS that formed by Reaction 4.4 is more than it should be present in matte. Therefore, 229.3 kg – 146.24 kg = 83.06 kg of FeS should be reacted by Reaction 4.5.

Fe_3O_4 formed by Reaction 4.7, as can be seen from magnetite balance, is 28.3 kg/t.conc. As a result, FeO amount needed for Reaction 4.7 is as follows:

$$\text{amount of } Fe_3O_4\times\frac{3\times72}{232}=28.3\times\frac{216}{232}=26.35\text{ kg/t.conc.}$$

SiO_2 in slag $=130.05$ kg.

In molar fraction:

$CuFeS_2$: $\frac{479.46}{2\times184}=1.303$ kg-mol (For Reaction 4.4);

FeS: $\frac{83.06}{88}=0.94$ kg-mol (For Reaction 4.5);

FeS_2: $\frac{297.3}{120}=2.478$ kg-mol (For Reaction 4.6);

FeO: $\frac{26.35}{3\times72}=0.12$ kg-mol (For Reaction 4.7);

SiO_2: $\frac{130.05}{60}=2.17$ kg-mol (For Reaction 4.8).

$$\begin{aligned}\text{Reaction heat }&=1.303\times22475+2.478\times163100+0.94\times111750\\&\quad+0.12\times25700+2.17\times10000=563276\text{ kcal/t.conc.}\end{aligned}$$

4.2.1.2 Heat of process air

Oxygen amount which is needed for Reactions 4.4-4.7 and oxygen amount which is calculated before as process air should be checked and compared.

From Reaction 4.4:

$$Needed\ Oxygen = mass\ of\ CuFeS_2 \times \frac{22.4}{368} = 479.46 \times \frac{22.4}{368} = 29.18\ Nm^3 / t.conc.$$

From Reaction 4.5:

$$Needed\ Oxygen = mass\ of\ FeS \times \frac{3/2 \times 22.4}{88} = 83.06 \times \frac{33.6}{88} = 31.71\ Nm^3 / t.conc.$$

From Reaction 4.6:

$$Needed\ Oxygen = mass\ of\ FeS_2 \times \frac{5/2 \times 22.4}{120} = 297.3 \times \frac{56}{120} = 138.74\ Nm^3 / t.conc.$$

From Reaction 4.7:

$$Needed\ Oxygen = mass\ of\ FeO \times \frac{1/2 \times 22.4}{3 \times 72} = 26.35 \times \frac{11.2}{216} = 1.37\ Nm^3 / t.conc.$$

Oxygen should be added to process with the excess amount, because some reactions with less energy capacity are not considered. Excess amount of oxygen is 5%.

$$Total\ Needed\ Oxygen = (29.18 + 31.71 + 138.74 + 1.37) \times 1.05 = 211\ Nm^3 / t.conc.$$

Oxygen amount that was calculated as process air before:

$$1012 \times \frac{21}{100} = 212.5\ Nm^3 / t.conc.$$

Error of calculation of needed oxygen:

$$\frac{212.5 - 211}{212.5} \times 100\% = 0.7\%$$

That error percentage is acceptable; therefore, calculations of heat balance can be continued. Oxygen amount in process air is chosen for the future calculations: $212.5\ Nm^3 / t.conc.$

Temperature of preheated air: $T=400^0C=673^0K$;

$$\left(H_{673^0K}-H_{298^0K}\right)_{O_2}=7.16\times673+0.50\times10^{-3}\times673^2+0.40\times10^5\times\frac{1}{673}-2313$$

$$=2791.58\ \text{kcal/kg-mol}=2791.58/22.4=124.62\ \text{kcal/Nm}^3;$$

$$\left(H_{673^0K}-H_{298^0K}\right)_{N_2}=6.66\times673+0.51\times10^{-3}\times673^2-2031=2682.17\,\text{kcal/kg-}$$

$$\text{mol}=2682.17/22.4=119.74\ \text{kcal/Nm}^3;$$

O_2 in air: $212.5\frac{Nm^3}{t.conc.}$;

N_2 in air: $1012\frac{Nm^3}{t.conc.}-212.5\frac{Nm^3}{t.conc.}=799.5\frac{Nm^3}{t.conc.}$.

$$\text{Sensible Heat in Process Air}=212.5\times124.62+799.5\times119.74$$

$$=122214\,\text{kcal/t.conc.}$$

4.2.1.3 Heat of lignite

Lignite composition as indicated in data from Eti-Bakır plant:

Volatile matter – 25%, Moisture – 14%, Ash – 15%, S – 1%.

By using wet basis of carbon balance we can determine amount of carbon in lignite:

100 = Fixed C + Volatile matter + Moisture + Ash + S

Fixed C = 100 – 25 – 14 – 15 – 1 = 45%

Dry basis:

Volatile matter + Fixed C + Ash = 25 + 45 + 15 = 85%

The total percentage must be increased to 100%:

Volatile matter $=25\times\frac{100}{85}=29.4\%$;

Fixed C $=45\times\frac{100}{85}=53\%$;

Ash $=15\times\frac{100}{85}=17.6\%$.

According to Schuhmann, 1952, lignite with indicated above Volatile matter, Fixed C and Ash composition has elemental composition as follows:
Lignite composition (lignite dust): 53% C, 5% H, 23.4% O, 1% S.

Lignite quantity as calculated in material balance part is 28.52 kg/t.conc.

$$\mathrm{C} - 53\% \Rightarrow 28.52 \times \frac{53}{100} = 15.12 \text{ kg/t.conc;}$$

$$\mathrm{H} - 6\% \Rightarrow 28.52 \times \frac{5}{100} = 1.43 \text{ kg/t.conc;}$$

$$\mathrm{O} - 40\% \Rightarrow 28.52 \times \frac{23.4}{100} = 6.67 \text{ kg/t.conc;}$$

$$\mathrm{S} - 1\% \Rightarrow 28.52 \times \frac{1}{100} = 0.29 \text{ kg/t.conc.}$$

Reactions:

$$C + O_2 = CO_2(g), \qquad -\Delta H_{CO_2} = 97200 \frac{kcal}{kg-mole}; \tag{4.9}$$

$$H_2 + \frac{1}{2}O_2 = H_2O(g), \qquad -\Delta H_{H_2O} = 57800 \frac{kcal}{kg-mole}; \tag{4.10}$$

$$S + O_2 = SO_2(g), \qquad -\Delta H_{SO_2} = 70960 \frac{kcal}{kg-mole}. \tag{4.11}$$

According to Reaction 4.9:

$$\frac{15.12}{12} = 1.26 \frac{kg - atom\ C}{t.conc.} = 1.26 \frac{kg - mole\ O_2}{t.conc.}.$$

According to Reaction 4.10:

$$\frac{1.43}{2} = 0.715 \frac{kg - mole\ H_2}{t.conc.}.$$

According to Reaction 4.11:

$$\frac{0.29}{32} = 0.009 \frac{kg - atom\ S}{t.conc.} = 0.009 \frac{kg - mole\ O_2}{t.conc.}.$$

H_2 which will react with O_2 in the lignite:

$$\frac{6.67}{32}=0.208\frac{kg-mole\ O_2}{t.conc.},$$

$$0.208\times 2=0.416\frac{kg-mole\ H_2}{t.conc.}.$$

H_2 reacting with O_2 in Air:

$$0.715-0.416=0.299\frac{kg-mole\ H_2}{t.conc.}.$$

Therefore, O_2 for the 2nd reaction:

$$\frac{0.299}{2}=0.15\frac{kg-mole\ O_2}{t.conc.}.$$

Combustion Heat of Lignite $=1.26\times 97200+0.15\times 57800+0.009\times 70960$

$=131781$ kcal/t.conc.

Per kg of lignite combustion heat is about $\frac{131781}{28.52}=4621$ kcal, which is close to industrial amount which is equal to 4800-5000 kcal/kg of lignite.

Needed air (oxygen and nitrogen) amount to combust lignite:

$$O_2=1.26+0.009+0.15=1.419\frac{kg-mole\ O_2}{t.conc.}=1.419\times 22.4=31.79\frac{Nm^3}{t.conc.},$$

$$N_2=31.79\times\frac{79}{21}=119.59\frac{Nm^3}{t.conc}=\frac{119.59}{22.4}=5.34\frac{kg-mole\ N_2}{t.conc.}.$$

Total needed Air $=151.38\frac{Nm^3\ Air}{t.conc.}$

$$\left(\mathrm{H}_{673^0\mathrm{K}}-\mathrm{H}_{298^0\mathrm{K}}\right)_{\mathrm{O}_2}=7.16\times 673+0.50\times 10^{-3}\times 673^2+0.40\times 10^5\times\frac{1}{673}-2313$$

$$=2791.58\ \text{kcal/kg-mol}=2791.58/22.4=124.62\ \text{kcal/Nm}^3;$$

$$\left(\mathrm{H}_{673^0\mathrm{K}}-\mathrm{H}_{298^0\mathrm{K}}\right)_{\mathrm{N}_2}=6.83\times 673+0.45\times 10^{-3}\times 673^2+0.12\times 10^5\times\frac{1}{673}-2117$$

$$=2701\ \text{kcal/kg-mol}=2701/22.4=120.58\ \text{kcal/Nm}^3;$$

Heat content of combustion air $= 31.79 \times 124.64 + 119.59 \times 120.58$

$= 18382$ kcal/t.conc.

Waste gas from combustion of lignite. From Reactions 4.9-4.11:

$$CO_2 - 1.26 \times 22.4 = 28.22 \frac{Nm^3}{t.conc.};$$

$$H_2O - 0.715 \times 22.4 = 16.02 \frac{Nm^3}{t.conc.};$$

$$SO_2 - 0.009 \times 22.4 = 0.2 \frac{Nm^3}{t.conc.};$$

$$N_2 - 119.59 \frac{Nm^3}{t.conc.};$$

Total waste gas from combustion of lignite $= 164.03 \frac{Nm^3}{t.conc.}$.

$T_{off\text{-}gas}=1263^0C=1536^0K$;

$$\left(H_{1536^0 K} - H_{298^0 K}\right)_{CO_2} = 10.57 \times 1536 + 1.05 \times 10^{-3} \times 1536^2 + 2.06 \times 10^5 \times \frac{1}{1536}$$

$$- 3936 = 14911 \text{ kcal/kg-mol} = 14911/22.4 = 665.67 \text{ kcal/Nm}^3;$$

$$\left(H_{1536^0 K} - H_{298^0 K}\right)_{H_2O} = 7.30 \times 1536 + 1.23 \times 10^{-3} \times 1536^2 - 2286$$

$$= 11829 \text{ kcal/kg-mol} = 11829/22.4 = 528.08 \text{ kcal/Nm}^3;$$

$$\left(H_{1536^0 K} - H_{298^0 K}\right)_{SO_2} = 11.04 \times 1536 + 0.94 \times 10^{-3} \times 1536^2 + 1.84 \times 10^5 \times \frac{1}{1536}$$

$$- 3992 = 15303 \text{ kcal/kg-mol} = 15303/22.4 = 683.17 \text{ kcal/Nm}^3;$$

$$\left(H_{1536^0 K} - H_{298^0 K}\right)_{N_2} = 6.83 \times 1536 + 0.45 \times 10^{-3} \times 1536^2 + 0.12 \times 10^5 \times \frac{1}{1536}$$

$$- 2117 = 9443 \text{ kcal/kg-mol} = 9443/22.4 = 421.56 \text{ kcal/Nm}^3;$$

Heat content of Waste Gas $= 28.22 \times 665.67 + 16.02 \times 528.08 + 0.2 \times 683.17$

$+ 119.59 \times 421.56 = 77796$ kcal/t.conc.

Available Heat of Lignite = Combustion Heat of Lignite + Heat content of Combustion Air – Heat content of Waste Gas $= 131781 + 18382 - 77796$

$$= 72367 \text{ kcal/t.conc.}$$

$$\text{Available Heat for 1 kg of Lignite } = \frac{72367}{28.52} = 2537 \text{ kcal.}$$

4.2.2 Outlet Heat

4.2.2.1 Heat of matte

According to literature, zinc and lead sulfides which are present in concentrate are changed to oxide form because of the high temperature in the combustion tower of furnace.

Mineralogical composition of 423 kg of matte:

Cu_2S in matte:

$$1000 \times \frac{Cu\ in\ conc. \times \frac{97}{100}}{100} \times \frac{160}{128} = 10 \times 19.62 \times \frac{97}{100} \times \frac{160}{128} = 237.89 \text{ kg.}$$

As mentioned at the beginning of calculations, 90% of matte in weight is a compound of Cu, Fe and S.

FeS in matte $= matte \times 0.9 - Cu_2S\ in\ matte = 423 \times 0.9 - 237.89 = 142.81$ kg;

Fe_3O_4 in matte $- 7.4\% \Rightarrow matte \times \frac{7.4}{100} = 423 \times \frac{7.4}{100} = 31.3$ kg;

Zn in matte $- 1.8\% \Rightarrow matte \times \frac{1.8}{100} = 423 \times \frac{1.8}{100} = 7.61$ kg;

ZnO in matte $= 7.61 \times \frac{81}{65} = 9.48$ kg;

Pb in matte $-0.6\% \Rightarrow matte \times \dfrac{0.6}{100} = 423 \times \dfrac{0.6}{100} = 2.54$ kg;

PbO in matte $= 2.54 \times \dfrac{223}{207} = 2.74$ kg.

In molar fraction:

Cu_2S -237.89 kg $\Rightarrow \dfrac{237.89}{160} = 1.487$ kg-mole;

FeS -142.81 kg $\Rightarrow \dfrac{142.81}{88} = 1.623$ kg-mole;

Fe_3O_4 -31.3 kg $\Rightarrow \dfrac{31.3}{232} = 0.135$ kg-mole;

ZnO -9.48 kg $\Rightarrow \dfrac{9.48}{81} = 0.117$ kg-mole;

PbO -2.74 kg $\Rightarrow \dfrac{2.74}{223} = 0.012$ kg-mole.

$T_{matte}=1162^0C=1435^0K$;

$$\left(H_{1435^0K} - H_{298^0K}\right)_{Cu_2S} = 20.32 \times 1435 - 4275 = 24884 \text{ kcal/kg-mol;}$$

$$\left(\mathrm{H}_{1435^0\mathrm{K}} - \mathrm{H}_{298^0\mathrm{K}}\right)_{\mathrm{FeS}} = 12.20 \times 1435 + 1.19 \times 10^{-3} \times 1435^2 - 2138$$
$$= 17819 \text{ kcal/kg-mol;}$$

$$\left(H_{1435^0K} - H_{298^0K}\right)_{Fe_3O_4} = 48.00 \times 1435 - 12650 = 56230 \text{ kcal/kg-mol;}$$

$$\left(\mathrm{H}_{1435^0\mathrm{K}} - \mathrm{H}_{298^0\mathrm{K}}\right)_{\mathrm{ZnO}} = 11.71 \times 1435 + 0.61 \times 10^{-3} \times 1435^2 + 2.18 \times 10^5 \times \frac{1}{1435}$$
$$- 4277 = 13935 \text{ kcal/kg-mol;}$$

$$\left(H_{1435^0K} - H_{298^0K}\right)_{PbO} = 16.00 \times 1435 + 180 = 23140 \text{ kcal/kg-mol.}$$

Heat content of Matte $= 1.487 \times 24884 + 1.623 \times 17819 + 0.135 \times 56230$
$+ 0.117 \times 13935 + 0.012 \times 23140 = 75422$ kcal/t.conc.

4.2.2.2 Heat of furnace slag

Mineralogical composition for 510.73 kg of Flash Furnace Slag.

Fe in slag -185.78 kg;

FeO in slag $=185.78\times\frac{72}{56}=238.86$ kg;

Cu in slag $-1.5\%\Rightarrow slag\times\frac{1.5}{100}=510.73\times\frac{1.5}{100}=7.66$ kg;

Cu_2S in slag $=7.66\times\frac{160}{128}=9.575$ kg;

Fe_3O_4 in slag $-6.5\%\Rightarrow slag\times\frac{6.5}{100}=510.73\times\frac{6.5}{100}=33.2$ kg;

SiO_2 in slag -130.05 kg;

Zn in slag $-3\%\Rightarrow slag\times\frac{3}{100}=510.73\times\frac{3}{100}=15.32$ kg;

ZnO in slag $=15.32\times\frac{81}{65}=19.09$ kg;

Pb in slag $-0.1\%\Rightarrow slag\times\frac{0.1}{100}=510.73\times\frac{0.1}{100}=0.51$ kg;

PbO in slag $=0.51\times\frac{223}{207}=0.55$ kg.

In molar fraction:

FeO -238.86 kg $\Rightarrow\frac{238.86}{72}=3.318$ kg-mole;

Cu_2S -9.575 kg $\Rightarrow\frac{9.575}{160}=0.06$ kg-mole;

Fe_3O_4 -33.2 kg $\Rightarrow\frac{33.2}{232}=0.143$ kg-mole;

SiO_2 -130.05 kg $\Rightarrow\frac{130.05}{60}=2.168$ kg-mole;

ZnO -19.09 kg $\Rightarrow \frac{19.09}{81} = 0.236$ kg-mole;

PbO -0.55 kg $\Rightarrow \frac{0.55}{223} = 0.002$ kg-mole.

$T_{slag}=1190^0C=1463^0K$;

$$\left(H_{1463^0K} - H_{298^0K}\right)_{FeO} = 11.66 \times 1463 + 1.00 \times 10^{-3} \times 1463^2 + 0.67 \times 10^5 \times \frac{1}{1463} - 3790 = 15455 \text{ kcal/kg-mol;}$$

$$\left(H_{1463^0K} - H_{298^0K}\right)_{Cu_2S} = 20.32 \times 1463 - 4275 = 25453 \text{ kcal/kg-mol;}$$

$$\left(H_{1463^0K} - H_{298^0K}\right)_{Fe_3O_4} = 48.00 \times 1463 - 12650 = 57574 \text{ kcal/kg-mol;}$$

$$\left(H_{1463^0K} - H_{298^0K}\right)_{SiO_2} = 14.41 \times 1463 + 0.97 \times 10^{-3} \times 1463^2 - 4455 = 18703 \text{ kcal/kg-mol;}$$

$$\left(H_{1463^0K} - H_{298^0K}\right)_{ZnO} = 11.71 \times 1463 + 0.61 \times 10^{-3} \times 1463^2 + 2.18 \times 10^5 \times \frac{1}{1463} - 4277 = 14309 \text{ kcal/kg-mol;}$$

$$\left(H_{1463^0K} - H_{298^0K}\right)_{PbO} = 16.00 \times 1463 + 180 = 23588 \text{ kcal/kg-mol.}$$

Heat content of Flash Furnace Slag $= 3.318 \times 15455 + 0.06 \times 25453 + 0.143 \times 57574 + 2.168 \times 18703 + 0.236 \times 14309 + 0.002 \times 23588 = 105012$ kcal/t.conc.

4.2.2.3 Heat of Off-Gas

Volume of off-gas at the outlet of reaction shaft as calculated above:

$SO_2 = 163.51\ Nm^3 / t.conc.$;

$O_2 = 10.12\ Nm^3 / t.conc.$;

$N_2 = 799.5\ Nm^3 / t.conc.$;

$H_2O = 3.02\ Nm^3 / t.conc.$

$T_{\text{off-gas}}=1263^0C=1536^0K$;

$$\left(H_{1536^0K}-H_{298^0K}\right)_{SO_2}=11.04\times1536+0.94\times10^{-3}\times1536^2+1.84\times10^5\times\frac{1}{1536}$$

$$-3992=15303\ \text{kcal/kg-mol}=15303/22.4=683.17\ \text{kcal/Nm}^3;$$

$$\left(H_{1536^0K}-H_{298^0K}\right)_{O_2}=7.16\times1536+0.50\times10^{-3}\times1536^2+0.40\times10^5\times\frac{1}{1536}$$

$$-2313=9890.4\ \text{kcal/kg-mol}=9890.4/22.4=441.5\ \text{kcal/Nm}^3;$$

$$\left(H_{1536^0K}-H_{298^0K}\right)_{N_2}=6.83\times1536+0.45\times10^{-3}\times1536^2+0.12\times10^5\times\frac{1}{1536}$$

$$-2117=9443\ \text{kcal/kg-mol}=9443/22.4=421.56\ \text{kcal/Nm}^3;$$

$$\left(H_{1536^0K}-H_{298^0K}\right)_{H_2O}=7.30\times1536+1.23\times10^{-3}\times1536^2-2286$$

$$=11829\ \text{kcal/kg-mol}=11829/22.4=528.08\ \text{kcal/Nm}^3;$$

Heat content of Off-Gas $=163.51\times683.17+10.12\times441.5+799.5\times421.56$

$$+3.02\times528.08=454805\ \text{kcal/t.conc.}$$

4.2.2.4 Heat of Dust

Mineralogical composition for 83.75 kg of Dust.

S in dust $-7\%\Rightarrow dust\times\frac{7}{100}=83.75\times\frac{7}{100}=5.86$ kg;

Cu in dust $-20\%\Rightarrow dust\times\frac{20}{100}=83.75\times\frac{20}{100}=16.75$ kg;

$CuSO_4$ in dust $=5.86\times\frac{160}{32}=29.3$ kg;

Cu in $CuSO_4$ $=29.3\times\frac{64}{160}=11.72$ kg;

Cu as CuO $=16.75-11.72=5.03$ kg;

CuO in dust $=5.03\times\frac{80}{64}=6.29$ kg;

Fe in dust $-25\%\Rightarrow dust\times\frac{25}{100}=83.75\times\frac{25}{100}=20.94$ kg;

Fe_3O_4 in dust $= 20.94 \times \dfrac{232}{168} = 28.92$ kg;

Zn in dust $-10\% \Rightarrow \mathit{dust} \times \dfrac{10}{100} = 83.75 \times \dfrac{10}{100} = 8.38$ kg;

ZnO in dust $= 8.38 \times \dfrac{81}{65} = 10.44$ kg;

Pb in dust $-5\% \Rightarrow \mathit{dust} \times \dfrac{5}{100} = 83.75 \times \dfrac{5}{100} = 4.19$ kg;

PbO in dust $= 4.19 \times \dfrac{223}{207} = 4.51$ kg;

SiO_2 in dust $-3\% \Rightarrow \mathit{dust} \times \dfrac{3}{100} = 83.75 \times \dfrac{3}{100} = 2.51$ kg.

In molar fraction:

$CuSO_4$ -29.3 kg $\Rightarrow \dfrac{29.3}{160} = 0.183$ kg-mole;

CuO -6.29 kg $\Rightarrow \dfrac{6.29}{80} = 0.079$ kg-mole;

Fe_3O_4 -28.92 kg $\Rightarrow \dfrac{28.92}{232} = 0.125$ kg-mole;

ZnO -10.44 kg $\Rightarrow \dfrac{10.44}{81} = 0.129$ kg-mole;

PbO -4.51 kg $\Rightarrow \dfrac{4.51}{223} = 0.02$ kg-mole;

SiO_2 -2.51 kg $\Rightarrow \dfrac{2.51}{60} = 0.042$ kg-mole.

$T_{dust}=T_{off\text{-}gas}=1263^0C=1536^0K$;

$$\left(H_{1536^0K} - H_{298^0K}\right)_{CuSO_4} = 18.77 \times 1536 + 8.60 \times 10^{-3} \times 1536^2 - 6361$$

$$= 42760 \text{ kcal/kg-mol;}$$

$$\left(H_{1536^0K} - H_{298^0K}\right)_{CuO} = 8.72 \times 1536 + 0.07 \times 10^{-3} \times 1536^2 + 0.73 \times 10^5 \times \frac{1}{1536}$$

$$- 2851 = 10756 \text{ kcal/kg-mol;}$$

$$\left(H_{1536^0K} - H_{298^0K}\right)_{Fe_3O_4} = 48.00 \times 1536 - 12650 = 61078 \text{ kcal/kg-mol;}$$

$$\left(H_{1536^0K} - H_{298^0K}\right)_{ZnO} = 11.71 \times 1536 + 0.61 \times 10^{-3} \times 1536^2 + 2.18 \times 10^5 \times \frac{1}{1536}$$

$$- 4277 = 15291 \text{ kcal/kg-mol;}$$

$$\left(H_{1536^0K} - H_{298^0K}\right)_{PbO} = 16.00 \times 1536 + 180 = 24756 \text{ kcal/kg-mol.}$$

$$\left(H_{1536^0K} - H_{298^0K}\right)_{SiO_2} = 14.41 \times 1536 + 0.97 \times 10^{-3} \times 1536^2 - 4455$$

$$= 19967 \text{ kcal/kg-mol;}$$

Heat content of Dust $= 0.183 \times 42760 + 0.079 \times 10756 + 0.125 \times 61078 + 0.129 \times 15291 + 0.02 \times 24756 + 0.042 \times 19967 = 19616$ kcal/t.conc.

4.2.2.5 Heat loss

Parameters and dimensions of furnace were taken from the actual furnace that is operating in Eti-Bakır plant.

Reaction shaft (Figure 4.3). Actual surface area will be 10% larger than the area calculated by dimensions on the drawing because of steel-work directly attached to the surface of reaction shaft.

The upper part of the reaction shaft, 1.44 m from the top of its sidewall, has heat loss of 10×10^3 kcal/m^{2}h, and the remaining part of reaction shaft has 25×10^3 kcal/m^{2}h.

Surface area:

A zone: $\pi R^2 = 3.14 \times \left(\frac{5.5}{2}\right)^2 = 23.75$ m^2;

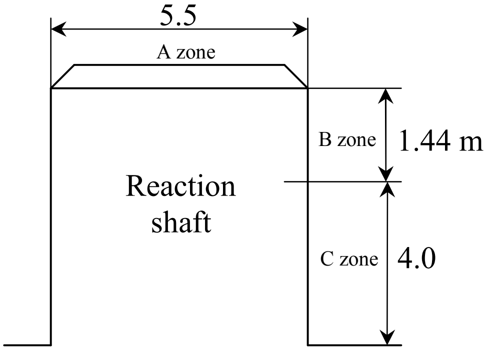


Figure 4.3. Reaction shaft of flash furnace

B zone: $2\pi Rh_1 = 2\times 3.14\times\left(\frac{5.5}{2}\right)\times 1.44 = 24.87\ \text{m}^2$;

C zone: $2\pi Rh_2 = 2\times 3.14\times\left(\frac{5.5}{2}\right)\times 4.0 = 69.08\ \text{m}^2$.

Ratio for unevenness of surface = 1.1.

Heat loss:

A+B zone $= (23.75 + 24.87)\times 1.1\times 10\times 10^3 = 534820$ kcal/h;

C zone $= 69.08\times 1.1\times 25\times 10^3 = 1899700$ kcal/h.

Heat Loss of Reaction shaft $= 534820 + 1899700 = 2434520$ kcal/h.

Up-take (Figure 4.4). Up-take has heat loss of 10×10^3 kcal/m^{2}h.

D zone: $\pi R^2 = 3.14\times\left(\frac{3.5}{2}\right)^2 = 9.62\ \text{m}^2$;

E zone: $2\pi Rh_3 = 2\times 3.14\times\left(\frac{3.5}{2}\right)\times 10.6 = 116.49\ \text{m}^2$;

Heat loss:

D+E zone $= (9.62 + 116.49)\times 1.1\times 5\times 10^3 = 693605$ kcal/h.

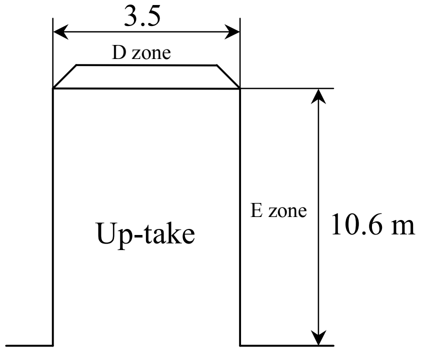


Figure 4.4. Up-take of flash furnace

Roof and Bottom of Furnace (Figure 4.5 and 4.6). Roof has heat loss of 5×10^3 kcal/m^{2}h and Bottom has heat loss of 5×10^3 kcal/m^{2}h.

Bottom $=18.7\times8=149.6$ m^2;

Roof = Bottom – A zone – D zone $=149.6-23.75-9.62=116.23$ m^2.

Heat loss:

Roof and Bottom $=116.23\times1.1\times5\times10^3+149.6\times1.1\times5\times10^3=1462065$ kcal/h.

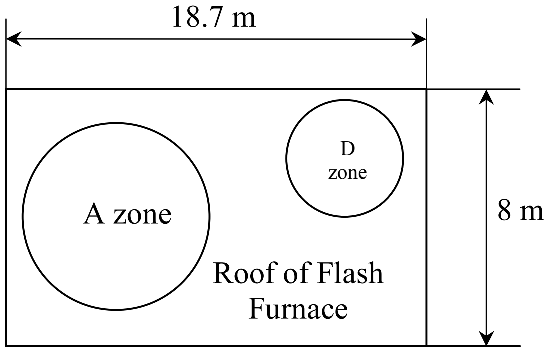


Figure 4.5. Roof of flash furnace

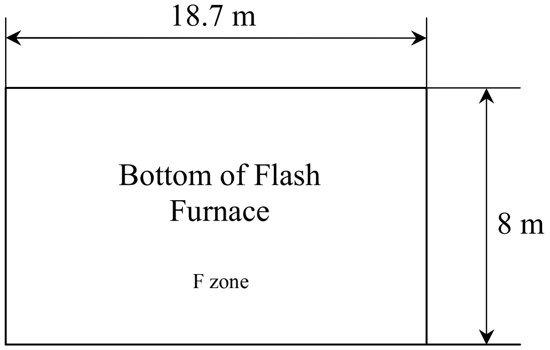


Figure 4.6. Bottom of flash furnace

Sides of Furnace (Figure 4.7). Sides of furnace have heat loss of 5×10^3 kcal/m^{2}h.

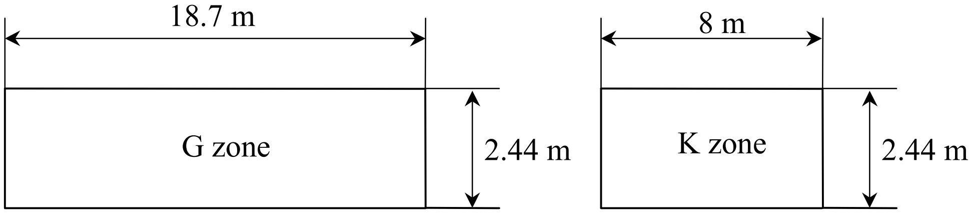


Figure 4.7. Sides of flash furnace

Sides of Furnace $= 2G + 2K = 2 \times 18.7 \times 2.44 + 2 \times 8 \times 2.44 = 130.296$ m^2.

Heat Loss:

Sides of Furnace $= 130.296 \times 1.1 \times 5 \times 10^3 = 716628$ kcal/h.

Total Heat Loss $= 2434520 + 693605 + 1462065 + 716628 = 5306818$ kcal/h

$= 5306818 / 30.4 = 174566$ kcal/t.conc.

4.2.3 Natural Gas Requirement

Composition of natural gas (NG) as mol.%: 85 CH_4, 8 C_2H_6, 3 C_3H_8, 1 C_4H_{10}, 1 CO_2, 0.5 O_2, 1 N_2, 0.5 S.

Basis: 1 Nm^3 of natural gas or $\frac{1}{22.4} = 0.0446$ kg-mol of NG

Reactions:

$$CH_4(g) + 2O_2(g) = 2H_2O(g) + CO_2(g), \tag{4.12}$$

$$-\Delta H_{CH_4} = 194910 \frac{kcal}{kg - mole};$$

$$C_2H_6(g) + 7/2O_2(g) = 3H_2O(g) + 2CO_2(g), \tag{4.13}$$

$$-\Delta H_{C_2H_6} = 347560 \frac{kcal}{kg - mole};$$

$$C_3H_8(g) + 5O_2(g) = 4H_2O(g) + 3CO_2(g), \tag{4.14}$$

$$-\Delta H_{C_3H_8} = 497980 \frac{kcal}{kg - mole};$$

$$C_4H_{10}(g) + 13/2O_2(g) = 5H_2O(g) + 4CO_2(g), \tag{4.15}$$

$$-\Delta H_{C_4H_{10}} = 647990 \frac{kcal}{kg - mole};$$

$$S(g) + O_2(g) = SO_2(g), \tag{4.16}$$

$$-\Delta H_{SO_2} = 70960 \frac{kcal}{kg - mole}.$$

In natural gas we have:

$0.0446 \times \frac{85}{100} = 0.03791$ kg-mole CH_4;

$0.0446 \times \frac{8}{100} = 0.00357$ kg-mole C_2H_6;

$0.0446\times\frac{3}{100}=0.00134$ kg-mole C_3H_8;

$0.0446\times\frac{1}{100}=0.00045$ kg-mole C_4H_{10};

$0.0446\times\frac{1}{100}=0.00045$ kg-mole CO_2;

$0.0446\times\frac{1}{100}=0.00045$ kg-mole N_2;

$0.0446\times\frac{0.5}{100}=0.00022$ kg-mole O_2;

$0.0446\times\frac{0.5}{100}=0.00022$ kg-atom S.

Combustion Heat of NG $=194910\times0.03791+347560\times0.00357$

$+497980\times0.00134+647990\times0.00045+70960\times0.00022=9604$ kcal.

Needed air (oxygen and nitrogen) amount to combust natural gas:

$$\mathrm{O_2}=0.03791\times2+0.00357\times\frac{7}{2}+0.00134\times5+0.00045\times\frac{13}{2}+0.00022$$

$$-0.00022=0.09794\ kg-mole\ O_2=0.09794\times22.4=2.1939\ Nm^3\ O_2,$$

$$N_2=0.09794\times\frac{79}{21}=0.3684\ kg-mole\ N_2=0.3684\times22.4=8.2522\ Nm^3\ N_2;$$

Total needed Air $=2.1939+8.2522=10.4461\ Nm^3$.

T=400^0C=673^0K;

$$\left(\mathrm{H}_{673^0\mathrm{K}}-\mathrm{H}_{298^0\mathrm{K}}\right)_{\mathrm{O_2}}=7.16\times673+0.50\times10^{-3}\times673^2+0.40\times10^5\times\frac{1}{673}-2313$$

$$=2791.58\ \text{kcal/kg-mol};$$

$$\left(\mathrm{H}_{673^0\mathrm{K}}-\mathrm{H}_{298^0\mathrm{K}}\right)_{\mathrm{N_2}}=6.83\times673+0.45\times10^{-3}\times673^2+0.12\times10^5\times\frac{1}{673}-2117$$

$$=2701\ \text{kcal/kg-mol};$$

Heat content of combustion air $= 2792 \times 0.09794 + 2701 \times 0.3684$

$= 1268\ \text{kcal/Nm}^3.$

Combustion product:

$$\text{CO}_2 = 0.03791 + 0.00357 \times 2 + 0.00134 \times 3 + 0.00045 \times 4 + 0.00045$$

$$= 0.05132\ kg-mole\ CO_2 = 0.05132 \times 22.4 = 1.1496\ Nm^3\ CO_2,$$

$$\text{H}_2\text{O} = 0.03791 \times 2 + 0.00357 \times 3 + 0.00134 \times 4 + 0.00045 \times 5$$

$$= 0.09414\ kg-mole\ H_2O = 0.09414 \times 22.4 = 2.1087\ Nm^3\ H_2O,$$

$$SO_2 = 0.00022\ kg-mole\ SO_2 = 0.00022 \times 22.4 = 0.0049\ Nm^3\ SO_2,$$

$$\text{N}_2 = 0.3684 + 0.00045 = 0.36885\ \text{kg}-\text{mole N}_2 = 0.36885 \times 22.4$$

$$= 8.2622\ Nm^3\ N_2;$$

Total waste gas from combustion of natural gas $= 11.5254 \dfrac{Nm^3}{Nm^3\ NG}.$

$T_{\text{off-gas}} = 1263^0\text{C} = 1536^0\text{K};$

$$\left(\text{H}_{1536^0\text{K}} - \text{H}_{298^0\text{K}}\right)_{\text{CO}_2} = 10.57 \times 1536 + 1.05 \times 10^{-3} \times 1536^2 + 2.06 \times 10^5 \times \frac{1}{1536}$$

$$- 3936 = 14911\ \text{kcal/kg-mol;}$$

$$\left(\text{H}_{1536^0\text{K}} - \text{H}_{298^0\text{K}}\right)_{\text{H}_2\text{O}} = 7.30 \times 1536 + 1.23 \times 10^{-3} \times 1536^2 - 2286$$

$$= 11829\ \text{kcal/kg-mol;}$$

$$\left(\text{H}_{1536^0\text{K}} - \text{H}_{298^0\text{K}}\right)_{\text{SO}_2} = 11.04 \times 1536 + 0.94 \times 10^{-3} \times 1536^2 + 1.84 \times 10^5 \times \frac{1}{1536}$$

$$- 3992 = 15303\ \text{kcal/kg-mol;}$$

$$\left(\text{H}_{1536^0\text{K}} - \text{H}_{298^0\text{K}}\right)_{\text{N}_2} = 6.83 \times 1536 + 0.45 \times 10^{-3} \times 1536^2 + 0.12 \times 10^5 \times \frac{1}{1536}$$

$$- 2117 = 9443\ \text{kcal/kg-mol;}$$

Heat content of Waste Gas $= 14911 \times 0.05132 + 11829 \times 0.09414$

$+ 15303 \times 0.00022 + 9443 \times 0.36885 = 5365\,\text{kcal}.$

Available Heat of Natural Gas = Combustion Heat of NG + Heat content of Combustion Air – Heat content of Waste Gas $= 9604 + 1268 - 5365 = 5507$ kcal/Nm^3 of natural gas.

4.2.4 Effect of leakage air

As in all metallurgical processes leakage of air is also present in flash smelter. Amount of that air actually can be taken as constant from plant and should be considered through the calculations of material and heat balance. For the Eti-Bakır plant that amount was chosen as 300 Nm^3 per t of copper concentrate by comparing SO_2 composition of calculated off-gas without consideration of leakage air and SO_2 composition of industrial off-gas.

Because amount of air leaking leaves the furnace as off-gas, heat loss by that air should be calculated and added to heat balance.

Volume of off-gas produced by leakage air at the output of reaction shaft is equal to the amount of leakage air, 300 Nm^3:

$$O_2 = 300 \times \frac{21}{100} = 63\ Nm^3 / t.conc.;$$

$$N_2 = 300 - 63 = 237\ Nm^3 / t.conc.;$$

$T_{off\text{-}gas}$=1263^{0}C=1536^{0}K;

$$\left(H_{1536^0K} - H_{298^0K}\right)_{O_2} = 7.16 \times 1536 + 0.50 \times 10^{-3} \times 1536^2 + 0.40 \times 10^5 \times \frac{1}{1536}$$
$$- 2313 = 9890.4 \text{ kcal/kg-mol} = 9890.4 / 22.4 = 441.5 \text{ kcal/Nm}^3;$$

$$\left(H_{1536^0K} - H_{298^0K}\right)_{N_2} = 6.83 \times 1536 + 0.45 \times 10^{-3} \times 1536^2 + 0.12 \times 10^5 \times \frac{1}{1536}$$
$$- 2117 = 9443 \text{ kcal/kg-mol} = 9443 / 22.4 = 421.56 \text{ kcal/Nm}^3;$$

Heat content of Off-Gas $= 63 \times 441.5 + 237 \times 421.56 = 127724$ kcal/t.conc.

4.3 Material and heat balances

By collecting all input and output heats in Table 4.2, we can get heat balance of Outokumpu Type Flash Smelting process in order to calculate required amount of fuel.

Table 4.2. Heat balance of Flash Smelting process without consideration of Natural Gas (for 1 ton of conc.)

	Inlet Heat	kcal	kJ
1	Heats evolved in exothermic reactions	563276	2356747
2	Heat of Process Air (preheated air T=400^{0}C)	122214	511343
3	Heat of Lignite	72367	302783
	Total:	**757857**	**3170874**
	Outlet Heat	kcal	kJ
1	Heat of matte (T=1162^{0}C)	75422	315566
2	Heat of furnace slag (T=1190^{0}C)	105012	439370
3	Heat of off-gas + leakage off-gas (T=1263^{0}C)	582529	2437301
4	Heat of dust (T=1263^{0}C)	19616	82073
5	Heat loss of Reaction Shaft	174566	730384
	Total:	**957145**	**4004695**

Amount of heat which should input in furnace as a fuel:

Total Outlet Heat – Total Inlet Heat = 957145 – 757857 = 199288 kcal;

For 1 ton of Cu concentrate charge, we need natural gas as fuel as indicated below:

$$\frac{199288}{5507} \approx 36.2\,\mathrm{Nm}^3 \text{ of natural gas for 1 ton of copper concentrate.}$$

Table 4.3 shows heat balance of Flash Smelting process with consideration of natural gas as fuel.

Air needed to burn Natural gas $=10.4461\times36.2=378.15$ Nm^3.

Off-gas from combustion of Natural gas $11.5254\times36.2=417.22$ Nm^3

Material balance of Flash Smelting process is shown in Table 4.4.

Table 4.3. Heat balance of Flash Smelting process with consideration of Natural Gas (for 1 ton of conc.)

	Inlet Heat	kcal	kJ
1	Heats evolved in exothermic reactions	563276	2356747
2	Heat of Process Air (preheated air T=400^{0}C)	122214	511343
3	Heat of Lignite	72367	302783
4	Heat of Natural Gas	199288	833821
	Total:	**957145**	**4004694**
	Outlet Heat	kcal	kJ
1	Heat of matte (T=1162^{0}C)	75422	315566
2	Heat of furnace slag (T=1190^{0}C)	105012	439370
3	Heat of off-gases (T=1263^{0}C)	582529	2437301
4	Heat of dust (T=1263^{0}C)	19616	82073
5	Heat loss of Reaction Shaft	174566	730384
	Total:	**957145**	**4004694**

Table 4.4. Material balance of Flash Smelting process

Materials	**Kg**	**Nm^3**
Inlet		
Copper concentrate	1000	
Flux	112.47	
Lignite	28.52	
Dust	72.83	
Natural Gas		36.2
Air: for process for lignite for natural gas		 1012 151.38 378.15
Total:	1213.82	1541.53

Table 4.4. (continued)

Outlet		
Matte	423	
Furnace slag	510.73	
Output Dust	83.75	
Gas: from process from lignite combustion from natural gas combustion from leakage air		 976.15 164.03 417.22 300
Total	1017.48	1857.4

CHAPTER 5

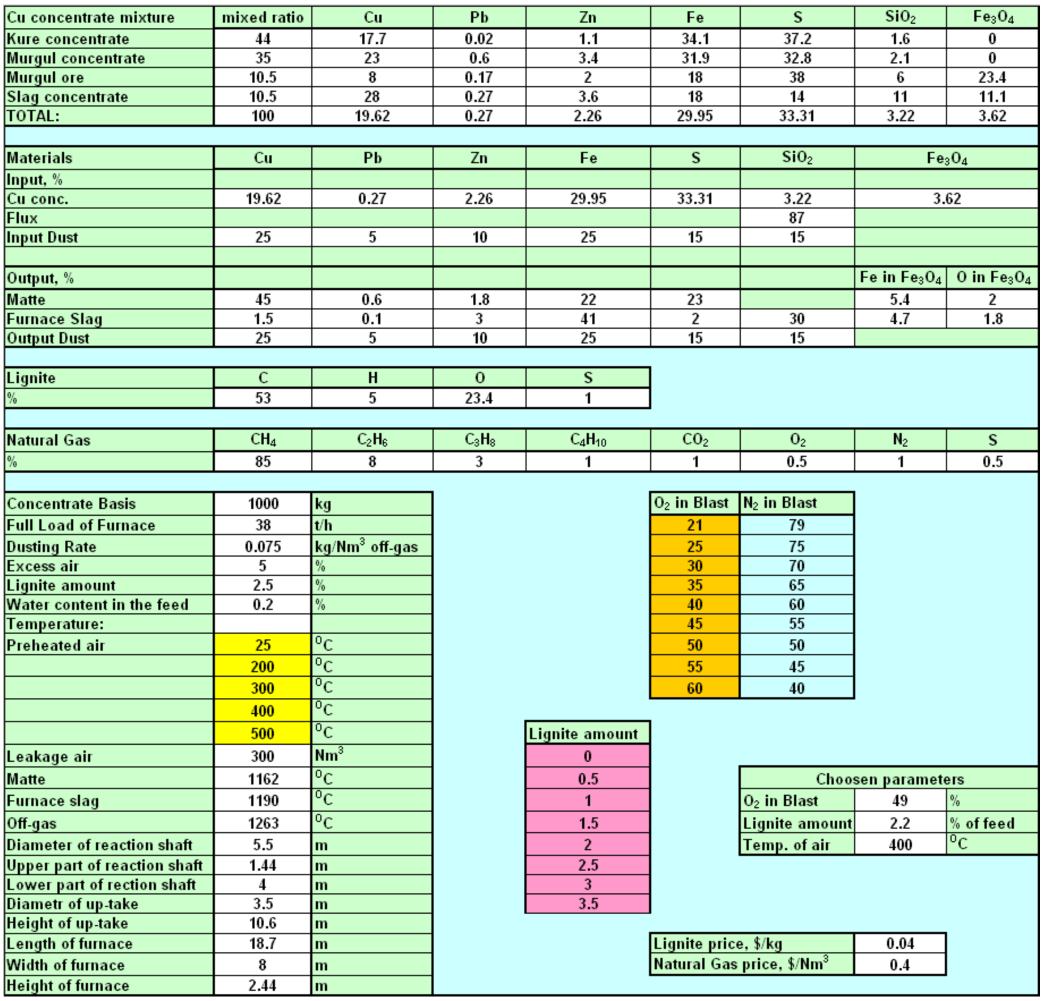
RESULTS AND DISCUSSION

Pyrometallurgical processes operate at high temperatures where reactions usually reach their equilibrium state within normal retention time of the process. Therefore, thermochemical calculations offer a useful possibility of estimating the effect of operation parameters on the performance characteristic of the process.

Thermochemical calculations do not reveal the whole truth about chemical processes; however, quite often they give a good estimate of what may happen if some process parameters are changed. Traditionally, thermochemical calculations have been hard to carry out manually; computer program makes them much easier.

In present work, computer program in Excel with the application of Visual Basic was written for proceeding calculations of material and heat balances to do optimization of flash smelting process of Eti-Bakır plant. In the calculations, all assumptions and modifications of program are the same as indicated in Chapter 4. Program consists of some sheets first of which is the Input sheet (Figure 5.1). By changing input data on this sheet, mass and heat balances of flash furnace at different preheating temperatures (yellow cells), compositions of oxygen enrichment of blast (orange cells) and lignite rates (red cells) can be obtained.

Through the discussion of this chapter parameters and curves will be represented with considering basis as 1000 kg of copper concentrate. Also, calculations of written program will be compared with the average material balance of smelting process of Eti-Bakır plant for the last 6 months.



Cu concentrate mixture	mixed ratio	Cu	Pb	Zn	Fe	S	SiO_2	Fe_3O_4
Kure concentrate	44	17.7	0.02	1.1	34.1	37.2	1.6	0
Murgul concentrate	35	23	0.6	3.4	31.9	32.8	2.1	0
Murgul ore	10.5	8	0.17	2	18	38	6	23.4
Slag concentrate	10.5	28	0.27	3.6	18	14	11	11.1
TOTAL:	100	19.62	0.27	2.26	29.95	33.31	3.22	3.62

Materials	Cu	Pb	Zn	Fe	S	SiO_2	Fe_3O_4	
Input, %								
Cu conc.	19.62	0.27	2.26	29.95	33.31	3.22	3.62	
Flux						87		
Input Dust	25	5	10	25	15	15		
Output, %							Fe in Fe_3O_4	O in Fe_3O_4
Matte	45	0.6	1.8	22	23		5.4	2
Furnace Slag	1.5	0.1	3	41	2	30	4.7	1.8
Output Dust	25	5	10	25	15	15		

Lignite	C	H	O	S
%	53	5	23.4	1

Natural Gas	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CO_2	O_2	N_2	S
%	85	8	3	1	1	0.5	1	0.5

Concentrate Basis	1000	kg
Full Load of Furnace	38	t/h
Dusting Rate	0.075	kg/Nm^3 off-gas
Excess air	5	%
Lignite amount	2.5	%
Water content in the feed	0.2	%
Temperature:		
Preheated air	25	^0C
	200	^0C
	300	^0C
	400	^0C
	500	^0C
Leakage air	300	Nm^3
Matte	1162	^0C
Furnace slag	1190	^0C
Off-gas	1263	^0C
Diameter of reaction shaft	5.5	m
Upper part of reaction shaft	1.44	m
Lower part of rection shaft	4	m
Diametr of up-take	3.5	m
Height of up-take	10.6	m
Length of furnace	18.7	m
Width of furnace	8	m
Height of furnace	2.44	m

O_2 in Blast	N_2 in Blast
21	79
25	75
30	70
35	65
40	60
45	55
50	50
55	45
60	40

Lignite amount
0
0.5
1
1.5
2
2.5
3
3.5

Choosen parameters		
O_2 in Blast	49	%
Lignite amount	2.2	% of feed
Temp. of air	400	^0C

Lignite price, $/kg	0.04
Natural Gas price, $/Nm^3	0.4

Figure 5.1. Input sheet of the computer program

5.1 Optimization of parameters

Operating parameters which are examined in this chapter with respect to economic justification include temperature of preheated air blast, oxygen enrichment of blast and lignite rate.

Parameters that describe present conditions of Eti-Bakır plant and through which the optimization of process can be done are as follows:
Preheated Air Temperature - 400^0C;
Air composition – 21%O_2, 79%N_2;
Lignite rate – 2.5 % of feed;
Matte grade - 45%Cu.

In order to do optimization of smelting process some parameters should be chosen as constants whereas other ones as variables. Listed parameters should be chosen as variables one by one and checked as they are really the optimum for the process. However, converter matte grade is not chosen as a variable in this work. Therefore, temperature of preheated air, oxygen enrichment of blast and lignite rate are chosen as variables.

A portion of the heat entering the furnace can be as preheated air, or preheated oxygen enriched air. The upper limit of preheating is determined by the equipment available and to some extent the ductwork which conveys the air from the preheater to the furnace. Most Outokumpu flash furnaces use preheated blast. The blast is preheated typically from 100 to 500^0C using hydrocarbon-fired or off-gas heated shell-and-heat tube exchangers. Hot blast ensures rapid Cu-Fe-S concentrate ignition in the flash furnace. It also provides energy for smelting. Modern highly oxygen enriched flash furnace occasionally use ambient (25^0C) blast. Concentrate ignition is rapid with this blast at all temperatures (Davenport et al., 2002).

In this work preheated air or air blast temperature is varied in the range of 25 to 500^0C. Material and heat balances at the mentioned temperature range are calculated by the program and relationship between consumption of natural gas and temperature range are determined.

In order to find out the optimum mode for the smelting process the oxygen enrichment of blast is chosen between 21 to 60%. Oxygen enrichment results in factors that affect operating costs of smelting which will be discussed later.

Range of lignite rate varies from 0 to 3.5% of feed through the optimization. When the optimization of exact value of lignite rate will take place factors that depend on that amount will be considered.

All parameters that are optimized in present work are changed and modified with respect to external energy source, i.e. consumption of natural gas. Because it is the main source to which expenses of plant is dependent, so consumption of natural gas will be minimized.

5.1.1 Temperature of preheated air as a variable

In this case temperature of preheated air is taken as variable whereas lignite rate is taken as a constant at 2.5% of feed and oxygen of air blast is taken as 21% (no oxygen enrichment). Main purpose of doing that is to observe conditions of smelting process at different temperatures of preheated air and to construct a curve which represents relations between needed natural gas volume and temperature of preheated air blast. Curve given in Figure 5.2 describes the effect of different temperatures of preheated air blast on needed natural gas volume.

As can be seen from Figure 5.2 using ambient temperature (25^0C) air blast for smelting process about 81 Nm^3/t.conc. of natural gas is needed which is really a high value. At the present condition of plant, which means air preheated to 400^0C, the needed amount of natural gas is 36.2 Nm^3/t.conc. which is a good value for the plant that uses normal air as a blast. Also temperature of preheated air can be increased to a level higher than 400^0C, but for that purpose additional energy for heating air blast will be needed, because as mentioned above to heat air blast to 400^0C at Eti-Bakır plant off-gas heat recovery system is used and it cannot be modified. As a result, preheating temperature of air blast should be kept the same, without any change, i.e. 400^0C.

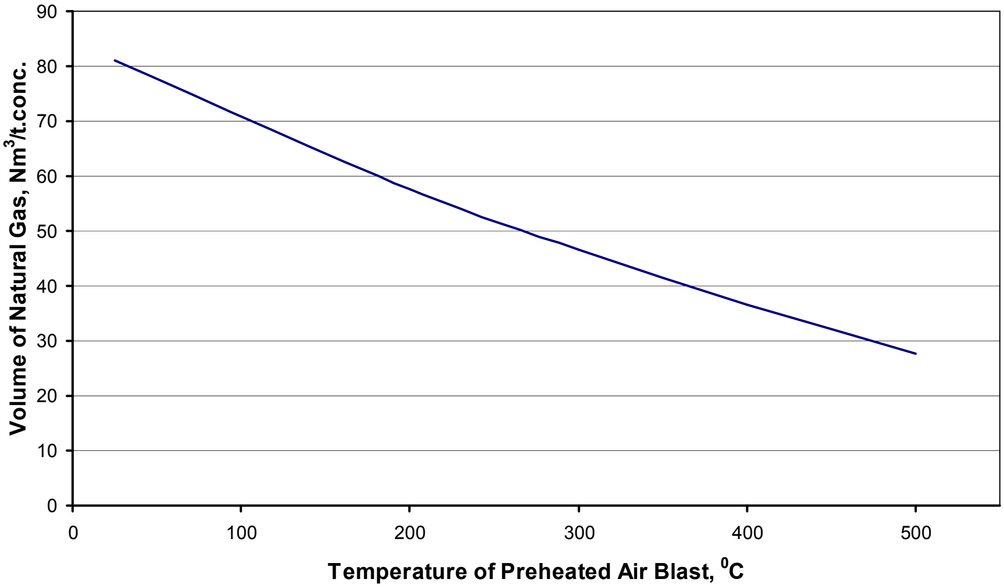


Figure 5.2. Relation between needed natural gas volume and temperature of preheated air blast at constant lignite rate and no oxygen enrichment of blast

5.1.2 Lignite rate and oxygen enrichment of air blast as variables

In this case lignite rate and oxygen enrichment of blast are taken as variables whereas temperature of preheated air blast is kept at a constant level which is 400^0C. Optimization of lignite rate and oxygen enrichment of blast should be done carefully and with consideration of matte grade, magnetite formation and other parameters which are also dependent on lignite rate and oxygen enrichment of blast.

By using the written program and giving to it different ranges of lignite rate and oxygen enrichment of blast at constant temperature of preheated air blast, curves which represent conditions of smelting process as well as relations between oxygen enrichment of blast and needed volume of natural gas are constructed and given in Figure 5.3.

In Figure 5.3 for eight different lignite rates relations are given and red point indicates conditions at which Eti-Bakır plant is working now. It is about 2.5% of charge feed rate with normal air as air blast and temperature of preheated air as 400^0C. By examining given curves with respect to matte grade and magnetite formation the optimum mode, even nearly autogenous mode, of flash smelter which is necessary in Eti-Bakır plant can be defined.

5.1.2.1 Matte grade control

Basic Outokumpu flash furnace strategy is to charge dried concentrate to the furnace at a prescribed rate and to base all other controls on this area. Having chosen concentrate feed rate, the flash furnace operator must next select the grade of his product which is matte, i.e. the extent of Fe and S oxidation.

Physically, matte grade is set by adjusting the:

$$\frac{\textit{oxygen in blast input rate}}{\textit{concentrate feed rate}}$$

ratio until the target matte composition is obtained. A large ratio gives extensive Fe and S oxidation and high-grade matte. A small ratio gives the opposite. Physically, the ratio is controlled by adjusting the rates at which air and oxygen enter the furnace at a constant concentrate feed rate (Davenport et al., 2002).

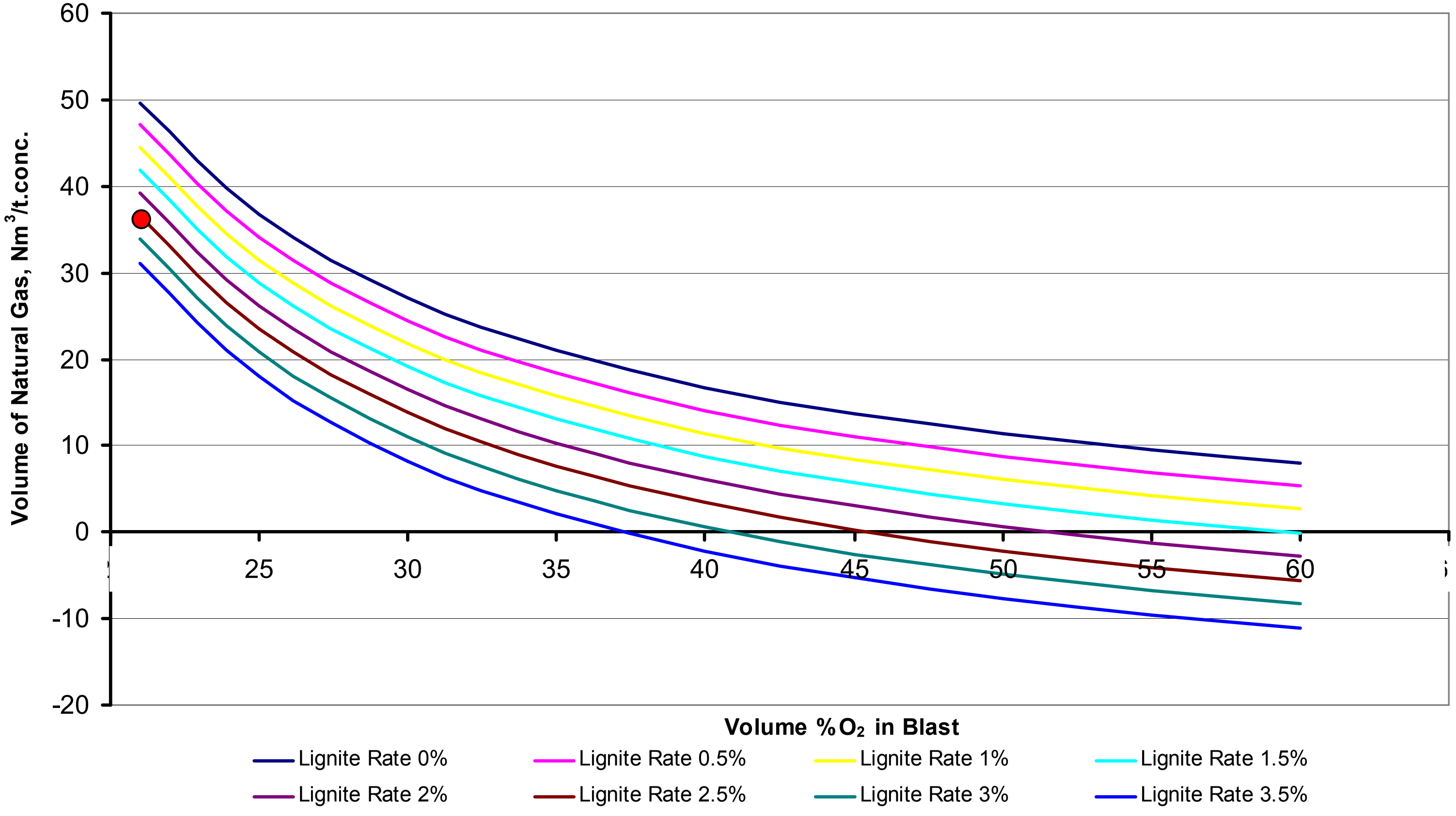


Figure 5.3. Relations between oxygen enrichment of blast and needed natural gas volume at constant temperature of preheated air blast 400^0C

In order to keep matte grade as a constant, according to ratio that is given above, with increasing oxygen enrichment of blast input, rate of blast should be decreased according to the relation that is indicated in Figure 5.4.

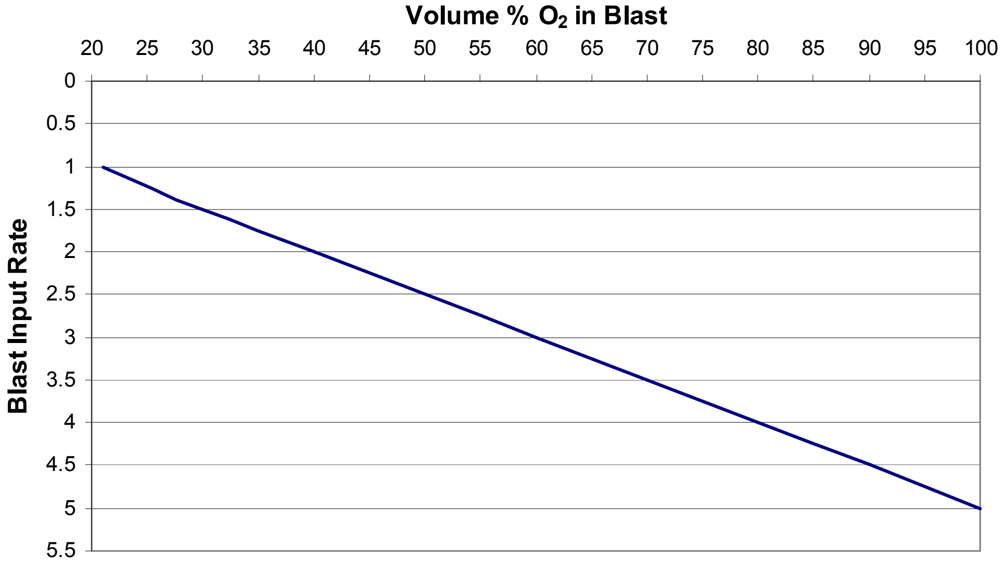


Figure 5.4. Relation between oxygen enrichment of blast and blast input rate

5.1.2.2 Magnetite formation criteria

Long flash furnace campaign lives require that magnetite-rich slag be deposited in a controlled manner on the furnace's walls and hearth. Magnetite slag deposition is encouraged by:

- highly oxidizing conditions in the furnace;
- low operating temperature;
- low SiO_2 concentration in slag.

It is discouraged by reversing these conditions and by adding coke, coal or lignite to the furnace (Davenport et al., 2002).

The formation of magnetite during copper smelting (Yazawa, 1974; Yazawa, 1979; Rosenqvist; Makipirtti, 1973; Yazawa and Eguchi, 1976) poses one of the most serious problems in copper smelting. A number of thermodynamic explanations regarding the behavior of magnetite are based on the following reaction (Yazawa, 1979):

$$FeS + 3Fe_3O_4 = 10FeO + SO_2 . \qquad (5.1)$$

While this reaction may occur in the lower region of the reaction shaft, magnetite formation in the upper region of the reaction shaft results from the following reaction:

$$6FeS + 10O_2 = 2Fe_3O_4 + 6SO_2 . \qquad (5.2)$$

Also the minimum matte grade of 45% which is kept in present work ensures a sufficiently high slag/matte ratio so that the suspension of furnace products, when impinged onto furnace walls, creates protective Fe_3O_4 layer on furnace refractory. This protective layer prevents excessive refractory wear and decreases furnace heat losses somewhat.

As mentioned above two contradictory criteria give us information that lignite should be present in smelting process to prevent formation of magnetite, and on the other hand, small amount of magnetite is needed for the smelting process to create protective layer for the refractory wear. As a result, lignite amount can be decreased from 2.5% of feed, but not much, because lignite is used in smelting process not only for preventing formation of magnetite but as a source of energy as well.

5.1.2.3 Effects of oxygen enrichment of blast

As already mentioned above, Eti-Bakır plant is using normal air as a blast, but it is important to go over the effects of oxygen enrichment of blast and make a decision whether it is really economically efficient to use oxygen enrichment of blast or not.

Oxygen enrichment will have many advantages for the plant. First of all, by oxygen enrichment volume of off-gas which is leaving the furnace will be decreased. In Figure 5.5 the relation between oxygen enrichment and off-gas volume defined by using the computer program with temperature of preheated air at 400^0C and lignite rate at 2.5% of feed is indicated.

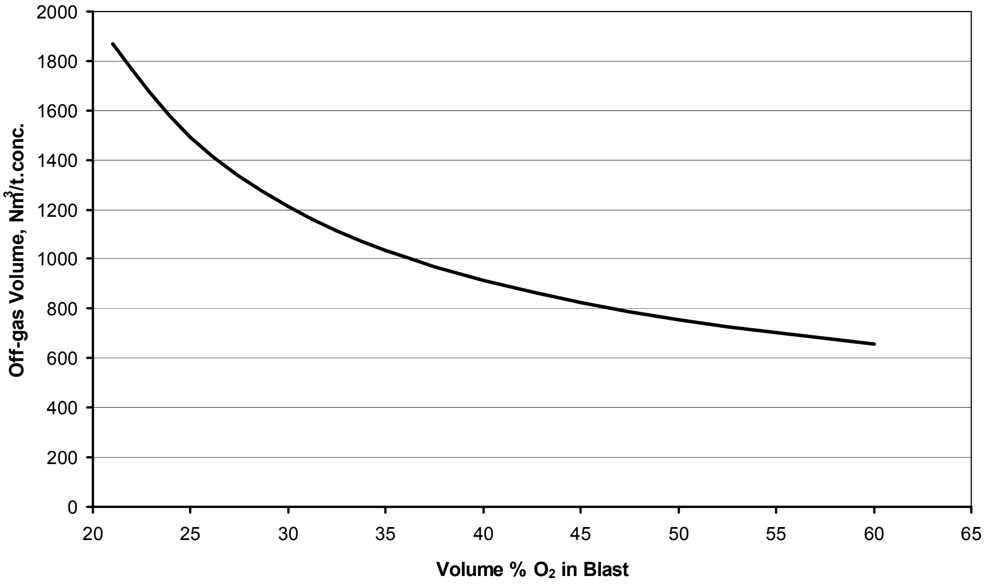


Figure 5.5. Volume of off-gas as a function of oxygen enrichment

As the off-gas volume decreased, the dust generation is also decreased. Effect of oxygen enrichment on dust generation is indicated on Figure 5.6.

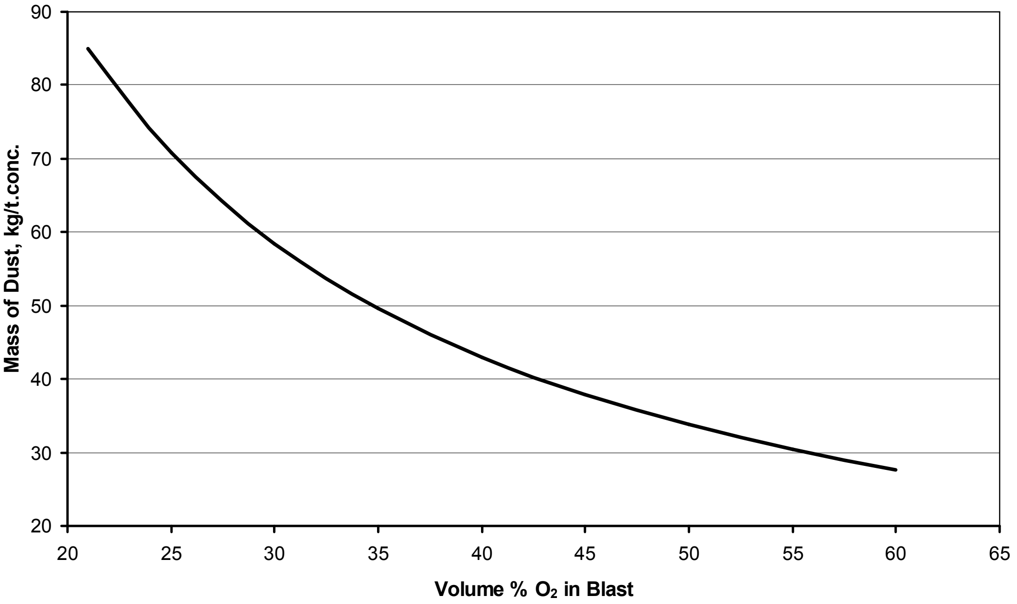


Figure 5.6. Effect of oxygen enrichment on dust generation

Also, because of the decreasing off-gas volume, oxygen enrichment results in decreasing recoverable heat in off-gases, which improves heat balance of the flash furnace. This relation is plotted in Figure 5.7.

One more economical advantage of oxygen enrichment of air blast is the possibility of constructing a smaller furnace with smaller heat losses. All of these factors affect operating cost and have been accounted for in the model. In addition, these factors have an impact on capital cost: Fans, dust conveying equipment, and structural steel are all reduced in size.

However, the flash furnace which is operating in Eti-Bakır plant has been already built and investments in it have been already done in early 1968, and it was built for normal air without oxygen enrichment. It means that up-take of furnace and all other design parameters are calculated for large amount of off-gas. So, by using oxygen enriched air blast, flash furnace has the potential to process more amount of feed, in other words, to produce more amount of matte and increase production of blister copper.

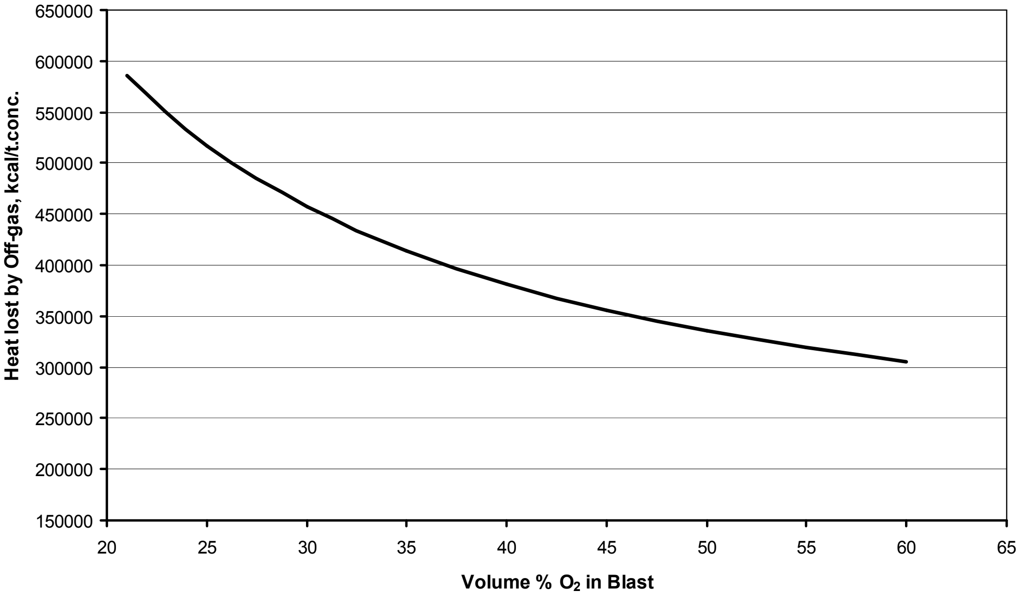


Figure 5.7. Effect of oxygen enrichment on heat content of off-gases

Metallurgical reason of using oxygen enriched air blast is to change flash smelting flame temperature. With increasing oxygen content of air blast, flash smelting flame temperature is also increased. This decreases magnetite formation and consumption of lignite which is also added for that purpose.

5.2 Checking for reliability of the computer program

Checking for reliability and property checking of the written computer program are important in present work, because main goal of the thesis is to optimize parameters of plant with the help of computer program. To get the exact optimum condition and to be sure that the chosen optimum condition is reliable, results that are obtained by computer program should be compared with the average industrial data of examined plant. As an average industrial data material balances for the last 6 months of Eti-Bakır plant are taken. Material balances by months from December 2007 to May 2008 with the comparison of calculated balances by computer program are given in APPENDIX A and average of that data are indicated in Table 5.1.

Table 5.1. Average material balance for one month of smelting process (industrial data)

	AVERAGE				
Materials	t	Cu, %	Fe, %	S, %	SiO_2, %
Input					
Kure Conc.	9614.45	17.82	34.88	37.35	1.49
Murgul Conc.	7719.21	22.59	31.54	31.58	1.93
Murgul Ore	1811.78	8.08	35.00	38.00	6.00
Slag Conc.	1514.16	23.58	22.40	12.07	10.33
Flux	3306.07				
Dust	1554.33	22.00			
Lignite	600.64				
Natural Gas, Nm^3	841910.50				
Process Air, Nm^3	25431622.67				
Output					
Matte	8868.88	43.51	25.74	19.75	
Furnace Slag	12127.69	1.35	39.70	1.51	32.04
Dust	1752.67	22.00			
Off-gas	41233333.33				

By entering to computer program the input amount of Küre concentrate, Murgul concentrate, Murgul ore and Slag concentrate and taking as basis elemental compositions indicated in Table 5.1, material and heat balances of the plant are calculated by the written computer program and given in Tables 5.2 and 5.3.

Table 5.2. Material balance of smelting process calculated by computer program

Tempereture of Preheated Air	400	^{0}C
Lignite Rate	2.5	% of feed
Materials	t	Nm^3
Input		
Copper concentrate	20659.60	
Silica Flux	3145.07	
Dust	1524.51	
Lignite	610.38	
Natural Gas		796152.65
Air Blast		32691272.59
for process		21135944.05
for lignite combustion		3233637.74
for natural gas combustion		8321690.80
TOTAL:	25939.56	33487425.24
Output		
Matte	8829.42	
Furnace Slag	11335.37	
Dust	1753.19	
Gas		39210750.39
from process		20326812.01
from lignite combustion		3504522.72
from natural gas combustion		9181535.66
TOTAL:	21917.97	39210750.39

Comparison of material balance of industrial data and calculated data by computer program are shown in Table 5.4. Also, for comparison calculated heat balance by computer program and heat balance of Outokumpu flash smelter given in Table 2.4 are shown in Table 5.5.

As can be seen from Table 5.4 percentage differences between data calculated by computer program and actual plant data are acceptable and written program can be used for optimization of parameters of smelting process.

Table 5.3. Heat balance of smelting process calculated by computer program (for 1 ton of conc.)

Heat	^{0}C	kcal	kJ
Input			
Exotermic Reactions		552859	2313162
Process Air	400	124238	519811
Lignite		74892	313347
Natural Gas		212348	888465
TOTAL:		964337	4034786
Output			
Matte	1162	76571	320373
Furnace Slag	1190	107511	449826
Off-gas	1263	585547	2449927
Dust	1263	20142	84276
Heat Loss		174566	730384
TOTAL:		964337	4034786

Table 5.4. Comparison of industrial data and computer data of material balance

	Industrial Data	Computer Data	Difference
Materials	t	t	%
Input			
Copper concentrate	20659.60	20659.60	0
Silica Flux	3306.07	3145.07	4.87
Dust	1554.33	1524.51	1.92
Lignite	600.64	610.38	1.6
Natural Gas (Nm^3)	841910.50	796152.65	5.43
Process Air (Nm^3)	25431622.67	24369581.79	4.18
Output			
Matte	8868.88	8829.42	0.44
Furnace Slag	12127.69	11335.37	6.53
Dust	1752.67	1753.19	0.03
Off-gas (Nm^3)	41233333.33	39210750.39	4.9

5.3 Choosing an optimal condition for smelting process

According to all mentioned criteria of formation of magnetite, matte grade control and oxygen enrichment the optimum mode of flash smelter ought to be possible to determine by Figure 5.3. In other words, the exact amount of lignite rate and oxygen enrichment of blast can be optimized now with respect to all information given above about formation of magnetite, matte grade control and oxygen enrichment.

Optimization of smelting process should be economically efficient and because of that nearly autogenous process have to be chosen as an optimum. It means that natural gas consumption should be nearly zero and from Figure 5.3 only region of x-axis should be examined for choosing the optimum amount of lignite rate and oxygen enrichment.

Table 5.5. Heat balance of Outokumpu flash furnace calculated by computer program and given in Table 2.4

Item	by computer program (air at 400^0C)	From Table 2.4 (air at 550^0C)
Input heat	10^5 kcal	10^5 kcal
Exotermic Reactions	5.6	5.3
Process Air	1.2	1.0
Lignite	0.7	-
Natural Gas	2.1	1.8
TOTAL:	9.6	8.1
	10^5 kcal	10^5 kcal
Output heat		
Matte	0.8 (45% Cu)	1.5 (50% Cu)
Furnace Slag	1.0	1.3
Off-gas	5.9	3.2
Dust	0.2	-
Heat Loss	1.7	2.1
TOTAL:	9.6	8.1

Matte grade is kept as constant by changing blast input rate when oxygen enrichment of blast is different. As indicated in Figure 5.4, increasing of oxygen enrichment of blast results in decreasing of blast input rate; because of that, too much increasing of oxygen in blast is not preferable. However, effects of oxygen enrichment, as indicated above, show that it is economically efficient for the plant. One more factor which should be considered through the optimization is that in practice many Outokumpu flash smelters are working with the range of oxygen enrichment of blast between 40 to 50%. Also, under the price and operating conditions minimum flash furnace energy cost should occur when flash furnace is producing required matte grade, in our case 45% Cu. This might not be always the case. Optimum conditions should always be re-determined whenever prices and operating constrains change.

In present work by calculating material and heat balances of smelting process of Eti-Bakır plant through the written program and by defining relations between needed volume of natural gas, for balancing heat values of furnace, and oxygen enrichment of blast with respect to lignite rates, according to Figure 5.3 optimum condition of smelting process is defined and indicated as a green point on Figure 5.8.

Green point describes the mode which is chosen as an optimum for the smelting process of Eti-Bakır plant and in numerical value can be stated as follows:
Temperature of preheated air – 400^0C;
Oxygen enrichment of blast – 49%
Lignite rate – 2.2% of feed;
Matte grade – 45% of Cu;
Process needs no natural gas (nearly autogenous).

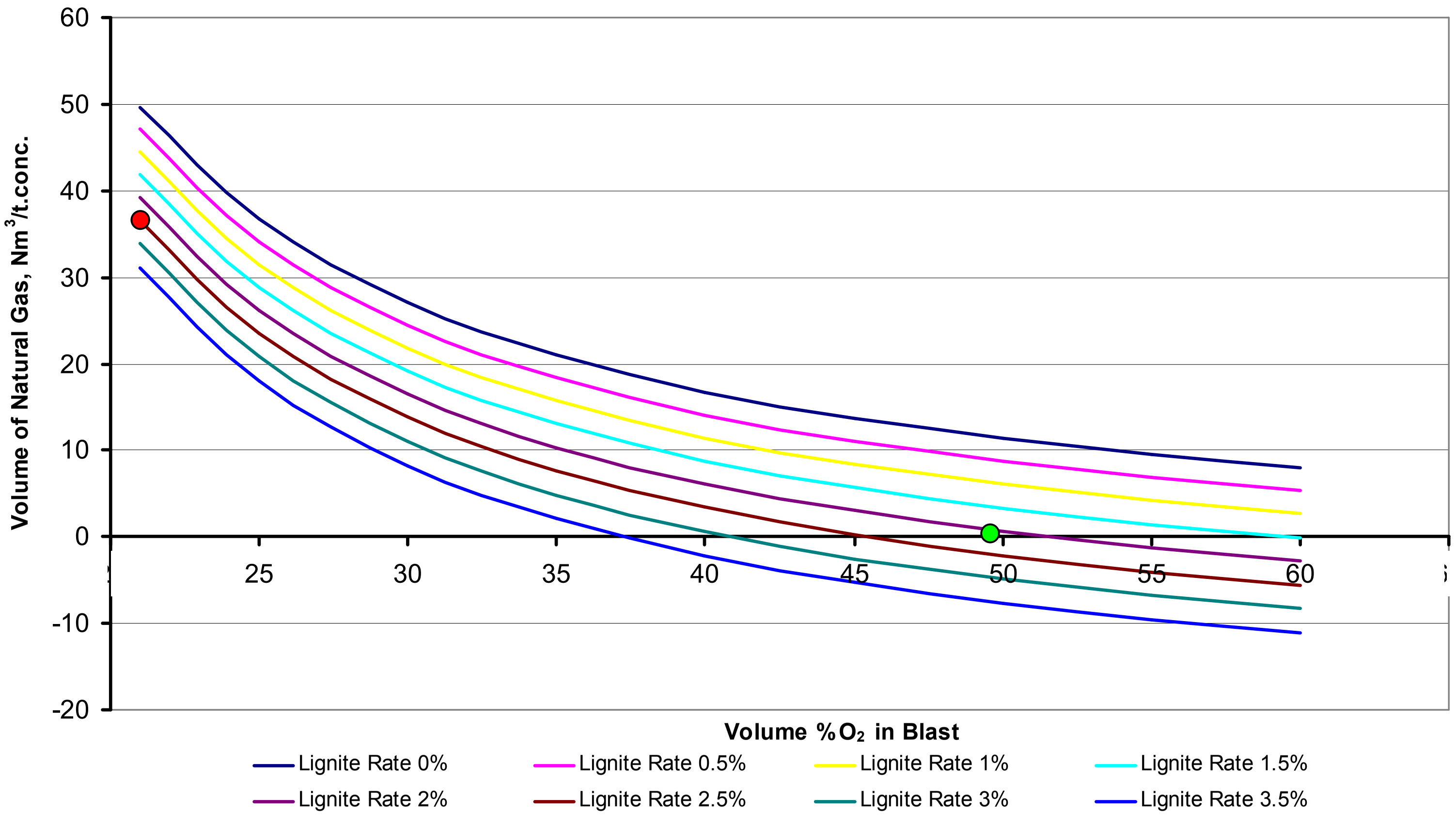


Figure 5.8. Relations between oxygen enrichment of blast and needed natural gas volume at constant temperature of preheated air blast 400^{0}C (with optimum natural gas shown)

5.4 Advantages of chosen condition of flash furnace

First of all, by increasing oxygen enrichment of blast to 49%; volume of off-gas (Figure 5.5), generation of dust (Figure 5.6) and heat loss by off-gas (Figure 5.7) will be decreased largely as shown in Table 5.6. Decreasing of volume of off-gas means that composition of SO_2 in it is increased, because nitrogen amount is decreased by oxygen enrichment, as a result, off-gas is sent to acid plant with higher amount of SO_2 in it.

Table 5.6. Comparison of optimum nearly autogenous smelting with optimum fuel-fired smelting

Parameters	Nearly autogenous smelting	Fuel-fired smelting
Volume of off-gas (Nm^3/t.conc.)	750	1900
Dust generation (kg/t.conc.)	35	85
Heat loss by off-gas (kcal/t.conc.)	340000	590000
Lignite amount (% of feed)	2.2	2.5
Natural gas (Nm^3/t.conc.)	0	36.2

Consumption of natural gas decreases to zero and for smelting only low amount of lignite is used as an external energy source, because of that new optimized process is called nearly autogenous instead of autogenous process. One other important advantage is that expenses for the fuel will be minimized and plant will not be dependent on natural gas (and so oil) prices in the world.

5.5 Needed financial expenses for required optimum condition

To obtain all the advantages that were mentioned above, in order to get oxygen enriched blast with composition of oxygen equal to 49%, oxygen plant in Eti-Bakır plant should be constructed. At a temperature of preheated air blast equal to

400^0C with 49% oxygen in it and lignite rate equal to 2.2% of feed to get a heat balance of flash smelting process, 19000 Nm^3/hr air blast is needed as calculated by program.

As an oxygen plant, membrane, adsorption or cryogenic system can be chosen. Each system has some advantages but cryogenic system is a new technology and appropriate for the needed capacity.

Cryogenic oxygen plants are designed for the production of 45-99.9 vol.% gaseous and liquid oxygen from atmospheric air (Figure 5.9). Gaseous mixture output is about 25-30000 Nm^3/hr and ambient temperature during operation is +5 to $+40^0C$, during storage is -20 to $+50^0C$. Plant useful life is about 150-200 thousand hours. Approximate capital cost of this plant with montage is about 15 million US Dollars.

Figure 5.9. Cryogenic oxygen plant (www.grasus.com)

5.6 Calculation of payback period of oxygen plant

In order to calculate payback period of suggested oxygen plant instead of using natural gas and substantial amount of lignite, the actual prices of natural gas and lignite are chosen as 0.4 $\$/\mathrm{Nm}^3$ for natural gas and 40 \$/ton for lignite. Annual extra expenses for natural gas and lignite at mode when furnace is working without oxygen enrichment of blast with consideration that plant is working 300 days in a year are as follows:

For natural gas:

$36.2\ \mathrm{Nm}^3/\mathrm{t.conc.} * 30.4\ \mathrm{t.conc./hr.} * 24\ \mathrm{hr.} * 300\ \mathrm{days} * 0.4\$/\mathrm{Nm}^3 = 3169382\ \$/\mathrm{year}$;

For lignite:

$(2.5\%-2.2\%)/100\% * 38\ \mathrm{t.feed/hr} * 24\ \mathrm{hr.} * 300\ \mathrm{days} * 40\ \$/\mathrm{ton} = 32832\ \$/\mathrm{year}$;

Total extra expenses:

$3169382\ \$/\mathrm{year} + 32832\ \$/\mathrm{year} = 3202214\ \$/\mathrm{year} \approx 3.2$ million US Dollars/year.

Payback period of cryogenic oxygen plant:

$$\frac{\text{Cost of oxygen plant}}{\text{Total extra expenses per year}} = \frac{15\ \text{million }\$}{3.2\ \text{million }\$} = 4.7\ \text{years}.$$

Therefore, payback period of oxygen plant with mentioned capacity is about 4.7 years. And also, if converters are changed to operate with oxygen enriched air and additional investments for the plant are done, the payback period will be shorter. This calculation excludes other changes that have to be made to the flash furnace and increasing of capacity.

5.7 Limitation of written computer program

Computer program was written for Eti-Bakır smelting plant for the production of low matte grade of 45% Cu. Most of the assumptions through the writing of a program, which were mentioned in Chapter 4, were taken from actual industrial smelting process of Eti-Bakır plant and should be changed in program algorithm for different plants.

5.8 Recommendation

According to the optimization of flash smelter done for Eti-Bakır plant by computer program, actions listed below should be taken:

1. Oxygen plant which will produce oxygen enriched blast of 49% oxygen with capacity 19000 Nm^3/hr should be constructed;
2. Produced oxygen enriched blast should be preheated to 400^{0}C and used in concentrate burner;
3. To keep matte grade as a constant blast input velocity should be decreased by 2.5 times (Figure 5.4);
4. Lignite rate should be decreased from 2.5% to 2.2% of feed.

CHAPTER 6

CONCLUSION

In this thesis work all industrial data of Eti-Bakır plant with Outokumpu type flash smelter were studied and by using that data computer program was written. By using written program mass and heat balances were done at different lignite rates and different compositions of oxygen in air blast. The relation between natural gas consumption, lignite rate and oxygen enrichment was studied.

To be sure that the chosen optimum condition is reliable, results that were obtained by computer program were compared with the average industrial data of examined plant. Errors of calculations of computer program were determined as acceptable and written program was used for the optimization of parameters of smelting process. In order to eliminate usage of natural gas as a fuel, the optimum condition for the smelting process of Eti-Bakır plant was found and recommended as:

- oxygen enriched air preheated to 400^0C;
- oxygen enrichment 49% ;
- lignite rate 2.2% of feed.

Payback period of cryogenic oxygen plant, when oxygen enriched air was used, was calculated as 4.7 years.

Written program can be used through the industrial calculations of material and heat balances of any plant which is using Outokumpu type flash smelter and producing low grade matte. Also, by recalculating material and heat balances of flash smelter by computer program, not only the optimized mode recommended above but also any required condition for the smelting unit can be obtained and characterized.

REFERENCES

Anderson B., Karlsson P., Hanniala P. (1980), “A Practical Design Paper on Outokumpu Flash Smelting Technology ”, Outokumpu Oy, Finland.

Anon. (1964), “Outokumpu Process for the Production of Elemental Sulfur from Pyrites”, Sulfur, No: 50, pp. 33-38.

Background report (1992), Primary Copper Smelting, U.S. Environmental Protection Agency.

Biswas A.K., Davenport W.G. (1980), Extractive Metallugy of Copper, Second Edition, Pergamon Press.

Bryk P., Ryselin J., Honkasalo J., Malstrom R. (1958), “Flash Smelting Copper Concentrates”, Journal of Metals, v. 10, pp. 395-400.

Bystrov, V.P. (2003), Vanyukov’s Process – Continuous, Cheap, Ecologically Safe. Moscow State Institute of Steel and Alloys, February.

Conde C.C., Taylor B., Sarma S. (1999), “Philippines Associated Smelting Electrostatic Precipitator Upgrade”, in Copper 99 – Cobre 99, Proceedings of the Fourth International Conference, v. V, Smelting Operations and Advances, edited by George D.B., Chen W.J., Mackey P.J., Weddick A.J., TMS, Warrendale, PA, pp. 685-693.

Copper Development Association, www.copper.org, last accessed date: 7 May 2008.

Davenport W.G., Jones D.M., King M.J., Partelpoeg E.H., (2001), Flash smelting: Analysis, Control and Optimization, TMS, Warrendale, PA, www.tms.org.

Davenport W.G., King M.J., Schlesinger M.E., Biswas A.K., (2002), Extractive Metallugy of Copper, Fourth Edition, Pergamon Press.

Davenport W.G., Partelpoeg E.H. (1987), Flash Smelting: Analysis, Control and Optimization, Pergamon Press.

Demetrio S., Santander N., Solar M. (1999), “The Copper Smelters of the 2010—a Vision of the Future”, in Copper 99 – Cobre 99, Proceedings of the Fourth

International Conference, v. V, Smelting Operations and Advances, edited by George D.B., Chen W.J., Mackey P.J., Weddick A.J. October 10–13, Phoenix, AZ, USA, pp. 295–303.

Elliot B.J., Robinson K., Stewart B.V. (1983), “Developments in Flash Smelting at BCL Limited” in Advances in Sulfide Smelting, v. 2, edited by Sohn H.Y., George D.B., Zunkel A.D., The Metallurgical Society of AIME, New York, pp. 875-898.

Fugii O., Shima N. (1971), “Reaction Shaft of Ashio Smelter’s Flash Furnace Utilizing High Oxygen Enriched Air”, in Extractive Metallurgy of Copper, v.1, edited by Yannopoulos J.C. and Agarwal S.C., The Metallurgical Society of AIME, New York, pp. 165-171.

Gößling S. (2001), “Entropy Balance of Industrial Copper Production: A Measure for Resource Use”, Thesis, Universität Hamburg, Institut für Experimentalphysik, January.

Goonan T.G., (2004), Flows of Selected Materials Associated with World Copper Smelting, U.S. Geological Survey Open-File Report 2004-1395.

Harkki S., Aaltonen O.A., Tuominen T. (1976), “High Grade Matte Production with Oxygen Enrichment by the Outokumpu Flash Smelting Method”, in Extractive Metallurgy of Copper, v.1, edited by Yannopoulos J.C. and Agarwal S.C., The Metallurgical Society of AIME, New York, pp. 488-507.

International Copper Study Group, www.icsg.org, last accessed date: 29 May 2008.

INCO Staff (1955a), “Oxygen Flash Smelting Swings into Commercial Operation”, Journal of Metals, v. 26, No: 6, June, pp. 742-750.

INCO Staff (1955b), “Oxygen Flash Smelting of the International Nickel Company”, Canadian Mining and Metallurgical Bulletin, v. 48, No: 517, May, pp. 292-300.

Juusela J., Harkki S., Andersson B. (1974), “Outokumpu Flash Smelting and its Energy Requirement”, Paper Presented in Symposium “Efficient Use of Fuels in Metallurgical Industries”, 9-13 December, Chicago, USA.

Juusela J.T., Makinen J.K. (1977), “Advanced Smelting of Copper Concentrates by the Outokumpu Flash Smelting Method”, The Second International Symposium on Management of Copper Resources, Lubin, Poland, 27-28 April.

Kelly T.D., Buckingham D.A., Di Francesco C.A., Porter K.E., Goonan T.G., Szonpek J.L., Berry C., Crane M. (2002), Historical Statistics for Mineral Commodities in the United States: U.S. Geological Survey Open-File Report 01-006.

Kemori K., Shibata Y., Fukushima K. (1985), “Thermodynamic Consideration for Oxygen Pressure in Copper Flash Smelting Furnace at Toyo Smelter”, Journal of Metals, May, pp. 24-29.
Kitap H. (2006), Blister Bakir Üretimi ve Dünya Bakır Piyasası, Zonguldak.

Kojo I.V., Jokilaakso A., Hanniala P. (2000), “Flash Smelting and Converting Furnaces: A 50 Years Retrospect”, Journal of Metals, 52 (2), pp. 57-61.

Krivsky W.A., Schuhmann R. (1957), Thermodynamics of the Cu-Fe-S System at Matte Smelting Temperatures. Trans. A.I.M.E., 209, 981-988.

Lilja L., Makitalo V.J. (1979), “Procedure for Producing a Suspension of a Powdery Substance and a Reaction Gas”, United States Patent, 4, 147, 535, 3 April.

London Metal Exchange, www.lme.co.uk, last accessed date: 23 May 2008.

Makipirtti S. (1973), Docent Lecture, Outokumpu Oy Report.

Muan A. (1955), Phase Equilibria in the System FeO-Fe_2O_3-SiO_2, Trans. A.I.M.E., 205, 965-976.

Nernes E.O., Talonen T.T. (1982), “Flash Smelting of Lead Concentrates”, Journal of Metals, v. 34, No: 11, pp. 55-59.

Niemela T., Harkki S. (1972), “The Latest Development in Nickel Flash Smelting at the Harjavalta Smelter”, Joint Meeting MMIJ-AIME, Tokyo.

Parker K.R. (1997), Applied Electrostatic Precipitation, Chapman & Hall, London, U.K.

Pritchard J.P., Hollis R. (1994), The Isasmelt copper-smelting process. Int. Miner. Met. Technol., 1, 125-128.

Rayan P., Smith N., Corsi C., Whiteus T. (1999), “Agglomeration of ESP Dust for Recycling to Plant Smelting Furnaces”, in Copper 99 – Cobre 99, Proceedings of the Fourth International Conference, v.V, Smelting Operations and Advances, edited by George D.B., Chen W.J., Mackey P.J., Weddick A.J., TMS, Warrendale, PA, pp. 561-571.

Reuleaux O. (1927), Reaktionen und Gleichgewichte im System Cu-Fe-S mit Besonderer Berücksichtigung des Kupfersteins. Metall und Erz 24, 99-111.

Rosenqvist T. (1971), "Thermodynamic of Copper Smelting", in Advances in Sulfide Smelting, v. 1, Basic Principles, edited by Sohn H.Y., George D.B., Zunkel A.D., pp. 239-255.

Schuhmann R. (1952), Metallurgical Engineering, Cambridge, Mass., Addison-Wesley Press.

The World Copper Factbook (2007), International Copper Study Group.

Toivanen T., Gronqvist P.O. (1964), "Nickel Refining in Finland", Canadian Mining and Metallurgical Bulletin, 57, pp. 653-658.

Vaarno J., Jarvi J., Ahokainen T., Laurila T., Taskinen P. (2003), "Development of a Mathematical Model of Flash Smelting and Converting Processes", Third International Conference on CFD in the Minerals and Process Industries, Melbourne, 10-12 December.

Wikipedia, The Free Encyclopedia, www.en.wikipedia.org/wiki/Copper, last accessed date: 13 May 2008.

Wu John C. 2002, The mineral industry of Japan, in Area reports – International – Asia and the Pacific: U.S. Geological Survey Minerals Yearbook 2000, v. III, pp. 13.1-13.34.

Yasuda M. (1974), "Recent Developments of Copper Smelting at Hitachi Smelter", The 103rd AIME Annual Meeting, Dallas, February, Paper No: 74-8.

Yasuda M., Yuki T., Kato M., Kawasaki Y. (1982), "Recent Flash Smelting Operations at the Saganoseki Smelter" in Copper Smelting, edited by George D.B. and Taylor J.C., Conference Proceedings, The Metallurgical Society of AIME, Annual Meeting, Dallas, 1982.

Yazawa A. (1974), "Thermodynamic Considerations of Copper Smelting", Canadian Metallurgical Quarterly, 13, v. 3, pp. 443-453.

Yazawa A. (1977), "Trends in Modern Copper Smelting Processes", Erzmetall, 30, pp. 511-518.

Yazawa A. (1979), "Thermodynamic Evaluations of Extractive Metallurgical Processes", Metallurgical Transactions, September, pp. 307-321.

Yazawa A., Azakami T. (1969), “Thermodynamic of Removing Impurities during Copper Smelting”, Canadian Metallurgical Quarterly, 8, pp. 257-261.

Yazawa A., Eguchi M. (1976), in Extractive Metallurgy of Copper, edited by Yannopoulos J.C. and Agarwal J.C., AIME, New York, pp.3.

APPENDIX A

DATA TAKEN FROM ETI-BAKIR PLANT AND CALCULATED BY COMPUTER PROGRAM BY THE LAST 6 MONTHS

Industrial data:

Table A.1. Material balance of flash smelter, December 2007

Materials	t	Cu, %	Fe, %	S, %	SiO_2, %
Input					
Kure Conc.	8844.39	17.76	34.12	37.20	1.60
Murgul Conc.	6778.79	22.43	32.00	33.00	2.00
Murgul Ore	1061.93	7.92	35.00	38.00	6.00
Slag Conc.	0.00	0.00	0.00	0.00	0.00
Flux	2846.00				
Dust	1367.00	22.00			
Lignite	108.00				
Natural Gas, Nm^3	743349.00				
Process Air, Nm^3	21000000.00				
Output					
Matte	6988.33	41.49	24.86	21.40	
Furnace Slag	9610.50	2.43	37.93	1.56	32.11
Dust	1562.00	22.00			
Off-gas	33500000.00				

Table A.2. Material balance of flash smelter, January 2008

Materials	t	Cu, %	Fe, %	S, %	SiO_2, %
Input					
Kure Conc.	10095.75	17.67	34.20	36.20	1.57
Murgul Conc.	8390.87	22.31	29.88	30.95	1.16
Murgul Ore	1418.34	8.02	35.00	38.00	6.00
Slag Conc.	399.06	27.62	26.80	26.54	10.53
Flux	3486.69				
Dust	1550.00	22.00			
Lignite	460.86				
Natural Gas, Nm^3	600418.00				
Process Air, Nm^3	26000000.00				
Output					
Matte	8260.37	43.84	23.63	20.54	
Furnace Slag	12771.50	1.63	42.30	1.38	30.10
Dust	1784.00	22.00			
Off-gas	40700000.00				

Table A.3. Material balance of flash smelter, February 2008

Materials	t	Cu, %	Fe, %	S, %	SiO_2, %
Input					
Kure Conc.	8759.56	17.71	34.90	37.69	1.30
Murgul Conc.	7663.40	22.64	32.00	30.30	2.20
Murgul Ore	1954.50	8.18	35.00	38.00	6.00
Slag Conc.	1957.42	28.15	26.14	11.35	12.56
Flux	3426.06				
Dust	1425.00	22.00			
Lignite	616.42				
Natural Gas, Nm^3	543304.00				
Process Air, Nm^3	26850000.00				
Output					
Matte	8557.55	44.20	26.09	16.63	
Furnace Slag	12757.50	1.27	39.01	1.43	33.51
Dust	1662.00	22.00			
Off-gas	41750000.00				

Table A.4. Material balance of flash smelter, March 2008

Materials	t	Cu, %	Fe, %	S, %	SiO_2, %
Input					
Kure Conc.	10292.29	17.74	36.25	39.20	1.06
Murgul Conc.	7817.24	22.63	31.91	32.80	2.07
Murgul Ore	2485.51	8.18	35.00	38.00	6.00
Slag Conc.	2481.10	28.94	26.14	11.35	12.56
Flux	3190.01				
Dust	1576.00	22.00			
Lignite	787.98				
Natural Gas, Nm^3	537392.00				
Process Air, Nm^3	27200000.00				
Output					
Matte	9751.00	44.43	26.57	18.91	
Furnace Slag	13877.00	0.91	40.89	1.31	31.95
Dust	1838.00	22.00			
Off-gas	45000000.00				

Table A.5. Material balance of flash smelter, April 2008

Materials	t	Cu, %	Fe, %	S, %	SiO_2, %
Input					
Kure Conc.	9758.84	17.91	34.90	37.69	1.30
Murgul Conc.	7621.60	22.56	31.41	32.21	1.71
Murgul Ore	2433.87	8.18	35.00	38.00	6.00
Slag Conc.	2433.87	27.19	25.88	10.42	13.58
Flux	3357.84				
Dust	1783.00	22.00			
Lignite	847.00				
Natural Gas, Nm^3	1803000.00				
Process Air, Nm^3	26160000.00				
Output					
Matte	9639.00	43.80	26.65	19.24	
Furnace Slag	12603.00	0.95	39.15	1.28	32.96
Dust	1920.00	22.00			
Off-gas	43300000.00				

Table A.6. Material balance of flash smelter, May 2008

Materials	t	Cu, %	Fe, %	S, %	SiO_2, %
Input					
Kure Conc.	9935.84	18.13	34.90	36.12	2.12
Murgul Conc.	8043.37	22.99	32.05	30.20	2.44
Murgul Ore	1516.52	7.97	35.00	38.00	6.00
Slag Conc.	1813.49	29.55	29.41	12.74	12.73
Flux	3529.80				
Dust	1625.00	22.00			
Lignite	783.56				
Natural Gas, Nm^3	824000.00				
Process Air, Nm^3	25379736.00				
Output					
Matte	10017.00	43.27	26.65	21.78	
Furnace Slag	11146.63	0.89	38.94	2.10	31.60
Dust	1750.00	22.00			
Off-gas	43150000.00				

Table A.7. Calculated material balance of flash smelter, December 2007

Materials	t	Nm^3
Input		
Copper concentrate	16685.11	
Silica Flux	2554.98	
Dust	1297.82	
Lignite	493.34	
Natural Gas		635395.05
Air Blast		27209282.79
for process		17954308.78
for lignite combustion		2613582.86
for natural gas combustion		6641391.15
TOTAL:	21031.25	27844677.84
Output		
Matte	7423.69	
Furnace Slag	8625.94	
Dust	1492.5	
Gas		32470002.60
from process		17304326.55
from lignite combustion		2832525.24
from natural gas combustion		7327617.81
TOTAL:	17542.13	32470002.60

Table A.8. Calculated material balance of flash smelter, January 2008

Materials	t	Nm^3
Input		
Copper concentrate	20304.02	
Silica Flux	3140.92	
Dust	1540.45	
Lignite	601.15	
Natural Gas		762075.98
Air Blast		32500010.10
for process		21349730.62
for lignite combustion		3184771.04
for natural gas combustion		7965508.44
TOTAL:	25586.54	33262086.08
Output		
Matte	8584.62	
Furnace Slag	11156.04	
Dust	1771.52	
Gas		38870718.61
from process		20539399.71
from lignite combustion		3451562.41
from natural gas combustion		8788550.49
TOTAL:	21512.18	38870718.61

Table A.9. Calculated material balance of flash smelter, February 2008

Materials	t	Nm^3
Input		
Copper concentrate	20334.88	
Silica Flux	3059.63	
Dust	1442.76	
Lignite	599.86	
Natural Gas		775448.30
Air Blast		31307835.51
for process		20024633.93
for lignite combustion		3177920.50
for natural gas combustion		8105281.08
TOTAL:	25437.13	32083283.81
Output		
Matte	8772.14	
Furnace Slag	11237.23	
Dust	1659.18	
Gas		37724188.26
from process		19236821.02
from lignite combustion		3444137.99
from natural gas combustion		8942765.25
TOTAL:	21668.55	37724188.26

Table A.10. Calculated material balance of flash smelter, Mart 2008

Materials	t	Nm^3
Input		
Copper concentrate	23076.14	
Silica Flux	3562.82	
Dust	1742.24	
Lignite	683.05	
Natural Gas		937562.07
Air Blast		37563601.80
for process		24145197.27
for lignite combustion		3618648.63
for natural gas combustion		9799755.90
TOTAL:	29064.25	38501163.87
Output		
Matte	9859.9	
Furnace Slag	12593.80	
Dust	2003.58	
Gas		44886853.84
from process		23229902.56
from lignite combustion		3921786.35
from natural gas combustion		10812322.93
TOTAL:	24457.28	44886853.84

Table A.11. Calculated material balance of flash smelter, April 2008

Materials	t	Nm^3
Input		
Copper concentrate	22248.18	
Silica Flux	3222.66	
Dust	1595.23	
Lignite	653.1	
Natural Gas		926719.06
Air Blast		35248111.40
for process		22101719.94
for lignite combustion		3459970.86
for natural gas combustion		9686420.60
TOTAL:	27719.17	36174830.46
Output		
Matte	9585.06	
Furnace Slag	12037.74	
Dust	1834.51	
Gas		42381258.72
from process		21269711.56
from lignite combustion		3749815.98
from natural gas combustion		10687277.18
TOTAL:	23457.31	42381258.72

Table A.12. Calculated material balance of flash smelter, May 2008

Materials	t	Nm^3
Input		
Copper concentrate	21309.22	
Silica Flux	3201.18	
Dust	1456.95	
Lignite	628.47	
Natural Gas		757414.26
Air Blast		31495761.24
for process		20249475.59
for lignite combustion		3329503.23
for natural gas combustion		7916782.42
TOTAL:	26595.82	32253175.51
Output		
Matte	9655.82	
Furnace Slag	11512.38	
Dust	1675.49	
Gas		38161954.43
from process		19425979.65
from lignite combustion		3608418.96
from natural gas combustion		8734789.82
TOTAL:	22843.69	38161954.43

APPENDIX B

X-RAY ANALYSIS

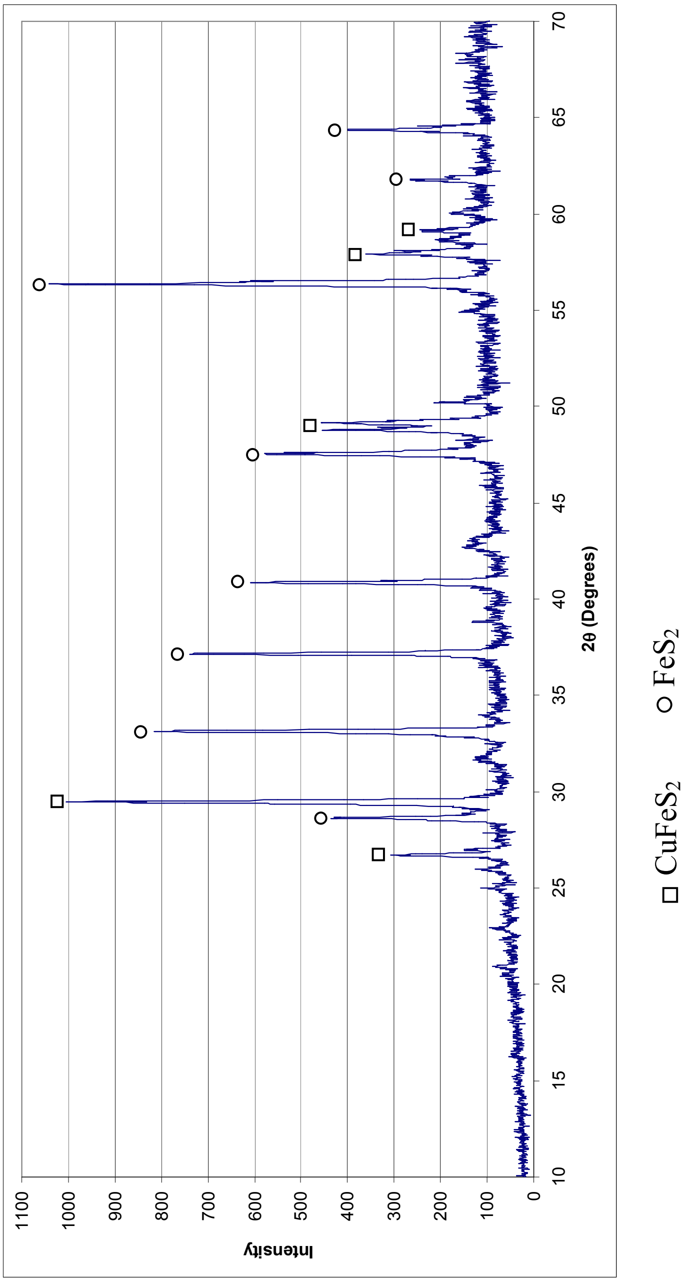


Figure B.1. XRD analysis of Murgul ore

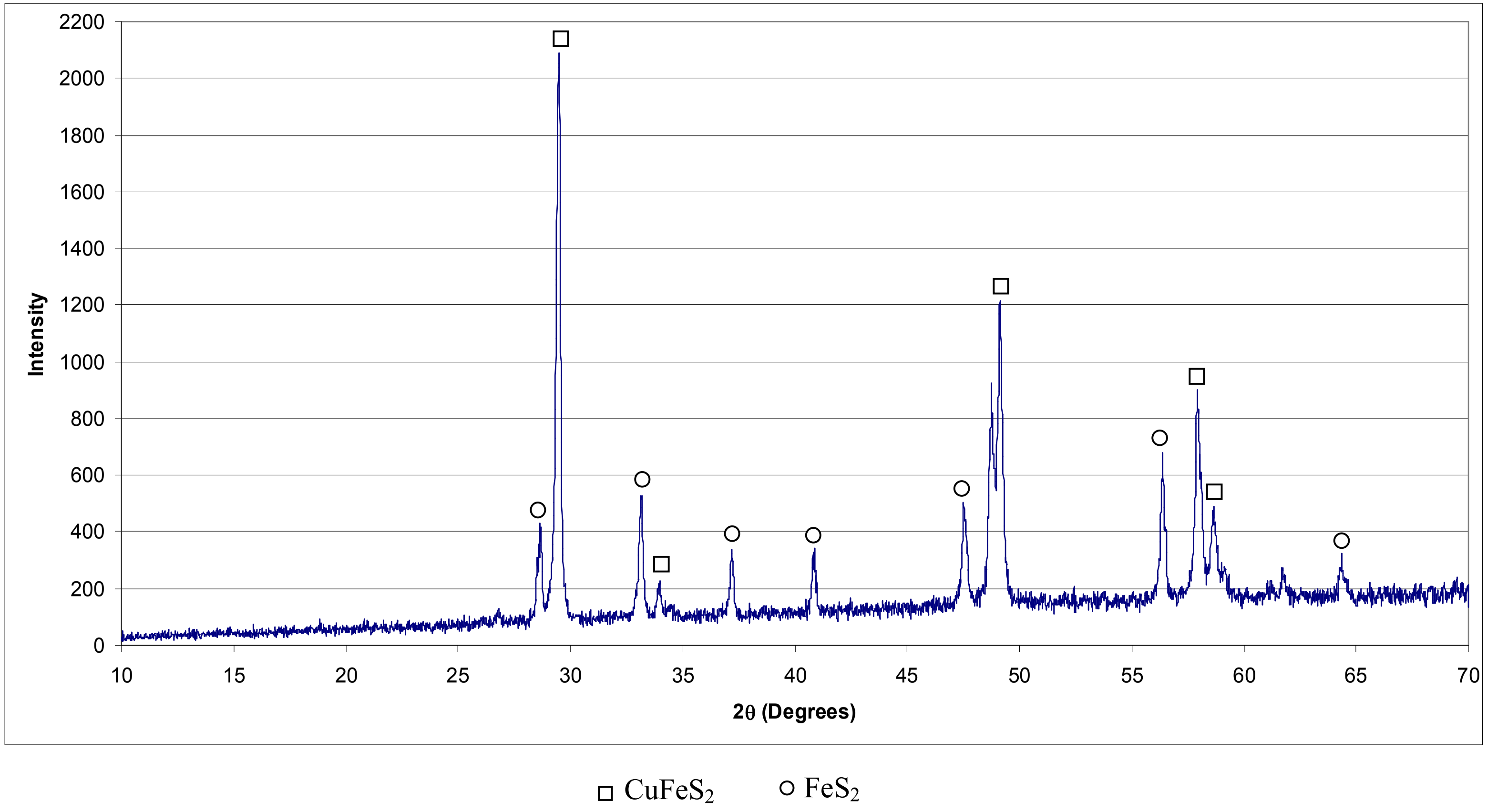


Figure B.2. XRD analysis of Murgul concentrate

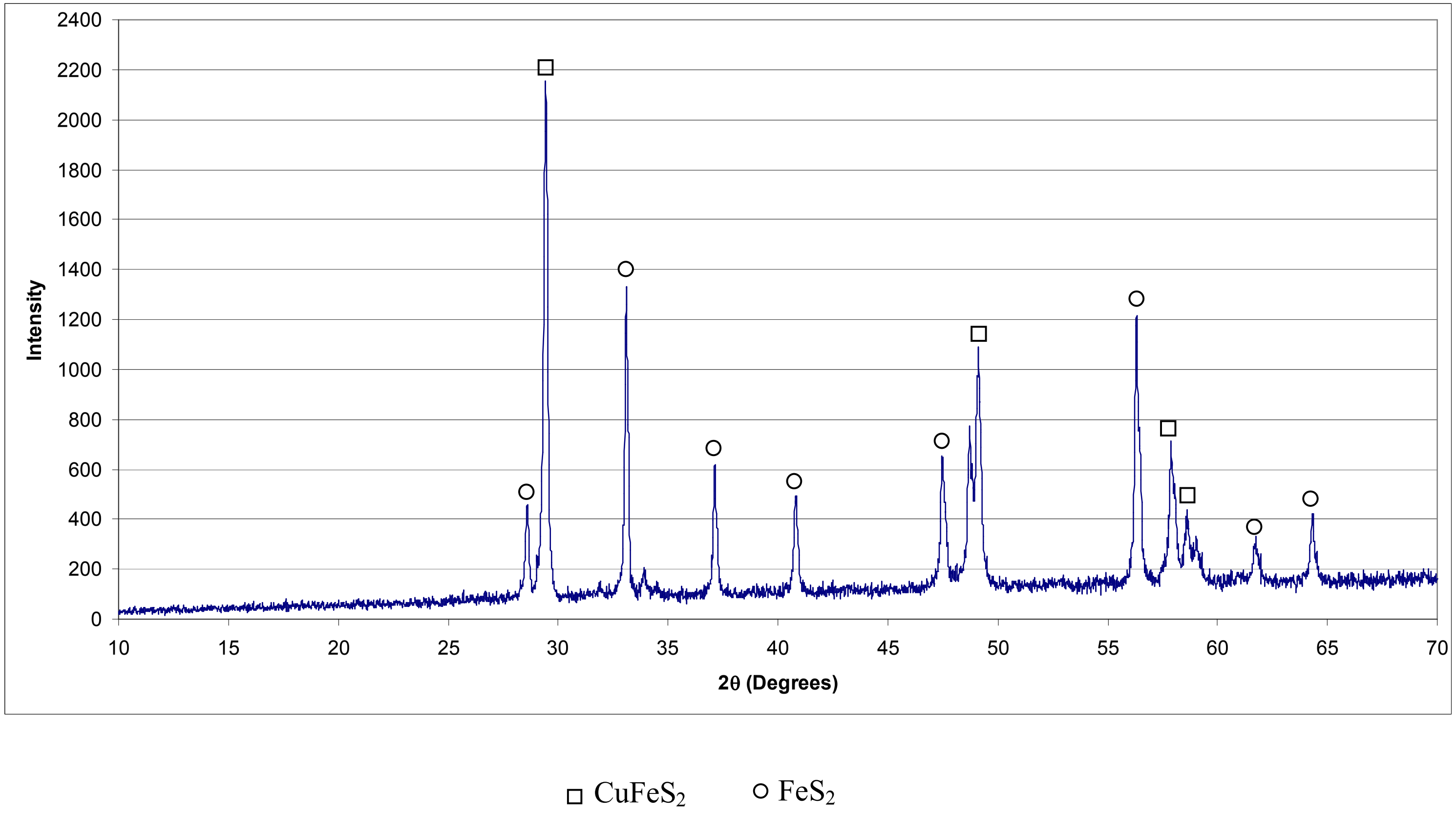


Figure B.3. XRD Analysis of Küre concentrate

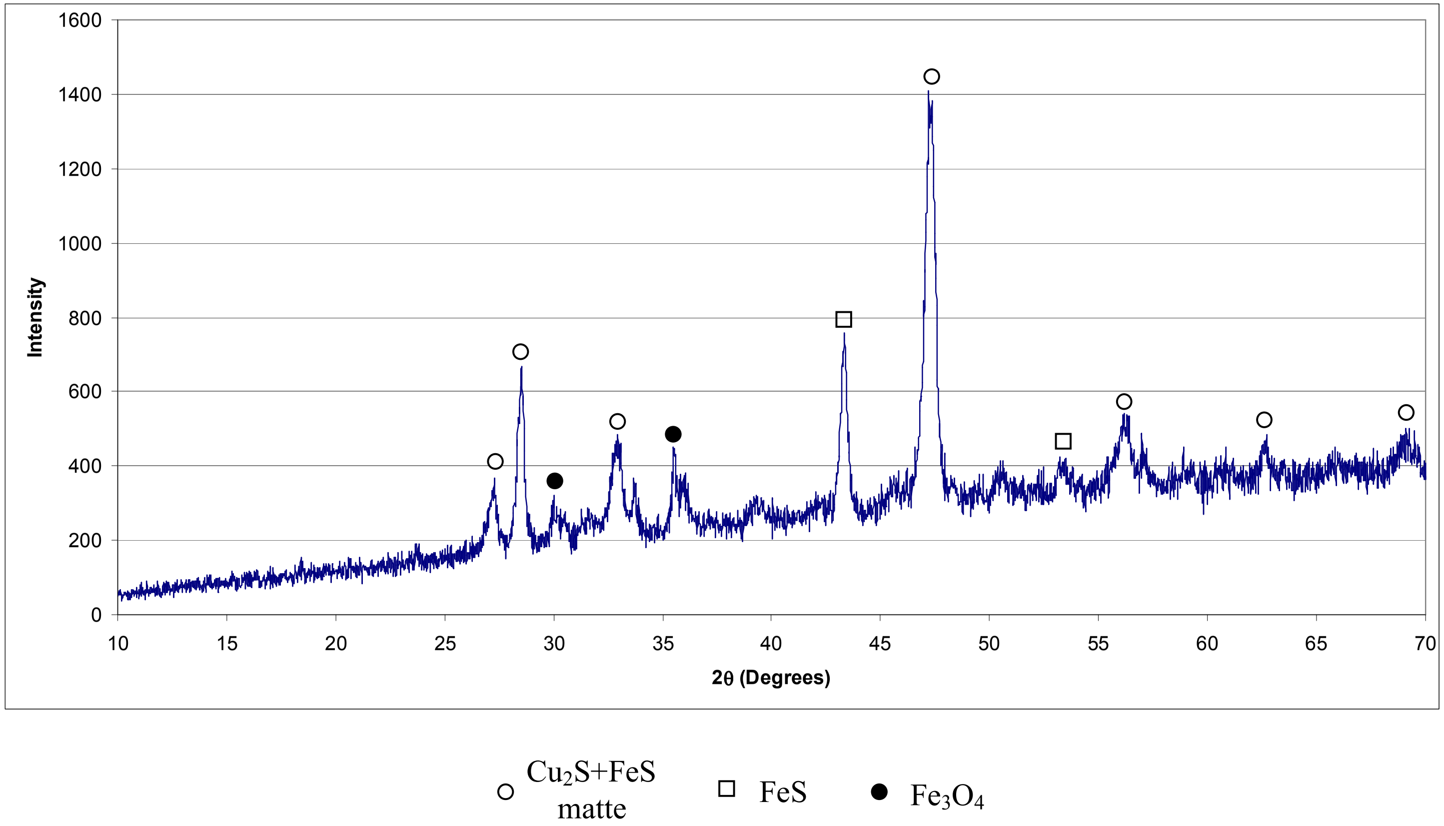


Figure B.4. XRD Analysis of Matte

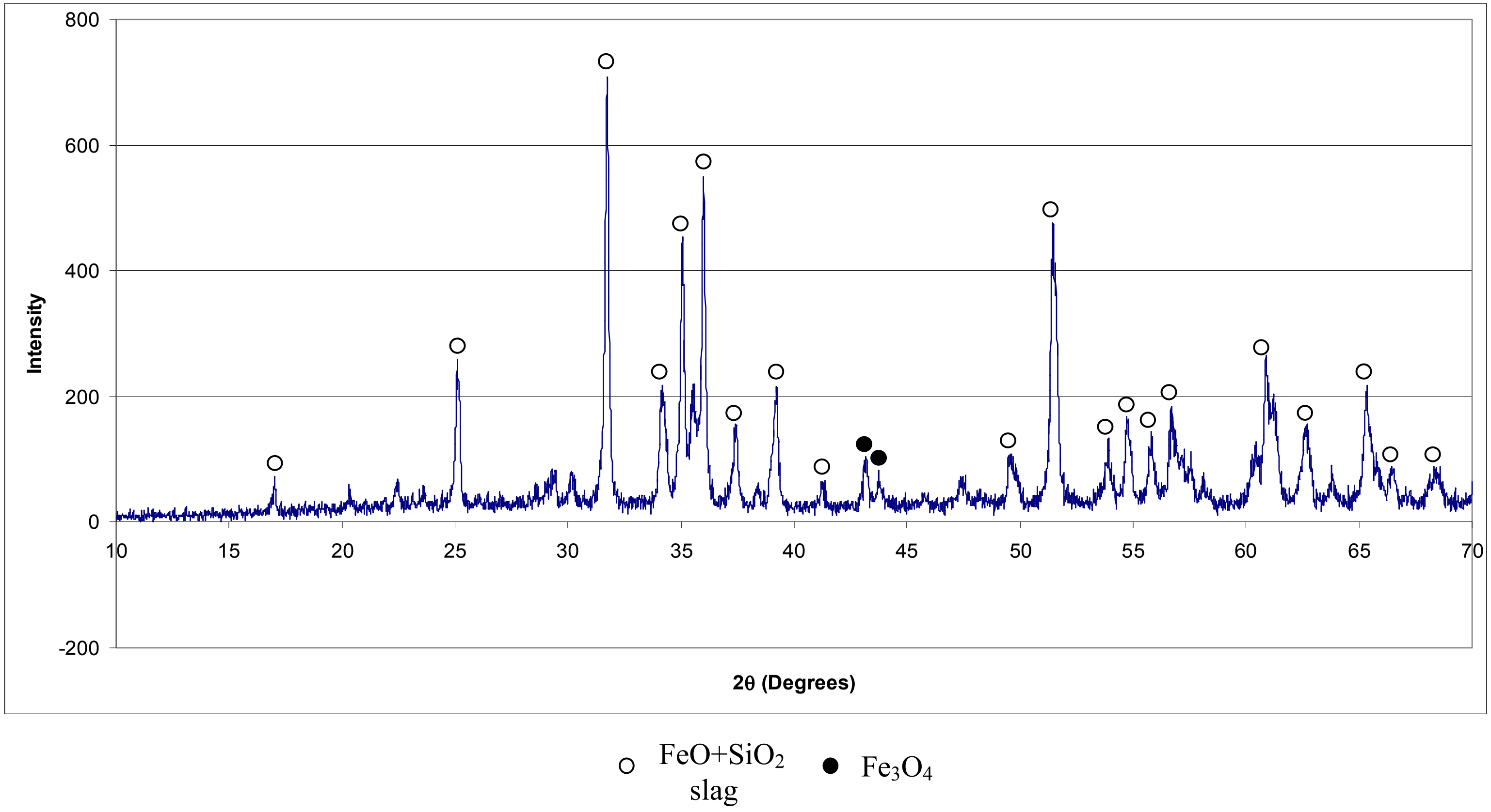


Figure B.5. XRD Analysis of Furnace slag

APPENDIX C

ALGORITHM OF COMPUTER PROGRAM

```
Function Materials(Basis_conc, Cu_conc, Cu_matte, Fe_conc, SiO2_conc, SiO2_flux, S_conc, Full_load, Cu_slag,
Dusting_rate, Excess_air, Coke_rate, Water_feed, O2_air, N2_air, Fe_as_Fe3O4_matte, Fe_slag, Fe_as_Fe3O4_slag,
Fe3O4_matte, Fe3O4_slag, Fe3O4_conc, Leakage_air)

Dim A(20), Fe3O4

A(0) = Basis_conc * Cu_conc * 0.97 / Cu_matte                                    'Matte quantity
A(1) = (A(0) * 0.9 - Basis_conc * Cu_conc * 0.97 / 100 * 160 / 128) * 56 / 88    'Fe in matte
A(2) = (A(0) * 0.9 - Basis_conc * Cu_conc * 0.97 / 100 - A(1))                   'S in matte
A(3) = Basis_conc * Fe_conc / 100 - A(1) - A(0) * Fe_as_Fe3O4_matte / 100        'Fe in slag
A(4) = 0.7 * A(3)                                      'SiO2 in slag, assumption, SiO2 in slag/Fe in slag=0.7
A(5) = (A(4) - 10 * SiO2_conc) * 100 / SiO2_flux                                 'Silica Flux
A(6) = Basis_conc * S_conc / 100 - A(2)                                          'S in Gas
A(7) = Basis_conc - A(0) - A(6) + A(3) * (Fe_slag / (Fe_slag + Fe_as_Fe3O4_slag)) * 16 / 56 + A(3) * (1 - Fe_slag /
(Fe_slag + Fe_as_Fe3O4_slag)) * (64 / 168) + A(5)                                'Slag quantity
A(8) = Full_load * 80 / 100                    'Conc load per hour, assumption, 80% of feed is copper conc
Fe3O4 = (A(1) * (Fe3O4_matte / 100) + A(7) * (Fe3O4_slag / 100)) - Basic_conc * (Fe3O4_conc / 100)  'Fe3O4 dificiency
A(11) = (A(6) * 22.4 / 32 + A(3) * (Fe_slag / (Fe_slag + Fe_as_Fe3O4_slag)) * 11.2 / 56 + Fe3O4 * (44.8 / 232)) * (1 +
Excess_air / 100) * 100 / O2_air                                                 'Volume of process air
A(12) = (Basis_conc + A(5)) * Coke_rate / (100 - Coke_rate)                      'Coke quantity
A(13) = Basis_conc + A(5) + A(12)                                                 'Total feed quantity
A(14) = A(6) * 22.4 / 32                                                          'SO2 in off-gas
A(15) = (A(11) - A(11) / (1 + Excess_air / 100)) * O2_air / 100 + Leakage_air * 21 / 100   'O2 in off-gas
A(16) = A(11) * N2_air / 100 + Leakage_air * 79 / 100                              'N2 in off-gas
A(17) = A(13) * Water_feed / 100 * 22.4 / 18                                       'H2O in off-gas
A(18) = A(14) + A(15) - Leakage_air * 21 / 100 + A(16) - Leakage_air * 79 / 100 + A(17)  'Total volume of off-gas from
                                                                                              reaction process
A(10) = A(18) * Dusting_rate                                                      'Input Dust quantity
A(9) = 1.15 * A(10)                                                              'Output Dust quantity
A(19) = Basis_conc + A(5) + A(10) + A(12)                                        'Exact Total feed quantity


Materials = A

End Function
```

```
Function Heat1(Basis_conc, Cu_conc, Fe_conc, T_air, C_coke, H_coke, O_coke, S_coke, T_gas, Fe3O4_matte, Zn_matte,
Pb_matte, T_matte, A_4, A_11, A_12, A_0, O2_air, N2_air, Cu_slag_conc, Cu_mix_rate, Fe_mix_rate, Fe_slag_conc,
Fe_matte, Fe3O4_slag, Fe3O4_conc, A_7, A_678, Total_mix)

Dim H_O2_air, H_N2_air, B(19), Heat_coke, Heat_coke_air, Heat_coke_waste, O2_aircoke, H_CO2_gas, H_H2O_gas,
H_SO2_gas, H_N2_gas, H_Cu2S_matte, H_FeS_matte, H_Fe3O4_matte, H_ZnO_matte, H_PbO_matte, FeS, FeO

B(0) = (Basis_conc * Cu_conc / 100 - Basis_conc * Cu_conc / 100 * (Cu_slag_conc * Cu_mix_rate / Total_mix) /
Cu_conc) * 184 / 64                                                                            'CuFeS2 in conc.
B(1) = (Basis_conc * Fe_conc / 100 - Basis_conc * Fe_conc / 100 * 5 / 100 - B(0) * 56 / 184) * 120 / 56 'FeS2 in conc
FeS = B(0) * 176 / 368 - A_0 * Fe_matte / 100 * 88 / 56
FeO = (A_0 * (Fe3O4_matte / 100) + A_7 * (Fe3O4_slag / 100) - Basis_conc * (Fe3O4_conc / 100)) * 3 * 72 / 232
B(2) = B(0) / (2 * 184) * 22475 + B(1) / 120 * 163100 + FeS / 88 * 111750 + FeO / (3 * 72) * 25700 + A_4 / 60 * 10000
                                                                                              'Reaction Heat
H_O2_air = (7.16 * (T_air + 273) + 0.5 * 10 ^ -3 * (T_air + 273) ^ 2 + 0.4 * 10 ^ 5 * 1 / (T_air + 273) - 2313) / 22.4
                                                                                              'Heat capacity of O2
H_N2_air = (6.83 * (T_air + 273) + 0.45 * 10 ^ -3 * (T_air + 273) ^ 2 + 0.12 * 10 ^ 5 * 1 / (T_air + 273) - 2117) / 22.4
                                                                                              'Heat capacity of N2
B(3) = A_11 * O2_air / 100 * H_O2_air + A_11 * N2_air / 100 * H_N2_air             'Heat content of Process Air
Heat_coke = A_12 * C_coke / 100 / 12 * 97200 + ((A_12 * H_coke / 100 / 2 - 2 * A_12 * O_coke / 100 / 32) / 2) * 57800 +
A_12 * S_coke / 100 / 32 * 70960
O2_aircoke = (A_12 * C_coke / 100 / 12 + A_12 * S_coke / 100 / 32 + (A_12 * H_coke / 100 / 2 - 2 * A_12 * O_coke / 100
/ 32) / 2) * 22.4
Heat_coke_air = O2_aircoke * H_O2_air + O2_aircoke * N2_air / O2_air * H_N2_air    'Heat content of comb air for coke

H_CO2_gas = (10.57 * (T_gas + 273) + 1.05 * 10 ^ -3 * (T_gas + 273) ^ 2 + 2.06 * 10 ^ 5 * (1 / (T_gas + 273)) - 3936) /
22.4
H_H2O_gas = (7.3 * (T_gas + 273) + 1.23 * 10 ^ -3 * (T_gas + 273) ^ 2 - 2286) / 22.4
H_SO2_gas = (11.04 * (T_gas + 273) + 0.94 * 10 ^ -3 * (T_gas + 273) ^ 2 + 1.84 * 10 ^ 5 * (1 / (T_gas + 273)) - 3992) /
22.4
H_N2_gas = (6.83 * (T_gas + 273) + 0.45 * 10 ^ -3 * (T_gas + 273) ^ 2 + 0.12 * 10 ^ 5 * 1 / (T_gas + 273) - 2117) / 22.4
Heat_coke_waste = A_12 * C_coke / 100 / 12 * 22.4 * H_CO2_gas + A_12 * H_coke / 100 / 2 * 22.4 * H_H2O_gas +
A_12 * S_coke / 100 / 32 * 22.4 * H_SO2_gas + O2_aircoke * N2_air / O2_air * H_N2_gas
B(4) = Heat_coke + Heat_coke_air - Heat_coke_waste                                 'Available Heat of Coke

B(5) = Basis_conc * Cu_conc / 100 * 97 / 100 * 160 / 128                           'Cu2S in matte
B(6) = A_0 * 0.9 - B(5)                                                            'FeS in matte
B(7) = A_0 * Fe3O4_matte / 100                                                     'Fe3O4 in matte
B(8) = A_0 * Zn_matte / 100 * 81 / 65                                              'ZnO in matte
B(9) = A_0 * Pb_matte / 100 * 223 / 207                                            'PbO in matte

H_Cu2S_matte = 20.32 * (T_matte + 273) - 4275
H_FeS_matte = 12.2 * (T_matte + 273) + 1.19 * 10 ^ -3 * (T_matte + 273) ^ 2 - 2138
H_Fe3O4_matte = 48 * (T_matte + 273) - 12650
H_ZnO_matte = 11.71 * (T_matte + 273) + 0.61 * 10 ^ -3 * (T_matte + 273) ^ 2 + 2.18 * 10 ^ 5 * (1 / (T_matte + 273)) -
4277
H_PbO_matte = 16 * (T_matte + 273) + 180

'Heat content of Matte
B(10) = B(5) / 160 * H_Cu2S_matte + B(6) / 88 * H_FeS_matte + B(7) / 232 * H_Fe3O4_matte + B(8) / 81 *
H_ZnO_matte + B(9) / 223 * H_PbO_matte

'Nedeed air for combustion coke
B(11) = O2_aircoke                  'O2 in air
B(12) = O2_aircoke * N2_air / O2_air      'N2 in air
B(13) = B(11) + B(12)                'Total Air
'Waste gas from combustion of coke
B(14) = A_12 * C_coke / 100 / 12 * 22.4                                            'CO2 in waste gas
B(15) = A_12 * H_coke / 100 / 2 * 22.4                                             'H2O in waste gas
B(16) = A_12 * S_coke / 100 / 32 * 22.4                                            'SO2 in waste gas
B(17) = B(12)                                                                      'N2 in waste gas
B(18) = B(14) + B(15) + B(16) + B(17)                                              'Total waste gas

Heat1 = B
End Function
```

```
Function Heat2(T_slag, Cu_slag, Fe3O4_slag, Zn_slag, Pb_slag, S_dust, Cu_dust, Fe_dust, Zn_dust, Pb_dust, SiO2_dust,
A_3, A_7, A_14, A_15, A_16, A_17, A_9, A_4, T_gas)

Dim C(14), H_FeO_slag, H_Cu2S_slag, H_Fe3O4_slag, H_SiO2_slag, H_ZnO_slag, H_PbO_slag, H_O2_gas,
H_H2O_gas, H_SO2_gas, H_N2_gas, H_CuSO4_dust, H_CuO_dust, H_Fe3O4_dust, H_ZnO_dust, H_PbO_dust,
H_SiO2_dust

C(0) = A_3 * 72 / 56                                                'FeO in slag
C(1) = A_7 * Cu_slag / 100 * 160 / 128                              'Cu2S in slag
C(2) = A_7 * Fe3O4_slag / 100                                       'Fe3O4 in slag
C(3) = A_7 * Zn_slag / 100 * 81 / 65                                'ZnO in slag
C(4) = A_7 * Pb_slag / 100 * 223 / 207                              'PbO in slag

H_FeO_slag = 11.66 * (T_slag + 273) + 10 ^ -3 * (T_slag + 273) ^ 2 + 0.67 * 10 ^ 5 * (1 / (T_slag + 273)) - 3790
H_Cu2S_slag = 20.32 * (T_slag + 273) - 4275
H_Fe3O4_slag = 48 * (T_slag + 273) - 12650
H_SiO2_slag = 14.41 * (T_slag + 273) + 0.97 * 10 ^ -3 * (T_slag + 273) ^ 2 - 4455
H_ZnO_slag = 11.71 * (T_slag + 273) + 0.61 * 10 ^ -3 * (T_slag + 273) ^ 2 + 2.18 * 10 ^ 5 * (1 / (T_slag + 273)) - 4277
H_PbO_slag = 16 * (T_slag + 273) + 180

'Heat content of Furnace Slag
C(5) = C(0) / 72 * H_FeO_slag + C(1) / 160 * H_Cu2S_slag + C(2) / 232 * H_Fe3O4_slag + A_4 / 60 * H_SiO2_slag +
C(3) / 81 * H_ZnO_slag + C(4) / 223 * H_PbO_slag

H_O2_gas = (7.16 * (T_gas + 273) + 0.5 * 10 ^ -3 * (T_gas + 273) ^ 2 + 0.4 * 10 ^ 5 * 1 / (T_gas + 273) - 2313) / 22.4
H_H2O_gas = (7.3 * (T_gas + 273) + 1.23 * 10 ^ -3 * (T_gas + 273) ^ 2 - 2286) / 22.4
H_SO2_gas = (11.04 * (T_gas + 273) + 0.94 * 10 ^ -3 * (T_gas + 273) ^ 2 + 1.84 * 10 ^ 5 * 1 / (T_gas + 273) - 3992) / 22.4
H_N2_gas = (6.83 * (T_gas + 273) + 0.45 * 10 ^ -3 * (T_gas + 273) ^ 2 + 0.12 * 10 ^ 5 * 1 / (T_gas + 273) - 2117) / 22.4

'Heat content of off-gas
C(6) = A_14 * H_SO2_gas + A_15 * H_O2_gas + A_16 * H_N2_gas + A_17 * H_H2O_gas + Leakage_air_heat

C(7) = A_9 * S_dust / 100 * 160 / 32                                'Cu2SO4 in dust
C(8) = (A_9 * Cu_dust / 100 - C(7) * 64 / 160) * 80 / 64            'CuO in dust
C(9) = A_9 * Fe_dust / 100 * 232 / 168                              'Fe3O4 in dust
C(10) = A_9 * Zn_dust / 100 * 81 / 65                               'ZnO in dust
C(11) = A_9 * Pb_dust / 100 * 223 / 207                             'PbO in dust
C(12) = A_9 * SiO2_dust / 100                                       'SiO2 in dust

H_CuSO4_dust = 18.77 * (T_gas + 273) + 8.6 * 10 ^ -3 * (T_gas + 273) ^ 2 - 6361
H_CuO_dust = 8.72 * (T_gas + 273) + 0.07 * 10 ^ -3 * (T_gas + 273) ^ 2 + 0.73 * 10 ^ 5 * (1 / (T_gas + 273)) - 2851
H_Fe3O4_dust = 48 * (T_gas + 273) - 12650
H_ZnO_dust = 11.71 * (T_gas + 273) + 0.61 * 10 ^ -3 * (T_gas + 273) ^ 2 + 2.18 * 10 ^ 5 * (1 / (T_gas + 273)) - 4277
H_PbO_dust = 16 * (T_gas + 273) + 180
H_SiO2_dust = 14.41 * (T_gas + 273) + 0.97 * 10 ^ -3 * (T_gas + 273) ^ 2 - 4455

'Heat content of Dust
C(13) = C(7) / 160 * H_CuSO4_dust + C(8) / 80 * H_CuO_dust + C(9) / 232 * H_Fe3O4_dust + C(10) / 81 * H_ZnO_dust
+ C(11) / 223 * H_PbO_dust + C(12) / 60 * H_SiO2_dust

Heat2 = C

End Function
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Function Heat3(T_gas, D_shaft, h1_shaft, h2_shaft, CH4_NG, C2H6_NG, C3H8_NG, C4H10_NG, CO2_NG, O2_NG,
N2_NG, S2_NG, O2_air, N2_air, A_8, T_air, D_side_take, h_side_take, Lenght_furnace, Width_furnace, Height_furnace,
Basic_conc)

Dim D(18), H_O2_air, H_N2_air, H_O2_gas, H_H2O_gas, H_SO2_gas, H_N2_gas, H_CO2_gas, Reaction_shaft,
Side_take_and_roof, Sides_and_bottom_heat

'Heat loss
Reaction_shaft = ((3.14 * (D_shaft / 2) ^ 2 + 2 * 3.14 * (D_shaft / 2) * h1_shaft) * 1.1 * 10 * 10 ^ 3 + 2 * 3.14 * (D_shaft /
2) * h2_shaft * 1.1 * 25 * 10 ^ 3) / A_8
Side_take_and_roof = (3.14 * (D_side_take / 2) ^ 2 + 2 * 3.14 * (D_side_take / 2) * h_side_take + Lenght_furnace *
Width_furnace - 3.14 * (D_shaft / 2) ^ 2 - 3.14 * (D_side_take / 2) ^ 2) * 1.1 * 5 * 10 ^ 3 / A_8
Sides_and_bottom_heat = ((2 * Lenght_furnace * Height_furnace + 2 * Width_furnace * Height_furnace + Lenght_furnace
* Width_furnace) * 1.1 * 5 * 10 ^ 3) / A_8
D(0) = (Reaction_shaft + Side_take_and_roof + Sides_and_bottom_heat) * Basic_conc / 1000
'CH4 content in natural gas
D(1) = (1 / 22.4) * CH4_NG / 100
'C2H6 content in natural gas
D(2) = (1 / 22.4) * C2H6_NG / 100
'C3H8 content in natural gas
D(3) = (1 / 22.4) * C3H8_NG / 100
'C4H10 content in natural gas
D(4) = (1 / 22.4) * C4H10_NG / 100
'SO2 content in natural gas
D(5) = (1 / 22.4) * S2_NG / 100
'Combustion Heat of Natural Gas
Heat_NG = D(1) * 194910 + D(2) * 347560 + D(3) * 497980 + D(4) * 647990 + D(5) * 70960
H_O2_air = 7.16 * (T_air + 273) + 0.5 * 10 ^ -3 * (T_air + 273) ^ 2 + 0.4 * 10 ^ 5 * 1 / (T_air + 273) - 2313     'Heat
capacity of O2
H_N2_air = 6.83 * (T_air + 273) + 0.45 * 10 ^ -3 * (T_air + 273) ^ 2 + 0.12 * 10 ^ 5 * 1 / (T_air + 273) - 2117   'Heat
capacity of N2
'Heat content of comb air for NG
O2_air_NG = 2 * D(1) + 7 / 2 * D(2) + 5 * D(3) + 13 / 2 * D(4) + D(5) - (1 / 22.4) * O2_NG / 100
Heat_NG_air = O2_air_NG * H_O2_air + (O2_air_NG * N2_air / O2_air) * H_N2_air
'Needed air for combustion NG
D(6) = O2_air_NG * 22.4                         'O2 in Air
D(7) = (O2_air_NG * N2_air / O2_air) * 22.4           'N2 in Air
D(8) = D(6) + D(7)                          'Total Air

'Waste gas from combustion of NG
D(9) = (D(1) + 2 * D(2) + 3 * D(3) + 4 * D(4) + (1 / 22.4) * CO2_NG / 100) * 22.4         'CO2 in waste gas
D(10) = (2 * D(1) + 3 * D(2) + 4 * D(3) + 5 * D(4)) * 22.4                                'H20 in waste gas
D(11) = D(5) * 22.4                                                                       'SO2 in waste gas
D(12) = D(7) + (1 / 22.4) * N2_NG / 100 * 22.4                                            'N2 in waste gas
D(13) = D(9) + D(10) + D(11) + D(12)                                                      'Total waste gas

H_CO2_gas = 10.57 * (T_gas + 273) + 1.05 * 10 ^ -3 * (T_gas + 273) ^ 2 + 2.06 * 10 ^ 5 * (1 / (T_gas + 273)) - 3936
H_H2O_gas = 7.3 * (T_gas + 273) + 1.23 * 10 ^ -3 * (T_gas + 273) ^ 2 - 2286
H_SO2_gas = 11.04 * (T_gas + 273) + 0.94 * 10 ^ -3 * (T_gas + 273) ^ 2 + 1.84 * 10 ^ 5 * (1 / (T_gas + 273)) - 3992
H_N2_gas = 6.83 * (T_gas + 273) + 0.45 * 10 ^ -3 * (T_gas + 273) ^ 2 + 0.12 * 10 ^ 5 * 1 / (T_gas + 273) - 2117
H_O2_gas = 7.16 * (T_gas + 273) + 0.5 * 10 ^ -3 * (T_gas + 273) ^ 2 + 0.4 * 10 ^ 5 * 1 / (T_gas + 273) - 2313

'Heat content of Waste Gas of NG
Heat_NG_waste = D(9) / 22.4 * H_CO2_gas + D(10) / 22.4 * H_H2O_gas + D(11) / 22.4 * H_SO2_gas + D(12) / 22.4 *
H_N2_gas

'Available Heat of Natyral Gas
D(14) = Heat_NG
D(15) = Heat_NG_air
D(16) = Heat_NG_waste

D(17) = Heat_NG + Heat_NG_air - Heat_NG_waste

Heat3 = D

End Function
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```
Function Heat(B_2, B_3, B_4, B_10, C_5, C_6, C_13, D_0, D_17, D_1, D_2, D_5, A_11, B_11, B_12, A_14, A_15, A_16,
A_17, B_14, B_15, B_16, O2_air, N2_air, D_3, D_4, D_9, D_12, O2_NG)
Dim E(21), O2_air_NG, D_10, D_11, H_N2_gas, H_O2_gas, Leakage_air_heat

'Inlet Heat
E(0) = B_2 + B_3 + B_4

'Outlet Heat
E(1) = B_10 + C_5 + C_6 + C_13 + D_0

'Heat deficiency
E(2) = E(1) - E(0)

'Natural Gas requirement, Nm^3/t.conc.
E(3) = E(2) / D_17

O2_air_NG = (2 * D_1 + 7 / 2 * D_2 + 5 * D_3 + 13 / 2 * D_4 + D_5 - (1 / 22.4) * O2_NG / 100) * 22.4

'Needed air for combustion NG
E(4) = E(3) * O2_air_NG                              'O2 in Air
E(5) = E(3) * (O2_air_NG * N2_air / O2_air)          'N2 in Air
E(6) = E(4) + E(5)                                   'Total Air


D_10 = (2 * D_1 + 3 * D_2 + 4 * D_3 + 5 * D_4) * 22.4
D_11 = D_5 * 22.4


'Waste gas from combustion of NG
E(7) = E(3) * D_9                        'CO2 in waste gas
E(8) = E(3) * D_10                       'H20 in waste gas
E(9) = E(3) * D_11                       'SO2 in waste gas
E(10) = E(3) * D_12                       'N2 in waste gas
E(11) = E(7) + E(8) + E(9) + E(10)       'Total waste gas

'Total needed air
E(12) = A_11 * O2_air / 100 + B_11 + E(4)     'O2 in total needed air
E(13) = A_11 * N2_air / 100 + B_12 + E(5)     'N2 in total needed air
E(14) = E(12) + E(13)                    'Total Air

'Total waste gas
E(15) = A_14 + B_16 + E(9)               'SO2 in waste gas
E(16) = A_15                             'O2 in waste gas
E(17) = A_16 + B_12 + E(10)              'N2 in waste gas
E(18) = A_17 + B_15 + E(8)               'H2O in waste gas
E(19) = B_14 + E(7)                      'CO2 in waste gas
E(20) = E(15) + E(16) + E(17) + E(18) + E(19)     'Total waste gas

Heat = E

End Function
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