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Magisterarbeit

Comparison of Several Furnace Concepts for the Pyrometallurgical Refining of Secondary Copper

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Kurzfassung

Gegenüberstellung von Eigenschaften des industriellen Ofen zur pyrometallurgischen Feuerraffinierung von sekundärem Kupfer

Ziel dieser Diplomarbeit ist es, einen Überblick über die relevanten Aspekte der Metallurgie des sekundären Kupfers zu geben, im Besonderen in Hinblick auf technische Bauart und prozessbezogene Parameter bei Drehrohr und Kippbaren Öfen.

Zu Beginn wird das Inputmaterial, z.B. Schrott, mit seinen Eigenschaften und grundsätzlichen Bedingungen für die Verbrennung sowie das Outputmaterial, das metallische Produkt des Prozesses, behandelt. Verschiedene Sorten von industriellen Öfen für die Feuerraffinierung von Schrott werden aufgezeigt, ihr Aufbau und ihr normaler Betrieb.

Die Metallurgie der Feuerraffinierung in Anodenöfen wird anhand der prozesstechnischen Einstellungen und der Logistik diskutiert, anschließend relevante Konzepte zum Einsatz von schützenden und feuerfesten Materialien beschrieben. Die Literaturrecherche wird ergänzt von praktischen Daten, welche von bereits im Betrieb stehenden Öfen stammt. Der Wirkungsgrad des Prozesses in den Anodenöfen wird gezeigt, weiter wird die Berechnung des Inputs an fossilen Brennstoffen anhand eines Beispiels demonstriert. Massen- und Energiebilanz wird für jede Produktionsstufe berechnet.

Drehrohrofen und kippbare Ofen, beide Anodenöfen, werden einander in Bezug auf Prozessmerkmale und Energieverbrauch gegenübergestellt. Schwierigkeiten, die mit dem Betrieb dieser Öfen verbunden sind, werden gezeigt. Ebenso wird auf das Verbesserungspotenzial und die dazugehörigen Optimierungsmethoden eingegangen.

Die Taguchi-Methode wird herangezogen und reduziert durch Zuhilfenahme statistischer Daten über die Variablen die notwendigen Experimente auf ein Minimum. Diskutiert wird außerdem der Einfluss der Reduktionsdüsen.

Das Hauptziel dieser Arbeit ist, eine Grundlage für weitere Untersuchungen auf diesem Gebiet, wie z.B. Simulationen der physikalischen Abläufe in den verschiedenen Raffinierungsprozessen, zu schaffen.

Abstract

Comparison of Several Furnace Concepts for the Pyrometallurgical Refining of Secondary Copper

The objective of this thesis is to review relevant aspects of the secondary metallurgy of copper, described in more detailed on behalf of the technical architectures and the operation parameters of the Rotary Furnace and the Tilting Furnace.

At first the input material i.e the recycling scrap characteristics and their general requirements of being processed, as well as the output material i.e the metallic product of the processes is discussed. Several types of furnaces for the pyrometallurgical treatment of recycling scrap are shown, their construction concept and typical processes.

The metallurgy of fire refining in anode furnaces is described on behalf of the furnace operational settings and process logistics. Relevant design concepts, construction features of shell and refractories are layed down. The documental research is complemented with practical data, taken from in-operation furnaces. The degree of efficiency of the anode furnace process is shown and the fossil fuel input required id calculated in an typical example. Mass and energy balances are treated in the sequences of operation are described.

Two different anode furnaces are compared: Tilting Heart Furnace and Rotary Furnace, in terms of operation features and energy consumption. Some of the most representative difficulties in connection with the operation of the furnaces are identified. It is also intended to allocate optimisation potential of anode furnaces as well as to identify a suitable optimisation method.

The concept of Taguchi’s method is proposed to deal with the problem of the numerous operational and design variables of the process and the furnace itself in order to minimise the number of experiments which are required to identify the impact of each variable. The impact of the refining nozzles on the furnace performance is discussed.

The final intention of this work, is to prepare the way for further investigations, which may consists of simulations of the phenomena in this particular type of processes and furnaces .

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Chapter 1 Background of Secondary Metallurgy Copper and Copper Scrap Characteristics

Copper’s natural occurrence is both in sulphides and oxide compounds. Fe, Zn, Pb, Ni, Mo are important companions in this ores. 85% of the world copper production is from sulphuric ores with 0.4 to 1% of Cu content. [2]

1.1 Type of Recycling Materials

Copper is a material which can be used over and over again, as it is impossible to tell recycled copper from primary copper. This means that resources can be conserved and energy saved at the same time. Recycling is effected by a combination of pyrometallurgical and hydrometallurgical (electrorefining) processes, in which base and noble impurities are removed.

More than 99% of copper is used in metallic form as copper metal or copper alloy. The principal advantages of recycling copper are:

(a) It permits the earth's copper resources to be consumed at a slower rate.

(b) It requires 5 to 50% of the energy required for extracting copper from ore, depending on the purity of the scrap.[3]

(c) It turns scrap into useful products rather than having it occupy space in waste disposal sites.

(d) It avoids some of the environmental problems of mining, milling and smelting, e.g. solid waste disposal and SO_2 control.

The different kinds of scrap are classified by their purity, their chemical composition, or by their origins, which establishes their physical condition.

Most copper scrap, however, is alloy scrap such as brass, bronze or nickel silver. If this scrap is very pure, it can be directly melted in alloy form.[1]

Besides these types of scrap, which are clearly defined by their origin, there are many kinds of mixed scrap such as scrap copper, which may be contaminated with plastics or organic materials.

If primary materials are charged together with the scrap, they often contain a high proportion of oxides and therefore have to be melted down under reducing conditions in shaft- or electric furnaces.

Scrap processing gives rise to many intermediate and by products such as flue dust, metal-rich slag, ash or mattes.

A widely used classification of copper scrap is:

(a) Primary Scrap:

This type of scrap is a residual material from several processing steps inside the copper plant and has a high copper content. For this scrap, a pyrometallurgical process (re-melting) is required.

(b) Secondary Scrap

- New Scrap:

This sort of scrap comes from the construction industry, the electrical industry and the automobile industry. The copper and its alloys are to be directly melted if they are very pure. The copper content is similar to new scrap. For this scrap, a pyrometallurgical process (re-melting) is required.

- Contaminated Scrap:

With most contaminated scraps, at least a pyrometallurgical refining is necessary, depending on . Contamination may be metallic (f.i. iron, …) or organic substances (f.i. cables, motor parts, switch gears,…). This sort of materials can be subdivided in subgroups:

Pyrometallurgical processes (re-melting and refining) and a hydrometallurgical process (electrorefining) is required.

Scraps are usually sized by mechanical cutting and pressing into bundles. The scrap also may be pre-processed by magnetic properties or density variations. Sometimes, thermal pre-treatment is inevitable to burn organic substances.

(c) Special Scrap Materials:

Copper containing copper-oxide materials developed from chemical processes, refining procedures, slags, ashes and filterdusts may also be fed to the recycling process of copper scrap.

In addition, more and more special materials or waste products are appearing, which require special processing routes. Examples of these are cable scrap, electronic scrap with its extremely complex composition, etching solutions from the circuits board industry, electroplating sludges or catalyst residues. [4]

1.2 Processing of Copper Scrap

Emphasis is mainly taken on pyrometallurgical processes. With only a few exceptions, e.g. leaching of intermediate products such as speiss and dross, hydrometallurgy has not yet become established as a route for copper production from secondary materials. Only in production of copper salts does hydrometallurgy play a major role.

The reasons are that:

- Copper scrap is generally a compact material and is therefore unsuited to direct hydrometallurgical processing and
- The final stage of copper refining, electrorefining, requires anodes which have been produced by pyrometallurgical means.

1.2.1 Scrap Cooper processing- general

The copper content is often over 90%. The material is melted in an anode furnace or a converter, depending on its impurity content, and then electrorefined. A particularly effective and energy-saving way of recycling scrap copper is to process it in a smelter, which also produces primary copper and has a converter where copper matte is blown [4].

1.2.2 Alloy scrap

Alloy scrap is based on copper alloyed in particular with zinc, tin, nickel or lead. Purely mechanical separation is not possible. The most common alloys are brass, bronzes and nickel silver. Brass mainly contains zinc in addition to some 50-90% copper.

A large proportion of the brass to be recycled can be directly remelted in the semi-finished products plant. Nickel silver comprises alloys containing, besides copper as the main constituent, nickel and zinc. Bronzes mainly contain tin in addition to copper, also zinc and lead.

Alloy scrap is almost exclusively processed in a converter, as the baser impurities are removed from the copper by oxidation and volatilization. However, processes for recovering the considerable proportions of alloying elements must also be available.

The scrap is first melted with coke and blown in an oxidising atmosphere in a scrap metal converter. This is usually done in a small converter that enables batch-wise processing of small quantities.

At a temperature of around 1200°C and by blowing in partly oxygen-enriched air, volatilization reactions for the more easily volatilized elements such as zinc and lead take place as well as oxidation reactions.

The slag from the process is copper-rich and is processed in a shaft or electric furnace. The flue dust is treated separately by melting in a reducing atmosphere in a rotary furnace with the addition of coke. The zinc is volatilized and after reoxidation in the gaseous phase, a marketable zinc oxide with a purity of around 95% is recovered. The metallic phase contains a tin-lead alloy, which is marketed as a solder under the name "mischzinn"[4].

1.2.3 Processing Methods of Complex Materials

The standard method of smelting complex raw materials is the shaft furnace process. For charging into the shaft furnace, the generally particulate materials are pelletized or briquetted.

Coke is added as reducing agent and limestone, iron oxide or sand as slag-forming fluxes. As a wide variety of materials are processed in shaft furnaces, it is very important to establish the correct mixture in such a way that a maximum metal recovery rate is achieved for the lowest possible loss of metal in the slag.

As not all the impurities accumulate in the slag or the flue dust but are also dissolved in the copper; a relatively impure copper with a copper content of around 75-80% is obtained.

This so-called "black copper" has to be refined in a converter. If materials containing a large amount of lead in addition to copper are to be processed, sulphur must be present. It "homogenises" the otherwise poorly miscible elements lead and copper through formation of copper-lead matte.

A major drawback of the standard process is the large volumes of off-gas, which necessitate a difficult and complex off-gas treatment process, and the poor external sealing of the system.

The Belgian firm Metallo-Chimique employs top-blown rotary converters (TBRCs) to process complex scrap. The advantage of the TBRC is that the metallurgical conditions can be geared to the different feed materials by adding different fluxes and reducing/oxidising agents. [4]

1.2.4 Oxide and Fine-Particle Secondary Materials

In addition to the types of scrap described above, there are other materials, mostly of low quality, which account for 1-2 % *of* total copper production. These include:

- Dross

  Dross forms when copper or alloys are melted down. Contact between the molten metal and air or oxygen results in the formation of metal oxides on the surface of the melt which have to be tapped off at intervals. As the oxides are viscous, droplets of metal become trapped in the dross and are often difficult to remove.

- Filter dust

  Again during melting of copper and alloys or smelting of primary materials, some of the copper is entrained in the stream of off-gas as oxide powder and collects in the off-gas cleaning system, where the oxide may be converted to sulphate by means of secondary reactions in the presence of SO_2 and air.

- Catalysts and carbon brush dust

  Copper-based catalysts are used in certain chemical reactions. They are recovered as secondary materials from time to time. Besides copper, they usually contain carbon, which has become deposited on the copper during the reaction. Another material consisting of carbon and copper is carbon brush dust from production of carbon brushes.

- Electroplating sludge

  In electroplating, the brightening chemicals are consumed, so the electroplating solution has to be discarded and its metal content precipitated. As this alkaline precipitation leads to the formation of hydroxides or basic salts, a sludge often containing over 50% water is obtained. Electroplating sludges frequently contain nickel and zinc as well as copper. Similar sludges are produced in alkali-based effluent treatment [6].

- Precipitated copper

  In converting copper-bearing solutions with ferrous scrap, the copper is precipitated and finally divided into metallic form and the baser iron is dissolved.

Apart from these materials, there are amounts of relatively low-quality copper-bearing residues whose complexity and copper content determines whether or not they can be profitably recycled [6].

Processing of the complex, often oxide-based, secondary copper-bearing materials requires, in addition to re-melting, reduction to a metallic intermediate product which can be refined in a converter. Reduction is generally brought about through the addition of carbon or carbon bearing secondary materials, but can also be accomplished by adding ferrous scrap.

1.2.5 Cable Scrap Processing

A large proportion of copper-bearing scrap stems from cable products. Where as the plastics content was formerly burned off, which caused serious environmental problems, nowadays cable is separated by mechanical means alone. It is charged into granulators where the cable is not only shredded in multiple stages, but the bond between the plastic covering and the copper is dissolved at the same time.

The separation is very efficient. The metal recovery rate is approx. 95% and purities of more than 99.5% being achieved in the copper fraction. The plastic can be re-used for making flowerpots or lane markings on motorway construction sites [7].

Problems are presented by lead sheathed cable. The lead sheath generally has to be removed manually before shredding and separation can be carried out.

1.2.6 Electronic Scrap Processing

Practically all appliances contain electronic circuits, when they are scrapped. Therefore, electronic components (mostly boards) will increasingly be sent for recycling.

The chemical composition and physical condition of this material make it very difficult to process and sample. Nevertheless, it pays to reprocess this material, as it contains not only around 20% copper but also gold, silver and palladium in amounts of up to 1,000 g/t [7].

The proximate analysis in the Table 1 shows, that the metals are tightly packed together, with plastics, optical fibres and ceramics.

Table 1 Composition of electronic boards [4]

Composition of electronic boards			
Organic Materials (max 25%)			
Plastics	(Polyethylene, polypropylene, PVC, Polyester, phenolic resins, polycarbonates)		< 25%
Additives			< 5%
Oxide materials (max 35%)			
Silicon Dioxide	15%	Alkaline (earth)Oxides	6%
Aluminia	6%	Other ceramics	3%
Metals (max 50%)			
Copper	20%	Zinc	1%
Iron	8%	Antimony	0.4%
Nickel	2%		
Tin	4%	Gold	500 g/t
Lead	2%	Silver	1000 g/t
Aluminium	2%	Palladium	50 g/t

A reprocessing method has to meet the following requirements:

- A high recovery rate for the valuable metals such as copper, silver, gold and platinum.
- Safe, environmentally harmless disposal of difficult-to-handle constituents such as halogens, plastics and heavy metals.
- Reliable valuation of the precious metal content.

Electronic scrap can be processed in different ways:

1.2.6.1 Selective leaching

If it is a matter of recovering gold and silver from the scrap, a selectively leaching can be used by treating the components with an alkaline cyanide solution and adsorbing the metals on activated carbon. The rapid recovery of the metal contrasts with a low yield, as only the proportion of the precious metal that is exposed to chemical attack is leached and not the proportion of the metal that is trapped inside a plastic matrix.

1.2.6.2 Mechanical pretreatment

A major problem is the plastics content of the electronic scrap. To separate out the valuable metals, mechanical pretreatment can be attempted. By means of crushing and physical separation steps, a high-metal fraction and a low metal fraction mainly consisting of plastic are obtained. However, complete separation is not achieved.

A prerequisite to achieve the major benefits, is that the complex plastic, which contains not only thermosetting plastics but also ceramics, organic additives, glass fibres and particles of metal, can be reused [8].

1.2.6.3 Incineration

Another way of removing the plastics content of electronic component scrap is to incinerate it. Its halogen content and the risk of dioxin formation mean that a temperature of over 1000°C, an additional post-combustion chamber and a complex flue gas cleaning system are required.

The incineration residue contains a high proportion of oxides and has to be melted under reducing conditions together with another copper-bearing material as a collector.

The drawbacks are the high off-gas rates and the pre-treatment of a relatively large amount of metal in the flue dust. The incineration is also difficult to control due to the rapid decomposition which takes place at over 200°C [9].

1.2.6.4 Pyrolysis

In pyrolysis, the plastic is decomposed at approx. 400-600°C in a hermetically sealed furnace. The pyrolysis gases mainly contain hydrocarbons and halogens and can be post-combusted in a separate combustion chamber.

The advantages of pyrolysis are the small amounts of flue gas, which can be effectively post-combusted, and the ease of control of the reaction, as pyrolysis is an endothermic process.

It's drawbacks are the incomplete removal of the halogen content of the feed material and the expensive hermetic scaling of the system in order to prevent the risk of an explosion and emissions of foul-smelling pyrolysis oils.

1.2.6.5 Processing in a converter

Processing in a converter, attempts to destroy the plastic content and collect the metals are in a copper matrix in one step. This however, is only achievable by firms who process large quantities of copper from other sources as well as electronic scrap.

A highly advantageous and environmentally friendly method of processing is to charge this scrap into a converter for production of primary copper. There the necessary high post-combustion temperatures are attained and a sophisticated off-gas cleaning system, installed for the demands of sulfuric acid production, minimizes emissions.

With optimum process control, over 90% of the precious metal content can be directly incorporated in the copper matrix, which can then be further processed as anode copper [8].

Comprehensive studies have shown that the amount of dioxin formed in this process is very low. If the volumes of material that have to be landfilled when employing leaching and mechanical pretreatment are taken into account, processing in a converter is the most environmentally friendly process currently available for processing computer scrap.

One drawback is the limited capacity. The quantity of electronic scrap that can be processed is tied to the converter capacity (charging, plastics content), the incoming volume of copper matte and the quantity and composition of the slag. Therefore only certain quantities and types of electronic scrap can be processed by this method.

1.2.7 Motor vehicle scrap

Although there is only 10 kg of copper on average in an old car and it is thus not one of the main constituents, it is nevertheless very important to the processing concept as it interferes with the processing of the steel from the car and lowers the quality of the steel produced.

This was one of the main reasons for the introduction of shredder technology in the sixties. Separation of the copper-bearing materials is carried out in the same way at every car scrapping and shredding firm. Large components such as radiators or generators are removed and the car is then cut up in the shredder and magnetically separated into ferrous and non-ferrous materials [4].

The non-ferrous metal fraction is often still separated by hand into the various alloys. Copper from dismantled cars is recovered in a wide variety of forms:

- As alloy scrap such as brass or bronze in radiators.
- As copper granules from cable stripping.
- As copper/iron scrap from the shredder, and, in future, as circuit boards from the car's electronic system.

These materials can be processed in anode furnaces, scrap metal converters or shaft/electric furnaces, depending on their composition.

In the recycling methods described so far, the emphasis has mainly been on pyrometallurgical processes. With only a few exceptions, e.g. leaching of intemediate products such as speiss and dross, hydrometallurgy has not yet become established as a route for copper production from secondary materials.

The reasons are, firstly, that copper scrap is generally a compact material and is therefore unsuited to direct hydrometallurgical processing and, secondly, that the final stage of copper refining. electrorefining, requires anodes which have been produced by pyrometallurgical means.

So copper is mainly recycled by pyrometallurgical methods. Only in production of copper salts does hydrometallurgy play a major role.

1.3 Description of the Furnaces used for pyrometallurgical processing of Copper and Converters used for Refining

1.3.1 Electric furnace

1.3.1.1 Description

The electric matte-smelting furnace is an electrically heated hearth furnace that performs the same functions as the reverberatory furnace(Figure 1). It smelts dried or roasted Cu-Fe-S concentrates and produces molten matte (50-60% Cu), molten slag and SO_2-bearing off-gas [5].

It also treats molten recycle converter slag for Cu recovery. The heat for the operation of the electric furnace is provided by passing electric current through molten slag between carbon electrodes. Their principal advantages over the reverberatory furnace were seen to be:

(a) A smaller production of off-gas due to the near absence of combustion gases in the furnace;

(b) A reasonable SO_2 concentration in the off-gas (5% SO_2) volume due to this small off-gas production.

Both advantages are useful from the $S0_2$ capture point of view. Also, electricity is occasionally a cheaper and more reliable source of energy than fossil fuel. The electric furnace is used extensively for recovering Cu from slags.

1.3.1.2 Construction Details

Electric furnace smelting is a submerged electrode process. The heat for heating and melting is generated by the passage of electric current through molten slag between submerged carbon electrodes. Recent Cu and Cu-Ni smelting furnaces are rectangular with six equispaced in-line self-baking carbon electrodes.

Dry charge (dry or roasted concentrate + flux + reverts) is added to the top of the slag through roof ports. Some Fe and S in the charge is oxidized by inleaked air when the concentrate falls into the furnace and while it rests on the surface of the blanket. This results in a matte significantly richer in Cu than the original concentrate.

The inleakage of air is due to a furnace draught of 1 to 3 mm water gauge (1 to 3 x 10^4 atmospheres) which keeps SO_2 gas from escaping the furnace into the workplace. The air enters through openings in the furnace structure, e.g. around the electrodes and charge ports.

The electric furnace is charged with dry materials. Charging of moist materials is avoided because moisture can occasionally cause steam or hydrogen explosions [10].

Molten converter slag is always recycled to the electric furnace for Cu recovery. It is poured from ladles down an inclined launder (10° slope) into the furnace. Care is taken not to impact the ingoing slag against the electrodes. Electric furnace slags typically contain 0.5 to 1.3 % Cu. They are tapped intermittently and discarded without further treatment. The furnace's molten matte is also tapped intermittently and sent forward to converting [5].

Electric-furnace smelting is started by placing slag, coke and steel beams or cables on the furnace hearth and in piles around each electrode. The furnace is then gently heated with fossil fuel burners to 'bake out' and heat the refractories. Voltage is then applied between the electrodes initiating current flow through the slag, coke and steel. The voltage and current are gradually increased until a pool of slag is formed, whereupon normal smelting is begun. Smelting can also be started with molten slag if another smelting operation is nearby.

The electric furnace sits on steel base plates (2.5 cm thick) seated on concrete or brick piers. The bottom of the furnace is cooled by natural convection of air beneath the furnace. The air can also be blown with fans if additional cooling is required.

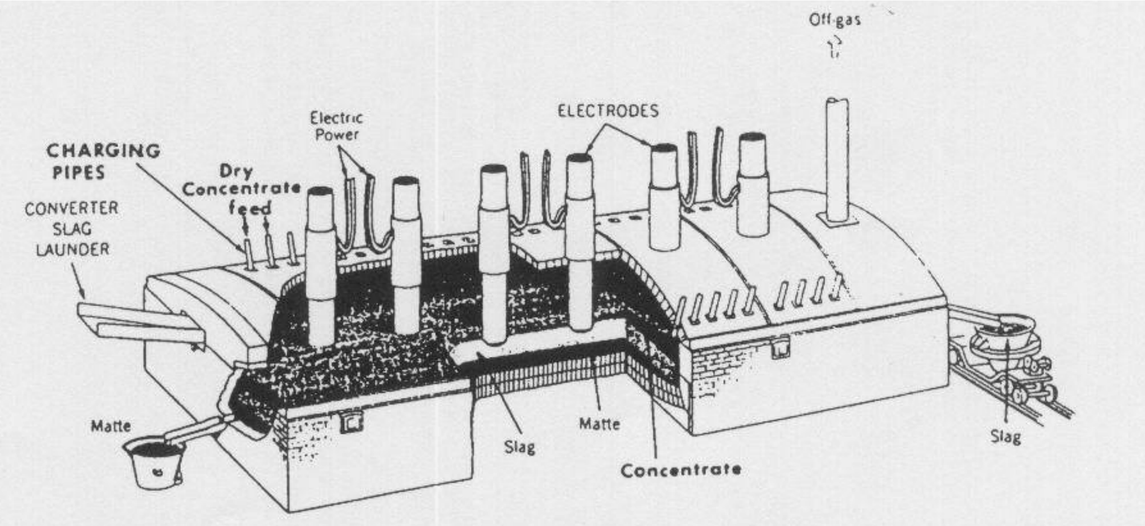
The roof and walls of the furnace are Magnesite or Chrome-Magnesite brick. The hearth is an inverted arch of Magnesite or chromemagnesite refractory backed below with insulating firebrick.

Recent Ni-Cu electric smelting furnaces are encased in a 2.5 cm thick welded steel shell. The furnace structure is kept under compression with a set of solid vertical beams and horizontal spring-loaded tie rods [9].

The pressure on the tie rods is kept between 25 and 150 psi during heat-up and operation to contain refractory expansion. Some expansion is reduced by inserting 'expansion papers' between courses of refractory bricks during construction. Refractory temperatures are monitored by thermocouples during start-up and operation.

Electric furnaces are operated with a thick (1.5 m) layer of slag. It permits the electrodes to be moved up and down for precise power and temperature control.

Figure 1 Electric Furnace [5]



1.3.2 Isamelt Furnace

1.3.2.1 Description

Isamelt smelting entails dropping moist pelletized solid feed into a tall cylindrical furnace while blowing O_2-enriched air through a vertical lance into the furnace's slag bath (Figure 2). The products of the process are matte/slag emulsion and a strong SO_2-bearing off-gas.

The emulsion is tapped periodically into an electric or fuel-fired settling furnace for matte/slag separation. The settled matte (58% Cu) is sent to conventional converting. The slag (0.6-0.7% Cu) is discarded [11].

The off-gas (35% SO_2 volume) is drawn from the top of the furnace through a vertical flue. It is passed through a waste heat boiler, gas cleaning and on to a sulfuric acid plant (or to the atmosphere). A small amount of oxygen is blown through the side of the smelting furnace (about half way up) to ensure that sulfur leaves the furnace as SO_2 rather than S_2, to avoid sulfur condensation in the gas cleaning system [12].

Most of the energy for smelting comes from oxidation of the concentrate charge. Additional energy is provided by combusting coal fines in the solid charge and oil or gas blown through the vertical lance.

Steady state operation consists of a continuous feeding of solid charge through the roof feed port and steady blowing of enriched air into the molten slag. The furnace is computer controlled to give a prescribed concentrate smelting rate while producing matte and slag of specified composition and temperature.

Matte/slag temperature is sensed by thermocouples imbedded in the furnace walls. It is controlled by adjusting the rate at which fossil fuel is supplied to the Isamelt lance. Matte and slag compositions are determined by X-ray fluorescence analysis of samples from each matte/slag tap.

1.3.2.2 Construction Details

The Isamelt furnace is a vertically-aligned steel barrel 13 m high and 3.5 m diameter. It smelts 1500 to 2000 tonnes of concentrate per day. It is lined inside with water-cooled copper slabs and chrome-magnesite refractory and Its roof can also be lined with water-cooled steel panels.

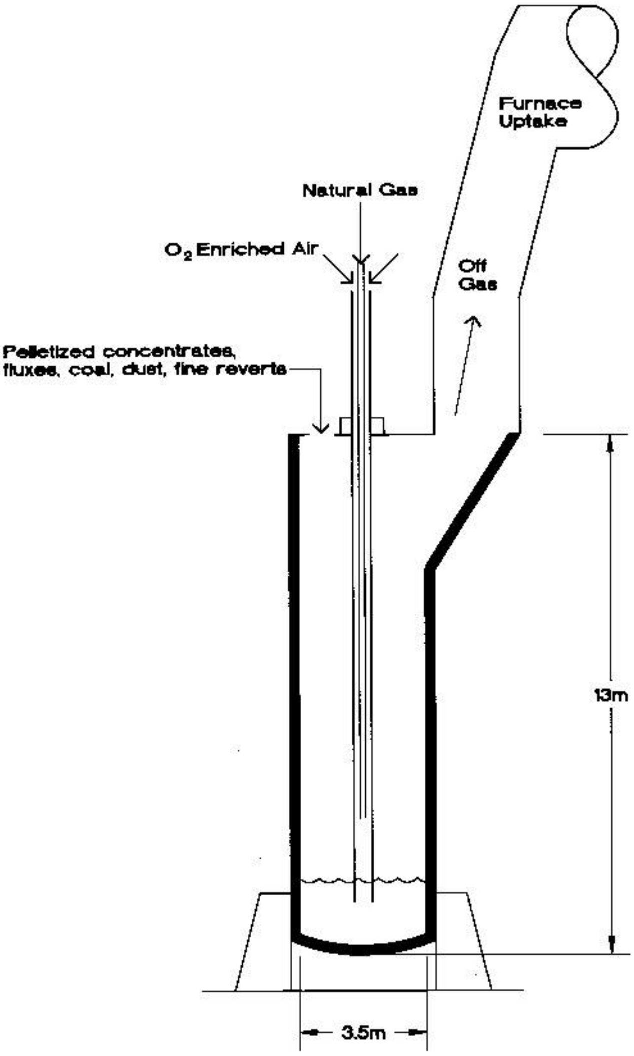
The Isamelt lance consists of a stainless steel outer pipe (1/2 m diameter) for O_2-enriched air and a steel inner pipe for oil or natural gas. The outer pipe is always immersed 1/3 m in the smelting furnace's slag. The inner pipe terminates about 1m above the slag surface [12].

The lance is cooled by swirling its O_2-enriched air in the annulus between the pipes. The swirled gas extracts heat from the outside pipe and causes a protective layer to freeze on the pipe surfaces. The swirling is created by a swirl plate in the annulus.

The immersed lance tip slowly erodes away. The lance is lowered to compensate for this erosion. It is replaced when approx. 1m has eroded (about every week). The old lance is removed and refurbished for future used by welding several 1 m sections of pipe to its bottom tip.

Use of cesium stainless steel pipe for the replaceable lance-tip sections has slowed lance erosion, increasing on-line smelting time.

Figure 2 Isamelt Furnace [5]



1.3.3 Vanyukov Furnace

1.3.3.1 Description

The smelting Vanyukov furnace is rectangular with tuyeres along both sides (Figure3), these tuyeres cannot be rotated out of the bath for maintenance and repair. The stationary nature of the Vanyukov furnace makes SO_2 capture simple and efficient.

Vanyukov matte smelting entails:

(a) Charging moist concentrates through two roof ports in the Vanyukov furnace.

(b) Blowing highly O_2-enriched air (70-90% O_2 volume) through tuyeres into the slag layer.

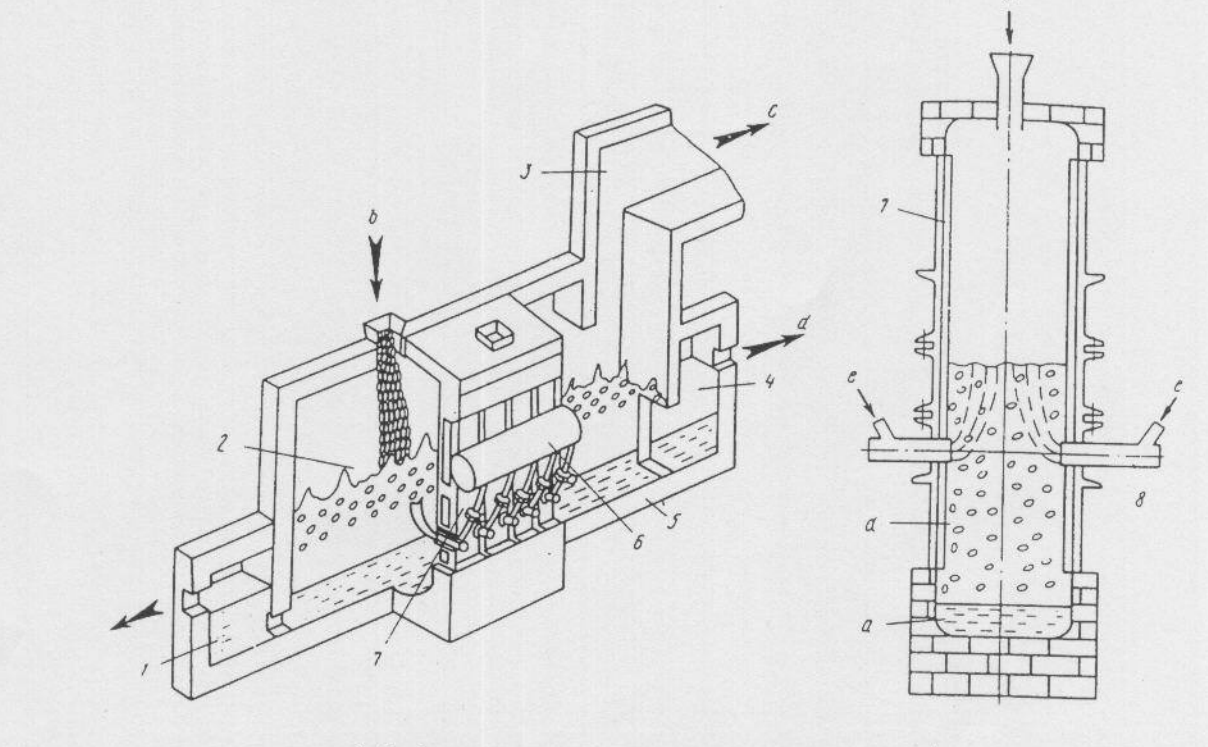
Its products are conventional: matte (50% Cu); slag (1.5-2% Cu); and off gas (30% SO_2 volume). The matte and slag exit continuously through syphons at opposite ends of the furnace. The matte is sent to conventional Peirce-Smith converting [6].

The slag flows into a small electric slag-cleaning furnace. It is discarded from the electric furnace at 0.6-0.7% Cu. Settled electric-furnace matte is sent to converting. The off-gas is drawn through an uptake at one end of the furnace roof. It is cooled, cleaned and sent to an acid plant or to the atmosphere [4].

1.3.3.2 Construction Details

A 10 m long x 2 m wide x 6 m high furnace smelts 1500 tonnes of concentrate per day. The furnace operators indicate that 2500 tonnes per day of concentrate should be possible with appropriate gas and slag handling capabilities. Campaign life is reported to be 10 to 12 months [6].

Figure 3 Vanyukov Furnace [20]



1.3.4 Blast furnace (Shaft Furnace)

1.3.4.1 Description

The blast or shaft furnace is well-suited for smelting high-grade, lumpy copper ore. If only fine concentrates are available, they must first be agglomerated by briquetting, pelletizing, or sintering. Due to this additional step and its overall low efficiency, in the last decades the blast furnace lost its importance for primary copper production [21].

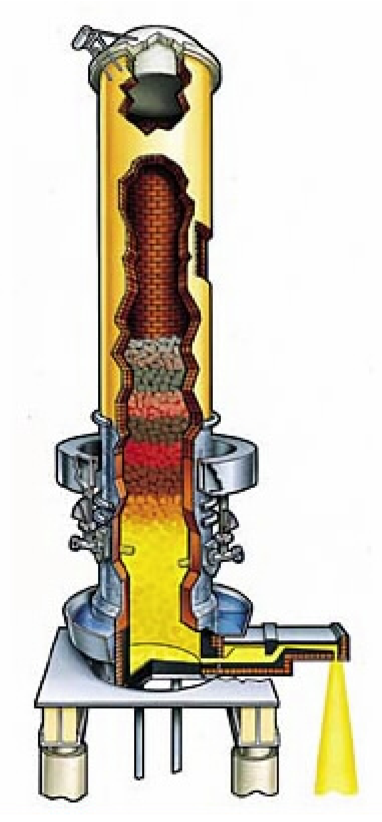
Smaller types of blast furnaces (Figure 4), however, are used to process such copper-containing materials as intermediate products (e.g., cement-copper or copper-oxide precipitates), reverts (e.g., converter slag, refining slag, or flue dusts), and copper-alloy scrap.

The furnace is charged with alternate additions of mixture (copper-containing materials and accessory fluxes such as silica, limestone, and dolomite) and coke (which serves as both fuel and reducing agent).

The usual mode of operation is reducing smelting, which yields two main products. Sulfide ores are used to produce a matte (40-50 wt% Cu) and a disposal slag (ca. 0.5 wt% Cu). In contrast, oxide ores are processed directly to impure black copper (~95 wt% Cu) and to a copper-rich slag [6].

The two ore types can be smelted together to produce matte and a slag with low copper content. Another product is top gas, which contains flue dust. Ores that contain high concentrations of arsenic and antimony also form speiss, which is difficult to decompose.

Figure 4 Shaft furnace [21]



1.3.4.2 Construction Details

The construction of the furnace is basically related to that of the iron blast furnace, but there are considerable differences in design, especially in size and shape.

The copper blast furnace is lower and smaller, and its cross section is rectangular. Recent developments in the steel industry have been adopted, including use of preheated air (hot blast), oxygen-enriched air, and injection of liquid fuels. [6]

There are three zones in the furnace:

1) The heating zone (the uppermost), where water evaporates and less stable substances dissociate.
2) The reduction zone, in which heterogeneous reactions between gases and the solid charge take place.
3) The smelting zone, where the liquid phases react.

1.3.5 Noranda and Teniente processes

The Noranda and Teniente smelting processes use large, 5 m diameter x 20 m long cylindrical furnaces. They provide O_2 for concentrate oxidation by injecting O_2-enriched air into the furnace's molten matte layer through submerged tuyeres along the length of the furnace. Solid charge is thrown into the furnace through an endwall or blown in through some of the tuyeres.

Most of the energy for heating and melting the charge comes from Fe and S oxidation. The Noranda process increase this heat by including coal in the charge and by burning natural gas. The Teniente process usually augments this heat by periodically adding molten lowgrade matte to the furnace as 'fuel'. Oxidizing this molten matte to super high grade matte provides extra heat for the process[5]

1.3.5.1 Noranda Process Description

The Noranda furnace is a horizontal steel barrel lined inside with about 40 cm of chrome-magnesite refractory. The furnaces at Noranda, Quebec and Salt Lake, Utah are 5 m diameter x 21 m long inside the 5 cm thick steel shell. The process entails:

(a) Continuously throwing coal and pelletized concentrates, flux, revert materials and scrap into one end of the furnace from a high-speed slinger belt.

(b) Blowing O_2-enriched air (40% O_2 volume) into the furnace's molten matte layer through 20 tuyeres, of 45 cm diameter, along the back of the furnace.

(c) Intermittently tapping slag from one end of the furnace and high grade matte from the bottom.

(d) Removing off-gas through a large mouth at the top of the furnace, into a water-evaporation gas cooler and then into electrostatic precipitators and sulphuric acid plant.

The process is continuous. The furnace always contains a layer of matte and, above it, a matte/slag mixture. The liquids above the tuyeres are violently turbulent due to rapid injection of air and oxygen through the tuyeres. The tuyeres are periodically cleared by pushing a steel bar through them.

The furnace is equipped with an automatic rotation mechanism. It rolls the tuyeres above the liquids in the event of a blower stoppage. The furnace can also be rolled out under manual control when smelting must be interrupted for maintenance or repair.

The new feed to the Noranda furnace at Noranda, Quebec includes up to 20% scrap. The scrap includes Cu, Ag and Au-bearing slag, ashes, residues (up to 14% moisture content), wire cables, precious metal ingots, jewelry, telephone scrap, automobile parts and precious metal computer and electronic scrap. The turbulence in the Noranda furnace causes these materials to be rapidly melted and their Cu, Ag and Au to be rapidly absorbed in the matte. Also, the high temperature of the process and the intensity of the smelting causes potentially harmful organic compounds to be oxidized to CO_2 and H_2O [15].

The Noranda process has proven to be an excellent tool for smelting large quantities of diverse scrap. This is due to its turbulent nature, its simple feed system and its ability to handle large (-10 cm) and moist materials [16].

1.3.5.2 Teniente Process Description

The Teniente process is similar to the Noranda process. Significant differences are:

(a) Molten 'seed' matte, usually from a reverberatory furnace in the smelter, are periodically added to the Teniente furnace as 'fuel' for concentrate smelting.

(b) Dry concentrate is injected through some of the tuyeres while moist concentrate is being charged above the bath.

(c) No coal is included in the furnace charge.

(d) 72 to 77% Cu matte is tapped through the feed end of the furnace rather than through the bottom.

The Teniente process developed from the practice of adding concentrate during Peirce-Smith converting in order to increase the smelting capacity of an existing smelter without constructing a new smelting furnace and to make use of the excess heat developed [5].

The use of 'seed' matte has been eliminated entirely in several Teniente furnaces, these furnaces inject almost all their concentrate (dry) through their tuyeres. Solid feed (concentrate, flux, recycle materials) is blown continuously onto the bath surface via a high-pressure 'Garr' gun. Most furnaces also continuously blow dry solid feed through four or five specialized tuyeres. Molten seed matte is added intermittently from ladles through the furnace mouth[13].

Smelting is begins in a cold furnace by preheating it with fossil fuel burners and adding molten matte from a reverberatory furnace. O_2-enriched air is then blown and the furnace is rotated to lower the tuyeres into the matte. Once oxidation and heat generation have begun, concentrate and flux feeding starts and smelting begins. The feed rate is gradually increased until full production is attained.

The principal product of the process is super high grade matte, 72 to 77% Cu. It is tapped into ladles through one end of the furnace and craned to Peirce-Smith converters for converting to blister copper. Slag is tapped from the opposite end of the furnace and sent to a slag cleaning process [18].

1.3.5.2.1 Construction Details

Teniente furnaces are 4 to 5 m in diameter and 14 to 22 m long (Santander et al., 1991). The furnace barrels are steel, 5 cm thick, lined with about *1/2* m of magnesite-chrome refractory. They have 30 to 50 tuyeres (5-6 cm diameter) along the back through which air or O_2-enriched air blast (30-32% O_2 volume) is blown.[17]

1.3.6 Outokumpu furnace (flash furnace)

1.3.6.1 Description

Operation of an Outokumpu flash furnace is begun by heating it with oil or natural gas burners at the top of the reaction shaft and around the settler walls (Figure 5). The heating is carried out carefully to prevent uneven expansion and breakage of the refractories. About one week is taken. Once the furnace is at smelting temperature, fossil fuel combustion is replaced by concentrate oxidation until full production is attained.

Cooper flash smelting entails blowing air, oxygen, dried Cu-Fe-S concentrate and silica flux into a 1250°c heart furnace. Once in the hot furnace, the sulphide mineral particles of the concentrate ($CuFeS_2$) react rapidly with the O_2 of the blast [5].

When extensive O_2 enrichment of the blast is practiced, the process is nearly or completely autothermal. The process is perfectly matched to smelting the fine particulate concentrates (50 µm) from froth flotation.

The goals of flash smelting are to produce a constant composition and a constant temperature molten matte for feeding to converters and gas rich enough in SO_2, as a by product, for efficient recovery as H_2SO_4.

The molten matte is sent to converters for oxidation-converting to molten metallic copper, the slag is usually sent to slag treatment for Cu recovery, and the off-gas is sent to heat, dust and SO_2 recovery.

The benefits of extensive oxygen-enrichment is a small fossil fuel requirement, small gas flows through the flash furnace and its gas handling systems. An other benefit it is a high concentration of SO_2 in off-gas, which is good for efficient SO_2 capture.

The Outokumpu furnace’s vertical entry of concentrate was designed specifically to impinge concentrate particles on the slag surface. However, this configuration does not completely stop fine materials from being blown through and out of the furnace.

1.3.6.2 Construction Details

The interior of an Outokumpu flash furnace consists mainly of MgO and Cr_20_3-MgO refractory bricks. These are backed on the outside by copper cooling jackets in areas of severe wear and by a 1-3 cm steel shell elsewhere. The roofs are usually unbacked Cr_20_3-MgO brick suspended from steel beams [5].

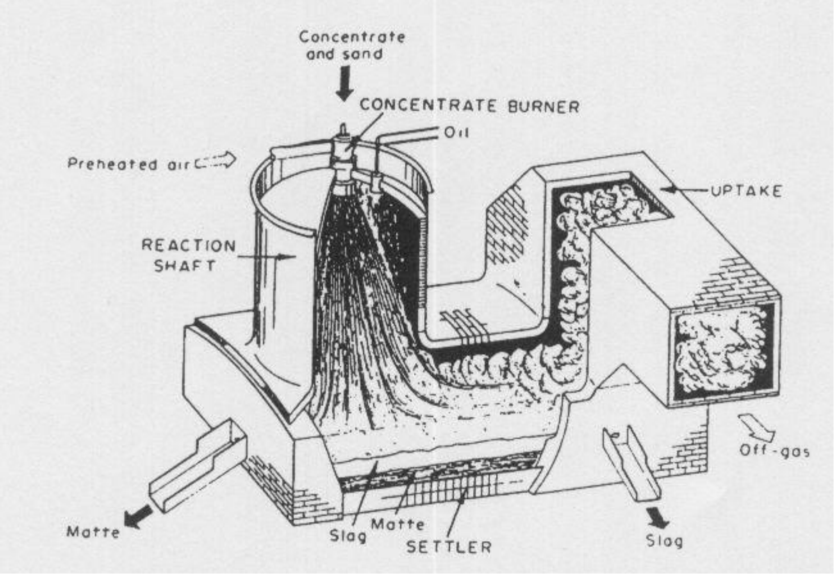
Outokumpu furnaces vary considerably in size and shape, however they all have the following five main features:

- Concentrate burners (one to four), which combine dry particulate feed with O_2-bearing blast and blow them downward into the furnace.
- A reaction shaft where most of the reaction between O_2 and the Cu-Fe-S feed particles takes place.
- A settler where molten matte and slag droplets collect and form separate layers.
- Water-cooled copper block tap-holes for removing matte and slag.
- An off-take for removing hot SO_2-bearing gases, 10 to 40% volume SO_2, from the furnace.

Large portions of the settler and off-take are water cooled to prevent overheating and weakening of the furnace structure. The cooling is usually provided by passing water through copper cooling jackets built into the furnace walls.

An important feature of the Outokumpu flash furnace is its concentrate burner, which creates a well distributed particle-gas suspension in the hot reaction shaft. Concentrate burners consist of two concentric pipes: Central pipe for the particulate solid feed and an annulus for the air/oxygen blast.

Figure 5 Outokumpu Furnace [20]



1.3.7 Inco Furnace (Flash Furnace)

1.3.7.1 Description

The Inco is also a flash smelting furnace in which the process uses commercial oxygen, 95 to 98% O_2 volume, rather than oxygen-enriched air. Its blast and particulate feed are blown horizontally into the furnace rather than downwards, and it is used to settle matte from molten converter slag (Figure 6).

Virtually all of the energy for smelting comes from oxidizing the Fe and S of the concentrate feed, very little, if any, fossil fuel is used.

The products of the process are conventional: liquid matte, liquid slag and SO_2-bearing offgas. The matte is sent to Peirce-Smith converting; the slag is sent to stockpile after a Cu-recovery step; and the off gas is sent to cooling, dust removal and SO_2 capture [5].

A small amount of oxygen is sometimes introduced into the gas off-take, through an oxygen lance. This oxidizes sulphur vapour which may be present in the off-take gas. Otherwise, the sulphur tends to condense on the gas cooling and dust collection equipment. The SO_2 is usually captured as sulphuric acid, sometimes as liquid SO_2.

Inco flash smelting is begun by slowly heating the furnace (1 week) to its operating temperature with temporary oil or gas burners. These burners are then replaced with concentrate burners and smelting is started.

Smelting can be halted for several days by replacing the concentrate burners with fossil fuel burners-keeping the furnace just hot enough to preserve refractory stability. Inco successfully operated its copper flash furnace on a 5-day smelting-week holding schedule for long periods of time[5].

1.3.7.2 Construction Details

The main advantage of the Inco process is the small size of its blast delivery and off-gas handling equipment. This is due to the near absence of N_2 in its blast and off-gas. Inco flash furnace is a Cr_20_3MgO refractory structure with copper water-cooling in high-wear areas [19]. The basic components of the furnace are:

- Concentrate burners, two at each end, through which commercial oxygen, dry concentrate, dry flux and ground recycle materials are blown into the furnace.

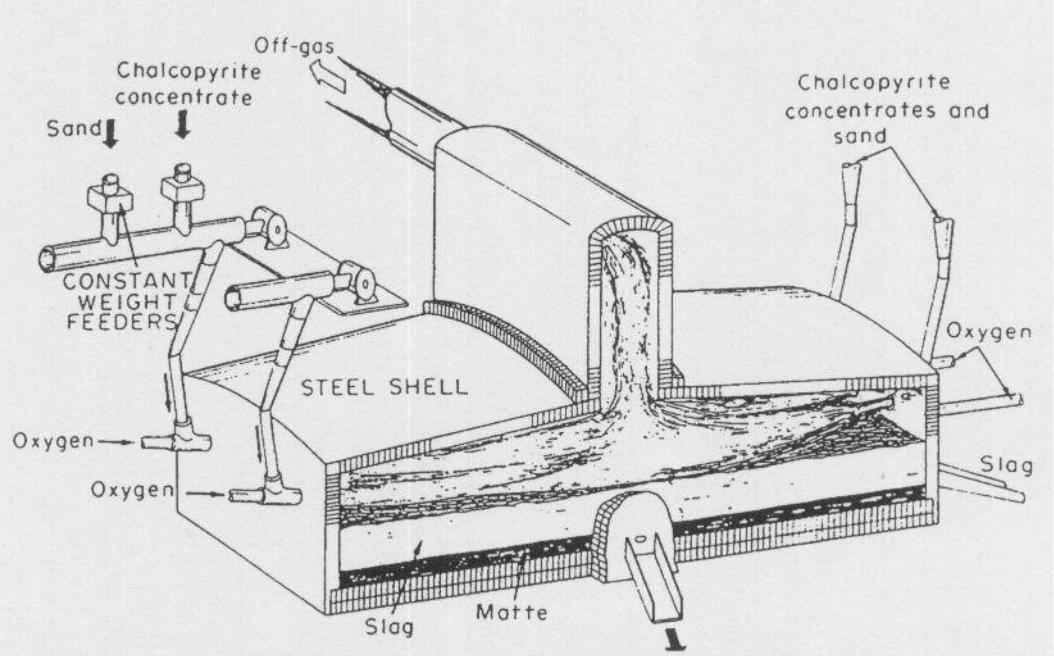
- A central off-take through which the off-gas is drawn into cooling, dust removal and SO_2 capture systems.
- Tap-holes for withdrawing matte and slag.

The concentrate burners are water-cooled ceramic-lined stainless steel pipes, about 1/4 m diameter and 1 cm thick. The oxygen blast is blown horizontally past a baffle, while concentrate and flux fall through a feed rate measurement system into the burner barrel.

The burners are inserted into the furnace through water-cooled copper collars in the furnace end-walls. They are readily removed for inspection and cleaning. The furnace is kept under strong draft while this is done.

The diameter of the burner barrel is chosen to produce an entry velocity of about $30x10^{-3}$ seconds into the furnace. This velocity gives a concentrate/oxygen flame which extends to the central gas off-take. The Burners are angled about 45 grades down and 5 grades inwards that their flame plays on the slag surface rather than on the furnace roof and walls[19].

Figure 6 INCO Furnace [5]



1.3.8 Kivcet Furnace (Cyclone smelting)

1.3.8.1 Description

Developments in power-plant technology have led to adoption of the cyclone principle by the metallurgical industry. The acronym KIVCET uses the initial letters of the following Russian terms: oxygen, vortex, cyclone, electrothermic. The development began in 1963, and the first plant was operated by Irtysh Polymetal Combine in Glubokoe, Kazakhstan.

The method is aimed at processing copper sulphide concentrates that contain considerable amounts of other metals. The essential part of the continuously operated plant is the smelting cyclone, in which the concentrates are fed vertically, and technical-grade oxygen (~95%) is blown in horizontally, so that reaction takes place rapidly above 1500°C [6].

The off-gas volume is small, and the percentage of SO_2 can be up to approx. 80%. Metals are recovered from the flue dust of both the separating chamber and the settler.

1.3.8.2 Construction Details

The furnace is divided to allow separating and settling of the reaction products, in this respect similar to a reverberatory furnace. In contrast to the separation chamber, the atmosphere in the electrically heated settler is maintained in a reducing state so that the slag does not need special post-treatment.

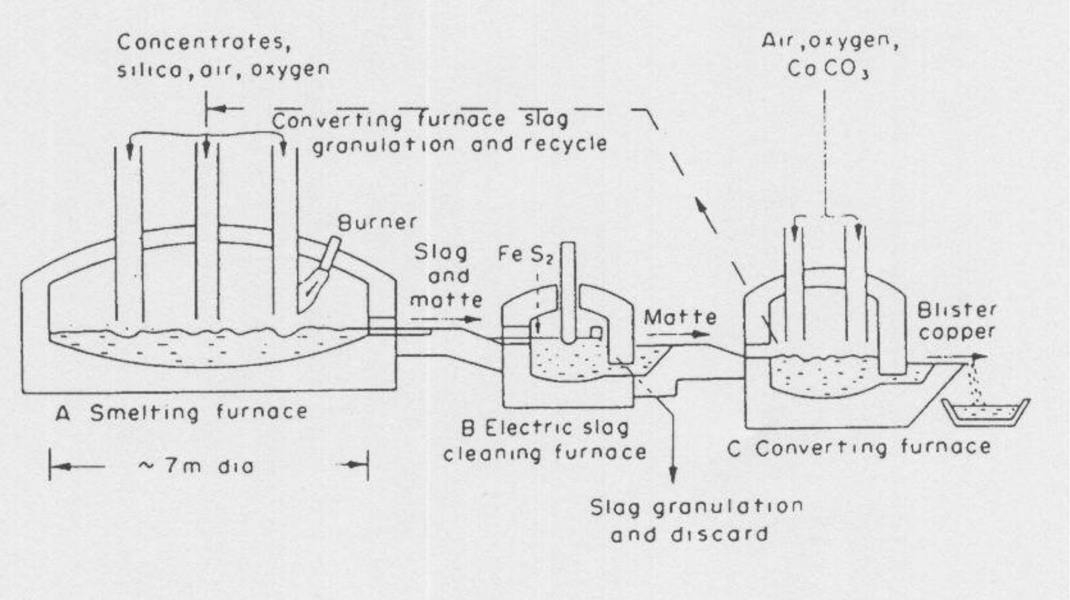
1.3.9 Mitsubishi procedure

In relation to all other fusion procedures the Mitsubishi procedure produces not 40-70% content of copper stone, but 98% content of Blister copper. A Mitsubishi plant consists of three furnaces, which are connected by heated gutters among themselves (Figure 7 & Figure 8). Into the melting furnace the dried concentrate, overcharge and oxygen-rich air are given up and melted [6].

The liquid-fusion mixture from stone and cinder arrives over a heated gutter into a setting off furnace, which is implemented as electrical furnace. By addition of pyrite and by reducing conditions and removable cinder is produced, which is granulated.

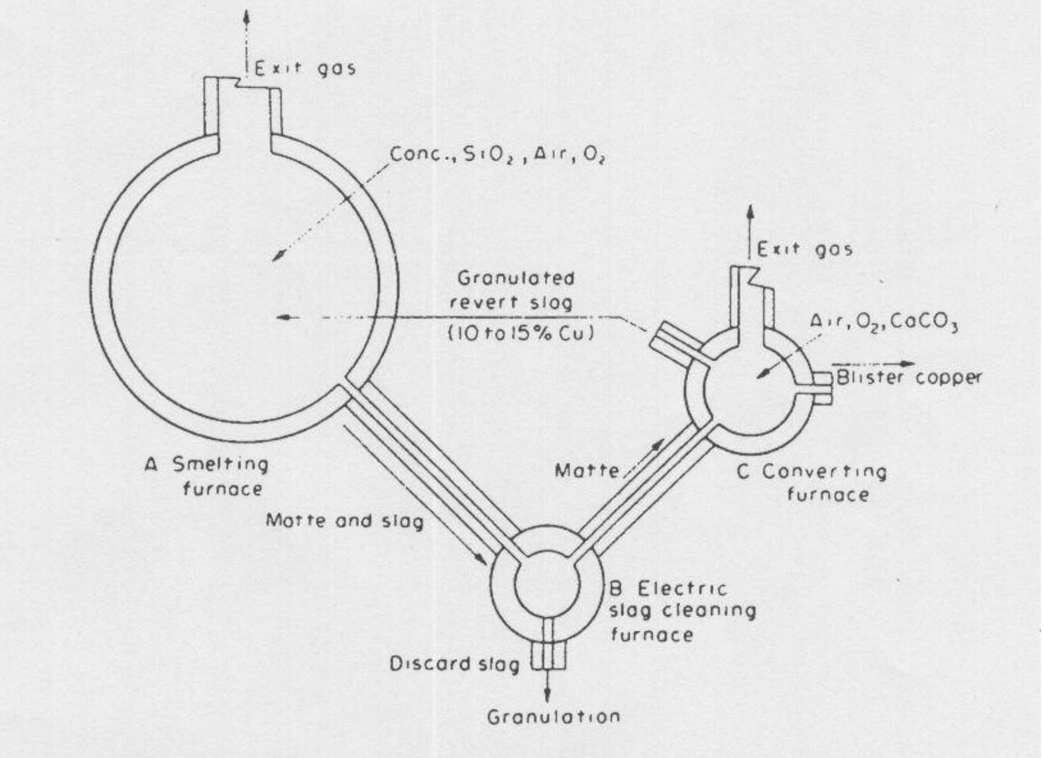
The copper stone arrived over a second heated gutter is produced into the conversion furnace where over several lances air and oxygen to be injected and Blister copper. The cinder of the conversion furnace contain about 10-15% Cu and into the melting furnace as granulates one gives up [20].

Figure 7 Mitsubishi procedure [20]



The advantage of the Mitsubishi procedure consists of the fact that Blister cooper is continuously produced. As disadvantage is to be stated that the investment cost are high and the heated gutters lead between the three furnace to a high energy consumption.

Figure 8 Mitsubishi furnace distribution [20]



1.3.10 Converter Types

The copper converter was invented in 1880 by Mabhes and David, based on the Bessemer converter, which had been used in the steel industry since 1855. This development led to the incorrect name "copper bessemerizing," although the true Bessemer process is a refining step. Originally, the copper converter was upright, and such obsolete units were in operation until the early 1980s. The following types are in use currently.

1.3.10.1 Pierce-Smith Converter

The P-S type (Figure 9 and Figure 10) has been the most important apparatus for converting for many decades, and the number in operation may be in the range of a thousand. It is a horizontal cylinder lined with basic bricks (magnesite, chrome - magnesite) that can be rotated about its long axis; blast air is blown through a horizontal row of tuyeres. In practice, the punching of tuyeres with special devices is necessary to maintain the flow of air. The largest vessels are 9 -11 m long with a diameter of 4-4.5 m [6].

Figure 9 Pierce-Smith converter [6]

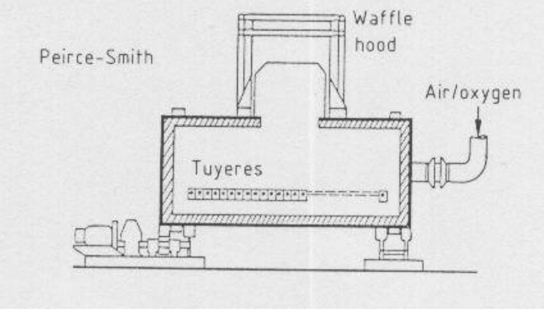
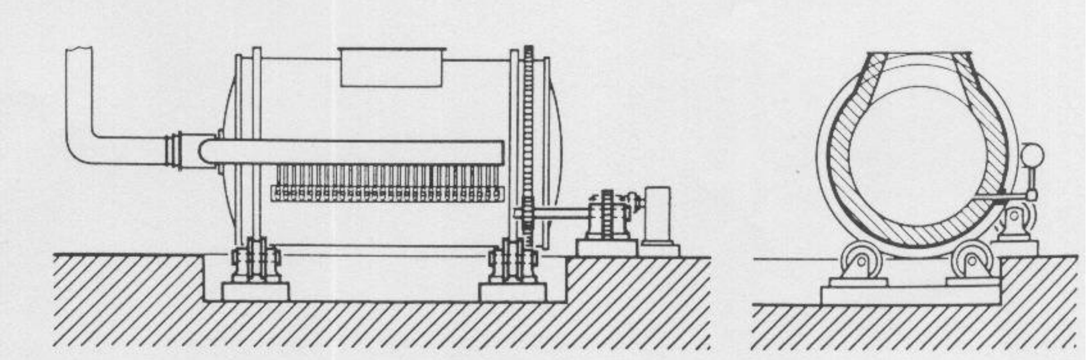


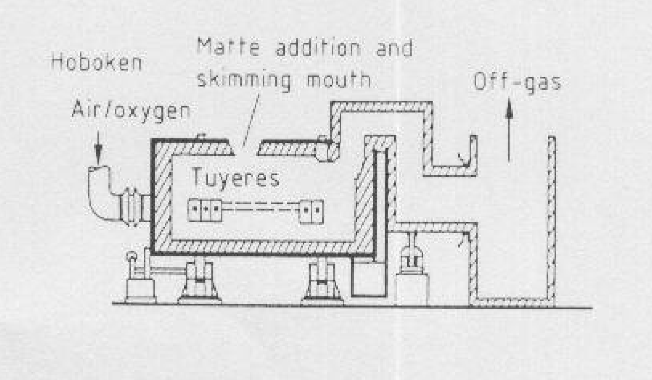
Figure 10 Pierce-Smith front and lateral views [6]



1.3.10.2 Hoboken Converter (Syphon converter)

This variation of the P-S type was developed years ago by Metallurgie Hoboken N.V., Belgium, but is now used by only a few smelters in Europe and in North and South America; larger units are operated at Glogow smelter in Silesia, Poland; Inspiration smelter in Arizona; and Paipote smelter (ENAMI), Chile . Its advantage is its freedom from sucking in air, so the off-gas can attain SO_2 levels up to 12%. Special features of the design are the small converter mouth and the syphon or goose neck that guides the off-gas and flue dust flow (Figure 11).

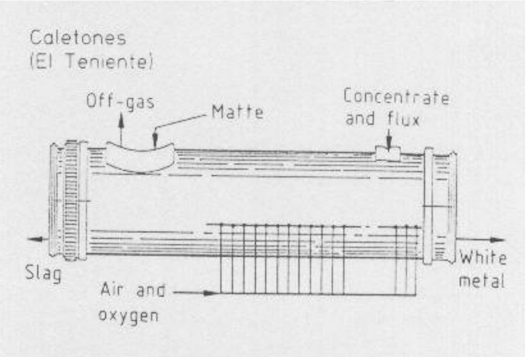
Figure 11 Hoboken converter [6]



1.3.10.3 Caletones or El Teniente Modified Converter (TMC)

Another modification longer than the P-S converter is the TMC (Figure 12). The main design differences are two separated mouths for charging and off-gas flow, and the lateral tap-holes for liquid slag and white metal. The latter is converted to blister copper in a conventional P-S converter. Further characteristics are testing for the direct smelting of concentrates in the converter with oxygen and the tendency to continuous operation. There are two units at Caletones smelter (ENAMI), El Teniente, Chile [6].

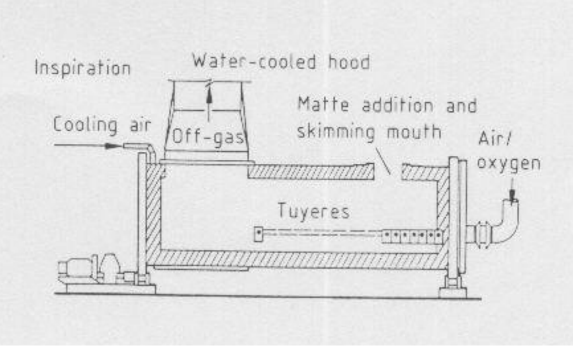
Figure 12 El Teniente modified converter TMC [6]



1.3.10.4 Inspiration Converter

Its design is similar to the Caletones type as it also has two mouths, the smaller for charging, the larger for the off-gas (Figure 13). The latter is well hooded in all operating positions.[6]

Figure13 Inspiration converter [6]



1.3.10.5 Top-Blow Rotary Converter (TBRC)

The TBRC, which is known in the steel industry as the Kaldo converter (Figure 14), was adopted by the nonferrous industry (first by INCO, Canada) because of its great flexibility. Air, oxygen-enriched air, or on occasion, commercial oxygen is blown through a suspended water cooled lance onto the surface of a charge of copper-containing materials.[6] In practice, the TBRC is used batchwise for special operations on a small scale:

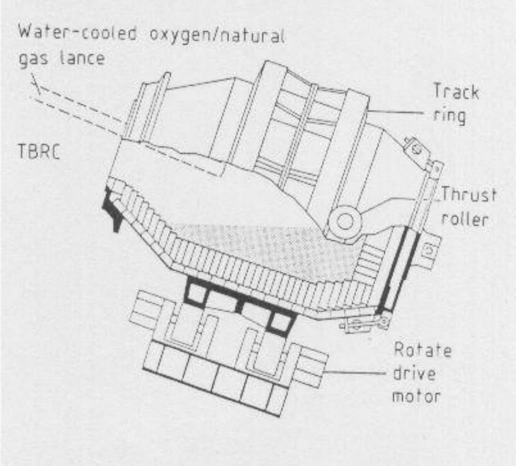
a) Converting copper matte with high levels of such impurities as bismuth and arsenic took place at the Tennant Creek smelter (Peko-Wallsend Ltd.), Australia, but it has been discontinued.

b) Direct smelting of concentrates (clean, complex, or dirty) to white metal or blister copper is performed at Ronnskar smelter (Boliden Metall AB), Sweden.

c) Slags from sulfide concentrate smelting and native copper are treated at Kamloops smelter (Afton Mines Ltd.), British Columbia, Canada.

d) Copper extraction from copper scrap and other secondary materials is also carried out.

Figure 14 Top Blow rotary converter [6]



1.3.10.6 Sirosmelt process

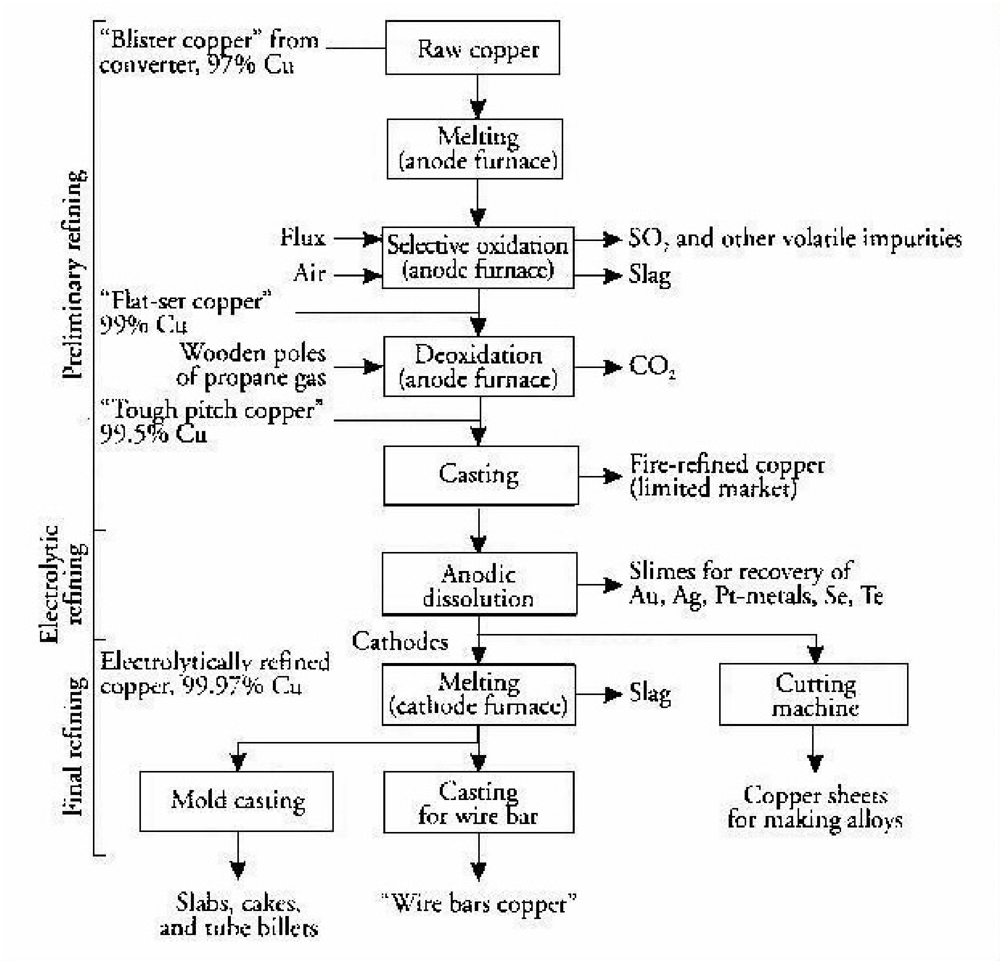
A new development, the Sirosmelt process operates batchwise, similar to the TBRC process when used for direct smelting and subsequent converting. Pelletized concentrates, air, and fuel are fed through a submerged lance into a special stationary furnace of circular design. After withdrawal of the primary slag, the matte is converted to white metal and then to blister copper in the same reactor. This concept of CSIRO, Australia, needs more testing before commercialisation.

Chapter 2 Fire Refining in the Secondary Metallurgy

This chapter deals with general concepts of fire refining and classification of anode furnaces (Diagram 1). The liquid blister copper from Peirce-Smith converting contains ~0.01 % S and 0.5% O while the blister copper from continuous and single-step smelting contains up to 1% S and ~ 0.3% [5].

At these levels the dissolved sulphur and oxygen would combine during solidification to form bubbles ('blisters') of SO_2 in newly cast anodes, making them weak and bumpy. In stoichiometric terms, 0.01% mass dissolved sulphur and 0.01% mass dissolved oxygen would combine to produce about 2 cm^3 of SO_2 (1083°C) per cm^3 of copper [5].

Diagram 1 Flow sheet for cooper refining [5]



At first the removal of the remaining sulphur and as much as possible of those impurities which are readily oxidised such as Al, Si, Mn, Zn, Sn, Fe, Ni, As, Sb, and Pb has to be effected by pyrometallurgical refining. However it is not possible to remove the precious metals that may be present in the raw copper by this method. The latter is done by electrolytic refining, where fire-refined copper is anodically dissolved and pure metallic copper is deposited on cathodes of pure Cu sheets, while impurities partially deposit at the bottom of the cell as slimes (Au, Pt metals, Se, Te) and partly go into solution (e.g., Ni).

Virtually all the copper produced by fire refining in furnaces and converters is subsequently electrorefined. It must, therefore, be suitable for casting into thin, strong, smooth anodes for interleaving with cathodes in electrorefinery cells (Diagram 1).

2.1 Fire refining

The fire refining process is done in a reverberatory furnace and is composed of two steps: the first is a selective oxidation of the remaining sulphur and the other impurities, and the second is deoxidisation, i.e., removal of oxygen in the molten metal which is in form of Cu_20. The amount of oxygen in molten copper is related to that of sulphur. The more sulphur is eliminated the more the oxygen content of the copper [5].

2.1.1 Selective oxidation

Copper is melted then compressed air is blown into the bath through pipes inserted through the side openings in the furnace. Some Cu_20 is immediately formed which is soluble in molten copper and reacts as follows:

With sulfur present in solution as Cu_2S to form SO_2 according to the reaction:

$Cu_2S+2Cu_2O\rightarrow 6Cu+SO_2$ Reaction 1

With impurity metals to form volatile oxides, e.g., As_2O_3, Sb_2O_3, or high melting point oxides which float on the surface. The reaction can be represented by the equation:

$M+Cu_2O \rightarrow MO+2Cu$ Reaction 2

Where M is the impurity metal. Usually, some SiO_2 is added to form a slag with these oxides, which is skimmed continuously [21].

When no more slag is formed, samples are then taken from the bath for physical examination. They are allowed to solidify and polished sections are then made. The oxidation process will be considered terminated when:

- No more gas bubble effects are found on the surface. This indicates that the sulphur content of the copper has decreased to an acceptable limit because gas bubbles form as a result of the escape SO_2 [21].
- The surface becomes brick red in colour, coarsely crystalline, lustrous, and brittle. This is because when molten copper is saturated with oxygen, it will contain 6 to 10% Cu_2O (0.6 to 0.9% oxygen); Cu_2O is red in colour. Also, the Cu—Cu_2O alloy freezes with the formation of an eutectic containing 3.45% Cu_2O, which on solidification will consist of coarse crystals of Cu_2O in a matrix of the eutectic [21].
- Copper produced after this operation is known as flat set copper and contains about 99% Cu. The metal is now ready for the next step.

2.1.2 Thermodynamic calculations

The following diagrams show the thermodynamic calculations of the oxidation of anode copper (Diagram 2 – 7). These calculations were done by the software Fact Sage. The base elements like iron, nickel and lead will be oxidised first. Also a lot of copper reacts to copper oxide which is reacts again with the base metals and is reduced to metallic copper. In the diagrams the oxidations characteristic of different metals is shown as a function of the oxygen potential. To give an overview the gas, slag and metal phase is indicated separately.

Diagram 2 Metal phase as a function of the oxygen potential

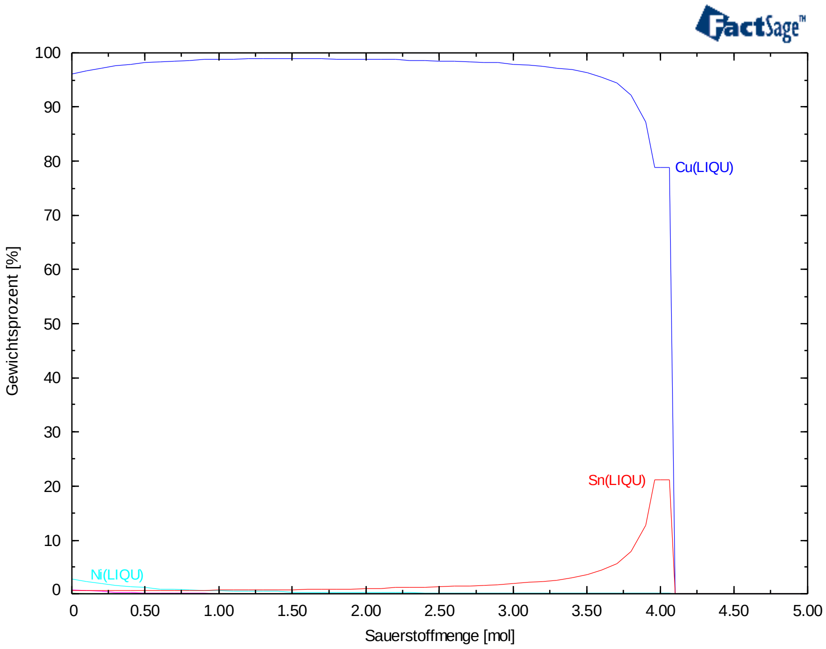


Diagram 3 Metal phase as a function of the oxygen potential (base metals)

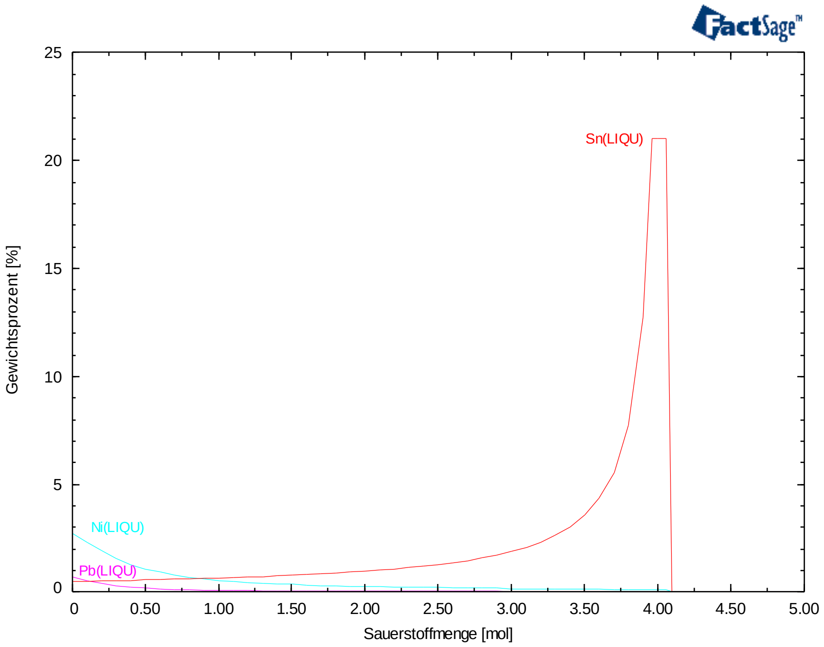


Diagram 4 Slag phase as a function of the oxygen potential

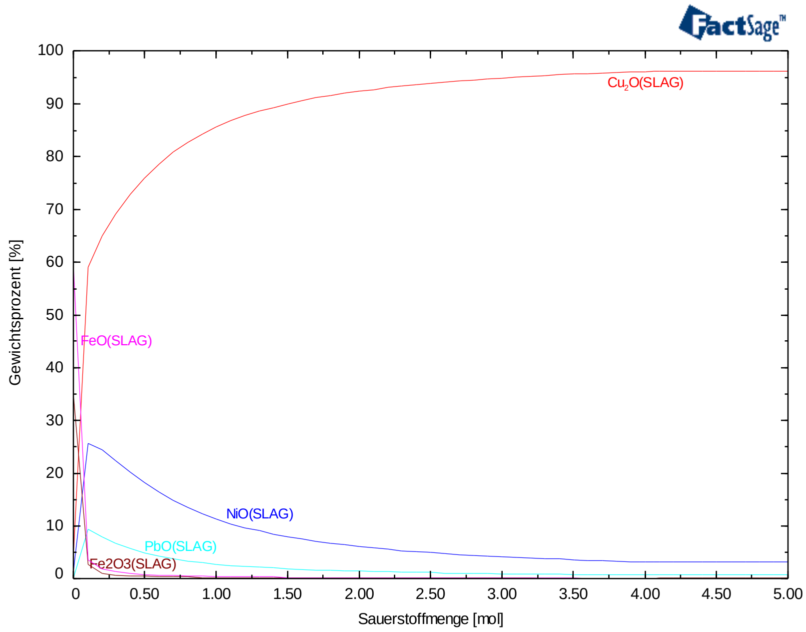


Diagram 5 Slag phase as a function of the oxygen potential (base metals)

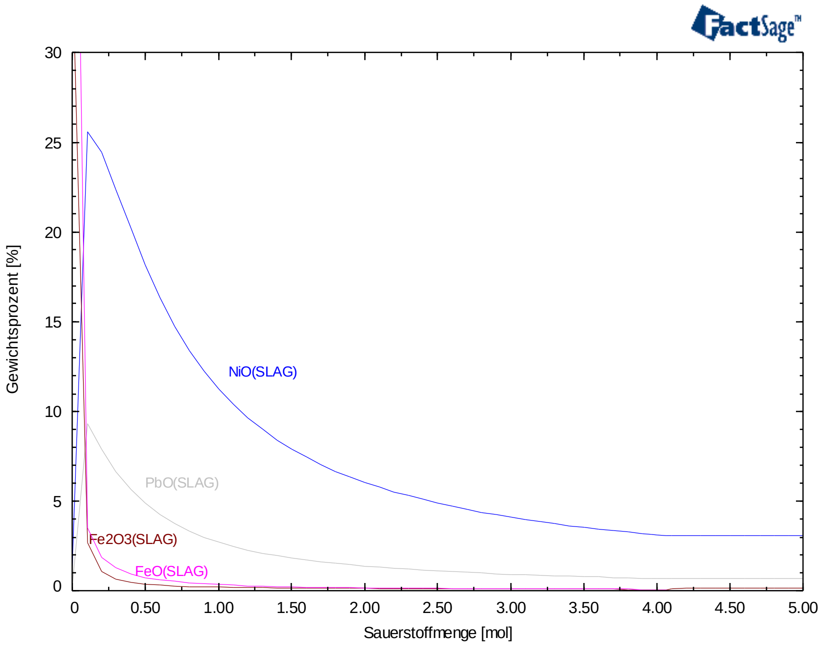


Diagram 6 Gas phase as a function of the oxygen potential

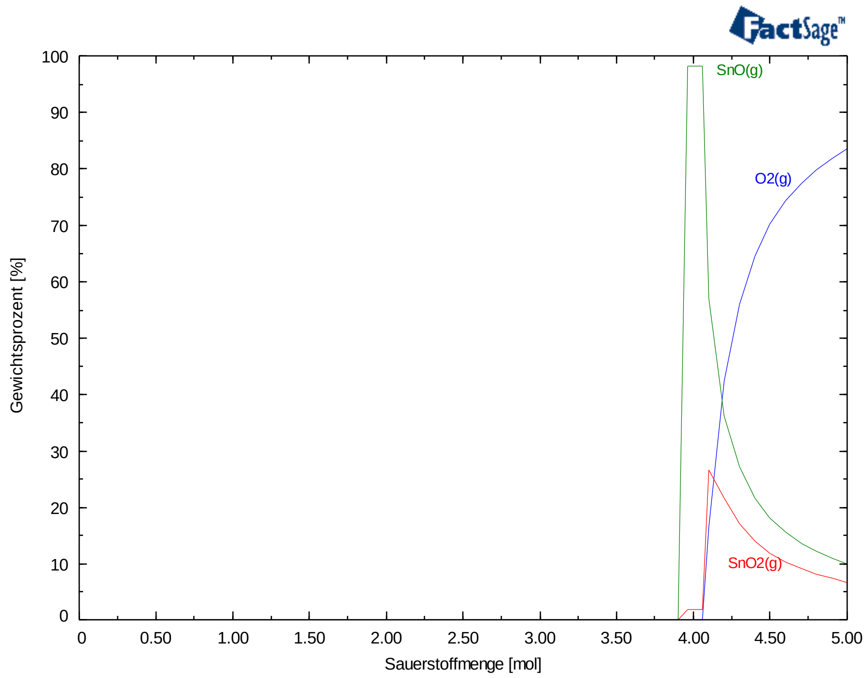
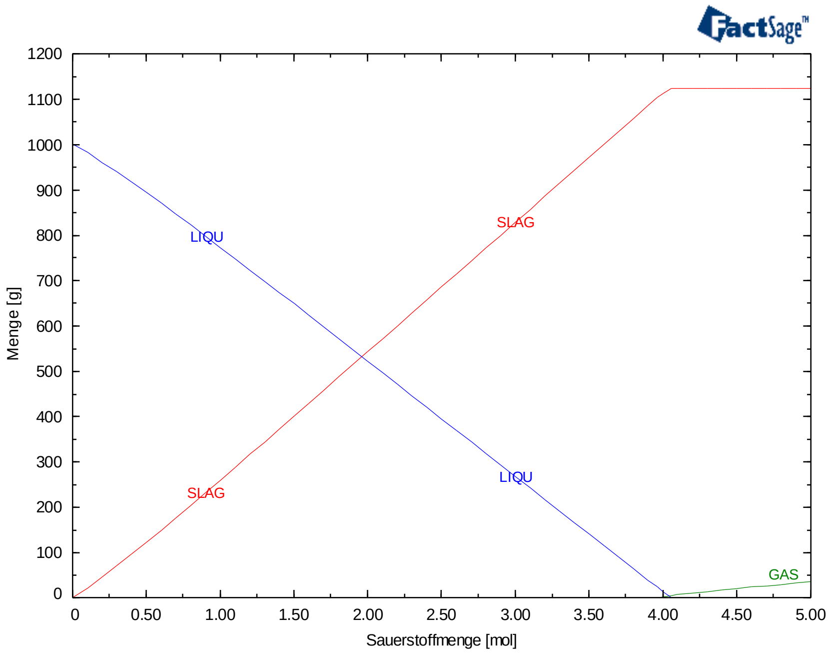


Diagram 7 Amount of phases as function of the oxygen potential



2.1.3 Deoxidation

This is the process whereby oxygen (or Cu_2O) dissolved in molten copper is removed. This may be accomplished in two ways:

Poling

In this method, wooden poles are submerged into the bath. The heat of the batch causes destructive distillation of the wood, the gases evolved (H_2O, H_2, CO, and hydrocarbons) stir the bath, and the reducing gases reduce Cu_2O to metallic copper. The poles used art usually green tree trunks 15 to 25 cm in diameter [21].

About six poles will usually suffice to treat 100 tons of copper. During the last stages of poling, the bath is covered with a layer of charcoal, wood, or low-sulphur coke to prevent reoxidation of the copper and to permit the operator to hold the melt at the proper temperature during casting. The process is now less frequently used.

Gaseous Reduction

In this method propane gas, C_3H_8, is injected through the bath to remove the oxygen. This process is more efficient than poling and is gaining wide acceptance [5].

As deoxidation proceeds, samples of the copper are cast and examined. When the copper has been deoxidized to the proper degree the sample has a metallic luster and a rose colour. Copper at this stage known as “tough-pitch copper”; it contains about 0.05% oxygen. A microscopic examination shows the $Cu—Cu_20$ eutectic at the boundaries of the large copper grains.

It is tough, malleable, and readily rolled, drawn into wire, etc. Most commercial metal is tough-pitch copper. As a rule, fire-refined anodes contain 99.2 to 99.6% C Removing too much of the oxygen gives the copper undesirable properties. It becomes porous and brittle and is difficult to cast. This is due to the dissolution of reducing gases (CO and H_2) in the molten copper. Completely deoxidized copper cannot be produced by reduction or poling. The production of such copper requires a special technique[21].

2.2 Definition of Anode Furnace and Classification

Fire refining is carried out in rotary refining furnaces resembling Peirce-Smith converters or less often, in hearth furnace. It is carried out at about 1200°C, which provides enough superheat for subsequent casting of anodes. The furnaces are heated by combusting fossil fuel throughout the process. About 2 to 3 x 10^6 KJ of fuel are consumed per tonne of copper [5].

The name Anode Furnace is derived from the refining process done in a Reververatory Furnace. The cooper coming from these furnaces, are usually cast into anodes for further refining.

Anode furnaces can be rectangular reverberatory furnaces or cylindrical, converter-similar aggregates. The oxidizing atmosphere is used over the flame adjusted for the reduction either fresh trunks or pole gases (natural gas CH_4).

In primary and secondary metallurgy of copper often uses a gas-smelting refining furnace. Different designs of refining and anode furnaces are:

- Stationer reverberatory furnace (stove reverberatory furnace)
- Tiltable reverberatory furnace (stove reverberatory furnace)
- Rotary furnace
- Hearth-shaft furnace

The process for the production of poured anodes can take place either continuously or intermittent.

Continuous processing:

A hearth-shaft furnace is used as pure fusion aggregate that operates continuously, the refining takes place in connection with two rotary furnace which work simultaneously, so liquid copper is always available for casting.

Intermittent processing:

The fire refining work is performed in an individual aggregate that could be a stationary or tiltable reverberatory furnace and subsequently cast from this aggregate into the anode casting facility.

2.2.1 Reverberatory Furnace (Hearth Furnace Refining)

The reverberatory furnace is a fossil-fuel heated hearth furnace. Reverberatory furnaces typically smelt 600 to 1100 tonnes of concentrate per day.

The reverberatory furnace dominated Cu matte smelting for much of the twentieth century. It was an excellent process for smelting the fine concentrates produced by flotation. It began to decline in the 1970's with the adoption of flash and other environmentally and energetically superior smelting processes.

Although the rotary furnace dominates copper fire refining in primary smelters, secondary (scrap) smelters tend to use hearth refining furnaces, which are better for melting solid scrap. Sulphur is removed by reaction of the scrap with the oxidizing flame above the bath and by air which is injected through a steel pipe moved manually around the surface of the newly-melted copper. Deoxidation is done by floating wooden poles on the molten copper. This reduction technique (called ‘poling’) is slow and costly and it is an important reason why rotary fire refining is used wherever possible [5].

Shell and Refractory-Lining of Furnace

The reverberatory furnace is rectangular in plan, typically 8 to 10 m wide, 30 to 35 m long and 3 or 4 m high, hearth to roof.

The furnace is essentially a refractory chamber supported on a solid foundation and held together by a steel superstructure. The walls and roof are erosion-resistant magnesite (MgO) or chrome-magnesite (Cr_20_3 MgO) bricks. The roof bricks are usually suspended from a steel superstructure above the furnace, often in sections for quick replacement. The brick walls are held in place by vertical steel beams (buckstays) connected across the top of the furnace by adjustable steel tie-rods.[5]

The furnace foundation is concrete or bedrock upon which layers of clay, sand, magnetite ore and high-magnetite slag are laid. The bath of the furnace usually rests on a layer of magnetite ore or highmagnetite slag. Cooling pipes through which cooling air is blown may be imbedded in the foundation to minimize erosion of the foundation. [28] The foundations typically last 20 or more years.

Smelting Process

Smelting is started by slowly heating the furnace hearth with the flames from lance burners inserted through the furnace roof. When the temperature reaches 500 to 700°C, the sidewalls are protected by piling concentrate against them, the main burners are lit and smelting begins [5].

Smelting is terminated by stopping the concentrate feed and draining the furnace of its matte and slag. The furnace is then allowed to cool at its natural rate.

Burners

The furnace charge is melted by continuous passage of hot combustion gases over the charge banks. Coal, oil and natural gas are burnt to produce the hot gases. The oxidant for the fuels is air, oxygen-enriched air or industrial oxygen. When air is used for the oxidant, it is often preheated 200 from to 400°C by heat exchange with reverberatory furnace off-gas [5].

Conventional reverberatory furnace design placed six to eight fossil fuel/air burners through the furnace end-wall from where the combustion gases swept down the length of the furnace. The oxidant gas was usually air, sometimes slightly oxygen enriched.

The 1970's and 1980's saw the endwall burners begin to be augmented by oxygen-fossil fuel burners playing downwards through the furnace roof [29, 30]. By the end of the 1980's some furnaces relied entirely on the downward-playing oxy-fuel burners with removal of the endwall burners.

The advantages of the oxy-fuel roof burners are:

(a) The burner flame is directed downwards onto the furnace charge, exactly where it is needed.

(b) The temperature of the oxy-fuel flame is hotter than an air-fuel flame-leading to faster heating, melting and concentrate-flux reactions.

(c) N_2 is absent so that smelting rate in an existing furnace can be increased without overloading the off gas handling system.

(d) The amount of heat carried out in the low-N_2 off gas is small, decreasing fuel consumption per tonne of furnace feed.

Off-gas

SO_2 concentration in reverberatory gas is also increased by using oxy-fuel burners, due to the decreased amounts of N_2 and fossil-fuel oxidation products in the offgas. The SO_2 increase is not substantial, however, because:

(a) Reverberatory furnaces are kept under considerable draft to prevent SO_2 emissions into the workplace.

(b) The draft draws air into the furnace and dilutes the SO_2 to – 2% volumen in the off-gas.

At this dilution, SO_2 cannot be efficiently or economically recovered as sulphuric acid. The changes encountered in the Chuquicamata reverberatory furnace during the switch from air-oil endwall burners to oxy-oil roof burners show significant improvements like a rise of 40% in smelting rate and a near 50% lowering of oil consumption. The major cost was provision of 300 kg of oxygen per tonne of charge [5].

Negative effects of the switch were an increase in Cu-in-discard slag from 0.7 to 0.9% Cu and an increase in refractory consumption from 1.2 to 1.8 kg per tonne of charge. On balance, however, the increased smelting rate and decreased oil consumption overwhelmed these disadvantages [5].

2.2.2 Tiltable stove reverberatory furnace

The tiltable stove reverberatory furnace (Figure 15) offers a universal applicability within the range of the anode casting line as single aggregate.

Both melting charged case-hardening material as well as refining the melted copper scrap iron to the casting finished anode copper takes place here. The load weights lie between 50 and 400 tons. The operating cycle is usually at 24 hours.

Whereby the cycle time as a function of the case-hardening material, process media and work logistics is to be regarded. Mixing scrap irons with an average copper content are used by > 92% Cu [31].

Beyond the openings of the furnace suction hoods are attached and connected by ducts to an afterburning chamber in order to suck diffuse off-gases and treat them together with the process off-gas

After going through the individual metallurgical process steps, refined copper is poured off through a tap hole by tilting the furnace onto the side of the anode casting machine.

An efficient heat transfer is ensured by a large (free) bath surface and a small bath depth as well as an arch construction reflecting radiate heat onto the bath.

During the charging procedure as a function of the furnace room, about 4 tons scrap iron are brought in with the help of a mobile charging machine by alternating one of the two openings at the side panel of the furnace container.

After latches of the charging procedure the front wall burners are operated with full load, around which scrap iron is to be melted as rapidly as possible, the next scrap hollow will be charged.

This happens until the furnace achieved the desired filling degree. Additionally silica is admitted to the process in the form of sand or glass break, in order to ensure the formation of an absorptive cinder. The temperature of the melt is with for instance 1200°C.

The middle specific thermal capacity of the pure copper: between 0 and 1000°C is with 0.4365 kJ/kgK, the fusion warm with 209 kJ/kg. However, the quality of the scrap iron is to be considered and the cinder quantity, therefore the values for the energy balance must be highly set, approx. 5-10% more [31].

After reaching liquid condition of the assigned copper, the furnace container is tilted by means of hydraulic cylinders, in oxidation/reduction position.

The refining nozzles (up to six pairs of nozzles) are turned under bath to start the oxidation phase with gaseous oxidation medium as air or oxygen.

By tilting motion, the reaction gases flow through a larger head of molten metal and thus a higher efficiency of the metallurgical reactions in the oxidation and reduction period. The oxygen concentration entered about 8,000 ppm toward end of the oxidation period [31].

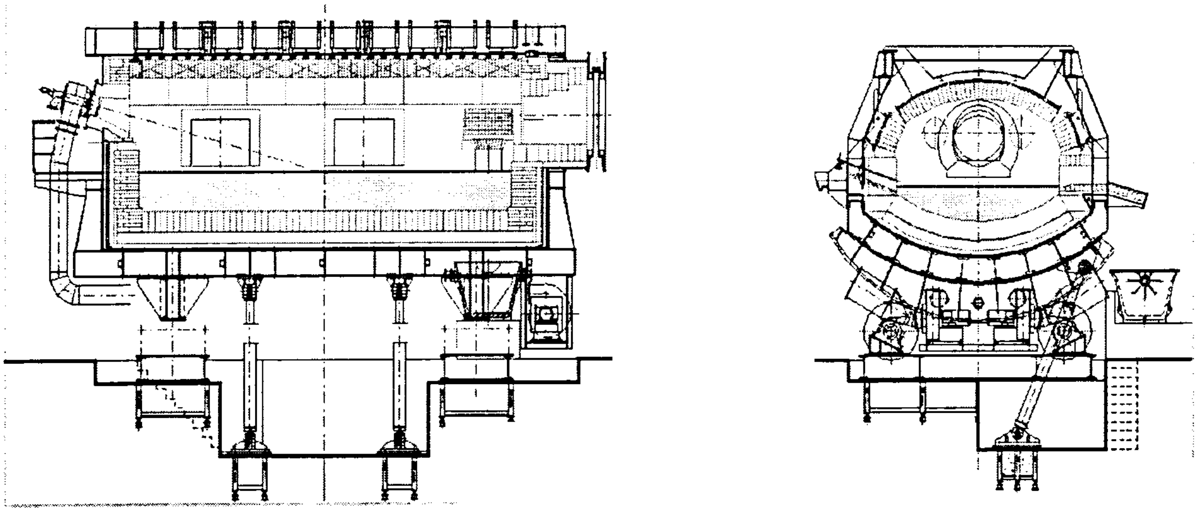
The slag formed contains unwanted accompanying elements, like lead, tin, zinc, nickel, etc. in oxidic form, are emptied by dumps in the furnace to the slagging off side in slag ladles.

The slag quantity developed is dependent upon case-hardening material, about 5% up to 10% of the load weight and exhibit in its consistency up to 30% Cu in the form of copper oxides [31].

The subsequent reduction period serves exclusively for the dismantling of the brought oxygen from the oxidation period. The oxygen concentration of approx. 8000 ppm reduces to less than1000 ppm. This is done again by means of dumps in the furnace in oxidation/reduction position and a nozzles suitable reduction medium (natural gas CH_4, hydrogen H_2) via the refining nozzles. The duration of the reduction depends on the oxygen concentration in the copper bath [31].

As soon as the adjustment has been completed the furnace is brought to the desired anode quality in pouring off position and copper in the casting machine poured. Depending upon capacity of the casting machine this procedure lasts up to seven hours.

Figure 15 Tiltable Reverberatory furnace [31]



2.2.3 The Rotary Furnace

The rotary refining furnaces resembles a Peirce-Smith converter (an horizontal metal cylinder), where the refining process is carried out at about 1200°C, which provides enough superheat for subsequent casting of anodes.

In a rotary refining furnace, air and hydrocarbon flow into a slow rate to provide precise control of copper composition. Only one or two tuyeres are used (depending on the charge's characteristics), the gas flow rates are 10 to 20 Nm^3/ min per tuyere at 2 to 5 atmospheres pressure [5].

Refining a 250-tonne charge of blister copper (0.01% S) takes 3 or 4 hours: an hour for air injection (sulphur removal) and two or three hours for hydrocarbon injection (oxygen removal). High-sulphur copper from continuous smelting and converting takes considerably longer (~5 hours) to desulphurize.

A typical sequence in rotary furnace refining is:

(a) Molten copper is delivered by crane and ladle from converters to the anode furnace until 200 or 300 tonnes are accumulated;

(b) The accumulated charge is then desulphurized by blowing air into the molten copper until the S-in-copper is lowered to 0.001%;

(c) The copper is deoxidized by blowing gaseous or liquid hydrocarbons into the molten copper bath.

Hydrocarbon blowing is terminated when the oxygen in copper concentration has been lowered to ~0.15% 0 (as detected by microscopic examination of copper test blocks or by measurement with disposable solid electrolyte probes [32]).

2.2.4 Mass and Energy Balances in a Copper Anode Furnace

This chapter describes a typical sequence operation, mass flow and energy calculations in an Anode Furnace (Hüttenwerke Kayser AG).

2.2.4.1 Process (Sequence operation)

The material contents of the charge in the second metallurgy can easily vary in composition from day to day. Nevertheless according to the experimental measurement, from the dissertation of Dr. B. Hanusch, from an average charge composition will be assumed the data presented in the mentioned work (Table 2 & Table 3). The mass and energy balances presented in this section will be used as a standard model that could be assumed in general terms for this investigation for the two different types of furnaces here presented.

Table 2 Material entry anode furnace [24]

Materials group	[t]	[%] v. E
Blister copper	55.0	16.3
Old copper	165.9	49.0
Copper granulates	9.0	2,7
Sum of the raw materials	230.0	68.0
Shaft furnace metal	2.9	0.8
Converter metal	69.2	20.5
Self cycle material (Casting scrap irons, King)	21.7	6.4
Anode Rests	10.8	3.2
Sum of intermediate products	104.6	30.9
Material Entry	334.6	98.9
Additives (Sand, Lime, Iron)	3.8	1.1
Total Entry	338.4	

Table 3 Material discharge anode furnace [24]

Material group	[t]	[%] v.A
Anoden	284.1	83.8
Refining cinders	31.1	9.2
Filter dust	4.8	1.4
Material for the Shaft furnaces (Cinders)	36.0	10.6
Könige	9.2	2.7
Anode forms	0.2	0.0
Casting waste	9.5	2.8
Self cycle material	18.9	5.6
Total Discharge	338.9	

In the anode stationer reverberatory furnace, the load takes approximately 24 hours starting from the charge and to be concluded in the pouring of anodes.

It is presented the sequence and the average times of each step of the reververatoy furnace operation:

- Loading time, 8 h
- Melt time, 3 h
- Oxidation and slagging off time, 6h
- Reduction time, 2 h
- Anode-pours time, 5h

The raw materials are brought in such a way into the furnace that they melt as fast as possible.[31] A typical sequence may be:

1. Hour: 60 t Old copper
2. Hour: 22 t Converter metal liquid;
9 t Copper granulates and shredder; 4 t surcharges
3. Hour: 20 t Old copper; 3 t shaft furnace metal;
51 converter metal firmly; 11 t casting scrap iron
4. Hour: 22 t Converter metal liquid
5. Hour: 601 Old copper
6. Hour: 20 t Converter metal liquid; 26 t old copper
7. Hour: 11 t Of anode scraps; 35 t Blister Copper
8. Hour: 11 t Of kings
Result: 20 t Blister Copper

2.2.4.1.1 Loading (Charging of the furnace with Recycling materials)

The raw materials (old copper of granulates shredder of blocks, self-cycles, etc), into are loaded Mulder boxes, which can be attached to a charging crane. After the charge doors are opened, the crane drives with the material hollows into the furnace and empties it through.

A substantial difference to a primary hut concerning the task of raw material is that the employment structure changes practically daily. The contents of the accompanying elements brought into the furnace are subject to strong fluctuations [24].

When slagging off the dross of the furnace some metal always runs along. Solidifies itself in the cinder pot, then develops into a copper cone, which can be separated from the cinder. The cone (king) is again used in a later load.

The deviation of the input charge in relation to the output charge results from adhering wetness and organic fraction in the entry and the oxygen bound in the discharge to the refining cinder.

2.2.4.1.2 Melting

After the anode reverberatory furnace is charge in approx. eight hours with the intended raw material quantity, the charge is melted over approximately three hours, until the surface is smooth.

Occupying procedure of the reverberatory furnace:

2.2.4.1.3 Oxidation and Slag Work

After melting the raw materials the pyrometallurgical refining of the copper melt oxidation work takes place. Filled pipes with low pressure blow wind (approx. 2.5 bar) are directed by the burner wall of the furnace toward the melt. The atmospheric oxygen contained in the blow wind oxidizes and clinkers the accompanying elements. With the help of the fluxing agents, given up when occupying, the refining cinder forms sand, if necessary lime and iron scrap.

When blowing air, melt and slag are whirled up and form sprayed particles, which interact with the furnaces atmosphere. With increasing oxidation duration the impulse transferred by the blowing pipes, shifts the slag in the furnace into a rotating motion, which finally seizes the entire melt surface. As soon as the slag is highly liquid, it is tapped. This procedure is performed several times and repeated during the oxidation phase.

Accordingly the composition of the copper portion changes; the dismantling of nickel takes place slower and the distribution quantities for the most important accompanying elements seem to remain almost unchanged.

For the refining period, almost three hours are needed to take up the cinder Fe, Al, Sn, Pb, Zn, Ni and Cu. At the same time the quantities of CaO, SiO_2 and Al_2O_3 drop out.

After approx. three hours of oxidation, trunks are dipped into the melt in order to agitate the melt. Remainders of firm raw materials arrive at the surface. Oxidation occurs for a long time, until the melt reach at a temperature of approx. 1220°C with an oxygen content about 11,000 ppm. The ladle sample may then contain no more sulphur. If the accompanying elements are under the content limits and the last cinder has been removed, the oxidation is terminated [24].

2.2.4.1.4 Reduction

After oxidation and slagging off, the oxygen drawn in the copper and the reduction takes place.

It is adjusted the oxygen content between 0.1 to 0.15% [O]Cu. After approx. two hours of pole duration, the metal pass is opened and protected for the following five hours become approx. 280 to 290 t anode copper [24].

2.2.4.1.5 Mass and Energy Calculations

The several stages in fire refining and the chemical reactions that occur, lead to changes in the concentration of materials in the bath as well as in the dross.

In this section this change will be followed as well as the energy requirements related.

The following mass balances are based on the experimental data from the dissertation of Herr Hanusch, in which 13 charges were considered (only the mean values for the mass balances as well as for the energy balances are used) (Table 4). From the source consulted, there are two types of experimental data, that according to the different air blowing procedures are divided in surface blowing procedure Surface blowing (Aufblasen) and injection blowing procedure (Einblasen).

For this report just the air injection will be taken into account, since the procedure is the standard procedure in the furnaces that will be compared in the following section.

The incoming material can be identified as in the Table 4:

Table 4 Incoming material [24]

Material	Not refined Metal		Starting dross Me		Starting dross Me_mO_n		Starting dross O_n	Sum
Units	%	[t]	%	[t]	%	[t]	[t]	[t]
Total material		311.8		13.0				324.8
Cu	96.9	302.1	11.7	1.52		1.71	0.19	303.6
Sn	0.39	1.23	1.05	0.14		0.17	0.04	1.36
Pb	0.45	1.40	1.21	0.16		0.17	0.01	1.56
Zn	0.32	1.01	3.34	0.43		0.54	0.11	1.44
Fe	0.94	2.93		1.26	12.49	1.62	0.36	4.19
N	0.75	2.35	0.96	0.12		0.16	0.03	2.48
SiO_2					46.8	6.06		6.06
CaO					10.6	1.37		1.37
Al	0.15	0.47		0.47	6.88	0.89	0.42	0.94
Mg	0.01	0.04		0.16	2.11	0.27	0.11	0.21
O	0.10	0.30						0.30
O_n						1.27		1.27

And for he output material the following table illustrates the results.

Table 5 output material [24]

Material	Anode Metal		Refined dross Me		Refined dross Me_mO_n		Refined dross O_n	Sum
Units	%	[t]	%	[t]	%	[t]	[t]	[t]
Total material		297.7				32.8		330.5
Cu	98.3	292.6	33.5	10.98		12.36	1.38	303.6
Sn	0.05	0.15	3.70	1.21		1.54	0.33	1.36
Pb	0.15	0.46	3.37	1.10		1.19	0.09	1.56
Zn			4.4	1.44		1.79	0.35	1.44
Fe				4.19	16.43	5.39	1.20	4.19
N	0.49	1.46	3.10	1.02		1.29	0.28	2.48
SiO_2					18.47	6.06		6.06
CaO					4.17	1.37		1.37
Al_2O_3				0.94	5.4	1.78	0.84	0.94
MgO				0.21	1.04	0.34	0.14	0.21
O								2.98
O_n							4.60	4.60

Fuel and Oxygen Needs

The fuel used in this calculation is standard oil. The amounts of oil and air will be given for each stage of the process in the Table 6.

Table 6 Fuel and Oxygen requirements [24]

Phase	Duration [h]	Oil amount [kg]	Air amount [Nm^3]	Oxygen amount [Nm^3]
Setting	1	1200	8246	1732
	2	1100	7241	1521
	3	1200	8246	1732
	4	1100	7241	1521
	5	1150	7743	1626
	6	1150	7743	1626
Melting	7	1150	7743	1626
	8	1100	7241	1521
	9	1100	7241	1521
Oxidation	10	1300	10202	2143
	11	1300	10679	2243
	12	1200	9674	2032
	13	1100	8670	1821
	14	1100	9146	1921

Energy Calculations

In this section the amounts of energy needed for heating, melting and over heating will be calculated according to the mass balances previously mentioned. For the general calculations, the following equations will be followed:

$$h_m = h_s + h_{sm} + h_{oh} \qquad \text{Eq.1}$$

$$H_m = m_{material}(h_m) \qquad \text{Eq.2}$$

Where: h_s Is the enthalpy at the solid phase, h_{sm} Is the enthalpy at the melting transition, h_{oh} Is the enthalpy from the overheating, h_m Is the total enthalpy, m Is the mass of material .

From the technical data consulted the values of the enthalpy of solid and liquid phase can be obtained. Since these values are in kJ/Kg, the masses will be transformed from tonnes to kilograms (1 ton = 1000 kg)

Then, the energy required for each metal fraction is shown in Table 8.

Table 8 Enthalpy required for the metal

Element	Temperature (K)	h_s (kJ/Kg)	h_{sm} (kJ/Kg)	h_{oh} (kJ/Kg)	h_m (kJ/Kg)
Cu	1473	463	204.3	58	725.30

The calculating of the total enthalpy needed per kg of metal, using the equation Eq2, is give in Table 9.

Table 9 Enthalpy per kg of metal

Element	Total mass in ton	Total mass in Kg	h_m (kJ/Kg)	H_m (kJ)
Cu	334.5	334500	725.30	24.261×10^7
Total				24.261×10^7

Efficiency of the Combustion Process

It is assumed that the entire process energy is supplied from the fuel. No preheating of gas and air is considered. Nevertheless the energy proportioned by the element’s reactions was subtracted from the energy calculated.

From the first statement, it is given:

$$H_n = H_m \qquad \text{Eq.3}$$

Since there is not an ideal system, the system efficiency should be taken into account. The following is to be used:

$$H_b(\eta_f) = \frac{H_n}{\eta_f} \qquad \text{Eq.4}$$

Where H_b Is the energy supplied by the fuel, η_f Is the efficiency of the combustion, H_n Is the energy needed, H_m Total energy in the metal, H_{Ex} Enthalpy of the exhaust gas.

In order to calculate the energy supplied by the fuel, the efficiency must be included in the calculation.

In order to calculate the energy supplied by the fuel, the efficiency must be included in the calculation:

The degree of efficiency describes the relationsship between the difference of energy input (from fuel and preheatede air) and energy output (offgas) divided on the Energy of the fuel input. Other losses, like wall losses are not considered in the first step. However they may required 5 to 10% of the total energy input, so they have to be calculated in the secon step.

$$\eta_f = \frac{H_{Fuel-IN} + H_{Air-IN} - H_{Offgas-OUT}}{H_{Fuel-IN}} \qquad \text{Eq.5}$$

Assuming no air preheating H_{air} ~ 0, an off-gas temperatures of 1200 °C and a stoichiometric operation (no excess air), Energy output is the equal to the off-gas loss. This may be roughly calculated as follows:

$$\eta_f = \frac{H_{Fuel-IN} - H_{Offgas-OUT}}{H_{Fuel-IN}} \qquad \text{Eq.6}$$

The energy requirements, in order to heat and melt the amount of copper given in one charge of 334.5 ton will be dived between the fourteen hours that the process last, this will yield an average melting rate in kg per hour and an average energy requirement in kJ per hour.

$$\frac{334.5\text{ ton}}{14\text{ h}} = 23.89\frac{ton}{h} = 23892.9\frac{kg}{h}$$

$$Hm = m_{cu}(hm)$$

$$Hm = (23892.9)(725.30)=17.329x10^6\frac{kJ}{h}$$

Calculating the energy supplied by the fuel, in this case the oil used for each hour of the process is taken from the dissertation of B. Hanusch given in kg we have:

Table 11 oil used per hour of operation

Hours of process	**Oil used (kg)**
1	1200
2	1100
3	1200
4	1100
5	1150
6	1150
7	1150
8	1100
9	1100
10	1300
11	1300
12	1200
13	1100
14	1100

The total amount of oil used per hour was 16250 kg, and calculating the mean amount of oil used per hour we have 1160 kg/h. Once the amount of oil is known it is possible to calculate the total energy given by the fuel by using the equation 7

$$H_{fuel}=m_{oil}(Hu) \qquad \text{Eq. 7}$$

Where Hu is the net calorific value of the oil used.

$$H_{fuel}=1160\frac{kg}{h}\ (35000)\frac{kJ}{Kg}$$

$$H_{fuel}=40.625x10^{6}\frac{kJ}{h}$$

Then, it is clear that the energy not used by the system and provided by the fuel is transmitted to the surrounding in form of off-gas and wall heating.

Energy not required by Cu = Energy supplied by fuel – Energy needed by the Cu (Wall loss is considered to be equal zero for simplicity reasons).

$$H_{Off-gas}=H_b-H_n=\frac{kJ}{h} \qquad \text{Eq. 8}$$

$$H_{Off-gas}=40.625x10^{6}-17.329x10^{6}=23.296x10^{6}\frac{kJ}{h}$$

An calculating the efficiency with this mean vale we have:

$$\eta_f=\frac{H_{Fuel-IN}-H_{Offgas-OUT}}{H_{Fuel-IN}}$$

$$\eta_f=\frac{40.625x10^{6}-23.29x10^{6}}{40.625x10^{6}}=0.4267=42.6\%$$

Chapter 3 Processes Analysis, Identification of Thermal Difficulties with the Potential to be Optimised Related to the Metallurgy of Copper Anode Furnaces

3.1 Introduction

In this chapter two types of refining cooper furnaces it will be compered. The tilting furnace with a 350 ton capacity and the rotary furnace with a 300 ton capacity. It is clear that a direct comparison is not possible due to differences in capacity of both furnaces. Nevertheless this comparison is attempted on a qualitative basis.

3.1.1 Measure of Empty Furnaces Chambers

The basic shape of the tilting furnace is a rectangular chamber in which the ceiling and floor are arched, in contrast to the cylindrical shape of the rotary furnace. It is of interest to notice that the height of both furnaces is almost the same in contrast to the total wall surface where the tilting furnace is greater than in the rotary furnace.

Table 12 Basic Characteristics of tilting and rotary furnace [31]

Characteristics	Tilting furnace 350 t		Rotary furnace 300t	
	Melting	Refining	Melting	Refining
Measures of empty furnace chamber				
Basic Geometry	Arched shaped floor		Circular shaped floor	
	Arched shaped covers		Arched side covers	
Width m	5.066		d=3.598	
Length m	11.962		11.30	
Height m	3.580		3.598	

Cross Section Area m^2	15.2	10.2
Furnace Chamber volume m^3	186.9	115.3
Extent furnace cross-section area m	~14.3	11.3
Wall surface total m^2	~201.5	145.3

3.1.2 Measures of Melted Bath

Comparing the two bath dimensions, there is a difference of almost 1.5m from the tilting furnace in relation to the rotary furnace. In contrast the bath volume difference is not that much, just ~ 0.4 m in favour of the rotary furnace.

Comparing the bath volume portion to the total furnace's volume, this relationship is greater in the rotary furnace (Table 13).

Table 13 Characteristics of tilting and rotary furnace bath [31]

Characteristics	Tilting furnace 350 t		Rotary furnace 300t	
	Melting	Refining	Melting	Refining
Measures of melted bath (max)				
Width m	5.066	~4.900	~3.550	
Length m	11.962		11.300	
Deepness m	1.030	~1.250	1.550	
Bath cross-section area m^2	4.12		3.7	

Bath volume m^3	49.3		41.8
Bath surface m^2	60.6	58.6	40.1
Portion of bath volume / furnace volume %	26.4		36.3

The rates comparing the surfaces and the volumes of the empty furnace's chambers, of the wall surfaces/bath volume and bath surface/bath volume are shown in the Table 14.

Of special interest is that the relationship of bath surface/bath volume is greater in the tilting furnace than in the rotary furnace.

Table 14 Characteristics of tilting and rotary furnace volume and surface [31]

Characteristics	Tilting furnace 350 t		Rotary furnace 300t	
	Melting	Refining	Melting	Refining
Rates surface/volume				
Wall surface/ empty furnace volume m^2/m^3	1.08		1.26	
Wall surface/ bath volume m^2/m^3	4.1		3.48	
Bath surface/ bath volume m^2/m^3	1.23	1.19	0.95	

3.1.3 Flame Room

The dimensions of both furnaces are almost the same in length and height, and differing in the cross section area and width. The portion of the total volume over bath used as a flame room is greater in the tilting furnaces than in the rotary furnace.

Table 15 Characteristics of tilting and rotary furnace flame room [31]

Characteristics	Tilting furnace 350 t		Rotary furnace 300t	
	Melting	Refining	Melting	Refining
Flame room over bath At max capacity				
Width m	5.066		3.598	
Length m	12.438		11.300	
Height m	2.550	~2.600	2.048	
Cross Section Area m^2	~11.1		6.5	
Portion of the total volume %	73.6		63.7	

3.1.4 Burners

The location and number of burners are the same, but the type of fuel is different, for the tilting furnace of 350 t, heavy oil or coal dust as possible fuels, in contrast to the natural gas used by the rotary furnace (Table 16). This characteristic can directly affect the exhaust emissions as well as the composition of the dross and the non ferrous particles in the Cu bath.

Table 16 Characteristics of tilting and rotary furnace burners [31]

Characteristics	Tilting furnace 350 t		Rotary furnace 300t	
	Melting	Refining	Melting	Refining
Burners for heating				
Burner location	Symmetric front walls		Symmetric front walls	
Number of burners	2		2	
Distance to the bath surface m	1.650	1/2	1.15/1.50	1.150/1.500
Fuel	Heavy Oil/ coal dust		Natural Gas	
Application of oxygen	Up to 1.250Nm^3	May vary	None	
Oxygenisation %	Up to 26			
Total amount of heat Kg/h	Max 2*1		Max 2x.05	
Total maximum amount of heat GJ/h	~80		37.2	
Furnace load GJ/m^3	~0.4		~0.3	

3.1.5 Tuyeres (Nozzles)

Even though the size of the tilting furnace is not the double of the rotary furnace, the quantity of nozzles installed and used in the tilting furnace are the double. Another characteristic related to the nozzles/lances is the use of a lance by the tilting furnace in the melting process, a characteristic that is not given in the rotary furnace. The Characteristics of tilting and rotary furnace tuyeres are summarised in Table 17.

Table 17 Characteristics of tilting and rotary furnace tuyeres [31]

Characteristics	Tilting furnace 350 t		Rotary furnace 300t	
	Melting	Refining	Melting	Refining
Nozzles for refining				
Arrangement	In front of the gates		Opposite side cinder gate	
Distance Nozzle bore - Bath surface m	0.0120	-0.0500	0.0120-0.015	-1.08
Blowing angle to the horizontal grads	18 under	0 horizontal	12 under	33 over
Number of nozzles	6		3	
Lateral distance of the nozzles m	1.098		1.450	
Characteristics	Tilting furnace 350 t		Rotary furnace 300t	
	Melting	Refining	Melting	Refining
Nozzles/ Lances by melting				
Distance Nozzle bore - Bath surface m	Lances by burner wall		None	
Blowing angle to the horizontal grads	when slagging off on bath			
Number of nozzles	2			
Lateral distance of the nozzles m				

The charging gates for the tilting furnace are two against one that is used in the rotary furnace. The charging system for the liquid input in both cases is a transport pan, nevertheless the discharging (pouring) gates are located in different places in the two furnaces. It is worthy to note, that the pouring angle is greater in the rotary furnaces than in the tilting furnace.

Table 18 Characteristics of tilting and rotary furnace Charging gates(1) [31]

Characteristics	Tilting furnace 350 t		Rotary furnace 300t	
	Melting	Refining	Melting	Refining
Charging entrance				
Size/ Number	2 gates 1.780x1.400		1 gate 1.5x1.0	
Arrangement	Long wall 5.124		Position 57° upward	
Charging system	Tilt hollow/ charge crane		Free case from open hollow	
Entry depth to furnace center m	~3.800		~2.800	

Table 19 Characteristics of tilting and rotary furnace Charging gates(2) [31]

Characteristics	Tilting furnace 350 t		Rotary furnace 300t	
	Melting	Refining	Melting	Refining
Charging entrance of the liquid input				
Size/ Number	Tranport launder		Closed intake gutter	
Arrangement	In charging gate		Middle Burner front wall	
Charging system	Transport Pan		pan over gate	

Table 20 Characteristics of tilting and rotary furnace Charging gates(3) [31]

Characteristics	Tilting furnace 350 t		Rotary furnace 300t	
	Melting	Refining	Melting	Refining
Liquid copper discharge				
Arrangement	Nozzle long side furnace center		Opposite side cinder gate	
Position of the Opening from the bath level m	-0.04	-1.2	0.010	~1.20
Angle of rotation Grad	0-29		0-45	

The cinder gates (Table 21), in the design of the rotary furnace allow the use of the same gate for charging as a cinder gate, reducing the possible heat losses and emissions related to gate operation. In contrast this type of gate in the tilting furnaces exists only for the goal of cinder removal.

Table 21 Characteristics of tilting and rotary furnace cinder gates [31]

Characteristics	Tilting furnace 350 t		Rotary furnace 300t	
	Melting	Refining	Melting	Refining
Cinder discharge				
Arrangement	Gate far from Charging gates		Cinder gate = Charge gate	
Size m	1x0.06		1.5x1.0	

Spill sheet over bath m	0.04	~0.6	1.100	~0.15
Angle of rotation for slagging off Grad		Up to 10		Up to 15

The movement capabilities are fully described in the following table; from it, is clear that the rotary furnace has a superior rotational grade of freedom (93°) against 39° of the tilting furnace. This characteristic can be of great influence at the refining phase where turbulence permits a better combination of the reducing and oxidising elements with the cooper bath.

Table 22 Characteristics of tilting and rotary furnace tilting and rotary angle [31]

Characteristics	Tilting furnace 350 t		Rotary furnace 300t	
	Melting	Refining	Melting	Refining
Tilt and max angle of rotation				
Charging Position Grad	0		0	
Refining Position Grad	16-18			48
Slag off Position Grad	0-10			45-30
Pouring Position Grad	0-29		0-45	
Total Trick tilting section Grad	39		93	

3.2 Oxidation Process

Following the refining process, the oxidation phase is to be before the reduction phase. For the oxidation process all the tuyere will be in operation. Even though the amount of air needed in the rotary furnace is lower than in the tilting furnace the percentage of oxidation speed is greater in the tilting furnace.

Table 23 Characteristics of tilting and rotary furnace Oxidation process [31]

Characteristics	Tilting furnace 350 t		Rotary furnace 300t	
	Melting	Refining	Melting	Refining
Oxidation process				
Nozzle application diameter m	0.017		0.02	
Number of nozzles	6		3	
Amount of air Nm^3/h	3500 at 6 bar		1500 at 6 bar	
Oxidation Time min/charge	3.0 (2.0-4.0)		4.0 (3.0-5.0)	
Specific air requirement Nm^3/t Cu	30		15-20	
Efficiency that O_2 conversion	~65.0		72.0 (57.3-86.5)	
Oxidation speed Cu % O_2/h	0.195		0.10 - 0.15	

For the reduction process, the method used is the injection of natural gas. In the tilting furnace it is a shorter reduction time than in the rotary furnace. This is a contrasting fact because the conversion efficiency in the rotary furnace is greater (Table 24).

Table 24 Characteristics of tilting and rotary furnace Reduction process [31]

Characteristics	Tilting furnace 350 t		Rotary furnace 300t	
	Melting	Refining	Melting	Refining
Reduction process				
Reduction gas	Natural Gas		Natural Gas	

Nozzle application diameter m	0.017	0.016
Natural gas portion Nm^3/h	2000 at 3 bar	700
Reduction Time min./Charge	60.0	90
Specific gas need Nm^3/t Cu	5,7	3,0 (2,8-3,5)
Efficiency gas conversion %	42.0	46.0
O_2 Dismantling speed % O_2 / h	0.59	0.2- 0.4

3.3 Parameter Identification Crossover Different Furnaces Architectures

During the design stage of an industrial furnace, thermodynamical, mechanical, geometrical, metallurgical and operation parameters have to be considered in order to obtain better results with the less investment possible. In response to this necessity engineers have developed simulation programs that allow a better understanding of the phenomena inside the furnaces.

Unfortunately, due to the variety of existing furnaces and their complexity. It is extremely difficult to use a single tool or model that could accurately describe and allow parameter variations to improve the operation and lifetime of the furnaces.

During this research, it was found different studies for specific types of furnaces were mostly based on numerical simulations. The advantage of this approach is that based on experimental data it is possible to have a better understanding of the physical-chemical nature of the reactions, and operation of the furnaces themselves.

Nevertheless this approach does not provide a global visualisation of the similarities that could be found in the operation of different types of furnaces.

This report intends to identify these similarities in the secondary metallurgy of cooper industry furnaces and form a base for the further development of a tool that could identify and give previews of the possible results, consequence of parameter variations.

This approach does not intend to replace the numerical simulations or thermodynamical modelling of the different furnaces, but to have a parameter-comparative crossover different furnaces architectures.

As background and start point methodology, the Taguchi's approach to parameter design will be taken as a guidance. The Taguchi's technique has been used as a tool in quality engineering, robust design and process design.

3.3.1 Taguchi's Approach to Parameter Design

Taguchi's approach provides the designer with a systematic and efficient approach for conducting experimentation to determine near optimum settings of design parameters for performance and cost.

The Taguchi method utilises orthogonal arrays to study a large number of variables with a small number of experiments. Using orthogonal arrays significantly reduces the number of experimental configurations to be studied.

In order to analyse the results, the Taguchi method uses a statistical measure of performance called signal-to-noise (S/N) ratio. The S/N ratio takes both the mean and the variability into account. The S/N equation depends on the criterion for the quality characteristic to be optimised [23].

Using the Taguchi method for parameter design, the predicted optimum setting need not correspond to one of the rows of the matrix experiment. Therefore, an experimental confirmation is run using the predicted optimum levels for the control parameters being studied. The purpose is to verify that the optimum conditions suggested by the matrix experiments do indeed give the projected improvement.

If the observed and the projected improvements match, the suggested optimum conditions will be adopted. If not, it will be concluded that the additive model underlying the matrix experiment has failed, and ways need to be found to correct that problem. The corrective actions include finding better quality characteristics, or S/N ratios, or different control factors and levels, or studying a few specific interactions among the control factors.

3.3.2 Design of Experiments

A designed experiment is an approach to systematically varying the controllable input factors and observing the effect these factors have on the output product parameters. As the stating point of this evaluation, a document research was driven in order to collect the most emblematic source of difficulties/problems in the cooper furnaces.

Up to now, just three different categories parameters will be analysed:

- Refractory lining
- Tuyeres (nozzles)
- Furnace Architecture and geometry

At the same time, these categories are divided into specific themes as follows:

- Refractory lining
  - (a) Material used in the lining
  - (b) Thickness of the refractory material
  - (c) Cooling system
- Tuyeres (nozzles)
  - (a) Type and diameters of nozzles
  - (b) Number of nozzles active
  - (c) Operation conditions

- Furnace geometry

  (a) Deepness and geometry of the metal bath

The chosen categories were taken into account based on the information compiled during the first step of this research. In the following part, a short description of the difficulties/problems found in these categories will take place in order to fundament the following parts of this investigation.

3.3.2.1 Refractory Lining

The refractory lining is constructed typically with 6” (152 mm) wedges in a staggered joint design with a thickness of 18” (450 mm) at the tuyere line and 15”(375 mm) or 13.5” (343 mm) in areas where the wear is less severe. It is interesting to note that the tuyere line is often installed with little or no expansion allowance. In contrast to the tuyere line, the rest of the lining may contain 1/10”-1/8” (2-3mm) expansion inserted for every foot of brickwork [27].

The expansion allowance required for the working face of the tuyere zone at operating temperature must be considered and located at the ends of the converter.

The endwall construction, therefore, becomes a very important factor in providing for a working lining that is adequately but not excessively tight.

Insufficient allowance for expansion to operating temperature will generate damaging compressive stress. In actual practice the refractory will possess a compressive strength of 30-50 MPa and an elastic modulus of 5-8x10^4 MPa [27].

If the brickwork is constrained at the tuyere line by more than 0.1%, the compressive strength is exceeded and the refractory will fail. The endwall may be built within the barrel brickwork or to the steel shell. In either case some movement must be expected as the tuyere line refractory expands to operating temperatures.

The tuyeres are commonly drilled with 6” centres which usually results in the presence of tuyeres that intersect brick joints. Refractory manufacturers have provided tuyere blocks that are ground to exact dimension size.

These blocks can be accurately positioned to ensure that drilling produces a tuyere with only one horizontal brick joint. It is thought that joint infiltration and wear can be minimized by this tuyere line construction.

It is certainly not difficult to visualize that joint penetration by matte and slag can lead to brick destruction at the working face of the lining. The tuyere line area opposite the mouth can cool considerably in out-of-stack periods. Furthermore, air injection is commenced before the tuyere line is rotated back into the bath. These cooling effects will lead to lining shrinkage at the tuyere area and the brick joints will open. Infiltration and solidification by matte/slag/copper can now prevent the re-expansion of the bricks and compressive stresses are induced in the working surface of the lining [27].

Anode copper refining furnaces are universally lined with refractories manufactured from magnesia and chrome ore. The refractory lining of these vessels wears more rapidly in the vicinity of the tuyeres. The lining of the copper converter in this high wear area must withstand complex combination of erosive factors including corrosion by fluid turbulent slag, mechanical damage by tuyere punching-thermal cycling and structural damage by alternating oxidizing and reducing conditions. The refractory recommended for these high wear areas has been the direct-bonded magnesia-chrome ore product ranging in magnesia content from 40-60%.

The sources of stress which affect the tuyeres area, the most vulnerable zone of the converters, have been listed and analyzed.

It was concluded that ‘stopping’ or hot-face spalling of the brick adjacent to the tuyeres zone was the primary cause of lining wear. Slag and/or copper metal penetration of brick joints and fractures, which formed parallel to the hot-face, were thought to result in the refractory loss [33].

Harris and Frechette supported most of this theory of wear, but were insistent that slag penetration of the joints and cracks was the major destructive mechanism [34]. These fractures were postulated to have formed due to several factors, namely:

(1) Differences in thermal expansion between the penetrated, densified hot-face of the lining and the unaffected refractory in the remainder of the lining;

(2) Damage caused by the punchers used to clear the tuyeres;

(3) Thermal shock generated by the cycling temperatures of the Peirce-Smith converter operation.

Slag corrosion has been cited as another critical factor in refractory loss. There is evidence to show that refractories high in chrome ore and direct-bonded with a spinel bond rich in chromic oxide will resist chemical corrosion by fayalite slags. It has been shown that fayalite slags react with the magnesia component of the refractory lining. In reducing conditions, fayalite will react with the magnesia according to the Eq8:

$$2FeO \cdot SiO_2 + 2MgO — 2MgO \cdot SiO_2 + 2FeO \qquad \text{Eq. 8}$$

Resulting in a solid solution of FeO and MgO and a solid solution of fayalite and forsterite.

There are reports, that converter tuyeres zone life is seriously compromised by slags with compositions richer in silica. It is thought that corrosion is accelerated by siliceous slags more likely to absorb the magnesia from the refractory lining.

However, there are some aspects of wear by slag corrosion which present a serious dilemma.

“It may be argued that since the chrome grains do not enter into reaction with the slag, but are presumably mechanically washed away, a high chrome brick is required. On the other hand, it is the magnesia which reacts with the slag and freezes it near the hot-face, so that a high magnesia brick might be considered desirable [27].

There is no doubt that high chrome bricks withstand corrosive attack by fayalite slags. However, slag penetrates significantly farther into a brick manufactured from a composition rich in chrome ore.

Most wear profiles of copper converters exhibit an area of the tuyeres zone which is relatively worse for weakening. The lining of the tuyeres zone opposite the mouth will generally be thinner than the rest of the eroded lining.

Bustos et al illustrated very clearly that the temperature of the lining can drop considerably during out-of-stack times during the skimming of slag or periods of time waiting for further matte charges. This accelerated wear opposite the mouth certainly may indicate that lining loss in this area is linked to thermal cycling [27].

It is assumed, then, that the removal of refractory by slag corrosion may not be the primary mechanism of lining erosion. The penetrated layer of the working face of the converter lining is lost by some means best described as pyroplastic failure. The slag that penetrates into the refractory brick matrix destroys the sintered bond of the brick.

The working surface of the lining, under compressive stress at operating temperature, can now deform and fractures at the limit of slag penetration into the brick. The frequency with which this hot-face spalling occurs and the thickness of the penetrated layer determinates the wear rate of the lining.

3.3.2.2 Tuyeres (nozzles)

The tuyeres zone of the converting and refining furnaces deteriorate more rapidly than the rest of the refractory lining. In general most of a refractory lining will not require replacing for a year or more, but the tuyeres are usually replaced every three to four months. The environment around the tuyere tip has been studied intensively to better understand the effect of thermal cycling and accretion growth on the refractory. However the chemical composition of the reacting air/matte and metal at the tuyeres zone has not been studied in depth. Some information exists to show the wide range of oxidizing and reducing reactants that are present during the converting process [26].

Air is injected into the molten charge of the converter at pressures between 13-17 psi (90-120 KPa). At these pressures air forms bubbles which rise vertically forming a spout or dome of turbulent liquid. The chemical composition of this reaction zone continually changes as the oxidation of iron progresses.

Percentage Out-of-Stack Time

During periods where skimming of slag or matte charging is taking place, the tuyere zone is out of bath, the refractory lining cools quite rapidly. A refractory lining that experiences extended periods of time out of the bath will suffer more severe thermal shock and subsequent stressing of the refractory lining. It has been suggested moreover that this cooling effect results in more severe accretion build-up which requires punching to be conducted more often. A combination of severe thermal cycling and more frequent punching will only increase the rate of refractory wear.[26]

Control of Temperature and Slag Chemistry

There is little doubt that higher silica slags can be responsible for corrosion of magnesia-based refractory especially at temperatures above 1280°C. It appears that overblowing blister copper has more damaging consequences. The campaign life of a converter with a severely worn tuyere line can be extended by confining its operation to slag blows.

Refractory wear is expected to occur more during the copper blow. Oxygen enrichment of injected air will result in higher temperatures at the tuyere area and higher temperature fayalite slag and/or copper oxide increases the refractory wear rate.

Tuyere Punching/Reaming Practice

Tuyere reaming or “dressing” is carried out between converter cycles to keep the tuyeres clean and retain high injection rates during blowing. However if the lining around the tuyeres is allowed to cool, the shrinkage of the refractory loosens the hot face of the brickwork. The tuyere reaming can result in the loss of thick portions of bricks, If tuyere reaming is conducted on a converter which is close to working temperature the lining is still tight and the accretions remain in a somewhat molten state [26].

3.3.2.3 Furnace Geometry

The brick lining of the rotary furnace, has individual sections with different radii. Considering the expansion of the ceramic ceiling in the cold and hot condition as well as an appropriate dimensioning of the radii of the ceiling (max radius do not cross, so the arch bricks may not slip out) a sufficiently high stability of the circulating brick lining is to be expected.

Depending upon demand of the brick lining by the bath and their movement (contact with copper or cinder) as well as the furnace atmosphere is different the wear. With the tilting furnace the following sections are to be differentiated:

- Side panels in bath level height: They are strongly stressed protecting the refining.
- Arched ceiling : It is exposed only to the furnace atmosphere. The service life is substantially higher than with the side panels.
- Bath sole: It is subject to the smallest wear. A higher attack of the sole can take place, where during the refining the bath surface reaches the sole.

There is no data present in reference to the service lives of the brick lining sections of the tilting furnace.

In the case of rotary furnace MKM the nozzles are submerged 2.30 m too 1.08 m gauge. rotary furnace, and 0,5m gauge for the tilting furnace [31].

The following repair work in the hot condition should be possible:

- Changes of the nozzle stones
- Lining and sole at the entrance into the charge and cinder opening
- Pass openings from the outside for the defined attitude of the maximum delivery

The brick lining is to be conceived in such a way that apart from the complete new installation from time and cost reasons also partial brick linings of critical sections (e.g. nozzle zone, parts of the front walls, cinder gate range, sections in the nozzle level) are possible.

3.3.3 Factors and Level for the Parameters Design

The factors up to now described are the main topics for several researches, however in order to propose a methodology to understand globally the operation and the most influent variables in the system, it is proposed to analyse just the variable “tuyeres”. Before the Taguchi technique will be used, supporting arguments are provided to ensure that the clearness of the chosen characteristics are the most important.

Up to now, from the literature consulted it is known that the number of tuyeres influence in the oxidation rate in the high sulphide mate processing:

“The No, 6 anode furnace was fitted with a second tuyere, in the location suggested by the CFD studies. The tuyere itself was of Noranda Horne standard design, but lacked the usual water-cooled copper block. The tuyeres are plumbed to 1.5” (38 m) natural gas and air supply lines by 1” (25 mm) flexible hoses. Natural gas supply is monitored by a mass flow meter, whose signal is converted to a volume readout by the distributed control system; air rate is determined by a correlation to supply pressure. During the deoxidation stage, copper was sampled periodically by dual pin-tube and by spoon sample.

At the time of writing, equipment modifications were incomplete and full flow capacity for two tuyeres was not yet available. A preliminary test in reduction mode was made, in which natural gas was delivered through two tuyeres but at a combined flow rate equal to that typically used for the single tuyere. Measured reactant efficiency during this test was lower than that found during single tuyere tests. While contrary to eventual test objectives, this initial finding is consistent with a bath mixing-controlled model; only half as much kinetic energy is delivered to the bath when the flow is divided through two tuyeres” [26].

During the experiments carried in the dissertation work of Dr Bernard Hanusch concerning different approaches to blowing oxygen rich air for the reduction phase in anode furnaces, different performance rates concerning to cooper oxidation were achieved. The data is shown in the following tables:

Table 23 Oxidation rate in the surface blowing (Aufblasen) [24]

Charge number	Cu % obtained
5.1.A	98.9
5.2.A	98.9
5.3.A	99.0
5.4.A	98.9
5.5.A	98.8
5.6.A	99.0
5.7.A	98.8
5.8.A	98.9
5.9.A	98.9
5.10.A	99.0
5.11.A	98.9
5.12.A	99.0
Media	98.9

Table 24 Oxidation rate in the injection blowing (Einblasen) [24]

Charge number	Cu % obtained
5.1.E	99.1
5.2. E	99.2
5.3. E	99.2
5.4. E	99.1
5.5. E	98.9
5.6. E	99.1
5.7. E	98.9
5.8. E	98.9
5.9. E	99.1
5.10. E	99.0
5.11. E	99.1
5.12. E	99.1
Media	99.1

Also as a injection technology, the COP KIN by RHI have been implemented in several Peirce-Smith-Converters and anode furnaces.

“Gas stirring systems, thought the furnace bottom, have been used in various metal industries for more than 30 years. The gas is purged through different types of plugs, including porous plugs, multihole plugs, and single pipe plugs. In the steel and aluminium industry, stirring the metal bath is a common practice. However, in the copper industry, whilst more gas stirring systems are being installed, they are mainly in anode furnaces or holding furnaces [25].

“In 2002, a COP KIN System was installed in one of the PS-Converters, at Boliden. In the first trial, only two porous plugs were used to determine if wear if the plugs in the converter would cause operational problems. After a normal operating period of 12 weeks, it was evident that no specific wear had occurred using the porous plugs. In the second trial, four plugs were installed and the operational safety and stability was evaluated [25].

It is suggested also that the temperatures of the lining surrounding the tuyeres could be keep in a “higher” temperature in order to reduce the thermal contraction-expansion variations that will lead to lining wear.

The thermal cycling of the tuyere tip is caused by the cooling effect of the injected air and the amount of time that the tuyeres are out of bath during periods of skimming and matte charging. The cooling effect of the air has been predicted to cause the accretion growth of frozen matte on the tuyere. This cooling of the refractory at the tuyeres zone is further compounded by the necessity to keep blowing during rotation of the converter while tuyeres are being removed or re-introduced into the molten charge.

During periods of out-of-stack time, as the converter is skimmed of slag or charged with matte, the tuyeres area can cool off very significantly. Mouth covers or secondary burners can reduce this effect, which is most severe opposite the mouth [27].

The oxygen mix during the operation of the furnace is considered also as a direct influencing factor in the tuyere lining corrosion, taking as a reference some experiments carried in the paper consulted:

“If the reaction is one hundred percent efficient, injected oxygen will be completely converted to sulphur dioxide, and the oxygen requirement at unit oxygen efficiency is

0.7 Nm^3 per kilogram sulphur removed. However, to calculate the amount of oxygen required, account must also be made of the oxygen solubility in copper. Unreacted oxygen may dissolve as Cu_2O to saturation at 7000 to 13000 ppm oxygen, depending on refining temperature. A separate slag phase will form from oxygen injected in excess of that required to saturate the copper. This slag may dissolve refractory components, and refractory corrosion may occur near the tuyere, even when the bath average dissolved oxygen has not reached saturation [26].

The temperature was taken in this proposed model as "uncontrollable factor" due to this research and experiments proposed are taking as a basis that the optimal temperature amounts were part of previous metallurgical calculations that settle the operations parameters and conditions of the furnace.

The size of the tuyeres could be an influencing factor in the performance rate of the oxidation process, unfortunately no literature data was found that directly deals with this field.

From the descriptions above mentioned, the following concrete variables are to be chosen to form the variables in the experiment's matrix array.

Table 27 Controllable factors in Taguchi's Model

Controllable factors	Levels		
A= Size of the tuyeres	Small	Medium	Large
B= Extra number of tuyeres	1	2	3
C= Location of tuyeres (height)	Under bath	Bath level	Over bath
D= Location of tuyeres (wide)	Close to the burners	In the middle of the bath chamber	In front of the burners

And for the out side array, the “uncontrollable factors” are:

Table 28 Uncontrollable factors in Taguchi’s Model

Uncontrollable factors	Levels		
Temperature surrounding the tuyere’s lining	Low Temperature	Middle Temperature	High Temperature
Oxygen rich mix	Low	Medium	High

It is of future works to take this matrix values into the experimental phase, and take some data from the in operation furnaces.

Summary

The objective of this thesis was to review relevant aspects of the secondary metallurgy of copper, described in more detailed on behalf of the technical architectures and the operation parameters of the Rotary Furnace and the Tilting Furnace.
As an example, an input material stream from real data, taken from the industry, was described. The general requirements of the process, as well as the output material characteristics and the energetic requirements were illustrated. The degree of efficiency of the anode furnace process was shown and the fossil fuel input required calculated in an typical example.

The metallurgy of fire refining in anode furnaces was described on behalf of the furnace operational settings and process logistics. Relevant construction features of shell and refractories were described.

Two different anode furnaces were compared: Tilting Heart Furnace and Rotary Furnace, in terms of operation features and energy consumption. Some of the most representative difficulties in connection with the operation of the furnaces were identified. Is to notice that as a critical components the following elements were found: Refractory lining, Tuyeres (nozzles) and the furnace Architecture and geometry.

And each of their components were also investigated and the basis of their relevance to this work were presented.

- **Refractory lining**

  Material used in the lining

  Thickness of the refractory material

  Cooling system

- **Tuyeres (nozzles)**

Type and diameters of nozzles

Number of nozzles active

Operation conditions

- **Furnace geometry**

Deepness and geometry of the metal bath

The final intention of this work, was achieved because the most relevant variables were identified, and now, it is possible to start the design of the experiments with a methodology that will reduce significantly the amount of experiments that have to be performed.

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