Report on Best Available Techniques (BAT)
in
Copper Production

FINAL DRAFT

Deutsch-Französisches Institut für Umweltforschung (DFIU)
French-German Institute for Environmental Research
University of Karlsruhe (TH)
o. Prof. Dr. O. Rentz
Dipl.-Ing. Martin Krippner, Dipl.-Ing. Stephan Hähre,
Dr. Frank Schultmann

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

Glossary

BAT	Best Available Techniques
BImSchV	BundesImmissionsschutzgesetz
DIN	Deutsche Industrie Norm
EN	European Norm
ESP	Electrostatic precipitator
EU	European Union
HMIP	Her Majesty´s Inspectorate of Pollution (UK)
IPPC/ IPPC-D	Integrated Pollution Prevention and Control/ IPPC-Directive
pH	pH-value
TA	Technical Instructions (Technische Anleitung)
TBRC	Top Blown Rotary Converter

Chemical Symbols

Ag	Silver
Al_2O_3	Aluminium oxide
As	Arsenic
CO	Carbon monoxide
CO_2	Carbon dioxide
Ca	Calcium
CaO	Calcium oxide, lime
Cd	Cadmium
Cu	Copper
F	Fluorine
Fe	Iron
FeO	Iron oxide
H_2SO_4	Sulphuric acid
MgO	Magnesium oxide, magnesia
MnO	Manganous oxide
Ni	Nickel
NO_2	Nitrogene dioxide
NO_x	Nitrogen (x) oxide
Pb	Lead
PCDD/ PCDF	Dioxine/Furane
S	Sulphur
Sb	Antimony
SiO_2	Silica, silicon oxide
SO_2	Sulphur dioxide
Zn	Zinc
ZnO	Zinc oxide

Units

µg	Microgramme
a	Year
DM	Deutsche Mark
GJ	Gigajoule
kg	Kilogramme
l	Litre
m	Metre
m^2	Square metre
m^3	Cubic metre
Nm^3	Norm cubic metre
mg	Milligramme
ng	Nanogramme
PPM	Parts per million
t	Ton
°C	Degrees Celsius
d	Day
g	Gramme
h	Hour
kWh	Kilowatt hour
Mio.	Million
MWh	Megawatt hour
Nm^3	Norm cubic metre (STP)
rpm	Rotations per minute
wt.-%	Weight-percent
vol.-%	Volume-percent

Definitions

Off-gas:	For the purpose of this report, off-gas is the carrier gas emitted from a plant or from an off-gas purification plant and containing gaseous or solid emissions or emissions in aerosol form. Carrier gases may be off-gases, for example from smelting units, or even air.
Aluminium bronze:	Alloys of copper and aluminium.
Anode copper:	Impure raw copper which has been cast to form anode plates and which is suspended in the electrolyte as the anode in the electrolytic copper production.
Blister copper:	Raw copper originating from the converter process in the primary extraction of copper and containing 96 - 99 % by mass of Cu.
Bronze:	Copper alloys which do not contain zinc as a major alloying.
ITE:	Total value for PCDD and PCDF calculated by a method specified in the appendix to the 17th Regulation on the Implementation of the Federal Law on Air-borne Pollution Prevention (ITE = international toxicity equivalent).
Burden:	Feedstock for blast furnace without coke, sometimes also referred to as charge.
German silver:	Copper-zinc-nickel alloy.
PCDD/PCDF:	Gaseous or dust bound emissions or aerosol emissions of polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF), whose presence and concentration are determined as specified in VDI 3499 Part 2.
Poling:	Refining method for deoxidizing oxygen-containing copper melts using wood or natural gas.
Clean gas:	For the purpose of this report, clean gas is the purified gas emitted at the last stage in an off-gas purification plant.
Red brass:	Copper alloys containing tin, zinc and lead.
Black copper:	Raw copper produced by reduction in a blast furnace, the Cu content is 70 - 80 % by mass.
Tombac:	Obsolete collective term for copper alloys containing 5 to 28 % by mass of zinc, modern term: brass. Tombac can be severely deformed by forging. Finely forged Tombac is referred to as fake gold foil.
White metal:	Tin-antimony-lead-copper alloy.
ITE:	Total value for PCDD and PCDF calculated by the method specified in the appendix to the 17th Regulation on the Implementation of the Federal German Law on Air-Borne Pollution Prevention (ITE = international toxicity equivalent)
Fugitive emissions:	For the purpose of this report, fugitive emissions arise from gases or particulate matter emitted to the surrounding air without being captured, purified or treated in any other way.

Stack emissions: For the purpose of this report, stack emissions arise when captured off-gases are emitted after purification (clean gas).

0 Preface

On September, 24th, 1996 the Council of the European Communities issued the Directive 96/61/EC on Integrated Pollution Prevention and Control (IPPC-D). This directive aims to achieve a high level of protection of the environment taken as a whole. It was enacted especially considering the common environmental goals of the EC, laid down in article 130r, EC-treaty (conservation and protection of the environment and improvement of environmental quality (i), protection of human health (ii), sustainable use of resources (iii), promotion of measures on an international level to handle regional or global environmental problems (iv)), and being aware of the fact that the implementation of an integrated concept of pollution prevention needs to be addressed by measures on a community level.

Annex I of directive 96/61/EC contains an extensive list of industrial activities to which the directive applies. According to this list, also industrial activities related to the production and processing of metals are subject to the measures within the IPPC (N° 2). The directive provides a general framework with principles for integrated pollution prevention and control. The goal of this integrated concept is to protect the environment taken as a whole by preventing and controlling emissions into all environmental media: air, water, and land. The necessity for drawing up information on best available techniques (BAT) for certain industrial activities is constituted by some of the measures laid down within the directive to attain the above mentioned goal:

- the definition of basic obligations, that operators of industrial activities have to comply with (art 3, esp. 3 a)).
- the requirement for the EC-member states to ensure compliance with these basic obligations by the operators (art 3, 4, 5).
- the definition of an approval procedure according to which permits should be granted, only if operators fulfil a number of requirements, further specified in the directive (art 3, 6, 7, 8).
- the reminder to the competent authorities, that a permit has to include emission limit values for at least a minimum number of substances explicitly named in Annex III. These emission limit values, or possibly equivalent parameters or technical measures, should be based on reference values derived from so-called Best Available Techniques (BAT, art 9(3)). The IPPC specifies explicitly, that BAT themselves are not binding, but only derived reference values.
- the specification of the term BAT in the IPPC as „the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole" (art 2.11).

- the obligation for the member states to provide the EC-commission with representative data and possibly information about BAT for the categories of industrial activities listed in Annex I (art 16.1). Furthermore the EC-commission is urged to maintain an information exchange between the member states and the concerned industries about BAT, related control measures, and developments in these fields (art 16.2). Additionally the member states have to ensure that the competent authorities follow or are informed of developments in BAT (art 11).

In particular the articles dealing with the definition of BAT and requiring an exchange of information on BAT are the motive for this document (esp. art 16.2). The goal of this study is to provide background information on BAT for environmental protection within the German primary and secondary copper production industry that serve as possible candidates BAT on an EU level. It gives information on environmental protection techniques but also production techniques on this performance. The further processing of copper is not included in this study. The paper is based also on literature study, but mainly on technical discussions with the experts of the German "Abstimmungsgruppe" co-ordinated by Mrs Dr. Pertersen, Umweltbehörde Hamburg.

The document is structured as follows:
Chapter 1 provides general information about the copper industry, including first indications of environmental concerns regarding the production of copper. Then basic information about the applied processes and techniques in the primary and secondary copper industry follows, and the main outputs and their sources are investigated (chapter 2). In Chapter 3, German copper production plants are described, including input/output levels and emission levels. Chapter 4 contains a list of German candidates BAT, i.e. techniques that are possibly candidates for being BAT on an EU level. Additionally, an overview of relevant legislation in Germany is provided in the Annex.

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1 General information

1.1 Production and use of copper

Germany is one of the main producers and users of non-ferrous metals in the European Community. Other important producers and users are France, Belgium, Italy, Spain, the Netherlands and the United Kingdom. Especially in copper production, Austria, Finland and Sweden also have an important share. In the following, information on production, use and recycling is given for the copper branch. The production of zinc and lead is dealt with in a separate report. The production of aluminium, other light metals or heavy metals is not in the scope of this study.

With a world-wide annual use of about 12 million tons, copper is the most important metallic material after steel and aluminium[1]. According to predictions for the coming years, the use of copper will retain an increasing tendency. In Europe, more than 3 million tons of copper per year are used. Germany is one of the most important copper producing and using countries in Europe and even in the world. In 1996, the production of copper amounted to about 671,000 tons of which 355,000 tons came from secondary raw materials [10]. The reported use in Germany amounted to about 955,000 tons of copper in 1996 [10], the calculated use amounted to 1,066,000 tons in 1995 [9]. Table 1-1 and Table 1-2 show the data for German copper production and use for different products and fields of application in Germany.

Table 1-1: Copper production in Germany

	1992 [t]	**1993** [t]	**1994** [t]	**1995** [t]	**1996** [t]
Total refined Cu (Σ)	581,682	632,079	591,859	616,387	670,790
Fire refining	*111,139*	*91,794*	*87,694*	*78,915*	*78,374*
Electrolytic refining	*470,543*	*540,285*	*504,165*	*537,472*	*592,361*
Cu cast alloys	58,805	52,542	57,502	58,047	53,916
Semi-finished products, Cu and Cu alloys	1,470,411	1,340,371	1,456,476	1,530,288	1,460,761
Conducting material	606,948	521,103	516,469	549,302	582,645
Castings, Cu and Cu alloys	89,427	71,988	81,068	86,842	73,768
Cu powder	10,490	9,414	10,416	11,130	11,158

Source: Bundesamt für Wirtschaft [10]

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[1] Detailed information on physical and chemical properties as well as the industrial uses of copper can be found elsewhere (c.f. [25], [86]).

Table 1-2: Industrial use of copper in Germany (1996)

User	[t/a]
Semi-finished plants	934,695
Powder industry	10,006
Foundries	4,588
Alloy producers	2,754
Iron and steel industry	1,524
Chemical industry	1,159
Total	**954,726**

Source: Bundesamt für Wirtschaft [10]

The main fields of application for copper products are power supply, telecommunications, the building industry, mechanical engineering, transportation and consumer goods. Figure 1-1 shows the different fields of application of German copper consumers.

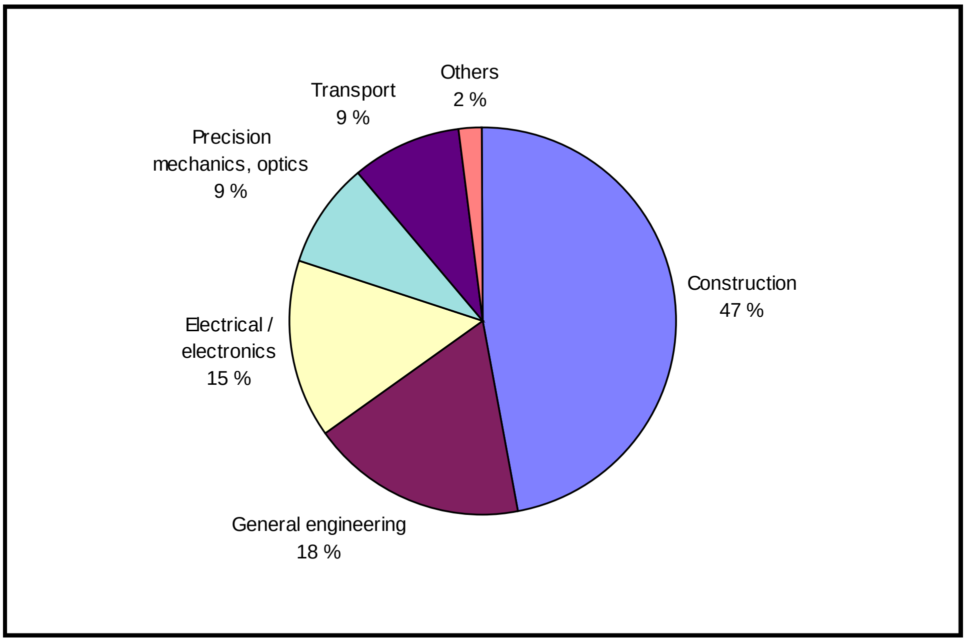

Figure 1-1: Main fields of application of copper products in Germany

Source: Wirtschaftsvereinigung Metalle [87]

Copper can be recycled without loss of quality. As Germany has almost none of its own ore resources of sufficient quality, the recycling of copper has always been of great importance. The recycling rate of copper world-wide is about 40 %. In Germany a recycling rate of about 46 % is achieved [64]. Figure 1-2 shows the average service life of various copper products and applications.

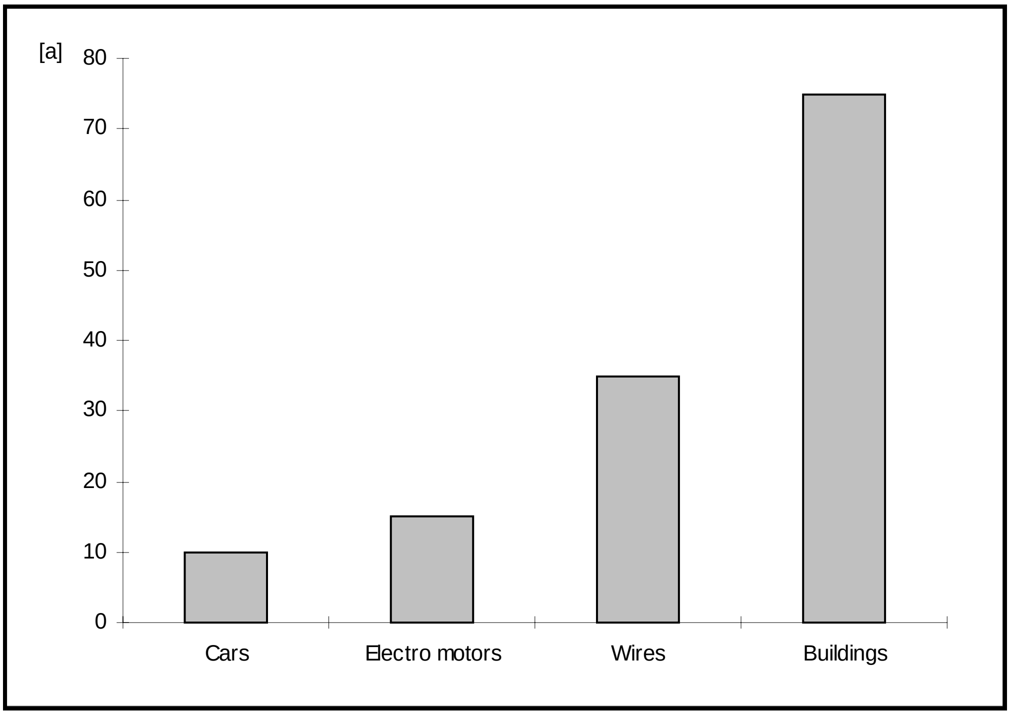

Figure 1-2: Average service life of copper materials in various applications

Source: Langner [49]

The average lifetime of copper products ranges from 6 - 8 years for cars and up to 60 - 80 years for buildings. If an average service life of copper products of 33 years is assumed, the recycling rate amounts to about 80 % [49].

1.2 First indication of environmental concerns regarding the production of copper

Plants producing non-ferrous metals such as copper are a source for certain emissions into the atmosphere and for discharges into water as well as for solid residues. A short description of relevant pollutants will be given in the following sections as a first indication. Emissions causing odours or noise have to be taken into account according to the IPPC-Directive. However these emissions have to be looked at on a plant by plant basis. Therefore they are not covered by the following sections.

1.2.1 Emissions into the atmosphere

The processing of non-ferrous metals is a source of different kinds of air polluting substances above all for gases and particulate matter. Depending on their origin two kinds of atmospheric emissions can be distinguished: stack emissions and fugitive emissions. Stack emissions arise mainly from furnaces and can usually be captured and cleaned by appropriate gas cleaning devices. Fugitive emissions are caused by open handling and storing of materials. Other sources are roofs and openings of production buildings as well as inadequately enclosed transport systems and leakages. Fugitive emissions should be avoided by hoods, closed transport systems and good housekeeping.

Osparcom [56] defines the following atmospheric contaminants to be taken into consideration for the (primary) production of non-ferrous metals:

- particulate matter,
- antimony, arsenic, cadmium, cobalt, copper, lead, mercury, nickel, selenium, tin, zinc, and
- chlorine, fluorine, nitrogen oxides, sulphur, sulphur dioxide and sulphuric acid mists.

Particulate matter arises during all smelting operations used in the non-ferrous metal industry. The precipitated flue dusts contain various metals and are treated internally or externally to recover the metal content. Sulphur dioxide emissions arise from the processing of sulphur containing raw materials and fuels in different production routes. According to the German Umweltbundesamt[2], the estimated emissions of sulphur dioxide in the German non-ferrous metal industry amounted to about 4,400 t/a in 1994, which accounts for 5.2 % of the sulphur dioxide emissions from the industrial processes[3] and for 0,15 % of the overall sulphur dioxide emissions in Germany. The estimated emissions of nitrogen oxides[4] amounted to about 1,200 t/a in 1994, which accounts for 5.1 % of the nitrogen oxide emissions from the industrial processes and for 0,05 % of the overall nitrogen oxide emissions in Germany. Copper plants covered by this study are a source of heavy metal emissions; different heavy metals and heavy metal compounds may be emitted [88]. Some processes in copper production are potential sources of dioxines and furanes (PCDD/PCDF). Different measures are available to control the PCDD/PCDF emissions from the copper plants, as shown, e.g. for secondary copper plants [75].

1.2.2 Potential releases into water

In the non-ferrous metal industry, water is used for different purposes mainly dependent on process specific constraints (see also [34], [56]). Controlled discharges, such as process effluent or cooling water take place through well defined ducts. They are usually treated in a waste water treatment plant before being released. In order to prevent uncontrolled discharges that may arise due to leakages or accidents measures such as collecting basins are applied. In general, surface run-off from the plant site is captured and treated either in a waste water treatment plant or in a special run-off water treatment plant. In non-ferrous metal plants, effluents may arise at different sources [24], mainly:

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[2] These calculations are based on estimated emission factors for sulphur dioxide (nitrogen oxides) which results from the processing of raw materials and the usage of different energy sources. The validity of these emission factors should be checked.

[3] Emissions caused by energy generation processes are not included in the figure for the industrial processes.

[4] NO_x given as NO_2.

- wet gas cleaning,
- slag granulation,
- hydrometallurgical treatment,
- electrolytic processes,
- cooling water, and
- surface run-off.

Osparcom [56] gives a list of potential contaminants into water and soil which could arise in the production processes of the (primary) non-ferrous metal industry:

- suspended solids,
- arsenic, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, thallium, tin, tungsten, zinc, and
- sulphate and sulphite.

In addition, the pH-value should be taken into account. Cooling water for indirect cooling from open cooling circuits and once-through systems is not contaminated and therefore does not have to be cleaned. Cooling water for slag granulation is led through a closed circuit without a conditioning agent and normally does not have to undergo demineralisation. Effluents from the demineralisation of closed cooling circuits are treated in a waste water treatment plant.

1.2.3 Solid materials generated

Besides the main products, solid materials generated in the non-ferrous metal industry are:

- slags,
- precipitates,
- residues from the production,
- dusts and sludges from gas cleaning, and
- sludges from the waste water treatment.

Residues for recovery are recycled in a production process, either in the same plant or in an external plant at a different location. In general, only a few residues arise in non-ferrous metal plants as the traditional aim of the process techniques is to close production loops to recover the metals contained and to generate marketable by-products. In the copper production industry only a minor amount of non-usable residues has to be disposed of.

2 Applied process technology and abatement techniques in copper production

Due to the large number of applied process technologies and abatement techniques in copper production and the existing site specific differences, in this technical study only brief descriptions of relevant processes and techniques are given.

2.1 Introduction and scope of the study

Integrated pollution prevention and control require the consideration and prevention and/or minimisation of all harmful impacts on the environment caused by industrial activities at the same time. Also the transfer of pollution from one environmental media to another has to be taken into account.

The goal of the IPPC-Directive (IPPC-D) is to prevent or control pollution caused by certain industrial activities, including primary and secondary production of copper (cf. Art 1 and Annex I). As mentioned in the preface of this paper, it therefore requires the member states of the EU, inter alia, to exchange information about BAT for these activities. Within the IPPC-D pollution is defined as "the direct or indirect introduction as a result of human activity, of substances, heat or noise into the air, water or land which may be harmful to human health or the quality of the environment, result in damage to material property, or impair or interfere with amenities and other legitimate uses of the environment" (cf. art 2.2). To achieve its goal the Directive lays down measures "to reduce emissions in the air, water and land from the above-mentioned activities, including measures concerning waste" (cf. art 1). „Best available techniques“ should be applied, in which „available techniques should mean those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions“. Summarising the provisions of the IPPC-D it can be concluded, that the identification of BAT for copper production requires an investigation of the underlying production systems and its economic context with particular respect to the emission of substances, heat, and noise caused by the system into the environmental media air, water, and land. Furthermore the considerations of Annex IV, IPPC-D, have to be taken into account, in particular the requirements of Annex IV.9 (consumption and nature of raw materials and energy efficiency of the processes).

Chapter 2 of the study gives a short description of processes and techniques applied in the production of copper and the most common inputs, outputs and emissions. Due to the high level of integration in copper production, a distinction between primary and secondary processing is difficult and cannot always be maintained. Furthermore, this report deals only with those steps of copper production which are normally carried out at the plant site: the preparation and handling of raw materials, the smelting or the hydrometallurgical treatment of the input charge and the refining of the raw metal produced[5]. In addition, the production of wire rod from copper cathodes using a cathode shaft furnace and the production of semi-finished cathodes from copper and copper alloys is covered.

2.2 Basic description of copper production

Copper is produced from various primary and secondary raw materials. The primary process uses sulphidic concentrates or sulphidic/oxide mixed ores, while secondary processes employ recycled oxidised or metallic products. The industry can be divided into two sections, secondary copper production and primary copper production with the additional use of secondary material. In the following, a general overview is given on the most common primary and secondary processes for copper production. To follow the scope of the study, emphasis is placed on processes operated in German plants.

2.2.1 Primary copper production

Primary copper can be produced by hydro-metallurgical processes or pyro-metallurgical processes. Approximately 10 % of the primary copper is produced by direct leaching of ores (hydro-metallurgical process). The pyro-metallurgical production of copper from primary material consists of several steps, which are summarised below[6]:

Smelting operations

- roasting
- smelting
- converting

Refining operations

- fire refining
- casting into anodes
- electrolytic refining

Preceding processes such as mining, crushing, grinding and concentrating steps, which normally take place at the mining location, are not in the scope of this study. Apart from the production of copper, the further processing following the electrolytic refining such as the fabrication of wire rod and the fabrication of semi-finished products is subject of this report. After a general process description (c.f. 2.2.1.1), typical outputs to the different environmental media are described in section (c.f. 2.2.1.2).

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[5] Mining and processing of ores are no longer carried out in Germany. Furthermore, these processes are applied at only very few sites in the EU.

[6] Detailed information on copper production can be found elsewhere (c.f. [8], [25], [86]).

2.2.1.1 General process description

Copper concentrates are today processed almost exclusively by pyrometallurgical methods[7]. Figure 2-1 shows a schematic overview of the primary copper production route. In the following first the raw materials, then the different production steps and process units of the primary copper production are described. The underlined terms refer to Figure 2-1.

Inputs for primary copper production

Nowadays sulphidic concentrates (copper content: 15 - 45 %) are the most important raw materials for the pyro-metallurgical primary copper production with a share of more than 85 %. To a small extent oxidic/sulphidic mixed ores and, more seldom, bituminous ores are processed. The sulphidic concentrates consist of complex copper/iron sulphides; they are obtained from ores containing 0.5 - 2 % copper by flotation. Further inputs used for primary copper production are fluxes **(**silicate, lime, sands, etc.), additives/reactants (iron, carbon, etc.) and recycled materials (scrap, drosses, lime sludges, used abrasive materials, slags, dusts, etc.).

Production units in primary copper producing plants

The **roasting** step, which is a heating process in an oxidising atmosphere, is applied to break down the complex sulphides to cuprous and ferrous sulphides and to convert the iron sulphide into iron oxide. The most common method is *partial roasting*, where 10 % of the iron and sulphur is oxidised. It is used as a preliminary stage of the smelting process only. *Sulphating roasting* is applied as a preliminary stage of a leaching process and is only in use in one plant [67]. During both roasting methods sulphur dioxide is formed and carried out with the furnace process gas. This roaster gas (SO_2-content of 10 - 14 % on average) is processed in a sulphuric acid plant after having been cleaned by electrostatic precipitators [56]. In Europe only partial roasting is used. The most common device for roasting is the fluidized bed roaster.

In the ***smelting*** step, roasted and unroasted[8] materials as well as slag forming fluxes (silica, limestone) are mixed and smelted under oxidising conditions into silicate slag and sulphidic copper matte. The produced slag contains the iron oxides and silicates as well as the gangue and the ash from the combustibles. The copper matte (copper content: 30 - 80 %) contains copper sulphide and iron sulphide in various portions as well as the precious metals and other accompanying elements.

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[7] Hydrometallurgical processing covers just a small part of the world-wide copper production and is not used in Germany. Therefore it is not discussed in this report.

[8] When unroasted raw material is smelted, a drying step can be necessary prior to smelting. Sludges from waste water treatment can be recycled via the drying process as well. Off-gases from drying are treated in electrostatic precipitators and wet scrubbers or fabric filters.

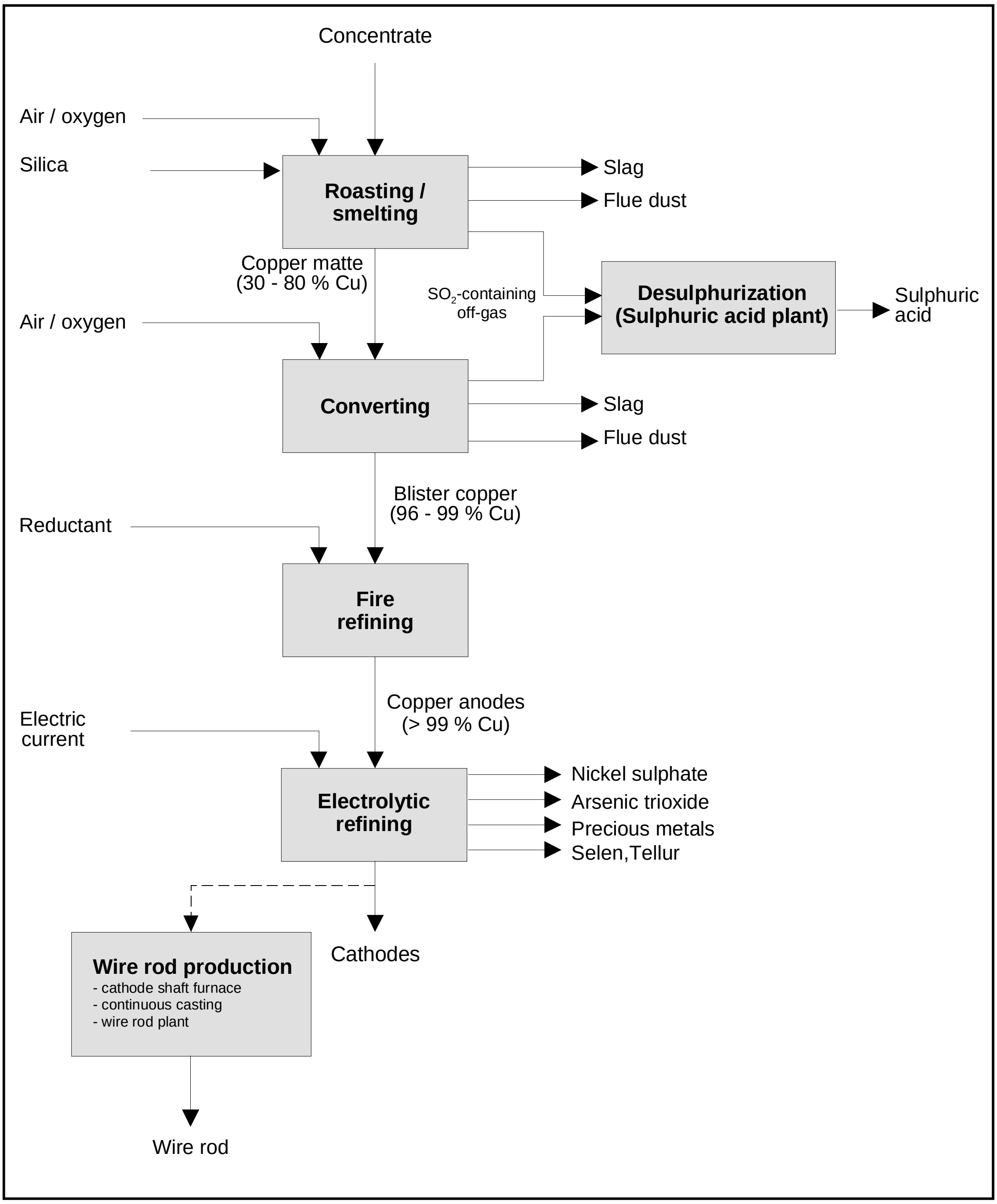

Figure 2-1: Primary copper production route

Source: Langner [49]

A furnace process gas, containing sulphur dioxide, is formed during smelting and further processed, after treatment for dust removal, in a sulphuric acid plant. If the copper content of the slag is too high, the recovery of copper e.g. in an electric furnace is possible. Otherwise the decopperised slag is marketed for e.g. road construction, hydraulic engineering or as a blasting media. Table 2-1 shows a typical composition of copper matte and slag produced in the smelting process.

Table 2-1: Composition of matte and slag from smelting operation

Components	Copper matte [wt-%]	Slag [wt-%]
S	20 - 25	-
Fe	6 - 40	-
Cu	29 - 70	0.3 - 0.8
SiO_2	-	29 - 40
FeO	-	32 - 50
Fe_3O_4	-	up to 10
CaO	-	up to 10
Al_2O_3	-	up to 10

Source: Winnacker-Küchler [86]

The main types of furnaces applied for smelting of roasted raw materials are reverberatory furnaces and electric furnaces. In 1994 reverberatory furnaces were used for about 25 % of the world-wide copper concentrate smelting [8]. Electric furnaces produce less off-gas, due to the fact that no additional fuel for heat production is added. Therefore it reaches a higher concentration of sulphur dioxide, which is favourable from an environmental point of view. But they can only be used economically, if cheap electric energy is available. In Europe, reverberatory furnaces are not used for primary smelting anymore.

Processes for ***combined roasting and smelting*** can be divided into bath smelting processes and flash smelting processes, these being the most widely adopted devices for the smelting of copper. Flash smelting accounts for most of the copper smelting in Japan, the United States and the European Community. Since 1970, about 30 new furnaces have been installed in addition to those already existing 7 [8].

The *Outokumpu process* is the standard process for smelting and is used most frequently today; about 30 furnaces are in operation world-wide. It is used for processing dry concentrates which are fed via a concentrate burner into the top of an upright reaction shaft together with the fluxes and the hot air. The molten particles are separated from the gas flow and fall into the molten bath at the bottom of the furnace. There the matte separates from the slag and is further processed in a converter. The slag is decopperised in a different process. Although the Outokumpu process is basically autogeneous, supplementary heating is needed in the settler. The advantages of the Outokumpu process are basically the high throughput rate achievable with one furnace, the high sulphur dioxide content in the off-gases, the good energy efficiency, which results in a reduction in fuel consumption in context with tonnage oxygen utilisation, and - as a result of the high matte grade - the reduced blowing time of the converters[56]. The *Inco process* (International Nickel Co.) processes a mixture of copper concentrate, which has been dried in a fluidised bed dryer, and oxygen, which is blown horizontally into the furnace from both ends. No additional heat is needed since the heat generated by the roasting of the concentrate is sufficient to support an autogeneous smelting process. In combination with the application of pure oxygen, the specific off-gas rate is very low and reaches a sulphur dioxide content of 75 – 80 vol.-%. Slag is removed continuously at the one end of the furnace whilst matte is discharged periodically from a side wall. Four Inco furnaces were in operation world-wide in 1994 [67]. In Europe, this process is not used [88].

The *Mitsubishi process* is a bath smelting process which combines roasting, smelting and converting in one continuously carried out process employing three interconnected furnaces. In the first furnace, dried concentrates, fluxes and air are charged, and a matte and a slag are produced. Slag and matte flow continuously into an electric furnace where they are separated. The matte flows into the converting furnace and is continuously processed into blister copper. This process is used in Japan and Canada [56] and is currently under construction in Indonesia and Korea [67]. The *Noranda process*, which is a cylindrical converter-type smelting furnace, is charged with pelletised concentrates and fluxes. The heat needed is supplied by natural gas or oil. The slag flows out continuously opposite the charging end and the matte is tapped periodically from the bottom of the furnace for further processing. Two Noranda furnaces are currently being used in Canada and in Australia [67]. The *El Teniente converter technology* for autogeneous smelting of copper concentrates uses the heat produced from the oxidation of the green charge for melting. Technical oxygen is used to produce a high grade matte, an off-gas with a high sulphur dioxide content and a slag with 6 - 8 % copper. Both wet and dried concentrates can be processed in the El Teniente converter. However, when charging wet concentrate, seed matte, produced in a separate smelting unit, i.e. a reverberatory furnace, needs to be added. The advantages of this technology are low capital investment and operating costs and low energy consumption [56]. Teniente furnaces are in operation in Chile, Peru and Samba and one is under construction in Thailand [67]. In the *Vanjukov process* the oxidising gas is not injected into the matte layer, but directly into the foaming slag. The process was commercialised in Russia in 1977; in 1992 five furnaces were producing about 400,000 tons of copper per year [56]. In the *Bayin process* the smelting and roasting processes are combined in a fixed rectangular furnace. The melting bath is divided into two parts into a smelting and a settling zone separated by a wall. The oxidising gas is injected through blast tuyères into the matte. It is operated at Lanzhau and has a capacity of 400 t of copper per day [56]. In Table 2-2, Langner [49] has summarised technical data for some of the described smelting processes.

Table 2-2: Technical data for different copper smelting processes

	Reverberatory furnace (green batch)	Outokumpu flash smelting	Inco	Mitsubishi (continuous)
Energy consumption [GJ/t Cu]	25.6	16.4	14.2	17.2
Copper content in the matte [wt.-%]	35	62	54	65
Oxygen feed rate [kg/t Cu]	0	480	790	390
Supplementary fuel [GJ/t Cu]	20.7	6.9	3.3	9.7
Off-gas rate [m³/t Cu]	17,700	5,300	3,800	5,100
SO_2 concentration*) [%]	3.8	13	20	14

*) More recent operating results indicate the following off-gas compositions, depending also on the percentage of ingress air: Outokumpu up to about 30 %, Inco up to about 80 %, Mitsubishi up to about 20 % SO_2.

Source: Langner [49]

To compare the overall energy consumption for the production of primary copper with different production processes, values on energy consumption according to [44] are shown in Table 2-3. The given values include the drying of the concentrate, the smelting using the different processes, the converting, the fire refining, the electrolytic refining and the production of sulphuric acid.

Table 2-3: Energy consumption of the primary copper production by use of different production processes

	Reverberatory furnace (green batch)	Outokumpu flash smelting	Inco	Mitsubishi (continuous)
Energy consumption [GJ/t Cu]	40.9	23.4*)	24.7	23.1

*) Converter slag is recycled to the flash smelter

The *Isasmelt process* is a rather new process technology using a top-entry lance submerging into the matte. Moist concentrate pellets, coal and fluxes are charged continuously into the furnace, whereas oxygen enriched air is injected through a lance which submerges into the slag. Both matte and slag are tapped simultaneously through a single hole into a settling furnace where they are separated. The main characteristics of the Isasmelt process are a high sulphur dioxide concentration in the off-gas, high specific smelting rates and a reduced fuel consumption. Four Isamelt furnaces are in operation in Australia, Europe, India and the USA. The *Contop process* is a new furnace concept which uses two furnaces, a flash cyclone smelter for producing copper matte and a continuous converter and refining furnace for producing anode copper. The inputs are injected tangentially into the cyclone and the reacting mixture falls into a settling chamber underneath where the different phases separate. Slag cleaning is carried out with oxygen and propane or methane as reductants. The matte flows into the converting and refining vessel which is separated into three chambers for converting, oxidation and reduction. This process is not in use, only in El Paso, USA, is a reverberatory furnace equipped with a cyclone burner and an injection system for natural gas. Table 2-4 shows the technologies currently used for copper smelting.

Table 2-4: Current copper smelting processes

Conventional technologies	Flash smelting	Bath smelting	New/emerging technologies
Oxy-fuel reverberatory furnace Electric furnace	Outokumpu Inco	Mitsubishi Noranda El Teniente Vanjukov Bayin	Isasmelt Contop

Source: Osparcom [56]

The ***converting*** of copper matte to blister copper is performed in a two-stage batch process. In the first step the remaining iron sulphide is oxidised by blowing in compressed air into the molten matte and then separated from the matte by forming a converter slag. In the second step the copper matte is partly converted into copper oxide, which then reacts to metallic copper (blister copper: copper content 96 - 99.5 %) with the remaining copper sulphide. Typical temperatures of the copper phase are between 1,150 and 1,250 °C. The resulting slag is skimmed off from the surface of the melt. The copper rich slag from the first converting step is removed before the second step and is returned to the smelting process to recover the copper content. The sulphur is oxidised to sulphur dioxide by the additional introduction of compressed air, iron, lead, zinc, nickel, arsenic, antimony and bismuth are removed by slagging or by volatilisation. The oxidation supplies enough heat to maintain the required temperature for the converting process, in order that no additional fuel is required. The typical composition of slags from copper smelting devices are shown in Table 2-5.

Table 2-5: Typical composition of copper smelting slags

Component [wt.-%]	Reverberatory furnace	Flash furnace	Noranda reactor	Pierce-Smith converter
Copper	0.4 - 0.6	1 - 1.5	8 - 10	3 - 5
Iron (total)	35	40	35	50
Silica	38	30	21	25
Magnetite	7 - 12	13	25 - 29	25

Source: following Fabian [25]

Mainly converters of the *Pierce-Smith* type (Figure 2-2) are used for this process. At this type, air or oxygen enriched air is blown into the copper matte through submerged tuyères.

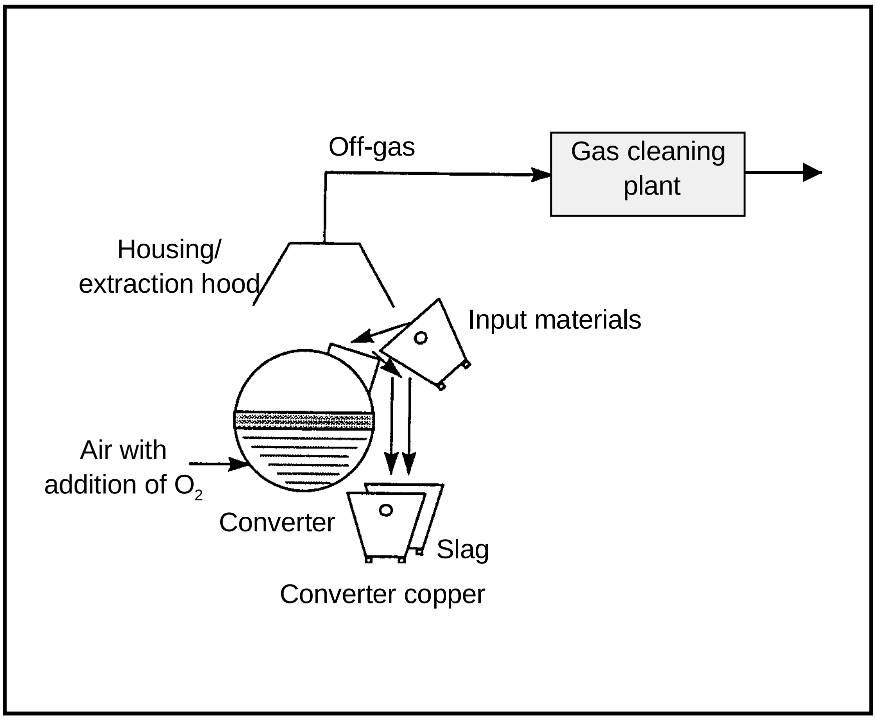

Figure 2-2: Pierce-Smith converter

Source: VDI-Richtlinie 2102 [75]

The off-gas is collected by a steel hood, led through a cooler, and then to an electrostatic precipitator and (usually) a sulphuric acid plant [8]. The *Hoboken* or *siphon converter* is another converter type with a different gas collection system, which is in use in only very few smelters. According to [56], it delivers an off-gas which is richer and more uniform than the off-gas from the Pierce-Smith converter. The *Kennecott-Outokumpu flash converter* treats ground, dried and high-grade granulate matte. It is a continuous working process which delivers a constant SO_2-concentration. Due to the constant concentration of SO_2 the off-gas can be handled easier in a sulphuric acid plant. One converter of this type went into operation in 1995 [67].

For sulphur recovery, dedusted off-gases can be treated in the ***sulphuric acid plant***, shown as an example in Figure 2-3.

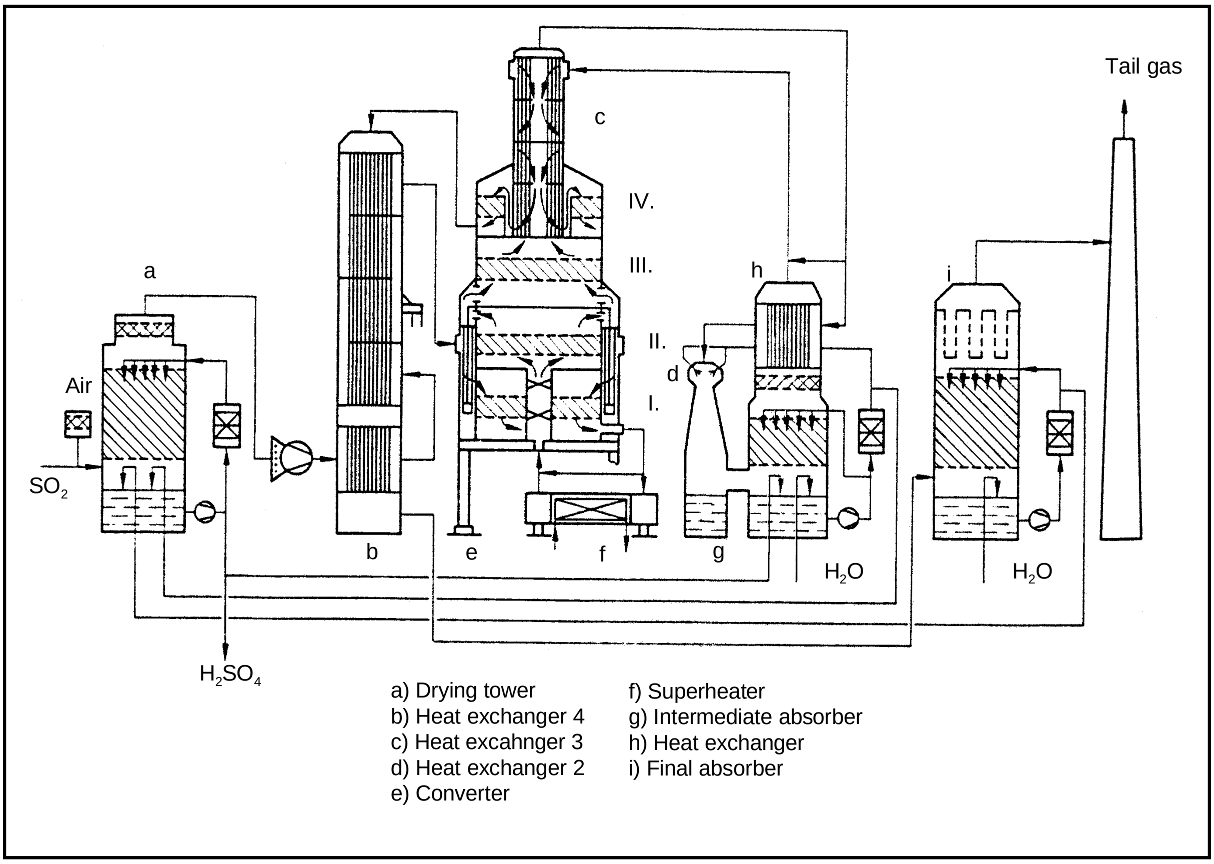

Figure 2-3: Double absorption contact plant

Source: Rentz [58]

Fire refining is a further purification process carried out in two steps. In the first step selective oxidation of the remaining sulphur and other impurities is achieved by blowing air through the molten metal. Thereby small amounts of a copper oxide containing slag are formed, where the oxidised impurities concentrate. They can be recirculated into the smelting furnace or the converter to recover the copper contained. The metals which are not oxidised (e.g. precious metals) remain in the copper phase and have to be removed by electrolytic refining. In the second step of the fire refining the oxygen content of the copper phase has to be reduced to the required final level. This deoxidisation step is achieved by blowing reductants in, such as natural gas, propane, naphta, reforming gas or ammonia through the molten phase or by addition of wood piles. The fire refined copper with a copper content of 99 % and above is cast into anodes. Most copper anodes are cast on a casting wheel in open anode-shaped impressions on the top of flat copper moulds. In 1994, continuous casting of anodes on a Hazlett casting machine was applied by 6 smelters and refineries [8]. The copper is thereby poured into the gap of two moving water-cooled steel belts and has to be cut out by a shear or a plasma torch.

Fire refining is carried out in rotary refining furnaces or in hearth furnaces (fixed or tiltable type (c.f. Figure 2-4)). Rotary furnaces dominate the fire refining in primary copper production, whereas for secondary copper production hearth refining furnaces are used, as they are better suited for the melting of solid scrap [8]. The Contimelt process, a continuous two-stage process, from which the copper can be directly casted into anodes on a casting wheel, is another technology used for fire refining of converter copper. Detailed information is given in chapter 2.2.2.1.

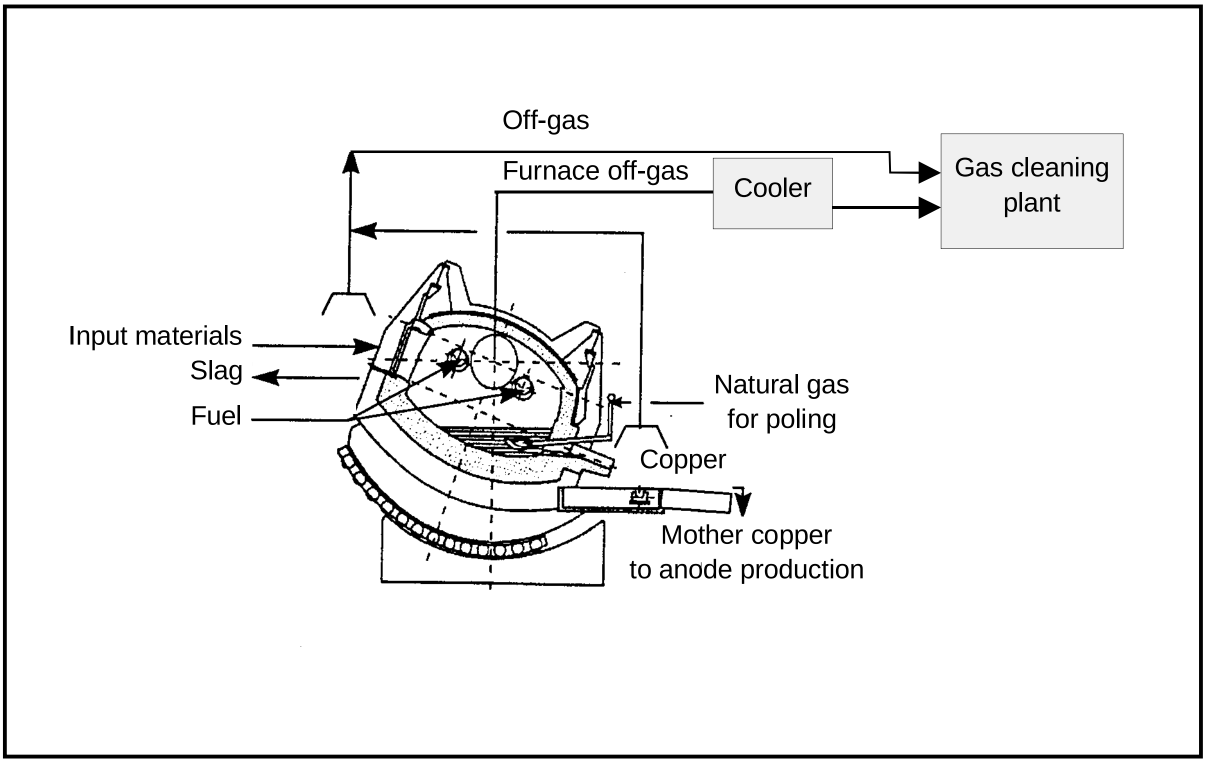

Figure 2-4: Reverberatory furnace plant for anode production (example for a plant having a tiltable furnace)

Source: VDI-Richtlinie 2102 [75]

To reach the desired high copper quality, further removing of impurities and the extraction of chemical elements, such as noble metals, nickel, selenium and tellurium takes place at the ***electrolytic refining***. The electrolytic process provides a copper which has the required properties due to a degree of purity of more than 99.99 %.

Thereby the copper anodes are dissolved in an electrolyte using electric current and the copper is deposited on the cathode as pure metal. The main processes involved are the following electrochemical reactions:

Anode: $Cu^{o} \rightarrow Cu^{2+}_{dissolved} + 2e^{-}$ $E_o = +0.34$ V

Cathode: $Cu^{2+} + 2e^{-} \rightarrow Cu^{o}$ $E_o = -0.34$ V

The electrolyte consists of dilute sulphuric acid containing dissolved copper and small additions of organic substances (1 - 5 g of organic materials such as glue, thiourea, gelatine and sulphite lye, per ton of copper [49]) in order to optimise the deposition characteristics.

Modern electrolytic plants using the *ISA process* employ permanent cathodes made of stainless steel, on which the copper is deposited and removed mechanically in the form of sheets. This technique avoids the expensive manufacturing of starter sheets and since this technique allows mechanisation and automatisation, the production capacity can be increased. The noble accompanying elements present in the copper anode, such as Ag and Au, and also lead are collected in the anode slime from which they are extracted in downstream process steps. The base elements, such as nickel (Ni), accumulate in the electrolyte, some of which is continuously drawn off for the purpose of extracting metals, including the nickel in the form of nickel sulphate, and then returned to the electrolysis plant.

The electrolyte is continuously circulated, in order, among other things, to establish uniform temperature conditions between 60 and 65 °C in the tanks and to continuously replenish additives. To keep the copper content constant, regulator tanks are included in the circulation system. The anodes used in these tanks are lead sheets on which fine bubbles of oxygen are formed by the following reaction.

Anode: $H_2O \rightarrow \frac{1}{2} O_2 + 2H^+ + 2e^-$
Cathode: $Cu^{2+}_{dissolved} + 2e^- \rightarrow Cu^o$

This oxygen produces an electrolytic spray above the surface of the tank and, because of the associated health risk in the case of inhalation, the tanks should be covered (oil, polyurethane beads, etc.) or provided with ventilation. In the case of vented tanks, a scrubber is provided downstream, if necessary, to purify the ventilation air.

For structural reasons, the floor area underneath the electrolytic tanks has to be protected from sulphuric acid attack by a suitable coating, thereby ensuring that the soil and ground water underneath the building are protected at the same time.

Waste water is not produced in copper electrolysis. Any leakage from the plant is collected and fed back to the electrolyte along with rinsing water to compensate for evaporation losses. The same applies to the scrubbing water if the decopperising tanks are operated with an extraction system. The anode scrap (approx. 12 - 16 % of the cast copper [64]) is recycled e.g. by charging them back into the converter or the anode furnace after washing off the anode slime.

2.2.1.2 Main outputs and environmental concerns of primary copper producing plants

The potential sources of stack and fugitive emissions into the air from primary copper production processes and the arising contaminants are summarised in Table 2-6.

Table 2-6: Potential sources of stack and fugitive emissions from primary copper producing plants

Process unit	Operation/source	Emission/main contaminants	f	s
Raw materials storage	Handling, storage, transport	Particulate matter	x	x
Dryer	Drying of flash smelting furnace-Feed	Particulate matter, gas		x
(Roasting) Smelting (incl. gas cleaning)	Leaks, cleaning operations	Gas, particulate matter, inorganic volatiles	x	
Converting (incl. gas cleaning)	Leaks	Gas, particulate matter	x	
Sulphuric acid plant	Off-gas from acid plant	Mist, gas		x
Electric slag cleaning furnace	Leaks	Particulate matter	x	x
	Off-gas	Gas, particulate matter		x
Anode furnace	Off-gas	Gas, particulate matter		x
	Leaks	Particulate matter	x	x
Electrolytic refining	Electrolysis cells/tanks/washing chambers	Mist		x
Continuous casting, wire rod plant	Material handling, off-gas from furnaces	Particulate matter, fumes		x

f: fugitive emissions; s: stack emissions

The potential sources of water pollution are summarised in Table 2-7.

Table 2-7: Potential sources of water pollution from primary copper production

Process unit	Operation/Potential source	Use/treatment options
General	Rain water from roads, yards, roofs, wet cleaning of roads	Waste water treatment plant
(Roasting) Smelting furnace (incl.gas cleaning)	Bleed of cooling water	Waste water treatment plant
Converter	Bleed of cooling water	Waste water treatment plant
Electric slag cleaning furnace	Bleed of cooling water	Waste water treatment plant
	Cooling water for slag granulation	Waste water treatment plant
Anode furnace (incl. casting wheel)	Bleed of cooling water	Waste water treatment plant
Sulphuric acid plant	Wet cleaning of roast gases	Waste water treatment plant
Water treatment plant (waste water/storm water)	Effluent treatment	Discharge, reuse as cooling water

The main solid outputs generated in primary copper production are summarised in Table 2-8.

Table 2-8: Outputs from primary copper producing plants

Process unit	Outputs	Use/treatment options
(Roasting) Smelting furnace (incl. gas cleaning)	Slags	Internal use or external use as construction material or abrasive manufacturing
	Dust	Internal use or bleed for external metal recovery
Converter (incl. gas cleaning)	Slags	Internal use or external use as construction material or abrasive manufacturing
	Dust	Internal use or bleed for external metal recovery
Electric slag cleaning furnace (incl. gas cleaning)	Slags	External use as construction material or abrasive manufacturing
	Dust	Internal use or bleed for external metal recovery
Sulphuric acid plant	Sulphuric acid	By-product for sale
Fire refining (incl. gas cleaning)	Slags	Internal use
	Dust	Internal use or bleed for external metal recovery
Electrolytic refining (incl. gas cleaning)	Anode slime	Internal precious metal recovery or sold for external treatment
	Anode scrap	Internal use
	Electrolyte bleed	Further processing for acid recovery and reuse as well as nickel sulphate to be sold
	Scrubber bleed	Recycled to the electrolyte
Waste water treatment plant	Sludges/residues	Internal recovery of metal content, waste disposal, sale product

2.2.2 Secondary copper production

Depending on the metal content and the type of feed, the smelting step to produce copper metal from secondary materials may comprise several stages, like reduction, oxidation/slagging and volatilisation, for upgrading the metal content and separating other components from copper. The subsequent fire and electrolytic refining is analogue to the primary copper production[9]. Depending on the purity and composition of the copper containing materials, they are added at different stages of the process. In the following sections, first a general process description of the secondary copper production is given (c.f. 2.2.2.1). Typical outputs to the different environmental media are then described in the section 2.2.2.2.

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[9] Process steps following the electrolytic refining such as founding, alloying, casting, etc., will not be described in this report.

2.2.2.1 General process description

In Figure 2-5, a schematic flowsheet for the secondary copper production is given. In the following sections the main input materials, the different production steps and process units of secondary copper production are described in detail. The underlined terms refer to Figure 2-5.

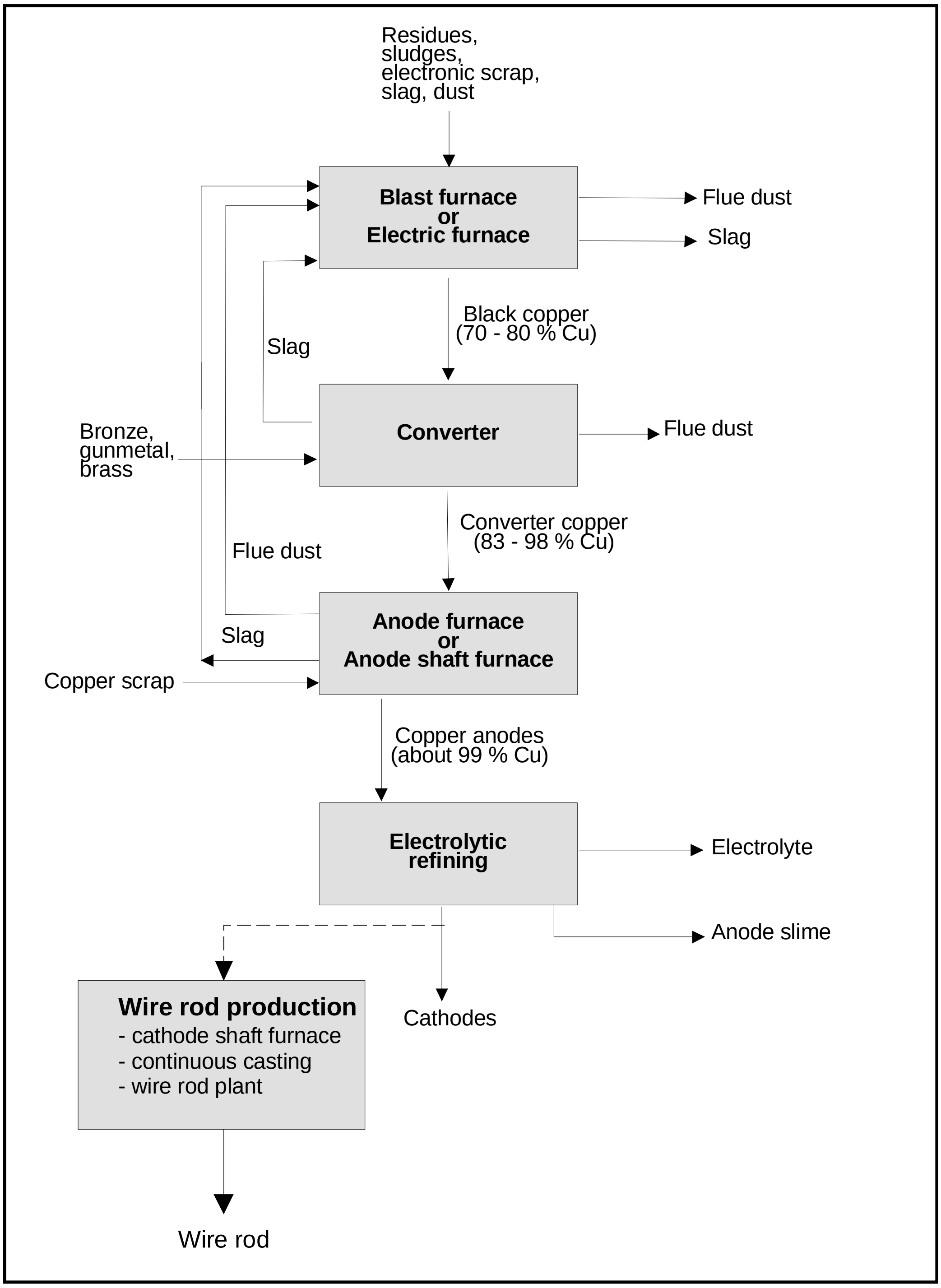

Figure 2-5: Flowsheet for secondary copper production

Source: following VDI-Richtlinie 2102 [75]

Inputs for secondary copper production

Inputs for secondary copper production are divided into:

- mainly metallic, oxidic and sulphidic raw materials,[10]
- fluxes and additives, and
- reductants (e.g. coal, coke, fuel oil, natural gas).

The most common raw materials for secondary copper production are metallic raw materials (different scraps from copper and copper alloys) and oxidic materials (copper-rich slags, ashes, drosses, dust and sludges).

Metallic materials

Pure copper scrap from manufacturing (fabrication scrap, wire scrap) or used product recycling can be remelted directly at the semi-finished products plant just as *alloy scrap* consisting of pure alloys (e.g. brass, bronze and nickel-silver). If not, the copper scrap is processed in a converter to remove zinc, tin and lead by oxidation and volatilisation. The converter copper is thereafter refined in an anode furnace and by electrolysis. *Copper scrap* can be contaminated with plastic and organic materials such as grease or with other metals such as lead and tin from soldered or brazed joints. Typical scraps are e.g. copper piping, sheets or iron-bearing electrical scrap (electric motors) or heating appliances (immersion heaters of washing machines). Another type of copper scrap is *copper-iron scrap* such as electric motors, plated scrap, circuit elements and switchboard units, telephone scrap, transformers, shredder materials. The processing depends on the composition and can take place in an anode furnace or in a converter followed by electrical refining. A variety of *special materials* such as cable scrap, electronic scrap etc. require special processing routes. When cables are sheathed with lead, the sheath has to be removed manually [49] and/or by segregation melting [67] before shredding. Depending on their chemical composition, the different scrap fractions can be added into the process at different stages.

Oxidic materials

Oxidic materials are of a low grade with a copper content from 10 - 60 %. These raw materials have to be reduced to a metallic intermediate product which then can be refined in a converter. Some typical oxidic raw materials are listed in the following.

Drosses result from the melting of copper and its alloys when molten material comes into contact with oxygen. A metal oxide is then formed on the surface and is skimmed off periodically. Droplets of metals become trapped in the dross. *Filter dust* containing copper

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[10] Sulphur containing raw materials are only processed if a sulphuric acid plant is installed for off-gas cleaning.

oxide are collected from the off-gas cleaning system. Other raw materials are *catalysts* from copper based catalysts. They contain carbon which forms a deposit on the surface during the use of the catalysts. *Electroplating sludge* and *waste water sludges* can also be recycled in secondary copper production. Table 2-9 shows some typical external recycling material for secondary copper production with the respective copper content and source.

Table 2-9: Major copper-containing external recycling materials

Type of material	**Cu-content** [wt-%]	**Sources**
Mixed copper sludges	3 - 10	Electroplating
Computer scrap	15 - 20	Electronics industry
Copper mono-sludges	10 - 30	Electroplating
Copper-iron material (lumpy or comminuted) from armatures, stators, rotors etc.	10 - 20	Electrical industry
Brass drosses, copper-containing ashes and slags	20 - 25	Foundries, semi-finished product plants
Red brass drosses, copper-containing and slags	20 - 25	Foundries, semi-finished product plants
Shredder material	60 - 65	Shredder plants
Copper-brass radiators	60 - 65	Cars
Mixed red brass scrap	75 - 85	Water meters, gear wheels, valves, taps, machine components, bearing boxes, propellers, fittings
Light copper scrap	88 - 92	Copper sheets, eaves, gutters, water boilers, heaters
Heavy copper scrap	90 - 96	Sheets, copper punchings, slide rails, wires, pipes
Mixed copper scrap	90 - 95	Light and heavy copper scrap
Copper granules	90 - 98	From cable comminution
Pure No. 1 scrap	99	Semi-finished products, wire, cuttings, strip

Source: Stelter [64]

Production units in secondary copper producing plants[11]

The standard technology for smelting secondary raw materials is the ***blast furnace process*** as shown schematically in Figure 2-6. It has a high flexibility in regard to raw material processing. The copper blast furnace is a shaft-type counter-current reactor in which the feedstock sinks downward from the top. The hot reaction gases flow upward from the bottom and heat the column of material. The shaft is sealed at the bottom by a crucible (a vessel lined with refractory material). The off-gas is extracted from the upper part of the shaft. In the case of furnaces having a closed throat at the top, the feedstock material is fed into the shaft via a transfer lock, while in the case of designs with an open throat, the feedstock material provides

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[11] The main parts of the process descriptions in this chapter are based on the current German VDI-Richtlinie 2102 [75].

a top seal itself. The furnace shell is either water-cooled over its entire height or in the lower part.

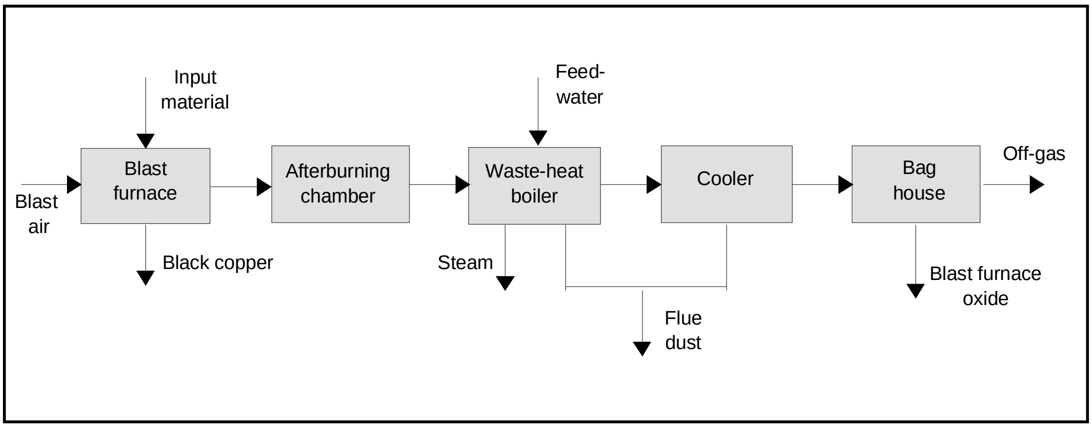

Figure 2-6: Treatment of blast furnace off-gas (secondary copper production)

The *feedstock* for blast furnaces includes secondary raw materials containing copper and noble metals originating from copper smelting and refining, copper foundries, the metal processing industry or mechanical concentrating plants for copper-containing materials (e.g. electronic scrap). The processed raw materials are, for example, copper-rich slags, copper drosses, filter or cyclone dusts, different sludges copper scrap, copper-iron scrap and copper-alloy scrap. Iron, lime and silica carriers are added to form the slag and coke is added as a fuel and for the purpose of reduction. As an example, the feedstock can be metered using a hopper system. Charging can be carried out in batches using buckets, or continuously at the head of the furnace. The transportation and charging systems are enclosed in order to prevent dust dispersal.

The blast furnace is operated using blast air (pre-heated and/or oxygen-enriched air). The molten phases of metal and slag collecting in the crucible are tapped off separately or together as a mixture. In the case of a combined run-off, the slag and metal are separated in a forehearth. The slag is granulated or poured into conical pots and mainly finds application as synthetic iron-silicate brick in the building industry or as a blasting material.

Some of the impurities present in the feedstock, such as zinc, lead and tin, are reduced, vaporised and oxidised by atmospheric oxygen above the stock column or in the subsequent exhaust gas passage and discharged with the furnace off-gases. After passing a controlled afterburning system[12], the reaction gases are fed to a gas cleaning plant via a waste-heat utilisation system. In a bag house, blast furnace oxide is precipitated. It is an important intermediate for metal extraction in other smelting plants or is sold directly as a product.

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[12] To remove the furnace off-gases safely and in an environmentally acceptable manner in the case of blast furnaces with an "unfired throat", it is necessary to fit an afterburning chamber in the downstream off-gas system, in which the afterburning of carbon monoxide and organic constituents (or compounds) is essentially carried out.

Emissions at the run-off of the blast furnace are collected by extraction hoods and fed to the gas cleaning plant.

By using a ***rotary converter*** instead of a blast furnace, the movements and the mass transfer, which are rather low in a blast furnace, can be increased. The rotary converter (TBRC) is operated batchwise. The heat for reduction is produced with the help of a flame from a water-cooled lance. Gas, heavy fuel and even powdery fuel can be used for the production of heat and as a reductant.

A rather new technology is the ***electric furnace***, which has the advantage that it produces smaller amounts of off-gas. Compared to the blast furnace, the raw material generally has to be pretreated as the electric furnace allows only a particle size of up to 100 mm and limited humidity. It is used in three different ways, depending on the raw material processed:

- Raw material with a low copper content as well as raw material consisting of oxides and sulphides are processed to copper matte, which is further processed in the converter to blister copper,
- raw material with a low copper content as well as raw material consisting of lead and sulphides is processed to copper-lead-matte, which is likewise processed in the converter to blister copper. The lead is removed with the slag which is used for lead recovery and
- raw material with a low copper content as well as raw material consisting of oxides is reduced to black copper,

For processing the latter, coke is likewise used as a reducing agent, but the melting heat is generated by electrical energy introduced by electrodes immersed in the molten slag, which provides electrical resistance. So the material usage per ton of black copper produced is less for an electric furnace than for a blast furnace and it emits correspondingly low amounts of off-gas. Since the electric furnace can be operated with a small amount of return slag, it is a comparatively small and well enclosed unit. Fugitive emissions occur during tapping and in the launders and these are extracted via off-takes ("subsidiary off-takes") and then fed to a gas cleaning plant. The separate purification of the subsidiary off-take waste air makes it possible, in the case of sulphur-containing feedstock, to purify the SO_2-containing furnace off-gas in the contact plant in which the SO_2 is converted into sulphuric acid.

The charge is prepared with a composition to suit the particular smelting program and fed into the furnace via an enclosed charging system. The molten product is tapped off via various tapping holes into buckets or ladles.

As in the blast furnace, zinc, tin and lead are essentially volatilised during the reducing smelting, discharged as oxides with the off-gas and precipitated in the gas cleaning plant. For the purpose of further purification, the off-gas may be fed to a contact plant after additional scrubbing. The precipitated flue dusts are processed further.

Besides the processing of the sulphidic phase (copper matte) in converters (c.f. 3.1.1.3), in secondary smelters a ***converter*** is used for further copper enrichment of the metal phase (black copper). This device is very flexible and can be used either for reduction as described above or for volatilisation, depending on the fuel air ratio.

The converter is operated in a batchwise manner, the feedstock consisting of alloy scrap (for example, bronze, red brass, brass, aluminium bronze, German silver, Tombac, tin alloys and various special alloys), suitable Cu-Fe scrap (copper content higher than 75 %) and also black copper and bronze from the in-house production, the latter being introduced partly in liquid state. Copper-rich return slags from the furnace for anode production and converter sectors can also be used, if possible in one heat, i.e. liquid.

Coke and iron-rich materials are used as fuel and as a reducing agent. The feedstock is introduced using so-called "boats" (for solid materials) and ladles (for molten materials), the latter also being used to collect the products, i.e. raw copper and slag. The boats and ladles for charging are transported by means of a crane. In some cases, cold material may be fed into the converter via a side charging hole during blowing.

Air, possibly enriched with oxygen, is blown into the bath from the rear through tuyéres. Because of their greater affinity for oxygen, the base metals (for example Fe, Al, Zn, Sn, Pb) largely undergo oxidation. Iron and aluminium are completely adsorbed by the slag, while zinc, tin and lead are only partly adsorbed by the slag as oxides and partly volatilised and discharged into the gas cleaning plant with the off-gases. The copper-containing slag is mainly recirculated to the blast or electric furnace. The off-gases are fed to a gas cleaning plant. The precipitated converter oxide can be used as an important intermediate for extracting the quantities of lead, zinc and tin contained in the feedstock or it can be sold directly as a product.

To collect or reduce the emissions occurring during charging and pouring, converters are enclosed or provided with extraction hoods. The waste air extracted from the housing or hoods is expediently used to convey the oxides, i.e. primary and secondary off-gases are removed together.

For refining the converter metal (further removal of accompanying elements), ***reverberatory (anode) furnaces (hearth type)*** are used, as they are better suited for the melting of solid scrap than rotary furnaces. This is an advantage since, in contrast to the primary copper production industry, in the secondary copper production industry copper scrap is used for the anode production on a large scale. The fixed or tiltable hearth-type furnaces are heated with fuel oil, gas and pulverised coal either individually or in combination. The combustion air is blown in cold or pre-heated and can, if necessary, be enriched with oxygen. The feedstock consists of converter copper (solid or molten), used copper material, in-house returns such as anode scrap from electrolysis and blister copper from primary smelting, if available.

Solid feedstock is introduced by means of charging machines, while liquid feedstock is poured in via launders. Reverberatory anode furnaces are operated batchwise, one charge involving loading, melting, refining and pouring.

After the feedstock has been melted completely, the melt is refined, i.e. the impurities are oxidised using air. In this process, traces of sulphur present in the raw copper are simultaneously oxidised to SO_2 and are then discharged with the off-gas. In the case of fixed furnaces, the air is blown onto the bath, while in the case of tiltable furnaces it is blown into the bath. The slag formed in this process is drained off, then the melt is heated to approximately 1,250°C and rendered pourable, i.e. the oxygen content (mainly present as Cu_2O) is reduced to about 0.1 %, under reducing conditions established by immersing wooden poles in the bath or blowing in reducing gases. The copper is cast in anode formats on a rotary casting machine.

The firing, and the amount and composition of the off-gases and also their dust content varies with the furnace phase. The off-gases are first fed to a heat exchanger (waste-heat boiler and tubular cooler) and then to a gas cleaning plant. To counteract corrosion due to SO_2 and off-gas humidity, lime (white lime hydrate) is blown into the off-gas. The precipitated dusts and the drained off slags are reused, generally in a blast furnace.

The ***Contimelt process***, developed by Norddeutsche Affinerie and Union Minière, is an energy-saving process for continuously melting and refining raw and used copper and also for casting refined copper as anodes. The plant consists of three units:

- hearth furnace equipped with a shaft for charging and pre-heating and for the oxidation of the molten copper,
- poling furnace for continuous reduction of the molten copper from the Contimelt furnace, and
- a casting plant for anode casting.

Natural gas is used as fuel and poling gas. The feedstock is transported by means of a skip into the shaft of the furnace and is pre-heated in the latter by the hot furnace off-gas. During the refining in the hearth of the furnace, a slag is produced which is drawn off and processed further. The refined, molten copper flows continuously via a launder into the poling and casting furnace and, after being poled with natural gas in the latter, it is fed via a launder to the casting plant.

The off-gas plant consists of a waste-heat boiler for generating steam, a heat exchanger for pre-heating the burner air, a cooler and a gas cleaning plant. Carbon containing lime, for example, may be introduced via a metering system for conditioning agents into the off-gas to adsorb organic constituents. Tapping holes and launders are provided with extraction hoods, via which diffuse emissions are likewise fed into the gas cleaning plant. The precipitated filter dust is recycled.

The remaining minor elements such as lead, nickel and precious metals are removed in the subsequent *electrolytic refining* as already described in section 2.2.1.1.

2.2.2.2 Main outputs and environmental concerns of secondary copper producing plants

The potential sources of stack and fugitive emissions into the atmosphere from secondary copper production processes and arising contaminants are summarised in Table 2-10.

Table 2-10: Potential sources of stack and fugitive emissions from German secondary copper producing plants

Process unit	Operation/source	Emission/main contaminants	f	s
Raw materials storage	Handling, storage, transport	Particulate matter	x	x
Blast furnace (incl. Gas cleaning)	Smelting/off-gas	Gas, particulate matter	x	x
Electric furnace (incl. Gas cleaning)	Smelting/off-gas	Gas, particulate matter	x	x
Converter (incl. Gas cleaning)	Converting/off-gas	Gas, particulate matter	x	x
Contimelt furnace	Smelting/refining	Gas, particulate matter	x	x
Electrolytic refining	Electrolysis cells/tanks/washing chambers	Mist		x
Continuous casting, wire rod plant	Material handling, off-gas from furnaces	Particulate matter, fumes		x

f: fugitive emissions; s: stack emissions

In the processing of secondary raw material, mostly the same liquid effluents occur as for primary copper production (c.f. 2.2.1.2), nevertheless the potential sources of water pollution are summarised in Table 2-11.

Table 2-11: Potential sources of water pollution from secondary copper production

Process unit	Operation/ Potential source	Use/treatment options
General	Rain water from roads, yards, roofs, wet cleaning of roads	Waste water treatment plant
Blast furnace	Bleed of cooling water	Waste water treatment plant
	Cooling water for slag granulation	Waste water treatment plant
Electric furnace	Bleed of cooling water	Waste water treatment plant
Converter	Bleed of cooling water	Waste water treatment plant
Contimelt furnace	Bleed of cooling water	Waste water treatment plant
	Cooling water for slag granulation	Waste water treatment plant
Anode furnace	Casting wheel	Waste water treatment plant
Water treatment plant (waste water/storm water)	Effluent treatment	Discharge/ reuse as cooling water

The main outputs generated in secondary copper production are summarised in Table 2-12.

Table 2-12: Outputs from secondary copper producing plants

Process unit	Outputs	Use/treatment options
Blast furnace	Blast furnace oxide (flue dust)	Internal recycling or sale for metal recovery
	Slags	External use as construction material or abrasive manufacturing
Electric furnace	Slags	External use as construction material
	Lead bullion	Further processing (refining)
Gas cleaning (furnace off-gas)	Dust	Recycling
Converter	Slags	Internal use or external reuse
Gas cleaning (converter off-gas)	Converter dust	Recycling
Contimelt furnace	Dust	Recycling
	Slags	Internal use or external reuse
Electrolytic refining	Bleed electrolyte	Further processing for acid recovery and reuse as well as nickel sulphate to be sold
	Anode slime	Internal recovery of precious metal or sold for external treatment
	Electrolyte bleed	Further processing for acid recovery and reuse as well as nickel sulphate to be sold
Gas cleaning (gas from refining)	Scrubber bleed	Recycled to the electrolyte
Tin-lead alloy plant	Tin lead alloy	Sale product
	Slags	Recycling or waste disposal
	Dust	Sale product (ZnO)
Waste water treatment plant	Sludges/residues	Internal recovery of metal content, waste disposal, sale product

2.2.3 Further processing of copper cathodes

Copper cathodes must be remelted and cast into shapes, because the structure of copper formed by the electrolytic refining is not suitable for working to semi-finished products. Cathodes are remelted in several types of special furnaces that perform the tasks of melting, post-refining (if necessary), holding and casting. In the following continuous processes to fabricate wire rod and processes for the fabrication of semi-finished products from copper and copper alloys are described.

2.2.3.1 Fabrication of wire rod

The most common *continuous rod casting* processes are further developments of the wheel-belt casting principle. Copper cathodes and recycling copper are melted in a shaft furnace. The molten copper is fed continuously via a launder to the grooved periphery of the casting wheel. After being shaved, the cast bar is fed to a rolling mill. The rolled rod is treated in a pickler with isopropanol, dilute sulphuric acid, water or steam rinsing to remove the oxidised surface and then coated with wax (c.f. Figure 2-7).

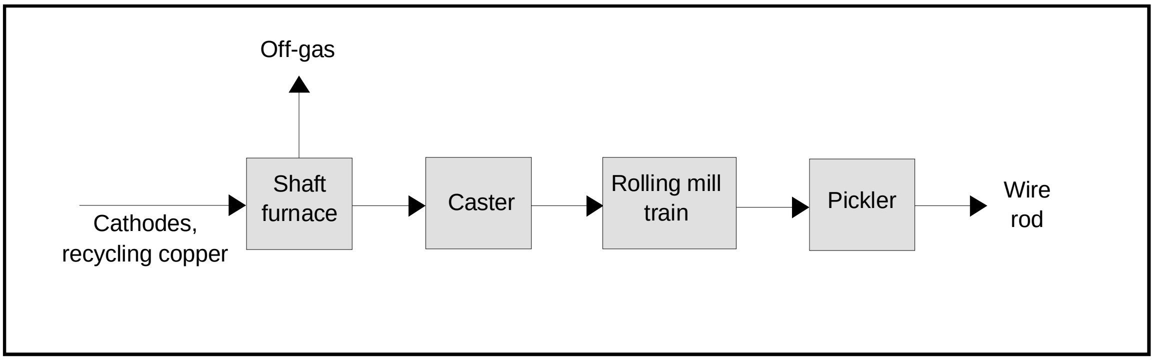

Figure 2-7: Wire rod plant

Another process to produce wire rod is the CONTIROD process. There, the copper is melted in a furnace and caste in a Hazellet-Caster. The caster is followed by a hot-rolling mill to produce wire rod which is sent to a coiler after being treated in a pickler. The basic concept of this process is shown in Figure 2-8.

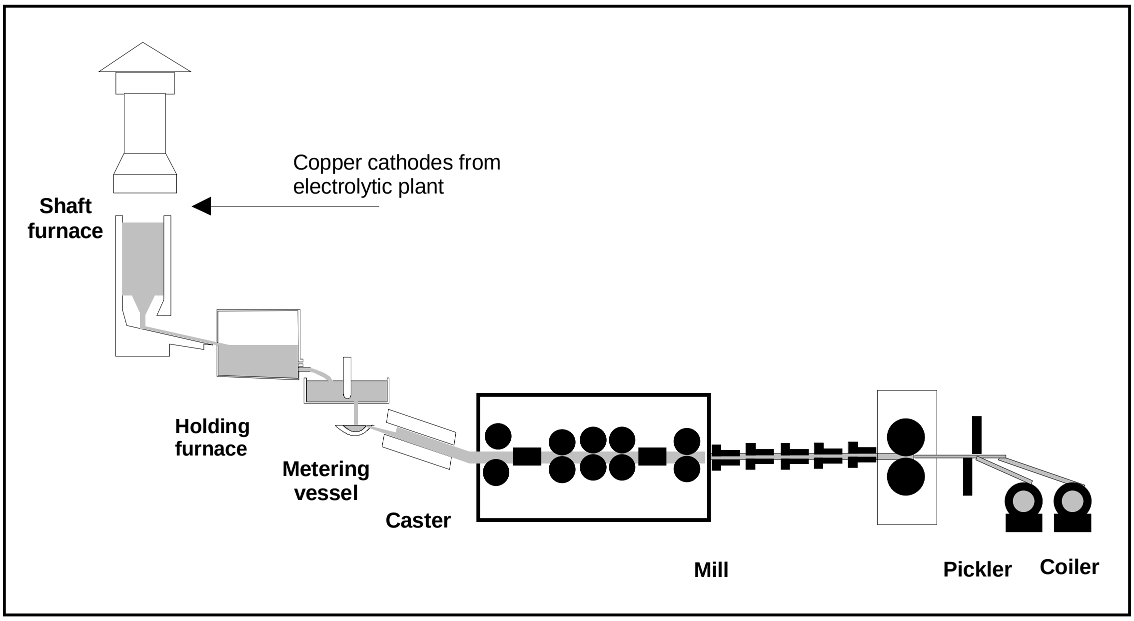

Figure 2-8: Basic concept of the CONTIROD process

Wire rod can also be produced by dip forming. With this process, a copper core wire (mother rod) is drawn through a molten bath of oxygen-free copper. Thereby additional copper solidifies on the surface to form a new rod. The rod produced is reduced in diameter in a mill under inert gas, so the copper wire is oxygen-free. About one third of the rolled wire is returned to form the core material.

2.2.3.2 Fabrication of semi-finished products from copper and copper alloys[13]

The following description represents a compilation of the most common processes and techniques for the fabrication of semi-finished products from copper and copper alloys including the applied abatement techniques.

Feed materials for the manufacture of semi-finished copper and copper alloy products are mainly: Copper cathodes, high grade copper scrap, fire-refined copper, copper alloy scrap, alloy metals, master alloys, etc. The main process steps for the fabrication of semis are illustrated as summary in Figure 2-9. The production steps for the different products are normally:

- Raw material processing,
- melting and casting,
- rolling mills for strips and sheets,
- extrusion and fabrication of tubes, rod and sections using different methods for working down,

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[13] Based on „Fabrication of Semi-Finished Products From Copper and Copper Alloys“, EUROMETAUX Copper Industry [66]

- annealing and pickling (this step is often integrated in other process steps), and
- degreasing (this step is often integrated in other process steps).

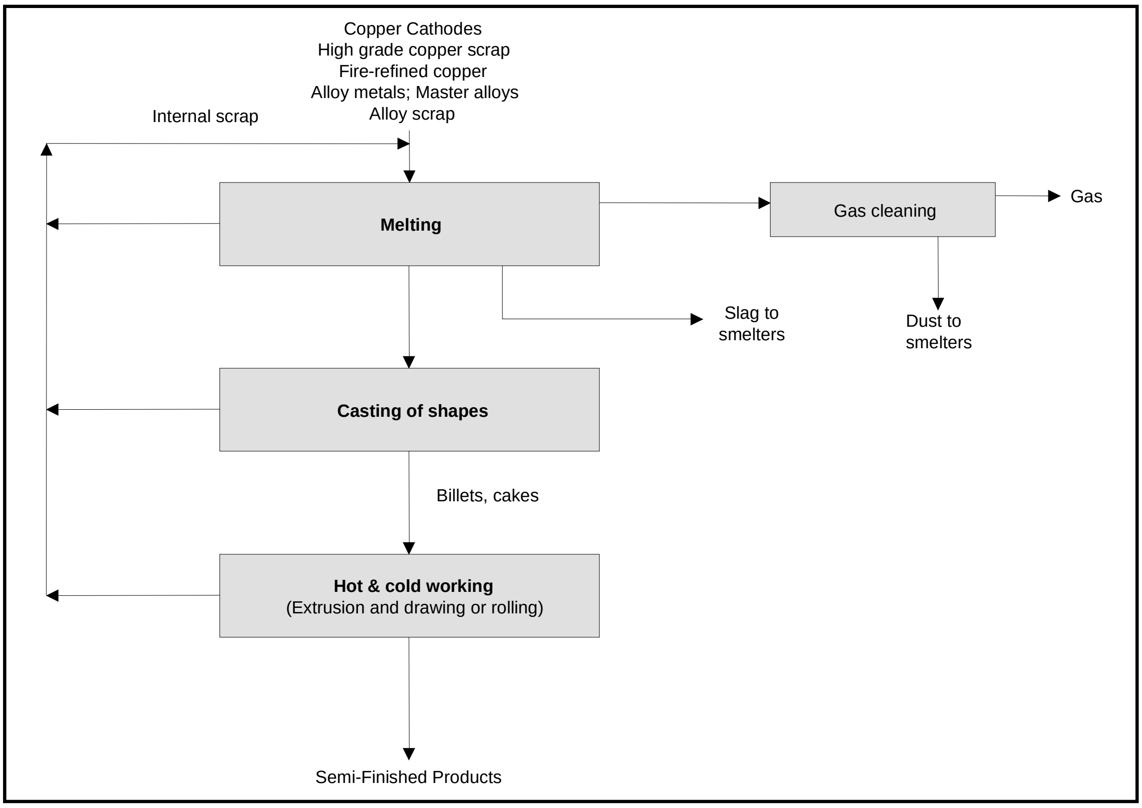

Figure 2-9: General flowsheet of semi-finished product fabrication

Source: [67]

Before charging into the melting furnace, raw materials like wires, punchings, cuttings, tubes etc. are pressed into blocks. Oil contaminated scraps are decreased or the off-gases of the furnace have to be treated in an afterburning chamber.

For melting, there are different kinds of furnaces in use: Batchwise operated electric furnaces are mainly used for copper alloy melting and to a lesser extend for unalloyed copper. Natural gas or fuel fired crucible, drum or hearth/reverberatory type furnaces are used for the discontinuous fire refining of the input materials. As in the fire refining step of the copper production, minor accompanying elements are reduced by an oxidation step and the oxygen content is reduced in the following reduction step by means of wood poles. If continuous operation and/or high capacity is necessary, shaft furnaces like the ASARCO furnace are in use. The ASARCO furnace is an energy saving melting facility, because the combustion gases of the natural gas fired burner are used to pre-heat the charge. Fire-refining and alloying are not possible in this furnace. The off-gases of the furnaces are collected and cleaned in a cyclone and a baghouse.

The molten copper is either directed directly to the casting units or to a holding furnace, where some alloying can take place. Then the materials are casted into billets or cakes/slabs in continuous or discontinuous casters. Discontinuous casting is always carried out in the vertical mode, continuous casting can be either in the vertical or horizontal mode. The basic principle is shown in Figure 2-10.

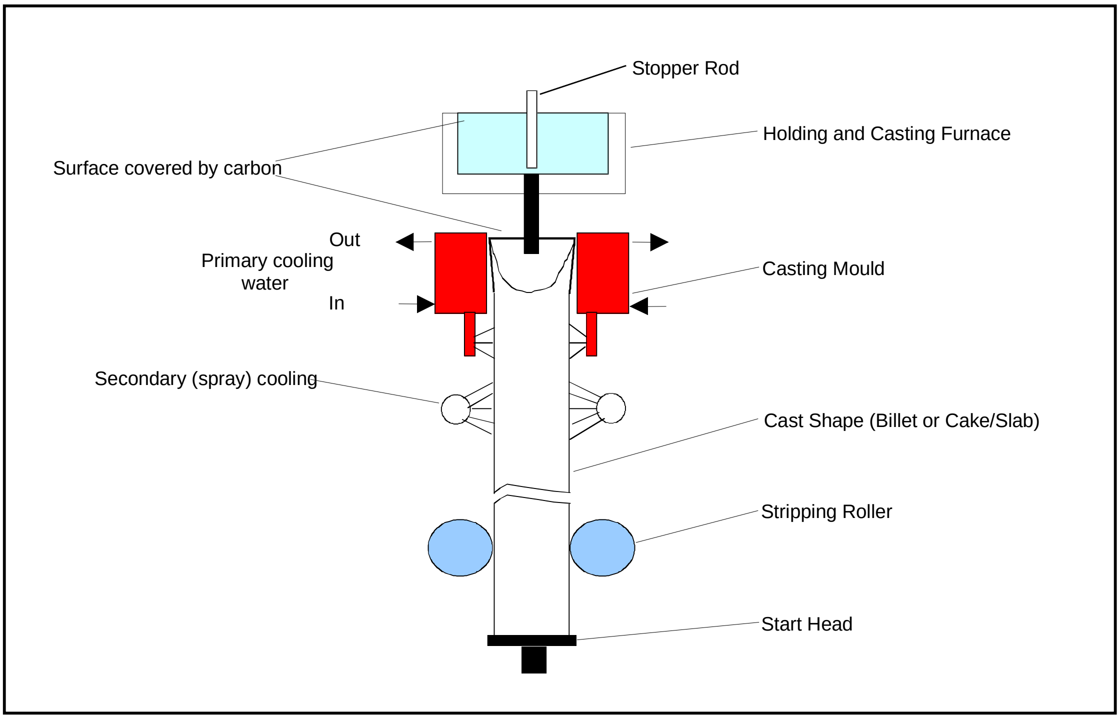

Figure 2-10: Principle of continuous or discontinuous casting

The casted slabs/cakes are used for the fabrication of sheets and strips by a rolling mill, billets are used for the fabrication of copper and copper alloy tubes, rods and sections by extrusion presses or rolling mills. The fabrication processes are described in detail in section 3.1.5.2.

2.2.3.3 Main outputs and environmental concerns of the further processing of copper

The main outputs generated in the casting and wire rod plants are summarised in Table 2-13.

Table 2-13: Outputs from the further processing of copper

Process unit	Outputs	Use/treatment options
Melting/holding furnace	Dust	Internal or external reuse
Caster	Cooling water	Waste water treatment plant, if necessary
Rolling mill train, pickler	Pickling acid	Recovery of copper content by electrowinning (electrical extraction), internal reuse
	Rolling emulsion	Treatment
	Cooling water	Waste water treatment plant, if necessary

2.2.4 Plants for copper production and further processing of copper cathodes

In Germany, one flash smelting process is in use for primary copper production, for secondary copper production, two plants use blast furnaces and one an electric furnace. Table 2-14 gives detailed information on German copper production plants.

Table 2-14: Copper production and recycling plants in Germany

	Norddeutsche Affinerie Aktiengesellschaft, Hamburg	**Hüttenwerke Kayser AG, Lünen**	**Mansfelder Kupfer und Messing GmbH, Hettstedt**
Primary smelter	Flash smelting furnace Electric furnace for slag purification Copper converters Anode furnace	-	-
Secondary smelter	Electric furnace Copper converters Contimelt plant Scrap converter/TLA plant	Blast furnaces Scrap converters Rev. anode furnaces Tin-lead alloy plant	Blast furnaces Scrap converters Anode hearth shaft furnaces Rotary anode plant
Electrolysis	ISA technology	ISA technology	Conventional technology
Further processing	Continuous casting Wire rod plant	-	Cathode shaft furnace Continuous casting Wire rod plant
Feed consumption [t/a]/**composition**	1,2 Mio (primary and secondary raw materials)	250,000 (secondary raw materials)	n. a.
Cu-cathode production capacity [t/a]	380,000	170,000	n. a.
Wire production capacity [t/h]	(60+40)	-	n. a.
Casting	(30+30)	-	n.a.
Main by-products	Sulphuric acid Slag Precious metals Lead	Zinc-oxide Tin-lead alloy Anode slime Copper sulphate Nickel sulphate Slag	n. a.
Certificates	ISO 9002	ISO 9002 ISO 14001 EMAS	n. a.
Dealt with in section	3.1	3.2	3.3

In Table 2-15 information about the products and capacity of main plants for further copper processing in Germany is given. German cable manufacturing plants are not mentioned in this Table.

Table 2-15 : Main plants for the further processing of copper

Company	Site	Production [t/a] (1996)	Production line	Employment
Deutsche Gießdraht GmbH	Emmerich	225,000 (1997)	Wire rod	-
Friedrich Kemper GmbH & Co KG, Kupfer und Drahtwerke	Duisburg	-	Bar, section and rod, strip/sections, wire rod, wire	-
MKM Mansfelder Kupfer und Messing GmbH, Hettstedt	Hettstedt	170,000	Sheet, plate, bar, section and rod, strip, foil, tube, wires	1,100
Norddeutsche Affinerie Aktiengesellschaft	Hamburg	350,000	Wire rod, billets, bar, section	2,100
Wieland Werke AG	Ulm, Vöhringen	307,000	Sheets, strip, tubes, rods, bars, wires, sections, finned tubes	3,800
KM Europa Metal AG	Osnabrück	225,000	Tubes, strips, sheets, specials	2,380
	Berlin	63,000	Brass products (tubes, wires, sections)	420
Schwermetall GmbH	Stolberg	261,000	Sheets	318
Prym	Stolberg	58,000	Strips, sheets, wires	417
Sundwinger Messingwerk	Hemer	12,000	Strips, sheets	450
Lacroix & Kress GmbH	Bramsche	-	Wire rod, wires	-

The locations of German copper production and main further processing plants are shown in Figure 2-11.

Figure 2-11: Locations of copper producing plants in Germany

3 Process technology, abatement techniques and present consumption/emission levels in German copper production

In the following, the copper producing plants operated in Germany are presented in detail. Based on the general description given in chapter 2, the process technology and abatement techniques applied are described. The present consumption and emission levels for each plant are given, if available.

3.1 Copper production at Norddeutsche Affinerie Aktiengesellschaft

Norddeutsche Affinerie Aktiengesellschaft (NA) was founded in Hamburg in 1866 and is today the largest copper producing plant in Western Europe with an annual output of at present 405,000 t/a of copper. NA is the only primary copper plant in Germany. It had a turnover of 2.15 billion DM and more than 2000 employees in 1996. Both primary copper (220,000 t/a) from copper concentrates (700,000 t of copper concentrates with an average copper concentration of about 31 % are processed yearly) as well as secondary copper (150,000 t/a) from different internal and external recycling materials are produced. An additional 35,000 t/a of external copper cathodes are purchased. Various by-products of copper production such as slags (at present 400,000 t/a), miscellaneous chemicals (e.g. sulphuric acid: 656,000 t/a) and precious metals (gold: 7.8 t/a, silver: 200 t/a) are obtained. In Figure 3-1 an overview of the copper production pathways at NA is given and in Table 3-1 the main input materials and products are listed.

In the following sections, detailed descriptions of the main process units of the NA plant are given, divided into:

- primary smelting plant,
- secondary smelting plant,
- electrolysis of primary and secondary copper,
- Southwire copper wire rod plant, and
- continuous casting of billets and slabs/cakes.

Finally, data on emissions and environmental concerns are summarised in section 3.1.7.

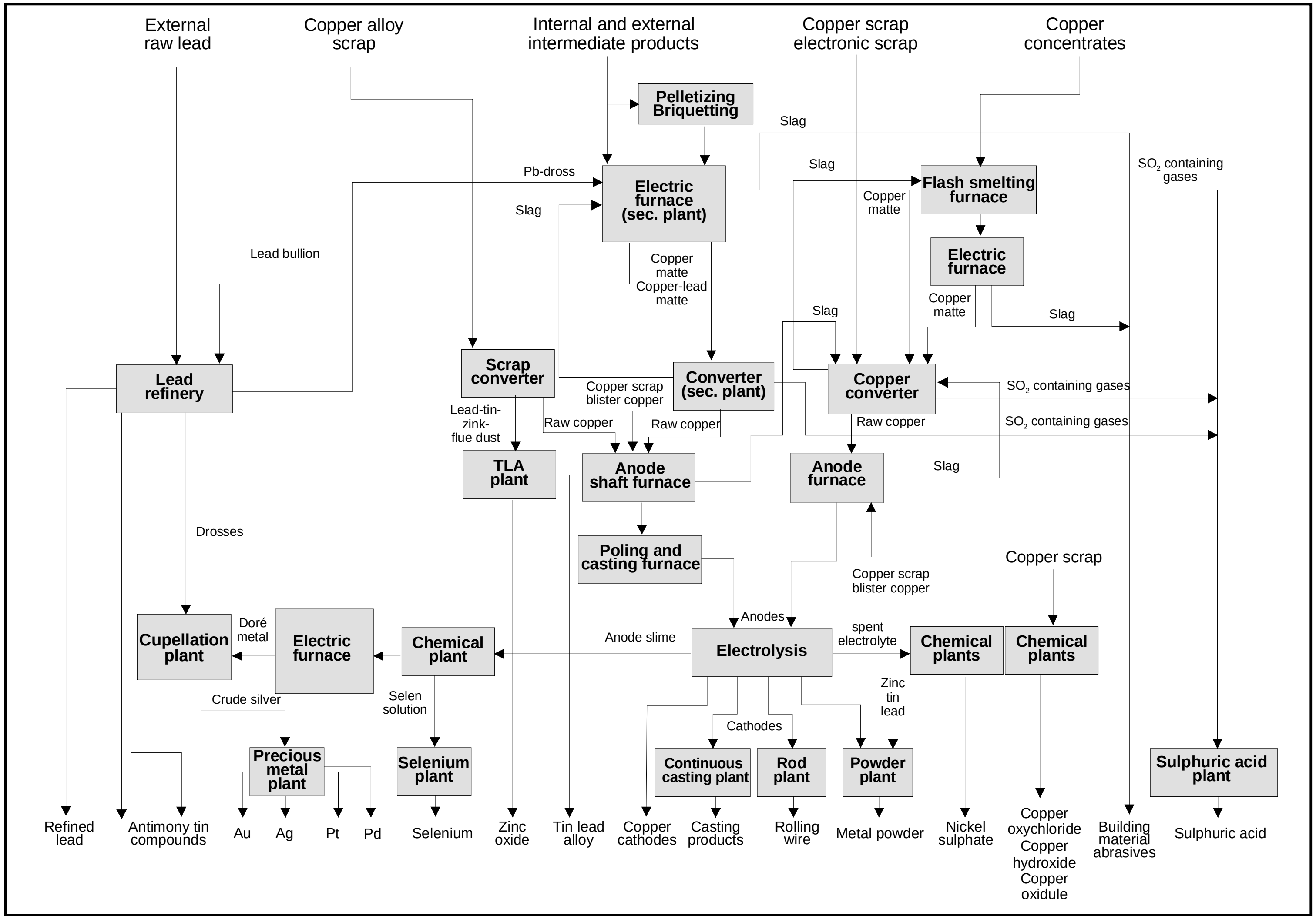

Figure 3-1: Copper production at Norddeutsche Affinerie Aktiengesellschaft

Source: Company information by NA [55]

Table 3-1: Input/output data from NA (1996)

Input materials	Quantity [t/a]
Copper concentrates	690,000
Copper scrap	95,000
Shredded material from electronic scraps	1,200
External intermediate products	86,000

Products	Quantity [t/a]
Electrolytic copper	370,000
Copper salts	6,500
Nickel sulphate	1,800
Precious metals	150
Refined lead	9,000
Sulphuric acid	660,000
Slags	410,000

Source: Company information NA, 1998

3.1.1 Primary smelting plant

3.1.1.1 Outokumpu flash smelting furnace

NA uses an Outokumpu flash smelting furnace for the processing of copper concentrates. The furnace was commissioned in 1972 and now has a permitted concentrate capacity of 950,000 t/a. The concentrates, which have a copper content between 30 and 34 %, are fed via a concentrate burner into the flash smelting furnace. The particle size is about 50 µm for the concentrate and 2 mm or less for the fluxes. 2,400 t/d of input material are fed into the furnace including 200 t/d of silica flux and recycled flash smelting furnace dust as well as 200 t/d of liquid converter slag from the Pierce-Smith converter (c.f. Figure 3-1). The use of oxygen enriched air amounts to 500 Nm³/min. Table 3-2 shows some process data for the Outokumpu flash smelter used at NA.

Table 3-2: Process parameter of the Outokumpu flash smelting furnace at NA

Blast details:	
Temperature [°C]	400 - 420
Oxygen enrichment [vol.-%]	> 45
Flow rate [m³/min]	420
Copper matte:	
Cu content [wt-%]	60 – 65
Temperature [°C]	1,200
Slag:	
Cu content [wt-%]	1 - 3
Fe content [wt-%]	37 - 42
SiO_2 content [wt-%]	30 - 32

Source: Biswas/Davenport [8], Langner [49]; company information NA, 1998

About 1,400 t/d of copper matte with an average copper content of about 65 % and an output temperature of about 1,200 °C are transferred to the Pierce-Smith converter for further processing. The flash smelting furnace slag (1,200 t/d) with a relatively high copper content of 1 - 3 % is processed in the electric furnace to reduce the copper content.

The off-gases from the Outokumpu furnace (40,000 - 60,000 Nm^3/h) leave the furnace at a temperature of 1,200 - 1,300 °C and a sulphur dioxide concentration of about 25 – 30 vol.-%. The off-gas is cooled in a waste-heat boiler and with recycled gas, which has a temperature of about 260 °C. With an off-gas temperature below 400 °C, the formation of sticky dusts is prevented. Part of the flue dust is thereby precipitated in the waste-heat boiler. The gas is then cleaned in a hot-gas electrostatic precipitator. After pre-heating the process air and the feed water for the waste heat boiler in a heat exchanger, the gas enters the sulphuric acid plant, where it is treated together with the dedusted off-gases from the converting operations. Figure 3-2 shows a diagram of the off-gas treatment applied for off-gases with a high content of sulphur dioxide at NA.

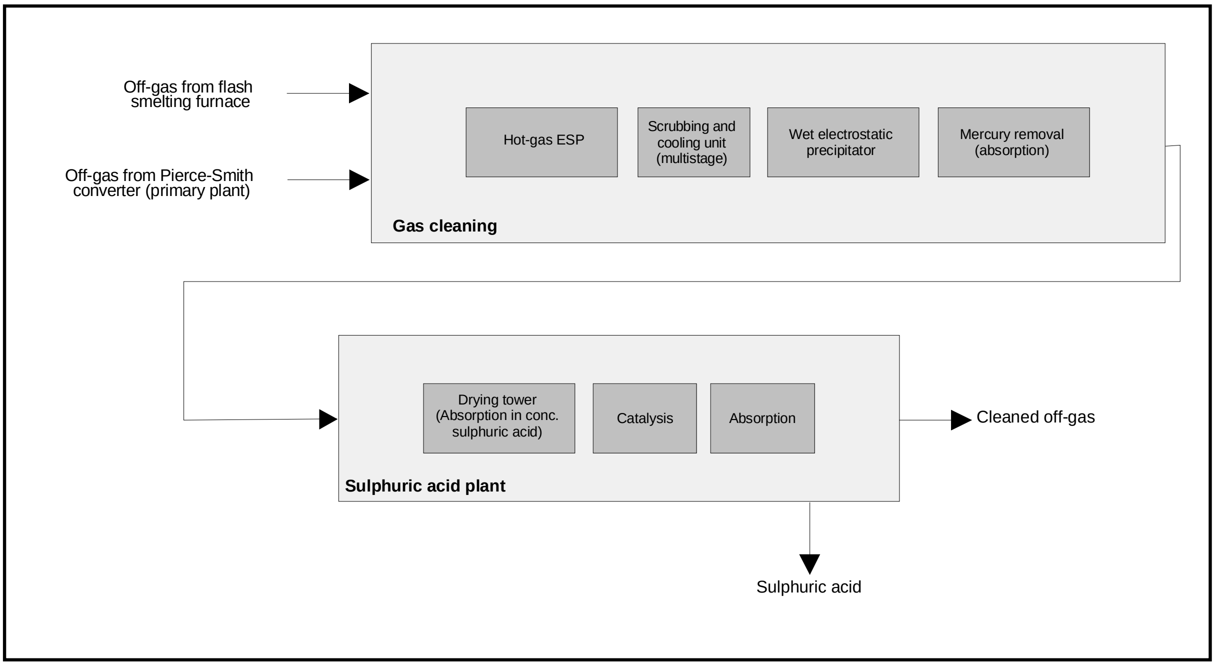

Figure 3-2: Treatment of Outokumpu flash smelting furnace and Pierce-Smith converter off-gas at NA

Source: Langner [49]

3.1.1.2 Electric furnace for slag cleaning (primary plant)

The slag produced in the flash smelting furnace contains about 1-3 % copper and is channelled to an electric furnace with a requirement of electrical energy of 50 kWh/t liquid slag for decopperising. During the slag cleaning process a C-bearing agent is added to the molten slag. The copper is collected at the bottom as a sulphide phase (matte) which is tapped and further treated in the converter process. 420 t/d of copper matte are recovered and sent for further processing to the converter. Depending on the market requirements, the 1,200 t/d of slag with a copper content of less than 0.8 % are either granulated (abrasives) or cast in slag pots, slowly cooled down and broken into lumps. The lumpy slag is used as a construction material. The dust arising during the slag cleaning (2 t/d) is sold for further processing.

The off-gas from the electric slag cleaning furnace (40,000 Nm^3/h) is afterburned, cleaned in a fabric filter and further cleaned together with the ventilation gases from secondary hoods above the furnace roof, the tapholes, launders and slag ladles as well as the doghouse for the matte ladle in a central baghouse.

The water used for granulation is operated in a closed circuit and cooled by cooling towers. Water from surface run-off is added if necessary, to make-up the required volume.

3.1.1.3 Pierce-Smith converter (primary plant)

The matte from the flash smelting furnace and the electric slag cleaning furnace is transferred in ladles by crane to the Pierce-Smith converters for conversion into blister copper by blowing with oxygen enriched air.

At Norddeutsche Affinerie’s primary smelter, 3 converters are installed with a capacity of 250 t each. Two converters are in operation while one is under repair.

The produced converter copper (230 t/charge) with a copper content of 98 - 99 % is further processed in the anode furnace. The slag formed during the slag blowing phase (200,000 t/a) is recycled in the flash furnace via a launder. When pouring slag the launder is enclosed by a removable hood and the gases are vented and dedusted in the central secondary gas handling system.

The heat generated during matte blowing is used for melting internal reverts like ladle skulls, etc., and copper scrap and/or tankhouse anode scrap. Scrap and flux are charged through the hood to the converter during blowing. In this way, the rolling of the converters in or out of the stack can be avoided, thus reducing uncontrolled gas releases into the surrounding air.

The SO_2 containing furnace process gases (95,000 Nm^3/h) are collected in water cooled primary hoods and have a temperature of about 1,250 °C. After being dedusted in an electrostatic precipitator, the heat content is used for the pre-heating of boiler feed water. Then it is conveyed to the sulphuric acid plant for further treatment. Depending on the chemical composition, the dust collected is recycled to the flash smelting furnace or - when e.g. rich in lead - transferred to the secondary smelter for treatment.

A secondary hood system at each converter ensures that the secondary gases arising during converter charging, skimming or metal pouring are collected. The secondary gases are cleaned in the central baghouse.

3.1.1.4 Anode furnace (primary plant)

NA uses two rotary anode furnaces with natural gas as a reductant for the pyrometallurgical refining of copper. The tap-to-tap cycle duration is 6 hours; 220 t of anodes with a copper content of 98.5 - 99.6 % can be produced per cycle. Oxidation lasts half an hour with an air flow rate of 10 Nm^3/min; reduction (poling) takes 3 hours and the flow rate of the reducing gas is thereby 10 Nm^3/min [8]. The 15 t of slag produced during the processing of one charge are recycled to the converter.

Anode casting is done by mould on a wheel at a rate of 80 tons per hour, the anodes have a mass of about 420 kg, which is controlled by automatic weighing [8].

For the prevention of fugitive emissions, a secondary hood system is installed. The captured gases are cleaned in a central fabric filter. The furnace off-gases (75,000 Nm^3/h) are afterburned during poling in a post-combustion chamber and are cleaned in a fabric filter after being cooled in an air to gas cooler to protect the filter media. The concentration of the main constituents in the cleaned furnace off-gas (measured as well as authorised values) are given in Table 3-3.

Table 3-3: Concentrations of main constituents in the cleaned off-gases from the anode furnace (primary plant)

Substance	Unit	Measured Value	Authorised value
SO_x (as SO_2)	mg/m^3	80 - 380	500 (Mean value of whole refining cycle)
	mg/m^3	2 - 700	1000 (hourly mean value)
NO_x (as NO_2)	mg/m^3	30 - 60	200
Cl^- (as HCl)	mg/m^3	< 2 - 20	30
C_{total}	mg/m^3	6 - 23	50 (if cold input material is used)
Particulate matter[*)]	mg/m^3	< 1 - 8	20

[*)] The main constituents of the particulate matter are given in Table 3-12

Source: Emission values which are accessible to the authority

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions (charging, pouring, poling etc.), different input materials and changes of the operating mode.

3.1.1.5 Sulphuric acid plant

The dedusted and combined off-gases from the smelter furnace, the Pierce-Smith converters of the primary smelter and the electric furnace in the secondary smelter enter a multi-stage scrubbing and cooling plant to remove any remaining particles and volatile compounds such as arsenic and halogens. These off-gases are combined with the scrubbed and cooled off-gases of the secondary plant converters (Pierce-Smith type), and are subsequently channelled to the mercury removal plant. After absorption of the moisture in concentrated sulphuric acid (the sulphur dioxide concentration in the off-gas amounts to between 6 - 8.4 vol.-% at this stage) and the catalytic conversion of sulphur dioxide to sulphur trioxide in the double contact plant, the gas is processed to sulphuric acid of different concentrations (94, 96, 98, 20 % SO_3, oleum). The production rate of the sulphuric acid amounts to about 2,000 t/d (100 %) sulphuric acid, the conversion rate for SO_2 to SO_3 is more than 99.6 % and the off-gas volume is up to about 290,000 Nm^3/h. The main constituents in these off-gases released into the surrounding air (measured values as well as authorised values) are given in Table 3-4.

Table 3-4: Concentrations of main constituents in the cleaned gas from the sulphuric acid plant

Substance	Unit	Measured value	Authorised value
SO_x (as SO_2)	mg/m^3	100 - 1100	1250
SO_3	mg/m^3	20 - 40	120
NO_x (as NO_2)	mg/m^3	20 - 45	50
Cl$^-$ (as HCl)	mg/m^3	2 - 7	10
F$^-$ (as HF)	mg/m^3	1 - 4	4.5
Class I (TA-Luft)			
Cd	mg/m^3	< 0.001 - 0.02	
Hg	mg/m^3	< 0.001 - 0.07	0.1 (daily average)
TI	mg/m^3	< 0.001 - 0.02	
Sum class I (TA-Luft)	**mg/m^3**	**0.001 - 0.11**	**0.2**
Class II (TA-Luft)			
As	mg/m^3	< 0.01 - 0.1	
Se	mg/m^3	< 0.01 - 0.02	
Sum class II (TA-Luft)	**mg/m^3**	**< 0.01 - 0.12**	**0.5**
Class III (TA-Luft)			
Sb	mg/m^3	< 0.01 - 0.03	1
Pb	mg/m^3	< 0.01 - 0.15	1
Cu	mg/m^3	< 0.01 - 0.09	1
Sum class III (TA-Luft)	**mg/m^3**	**< 0.01 - 0.027**	**1**
PCDD/PCDF	**ng ITE/m^3**	**0.001 - 0.01**	**< 0.02**

Source: Emission values which are accessible to the authority

If substances of several classes are present, the mass concentration in the emitted gas should not exceed a total of 1 mg/m^3 for coinciding class I and II substances as well as a total of 5 mg/m^3 for coinciding class I and III or class II and III substances. The emissions of substances class I - III have to be determined as a sum of the particulate matter, the vapour and the gas share of the respective element and its compounds (according to TA Luft [1]). More information about the German regulations can be found in section 6.1.2.

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions and changes of the operating mode.

3.1.2 Secondary smelting plant

3.1.2.1 Electric furnace (secondary plant)

Since 1991, NA has been using the electric furnace technology for the processing of smelter intermediates as well as external recycling materials. This resistance type furnace with a nominal capacity of 8 MVA replaced four blast furnaces operated up to then. The electric furnace with a height of 3.3 m and a diameter of 7.4 m reaches a melting capacity of 8 - 25 t/h [40] and 25 - 60 kg coke are required per ton of burden. As the electric furnace puts higher demands on the physical properties of the charge than the blast furnace, the input material is limited to a size of 100 mm and a humidity of < 3 %. A pretreatment of the raw materials can therefore be necessary (e.g. pelletising). Up to 10 t of copper matte with a copper content of 55 - 63 % are produced per hour which are further processed in the converter. The 13 t of slag arising during one hour have a low copper content of about 0.7 % and can be sold as construction material. The off-gas, with a volume of 15,000 Nm^3/h and a temperature of about 1,200 °C, enters the off-gas system, which is composed of a cooling device and a fabric filter. Additional treatment is necessary when the concentration of sulphur dioxide exceeds 800 mg/Nm^3. In this case, e.g. during the melting stage, the off-gas is led to the sulphuric acid plant. The flue dust, which contains high concentrations of zinc and lead, is marketed or recycled. Secondary hoods are installed to capture fugitive emissions, which can occur during charging and transfer operations. The secondary off-gas has a volume up to 150,000 Nm^3/h [72].

The electric furnace is cooled with conditioned river water, which is recirculated in a closed cooling circuit. The water is cooled down in cooling towers, whereby a circuit water bleed of about 10 m^3/h is necessary. In Table 3-5 the formerly used blast furnaces (i.e. two blast furnaces which together have the same capacity as one electric furnace) are compared to the newly installed electric furnace.

Table 3-5: Data for the formerly used blast furnaces and the new electric furnace

	Blast furnace	Electric furnace
Yield of metal	Lower	High, due to better reduction
Requirement for recycling slags	Yes	No
Quality of raw materials	High flexibility	Lower flexibility
Process control system	Undemanding	Demanding
	2 blast furnaces	**1 electric furnace**
Off-gas (melting stage) [m^3/h]	100,000	15,000
Secondary hoods (melting stage) [m^3/h]	125,000	150,000
Cooling water [m^3/h]	350	10
Emissions (estimation from measurements)		
CO [t/a]	20,000	10
SO_2 [t/a]	1,300	20
Particulate matter [t/a]	14.5	1.5
Pb [t/a]	1.7	0.4
As [t/a]	0.8	0.04

Source: Velten [72]

3.1.2.2 Pierce-Smith converter (secondary plant)

The copper matte and the copper lead-matte from the electric furnace are further processed in the Pierce-Smith converter of the secondary smelter with a capacity of 35 t Cu/charge (c.f. Figure 3-1). 30 - 60 t per charge of converter copper with a copper content of 97 % is produced and further processed in the anode shaft furnace, the 20 - 40 t per charge of slag as well as the 0.5 - 2.5 t per charge of dust are re-fed to the electric furnace. The off-gas volume of 30,000 Nm^3/h is used for steam generation in a waste heat boiler, dedusted in an ESP and led to the sulphuric acid plant.

3.1.2.3 Scrap converter (Pierce-Smith type)

NA operates three scrap converters of the Pierce-Smith type using the so called Knudsen process. Raw material, such as alloy scraps and shredder material with a copper content between 60 and 90 %, is charged into the converter as well as black copper from the electric furnace. The converters have a capacity of approximately 15 t each and about six batches are processed per day. The converter metal with a copper content of approximately 97 % (7 - 10 t per charge) is further processed in the Contimelt process as well as in the matte converter at the primary smelter. The 2 - 4 t per charge of converter slag, containing approximately 30 % of copper, are returned to the electric furnace for recycling. The off-gas volume of 50,000 - 80,000 Nm^3/h is cleaned in a fabric filter. Since zinc, lead and tin are volatilised during the process, the collected flue dust (2 - 3 t per charge) has a high content of these metals and is therefore processed in the tin-lead alloy plant.

The particulate matter content and its main constituents in the raw furnace off-gas are shown in Table 3-6, the concentrations of the main constituents in the cleaned off-gases can be seen in Table 3-7.

Table 3-6: Particulate matter content and its main constituents in the raw off-gases from the scrap converter (secondary plant)

Particulate matter	
Total [mg/m^3]	10,000 - 30,000
Pb [wt.-%]	5 - 30
Zn [wt.-%]	25 - 70
Sn [wt.-%]	1 - 20

Table 3-7: Concentrations of main constituents in the cleaned off-gases from the scrap converter (secondary plant)

Substance	**Unit**	**Measured Value**	**Authorised value**
SO_x (as SO_2)	mg/m³	200 - 500	800
NO_x (as NO_2)	mg/m³	20 - 30	500
PCDD/PCDF	ng/ m³	< 0.1	< 0.5
Particulate matter[*)]	mg/m³	<1 - 10	20

[*)] The main constituents of the particulate matter are given in Table 3-12.

Source: Emission values which are accessible to the authority

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions (charging, blowing, pouring, etc.), different input materials and changes of the operating mode.

3.1.2.4 Tin-lead alloy plant

In the tin-lead alloy plant, technical zinc oxide and tin-lead alloy are produced from oxides arising during the smelting and converting processes. The converter flue dust and, if the tin content is high enough, also the electric furnace flue dust are mixed with fluxes (sodium carbonate) and reductants (anthracite coal) and are fed to a Dörschel furnace (25 t dust per charge). The heat is supplied by an oil burner with a fuel consumption of 200 l/h. The collected flue dust has a high content of zinc oxide, since the zinc content of the input materials is transferred to the flue dust as zinc oxide. The remaining metal phase of 10 t per charge consists mainly of tin (20 - 50 %) and lead (50 - 80 %) which is refined and cast into ingots and then sold. 8 t of slag, consisting mainly of caustic soda and zinc, is processed in the flash furnace.

The furnace is equipped with secondary hoods to avoid fugitive emissions. The arising ventilation gases of these hoods with a volume of 15,000 - 36,000 Nm^3/h are cleaned in the central system. The furnace off-gas (25,000 - 35,000 Nm^3/h) is cleaned in a fabric filter. The concentration of the main constituents in the cleaned furnace off-gas can be seen in the following Table.

Table 3-8: Concentration of the main constituents in the cleaned furnace off-gas from the tin-lead alloy plant

Substance	Unit	Measured value	Authorised value
SO_x (as SO_2)	mg/m^3	n.d.	800
NO_x (as NO_2)	mg/m^3	40 - 100	500
Particulate matter	mg/m^3	2 - 8	20

*) The main constituents of the particulate matter are given in Table 3-12

Source: Emission values which are accessible to the authority

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions (charging, pouring, etc.), different input materials and changes in the operating mode.

3.1.2.5 Contimelt process

NA uses the Contimelt process for the fire refining of the converter copper from the electric furnace path and from the scrap converter. Pure scrap including anode scrap and blister copper are fed at this stage and melted in the furnace as well. Figure 3-3 shows a schematic view of the Contimelt process.

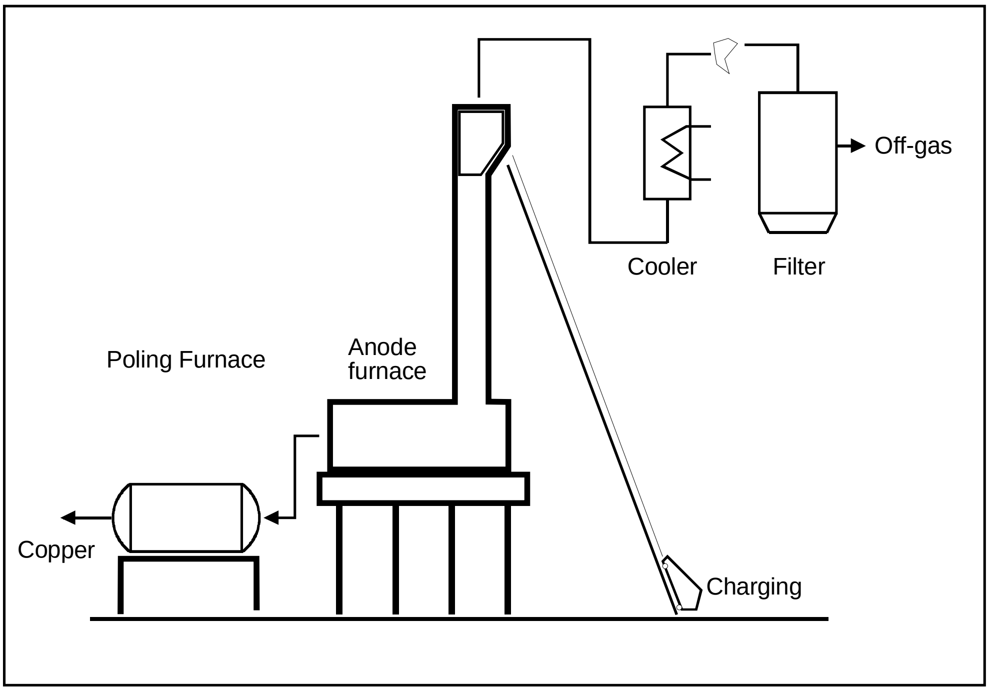

Figure 3-3: The Contimelt process for fire refining of secondary copper

Source: Langner [49]

The two-stage process comprises a shaft, which is placed on a hearth furnace, and a continuously processed poling furnace, from which the copper is cast into anodes on a casting wheel. The production capacity of the Contimelt plant is about 80 t/h of anode copper with a copper content of 98 - 99 %. 30 Nm^3/t of natural gas are needed for the heat supply and 8 Nm^3/t as a reducing agent. The slag from the Contimelt process with a copper content of 55 - 70 % is recycled to the converter of the primary smelter (c.f. Figure 3-1).

An integrated concept for the utilisation of heat has been implemented in the Contimelt plant. The hot off-gas from the hearth furnace travels in counterflow to the feedstock materials so that its energy content is utilised to pre-heat the latter and save fuel. After the anode shaft furnace off-gas has been combined with the hot off-gas from the downstream poling and casting furnace, the residual heat content is used for heat steam generation in a waste heat boiler and to pre-heat the process air. Then carbon containing lime is injected into the off-gas (140,000 Nm^3/h) to adsorb organic constituents before it is cleaned by a fabric filter. In Figure 3-4 the energy flows of the Contimelt process are presented in the form of a Sankey diagram.

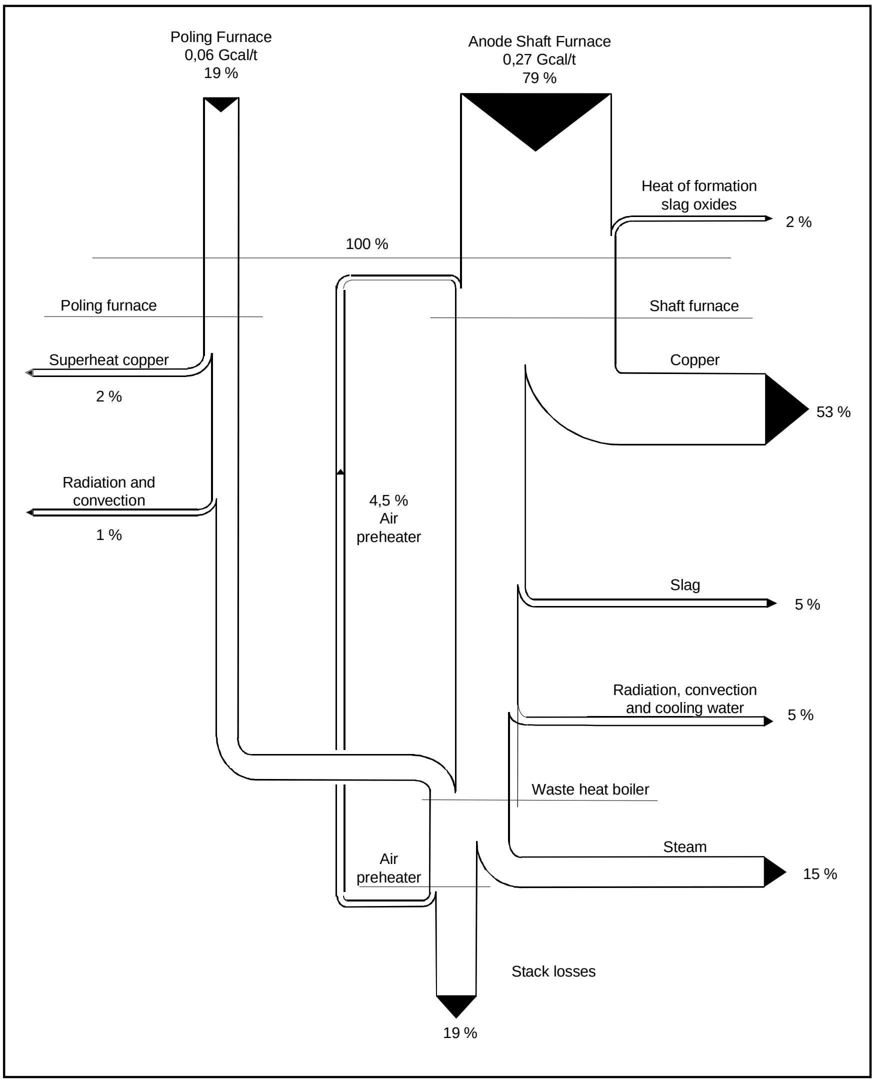

Figure 3-4: Energy flows in the Contimelt process

Source: Company information NA, 1998 [55]

Since the secondary hood system installed to prevent fugitive emissions is part of a central system, these emissions are shown in Table 3-11.The values of the main constituents in the cleaned furnace off-gases can be seen in Table 3-9.

Table 3-9: Concentrations of the main constituents in the cleaned furnace off-gases from the Contimelt process (secondary plant)

Substance	Unit	Measured value	Authorised value
SO_x (as SO_2)	mg/m³	50 - 520	570
NO_x (as NO_2)	mg/m³	50 - 960	1000 (mean value of daily operation period referring to 2 shift operation)
	mg/m³		800 (mean value of daily operation period)
	kg/d		1700 (referring to 2 shift operation)
CO	mg/m³	< 500	500 (mean value of daily operation period referring to 2 shift operation) 700 kg/h (if post-combustion breaks down)
PCDD/PCDF	ng ITE/m³	< 0.1 - 0.4	0.1 (value for orientation)
Particulate matter	mg/m³	< 1 - 8	20

[*)] The main constituents of the particulate matter are given in Table 3-12.

Source: Emission values which are accessible to the authority

3.1.3 Electrolysis plant for primary and secondary copper

NA uses the ISA technology for the electrolytic refining of anode copper with a production capacity of about 380,000 t/a of cathode copper. This process is operated with about 60,000 stainless steel plate cathodes and 1080 electrolytic cells. The current density is between 300 and 330 A/m² and a current efficiency of 95 - 98 % is reached. A low cell voltage (< 300 mV) is achieved by monitoring the glue content in the electrolyte and a short anode-anode distance of 95 mm. The cell current amounts to 35,000 A. The power consumption of the tankhouse amounts to 300 - 350 kWh/t copper. The anodes, which have a copper concentration of 98.5 - 99.6 %, have a weight of about 420 kg and a lifetime of 21 days. The anode scrap (about 11 % of the anode mass) is recycled. The cathodes have a plating time of 7 days. The electrolyte has a concentration of about 150 - 200 g/l of sulphuric acid and about 40 - 50 g/l of copper. The concentration of glue is automatically controlled by the Collamat® glue control system. 70 - 100 kg of steam per hour are needed to keep the temperature of the electrolyte between 55 and 65 °C. In Table 3-10 the distribution of accompanying metals in the anodes and cathodes is shown for the ISA technology used at NA.

Table 3-10: Accompanying metals in anodes and cathodes at NA

Element	**Anode** [g/t]	**Cathode** [g/t]
Ag	720	9
Se	510	< 0.5
Te	130	< 0.5
As	760	< 1
Sb	330	< 1
Bi	60	< 0.5
Pb	990	< 1
Ni	1,080	< 3

Source: Langner [49]

5 - 10 kg of anode slime is obtained per ton of anode processed, which is further treated to recover the precious metals (c.f. Figure 3-1).

3.1.3.1 Secondary hood system

As in the plant descriptions above, some of the furnaces of the primary as well as the secondary copper production line are equipped with secondary hoods in order to prevent fugitive emissions. The suction is provided directly at the source to optimise the reduction of fugitive emissions. Alternatively, the air could be suctioned at the ridge, but therefore, a large volume of air has to be handled which cannot be cleaned effectively in a fabric filter. Other disadvantages are likewise high energy consumption, high investment, more waste (used filter media) and especially the worse conditions at individual working places. In addition, the applied system reduces the heat input in the aisle. So the lift of the air in the aisle is reduced, which reduces the emission through the ridge.

Depending on the SO_2 content in the suctioned air from the primary smelter, dry sorption (injection of $Ca(OH)_2$) is applied before the gas stream is cleaned in fabric filters. The calcium hydroxide is re-circulated to improve its conversion and so to minimise the amount of solid material arising during the gas-cleaning. The air flow rate is controlled via a closed-cycle control system by reducing dampers and ventilators with speed control in order to minimise the energy consumption. 580,000 Nm^3/h of secondary gases are captured and cleaned in fabric filters. Thereby 13.6 GWh/a of electrical energy are consumed and 700 kg of dust are collected per hour.

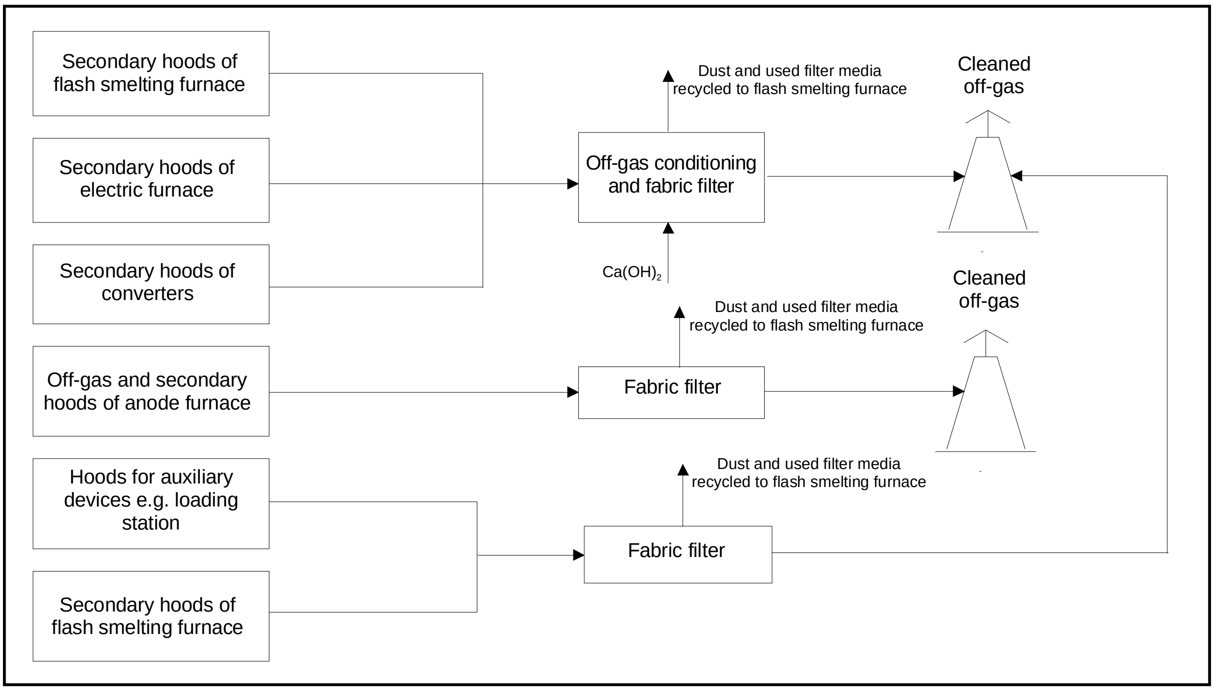

Figure 3-5: Secondary hood system of the primary smelter

All solid materials arising during the gas-cleaning are recycled to the flash smelting furnace. The concentrations of the main constituents in the cleaned gas stream are shown in Table 3-11.

Table 3-11: Concentrations of the main constituents in the cleaned gas from the central fabric filter

Substance	Unit	Measured value	Authorised value
SO_x (as SO_2)	mg/m³	20 - 600*)	500
	kg/h	111 (1996)	155 (annually mean value)
Particulate matter**)	mg/m³	< 1 - 7	10

*) Continuously measured value (c.f. section 4.1.1)

**) The main constituents of the particulate matter are given in Table 3-12.

Source: Emission values which are accessible to the authority

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions (charging, pouring, etc.), different input materials and changes in the operating mode.

3.1.4 Characteristics of fabrics filters at NA

In the following Table, the measured and authorised values of the constituents in the particulate matter content in off-gases released into the ambient after being cleaned in a fabric filter are given.

Table 3-12: The main constituents in the dust content of the off-gas after treatment in a fabric filter

Substance	Unit	Measured value	Authorised value
Class I (TA-Luft)			
Cd	mg/m³	< 0.01 - 0.1	0.2
Hg	mg/m³	< 0.01 - 0.2	0.2
Tl	mg/m³	< 0.01	0.2
Sum class I (TA-Luft)	**mg/m³**	**< 0.03 - 0.2**	**0.2**
Class II (TA-Luft)			
As	mg/m³	< 0.01 - 0.8	1
Ni	mg/m³	< 0.01 - 0.3	1
Co	mg/m³	< 0.01 - 0.1	1
Se	mg/m³	< 0.01 - 0.9	1
Te	mg/m³	< 0.01 - 0.1	1
Sum class II (TA-Luft)	**mg/m³**	**< 0.05 - 1**	**1**
Class III (TA-Luft)			
Sb	mg/m³	< 0.01 - 0.5	5
Pb	mg/m³	0.1 - 2	5
Cr	mg/m³	< 0.01 - 0.1	5
Cu	mg/m³	0.02 - 2	5
Sn	mg/m³	< 0.01 - 1	5
Sum class III (TA-Luft)	**mg/m³**	**< 0.15 - 5**	**5**

Source: Emission values which are accessible to the authority

If substances of several classes are present, the mass concentration in the emitted gas should not exceed a total of 1 mg/m^3 for coinciding class I and II substances as well as a total of 5 mg/m^3 for coinciding class I and III or class II and III substances. The emissions of substances class I - III have to be determined as a sum of the particulate matter, the vapour and the gas share of the respective element and its compounds (according to TA Luft [1]). More information about the German regulations can be found in section 6.1.2.

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions (charging, blowing, pouring, poling etc.), different input materials and changes in the operating mode.

3.1.5 Further processing of copper at NA

3.1.5.1 Southwire copper wire rod plant

Cathodes from NA's copper electrolysis are the main input of a continuously operating shaft furnace. The other feed materials are recycled, i.e. off-specification or damaged wire rod and bar from cropping operations during the start up and shut down of the process (c.f. Figure 3-6).

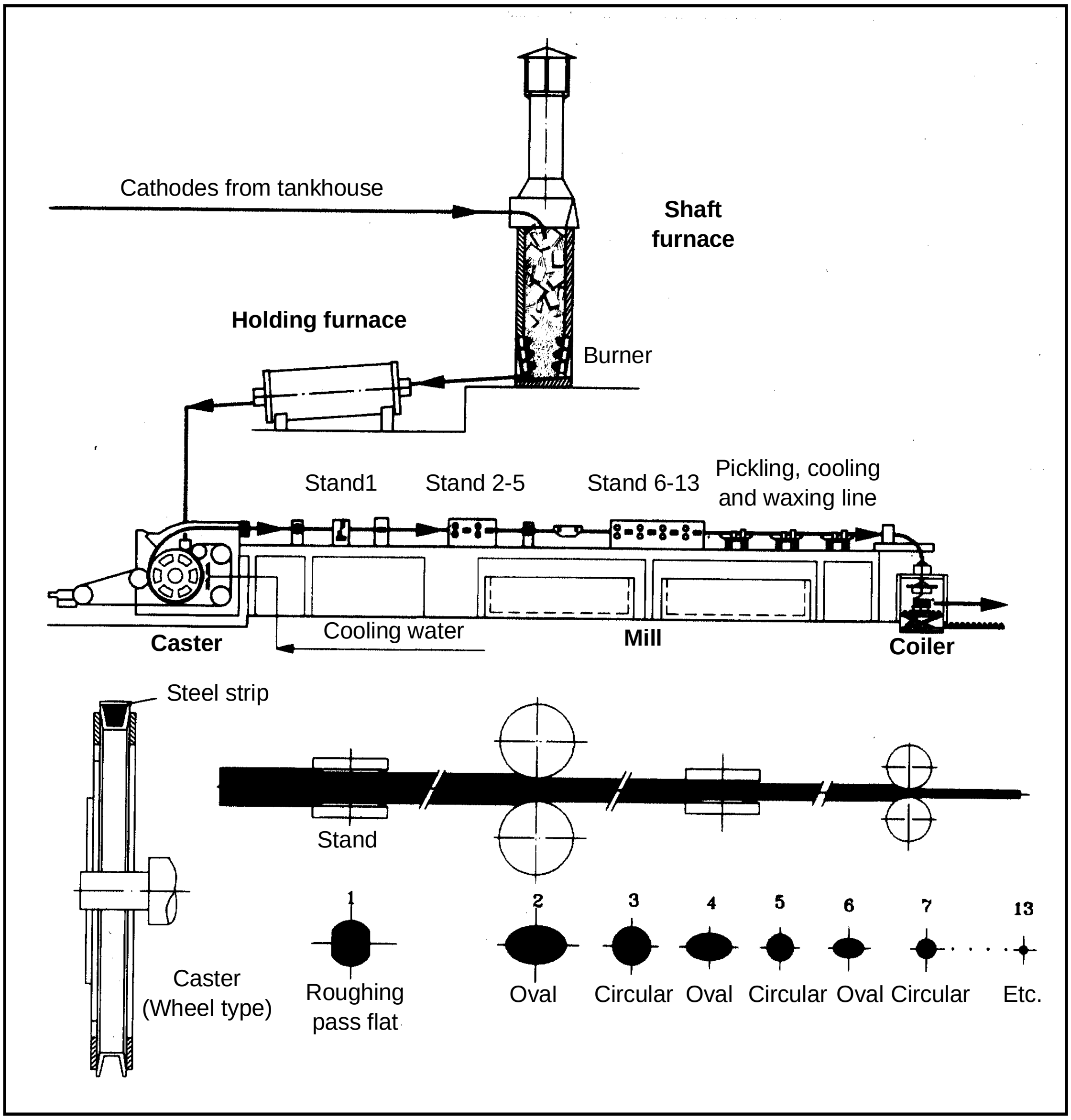

Figure 3-6: Southwire copper wire rod plant at NA

Source: company information NA, 1998

Bundles of cathodes are loaded into a bucket elevator as well as scrap bar, scrap wire, copper ingots (pigs) and copper shavings, produced when the edges of the cast bar are trimmed prior to rolling. Coils of reject rod are also charged via a cutter. The buckets are raised by an overhead crane and hoisted above the opening of the furnace and then emptied.

The feed materials are melted by natural gas fired burners arranged in rows around the furnace shell. It is essential that oxygen is not introduced into the copper during the melting operation. Consequently, the fuel is burnt under closely controlled combustion conditions to maintain a slightly reducing atmosphere. Thus, the off-gases from the furnace contain small quantities of carbon monoxide (less than 0.5 vol-%). Independent control of the fuel/air ratio is provided for each burner. The off-gas of the shaft furnace is cleaned in a bag house and the separated dust is processed in the flash smelter furnace.

The holding furnace, which is fired with natural gas, serves as a reservoir to provide a constant flow of metal to the casting process and, if required, can be used to superheat the metal. The molten copper flows from the holding furnace via a gas-fired launder to a pot with a pouring spout, which feeds the grooved periphery of the casting wheel. A water cooled steel band encloses half of the circumference of the wheel, forming the casting cavity in which the molten copper solidifies to form a trapezoidal bar. Acetylene, burnt with air, produces a soot dressing for the casting wheel and steel band.

After being bevelled and shaved, the cast bar is fed by pinch rolls to a rolling mill consisting of a roughing section and one finishing section, which reduces the bar to its final diameter. A special emulsion in water is used as a rolling fluid; the fluid is re-circulated and continuously filtered to remove copper fines and oxide scale.

Subsequently the wire rod is pickled with a solution of isopropanol and later followed by acid pickling with diluted sulphuric acid. Then the residual acid is washed off the rod surface by water spray and cooled. In the next stages the rod is dried by compressed air, coated with wax and coiled on pallets. These coils are weighed automatically and then taken to an automatic packing unit, where they are strapped and covered with the heat-shrunk polyethylene film. The copper contained in the pickling acid is recovered in a small electrowinning facility, and then decopperised acid is channelled back to the pickling equipment.

Cooling water is required for the caster and for different temperature control purposes of the mill process, i.e. pickle lubrication or rolling emulsion. Direct cooling is applied at the caster and indirect cooling at the mill. River water is used in an open circuit concept. The discharge of cooling water back to the river depends on the volume of fresh water needed to control the temperature. With this concept biocides are not required. The water used amounts to approximately 25 m^3/t.

3.1.5.2 Continuous casting of Copper Billets and Slabs/Cakes

The production of copper billets and cakes/slabs is another important production line of Norddeutsche Affinerie. The cakes are used for sheet and strip rolling while the billets are applied for extrusion and fabrication of tubes and sections.

Billets and cakes are produced in different copper qualities depending on the final application. Typical qualities are: ETP copper - oxygen containing copper - has a high conductivity in line with low impurity levels; phosphorised copper with improved properties related to brazing, welding and corrosion resistance; low oxygen or oxygen free copper; low alloyed copper - mostly silver alloyed. In Table 3-13, some data of the continuous casting plant are given.

Table 3-13: Continuous casting plant data

Melting furnaces:	
Number	2
Type	Cathode shaft furnace, gas fired
Melting rate	30 t/h max, each
Off-gas cleaning	Baghouse
Casting/holding furnace	
Number	3
Type	Induction furnace
Caster	
Number	3
Type	Continuous caster, multi-strand for billet casting
Casting rate	5 - 30 t/h, depending on shape, copper quality, number of strands

Normally both shaft furnaces, each serving one caster, are in operation continuously for 24 hours per day. Cathodes and other high purity copper casting scrap and chips from cutting cakes and billets to length are charged by skip hoist to the shaft furnaces. The molten copper is transferred by launder from the shaft to the holding and casting furnace. Alloying elements or phosphorus (as copper alloy) are dosed to the launders and evenly distributed in the molten copper within the holding furnace. From the holding furnace the copper is dosed into the casting moulds of the vertical casters.

The solidified copper, leaving the casting mould, forms a continuous, cake or billet strands which are cut to length by a flying saw as the cast strands come down. The product castings are inspected on roller conveyors and then transported to the open storage area for shipment. Products normally are shipped by truck and railway, occasionally also by ship.

The cast strand is cooled by river water from the Elbe. The water is partly recirculated; the bleed is discharged after settling and separation of solids.

3.1.6 Waste water treatment plant

All waste waters arising at NA are treated in a central waste water treatment plant. The plant with an energy consumption of 9 - 13 kWh/m^3 waste water is mainly designed to minimise the arsenic content in the waste water and process water, precipitation water and direct cooling water are treated and discharged separately. 15 - 25 kg sludge per m^3 waste water arise (mainly depending on the arsenic content in the waste water) with an arsenic content of 5 - 15 % and an iron content of 20 - 35 %. In Table 3-14 the concentrations of the main constituents in the raw waste waters are given. Since the waste waters discharged from the central waste water treatment plant arise in the primary and secondary plant and therefore have to be seen as overall emissions into the water from NA, the concentration of pollutants are shown in the next section.

Table 3-14: Concentrations of the main constituents in the untreated waste water at NA

	Main components before treatment [mg/l]					
	Cu	**Pb**	**As**	**Ni**	**Cd**	**Zn**
Process water	2,000	500	10,000	1,000	500	1,000
Precipitation water*)	15 - 30	< 5	< 2	< 2	< 0.5	< 2
Direct cooling water	< 3	< 0.5	< 0.1	< 0.1	< 0.05	< 0.5

*) Calculated back from the analysis of the precipitated sludge

Source: Emission values which are accessible to the authority

3.1.7 Summarised data on outputs and environmental concerns at NA

Emissions into the air

Table 3-15 shows the emissions at Norddeutsche Affinerie Aktiengesellschaft. The given concentrations include all captured emissions, the given loads are calculated values and include all captured emissions (from stacks and exhaust pipes) and fugitive emissions from baghouses, cooling towers, ridges, storage and loading places as well as from traffic areas. The calculations are based partly on measured values and partly on emission factors.

Table 3-15: Total emissions from copper production at NA (primary and secondary plant), 1996

Main components	**Particulate matter**	**SO_2**	**Cu**	**Pb**	**As**
Loads [g/t]	168	$5.55 \cdot 10^3$	29	7	2.5
Concentration [mg/Nm^3]	2 - 10	0 - 1250	0.01 - 5*)	0.01 - 5*)	0.01 - 1**)

*) In total with several substances of the same class TA Luft (Sb, Pb, Cr, Cn, F, Cu, Mn, Pt, Pd, Rh, V, Sn)

**) In total with several substances of the same class TA Luft (As, Co, Ni, Se, Te)

Source: Emission values which are accessible to the authority

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions, different input materials and changes in the operating mode (e.g. start-up and shut-down operations). More information about measurements, to ensure that the emissions specified are representative, mutually comparable and clearly describe the relevant operating state of the plant, can be found in section 4.1.1.

Waste water

In Table 3-16 measured values and in Table 3-18 authorised values on the annual use of water and the pollutants in the three separately captured, treated and discharged waterstreams in 1996 are given. The concentrations of the various substances are determined by qualified composite samples. The samples are taken and analysed according to the German regulations. (c.f.6.1.2.2)

Table 3-16: Pollutants in the three separately discharged waterstreams at NA (primary and secondary plant) based on measured values from 1996

	Flow	**Main components** [mg/l]					
	[m³/a]	**Cu**	**Pb**	**As**	**Ni**	**Cd**	**Zn**
Process water	72,000	0.01-0.2	0.001-0.04	0.01-0.1	0.004-0.15	0.0001-0.1	0.01-0.2
Precipitation water	322,000	0.01-0.4	0.005-0.2	0.003-0.07	0.002-0.4	0.0002-0.1	0.03-0.4
Direct cooling water	11,300,000	0.01-0.25	0.001-0.1	0.001-0.1	0.002-0.06	0.0001-0.003	0.02-0.5
Cooling water (total)	82,000,000						

Source: Emission values which are accessible to the authority

Table 3-17: Authorised pollutant concentrations in the three separately discharged waterstreams at NA (primary and secondary plant), 1996

	Flow	**Main components** [mg/l]					
	[m³/a]	**Cu**	**Pb**	**As**	**Ni**	**Cd**	**Zn**
Process water	100,000	0.3	0.2	0.1	0.5	0.1	1
Precipitation water	-	0.5	0.5	0.1	0.5	0.2	1
Direct cooling water	16,000,000	0.1 – 0.5	0.1 - 0.3	0.1	0.1	0.005	1

Source: Emission values which are accessible to the authority

In Table 3-18 the measured overall pollutant rate of waste water discharged from NA in 1996 is given.

Table 3-18: Overall pollutant rate of waste water discharges from NA based on measured values from 1996

Main components	**Cu**	**Pb**	**As**	**Ni**	**Cd**	**Zn**
Overall pollutant rate [g/t]	2.3	0.3	0.23	0.1	0.05	0.8

Source: Emission values which are accessible to the authority

Main intermediates, by-products and residues

In Table 3-19 an overview of the main intermediates, by-products and residues is given.

Table 3-19: The main intermediates, by-products and residues from copper production at NA

Process unit	**By-product/residue**	**Amount** [t/a]	**Use/treatment option**
Primary plant:			
Flash smelting furnace	Dust	100,000	Internal use at the flash smelting furnace
	Slag	400,000	Further processing in the electric furnace
Electric furnace	Dust	400	External use for Zn/Pb production
	Slag	400,000	External use as construction material
Copper converter	Dust	4,000	Internal recycling to the flash smelter or electric furnace (sec. plant)
	Slag	150,000	Internal use at the flash smelting furnace
Anode furnace	Dust	200	Internal use at the flash smelting furnace
	Slag	20,000	Internal use at the copper converter
Sulphuric acid plant	Sulphuric acid	656,000	By-product for sale
Secondary plant:			
Electric furnace	Dust	10,000	By-product for sale
	Slag	40,000	External use as construction material
Converter	Dust	400	Internal use at electric furnace
	Slag	10,000	Internal use at electric furnace
Contimelt process	Dust	1,000	Internal use at the flash smelter/electric furnace
	Slag	2,000	Internal use at copper converter
Scrap converter/TLA plant	Dust	1,000	Further processing in TLA plant
	Slag	2,000	Internal use at the electric furnace
Others:			
Electrolysis	Anode slime	3,000	Internal use at the chemical plant for the recovery of precious metals and Se, Te, Pb
	Final liquor	35,000 m^3	Internal use at the chemical plant for the production of nickel sulphate, As_2O_3
Process waste water treatment plant	Sludge	1,500	Dumping as hazardous waste
General	Household refuse	400	

Source: Company information NA, 1998

3.2 Secondary copper production at Hüttenwerke Kayser AG

Hüttenwerke Kayser AG (HK), located in Lünen, was founded in 1861 and is today the largest secondary copper producing plant in the world with a turnover of 1 billion DM and about 700 employees. In 1997 250,000 t of raw materials such as copper scrap, residues, slags, etc. were processed to 176,000 t of Grade A cathodes, which accounts for more than eight percent of the world-wide secondary copper production. By-products from secondary copper production are slags, zinc oxide, tin-lead alloy, copper and nickel sulphate and anode slime containing precious metals. In Figure 3-7 a scheme of the pathways for secondary copper production at HK is given and in Table 3-20 the main input materials and products are specified.

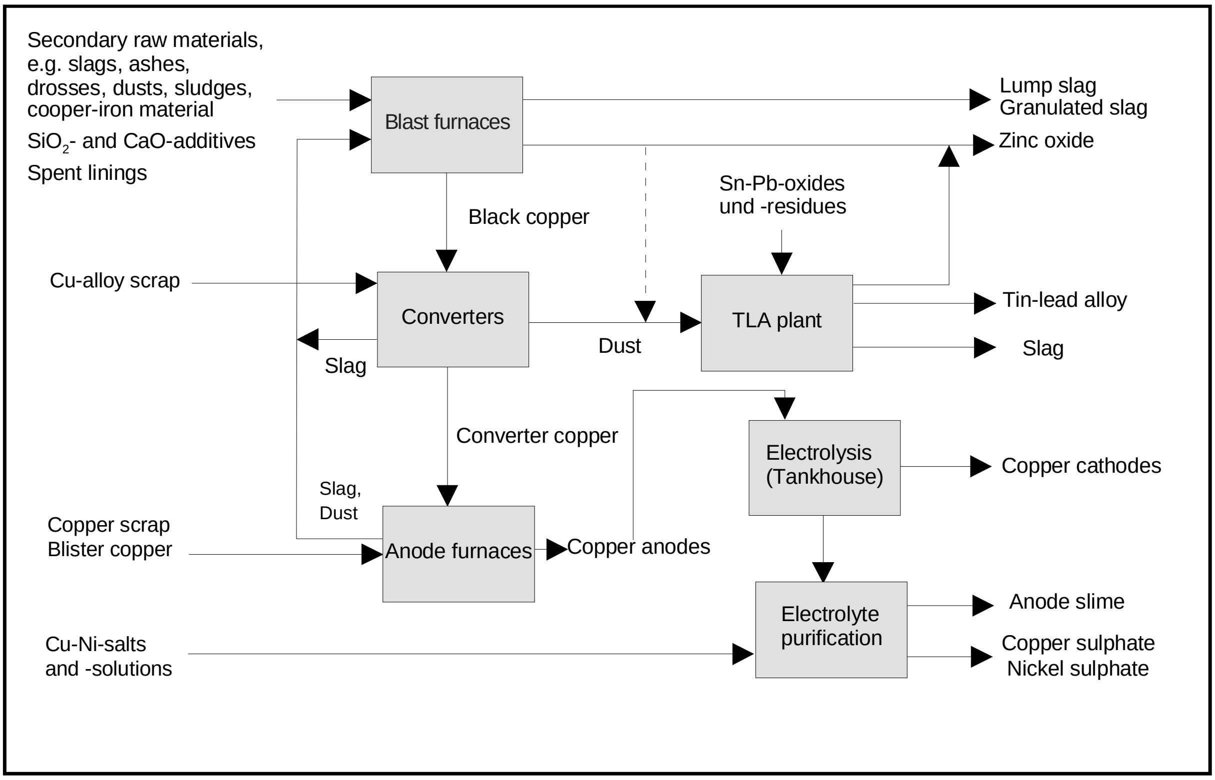

Figure 3-7: Copper recycling at Hüttenwerke Kayser AG

Source: Meyer-Wulf/Nolte [52]

Table 3-20: Input/output data from Hüttenwerke Kayser AG (1997)

Input materials	Quantity [t/a]
Copper scrap*)	130,000
Blister copper	20,000
Copper alloy scrap*)	35,000
External intermediate materials (e.g. slags, dusts, ashes, sludges, sweepings, etc.)	40,000
Copper-iron material	25,000
Limestone	13,000
Silica	11,000
Coke	25,000
Coal	15,000
Fuel (oil)	11,000

Products	Quantity [t/a]
Copper cathodes	176,000
Copper sulphate	2,200
Nickel sulphate	2,400
Zinc oxides	9,000
Lead-tin alloys	3,700
Anode slime	1,000
Slag	80,000

*) including electronic scrap

Source: Nolte[54] and company information HK

The main input material is copper scrap in the form of plates, tubes, wire, etc. and copper alloy scrap (bronze, brass). Another group consists of external intermediate materials (e.g. slags, dusts, ashes, sludges, sweepings, etc.). Blister copper from primary smelters is added at a level of 10% of the feed. 13 % of the materials treated at HK in 1995 originated from electronic scrap processing [54]. The main share consists of relais scrap, scrap from electronic scrap processing of household appliances and granulates from cable disassembly. The processed raw materials have to be free from PCB and mercury. Organics as well as harmful constituents such as arsenic, antimony and cadmium are limited. The copper content varies within a range between 94 % (granulate from cable assembly) and 1.5 % (shredded iron from household appliances, electronic scrap).

3.2.1 Blast furnaces

Various oxidic materials such as ashes, drosses, dusts and sludges, different copper-iron containing materials with an average copper content of 20 - 30 % as well as internal recycling slag from converter and anode furnace are processed in three blast furnaces using coke as fuel and reductant. Silica and limestone and iron are added for slag formation. Black copper and a slag which is poor in copper are produced. 150 - 180 tons of feed material are charged per furnace and day of operation. The raw materials are commuted or compacted if necessary. In 1996, the blast furnaces had a throughput of 148,000 t, of which 67,000 t was from secondary material. A schematic view of the blast furnace operation is given in Figure 3-8.

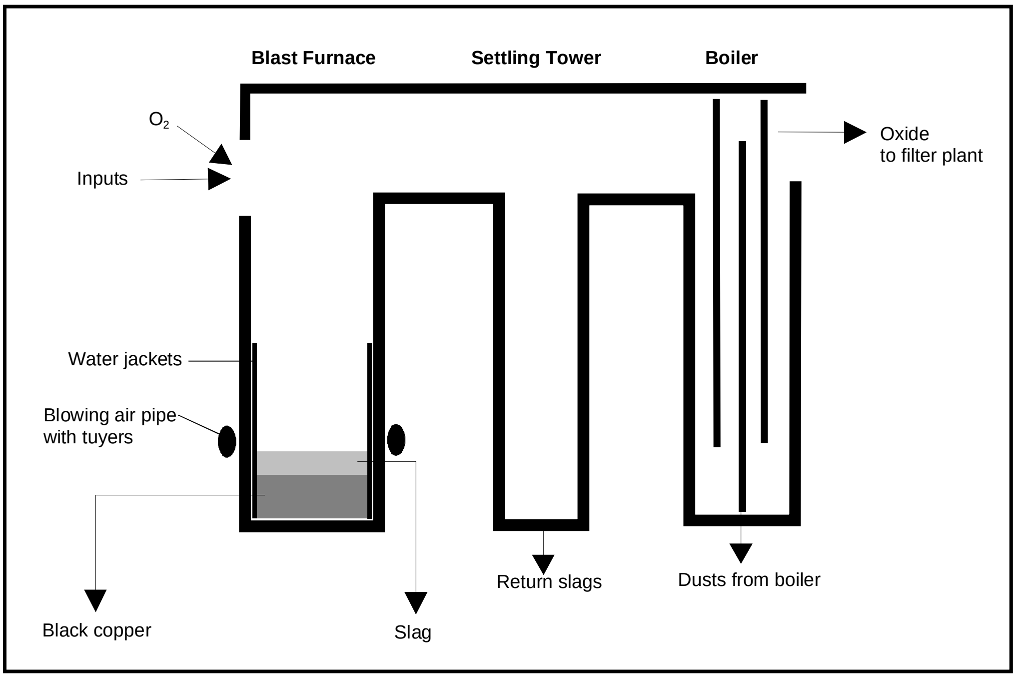

Figure 3-8: Schematic view of a blast furnace at HK

Source: Nolte [54]

The black copper fraction with a copper content of 70 - 80 % is tapped into a holding furnace and then led to the converter for further processing. The blast furnace slag, which has a rather low copper content and a high density, is marketed in granulated form (15,000 t/a) or as lump slag (50,000 t/a) for construction purposes or as blasting media. In order to maintain the required mechanical properties of the slag, the chemical composition must be kept in a fixed range. Table 3-21 shows the typical chemical composition of blast furnace slag produced at HK.

Table 3-21: Chemical composition of blast furnace slag from HK

Substance	**FeO**	**SiO_2**	**CaO**	**Al_2O_3**	**MgO**	**Na_2O**	**Zn**
Share [wt.-%]	32 - 38	20 - 25	14 - 17	10	3	2	4 - 8

Substance	**Cu**	**Sn**	**Pb**	**Ni**	**As**	**Cd**
Share [wt.-%]	0.7 - 1.2	0.5 - 1.0	0.2 - 0.4	0.1	< 0.1	< 0.1

Source: Meyer-Wulf/Nolte [52]

The heavy metals, which are still present in significant quantities, are hardly leachable under normal conditions, so that this slag can be used in similar ways to primary copper slag in many fields of application.

A further product from the blast furnace is zinc oxide with a zinc content of 60 - 70 %. Zinc evaporates at the existing temperatures in the blast furnace (about 1,250 °C in the lower part of the shaft) and a part of it is carried out with the furnace process gas where it is converted to zinc oxide. Lead and tin are found in the flue dust as well. Depending on the tin content, the flue dust collected in the baghouse is further processed in the tin-lead alloy plant or, in the case of a low tin content, sold as raw material for external processing. Some further process parameters of the blast furnace are shown in Table 3-22.

Table 3-22: Process parameters of the blast furnace

Process data	**Typical value or range**
Burden throughput [t/h]	5 - 20
Requirement of coke [kg/t burden]	100 - 120
Requirement of process air [Nm^3/t burden]	5,000 - 12,000
Requirement of natural gas for support of post-combustion*) [Nm^3/t burden]	3 - 10
Intermediates and by-products	
Black copper (further processed in converter [kg/t burden]	200 - 400
Slag (sold as construction material or for abrasive manufacturing) [kg/t burden]	400 - 600
Dust (processed in TLA plant) or directly sold as zinc oxide) [kg/t burden]	20 - 50

*) Natural gas necessary to support the throat gas afterburning in the case of a "cold feed".

To support the volatilisation and oxidation of the accompanying metals such as zinc, tin and lead, the furnaces are operated with top gas temperatures of about 1,000 °C and more. Figure 3-9 shows the off-gas treatment operated at HK for the three blast furnaces.

The air, which is needed for the oxidation of fugitive metals and furnace process gases (e.g. carbon monoxide, low temperature carbonisation gases and the volatilised metals), is suctioned through the charging door. The off-gases pass a settling chamber which also serves as a post-combustion chamber. The heat content of the furnace process gas is used for producing steam in a boiler. The temperature of the off-gases is then about 300 - 400 °C. Before the gases with a volume of 50,000 - 100,000 Nm^3/h are dedusted by filtration, further cooling is necessary. This is achieved by leading the gases through a tubular cooler and by subsequent mixing with cold off-gas from the secondary hoods in a mixing chamber. The off-gases, which now have a temperature of about 120 °C, are dedusted in a bag house.

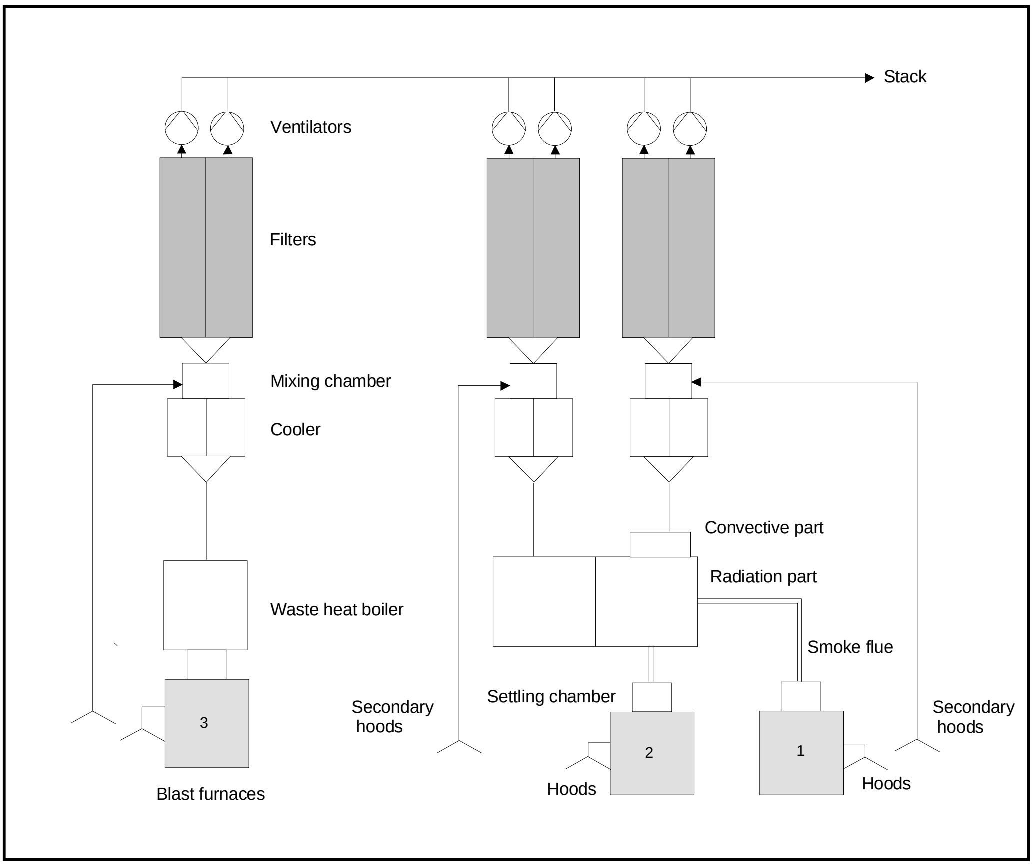

Figure 3-9: Off-gas treatment from blast furnaces at HK

Source: Meyer -Wulf [51]

In the past, the top gas temperature varied between 800 and 1,100 °C, and PCDD/PCDF emissions were between 2 and 30 ng/Nm^3 [14]. Since 1990 additional oxygen has been injected into the top area of the blast furnace which led to a higher level of temperatures and a considerable reduction of PCDD/PCDF emissions because of the improved post-combustion[14]. Values lower than 0.5 ng/Nm³ have been achieved. The particulate matter content as well as its main constituents in the raw off-gases can be found in Table 3-23. Measured and authorised emission values of the cleaned off-gases are given in
Table 3-24.

Table 3-23: Particulate matter content and its main constituents in the raw off-gases from the blast furnace

Particulate matter	
Total [mg/m^3]	20,000 - 30,000
Pb [wt.-%]	10 - 40
Zn [wt.-%]	30 - 60
Sn [wt.-%]	1 - 5

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[14] A detailed description regarding the decrease of PCDD/PCDF emissions by oxygen injection can be found in Meyer-Wulf [51] and Bußmann [14].

Table 3-24: Concentrations of main constituents in the cleaned off-gases from the blast furnace

Substance	Unit	Measured Value	Authorised value
SO_x (as SO_2)	mg/m³	50 - 150	800
NO_x (as NO_2)	mg/m³	30 - 100	500
PCDD/PCDF	ng/ m³	< 0.5	< 0.5
Particulate matter*)	mg/m³	< 1 - 8	20

*) The main constituents of the particulate matter are given in Table 3-31.

Source: Emission values which are accessible to the authority

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions (charging, blowing, pouring, etc.), different input materials and changes in the operating mode.

3.2.2 Scrap converters (Pierce-Smith type)

HK operates two converters of the Pierce-Smith type using the Knudsen process. Black copper from the blast furnaces as well as further raw material such as alloy scraps and shredder material with a copper content between 60 and 80 % is charged into the converter. The converters have a capacity of approx. 35 t each and four to six batches are processed per day and converter. 8 - 25 t per charge of converter metal with a copper content of approx. 95 % are further processed in the anode furnace. The converter slag, containing approx. 30 % of copper, is returned to the blast furnace. Zinc, lead and tin are volatilised and oxidised by the process air. The flue dusts collected in the baghouse are processed in the tin-lead alloy plant.

The particulate matter content in the raw off-gas (80,000 - 150,000 Nm^3/h) and its main constituents are shown in Table 3-25. Measured and authorised emission values of the cleaned scrap converter off-gas are given in Table 3-26.

Table 3-25: Particulate matter content and its main constituents in the raw off-gases from the scrap converter

Particulate matter	
Total [mg/m^3]	10,000 - 30,000
Pb [wt.-%]	5 - 30
Zn [wt.-%]	25 - 70
Sn [wt.-%]	1 - 20

Table 3-26: Concentrations of the main constituents in the cleaned off-gases from the scrap converter

Substance	Unit	Measured Value	Authorised value
SO_x (as SO_2)	mg/m³	200 - 500**)	800
NO_x (as NO_2)	mg/m³	20 - 30	500
PCDD/PCDF	ng/ m³	< 0.1	< 0.1
Particulate matter*)	mg/m³	< 1 - 10	20

*) The main constituents of the particulate matter are given in Table 3-31.

**) Typical mean value of a charge

Source: Emission values which are accessible to the authority

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions (charging, blowing, pouring, etc.), different input materials and changes in the operating mode.

3.2.3 Reverberatory anode furnaces

Scrap with an average copper content of 90 to 95 % together with the metal phase from the converter is fed into the anode furnace and refined by oxidation. For this purpose HK operates two reverberatory furnaces: a stationary furnace, where the oxidation is accomplished by top blowing, which has a capacity of 300 t/d of anode copper and a new tilting furnace (since 1995) where the air is injected by nozzles and which produces 400 t/d. The two-component burners are fired with oil and lignite. For deoxidisation, wood is used in the stationary furnace and in the tiltable furnace natural gas is blown into the molten phase. The refined copper is cast into anodes on two casting wheels and is further refined in the electrolysis plant.

Further products resulting from fire refining are a slag with a copper content of about 30 %, which is re-fed into the blast furnaces, and filter dust with a copper content of 15 to 25 %, which is recycled in the blast furnace.

A secondary hood system is installed to prevent fugitive emissions. The heat of the furnace off-gas is used to generate steam in a waste heat boiler before the off-gas is cleaned by a fabric filter. The particulate matter content in the raw furnace off-gas and its main constituents are shown in Table 3-27. Measured and authorised emission values of the cleaned off-gas are given in Table 3-28.

Table 3-27: Particulate matter content and its main constituents in the raw off-gases from the reverberatory anode furnace

Particulate matter	
Total [mg/m^3]	1,000
CaO[*)] [wt.-%]	30 - 50
Pb [wt.-%]	2 - 6
Zn [wt.-%]	5 - 15
Cu [wt.-%]	15 - 25
As [wt.-%]	0.5 - 5[**)]

[*)] from off-gas conditioning

[**)] depending on type of raw materials

Table 3-28: Concentrations of main constituents in the cleaned off-gases from the reverberatory anode furnace

Substance	Unit	Measured Value	Authorised value
SO_x (as SO_2)	mg/m³	150 - 500[**)]	800
NO_x (as NO_2)	mg/m³	100 - 500	500
PCDD/PCDF	ng/ m³	< 0.1	< 0.1
Particulate matter[*)]	mg/m³	1 - 10	20

[*)] The main constituents of the particulate matter are given in Table 3-31.

[**)] Typical mean value of a charge

Source: Emission values which are accessible to the authority

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions (charging, pouring, poling etc.), different input materials and changes in the operating mode.

3.2.4 Electrolysis plant

In 1994 an electrolysis plant according to the ISA technology was installed to replace the old conventional one. The capacity is about 170,000 t/a of cathode copper with a current density of approx. 310 A/m² [22]. In Table 3-29 the accompanying metals contained in anode copper and the copper cathode from the electrolysis plant at HK are shown.

Table 3-29: Accompanying metals in anodes and cathodes at HK

Element	**Anode** [wt.-%]	**Cathode** [g/t]
Ag	0.06	10
Se	0.005	0.1
Te	0.002	< 0.1
As	0.07	0.7
Sb	0.07	< 1
Pb	0.2-0.4	< 1
Sn	0.08	< 1
Ni	0.3-0.5	1
O_2	0.15-0.22	-

Source: Dobner [22], Dobner/Schwill [23]

In comparison with Table 3-10 it can be seen, that anodes from secondary smelting are different from the primary ones, but cathodes are very similar and so they have the same quality.

The anode slime, which results from the precipitation of lead sulphate and insoluble precious metals, has a content of 5 - 10 % of precious metals. It is further processed in subsequent processes to recover the precious metals such as silver, gold, platinum and palladium. 1,000 t of anode slime were obtained in 1997 [52]. The sludge is pretreated (elimination of copper and zinc, partial dewatering) before it is marketed.

3.2.5 Electrolyte purification[15]

Nickel is dissolved during electrolysis and has to be removed from the electrolyte (tankhouse bleed) in a special auxiliary plant. To maintain a nickel concentration of approximately 20 g/l, 120 - 130 m³ of electrolyte are withdrawn per day and purified. In the case of 203,000 t/a anode feed and a nickel content of approximately 0.5 %, and considering an anode scrap return of 13 %, about 880 t/a of nickel have to be withdrawn from the system via anode slimes and bleed. With an extraction rate of 85 % in the electrolyte purification plant, 110 m³/d of bleed and 35 m³/d of liquor from anode slime leaching have to be treated.

The main stages in the purification of the electrolyte are copper sulphate recovery via evaporation process, further decopperisation in liberator cells and nickel sulphate recovery via evaporation processes. There are three sales products which can be gained from electrolyte purification:

- fine copper sulphate ($CuSO_4 \cdot 5H_2O$)

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[15] A detailed description of the electrolyte purification can be found in Dobner [22].

- crude nickel sulphate ($NiSO_4 \cdot 2H_2O$)
- fine nickel sulphate ($NiSO_4 \cdot 6H_2O$).

About 2,000 t/a of nickel sulphate and 2,000 t/a of copper sulphate are recovered from the electrolyte. Elutriation from condensing and cooling has to be treated by the precipitation of arsenic.

3.2.6 Tin-lead alloy plant

In the tin-lead alloy plant, technical zinc oxide and tin-lead alloy are produced from oxides arising during the smelting and converting processes. The converter flue dust and, if the tin content is high enough, also the blast furnace flue dust are mixed with fluxes (soda) and reductants (anthracite coal or petrol coke) and are fed to two hearth furnaces. The heat is supplied by oil burners. Zinc is transferred to the flue dust as zinc oxide and is collected in bag filters. The remaining metal phase consists mainly of tin and lead which is refined and cast into ingots. 3,500 t of tin-lead alloy with a composition of 30 % tin and 70 % lead were produced in 1997 and sold for the production of soft solder. The slag, consisting mainly of caustic soda, zinc and sulphur, has to be dumped [27]. Other residuals such as drosses and skimmings are recycled in the copper recovery process steps.

The off-gases from the TLA plant are cleaned by a fabric filter before being released into the surrounding atmosphere. Measured and authorised emission values of the cleaned gas are given in Table 3-30.

Table 3-30: Concentrations of main constituents in the cleaned off-gases from the TLA plant

Substance	Unit	Measured value	Authorised value
SO_x (as SO_2)	mg/m³	n.d.	400
NO_x (as NO_2)	mg/m³	30 - 50	200
PCDD/PCDF	ng ITE/m³	< 0.1	< 0.1
Particulate matter	mg/m³	5 - 20	20

*) The main constituents of the particulate matter are given in Table 3-31.

Source: Emission values which are accessible to the authority

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions (charging, pouring, poling etc.), different input materials and changes in the operating mode.

3.2.7 Characteristics of fabric filters at HK

All off-gases arising at processes at HK are cleaned in a fabric filter before being released into the surrounding atmosphere. The measured and authorised values of the constituents in the particulate matter content in these off-gases are shown in Table 3-31.

Table 3-31: Main constituents in the dust content of the off-gas after treatment in a fabric filter

Substance	Unit	Measured value	Authorised value
Class I (TA-Luft)			
Cd	mg/m³	< 0.01 - 0.1	0.2
Hg	mg/m³	< 0.01 - 0.2	0.2
Tl	mg/m³	< 0.01	0.2
Sum class I (TA-Luft)	**mg/m³**	**< 0.03 - 0.2**	**0.2**
Class II (TA-Luft)			
As	mg/m³	< 0.01 - 0.8	1
Ni	mg/m³	< 0.01 - 0.3	1
Co	mg/m³	< 0.01 - 0.1	1
Se	mg/m³	< 0.01 - 0.9	1
Te	mg/m³	< 0.01 - 0.1	1
Sum class II (TA-Luft)	**mg/m³**	**< 0.05 - 1**	**1**
Class III (TA-Luft)			
Sb	mg/m³	< 0.01 - 0.5	5
Pb	mg/m³	0.1 - 2	5
Cr	mg/m³	< 0.01 - 0.1	5
Cu	mg/m³	0.02 - 2	5
Sn	mg/m³	< 0.01 - 1	5
Sum class III (TA-Luft)	**mg/m³**	**< 0.15 - 5**	**5**

Source: Emission values which are accessible to the authority

If substances of several classes are present, the mass concentration in the emitted gas should not exceed a total of 1 mg/m^3 for coinciding class I and II substances as well as a total of 5 mg/m^3 for coinciding class I and III or class II and III substances. The emissions of substances class I - III have to be determined as a sum of the particulate matter, the vapour and the gas share of the respective element and its compounds (according to TA Luft [1]). More information about the German regulations can be found in section 6.1.2.

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions (charging, blowing, pouring, poling etc.), different input materials and changes in the operating mode.

3.2.8 Waste water treatment

The present waste water situation at HK is characterised by collecting process water, precipitation water and cooling water in a mixed water drain and by fed them through the municipal sewage system to a communal waste water treatment plant. Parts of the waste water stream are pretreated at HK before the final treatment is carried out at the communal waste water treatment plant. Currently, the waste water system at HK is modified in order to fulfil the requirements of the 39th annex of the Abwasserverordnung (AbwV) [84]; especially the multiple use of waters will be intensified.

Since the waste waters discharged from the communal waste water treatment plant arise at all processes carried out HK, the concentration of pollutants are shown in the next section.

3.2.9 Summarised data on outputs and environmental concerns at HK

Emissions into the air

Table 3-32 shows the main stack emissions from the different process units at Hüttenwerke Kayser AG. The given values are the mean values of a charge.

Table 3-32: Stack emissions from secondary copper production at HK, measured values

Process unit	**Flow** [m³/h]	**Clean gas** **Particulate matter** [mg/m³]	**SO_2** [mg/m³]	**NO_x** [mg/m³]	**CO** [mg/m³]	**PCDD/PCDF** [ng/m³]
3 blast furnaces (incl. secondary hoods)	200,000 - 250,000	1 - 20	50 - 150	30 - 100	20 - 100 (500)*)	< 0.5
2 scrap converters	150,000 - 300,000	1 - 10	200 - 500 (1,600)*)	20 - 30	30 - 80 (300)*)	< 0.1
2 rev. Anode furnaces	100,000 - 150,000	1 - 10	150 - 500 (1,600)*)	100 - 500	20 - 80	< 0.1
Tin-lead alloy plant	30,000 - 40,000	1 - 20	n.d.	10 - 100	10 - 30	< 0.1

*) peak value

Source: Emission values which are accessible to the authority

In Table 3-33 the calculated overall values of both, stack and fugitive emissions, can be seen. The calculations are based partly on measured values and partly on emission factors.

Table 3-33: Total emission from copper production at HK, calculated values

Main components	**Particulate matter** [kg/t]	**SO_2** [kg/t]	**NO_x** [kg/t]	**CO** [kg/t]	**Pb** [g/t]	**As** [g/t]	**Cu** [g/t]	**Zn** [g/t]
Overall loads	0.47	3	1	2	50	1	50	100

Source: Emission values which are accessible to the authority

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions, different input materials and changes in the operating mode (e.g. start-up and shut-down operations). More information about measurements to ensure that the emissions specified are representative, mutually comparable and clearly describe the relevant operating state of the plant can be found in section 4.1.1.

Waste water

In Table 3-34 data on the waste water from HK after treatment in a communal waste water treatment plant is given.

Table 3-34: Pollutants (based on measurements) from HK

Main components	Cu	Pb	As	Ni	Cd	Zn
Overall pollutant rate [g/t]	1.0	0.5	0.1	0.3	< 0.01.	0.2

Source: Emission values which are accessible to the authority

Main intermediates, by-products and residues

In Table 3-19 an overview of the main intermediates, by-products and residues is given.

Table 3-35: Main intermediates, by-products and residues from copper production at HK

Process unit	By-product/residue	Amount [t/a]	Use/treatment option
Blast furnace	Zinc oxide	7,500	Partly internal use at the TLA plant, partly external use for the production of zinc metal and chemicals
	Slag	80,000	External use as construction material or abrasive manufacturing
Scrap converters	Zinc oxide	8,500	Internal use at the TLA plant
	Slag	20,000	Internal use at the blast furnace
Rev. Anode furnaces	Dust	1,000	Internal use at the blast furnace
	Slag	20,000	Internal use at the blast furnace
Electrolysis	Anode slime	1,000	External use for the recovery of precious metals and Se, Te, Pb
	Nickel sulphate	2,400	By-product for sale
	Copper sulphate	2,200	By-product for sale
TLA plant	Tin-lead alloy	3,700	By-product for sale
	Zinc oxide	5,000	External use for the production of zinc metal and chemicals
	Caustic slag	3,000	Dumping
General	Household refuse	200	

Source: company information Hüttenwerke Kayser AG, 1998

3.3 Copper production at Mansfelder Kupfer und Messing GmbH, Hettstedt

At Hettstedt copper has been processed for centuries. The mining of copper schist in the area of Hettstedt goes back to the end of the 12th century. Already at the end of the middle ages, Hettstedt was one of the most important metallurgical plants of its region. The processing of copper schist from this area was carried out until 1990. The production of secondary copper at the present site of Mansfelder Kupfer und Messing GmbH Hettstedt (MKM) started in the seventies.

In 1996, 105,000 tons of copper containing raw materials such as copper containing scrap, copper containing residues (drosses, slags, sludges, dusts), brass scrap, copper containing iron scrap and copper granulates were processed to 60,000 tons of copper cathodes. The produced copper is further processed in a wire rod plant and a continuous casting plant as well as in a newly installed wire rod and strip plant. In Figure 3-10 a scheme of the pathways for the secondary copper production at MKM is given and in Table 3-36 the main input materials and products are specified.

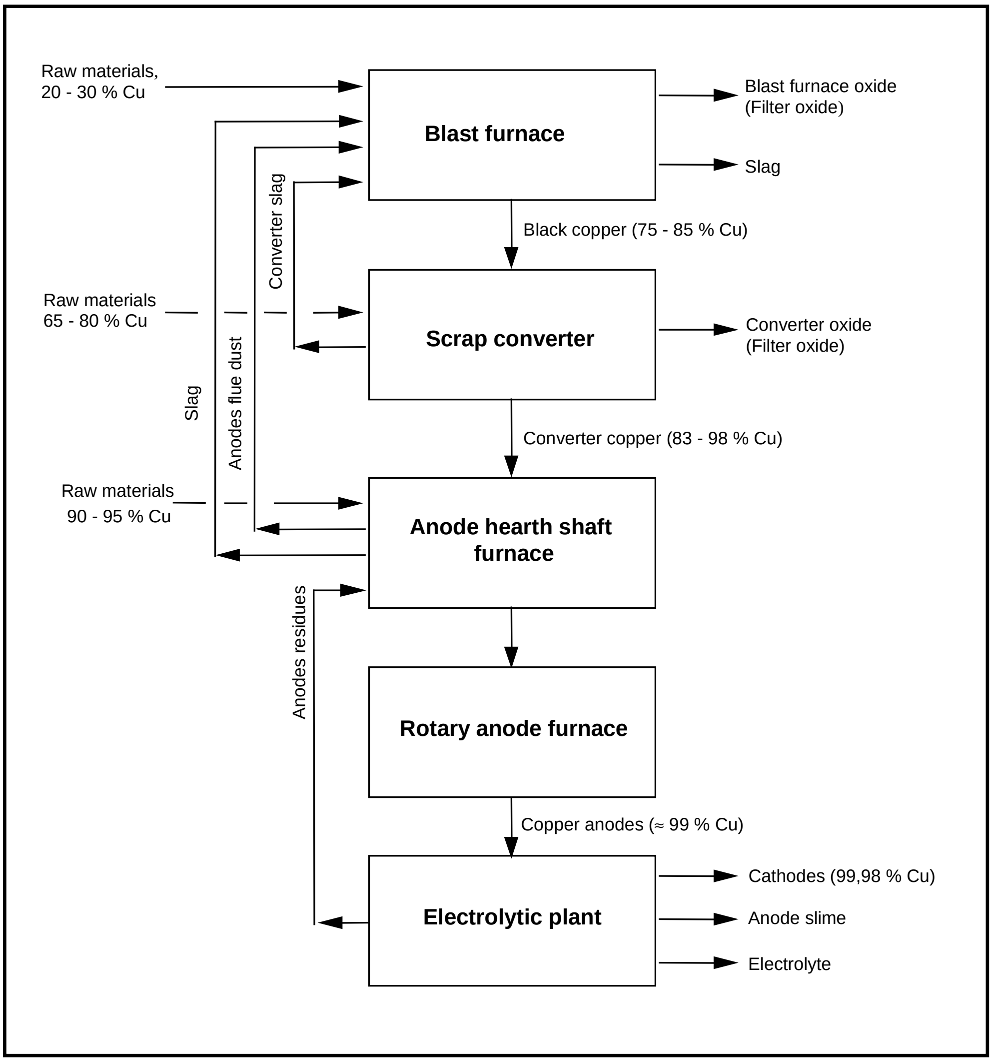

Figure 3-10: Copper Production at MKM GmbH, Hettstedt

Table 3-36: Input/output data from Mansfeld Kupfer und Messing GmbH (1996)

Input materials	Quantity [t/a]
Drosses/slags	40,000
Copper-iron containing scrap	7,000
Brass scrap	20,000
Refining scrap	40,000
Granulated copper	1,000
Coke	10,000
Limestone	4,500
Natural gas	n.a.
Silica	2,000
Wood	900

Products	Quantity [t/a]
Copper cathodes	60,000
Nickel sulphate	800
Slags	35,000
Flue dust	5,000

Source: Company information MKM, 1996

3.3.1 Blast furnace

Since 1995, MKM has been operating a new blast furnace with a maximum melting capacity of 8.45 t/h (referring to the input material). There, copper containing secondary raw materials are processed together with limestone and coke to 2.5 - 3 t/h of black copper. The input materials of the blast furnace are specified in Table 3-37.

Table 3-37: Input materials for blast furnace

Input materials	Amount [t/a]
Drosses, slags	40,000
Copper-iron containing scrap	7,000
Filter oxide from afterburning chamber and cooler	1,200
Filter oxide from anodes shaft furnace	150
Coke	7,000
Limestone	4,200

Source: Company information MKM, 1996

The produced black copper with a copper content of 75 - 85 % is further processed together with additional metal in the converter. The blast furnace slag is used for construction purposes. Table 3-38 shows the typical chemical composition of the blast furnace slag produced at MKM. In 1996, about 15,200 t of black copper and 30,000 t of slag were produced.

Table 3-38: Chemical composition of blast furnace slag from MKM

Substance	**FeO**	**SiO_2**	**CaO**	**MgO**	**Cu**	**Ni**	**Pb**	**Zn**
Share [wt.-%]	25 -30	22 -32	8 -12	0,5 -3	1 -4	0,1 -1	0,5 -2	5 -15

Source: Company information MKM, 1996

The furnace off-gas (Gichtgas) is afterburned with additional oxygen and natural gas in a post-combustion chamber which also serves as a settling chamber at about 1,000 °C. The heat of the off-gas is used for steam production in a waste heat boiler, before the off-gas is cooled with air in a tubular cooler and then sent to a purification plant. There, adsorption is used to deposit dioxines and furanes (PCDD/PCDF), after the off-gas is dedusted in a fabric filter. The released clean gas (32,000 m^3/h) has a temperature of about 90 °C and an oxygen content of 14.9 vol.-%. In Table 3-39 the measured and authorised emission values of the clean gas are given.

The off-gas of the settler is dedusted in an extra filter and is released into the surrounding atmosphere via a separate stack. The concentration of particulate matter in the clean gas is 2 mg/m^3 as a yearly average (emission declaration 1996). Figure 3-11 shows a schematic view of the blast furnace process.

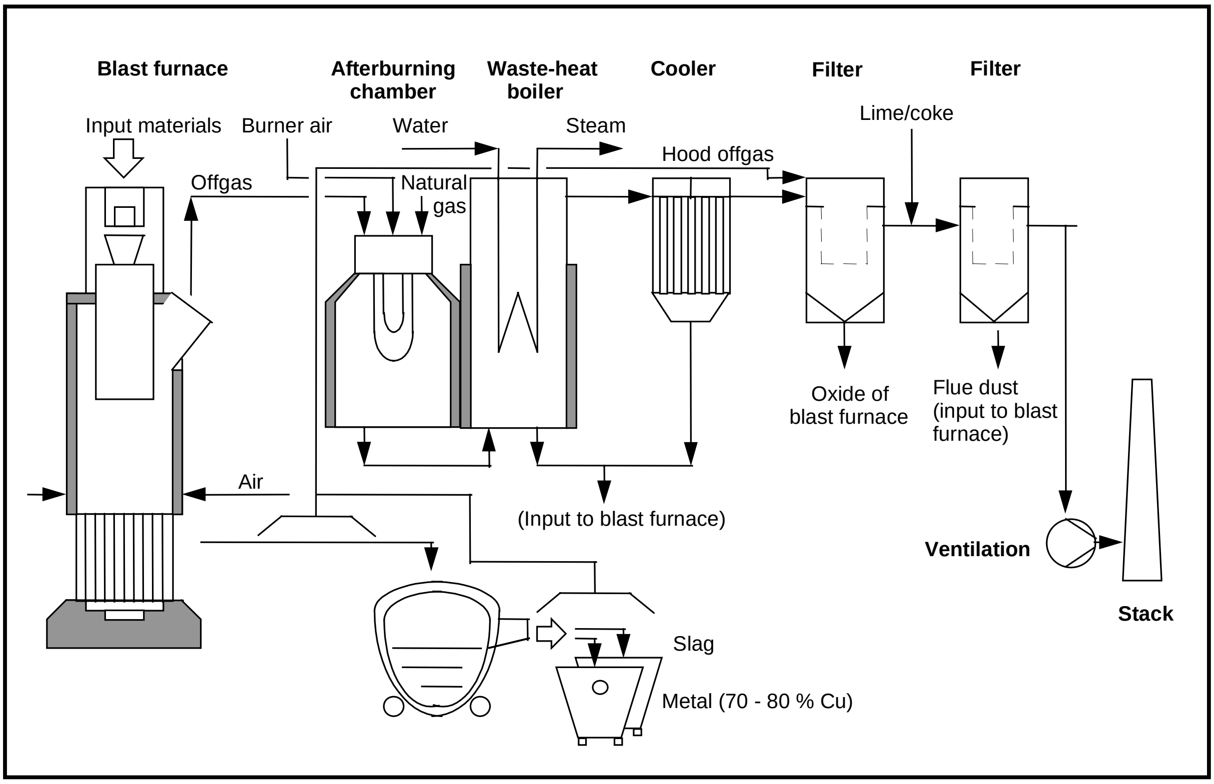

Figure 3-11: Blast furnace process

Table 3-39: Concentrations of main constituents in the cleaned off-gas from the blast furnace

Substance	Unit	Measured value	Authorised value
SO_x (as SO_2)	mg/m³	50	800
NO_x (as NO_2)	mg/m³	47	500
CO	mg/m³	19	50
C_{total}	mg/m³	3	50
PCDD/PCDF	ng (ITE)/m³	< 0.5	< 0.5**)
Particulate matter*)	mg/m³	3	10

*) The main constituents of the particulate matter are given in Table 3-47

**) Value to be achieved: 0.1 ng (ITE)/m³

Source: Emission values which are accessible to the authority

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions (charging, blowing, pouring, etc.), different input materials and changes in the operating mode.

The dust arising in the post-combustion chamber as well as the dust arising in the waste heat boiler and the tubular cooler is recycled to the blast furnace. In 1996, the following amounts of dust were collected and recycled to the blast furnace:

- 550 t from the post-combustion chamber,
- 100 t from the waste heat boiler, and
- 100 t from the tubular cooler.

The filter dust (1,300 t in 1996) with a high content of zinc and lead is sold for hydro- and pyro-metallurgical processing. The metallic components of this filter dust are given in Table 3-40.

Table 3-40: Metallic components of filter-oxide from blast furnace

Substance	Zn	Pb	Cu	Sn	Ni
Share [wt.-%]	20 - 50	5 - 20	2 - 12	0.2 - 4	0.1 - 1

Source: Company information MKM

The lower part of the blast furnace is cooled by cooling water. Thereby 400 m^3 per year of so-called changing water has to be discharged.

3.3.2 Converter

The converter plant in operation since 1972 consists of two drum type converters (capacity: 20 t of input material) with a post-combustion chamber, ducted cooling, a gas cleaning plant as well as auxiliary plants such as a cooling water supply, an air supply and an electrical load center. One converter is in operation while one is on stand-by or is being relined. In Figure 3-12 a schematic view of a converter is shown.

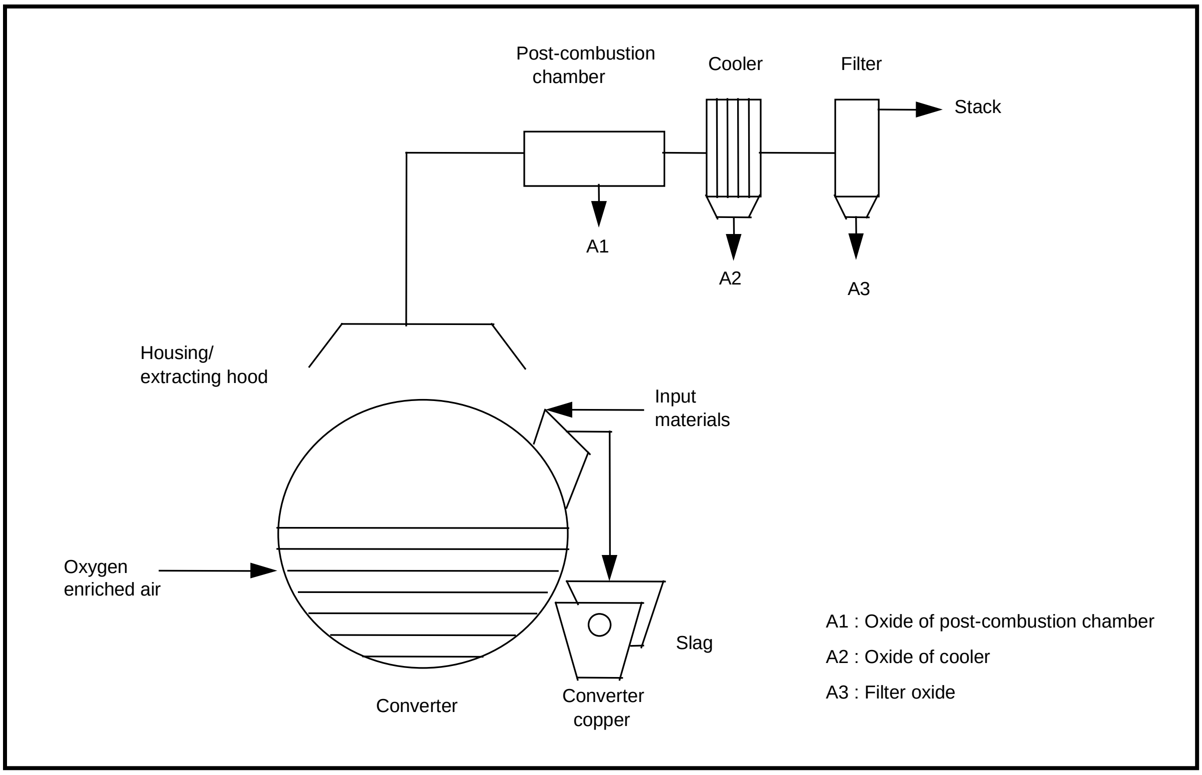

Figure 3-12: Schematic view of converter process

The black copper of the blast furnace is used as flush material and is processed together with brass scrap, copper containing drosses, refining scrap and coke as well as other fluxes. The input materials are blown to converter copper by use of a special mixture of oxygen and nitrogen. The input materials for the converter are specified in Table 3-41. In 1996 about 21,000 t of converter copper were produced.

Table 3-41: Input materials for converter

Input materials	Amount [t/a]
Black copper	15.200
Brass scrap	20.000
Anodes scrap	250
Coke	3.000
Silica	1.700

Source: Company information MKM, 1996

Between 12 t and 13 t of converter copper with a copper content of 92 - 98 % are produced per batch and are sent to the anode furnace for further refining. The converter slag produced (about 18,500 t in 1996) is mainly recycled to the blast furnace to recover its copper content. The accompanying metals in the converter slag are shown in Table 3-42.

Table 3-42: Accompanying metals in the converter slag

Substance	**Cu**	**Ni**	**Pb**	**Zn**
Share [wt.-%]	15 - 35	1 - 30	1 - 5	5 - 15

Source: Company information MKM, 1996

The off-gas arising during blowing is captured by hoods and sent to a post-combustion chamber together with secondary air with the aim of oxidising the volatile metal components in the off-gas, whereby, temperatures of 800 - 1,300 °C are reached. This off-gas with a volume of 100,300 m³/h is divided into partial currents and cooled with air before being combined and directed to a baghouse. The dedusted gas is released into the surrounding atmosphere at a temperature of 65 °C. The measured and authorised emission values of the clean off-gas are given in Table 3-43.

Table 3-43: Emissions in clean gas of the converter

Substance	**Unit**	**Measured value**	**Authorised value**
SO_2	mg/m³	300	800
NO_x	mg/m³	27	500
CO	mg/m³	173	-
PCDD/PCDF	ng (ITE)/m³	n.a.	0.5
Particulate matter*)	mg/m³	6	20

*) The main constituents of the particulate matter are given in Table 3-47.

Source: Emission values which are accessible to the authority

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions (charging, blowing, pouring, etc.), different input materials and changes in the operating mode.

The dust collected at the post-combustion chamber as well as the dust settled in the coolers is recycled to the blast furnace. The filter dust from the baghouse (3,650 t in 1996) can be sold as so-called filter oxide due to its high zinc content and it is used as a raw material in the secondary zinc production industry. The metallic accompanying metals in the filter oxide are shown in Table 3-44.

Table 3-44: Metallic accompanying metals in filter-oxide of the converter

Substance	**Cu**	**Ni**	**Pb**	**Zn**	**Sn**
Share [wt.-%]	2 - 10	0.1 - 1	5 - 20	45 - 65	0.2 - 4

Source: Company information MKM, 1996

The cooling water for the hoods of the converters and the charging chutes is operated in a closed circuit. A necessary bleed of 215 m^3 per year has to be discharged as waste water.

3.3.3 Anode plant

The converter copper produced in the converter is fire refined in the anode furnace together with additional raw copper material. Until now, this process step was carried out by 3 fixed-head reverberatory furnaces. Currently a new anode plant with an authorised capacity of 99,500 t/a anode copper is in test operation. The anode copper should have a copper content of about 99 %. A principal flow sheet of the new anode plant can be seen in Figure 3-13.

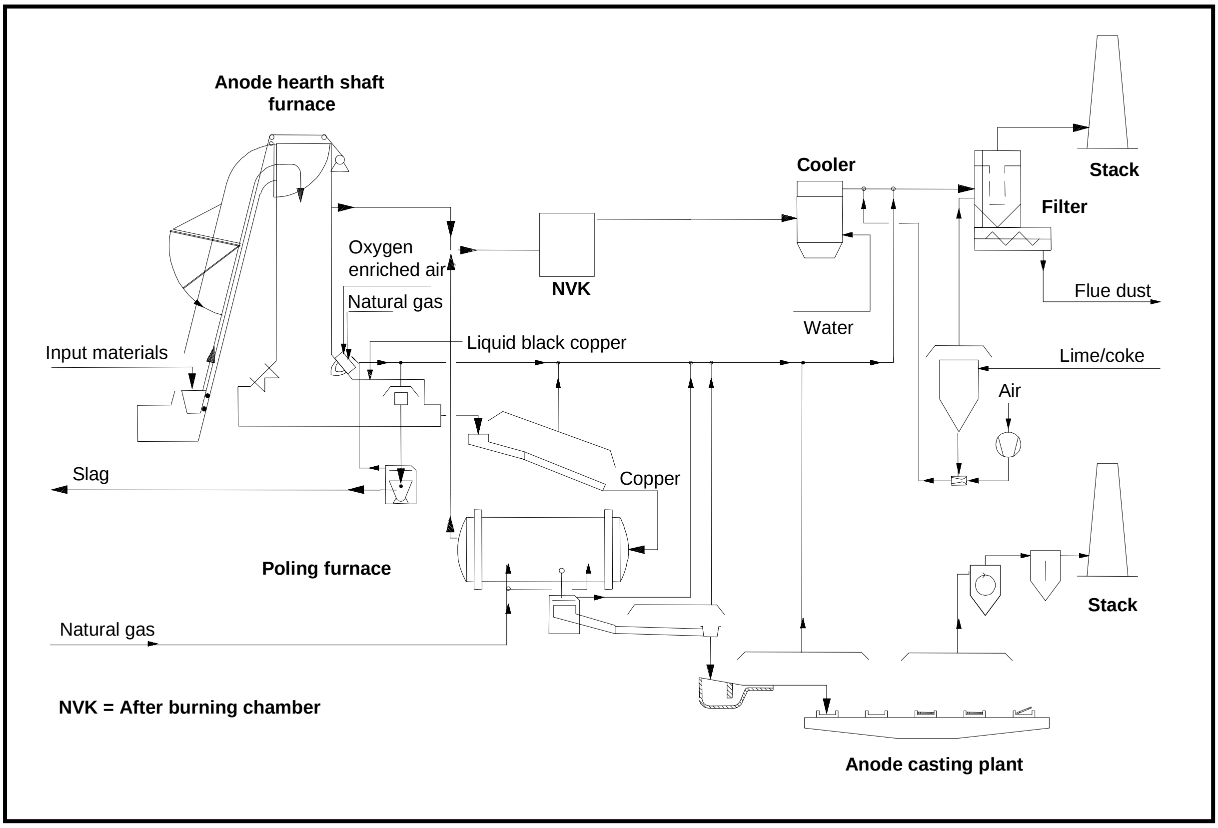

Figure 3-13: Flow sheet of the new anode plant

Besides the gas cleaning facilities, the plant consists of 3 units:

- the melting furnace,
- the refining furnace, and
- the anode casting machine.

The melting furnace with a melting capacity of 30 t/h is an open-hearth furnace with a shaft stacked up. The furnace is charged with solid material (about 240 t /d) via the shaft. A natural gas/air burner is installed in the lower part of the shaft to melt the input material. Oxygen enrichment of the burner air is possible. The molten copper accumulates in the hearth of the melting furnace (capacity: about 80 t). There, the liquid converter copper is poured in directly (70 - 80 t per day). In Table 3-45 the maximum input materials according to the operation permit of the competent authority are given.

Table 3-45: Input materials of anode hearth shaft furnace

Input materials	**max. amount** [t/a]
Refined copper	58,000
Brass scrap	1,500
Blister (black copper)	10,000
Granulated copper	4,000
Converter copper	24,000
Anode residues from electrolysis plant	11,000
Casting residues	310
Anode copper	600
Silica	7,000
Charcoal	50

Source: Company information MKM

The slag produced in the melting furnace is recycled to the blast furnace after mechanical preparation. 4,000 t of slag with a copper content of 15 - 32 % are expected.

The superheated melt is transferred from the melting furnace to the refining furnace via a skimmer tap. The refining furnace is a rotary or drum furnace with a capacity of 300 t and is also equipped with a natural gas/air burner. After the oxidation of the copper with air, the reduction (poling) is applied by blowing in natural gas. The slag arising during the oxidation as well as the reduction step (expected amount: 7,500 t) is recycled to the shaft furnace.

The refined copper is directed to the continuous casting machine (capacity: 50 t/h) via a launder and a metering vessel. The continuous bar is hydraulically cut into anodes, which are cooled in a cooling tunnel by water spray before being sent to the electrolytic plant. The water vapour arising during the cooling of the casting machine is captured by hoods and directed to a wet separation plant.

The off-gases of the melting furnace and the refining furnace are afterburned in post-combustion chambers at a temperature of at most 900 °C. The off-gas of the refining furnace is then used to pre-heat the burner air up to approximately 400 °C, before the off-gases of both furnaces are cooled in a quench cooler. Afterwards, they are treated in a gas cleaning plant that consists mainly of an adsorption filter plant and a fabric filter. In the adsorption filter plant, a mixture of dust from lignite coke and lime hydrate is injected into the off-gas mainly to reduce the emission of dioxines and furanes (PCDD/PCDF). The emission values in the clean gas with an expected volume of 97,000 m3/h shown in Table 3-46 are authorised.

Table 3-46: Emission values in the clean gas of anode furnace and poling furnace

Substance	Unit	Authorised value
Cd, Hg, Tl	mg/m³	0.2
As, Co, Ni, Se	mg/m³	1
Sb, Pb, Cr, Cu, Mn, Sn, V	mg/m³	5
NO_x	g/m³	0.5
HCl	mg/m³	30
HF	mg/m³	5
C_{total}	mg/m³	50
PCDD/PCDF	ng (ITE)/m³	< 0.5
Particulate matter*)	mg/m³	10

*) The main constituents of the particulate matter are given in Table 3-47.

Source: Emission values which are accessible to the authority

To avoid fugitive emissions, all holes at the smelting furnace and the refining furnace as well as the metering vessel are equipped with hoods or enclosures. The captured ventilation gases are directed to the gas cleaning system.

Cooling water is necessary to cool both furnaces, to quench the hot furnace off-gases and also to cool the casting machine, the anode cutting facility and the cast and cut anodes. The different cooling waters are operated in a closed circuit and are conditioned depending on their application. The arising waste water is used to operate the quench cooler, so the discharge of waste water is not necessary. The copper containing residues arising both, at the cooling tunnel to cool the cast anodes and during operation of the quench cooler, can be recycled to the blast furnace.

3.3.4 Electrolytic plant

The electrolytic refining of the copper anodes is carried out by a conventional electrolytic plant. The produced copper cathodes have a copper content of 99.98 %. Currently, this plant has a production capacity of 60,000 t/h copper cathodes. As by-products, anode slime and raw nickel sulphate are produced.

3.3.5 Characteristics of fabric filters at MKM

All off-gases arising from processes at MKM are cleaned in a fabric filter before being released into the surrounding atmosphere. The measured and authorised values of the constituents in the particulate matter content in these off-gases are shown in Table 3-47.

Table 3-47: Main constituents in the dust content of the off-gas after treatment in a fabric filter

Substance	Unit	Measured value	Authorised value
Class I (TA-Luft)			
Cd	mg/m³	< 0.01 - 0.1	0.2
Hg	mg/m³	< 0.01 - 0.2	0.2
Tl	mg/m³	< 0.01	0.2
Sum class I (TA-Luft)	**mg/m³**	**< 0.03 - 0.2**	**0.2**
Class II (TA-Luft)			
As	mg/m³	< 0.01 - 0.8	1
Ni	mg/m³	< 0.01 - 0.3	1
Co	mg/m³	< 0.01 - 0.1	1
Se	mg/m³	< 0.01 - 0.9	1
Te	mg/m³	< 0.01 - 0.1	1
Sum class II (TA-Luft)	**mg/m³**	**< 0.05 - 1**	**1**
Class III (TA-Luft)			
Sb	mg/m³	< 0.01 - 0.5	5
Pb	mg/m³	0.1 - 2	5
Cr	mg/m³	< 0.01 - 0.1	5
Cu	mg/m³	0.02 - 2	5
Sn	mg/m³	< 0.01 - 1	5
Sum class III (TA-Luft)	**mg/m³**	**< 0.15 - 5**	**5**

Source: Emission values which are accessible to the authority

If substances of several classes are present, the mass concentration in the emitted gas should not exceed a total of 1 mg/m^3 for coinciding class I and II substances as well as a total of 5 mg/m^3 for coinciding class I and III or class II and III substances. The emissions of substances class I - III have to be determined as a sum of the particulate matter, the vapour and the gas share of the respective element and its compounds (according to TA Luft [1]). More information about the German regulations can be found in section 6.1.2.

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions (charging, blowing, pouring, poling etc.), different input materials and changes in the operating mode.

3.3.6 Further processing of copper at MKM

No information is available about further processing of copper at MKM.

3.3.7 Summarised data on outputs and environmental concerns at MKM

Emissions into the air

Table 3-48 shows the main emissions from the different process units at MKM.

Table 3-48: Stack emissions (max. measured values) from secondary copper production at MKM

Process unit	Flow [m^3/h]	Particulate matter [mg/m^3]	SO_2 [mg/m^3]	CO [mg/m^3]	NO_x [mg/m^3]	PCDD/PCDF ng (I-TE)/m^3
1 blast furnace	32,000	3	50	20	50	< 0.5
1 converter	100,000	6	300	175	30	n.a.
Anode furnace*)	11.000 - 15.000	3 - 6	20 - 200	10 - 80	10 - 160	n.a.

*) Emissions are given for the 3 reverberatory furnaces (old anode plant)

Source: Emission values which are accessible to the authority

In Table 3-49 the specific stack emission can be seen. Thereby the annual emission load is related to the annually produced amount of shaft furnace copper (shaft furnace), black copper (converter) or anode copper (anode plant). Fugitive emissions are not included in these values.

Table 3-49: Specific stack emissions of different process units at MKM

Component	Particulate matter [kg/t]	SO_2 [kg/t]	NO_x [kg/t]	CO [kg/t]	Pb [g/t]	As [g/t]	Zn [g/t]	Cu [g/t]	Cd [g/t]	Ni [g/t]	Sn [g/t]
Blast furnace	0.15	0.08	0.7	0.3	18	0.1	5	25	0.2	3	6
Converter	0.26	11.8	1.0	6.8	31	0.1	13	17	1	1	15
Anode furnace*)	0.08	0.26	0.8	0.2	14	2	4	26	0.3	2	4

*) Emissions are given for the 3 fixed-hearth reverberatory furnaces (old anode plant)

Source: Emission values which are accessible to the authority

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions, different input materials and changes in the operating mode (e.g. start-up and shut-down operations). More information about measurements to ensure that the emissions specified are representative, mutually comparable and clearly describe the relevant operating state of the plant can be found in section 4.1.1.

Waste water

From the cooling circuits of the shaft furnace and the converters, 615 m^3 are directed to the draining ditch. The cooling water from the anode hearth shaft furnace, the refining furnace and the casting machine is operated in a closed circuit. The necessary bleed is partly used in the quench cooler.

Main intermediates, by-products and residues

In Table 3-50 an overview of the main intermediates, by-products and residues is given.

Table 3-50:Main intermediates, by-products and residues from copper production at MKM

Process unit	By-product/residue	Amount [t/a]	Use/treatment option
Blast furnace	Slag	30,000 - 35,000	Sold as construction material
	Oxide from afterburning chamber, boiler and cooler	700 - 800	Internal use at the blast furnace
	Filter oxide	1,000 - 1,300	External use
Converters	Slag	17,000 - 19,000	Internal use at the blast furnace
	Oxide from afterburning chamber	250 - 300	Internal use at the blast furnace
	Oxide from cooler	100	Internal use at the blast furnace
	Residues	300	Internal use at the blast furnace
	Filter oxide	3,500 - 3,700	External use
Anode furnace*)	Anode copper residues	7,000 - 8,000	Internal use at the blast furnace
	Filter oxide	150	Internal use at the blast furnace
	Residues from furnace	200	Internal use at the blast furnace
Electrolysis	Anode slime	360	External use
	Nickel sulphate	700	External use
General	Household refuse	n.a.	

*) By-products and residues are given for the 3 fixed-hearth reverberatory furnaces (old anode plant)

Source: Company information MKM, 1996

3.4 Fabrication of wire rod at Friedrich Kemper GmbH & Co KG, Duisburg and Lacroix & Kress GmbH, Bramsche

At Friedrich Kemper GmbH & Co KG, Duisburg and Lacroix & Kress GmbH, Bramsche, the dip forming wire rod process is used for the further processing of copper. In this process, a copper core wire of 9 - 12.5 mm diameter (mother rod) is drawn through a molten bath of oxygen-free copper. Thereby additional copper solidifies at the surface to form a new rod of about 20 mm diameter. A special induction furnace is used for this process.

The rod produced in the furnace is reduced in diameter in a mill under inert gas, so the copper wire is oxygen-free. About one third of this wire is returned to form the core material. The basic concept of the process is shown in Figure 3-14.

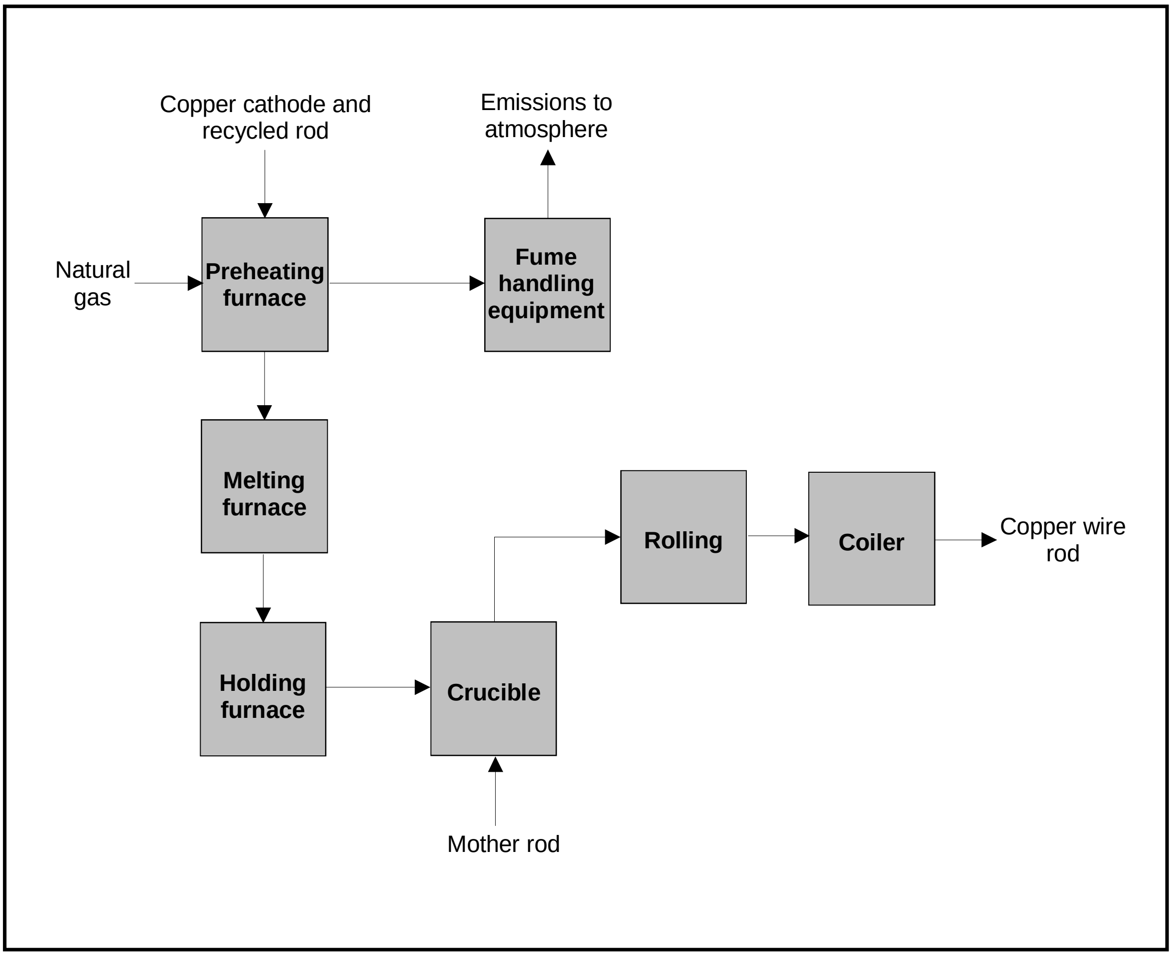

Figure 3-14: Basic concept of the dip forming copper wire rod plant

The main input material to the process is cathode copper as well as recycled scrap; both are charged automatically into a gas fired rotating drying furnace. There, the charge is conditioned and pre-heated up to 800 °C. This pre-heated feed material is discharged into a channel induction melting furnace with a capacity of 5 - 10 t/h providing copper at about 1,100 °C to the holding furnace and crucible. To ensure there is a constant level of molten metal in the crucible, it is attached to the holding furnace. Mother rod is drawn through an inlet die at the base of the crucible, increasing the diameter by drawing the core wire through the metal pool. The final diameter of the cast rod produced is controlled through the upper die, e.g. at < 20 mm dia before being directed via dancers to a three stand rolling mill. There, 8.0 mm and 12.5 mm rod is produced and coiled to 3,5 t palletised coils.

3.5 Fabrication of semi-finished products from copper and copper alloys[16]

There are numerous German fabricators of copper and copper alloyed semi-finished products. Size of the companies and the product range differ significantly so that not all fabrication facilities can be described. The following description represents a compilation of the most common processes and techniques for the fabrication of semi-finished products from copper and copper alloys including the applied abatement techniques. Not all German fabricators will be dealt with in this section. The descriptions and explanations will be restricted to plants which have melting and casting shops integrated with extrusion and/or mills. The general concept of the semi-finished product fabrication is shown in Figure 3-15.

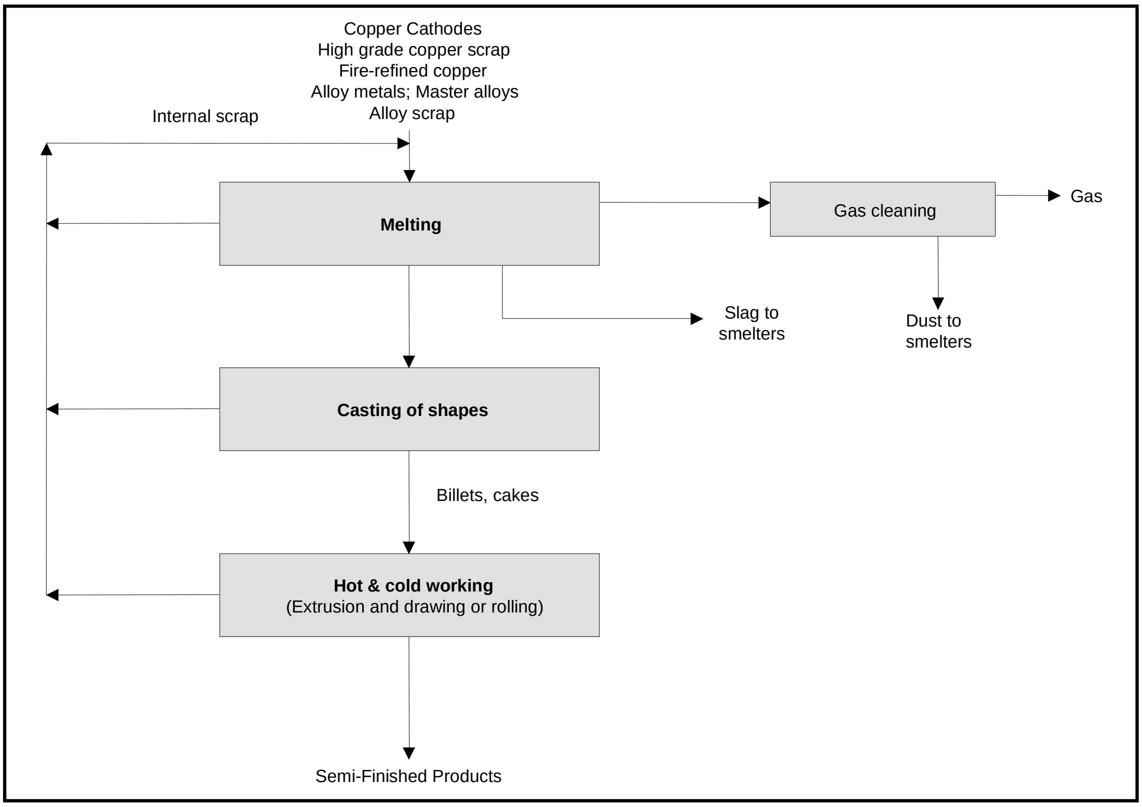

Figure 3-15: General flowsheet of semi-finished product fabrication

As raw material only metallic components are used. Some materials may be slightly contaminated with oil, paper and/or dirt. The following list shows the metallic components typically used as feed in meltshops of a semis fabrication plant :

- Cathodes,
- wire bars,
- ingots (copper and alloys),

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[16] Based on Traulsen, H.: „Fabrication of Semi-Finished Products From Copper and Copper Alloys“, EUROMETAUX Copper Industry [66]

- anodes (only for fire refining),
- swarf (usually returned from customers), and
- scraps from own factory, customers, other factories or from other sources.

The scraps are classified in technical and commercial (e.g. customs) specifications. The incoming raw material is controlled by scanners for radioactivity and by visual control for the compliance with the specification. This is true for a increasing number of factories.

The storage of raw material is done outdoors and indoors; outdoors storage areas are protected by a hard surface, in most cases concrete slabs. The rainwater is collected and treated by settling before discharge. Swarf, oil contaminated scrap and fines are stored indoors to avoid rainwater contamination.

Raw materials like wires, punchings, cuttings, tubes, etc are pressed to blocks. Oil contaminated scraps are processed for decreasing before melting. This can be done by washing with detergents and drying or heating in a rotary kiln. The distilling oil can be used as a fuel substitute or it is burned in an afterburner. Swarf is not pre-treated but charged directly

3.5.1 Melting

The input materials are handled by cranes or fork lifters for transport to the smelter. Different scrap types and alloy metals are selected with the objective to compose the correct feed for the specific charge to be processed. The melting furnaces may be distinguished by the energy sources applied: Electrically heated and (natural) gas- or fuel-fired units to melt the metallic feed. Furthermore, the melting and casting rate may determine the type of furnace and casting equipment selected: High production rates may lead to the use of a continuously melting shaft furnace and continuous casting equipment; batchwise melting and discontinuous casting may be preferred for copper alloys or special copper shape casting.

When using electric power for melting induction furnaces are applied. Both, coreless or channel type induction furnaces, are in use. Capacities of electric furnaces may range between 0.5 and 15 t of metal. Electric furnaces are mainly used for copper alloy melting and to a lesser extend for unalloyed copper. Typical data of a slab fabrication plant are compiled in Table 3-51 as an example.

Table 3-51: Typical data of an Electric furnace based discontinuous casting plant

Product	
Alloy	Brass
Shape	Slab
Dimensions	720 mm W x 130 mm H x 6500 mm L
Melting unit	
Type of furnace	Coreless induction furnace
Number of furnaces	2
Capacity	12 t metal
Power rating	2.8 MW each
Power consumption	165 – 184 kWh/t
Holding furnace	
Type of furnace	Channel type
Capacity	8 t
Caster	
Type	Discontinuous
N^o strands cast parallel	3
Primary cooling /mould	Indirectly water cooled copper mould
Secondary cooling	Direct spray cooling
Cooling water system	Primary: Once-through concept Secondary: Returned to water treatment plant
Off-gas handling	
Volume	Approx. 50,000 Nm^3/h
Cleaning by	Cyclone followed by baghouse

The melting furnace operation is discontinuous: Normally the total amount of the feed materials is charged to the furnace and melted down. As the furnace charge is carefully pre-adjusted, only slight corrections of the alloys are necessary before casting. When the material is completely molten and the composition correctly adjusted the melt is ready for casting. Frequently the melt is not directly cast from the melting unit but transferred to a holding and casting furnace and then casted. Such furnaces have less electric power installed so that energy is saved. The main purpose of this concept is to make the melting unit rapidly available for melting the next charge. So casting can be carried out while the melting furnace melts down the next charge. Depending on the type of alloy and the furnace capacity a batch may last between 0.5 and 2.5 hours.

The electric furnaces are lined with silicate or phosphate based brickwork, but also alumina or silicate castable refractory masses or refractory concrete are in use. The gases and fumes from the electric furnaces are capture by adequate hooding systems and dedusted in bag houses. The dust is sold to secondary smelters for metal recovery.

Natural gas- or fuel-fired crucible, drum or hearth/reverberatory type furnaces are also applied in the different semi's operations. These types of furnaces are used for melting and fire-refining of copper and not for alloying. The furnaces are also operating batchwise. The material of a complete charge is added in portions during melting. Drum type furnaces in use have capacities of 5-20 t.

The fire-refining practice applied covers an oxidation phase to remove minor elements and an reduction phase to adjust the oxygen content in the metal. The oxidised copper is reduced by means of wood poles which are inserted into the molten bath and held in position by crane. The refined copper is tapped into ladles and transferred to holding furnaces for casting. The off-gases are collected in adequate gas handling systems and cleaned in baghouses. The dust and the slag formed during the refining process are shipped to third parties for treatment and metal recovery.

The refining furnace is bricklined with magnesite based bricks. The campaign of a furnace may have a lifetime of more than 2 years (e.g. up to 5 years) before it needs to be relined. Used brickwork bricks are separated into a contaminated part, which is shipped with the slag for recovery, and a less contaminated portion which can be used as building material on deposit sites.

For continuous operation and/or high production rates mostly shaft furnaces, like the ASARCO furnace, are selected. These furnaces are equipped in the lower (crucible) part with one to three rows of air/gas burners. The shaft furnace is charged from the top. The combustion gases, raising in the shaft, are pre-heating the charge which finally melts in the crucible area; the molten copper flows out through an open tapping slot.

The ASARCO furnace is a continuous smelting unit for copper and not suitable for refining or alloying. Therefore, the charge composition requires close control to maintain the metal quality. As fuel for the ASARCO furnace mostly natural gas is used. The combustion air may be enriched with oxygen to improve the melting capacity. Reducing conditions are maintained within the furnace in order to control the oxygen content in the metal at low levels. The melting rate of such units is between 5 and 25 t/h. The furnace is lined with silicon carbide refractory. The molten copper is normally transferred by ladle to the casting units. It will be either tapped directly into the ladles or to a holding furnace, where some alloying can take place.

Compared to other melting facilities, the ASARCO furnace is an energy saving process, since the combustion gases are utilised to pre-heat the charge. If the charge is contaminated by oil, an afterburning chamber is necessary for off-gas cleaning, since the organic compounds are thermally cracked and vaporised. One shaft furnaces is used for example at KME located in Osnabrück. Typical data of an ARSACO shaft furnace based plant are given in Table 3-52.

Table 3-52: Typical data of an ASARCO shaft furnace based plant

Shaft furnace	
Melting rate	20 to 25 t/h
Input	Cathodes, internal fabrication scrap
Mode of operation	Continuous melting
Fuel	Natural gas
Consumption	930 Nm³/h
Holding furnace	
Number	2
Capacity	80 t each
Heated by	Natural gas, 600 Nm³/h, each
Caster	
Type	Vertical, continuous
Mould	Indirectly water cooled mould
Production rate	20 t/h
Cooling water system	Closed cooling water circuit with cooling tower; solid separation by settling, de-watering by means of a mobile filter press; recirculation of the solids
Off-gas handling	
Volume	12,000 Nm³/h
Afterburning	Applied, 220 Nm³/h gas
Gas Cooling	Indirectly by pre-heating combustion air
Cleaning	Baghouse

Controlled handling of the off-gases from the furnaces is common practice in the casting shops. The gases are collected in specifically designed gas handling systems and cleaned in bagfilters which are combined with cyclones as a first dedusting step. The collected dust is recycled to other operations for pyro- or hydrometallurgical treatment and metal. Frequently the gas handling systems of shaft furnaces are equipped with an afterburning system for the elimination of hydrocarbons and for conversion of carbon monoxide in carbon dioxide. Then the off-gas handling system includes a heat recovery system before the off-gas is cleaned in bagfilters. For heat recovery combustion air pre-heaters or boilers are used.

Electric furnaces of the channel type are mainly used to melt larger charges. Coreless type induction furnaces are in application for alloy melting/casting or as casting furnaces in combination with separate melting units and casting machines. The metal produced and cast covers the full range of industrially applied copper alloys, low alloyed copper e.g. with silver or tin, and the different copper qualities, like oxygen-free, phosphorous desoxidised, ETP copper. Special alloys are CuNi, CuZnPb, CuNiZn, CuCoBe, and similar. During processing (melting, grinding) of these alloys special care is required to control fume and dust development. For the production of oxygen-free copper induction furnaces are used. The induction furnace is normally combined with a semi-continuous caster for billets or cakes.

Emissions during all melting operations can be reduced by removing as much of non-metallic material as practicable, e.g. centrifuging and thermal de-oiling of swarf in a rotary kiln. Techniques for thermal swarf handling are: Melting with slow feed and afterburning of the off-gases, de-oiling using indirectly heated dryers with separate afterburners holding the combustion gases at 850 °C for minimum 2 seconds.

3.5.2 Casting

Conventional casting processes

The conventional way for semi-finished product fabrication is via casting of billets and cakes/slabs which are then further processed. The most widely spread methods in use for production of shapes like cakes/slabs and billets at higher rates are discontinuous casting and continuous casting.

Discontinuous casting is carried out in the vertical mode. Continuous casting can be either in the vertical or horizontal mode. In most cases the casting unit is not directly fed from the melting furnace. Depending on the type of operation and the production rate, holding/casting furnaces and/or heated tundishes are installed in-between melting unit and caster.

The normal shapes produced are billets for the production of tubes, rods and section and cakes/slabs for the production of sheets and strips. The cast strand on vertical or horizontal casting units is cut using the flying saw technique.

In a discontinuous casting unit the format length is determined by the depth of the casting pit. After reaching the maximum format length, casting is interrupted and the cast shapes is extracted by crane or elevator. Then the moulds are prepared and the next casting cycle starts. All casting operations need direct cooling water for final solidification and cooling down of the cast strand down to temperatures allowing further handling. The cooling water normally is recycled after sedimentation and separation of particulates (casting scales). The scales are recirculated to a smelter for processing if not directly reused in the casting shop. Most of the equipment components are movable by hydraulic systems.

Special Processes

A special ASARCO casting process, using graphite casting dies, is occasional applied for direct casting of tubes, rods and sections from high alloyed copper. With this process, very narrow tolerances as close as possible to the final dimensions can be casted. Typical constituents in the copper alloys cast by this process are lead, tin, silicon and nickel.

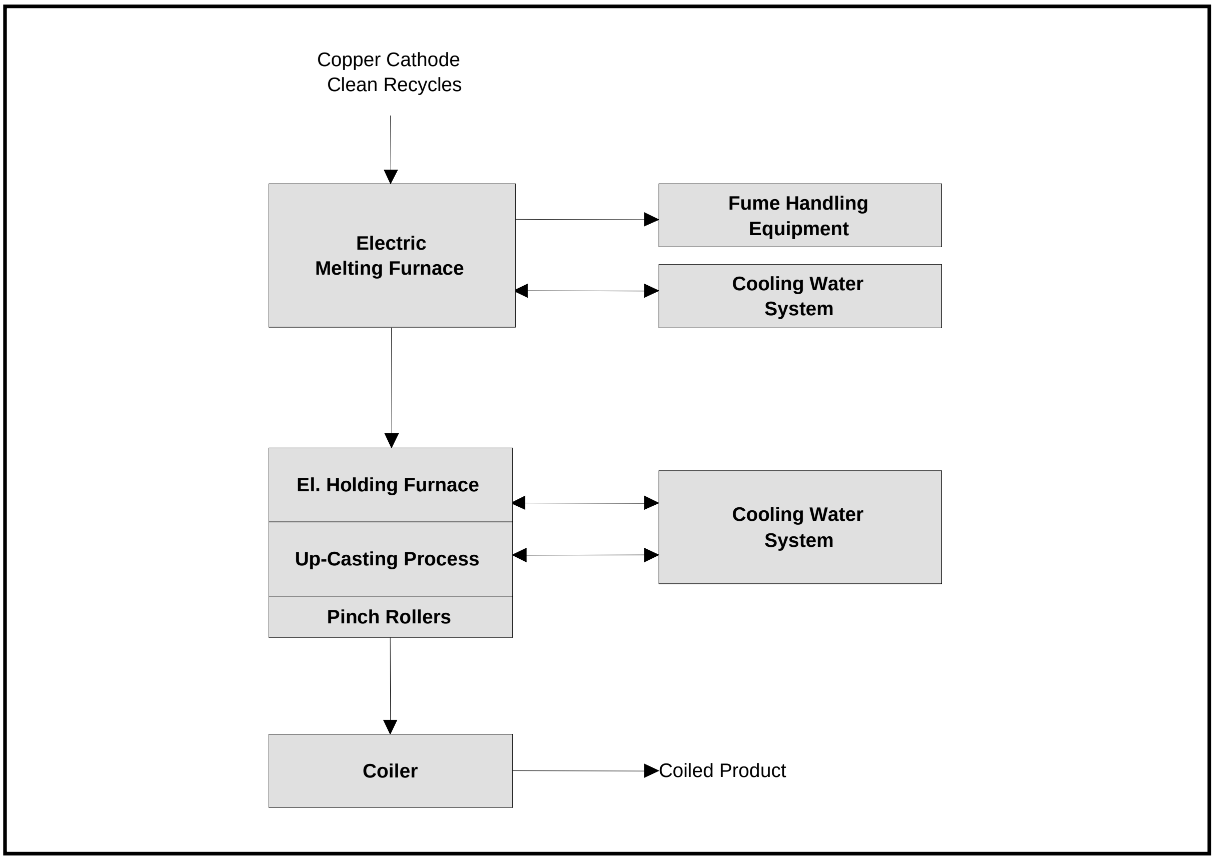

Figure 3-16: Simplified flow diagram of an upcast process

An upward casting method is used at Wieland-Werke AG for the fabrication of wires made from copper alloys. The diameter of the wires ranges from 16 up to 24 mm. The principle of the method is explained in Figure 3-16. After melting in an electric furnace, the liquid alloy is transferred to the holding furnace. The casting direction is vertically upwards. The metal is continuously drawn through a vertical die; the lower end of the die reaches into the melt, while the upper end is surrounded by a water-cooled jacket. The solidified wires are moved upwards through the pinch rolls of the withdrawal machine. The output of one cooler unit is limited by its cooling efficiency. As one single strand is not sufficient to meet capacity requirements, a multi-strand unit is in use.

3.5.3 Fabrication of Sheet and Strip

Cakes from the cast shop are in most cases the starting material for the fabrication of sheets and strips. The key elements of the fabrication process for flat products are the hot and subsequent cold rolling operations. In detail the fabrication process comprises the following steps, which are also illustrated in some detail in Figure 3-17.

- Pre-heating,
- hot rolling and milling,
- intermediate annealing,
- cold rolling,

- pickling, washing and drying,
- re-rolling and strand annealing,
- Finishing, and
- for sheets: Cutting to length,
- for strips: Cutting to width.

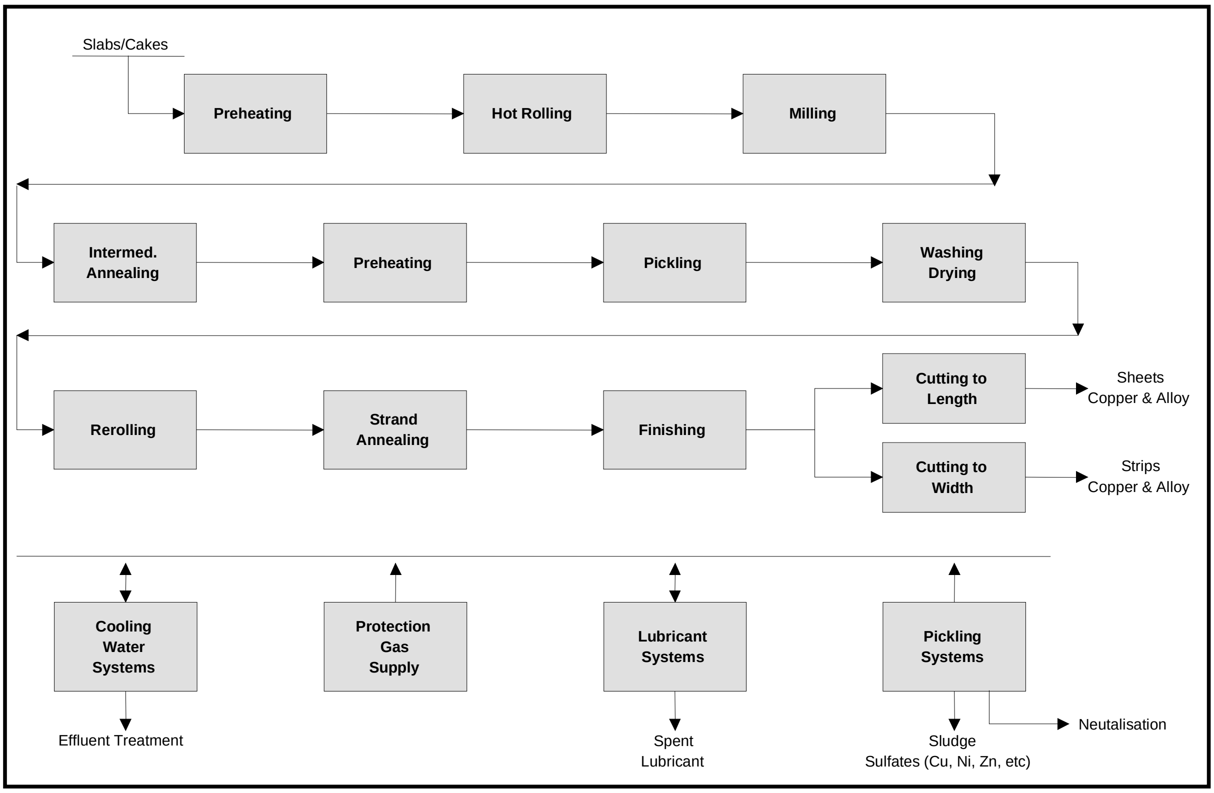

Figure 3-17: Fabrication of sheets and strips of copper and copper alloys

Normally the slabs/cakes are pre-heated prior to hot rolling in gas- or oil-fired furnaces. In some plants the off-gas is used for heat recovery.

The hot rolling is usually done with a dual rolling mill equipped with benches up to 200 m and a final coiling device. The width of the rolled product is up to 1,400 mm, the thickness of the slabs is reduced from approximately 250 mm down to approximately 10 mm. The cooling water for the rolls has small amounts of lubricant added for improving the attachment to the steel rolls. The vapour generated is vented and the vent gas is demisted prior to release to atmosphere.

The hot rolling of the cast slabs takes only a short time per slab and is determined by the slab weight. There is no loss of metal during hot rolling so slab and coils weight are identical. The hot rolling mill does not require protection gas. The noise development during rolling is controlled by protective measures. The surface and side milling units installed after hot rolling are equipped with ventilation and dust filtration systems. The loss of material is around 5 %, the chips are recycled for metal recovery. The surface milling requires protective measures against noise emissions.

Further cold rolling operations result in a hardened metal. In most cases the coil is annealed prior to cold rolling. Annealing is done under reducing conditions to avoid oxidation. As protection gas exogas or nitrogen/hydrogen mixtures are in use. Exogas is produced at site from natural gas in a special reactor which is indirectly fired. N_2 and H_2 are purchased and stored at site in special tanks. The N_2/H_2 protection gas mixtures are produced from the storage tanks by mixing the components in the ration required. For annealing before cold rolling usually bell type furnaces are used with electric heating or indirectly fired by natural gas or fuel oil. Tower type furnaces are applied for intermediate annealing of pre-rolled coils. They are heated by natural gas and are operated with protection gas. Strand annealing furnaces are in use for final and also for intermediate annealing. This method is a so-called touchless annealing process, surface oxidation is avoided by applying protection gas. In some cases, heat content of the off-gases is utilised to pre-heat combustion air or to generate steam. Prior to annealing the material will be degreased after the coiling by washing with water which contains detergents. The used solutions are cleaned by ultra-filtration.

After annealing the material is normally pickled in line in order to remove residual surface contaminants and oxides. For pickling purposes systems of sulphuric acid as well as mixtures from sulphuric and nitric acid are in use. The burden generated during usage of nitric acid is treated in a gas cleaning system (scrubbing with caustic soda). The pickling is done in continuous lines or in automatic processing, the acid is changed from time to time, the criteria is the pickling result. The spent acid is given to recovery. The pickling is vented for workers protection. Connected with the pickling bath a rinsing system is attached working with rotating brushes, water and at last with deionised water to get a clean and acid free surface. The rinsing water is given to the waste water treatment plant. Sludges are separated from the pickling media and disposed of or recycled. After washing the handling steps following are drying and coiling.

The sheet thickness is further reduced by stepwise cold rolling operations on different reversing mills. For cold rolling different types of mills called Duo, Quarto, Sexto, Sendzimir (12 rolls) are in use. Rolling mill designs as single-stand which are combined to an in-line multi-stand rolling mill are also applied. It depends on the thickness of the sheet on the coils and on the finishing status the coil has already been reached which combination of the different types is applied.

During cold rolling an emulsion or oil is used for roll protection. Therefore, the roll stands are vented and the ventilation gases are cleaned by mechanical filters, wet electrostatic precipitators or scrubbing. The emulsion and the oil is cleaned from metal and cracked oil particles by paper or textile band filters. Alternatively, the rolling mill coolant liquid is mixed with inert adsorbing agents and filtered. The duration of use for the original emulsion or oil may reach several years before it has to be replaced.

Also after cold rolling the surface of the rolled products is degreased by water containing washing agents. The washing solution is cleaned by ultra-filtration and reused. The oil separated from the washing water is given to authorised external companies for further treatment.

For strip fabrication special cutting units are available to cut the rolled and finished sheet coils into strips of the defined width. Table 3-53 compiles some typical data for the fabrication of brass strips by hot and cold rolling.

Table 3-53: Typical data of a facility to roll brass strips

Hot rolling	
Type of mill	Mainly Duo
Dimensions start	250 - 130 mm thickness, 450 - 1.000 mm width
Final dimensions	15 - 12 mm thickness, 450 - 1.000 mm width
Temperature	750 - 800 °C
Rolling force	Abt. 10 - 12 kN/mm sheet width
Surface milling	0,3 - 0,7 mm cutting of both surfaces
1st Cold rolling	
Type of mill	Mainly Quarto
Rolling force	Abt. 15 - 20 kN/mm sheet width
Dimension reduction and rolling speed	Reduction 15 mm to 4 mm thickness in multiple passes, speed 100-200 m/min
Conversion ratio	70 - 80 %
Annealing*) (recrystallisation)	
Temperature	550 - 600 °C
2nd and final rolling	
Type of mill	Mainly Quarto, alternatively, depending on sheet thickness, Sexto or stands with 20 rolls are used
Rolling force	Abt. 2 - 1o kN/mm sheet width, depending of type of mill used
Rolling speed	Reduction 4 to 1 mm: 300 - 500 m/min, multiple passes Reduction 1 to 0,1 mm: 500 - 1000 m/min, multiple passes
Cutting of sheets to strips	
Type of equipment	Longitudinal strip cutting machine

*) Annealing required after every conversion ratio of more than 70-80 %.
Annealing temperatures selected depending of material properties to be achieved.

The described concept for sheet and strip fabrication, based on hot and cold rolling corresponds to the conventional concept and is also suitable for high production rates. However, there are concepts industrially applied or under development for direct casting of sheets or strips followed by cold rolling. Such concepts bypass the hot rolling operation. One method is the horizontal casting used for copper alloy strip production. These concepts are also applied for rod and profile casting. Furthermore, different other systems have been proposed for continuous strip and sheet casting and some are under development.

3.5.4 Fabrication of Copper and Copper Alloy Tubes, Rods and Sections

The fabrication process lines can be subdivided into two product groups, with each product group following the same process steps. The groups are copper tubes in straight length and coils and copper alloy tubes as well as copper and copper alloy rod and sections. In both cases the start material for the fabrication process are copper and/or copper alloy billets. The production concept of copper tubes (c.f. Figure 3-18) is somewhat different from the production concept required for the fabrication of copper alloy tubes, rods and sections (c.f. Figure 3-19).

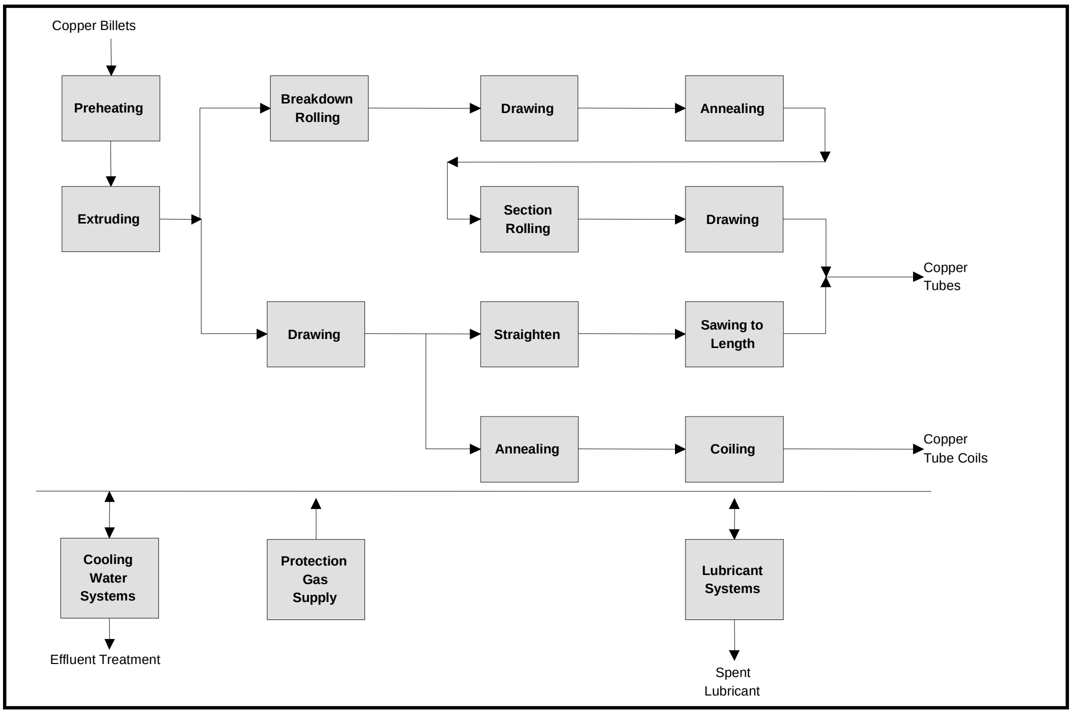

Figure 3-18: Fabrication of copper tubes

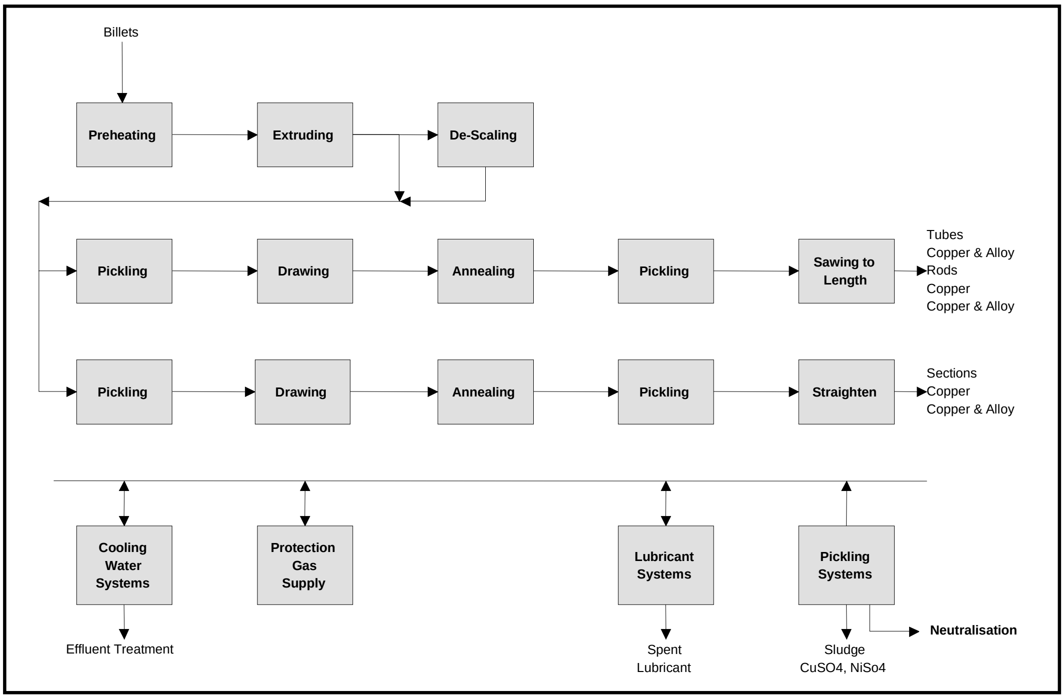

Figure 3-19: Fabrication of copper alloy tubes and rod/sections from copper and copper alloys

The billets in a first stage are electrically or indirectly pre-heated by gas-fired units. Starting from pre-heated billets, hydraulically operated extrusion presses are used for pressing unfinished tubes from copper and copper alloy as well as for the production of copper alloy rods and sections. For the fabrication of copper tubes different processes are industrially applied:

- Tube extrusion followed by multi-step drawing to size,
- tube extrusion followed by breakdown rolling followed by several steps of drawing to size, and
- hot piercing mill followed by breakdown rolling and drawing to size.

The process concept applied depends of the type of product to be fabricated. For billets, which are extruded or rolled to tubes with thick walls, breakdown rolling has normally the preference as first size reduction step. For tubes extruded to thin walls, tube drawing machines are applied. For the fabrication of copper alloy rods and sections material extruding in coils or straight length, cleaning and pickling, drawing to size using drawbenches or continuous drawing machines, heat treatment for certain alloys and straightening and sawing are normally the sequences of the fabrication process.

The whole process, started by the extrusion press or the hot piercing mill, is a sequence of (mostly) reducing steps changing shape and size. During these processing steps the tools of the equipment for size and shape changing are cooled and protected by adequate media, using emulsions for the breakdown rolling and lubricants for the drawing units. The emulsions for the breakdown rolling are cleaned up by filtration, thus increasing the life time and reducing the amount of lubricant to be disposed for treatment. However, the lubricants used for the drawing steps are completely lost with the product and no oily materials have to be rejected from the drawing processes.

Annealing may be required as intermediate operation during the stepwise size reduction process in order to enable the fabrication of the different finished products of copper and copper alloys. For annealing a reducing atmosphere has to be maintained exogas or N_2/H_2 mixtures using as protection gas. Exogas is produced in reactors at site, N_2/H_2 mixtures are generated by mixing of pure gases which are purchased and stored at site in special tanks. Annealing furnaces in use have inductive electrical or indirect gas-fired heating. Also pickling or degreasing operations may be required as finishing procedure for the products. As pickling solution, mainly sulphuric acid is used, for some special alloys mixtures of nitric and sulphuric acid are applied.

For degreasing the tubes after the final working down step chlorine/hydrocarbons or aliphatic hydrocarbons are in use. For some special products also alkaline solutions can be applied. Chlorine hydrocarbons require gas capture and cleaning. Special chemicals are in use to obtain special high standard surfaces of specific products. The chlorine/hydrocarbons containing vent gases from degreasing of the tubes after the final processing stage are treated in a reactor by passing through active carbon or resin. Loaded carbon is re-generated by treatment with steam, resin by treatment with hot air.

The fabrication scrap produced during the different size reduction steps is reused in the melting and casting shop. Cooling water is required for extrusion and for different other purposes. The cooling water for direct or indirect cooling is provided in once-trough systems or from circuits with re-cooling in cooling towers. Blowdowns are treated; solids as scale and oxides are separated and recycled.

3.5.5 Waste water treatment

The effluent treatment concepts in use are depending of the type and range of contamination of the waste water. In general oil separation is applied prior to discharge.. Process water like rinse water from pickling, laboratory effluent waters, waters from polishing operations and used galvanic waters from tool preparation are treated by chemical and physical operations in a waste water treatment plant (neutralisation with lime and optional ironsulphate; additional reduction of metals with sandfilter and ion exchanger). The arising sludges are de-watered on filter presses or similar. The surface water is collected and solids and oil are removed in a settler prior to discharge. Indirect cooling waters are not contaminated by metals, the blowdown from the cooling towers are discharged to the sewer. If direct cooling is applied with a closed system, the cooling water is completely recycled and only treatment sludge occurs. If direct cooling water passes through after treatment without reuse or only partly reuse, waste water as well as treatment sludge occur.

3.5.6 Summarised data on outputs and environmental concerns of the fabrication of semi-finished products

Emissions into the air

Table 3-54 shows stack emissions into the air from the fabrication of semi-finished products (annual average concentration).

Table 3-54: Emissions from the fabrication of semi-finished products (annual average concentration)

Process unit		**Particulate matter** [mg/m^3]	**CO** [mg/m^3]	**TOC** [mg/m^3]
Melt shop:	Electric furnace	< 10	-	< 20
	Rotary furnace	< 10	-	< 50
	Shaft furnace (ASARCO type)	< 10	< 100*)	< 20
Rolling mill:		-	-	< 50
Milling:		< 10	-	-

*) With afterburner (afterburning depending on type of feed (oil/organic content))

Source: Emission values which are accessible to the authority

The annual average concentrations represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions (charging, blowing, pouring, poling etc.), different input materials and changes in the operating mode.

In Table 3-55 specific emissions from the fabrication of semi-finished products are given. They include the emissions from all cleaned off-gases captured by hoods and from cleaned ventilation gases (arising from venting the shed). Fugitive emissions are not included.

Table 3-55: Specific emissions from the fabrication of semi-finished products (annual average loads)

		Particulate matter [g/t]	**CO** [g/t]	**TOC** [g/t]	**Oil mist** [g/t]	**PCDD/PCDF** [µg/t TE]***)
Melt shop:	Electric furnace	< 70	-	< 80	-	< 5
	Rotary furnace	< 50	-	< 11	-	< 10
	Shaft furnace (ASARCO Type) without afterburner*) with afterburner*)	< 12	 < 10,000 < 45	-	-	< 10
Rolling mill:		-		< 100	< 30**)	
Milling:		< 20				

*) Afterburning depending on type of feed (oil/organic content)

**) Usually included in value for TOC

***) Values according to Krüger [45]

In Table 3-56 the main constituents in the dust content of all furnace off-gases cleaned in fabric filters are given.

Table 3-56: Main constituents in the dust content of off-gas cleaned in a fabric filter

Substance	Unit	Measured value			Authorised value
		Electric Furnace	**Rotary Furnace**	**Shaft furnace**	
Class I (TA Luft)					
Cd	mg/m^3	< 0.006	< 0.1	< 0.1	
Hg	mg/m^3				
>Tl	mg/m^3				
Sum Class I (TA Luft)	**mg/m^3**	**< 0.2**	**< 0.2**	**< 0.2**	**0.2**
Class II (TA Luft)					
As	mg/m^3	< 0.025	< 0.005	< 0.005	
Ni	mg/m^3	< 0.003	< 0.003	< 0.003	
Co	mg/m^3				
Se	mg/m^3				
Te	mg/m^3				
Sum Class II (TA Luft)	**mg/m^3**	**< 1**	**< 1**	**< 1**	**1**
Class III (TA Luft)					
Sb	mg/m^3				
Pb	mg/m^3	< 0.1	< 0.05	< 0.05	
Cr	mg/m^3	< 0.007			
Cu	mg/m^3	< 0.5	< 0.6	< 0.6	
Sn + Mn	mg/m^3	< 0.05			
Sum Class III (TA Luft)	**mg/m^3**	**< 5**	**< 5**	**< 5**	**5**

Source: Emission values which are accessible to the authority

If substances of several classes are present, the mass concentration in the emitted gas should not exceed a total of 1 mg/m^3 for coinciding class I and II substances as well as a total of 5 mg/m^3 for coinciding class I and III or class II and III substances. The emissions of substances class I - III have to be determined as a sum of the particulate matter, the vapour and the gas share of the respective element and its compounds (according to TA Luft [1]). More information about the German regulations can be found in section 6.1.2.

The measured values represent the typical range. However, the results of single measurements can be higher than the given range and reach the authorised values depending on different operation conditions (charging, blowing, pouring, poling etc.), different input materials and changes in the operating mode.

The specific emission values (annual average) of substances in the dust content of off-gases cleaned in a fabric filter are given in Table 3-57.

Table 3-57: Specific emissions of the main constituents in the dust content of the off-gas cleaned in a fabric filter (annual average loads)

Substance	Unit	Value (calculated)		
		Electric furnace	Rotary furnace	Shaft furnace
Cd	g/t	0.05	0.5	0.2
As	g/t	0.2	0.03	0.01
Ni	g/t	0.03	0.02	0.005
Pb	g/t	1	0.3	0.1
Cr	g/t	0.05	-	-
Cu	g/t	3.5	3	1
Sn - Mn	g/t	0.4	-	-

Waste water

In Table 3-58 data on the concentration of contaminants in the waste water (process, cooling and surface water) from the fabrication of semi-finished products is given (annual average).

Table 3-58: Pollutants in the different waste water streams from the fabrication of semi-finished products (annual average)

Item	Units	Value
pH	Units pH	6.5 – 9.5
Copper	mg/l	< 0.5
Cadmium	mg/l	< 0.2
Lead	mg/l	< 0.5
Mercury	mg/l	< 0.05
Nickel	mg/l	< 0.5
Tin	mg/l	< 2
Chromium total	mg/l	< 0.5
Arsenic (As)	mg/l	< 0.3
Zinc	mg/l	< 2
Suspended solids	mg/l	< 100
COD[*)] (COD : TOC = 4 : 1)	mg/l	< 100

[*)] COD only for discharge into waters, for discharge to sewer no limits are required

In Table 3-59 the amount of contaminants discharged per year with the process water of a plant are given as an example. A volume of 35,000 m^3/a process water are discharged at this plant. The values are real figures and not calculated on the basis of statutory limits.

Table 3-59: Contaminants discharged per year with the process water of a semis fabrication plant (example)

Substance	Unit	Value
Cu	kg/a	11
Ni	kg/a	3
Zn	kg/a	25
Pb	kg/a	1
Cr	kg/a	1
As	kg/a	0.01
Cd	kg/a	0.01
Hg	kg/a	0.01
Sn	kg/a	1

In the amount of solids and oil in the surface water of the hardened water-proof storage place are given as an example. At this plant, 60,000 m^3 of surface water are discharged per year.

Table 3-60: Solids and oil discharged per year with the surface water of a semis fabrication plant (example)

Substance	Unit	Value
Cu (solid)	kg/a	< 6
HC (Hydrocarbon)	kg/a	< 10

Main residues

In Table 3-61 an overview of the main residues is given.

Table 3-61: Main residues from the fabrication of semi-finished products

Process unit	Residue	Use/treatment option
Melting/casting shop	Dust	Recycled to smelter for metal recovery.
	Refractory	Partly used for construction, balance dumped.
	Slag	Recycled to smelter for metal recovery.
	Scale	Recycled to smelter for metal recovery or internal use.
Hot rolling mill	Scale	Recycled to smelter for metal recovery.
	Milling chips	Internal recycle.
	Used emulsion/oil	Given to authorised companies for treatment.
Cold rolling mill	Used emulsion/oil	Given to authorised companies for treatment.
Pickling	Sludge	Recycled for metal recovery.
De-greasing	Sludge (CHC containing)	Given to authorised companies for treatment.
	Used detergents	Given to authorised companies for treatment.
	Used oil	Given to authorised companies for treatment.
Direct cooling water treatment	Sludge	Discarded
General	Used packing materials	Given to authorised companies for treatment.

4 German candidate best available techniques (BAT) for integrated pollution prevention and control in the copper production

In this chapter, German *best available techniques* (BAT) will be described that serve as possible candidates for the later determination of best available techniques on an EU level. For the identification of the German BAT, the IPPC-Directive, that is to say the definition of BAT in Art. 2.11 IPPC-D, serves as a basis:

"Best available techniques should mean the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole: Techniques should include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned, available techniques should mean those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator. Best should mean most-effective in achieving a high general level of protection of the environment as a whole." According to the IPPC-Directive, in the identification of BAT special consideration should be given to the following items listed in Annex IV:

- "the use of low-waste technology",
- "the use of less hazardous substances",
- "the furthering of recovery and recycling of substances generated and used in the process and of waste, where appropriate",
- "comparable processes, facilities or methods of operation which have been tried with success on an industrial scale",
- "the nature, effects and volume of the emissions concerned",
- "the commissioning dates for new or existing installations",
- "the consumption and nature of raw materials (including water) used in the process and their energy efficiency",
- "the need to prevent or reduce to a minimum the overall impact of the emissions on the environment and the risk to it", and
- "the need to prevent accidents and to minimise the consequences for the environment".

On basis of the processes used in the German copper production industry described in chapter 3, proposed emission guide values for BAT are given in this chapter. These values can be reached with the process units in combination with abatement techniques. Since this paper deals only with German techniques, only German BAT are described which work within the proposed emission guide values. They should be seen as one possible combination of process unit and abatement technique, other combinations of process and abatement techniques in operation within Europe are not excluded.

4.1 General provisions and requirements for the prevention and control of environmental pollution

In the following sections the monitoring of emissions and general measures, which can be applied to prevent and control emissions into the air as well as discharges of waste water and to prevent the formation of solid wastes are presented. In addition measures and general rules for other areas of environmental concerns as noise, plant safety and energy aspects are described. Only a short overview will be given; detailed technical information can be found elsewhere e.g. in [56], [88].

4.1.1 Monitoring of emissions

The following section is intended to ensure that emissions are measured in such a way that the results are representative, mutually comparable and clearly describe the relevant operating state of the plant.

Measurement Planning

The objective and scope of measurements are governed by the requirements in the approval decision or by particular events. In principle, the measurements serve to determine substances in the clean gas. Measurement planning should take account of the mode of operation and the operating state of off-gas purification plants, operating conditions in the plant (continuous, discontinuous, start-up and shut-down operations, load change) and the effect of thermodynamic interference factors. These data form the basis for determining the selection of operating conditions at which the highest emissions will presumably be recorded, the number and duration of the measurements, the method of measurement to be chosen, and the position of the measurement locations and points.

In the case of continuous and batchwise operation, a sample collection time or measurement time of half an hour (half-hour mean value) is, as a rule, necessary. If dust contents are low or if PCDD/PCDF are to be determined, other measurement times and, consequently, other reference times may be necessary because of the limitation of detection. In particular cases, for example batch operation, the measurement time and, consequently, the averaging time should be appropriately modified. For continuous operation and only slight fluctuations in the emission characteristics, at least 3 individual measurements should be performed at the highest emission level. If it is anticipated that the emission level will be very variable during continuous operation, at least 6 measurements should be carried out, the sampling and averaging time being limited to the emission phase.

Sampling Locations

The sampling points should meet the requirements of Guidelines VDI 2066 Part 1 [77]and VDI 2448 Part 1 [80]. According to the latter, the sampling points

- should be clearly marked,
- should have, if possible, have a disturbance-free flow in the measurement section,
- should have measurement openings that can be closed,
- should have the required energy supplies,
- should have sufficiently large working platforms, and
- should ensure that the requirements for safety at work are met.

Measured Variables, Methods of Measurement and Instruments

Measurements of the components specified in Table 4-1, where the VDI guideline is quoted in which the methods of measuring the components are described, should be carried out to characterise the emission behaviour of a plant, where the off-gas is removed via a known outlet:

Table 4-1: VDI guidlines on emission measurements

Component	VDI Guideline or DIN Standard
Total dust	VDI 2066 [77]
Dust constituents Cd, Cr, Cu, Pb, Zn	VDI 2066 [77] VDI 2268 [81]
As	VDI 2066 [77] VDI 2268 [81]
Total organic carbon	VDI 3481 [78]
Sulphur dioxide	VDI 2462 [79]
PCDD/PCDF	DIN EN 1948 [21], [76]

The parameters sulphur oxides (mass flow > 50 kg/h) and total dust (mass flow > 2 kg/h) should be continuously observed using an approved measurement apparatus, the suitability of which has been tested and, as a rule, evaluated using an emission evaluation computer.

The reference quantities necessary for evaluating and assessing the continuous measurement should also be continuously observed. The continuous measurement of these parameters may be dispensed with, if experience shows they are subject to only small fluctuations. The instruments should be calibrated after installation of a measurement location and then every 5 years, and should be checked once a year for serviceability.

Reference Quantities

To convert the emission concentrations obtained to standard conditions (p_o = 1013 hPa, T_o = 273 K, $p(H_2O)$ = 0 hPa), the volumetric off-gas flow (in order to calculate the emission mass flow), the off-gas temperature, the water vapour content of the off-gas, the static pressure in the off-gas duct and the atmospheric pressure should be determined as off-gas parameters.

Measurement Result Evaluation and Measurement Report

All the emission measurement results should be reported as masses, in mg/m^3 or, for PCDD/PCDF, in ng/m^3 (ITE), of the emitted components, relative to the volume of the off-gas in the standard state after subtracting the water vapour content. From the measured values of instantaneous samples for gaseous components, the measurement result should be determined as a half-hour mean value or as a computed half-hour mean value. From the measured values of individual measurements of particulate emissions, the measurement result should be reported as a half-hour mean value or, if the sampling time is longer, as a mean value for the sampling time.

Continuously determined measurements should be evaluated as follows:
From the measured values, the half-hourly mean value should always be determined for each consecutive half hour. The half-hourly mean values should, if necessary, be converted to the respective reference quantities, assigned to at least 20 class intervals and stored as a frequency distribution. A daily mean value for the daily operating time should be calculated from the half-hourly mean values for each day of the year. The emission limits are deemed to be met if none of the daily mean values do not exceed the specified concentration by mass, 97% of all the half-hour mean values exceed 6/5 of the specified concentration by mass and none of the half-hour mean values exceed twice the specified concentration by mass. Any measurement report and measurement protocol drawn up should conform to Guideline VDI 2066 Part 1 [77] and should in particular contain:

- the objective,
- general information on the measurements,
- a description of the plant, its state and operating data,
- operating conditions during the measurement,
- information on the measurement planning,
- sampling locations,
- methods of measurement,
- tabular presentation of the individual measurements,
- evaluation of the results,
- consideration of errors,
- presentation of the quality assurance measures, and
- an abstract.

Determination of specific emission values

If emissions are stated as specific emissions, it should be defined properly which emission sources (stack emissions/fugitive emissions) are included. Often only stack emissions are base of the calculation of specific emissions. This is not sufficient, since nowadays the stack emissions of copper smelting plants are cleaned so efficient that the total released emissions in Germany are determined mainly by fugitive emissions. If the calculation of specific emissions are only based on stack emissions, all measures to minimise fugitive emissions by capturing and cleaning them result in an increase of the specific emissions although the total emissions released are reduced.

4.1.2 Techniques to prevent and control emissions into the atmosphere

In chapter 2 general information on the main emissions into the air from copper production plants is given, whilst in chapter 3 detailed information is provided. In this section, general measures and techniques to minimise emissions as well as end of pipe measures to reduce the content of pollutants in off-gases from the copper production industry are summarised. Since process integrated measures, that prevent the formation of contaminants during the production process, are mainly process specific, they are dealt with in section 4.2.

The emissions are subdivided into stack and fugitive emissions. Stack emissions are captured emissions, which can usually be treated with appropriate gas cleaning devices. Sources for fugitive emissions are roofs and openings of production buildings as well as inadequate enclosed transport system and leakages. They also can arise during open handling and storing of materials.

4.1.2.1 Measures to prevent fugitive emissions

The contribution of fugitive emissions to the total emissions from a process site can be very significant and, if appropriate cleaning of the captured gases is applied, in most cases exceed the stack emissions. Several general measures are used to prevent fugitive emissions from storage, handling and transfer operations of dusty materials, from production processes (mainly furnaces) and from recycling operations. It should be mentioned, that, as a rule, these measures are wide-spread, although their realisation depends strongly on the site-specific constraints.

Storage, handling and transfer operations of dusty materials

During storing, handling and transport of materials consisting of fine particles such as ore concentrates, drosses and filter dusts, emissions of particulate matter can occur. When these dusty materials are stored, the following measures can help to reduce fugitive emissions:

- roofing and complete side coverage for the storage of bulk goods including secondary facilities,

- capturing of exhaust air and adequate cleaning (c.f. 4.1.2.2),
- storage in closed containers (protection against wind-blown emissions),
- coverage of the surface, e.g. with mats,
- planting,
- establishing overgrown earth embankment, windbreak plantings or windbreak hedges, and
- continual maintenance of a sufficient moisture level on the surface, i.e. with sprinkler devices.

For the handling of dusty materials, the following measures can be applied to reduce fugitive emissions:

- installation of exhausters and dedusters at main emission relevant parts, i.e. stationary reception, transfer and discharge points of dried ore concentrates, shovel loaders and transport units, downspout of loading facilities,
- complete enclosure of the machinery, equipment and other facilities used for the treatment or production of dusty goods, and
- dusts can be received wetted and/or in sealed containers or in enclosed vehicles.

When dusty materials are transported, fugitive emissions can be reduced by the following measures:

- usage of adequate transport facilities, like covered conveyor belts or closed recycling systems for filter dusts) and collection of remaining dust containing air,
- usage of underfed conveyors,
- reduction of vehicle contact with the stockpile,
- roads should be well constructed, well maintained, kerbed, cambered and equipped with drains to obtain a maximum run-off and collection of water,
- regular cleaning of access roads with cleaning machines,
- keeping roads wet and cleaning when appropriate,
- reducing speed for vehicles at the plant site,
- careful on-site traffic management (e.g. minimisation of number of private vehicles passing, restriction of vehicles to designated functions and areas), and
- careful cleaning of vehicles, especially their wheels, before leaving the concentrate storage buildings.

Operation of production and recycling units

To prevent fugitive emissions during operation of production and recycling units, devices for the extraction of process gases should be installed at emission sources such as furnaces, launders, melting pots, crushers for recycling material, etc. The extraction volumes of these devices should be sufficient to cope with abnormal operation conditions and overloads. The captured off-gases have to be cleaned adequately(c.f. 4.1.2.2). Encapsulating measures can include:

- lock chambers on charging systems,
- close hooding at tapping points,
- housing for ladles during tapping,
- enclosure of hot metal material handling, and
- arrestment devices for crushers.

To prevent emissions of particulate matter in the working area, high capacity vacuum cleaning systems should be used.

4.1.2.2 Measures to prevent and control stack emissions

In order to control stack emissions, measures to clean the gas streams before being released should be applied. Depending on their physical state, contaminants contained in the gas streams can be classified in two groups:

- gases and vapours, and
- particulate matter.

For their removal from the gas streams (raw gas, exhaust air, process gas), different gas cleaning devices are available as shown in the examples in Table 4-2. Normally dry off-gas cleaning is applied. Only when gaseous compounds or vapours such as e.g. mercury vapour have to be precipitated, a wet gas cleaning may be necessary.

Table 4-2: Selection of gas cleaning devices

Removal of ...	Gas cleaning device	Remark / example	Reference
Particulate matter	Settling chambers		
	Cyclones	Used as pre-precipitator device	VDI 3676
	Electrostatic precipitators - Dry - Wet	- Dedusting of SO_2-containing off-gases (dry/wet ESP) - off-gas from slag granulation (wet ESP)	VDI 3678
	Scrubber (Venturi)	Usage of water requires - water treatment - corrosion control	VDI 3679
	Fabric filter	- selection of adequate filter materials (elevated temperatures)	VDI 3677
Gaseous contaminants and vapours	Absorption into a liquid using packed, plate or spray towers	Boliden/Norzink process for removal of mercury	VDI 3675
	Adsorption on a solid in a fixed bed	Lead sulphide process for removal of mercury	VDI 3674
	Chemical conversion using catalytic reactors		VDI 3476

When choosing a gas cleaning device, the following criteria have to be considered in each specific case:

- process and operation characteristics,
- raw gas characteristic: temperature, humidity, composition, flow, etc.,
- dust characteristic: mass flow, grain size distribution, etc.,
- space requirements,
- separation efficiency, clean dust content, and
- operation safety, capital expenditure and operation costs.

As an example, different gas cleaning techniques to remove certain gaseous contaminants and vapours are shown in Table 4-3. Sulphuric acid plants are used in the copper production industry with the primary function to remove sulphur dioxide from the off-gas.

Table 4-3: Techniques to remove gaseous contaminants

Substance to remove	Process	Remarks
Sulphur dioxide	Recovery of sulphuric acid in - Single contact plant - **Double contact plant**[1)] - Wet catalysis - Processes based on NOx	- minimum concentration of SO_2 necessary - steady off-gas conditions necessary
	Recovery as liquid sulphur dioxides by - Condensation processes - Absorption processes	
	Recovery as elemental sulphur	
	Dry sorption of SO_2 by calcium oxide	- SO_2 concentration too low for contact acid plant - unsteady conditions
Mercury vapour	Wet absorption processes: - Selenium filter - **Boliden/Norzink**[1)] - Outokumpu process - Sodium thiocynate process	- subsequent sulphuric acid recovery Scrubbing with H_2SO_4
	Dry adsorption processes - Activated carbon filter - Lead sulphide process	
Carbon monoxide	**Afterburning chamber**[1)]	

[1)]: These techniques are applied in the German copper production industry.

4.1.3 Water management

In chapter 2 general information on the main water discharges and their contaminants from copper production plants is given, whilst chapter 3 provides detailed information. In this section, general measures and techniques to prevent uncontrolled discharges, different cooling water concepts, as well as end-of pipe treatment techniques to reduce the content of pollutants in the effluent are summarised.

In general, measures in order to prevent accidents (c.f. 4.1.7) and devices to avoid uncontrolled discharges due to leakages or accidents are necessary. These devices should include facilities to contain process waters, site drainage waters, emergency fire water and chemically contaminated waters. Bunding of storage tanks or double walls for tanks are essential in many cases, where there is a risk to controlled waters, sewers and drains, and on-site effluent treatment plants. Shared bunds are possible in cases where the materials stored are not incompatible. Bund capacities should always have sufficient volume for the maximum storage. High level alarms and trip switches on storage tanks should be designed to an appropriate integrity. These devices as well as the bunds should be inspected on a regular basis, especially where corrosive substances are involved.

The main liquid effluents arising in the copper production industry are from cooling water for cooling furnaces and sulphuric acid plants, slag granulation and surface run-off. An additional source of waste water are wet gas cleaning operations. So, to minimise the amount of waste waters, this kind of gas cleaning should only be carried out if it is not possible to clean the gas sufficiently with dry gas cleaning devices.

Cooling water concepts

The waste water situation in copper production plants is strongly determined by site specific conditions [75]. The main location dependent factor is the availability of water, especially for cooling purposes. If the smelting plant is situated alongside a river containing sufficient water, the cooling of furnaces, runners, burners etc. is carried out in temperature-controlled, open recirculating systems without re-cooling (once-through cooling). The heat is removed by heating the cooling water. If water resources are in short supply, cooling is carried out in a closed recirculating system, with recooling by means of cooling towers. The latter are operated, as a rule, as spray towers and the heat is removed by evaporating the water. Cooling water used in closed recirculating systems must, as a rule, be conditioned to prevent the growth of algae, corrosion etc. In addition, elutriation of the recirculation water is necessary in order to keep the salination within limits. The elutriation water contains agents and increased concentrations of substances introduced into the recirculatory cooling system with the make-up water.

Purification of indirect cooling water, i.e. cooling water not polluted by the product, in an open recirculatory cooling system is not necessary. Polluted cooling water from the elutriation of the recirculating systems or from casting plants may need treatment. The slag granulation water is always recirculated without a conditioning agent and elutriation is often not necessary.

End-of-pipe treatment of waste water

Contaminated water generated by the copper production industry is usually characterised by the presence of elevated metal concentrations (for example lead, copper, tin, zinc, cadmium, mercury, and nickel), elevated elements like arsenic as well as suspended solids. So the end-of-pipe treatment techniques used in this industry are applied in order to minimise the concentration of these pollutants in final effluent discharges to the aquatic environment. Depending on the site specific conditions, the plant can be connected to an urban waste water system where the end-of-pipe treatment is applied or the treatment is carried out in a central waste water treatment plant at the plant site. Because of different pollutant loads, the effectiveness of the end-of-pipe treatment can be improved by separating cooling water, surface runoff water from roofs and roadways and stockyard as well as process water.

If the treatment is carried out at the plant site, the waste water from the different production plants is usually brought together in a collecting tank. If necessary, surface water is collected in a separate tank and is then usually supplied to the collecting tank to guarantee a more constant flow. Only a few companies treat their surface water in an extra facility. The tank for the surface water has to be dimensioned to handle worst-case rainfalls. In the collecting tank, oil, grease and plastics are removed mechanically. The subsequent treatment is based on chemical precipitation and neutralisation, sedimentation and filtration or centrifugation. Devices for this treatment are described in Table 4-4 [24].

Table 4-4: Devices for waste water treatment

Process step	**Principle**	**Device**	**Remark**
Precipitation and neutralisation	**Chemical precipitation**: forming of insoluble compounds by addition of precipitants, adjustment of pH	Precipitation reactor, tanks	To remove heavy metals, hydroxides and afterwards sulphides are used as precipitants; ferric sulphate is used to eliminate the surplus sulphide
Solids separation	**Sedimentation**: Settling due to gravity, often use of additional flocculants	Clarifier, two compartment tank	Coagulants: polymers
Polishing step	**Filtration**	Gravity filter with a sand bed	
Precipitate dewatering	**Filtration, centrifugation**	Belt filter, vacuum filter (rotary drum filter), filter press, cyclone	Dewatered sludge is recycled to the metal production process or dumped

Especially where large discharges of effluent with high or low pH are possible, consideration should be given to a two or three stage pH control system. Dosing systems are unable to cope with effluent with extreme pH; therefore, an intermediate facility capable of storing acidic or alkaline effluent should be installed with an automatic control, if such effluents are likely.

In selecting an appropriate separation technique, consideration should be given to such factors as:

- current industry practice for the same or similar waste waters,
- ability to produce an effluent with the desired characteristics,
- characteristics of the concentrated solids that are produced,
- mechanical simplicity,
- reliability of equipment operation,
- controllability of the process,
- space requirements, and
- investment and operating costs.

4.1.4 Management of by-products and wastes

In chapter 2 general information on solid material arising from the production of copper in the different process units are given and in chapter 3 detailed information is provided. In this section, the treatment options for solid materials to minimise the amount of wastes are summarised.

In copper production, only small amounts of waste material arise compared to the throughput of raw materials because it has traditionally been the objective of the processing technology to produce as many constituents as possible in a marketable form and thereby to close the material cycle. This may be done within one company or in co-operation with other companies. The various chemical and physical properties of the substances are used to extract the individual constituents. These are, for example:

- distribution of substances between the molten and gas phase: in copper metallurgy, zinc, lead, tin, cadmium, arsenic and their compounds, in particular, are volatilized, discharged from the production process with the off-gas and collected in gas cleaning plants in the form of flue dusts and extracted from the latter,
- different distribution coefficients of molten materials in non-miscible molten phases (for example, matte and slag),
- non-miscibility and insolubility of solid phases in liquid phases: separation of solid substances from melts (for example, liquations, dross, skimmings) or from aqueous solutions (sludges, precipitations).

In this way, even traces of substances in the raw materials can be obtained in a marketable form.

In primary production, the copper concentrate contains mainly copper, iron and sulphur. Silica is added as a flux. Consequently, besides copper, iron silicate slag and sulphuric acid are produced in quantities, which are even higher than the copper production. Sulphuric acid is widely used e.g. in the chemical industry. The iron silicate slag is either granulated or produced in the form of lumps, which may be crushed and screened according to the customer demand. Granulated iron silicate is used as a quartz-free blasting agent or as a construction material (as a substitute for special sand qualities). Iron silicate lumps are used for various construction purposes, e.g. embankment construction of waterways, breakwaters, dams as well as for road construction. In any case, slag production is carried out with regard to common product standards, such as DIN EN ISO 11 126 Part 3 and VBG 48 for blasting materials as well as [83] and different technical guidelines for construction materials. The same goes for iron silica slag from secondary production, which has a similar chemical and mineral composition and which can be used in the same fields of application.

Other by-products from primary and secondary copper production are noble metals, lead, tin i.e. tin lead alloy, zinc oxide, nickel sulphate, selenium and other metals or metal compounds.

Metal wastes arise only if the demand is not sufficient, which is the case with arsenic. This is why a surplus of arsenic compounds are safely disposed of in underground disposal sites. Other wastes which cannot be avoided are sludges from the waste water treatment plants or from the cooling water treatment, sweepings from paved areas and plants, used operation materials such as filter materials, conveyor belts, pallet wood, paper, oils, emulsions, ion exchangers from the boiler feed-water treatment, packaging materials, insulating materials, furnace linings etc. If possible, those wastes should be used in recovery operations. Typically sludges from the waste water treatment plant, sweepings from paved areas and plants, filter materials and insulating materials are recirculated to the smelter. According to the European guideline 75/442/EEC, recovery operations are

- Use as a fuel (other than in direct incineration) or other means to generate energy,
- Solvent reclamation / regeneration,
- Recycling / reclamation of organic substances which are not used as solvents, and
- Recycling / reclamation of metals and metal compounds, etc.

This means wastes can be utilised in a material manner or can be used for the generation of energy. Priority should be given to this kind of utilisation with less environmental impact. Only if recovery is not possible according to the rules and without causing damage, wastes should be disposed of. This should be done in an approved manner in adequate facilities at the production site or at the nearest available site and it should be specified how the accumulation and storage of waste has to be controlled.

4.1.5 Energy aspects

In general, the optimal solution in terms of energy management depends on the specific conditions existing at the site. An appropriate way of finding this solution is to draw up an energy utilisation concept which combines technical and economic objectives and eliminates information deficits. This general concept specifies economically feasible measures to be taken to optimise energy use and is structured as follows:

1. Overview of the plants operated at the site and of their energy demand in terms of fuel and power demand.
2. Information on energy use inside the plants prior to site-specific optimisation, particularly
   - types and amounts of energy supplied to and removed from the plant, the most important reactions and their enthalpies including main parameters,
   - description of the plant; energy balance, flow charts.
3. Description of energy use inside the plant after its energetic optimisation (as under 2. above), including description of envisaged measures.

In the copper production industry, several measures are applied in order to minimise energy consumption or to recover the waste heat that is produced. To minimise the energy consumption of the processes, the fuel value of the feed material is used to decrease the amount of energy needed. Hot charging of intermediate products where possible or continuously working plants minimise the additional energy supply, since the material has not to be remelted in every process step. The surplus reaction heat can be used as a substitute for fossil fuel or to melt additional scrap or internal reverts.

The utilisation of waste heat has a long tradition for some types of furnaces, but in some cases it is difficult, with the result that no effective solutions exist today for various subregions. In general the devices for using the waste heat are designed in order to maintain plant availability, so they are not optimised with regard to maximising the energy efficiency.

In the case of fire-top blast furnaces or those with off-gas afterburning and also in the case of anode reverberatory furnaces, the off-gas temperatures are between 1,000 °C and 1,200 °C, so the heat in the off-gas can be used to generate steam in waste-heat boilers. In the Contimelt plant an integrated concept for the utilisation of heat has been implemented to save fuel and also to generate steam. The steam generated is generally used in-house, e.g. for heating the electrolyte, for providing hot water in the washroom and for heating the building.

4.1.6 Noise aspects/abatement techniques

In the planning and operation of installations, all *technical*, *structural*, *organisational* and *planning-related* measures must already be taken into account during the planning phase, in a manner appropriate to the respective local operating situation and in consultation with acoustic experts. Acoustic experts should be consulted throughout construction and their advice should be taken into particular account. Use should primarily be made of technical and planning-related noise prevention measures. In general the following measures have to be considered:

Technical measures

- Obtaining information at an early stage about noise emissions of machinery, installations and parts thereof, and of work and production processes,
- use of low-noise machines and processes,
- reduction of noise generation and transmission,
- reduction of sound emission of, e.g. by the use of sound absorbers, and
- maintenance of machinery and soundproofing equipment.

Structural measures

By means of secondary soundproofing measures, such as encapsulation, absorbing walls and buildings, further noise reduction can be achieved. The absorption of air-borne sound by space-enclosing structural components primarily depends on their surface mass and good sealing. Structural measures to reduce the transmission of structure-borne sound (e.g. partition joints, appropriate foundations) are necessary, if a high level of structure-borne sound is expected to emanate from the building as a result of e.g. noise emission from machinery, rolling operations or vibration.

Organisational and planning-related measures

Additional reductions in noise emissions as a function of local conditions can be achieved by organisational and planning related measures, such as accumulating high-noise sources and increasing the distance between noise sources and affected areas. In addition, operation restrictions may have to be imposed in special cases to reduce noise emissions. The exploration of suitable sites under consideration of the existing noise sources is of particular importance. Noise emissions from traffic to and from installations, which arise in connection with their operation, must likewise be taken into account.

4.1.7 Plant safety aspects

The general policy for the prevention of, preparedness for and response to industrial accidents is based on the following principles:

Prevention principle

- The plant should be constructed and operated in such a way as to prevent the uncontrolled development of normal operation,
- the plant should be constructed and operated in such a way that the consequences of accidents are reduced, and
- the plant should be constructed and operated according to the best available safety techniques (state of the art safety technology).

Consideration of complex systems in process industries

Complex systems can only be sufficiently examined by means of systematic, logical methods. This is taken into account by applying:

- systemanalytical investigation methods,
- detailed safety analysis considering the conditions of the individual case.

Appropriateness of means

Safety requirements are graded according to "type and scope of hazards to be expected". To this end, rules are set up for:

- substances relevant to accidents (substance criteria, list of substances),
- industrial activities relevant to accidents (list of plants).

The objective dependence of the disaster potential upon the quantity of hazardous substances is considered by a quantity threshold concept that defines staged safety requirements as a function of quantity.

4.1.8 Plant operation and decommissioning

Operational control plays an important role in the reduction of emissions. Special attention should be paid to the maintenance of equipment, malfunctions and breakdowns as well as supervision and training [88].

With regard to the cessation of activities, and in order to avoid any pollution risk and to return the site of operation to a satisfactory state, soil protection is of major importance. An integrated approach requires that at least measures should be taken:

1. To minimise the amount of soil that needs to be excavated or replaced due to construction measures and to make sure that excavated soil material is treated carefully (in order to avoid harmful changes of soil properties),
2. to minimise the additional input of substances into the soil during the operation phase of a facility (e.g. additional input due to deposition of airborne substances should not lead to precautionary soil levels being exceeded and spillages should be avoided);
3. to ensure a clean closure when a facility is shut down, e.g. clean up and rehabilitation or securing of contaminated soil, soil securing, with regard to the future use of the area. Natural soil functions should be safeguarded, if feasible.

4.2 Candidate BAT for copper production

Within the framework of integrated pollution prevention and control, first of all the above-mentioned general techniques and rules as described in section 4.1 should be considered for each plant operation. In this section the proposed emission guide values for BAT are given on the basis of the explanations in chapter 3. Since this paper deals only with German techniques, only German BAT are described which work within the emission guide values. They should be seen as one possible combination of process unit and abatement technique, other combinations in operation within Europe are not excluded.

The process units are described in a modular way, since the copper production industry is too complex and primary and secondary plants are too closely connected to describe the production line for primary and secondary copper production as a whole.

Table 4-5: Overview of section 4.2

Process unit	Emission guide values	Emission guide values for cleaned gas from secondary hoods	German BAT for this process unit
Smelting and converting (primary plant)	Table 4-13	Table 4-15	Outokumpu flash smelting furnace and Pierce-Smith converter
Fire refining including anode casting (primary plant)	Table 4-8	Table 4-15	Rotary anode furnace
Smelting of sulphidic materials (secondary plant)	Table 4-13	Table 4-15	Electric furnace
Smelting of oxidic materials (secondary plant)	Table 4-9	Table 4-15	Blast furnace
	Table 4-13	Table 4-15	Electric furnace
Converting (secondary plant)	Table 4-13	Table 4-15	Pierce-Smith converter
Scrap converting (secondary plant)	Table 4-10	Table 4-15	Pierce-Smith converter
Fire refining including anode casting (secondary plant)	Table 4-11	Table 4-15	Contimelt plant Reverberatory anode furnace Anode hearth shaft furnace with drum furnace
Electrolytic refining (primary and secondary plant)	-	-	-
Sulphuric acid plant	Table 4-13	-	-
Tin-lead alloy plant	Table 4-14	-	Dörschel furnace
Secondary hood system	Table 4-15	-	-
Fabrication of semi-finished products from copper and copper alloys	-	-	Table 4-16
Waste water treatment plant	Table 4-17	-	-

Primary copper production

In Figure 4-1 the flow sheet of a primary copper production plant including the principle process units is shown. All flows ending inside the dotted line are processed within the plant. The flows crossing the dotted line are sold as a product or for further processing.

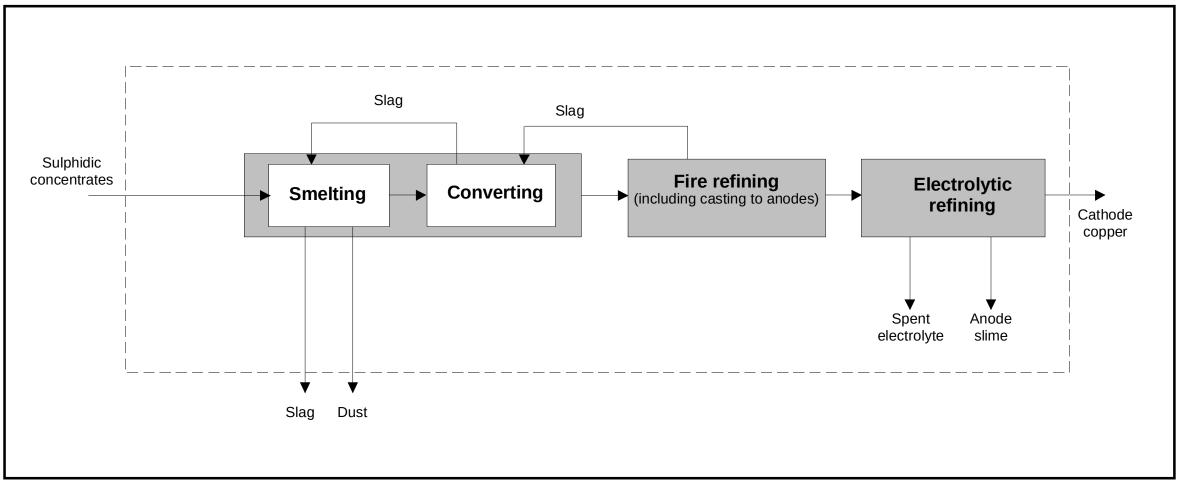

Figure 4-1: Primary copper production plant

In Table 4-6 the German BAT for these process units including techniques for waste heat recovery and off-gas cleaning are summarised.

Table 4-6: German candidates BAT for the primary copper production

Production step	Process technique	Applied techniques to prevent emissions	Applied techniques for minimisation of energy supply and waste heat recovery
Smelting and converting	Outokumpu flash smelting furnace	Secondary hood system, hot gas ESP, sulphuric acid plant	Waste heat boiler, pre-heating of process air
	Pierce-Smith converter	Secondary hood system, ESP, sulphuric acid plant	Remelting internal reverts and copper scrap, air to gas cooler for pre-heating of boiler feed water
Fire refining (including anode casting)	Anode furnace (rotary type) including casting wheel	Post-combustion chamber (during poling), fabric filter	-
Electrolytic refining	Electrolytic plant	Mist collector for exhaust air from regulator tanks	-

Secondary copper production

In Figure 4-2 the flow sheet of a secondary copper production plant including the principle processes is shown. All flows ending inside the dotted line are processed within the plant. The flows crossing the dotted line are sold as a product or for further processing.

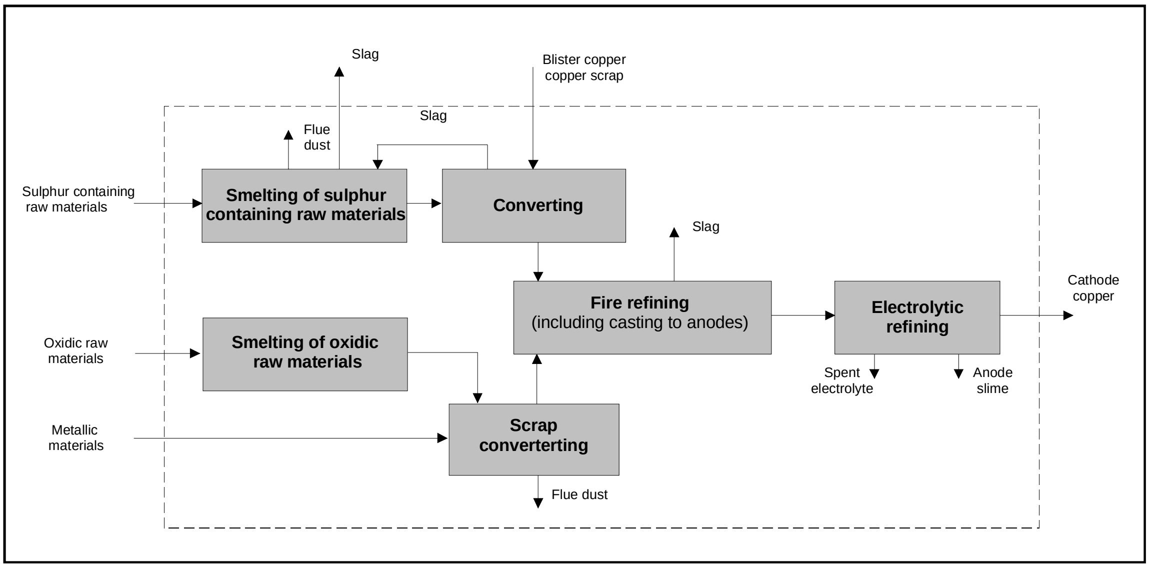

Figure 4-2: Secondary copper production plant

In Table 4-7 the German BAT for these process units including techniques for waste heat recovery and off-gas cleaning are summarised.

Table 4-7: German candidates BAT for the secondary copper production

Production step	Process technique	Applied techniques to prevent emissions	Applied techniques for minimisation of energy supply and waste heat recovery
Smelting	Blast furnace	Secondary hood system, settling chamber (serves also as post-combustion chamber), fabric filter	Waste heat boiler, tubular cooler
	Electric furnace	Secondary hood system, sulphuric acid plant	-
Converting	Pierce-Smith converter	Secondary hood system, ESP, sulphuric acid plant	Waste heat boiler if premitted by the temperatur conditions
	Scrap converter, Pierce-Smith type	Secondary hood system	Waste heat boiler if premitted by the temperatur conditions, tubular cooler
Fire refining (including anode casting)	Contimelt process	Secondary hood system, post-combustion chamber, adsorption filter, fabric filter	Pre-heating of feedstock, waste heat boiler, pre-heating of process air
	Reverberatory anode furnace (hearth type)	Secondary hood system, fabric filter	Waste heat boiler
	Combination of anode hearth shaft furnace and drum furnace	Secondary hood system, post-combustion chamber, adsorption filter, fabric filter	Pre-heating of process air
Electrolytic refining	Electrolytic plant	Mist collector for exhaust air from regulator tanks	-

In the following sections, reference emission limits are proposed for these units and German BAT operating within these limits are summarised.

4.2.1 Smelting and converting (primary plant)

The off-gases of the smelting and converting units are sent to a sulphuric acid plant, so the proposed emission guide values are given in Table 4-13. Both units should be equipped with a secondary hood system to prevent fugitive emissions. The maximum efficiency of the converters can be reached by optimising the capacity and number of the installed converter units. The proposed emission guide values for the off-gases from the secondary hood system are given in Table 4-15.

German BAT for the smelting and converting (primary plant): The Outokumpu flash smelting furnace and the Pierce-Smith Converter

The Outokumpu flash smelting furnace achieves a comparatively high throughput rate with one furnace. Since it is operated with oxygen enriched air to burn as much sulphur contained in the raw material as possible, it has a high sulphur oxide content in the off-gas, the fuel consumption is reduced and a high matte grade can be achieved (Cu content: 65 wt-%). The furnace off-gas is used for heat generation in a waste heat boiler and to pre-heat the process air. Then it is dedusted by a hot gas ESP and sent to a sulphuric acid plant. Hoods are installed to prevent fugitive emissions. The produced slag is sent to an electric slag cleaning furnace to lower its copper content.

The blowing time of the Pierce-Smith converter is very short, since a high matte grade can already be achieved in the Outokumpu flash smelting furnace. The reaction heat produced in the converter is used to remelt internal reverts and copper scrap. Before the converter off-gases are dedusted in a hot gas ESP, the heat is used by an air to gas cooler to pre-heat boiler feed water. A secondary hood system is installed to prevent fugitive emissions.

4.2.2 Fire refining including anode casting (primary plant)

Furnaces for fire refining should be equipped with secondary hoods to prevent fugitive emissions. Proposed emission guide values for the off-gas from these hoods can be found in Table 4-15. The following emission guide values are proposed for the cleaned furnace off-gases:

Table 4-8: Proposed emission guide values for the cleaned off-gases from fire refining plants (primary plant)

Substance	Unit	Proposed emission guide values
SO_x (as SO_2)	mg/m³	500[**)]
NO_x (as NO_2)	mg/m³	200
Cl^- (as HCl)	mg/m³	30
C_{total}	mg/m³	50[***)]
Particulate matter[*)]	mg/m³	10

[*)] The main constituents of the particulate matter are given in Table 4-12.

[**)] Mean value of whole refining cycle

[***)] if cold input material is used

German BAT for the fire refining (primary plant): The rotary anode furnace

The anode furnace (rotary type) is German BAT for fire refining of the converter copper, since the rotary type is well suited for input materials that are charged in liquid form. During poling, the furnace off-gas is afterburned in a post-combustion chamber and sent to a fabric filter after being cooled in a gas cooler to protect the filter media. To prevent fugitive emissions, a secondary hood system is installed.

4.2.3 Smelting of sulphur containing raw materials (secondary plant)

If the SO_2 content exceeds 800 mg/m^3, the furnace off-gases should be sent to a sulphuric acid plant. Therefore the emission guide values of the off-gases can be found in Table 4-13. The secondary hoods installed to prevent fugitive emissions are part of a central system. The proposed emission guide values of these ventilation gases are given in Table 4-15.

German BAT for the smelting of sulphur containing raw materials (secondary plant): The electric furnace

Since no fuel has to be burned for heat supply, the electric furnace produces comparatively small amounts of off-gas and, if the raw material contains sulphur, a high concentration of sulphur dioxide is reached in the off-gas, so it can be fed to a sulphuric acid plant. It is a comparatively small and well enclosed unit, because it can be operated with only small amounts of return slags, but the raw material has to be pretreated and it puts higher demands on the physical properties than the blast furnace. The furnace off-gas is treated in a sulphuric acid plant and fugitive emissions are prevented by the secondary hood system.

4.2.4 Converting (secondary plant)

To reach the maximum efficiency, the capacity and number of the installed converters should be optimised. The off-gases of the converting units have a relatively high SO_2content, therefore they should be sent to a sulphuric acid plant. The units should be equipped with a secondary hood system to prevent fugitive emissions. The proposed emission guide values for the converter off-gas are shown in Table 4-13 and the emission guide values for the off-gas from the secondary hood system are given in Table 4-15.

German BAT for the converting (secondary plant): The Pierce-Smith converter

The Pierce-Smith converters are used for further processing of the copper rich phase of the electric furnace. The off-gas is used for pre-heating of the waste heat boiler feed water or for steam generation in a waste heat boiler, dedusted in a hot gas ESP and sent to a sulphuric acid plant. The fugitive emissions are reduced by secondary hoods.

4.2.5 Smelting of oxidic raw materials (secondary plant)

The smelter to process oxidic raw materials should be equipped with secondary hoods to avoid fugitive emissions. The proposed emission guide values of this system are given in Table 4-15. Proposed emission guide values for the cleaned furnace off-gas are shown in Table 4-9.

Table 4-9: Proposed emission guide values in the cleaned off-gases for the smelting of oxidic raw materials (secondary plant)

Substance	Unit	Proposed emission guide values
SO_x (as SO_2)	mg/m³	800
NO_x (as NO_2)	mg/m³	500
PCDD/PCDF	ng/m³	< 0.5
Particulate matter*)	mg/m³	< 10

*) The main constituents of the particulate matter are given in Table 4-12.

German BAT for the smelting of oxidic raw materials (secondary plant): The blast furnace

The advantage of the blast furnace in secondary copper production is its high flexibility with regard to the raw material processed. At existing plants, additional oxygen is injected into the top area of the furnace that improves post-combustion to reduce the emission of dioxines and furanes (PCDD/PCDF). At new plants, a specific post-combustion is applied in order to reduce these emissions. The furnace off-gases pass a settling chamber that also serve as a post-combustion chamber before the heat is used for steam generation in a waste heat boiler. Then the gases are cooled by a tubular cooler and mixed with cold off-gas before they are cleaned together with the ventilation gases of the secondary hood system installed to prevent fugitive emissions in a fabric filter.

4.2.6 Converting of scrap (secondary plant)

The capacity and number of installed converters should be optimised in order to reach the maximum efficiency. A secondary hood system should be installed to prevent fugitive emissions. The proposed emission guide values of the ventilation gases from secondary hoods are given in Table 4-15. The proposed emission guide values for the furnace off-gas are shown in Table 4-10.

Table 4-10: Proposed emission guide values in the cleaned off-gases from a scrap converter (secondary plant)

Substance	Unit	Proposed emission guide values
SO_x (as SO_2)	mg/m³	800
NO_x (as NO_2)	mg/m³	500
PCDD/PCDF	ng/m³	< 0.5
Particulate matter*)	mg/m³	< 10

*) The main constituents of the particulate matter are given in Table 4-12.

German BAT for the converting of scrap (secondary plant): The Pierce-Smith converter

A converter of the Pierce-Smith type is German BAT in the secondary copper production to process black copper from the blast furnace as well as further raw material such as alloy scraps and shredder material by using the Knudsen process. The off-gas is cleaned in a fabric filter and secondary hoods are installed to reduce fugitive emissions.

4.2.7 Fire refining (secondary plant)

For fire refining, the emission guide values shown in Table 4-11 are proposed. The proposed emission guide values for the off-gas from the secondary hood system that should be installed to prevent fugitive emissions are given in Table 4-15.

Table 4-11: Proposed emission guide values for the cleaned off-gases for the fire refining (secondary plant)

Substance	Unit	Proposed emission guide values
SO_x (as SO_2)	mg/m³	800
NO_x (as NO_2)	mg/m³	800
CO	mg/m³	500
PCDD/PCDF	ng/m³	< 0.5
Particulate matter*)	mg/m³	< 10

*) The main constituents of the particulate matter are given in Table 4-12.

German BAT for the fire refining (secondary plant): The Contimelt process

The Contimelt process is used for continuous melting and fire refining of the converter copper from the electric furnace path and from the scrap converter. It comprises an anode shaft furnace and a subsequent poling furnace, from which the copper is cast into anodes on a casting wheel. The process is energy-saving, because the copper is melted and refined continuously. An integrated concept for the utilisation of heat has been implemented in the

Contimelt plant. The hot off-gas from the hearth furnace travels in counterflow to the feedstock materials so that its energy content is utilised to pre-heat the latter and save fuel. After the anode shaft furnace off-gas has been combined with the hot off-gas from downstream poling and casting furnace, the residual heat content is used for heat steam generation in a waste heat boiler and to pre-heat the burner air. Then carbon containing lime is injected into the off-gas (140,000 Nm^3/h) to adsorb organic constituents before it is cleaned by a fabric filter. To reduce the fugitive emissions, the furnaces are equipped with secondary hoods.

German BAT for the fire refining (secondary plant): The reverberatory anode furnace

The reverberatory anode furnace (hearth type) is used for fire refining of converter copper and additional copper scrap, since it is better suited for the melting of solid scrap than the rotary type. A secondary hood system is installed to prevent fugitive emissions.

German BAT for the fire refining (secondary plant): The Anode hearth shaft furnace and the drum furnace

In the anode hearth shaft furnace black copper is processed together with additional raw copper material. It is an open-hearth furnace with a shaft stacked up. Oxygen enrichment of the burner air is possible. The superheated melt is transferred to the refining furnace which is a rotary drum furnace where reduction is applied by blowing in natural gas. The off-gases of both furnaces are afterburned in post-combustion chambers. The off-gas from the refining furnace is then used to pre-heat the burner air, before the gases of both furnaces are cooled in a quench cooler. Afterwards they are treated in a gas cleaning plant that consists mainly of an adsorption filter plant and a fabric filter. To avoid fugitive emissions, all holes at both furnaces are equipped with hoods or enclosures.

4.2.8 Electrolytic refining (primary and secondary plant)

Electrolytic refining should be carried out in an electrolytic plant, whereby the ground should be protected against acidic leakage. Therefore appropriate materials should be used (e.g. lead). Storage tanks should be bunded or double wall tanks should be used. Bund capacities should always have sufficient volume for the maximum storage. Any leakage from the plant as well as scrubbing water from extraction systems should be fed back to the process.

The electrolyte should be conditioned in an appropriate way, e.g. when the copper content in the electrolyte is reduced electrochemically, the copper content in the last process step with the lowest copper content should be monitored permanently, and the electricity supply of the process should be cut down automatically if the concentration of copper is less than 1.5 g/l.

4.2.9 Auxiliary plants

In the following section, facilities for further treatment of by-products and cleaning facilities for waste water and off-gases are described.

4.2.9.1 Fabric filters

All furnace off-gases and off-gases from secondary hoods that do not pass the sulphuric acid plant are cleaned in fabric filters. The proposed emission guide values for the dust content in the filtered gas is given in the respective sections. In Table 4-12, the emission guide values for the main constituents in dust are given. They are proposed for all fabric filters, since the differences between single measurements at the same filter are more significant than the differences of fabric filters cleaning the off-gases of different processes.

Table 4-12: Proposed emission guide values for the off-gases after treatment in a fabric filter

Substance	Unit	Proposed emission guide values
Class I (TA-Luft)		
Cd	mg/m³	0.2
Hg	mg/m³	0.2
Tl	mg/m³	0.2
Sum class I (TA-Luft)	**mg/m³**	**0.2**
Class II (TA-Luft)		
As	mg/m³	1
Ni	mg/m³	1
Co	mg/m³	1
Se	mg/m³	1
Te	mg/m³	1
Sum class II (TA-Luft)	**mg/m³**	**1**
Class III (TA-Luft)		
Sb	mg/m³	5
Pb	mg/m³	5
Cr	mg/m³	5
Cu	mg/m³	5
Sn	mg/m³	5
Sum class III (TA-Luft)	**mg/m³**	**5**

If substances of several classes are present, the mass concentration in the emitted gas should not exceed a total of 1 mg/m^3 for coinciding class I and II substances as well as a total of 5 mg/m^3 for coinciding class I and III or class II and III substances. The emissions of substances class I - III have to be determined as a sum of the particulate matter, the vapour and the gas share of the respective element and its compounds (according to TA Luft [1]). More information about the German regulations can be found in section 6.1.2.

4.2.9.2 Sulphuric acid plant (double absorption contact plant)

As mentioned regarding process units above, some off-gas streams should be directed to the sulphuric acid plant for further treatment. The sulphuric acid plant should have a conversion rate higher than 99.6 %. The ground at the plant site as well as at the loading station for the sulphuric acid should be protected in an appropriate way against acid leakages. Storage tanks should be bunded or double wall tanks should be used. Bund capacities should always have sufficient volume for the maximum storage. The proposed emission guide values for the off-gas from a sulphuric acid plant are given in Table 4-13.

Table 4-13: Proposed emission guide values for the cleaned off-gases from a sulphuric acid plant

Substance	Unit	Proposed emission guide values
SO_x (as SO_2)	mg/m³	1250
SO_3	mg/m³	120
NO_x (as NO_2)	mg/m³	50
Cl^- (as HCl)	mg/m³	10
F^- (as HF)	mg/m³	4.5
Class I (TA-Luft)		
Cd	mg/m³	0.2
Hg	mg/m³	0.2
Tl	mg/m³	0.2
Sum class I (TA-Luft)	**mg/m³**	**0.2**
Class II (TA-Luft)		
As	mg/m³	0.5
Se	mg/m³	0.5
Sum class II (TA-Luft)	**mg/m³**	**0.5**
Class III (TA-Luft)		
Sb	mg/m³	1
Pb	mg/m³	1
Cu	mg/m³	1
Sum class III (TA-Luft)	**mg/m³**	**1**
PCDD/PCDF	**ng ITE/m³**	**< 0.5**

If substances of several classes are present, the mass concentration in the emitted gas should not exceed a total of 1 mg/m^3 for coinciding class I and II substances as well as a total of 5 mg/m^3 for coinciding class I and III or class II and III substances. The emissions of substances class I - III have to be determined as a sum of the particulate matter, the vapour and the gas share of the respective element and its compounds (according to TA Luft [1]). More information about the German regulations can be found in section 6.1.2.

4.2.9.3 Tin-lead alloy plant

Collected flue dust from secondary copper production is processed in a tin-lead alloy plant. Proposed emission guide values for this kind of plant can be seen in Table 4-14.

Table 4-14: Proposed emission guide values for the cleaned off-gases from a tin-lead alloy plant

Substance	Unit	Proposed emission guide values
SO_x (as SO_2)	mg/m³	800
NO_x (as NO_2)	mg/m³	500
PCDD/PCDF	ng/m³	< 0.5
Particulate matter*)	mg/m³	< 10

*) The main constituents of the particulate matter are given in Table 4-12.

German BAT for TLA plants: The Dörschel furnace

Flue dusts with a high content of tin, lead and/or zinc are fed to a Dörschel furnace which is heated by an oil burner. The zinc is transferred to the flue dust as zinc oxide and is collected in fabric filters. The remaining phase consists mainly of tin and lead.

4.2.9.4 Secondary hood system

All furnaces should be equipped with a secondary hood system in order to prevent fugitive emissions. The proposed emission guide values for off-gases from these systems are shown in Table 4-15.

Table 4-15: Proposed emission guide values for the cleaned off-gases from secondary hood systems

Substance	Unit	Proposed emission guide values
SO_x (as SO_2)	mg/m³	500
Particulate matter*)	mg/m³	< 10

*) The main constituents of the particulate matter are given in Table 4-12.

4.2.10 Fabrication of semi-finished products from copper and copper alloys

In Table 4-16 the German BAT for melting and casting in the fabrication of semi-finished products from copper and copper alloys is given.

Table 4-16: German BAT for melting and casting in the fabrication of semi-finished products

Equipment	Feed	Abatement
Shaft furnace (Asarco type)	Scrap & cathodes	Afterburner & fabric filter.
	Cathodes	Fabric filter.
Electric furnace	Cathodes,	Fabric filter.
	Cathodes, scrap, alloy scrap, master alloys, alloy metals	Cyclones (spark arresting), fabric filter.
Rotary furnace	Scrap, cathodes	Fabric filter.

4.2.10.1 Waste water treatment plant

In the following Table, proposed emission guide values for pollutants in discharged waste waters from both, primary and secondary plants, are given.

Table 4-17: Proposed emission guide values for pollutants in discharged waste waters (primary and secondary plant)

Substance	**Cu**	**Pb**	**As**	**Ni**	**Cd**	**Zn**
Proposed emission guide values[mg/l]	0.5	0.5	0.1	0.5	0.2	1

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6 Annex

6.1 Information on current legislation relevant to the copper production industry

6.1.1 Introduction

Various regulations concerning environmental standards have to be complied with related to the erection and operation of copper production plants, since the copper production industry is a consumer of energy and a potential source of air and water pollution as well as solid wastes. Consequently, the immediate environmental concerns are the usage of energy, control of air pollution (particularly CO, SO_x, NO_x and heavy metals), solid waste disposal and recycling, waste water emissions and - more recently with the increased amounts of recycled contaminated scrap metals - also harmful organic emissions. Existing regulations lay down standards for

- the use of raw materials,
- energy consumption and usage of waste heat,
- air quality,
- water quality,
- waste management and disposal of hazardous materials, and
- noise quality, vibration, smell.

Since this report deals only with the German copper production, the following sections give a brief overview of the current German legislation for copper production plants. In addition, a rough overview of important regulations on an international level is given. Legislation on a European level is excluded.

6.1.2 Regulations on a German level[17]

Important regulations relevant for copper production plants in Germany are laid down in the BImSchG (Federal Immission Control Act), the WHG (Federal Water Act) and the KrW-/AbfG (Federal Recycling and Waste Management Act). Germany uses a segregated media permitting system for different environmental media, but the final decision on an application is reached by the assessment of environmental impacts on all media by the local authorities. Also noise requirements are considered in the licensing procedure Germany aims at favouring pollution prevention. The „precautionary principle" has a legal status which

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[17] This section summarises information on the German legal framework. However, a complete discourse on all the regulations is not intended in this study. The regulations may be found in corresponding laws, ordinances, or other documents.

permits the settings of standards. Legal standards are not subject to any negotiation in the licensing process in Germany.

In compliance with the federal structure of Germany, the implementation of environmental laws and decrees is under the responsibility of the federal states (Bundesländer), which may take into account local requirements and implement the administrative procedure differently. For new plants and also for major changes of existing plants a permission procedure with participation of the public has to be fulfilled. During the licensing procedure also an environmental impact assessment may be required (c.f. Gesetz über die Umweltverträglichkeitsprüfung (UVPG)).

Table 6-1 gives an overview of the German legal basis and regulations for environmental protection in Germany alongside the production line. In the following, a selection of the most important acts, regulations and requirements are presented.

Table 6-1: Legal basis and main regulations alongside the production line

Area	Legal basis	Regulations and ordinances
Authorisation	Genehmigungsrecht	Bundes-Immissionsschutzverordnungen, ...
Transport	Verkehrsrecht	- Gefahrgutverordnung Straße - Gefahrgutverordnung Schiene - Gefahrgutverordnung Binnenschifffahrt
Health and safety at work	Chemikaliengesetz (ChemG)	- Chemikalienverbotsordnung - Gefahrstoffverordnung
	Gewerbeordnung	- TA Lärm - Arbeitsschutzgesetz - Arbeitsstättenverordung und -richtlinien
Emissions	Bundes-Immissionsschutzgesetz (BImSchG)	- Bundes-Immissionsschutzverordnungen - Bundes-Immissionsschutzverwaltungsvorschriften (TA Luft, TA Lärm)
	Wasserhaushaltsgesetz (WHG)	- Abwasserverordnung (AbwV) - Indirekteinleiterverordnungen oder Abwassergesetze der Länder - Anlagenverordnungen der Länder - Katalog wassergefährdender Stoffe - Lagerung und Transport wassergefährdender Stoffe (VAWS)
Waste Prevention and Treatment	Kreislaufwirtschaftsgesetz (KrW.-/AbfG)	TA Abfall TA Siedlungsabfall
Environmental management		Öko-Audit ISO 14000

6.1.2.1 German regulations concerning the air quality

The basic law for air pollution control is the Federal Immission Control Act (Bundes-Immissionsschutzgesetz BImSchG). It primarily aims towards the protection of the medium air, but it also applies to the media water and soil in case pollution is transferred via the medium air. The BImSchG is specified by 21 ordinances and the Technical Instructions on Air

Quality (TA Luft). Especially the TA Luft as a prescription for the authorities specifies in more detail requirements to be met by installations subject to licensing.

Federal Immission Control Act (Bundes-Immissionsschutzgesetz, BImSchG)

The BImSchG is the legal instrument for monitoring air pollution. Immission as defined within the law comprises air pollutants, and also noise, vibration, light, heat, radiation and associated factors affecting humans as well as animals, plants or other things. This concept already implements the idea of cross-media effects to a certain extent. The BImSchG requires federal authorities to issue ordinances identifying the types of facilities, which are subject to licensing, set licensing requirements for these facilities, and impose emission limit values and technical control requirements for all facilities, whether licensed or not.

Especially article 5(1)3 BImSchG aims at the avoidance and minimisation of wastes and residues. The paragraph emphasises the cross-media effects of industrial production. The concept of "state of the art technology" defined in the BImSchG is similar to the one of BAT:

State of the art as used herein shall mean the state of development of advanced processes of facilities or modes of operation which is deemed to indicate the practical suitability of a particular technique for restricting emission levels. When determining the state of the art, special consideration shall be given to comparable processes, facilities or modes of operation that have been successfully proven in practical operation. (Article 3 paragraph 6 BImSchG)

In principle, "state of the art technology" is stated in terms of emission limits set by the licensing authority, the choice of technology to comply with the emission limit levels is left to industry. Necessary precautions against harmful effects on the environment are to be taken in particular by using control measures corresponding to the state of the art. Depending on the mass flow, some substances have to be measured continuously (eg. SO_x, NO_x, and particulates).

Technical Instructions on Air Quality (TA Luft):

The Technical Instructions on Air Quality (TA Luft) [1] have been set up as general administrative regulations in connection with the §48 BImSchG [cf. 19]. The TA Luft further specifies the requirements to be met by installations subject to licensing if not specified in one of the other regulations. Therefore, it prescribes limit values for virtually all air pollutants as well as structural and operational requirements designed to limit diffuse emissions. It establishes standards as well as assessment procedures for *immissions* (as suspended particles in [mg/Nm^3] and as dust deposition [g/(m^2 d)]) and *emissions* [1]. Existing melting plants had to comply with the TA Luft (as at 1986) requirements by 1994. For the new federal states, the requirements had to be met before 1996, and in special cases by 1999. Table 6-2 shows the limits for main emission control requirements or, if specific regulations for non-ferrous metal production plants exist, it gives the corresponding more specific requirements laid down in the TA Luft, which are aimed at the avoidance and minimisation of air pollution.

The potentially emitted substances are split into 3 classes, whereby class I substances are the most toxic and while Class III are the least harmful. The emission limit values contained in the TA Luft represent the BAT for technical measures for reducing emissions (dating from 1986). These quality values were developed referring to scientific findings and research taking into account toxicological, bioaccumulative and epidemiological aspects. The required concentration limits are given in mass of emitted substances related to the volume of emitted gas under standard conditions (0°C, 1013 mbar) after subtraction of the water vapour content and for a prescribed measuring time and statistic evaluation.

Table 6-2: Emission control requirements laid down in the TA Luft

Emitted substance (TA Luft section)	**Class**	**Substances**		**Mass flow threshold [g/h]**	**Concentration limit [mg/Nm^3]**
Dust containing waste gases (3.3.3.3.1 a))		dust containing waste gases are to be captured as far as possible and to be fed to a gas cleaning system, if necessary to comply with further requirements.			
Inorganic dust particles (3.1.4)	I	(e.g. Cd, Hg, Tl)	sum of substances	1	0.2
	II	(e.g. As, Co, Ni, Te, Se)	- " -	5	1
	III	(e.g. Sb, Pb, Cr, F, Cu, Mn, Pt, Pd, Rn, V, Sn)	- " -	25	5
	I+II		- " -		1
	I+III, II+III		- " -		5
Vaporous or gaseous inorganic substances (3.1.6)	I	(e.g. AsH_3)	per substances	> 10	1
	II	(e.g. HF, Cl_2, H_2S)	- " -	> 50	5
	III	(e.g. Cl-compounds as HCl)	- " -	> 300	30
	IV	(e.g. SO_2, NO + NO_2 as NO)	- " -	> 5.000	500
Organic substances (3.1.7)	I	(e.g. Chlormethane)	Classification	> 100	20
	II	(e.g. Chlorbenzene)	according to	> 2.000	100
	III	(e.g. Alkylalcohols)	Annex E of TA Luft	> 3.000	150
Carcinogens	I	(e.g. asbestos, benzo(a)pyren)		≥ 0.5	0.1
	II	(e.g. arsenic trioxide, dimethylsulfate)		≥ 5	1
	III	(e.g. Acrylonitrite, benzene)		≥ 25	5
Carbon monoxide (3.3.3.3.1)		should be utilised or burned as far as possible.			

If inorganic dust particles of several classes are present, the mass concentration in the emitted gas should not exceed a total of 1 mg/Nm^3 for coinciding class I and II substances as well as a total of 5 mg/Nm^3 for coinciding class I and III or class II and III substances.

If organic substances in several classes are present, the mass concentration in the emitted gas should not exceed a total of 0.15 g/Nm^3 with a total mass flow of 3 kg/h or more.

Furthermore, for facilities producing non-ferrous unrefined metals, particle emissions in the emitted gases at a mass flow of 0.2 kg/h and more should not exceed 20 mg/Nm^3. Sulphur dioxide and sulphur trioxide in the emitted gas should, indicated as sulphur dioxide, should not exceed 0.80 g/Nm^3 at a mass flow of 5 kg/h or more[18]. When using solid or liquid fuels, a sulphur mass content of 1 %, which is given for solid fuels with a lower calorific value of 29.3 MJ/kg, should not be exceeded.

No daily mean value of the respective emitted substances should exceed the required emission limits, 97 % of all half-hourly mean values should not exceed 6/5 of the required emission limits, and all half-hourly mean values should not exceed the required emission limits by more than twice.

Since the TA Luft stems from 1986, the local authorities demand stricter emission limit values.

Ordinance on installations subject to licensing (4. BImSchV)

In addition to these emission limits for certain substances shown in Table 6-2, special requirements for copper production plants are laid down in section IV of the Bundes-Immissionsschutzgesetz (Verordnung über genehmigungsbedürftige Anlagen, 4. BImSchV) [11] for:

- Roasting and sintering of copper ores,
- Production of copper crude metal, and
- Electrolytical production of copper.

Technical Instruction on Noise Abatement:

The Technical Instruction on Noise Abatement (TA Lärm) [4] sets the limits for noise emissions from the operation of a facility permitted in various areas. Permission for the construction, operation or altering of a facility is granted only if the emission limits allowed for a specific area are not exceeded and if state-of-the-art noise protection measures are employed.

6.1.2.2 German regulations concerning the water quality

With respect to water management, each discharge, wherever it is located, has to comply with the Federal Water Act (Wasserhaushaltsgesetz, WHG [31]). The WHG is the legal instrument for water management, analogous to the BImschG for air pollution control. It applies to waste water generated by various industrial processes, including the non-ferrous metal industry. According to the WHG, the use of surface, coastal, and ground waters requires the approval of

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[18] Sulphuric acid plants are dealt with in a different section of the TA Luft. A conversion factor of at least 99.5 %/99.6 % for varying/constant gas conditions should be maintained. In addition, a sulphur trioxide limit value in the off-gas of 60 mg/Nm³ for constant gas conditions resp. 120 mg/Nm³ in all other cases should not be exceeded [1].

the competent authority. Water protection legislation in Germany is implemented by the Ordinance on Waste Water (Abwasserverordnung, AbwV) Besides the minimum requirements concerning waste water treatment (c.f. Table 6-3), requirements concerning techniques of analysis and measurement as well as limits for the content of specific substances are laid down in the Annexes of the AbwV for different industries. The production of copper as part of the non-ferrous metal industry is dealt with in Annex 39 of this regulation [84]. In addition, the Federal Ministry of Environment has published explanations and comments on this Annex [12]. Depending on the local conditions, more stringent requirements can be established by the authorities.[19] Table 6-3 gives the main restrictions established in Annex 39 of the AbwV, especially for copper production plants.

Table 6-3: Limit values for discharges into water for copper production plants

	Limit value**) [mg/l]	**Load limit value*****) [g/t tonne produced]
Cadmium	0.2	3*)
Mercury	0.05	1*)
Zinc	1	30*)
Lead	0.5	15*)
Copper	0.5	10*)
Arsenic	0.1	2*)
Nickel	0.5	15*)
Thallium	1	-
Chromium, total	0.5	10*)
Chromium VI****)	0.1	-
Cobalt	1	-
Silver	0.1	-
Tin	2	-
Cyanide (freely available) ****)	0.1	-
Sulphide (dissolved)	1	-
AOX	1	-
Fish toxicity as thinning factor G_f	4	-
COD	-	1,500
Iron	-	100

*) Only valid for plants with a daily production capacity of more than 10 tons.

**) Qualified random sample or 2 hours composite sample; three from four samples have to comply with the limit and no value more than 100% exceeding the limit value

*****)** The load limit is calculated with the permitted production capacity and the limit values given by permission

****) This limit value is valid for the location where the waste water arises (c.f. [84]) .

Source: Annex 39, Abwasserverordnung [12]

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[19] Each of the 16 Federal states has its own legislation which both the Federal Law and adds to it.

The required load values shall be production-specific loads in relation to the production capacity on which the water discharge licence is based. It shall be determined by the 2 hours composite sample or the qualified random sample. The qualified random sample shall refer to a composite sample of at least five random samples taken over a maximum period of two hours at intervals of no less than two minutes, and blended. A composite sample shall refer to a sample which is taken continuously over a given period, or a sample consisting of several samples taken either continuously or continuously over a given period and blended. A random sample shall refer to a single sample taken from a waste water flow.

Waste water from cooling systems for the indirect cooling of industrial processes is excluded from this regulation and subject to the provisions laid down in Annex 31, AbwV [12]. Table 6-4 gives the relevant requirements for discharges from cooling circuits in Annex 31 [84]. If the stated values are not observed, approval for the discharge of waste water will be denied.

Table 6-4: Requirements for discharges from cooling circuits of industrial processes

Hazardous Substances	**Minimal Requirements*)**
COD	40 mg/l
Phosphor compounds, given as P	3 mg/l
Zinc	4 mg/l
AOX	0.15 mg/l
Available residual chlorine	0.3 mg/l
Chromium compounds	must not be contained
Mercury compounds	must not be contained
Nitrite	must not be contained
Metal organic Compounds (Metal-Carbon-Compound)	must not be contained

*)Qualified random sample or 2 hours composite sample

Source: Annex 31, Abwasserverordnung [12] or [84]

The WHG is furthermore complemented by the waste water levy act (Abwasserabgabengesetz: AbwAG) [29]. The tariffs are related to the mass and possible hazard of the discharged waste water according to Table 6-5. For the discharge of sewage, that exceeds the mentioned threshold values for concentrations or annual freights, the discharging party has to pay a fee related to the given units of measurement.[20]

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[20] Currently a levy of 70 DM per unit of hazards has to be paid

Table 6-5: Thresholds according to the waste water levy act

Hazardous Substances	**Units of measurement (relating to a unit of hazard)**	**Threshold values**	
		Concentrations	**Annual freights**
Oxydizable substances (given as COD)	50 kg Oxygen	20 mg/l	250 kg
Phosphor	3 kg	0.1 mg/l	15 kg
Nitrogen	25 kg	5 mg/l	125 kg
Organic Halogen compounds as AOX	2 kg Halogen, calculated as Cl	100 µg/l	10 kg
Mercury & compounds.	20 g	1 µg/l	0.1 kg
Cadmium & compounds	100 g	5 µg/l	0.5 kg
Chromium & compounds	500 g	50 µg/l	2.5 kg
Nickel & compounds	500 g	50 µg/l	2.5 kg
Lead & compounds	500 g	50 µg/l	2.5 kg
Copper & compounds	1000 g	100 µg/l	5 kg
Fish toxicity	3,000 m^3 discharges divided by G_F	G_F =2 (dilution factor for non-lethal quantity for fish from the discharge)	

Source: Abwasserabgabengesetz [29]

6.1.2.3 German regulations concerning the waste management and disposal of hazardous materials

Waste legislation in Germany is laid down in the Act on Waste Prevention and Treatment (Gesetz zur Vermeidung, Verwertung und Beseitigung von Abfällen, GVVB [32]). It is applied to the use and storage of waste, i.e. to substances to be disposed of by the processor or to substances whose proper treatment is necessary to protect the environment. Additional requirements refer to waste from particular installations.

Legislation laying down measures aiming towards "avoidance, utilisation and disposal" of waste is set down in the Recycling and Waste Management Act (Kreislaufwirtschafts- und Abfallgesetz, KrW-/AbfG [30]), which came into force in October 1996 and is the most important part of the new GVVB. It broadens the entire national waste concept and sets new priorities with regard to the avoidance of and the duty to utilise waste. The KrW-/AbfG also codifies manufacturer's product responsibility.

For administrational procedures, technical guidelines on waste (TA Abfall) [2] and on municipal waste (TA Siedlungsabfall) [3] are of relevance. The TA Abfall regulates planning, licensing, construction and operation of waste disposal facilities [62]. Facilities for treating waste have to fulfil requirements regulated in special decrees, based on Art. 5 BImSchG.

A working group of the federal states on waste (Länderarbeitsgemeinschaft Abfall, LAGA) issued a categorisation of waste types, comprising 589 types of waste, of which 333 have priority for control [46] (*LAGA-Abfallartenkatalog*). This catalogue was valid till 12/31/1998 and has been replaced by the European waste catalogue (EWC) in the following [50]. To facilitate the change from the LAGA catalogue to the EWC, the German *LAGA* worked out an interim catalogue (*LAGA-Umsteigekatalog*) [47]. Following this categorisation, the following types of waste may arise within the copper production industry (cf. [46, 47]):

- Slag from non-ferrous metal melting,
- Plant residues (runner breaks, ladle breaks, converter breaks, refractory breaks, etc.),
- Sludges from non-ferrous metallurgy,
- Filter dust.

6.1.2.4 International regulations (overview)[21]

In this section, a rough overview of important regulations on an international level effecting the copper production industry is given. International regulations and agreements have been worked out on different levels. Besides the European level, which is not further considered in this chapter, the different international committees of the United Nations like UNEP, UNCED, UNECE, WHO, IFCS have to be mentioned. In addition, the OECD is working in the field of environmental protection. Important international regulations, effecting the pollution of the different environmental media are e.g.:

Long Range Treaty on Air Pollution (LRTAP):
International efforts to reduce the adverse effects of the transboundary acidification on forests, aquatic ecosystems, and human health, by way of internationally co-ordinated emission reductions, were undertaken in the 1979 Convention on Long Range Transboundary Air Pollution (LRTAP). After coming into force in 1983, the LRTAP Convention was augmented by (1) the 1984 Protocol on long-term financing; (2) the 1985 Helsinki Protocol reducing sulphur emissions or their transboundary fluxes by at least 30%; (3) the 1988 Sofia Protocol on the freezing of the emission of nitrogen oxides; (4) the 1991 Geneva Protocol on the control of the emission of volatile organic compounds; and (5) the 1994 Oslo Protocol on the further reduction of the emission of sulphur dioxide.

Basel Conventions:
The Basel Conventions declare the responsibility of OECD states regarding the control of transboundary movements of hazardous wastes and their disposal. It was adopted in March 1989 and entered into force in May 1992. In 1996, more than 100 countries plus the EC are parties to the Convention. The conventions comprise Technical Guidelines for waste management activities. In this guidelines materials are divided into substances with a ban for

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[21] This section summarises information on international regulations effecting the non-ferrous metal industry. However, a complete discourse on all the regulations is not intended in this study. The regulations may be found in corresponding laws, ordinances, or other documents. A more detailed summary can be found in [43]

export (list A) and substances which still can be exported to non-OECD countries. A decision adopted by the parties in 1994 prohibits with immediate effect the export from OECD countries of hazardous wastes destined for final disposal in non-OECD countries. The decision also phased out similar exports destined for recycling or recovery operations before banning them completely on 31 December 1997.

OECD-Council decision on Transfrontier Movements of Hazardous Wastes:
As a reaction of the "Basel Convention" of the United Nations, the council of the OECD ratified the council decision C 88(90). A three-tiered system was proposed to delineate controls to be applied to transfrontier movements: Wastes destined for recovery operations included on the green list would move among OECD Member countries toward recovery operations subject to all existing controls normally applied in commercial transactions. A notification procedure would exist for wastes destined for recovery operations included in the yellow list and wastes destined for recovery operations included in the amber list or red list would be subject to stricter or more rigorous controls.

Protection of the aquatic environment:
There are several international activities concerning the protection of the aquatic environment. The most important ones are the the Oslo Paris Commission (OSPARCOM) for the protection of the maritime environment of the North Sea and the Northeast Atlantic and the Helsinki commission of the countries bordering the East Sea (HELCOM) for the protection of their maritime environment.

In addition, there exist several international agreements on the pollution prevention of the main European seas (Nordseeschutzkonferenz), lakes (Bodensee) and rivers (e.g. Rhine (IKSR), Elbe(IKSE), Donau (IKSD), Oder (IKSO)) [43]. For example, there are two international agreements dating from 1978 concerning the pollution prevention of the River Rhine referring to chemical contamination and chlorides [68].

Global Environment Monitoring System (WHO/UNEP)
UNEP and WHO operate the GEMS (Global Environment Monitoring System) environmental pollution monitoring programmes for urban air quality (AIR), food, human exposure assessment location (HEAL), and water. The objectives of GEMS as defined at its inception are:

- to strengthen monitoring and assessment capabilities in the participating countries,
- to increase the validity and comparability of environmental data and information,
- top produce global/regional assessments in selected fields and compile environmental information at a global level.