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The Current State of Copper Metallurgy and Its Raw Material Base

Shokhrukh Toshpo'latovich Khojiev[1], Mohichehra Saburovna Ergasheva[2], Shamshod Farkhod o'g'li Khamroqulov[2], Javokhir O'tkir o'g'li Khamroev[2]

[1]Senior Lecturer of the Department of Metallurgy, Tashkent State Technical University,
[2]Students of the Department of Metallurgy, Tashkent State Technical University,
E-mail: hojiyevshohruh@yandex.ru

Abstract: *Sources of copper production are ores, their enrichment products - concentrates - and secondary raw materials. The share of secondary raw materials currently accounts for about 40% of the total copper output. Copper ores are almost entirely polymetallic. Possible natural companions of copper, like other heavy non-ferrous metals, are the elements of the 4th-6th long periods of the Mendeleev's periodic system. Valuable companions of copper in ore raw materials in various combinations can be about 30 elements. The most important of them: zinc, lead, selenium, tellurium, cadmium, nickel, cobalt, gold, silver, sulfur, germanium, rhenium, thallium, indium, molybdenum, iron. In cases where copper-bearing ores contain significant amounts of other satellite metals, commensurate with the copper content, they are called copper-nickel, copper-zinc, copper-lead-zinc, etc. All types of ores are used in copper production: sulfide (solid and disseminated), oxidized, mixed and native. However, the main copper raw material is sulfide phenocrysts, the reserves of which in the subsoil are the largest. 85 - 90% of all primary copper is currently obtained from sulfide ores.*

Keywords— metallurgy, copper, pyrometallurgy, ore, concentrate, charge, raw materials, production, mineral.

1. INTRODUCTION

Copper is a red metal, has a cubic face-centered crystal lattice (lattice type 2), density 8.93 g/cm ^{3}, $T_{melting}$ = 1083 ºC. Copper has high plasticity, electrical and thermal conductivity, resistant to chemical environments. The mechanical properties of copper are relatively low. So, in the cast state, copper has Gv = 150 ... 200 MPa, d = 15 ... 20%. In nature, copper occurs in the form of minerals and chemical compounds with oxygen ($CuCO_3 \cdot Cu(OH)_2$, Cu_2O) and sulfur (Cu_2S, CuS, $CuFeS_2$). The most widespread deposits of ores are in the form of sulfur compounds (80% of world reserves). The earth's crust contains only about 0.01% copper. Currently, copper ores are mined by the mine method. About 50% of all produced copper is used in the electrical industry, about 40% in alloys (bronze and brass), 10% in chemistry and other industries [1-7].

2. MODERN METHODS OF COPPER PRODUCTION

For the production of copper ores are used containing 1 ... 6% Cu, as well as waste of copper and its alloys. Copper ores are considered rich if they contain more than 2% Cu [8].

There are two ways to produce copper.

1. Pyrometallurgical.
2. Hydrometallurgical.

The main method is pyrometallurgical. It consists of the following main stages.

2.1. Beneficiation of copper ores. Produced in most cases by flotation. Its essence is as follows. Mineral oils (reagents) are added to the crushed ore (grain diameter 0.5 ... 0.05 mm), which cover the ore minerals with an oily film and make them not wetted with water. This helps to separate the ore from the waste rock. Get a copper concentrate containing 15 ... 20% Cu [9-15].

2.2. Cinder production (concentrate roasting). Dried copper concentrate is subjected to roasting. It is produced for the purpose of partial removal of sulfur, as well as arsenic, antimony and other impurities associated with copper ores. Firing is carried out in furnaces, the action of which is based on the principle of a "fluidized" bed [16-19]. In the process of heating the concentrate to 800ºC in the presence of atmospheric oxygen, sulphides are oxidized, and the sulfur content in the concentrate is almost halved against the original (the content of copper sulfide increases):

$$FeS + O_2 \rightarrow Fe_2O_3 + SO_2\uparrow;$$
$$Cu_2S + O_2 \rightarrow Cu_2O + SO_2\uparrow;$$
$$Cu_2O + FeS \rightarrow Cu_2S + FeO.$$

The resulting product (cinder - Cu_2S, FeS, FeO) enters the furnace to obtain from it an alloy rich in copper content (matte). Sulfur-rich exhaust gases from the furnace are used to produce sulfuric acid. Concentrates with a copper content of up to 25% are fired. At a higher copper content, the concentrate is melted without roasting [20].

2.3. Obtaining a copper matte. Reflective furnaces are used to obtain copper matte. As a result of heating the cinder to 1200 ... 1300 ºC in an oxidizing atmosphere (the furnace is lined with dinas bricks), it melts. In this case, the reactions of the formation of copper oxide (Cu_2O) and its reaction with iron sulfide proceed with the formation of copper sulfide. As a result, the melt stratification occurs: at the bottom, heavier compounds are collected, which are sulfides of Fe and Cu - primary copper matte (FeS + Cu_2S - up to 50% Cu; 20 ... 40% Fe; 20 ... 25% S; up to 8% O_2 and impurities Au, Ag, Pb, Zn, Ni and others); top - slag, consisting of oxides (Fe_2O_3, Fe_3O_4, FeO, SiO_2, Al_2O_3) [21-23].

2.4. Converting copper matte (producing blister copper). The molten matte is poured into a horizontal converter (with a capacity of up to 100 tons) and blown with compressed air through a series of tuyeres made in a magnesite lining along the entire length of the converter [24]. In this case, the oxidation of Fe and Cu sulfides and the transfer of oxides to slag occurs.

The purging process is divided into two stages:

$$FeS+O_2 \rightarrow FeO+SO_2$$
$$Cu_2S+O_2 \rightarrow Cu_2O+SO_2$$
$$Cu_2O+FeS \rightarrow Cu_2S+FeO$$

During this period, quartz sand is loaded into the converter, which slags iron oxide:

$$SiO_2+FeO \rightarrow FeO \cdot SiO_2$$

At the end of the first stage of blowing, no FeS remains in the metal, and the so-called white matte (Cu_2S) is obtained. In the second stage, the following processes take place [25]:

$$Cu_2S+O_2 \rightarrow Cu_2O+SO_2$$
$$Cu_2O+Cu_2S \rightarrow Cu+SO_2$$

The result is blister copper containing up to 3% impurities, including noble metals (97.5 ... 99.5% Cu; 0.3 ... 0.5% S; 0.3 ... 0.5% Ni; impurities Au, Ag, As, Bi, Te and others). Such copper is not suitable for production. It is fragile, has low electrical and thermal conductivity. Therefore, it requires further processing [26-30].

2.5. Fire refining of copper. Produced in order to remove as many impurities as possible. Fire refining is carried out in reverberatory furnaces. In this case, blister copper is melted and the metal bath is blown with air through the tubes. Copper oxidation occurs: $Cu + O_2 \rightarrow Cu_2O$. In this case, such impurities as Fe, Al, Si, Zn, Pb are completely oxidized and either pass into slag or volatilize $Me + Cu_2O \rightarrow MeO + Cu$; Ni, Sb, As with their high content are removed only partially, Au and Ag remain completely in the metal. By the end of refining, the Cu_2O content reaches 8%. To restore copper, birch poles are introduced into the bath and the melt is stirred ("teasing" the copper) [31-33].

Wherein:

$$Cu_2O+C \rightarrow Cu+CO\uparrow;$$
$$Cu_2O+CO \rightarrow Cu+CO_2\uparrow;$$
$$Cu_2O+H_2 \rightarrow Cu+H_2O\uparrow.$$

The obtained copper with a purity of 99.0 ... 99.5% is poured into ingots or ingots in the form of anode plates with a thickness of 30 ... 45 mm for subsequent electrolytic refining.

2.6. Electrolytic copper refining. Produced to obtain copper, pure from impurities (99.95% Cu). Electrolysis is carried out in baths lined with vinyl plastic or lead from the inside. Anodes are made of fire-refined copper, cathodes are made of thin sheets of pure copper. The electrolyte is an aqueous solution of $CuSO_4$ (10 ... 16%) and H_2SO_4 (10 ... 16%). When direct current is passed, the anode dissolves, copper goes into solution, and copper ions are discharged at the cathodes, precipitating by a layer of pure copper: $Cu^{2+} + 2\bar{e} \rightarrow Cu^0$. Impurities (Bi, Te, As, Sb, Se, Au, Ag) are deposited on the bottom of the bath in the form of sludge, which is removed and processed to recover precious metals. The cathodes are unloaded in five to twelve days, when their mass reaches 60 ... 90 kg. They are thoroughly washed and remelted in electric furnaces. Copper is obtained with high purity of the following grades MO (99.95% Cu), M1 (99.9% Cu), M2 (99.7% Cu), M3 (99.5% Cu), M4 (99.0% Cu) [34-40].

3. RAW MATERIAL BASE FOR COPPER PRODUCTION

More than 250 copper minerals are known. Most of them are rare. The greatest industrial importance for the production of copper is a small group of minerals, the composition of which is given in table 1.

In modern practice, ores are usually mined with a content of 0.8 - 1.5% Cu, and sometimes even higher. However, for large deposits of disseminated ores, the minimum copper content suitable for development in modern conditions is 0.4 - 0.5%. Along with copper minerals, sulfides of other heavy non-ferrous metals (zinc, lead, nickel) and iron are found in ores in greater or lesser amounts.

Iron can be present both in the form of independent and in the form of complex sulfides such as chalcopyrite and bornite. The main natural iron sulfides are pyrite FeS_2 and pyrrhotite $Fe_{1-x}S$ (often Fe_7S_8) [41].

Table 1. Main minerals of copper

Minerals	Cu content,%
Chalcopyrite $CuFeS_2$	34,5
Covellin CuS	66,4
Chalcocite Cu_2S	79,8
Bornite Cu_5FeS_4	63,3
Malachite $CuCO_3 \cdot Cu(OH)_2$	57,4
Azurite $CuCO_3 \cdot 2Cu(OH)_2$	55,1
Cuprite CuO	88,8
Chrysocolla $CuSiO_3 \cdot 2H_2O$	36,2
Native copper Cu, Au, Ag, Fe, Bi, etc.	before 100

Chalcopyrite, covellite, bornite and pyrite belong to the so-called higher sulfides. They contain an excess of sulfur in excess of the stoichiometric content corresponding to the valence ratios. When heated, higher sulfides dissociate with the formation of lower ones (Cu_2S and FeS) and the release of elemental sulfur vapors.

In addition to ore minerals, copper ores contain waste rock in the form of silica, alumina, calcite, various silicates, etc.

Due to the low copper content and the complex nature of ores, in most cases, direct metallurgical processing is unprofitable, therefore they are usually preliminarily subjected to flotation concentration [42].

Table 2. Approximate composition of copper-containing concentrates,%

Concentrate type	Cu	Pb	Zn	Fe	S	SiO_2	Al_2O_3	CaO
Copper	13,5	-	0,5	36,5	39,0	2,7	3,4	0,5
Copper	36,5	1,5	1,1	7,1	17,0	25,5	7,2	2,4
Copper-zinc	15,7	0,8	6,8	31,6	40,4	0,7	-	0,2
Copper Nickel	24,7	-	-	34,9	32,6	1,7	1,5	0,7

When enriching copper ores, the main product is copper concentrates containing up to 55% Cu (usually 10-30%). The extraction of copper into concentrates during flotation ranges from 80 to 95%. In addition to copper ores, pyrite concentrates and sometimes concentrates of a number of other non-ferrous metals (zinc, molybdenum, etc.) are obtained during the enrichment of ores. The approximate composition of flotation copper concentrates is shown in Table 2.

Flotation concentrates are fine powders with a particle size of less than 74 microns with a moisture content of 8 - 10%.

The copper industry is one of the leading sub-branches of non-ferrous metallurgy in the Soviet Union. The output of copper in our country is constantly growing, and the technology for its production is constantly being improved.

The leading place in the further increase in copper production in the CIS is occupied by the regions of the Arctic Circle, Kazakhstan, Central Asia and Siberia. On the basis of numerous large deposits, the Norilsk, Balkhash, Almalyk and Dzhezkazgan mining and metallurgical plants operate. As before, an important place in the production of copper is occupied by the Ural copper smelting and copper refining enterprises [43].

The copper industry is developing rapidly abroad. The largest copper producer among the capitalist and developing countries is the United States. Copper production is rapidly developing in Japan, which imports almost all raw materials from Asia, Oceania and Australia. Copper is produced in large quantities in Chile, Zambia, Canada and the Federal Republic of Germany.

For the processing of copper-containing raw materials, both pyro- and hydrometallurgical processes are used. In the total volume of copper production, pyrometallurgical methods account for about 85% of the world production of this metal. In the CIS, copper is obtained by the hydrometallurgical method only on a very small scale.

Pyrometallurgical technology provides for the processing of raw materials (ore or concentrate) into blister copper, followed by its mandatory refining. If we take into account that the bulk of copper ore or concentrate consists of copper and iron sulfides, as well as gangue minerals, then the ultimate goal of copper pyrometallurgy - the production of blister copper - is achieved through the almost complete removal of waste rock, iron and sulfur.

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Obtaining blister copper in industrial conditions can be carried out in several ways. The diagram shown in Fig. 1 shows that the removal of iron and sulfur by oxidation can be carried out in three (roasting, melting, converting), two (melting, converting) or one stage (melting for blister copper) [12].

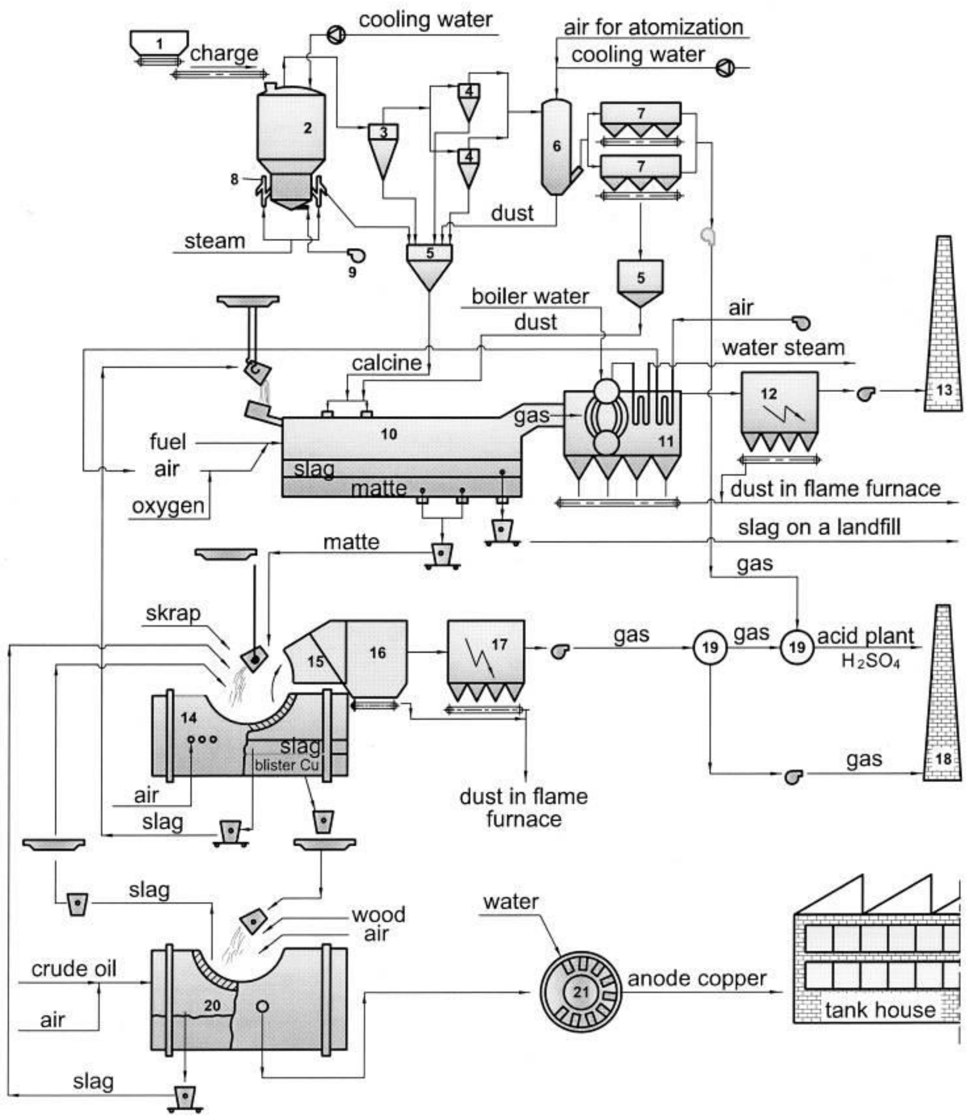

Fig.1. Basic technological scheme of pyrometallurgical production of copper from sulfide ores

The most common technology for producing copper to date provides for the mandatory use of the following metallurgical processes: smelting for matte, converting copper matte, fire and electrolytic refining of copper. In some cases, before smelting, an oxidative roasting of sulphide raw materials is carried out.

Matte melting can be carried out in a reducing, neutral or oxidizing atmosphere. In the first two cases, it is impossible to regulate the degree of desulfurization, and the content of copper in the mattes will slightly differ from its content in the initial charge.

Under the conditions of oxidative smelting, mattes of any given composition can be obtained. This is achieved by oxidizing mainly iron sulfides, followed by slagging of its oxides.

An increase in the degree of desulfurization by any means always leads to the enrichment of the matte with the base metal, and, consequently, to a decrease in its amount.

There are many varieties of smelting copper ores and concentrates, differing in technological features and hardware design. The most widespread method of smelting for matte in copper today is smelting in reverberatory furnaces. A close analogue of reflective smelting is smelting in electric (ore-thermal) furnaces. Until now, the oldest method of extracting copper from ores - smelting in shaft furnaces, has retained its practical significance.

The listed methods of melting for matte, despite their widespread use, do not meet modern requirements and require replacement. The main direction in the development of the technology for the processing of sulphide raw materials is the development of new, more modern and more economical technological schemes based on autogenous processes. The introduction of autogenous processes into the practice of metallurgy of heavy non-ferrous metals, including the production of copper, makes it possible to simplify the technology by combining the processes of roasting, melting into matte and partially or completely the conversion process in one technological cycle. This makes it possible to increase the complexity of the use of raw materials, completely eliminate or drastically reduce fuel consumption, improve many technical and economic indicators and prevent environmental pollution with harmful substances.

The raw material for the production of blister copper is sulphide copper concentrate, copper cakes of the zinc plant, cement copper from the heap leaching section. Together with copper raw materials, gold-containing concentrates and, in a small amount, other materials containing precious metals (molybdenum cakes, sands of the CEP, concentrate of the gold section) are processed. The smelting fluxes are limestone and quartz ore.

4. CHARGE PREPARATION

Charge Sulfide copper concentrate complies with GOST 48-77-74 grades KM 6 and KM 7.

Copper concentrate is composed of the following minerals: chalcopyrite, chalcocite and pyrite. Copper in minerals is distributed between chalcopyrite and chalcocite as 9:1. The moisture content in dried concentrates should not exceed - 6%, the concentrate should contain at least 80% of particles of class minus 74 microns (200 mesh).

Before being used in the production of blister copper, the concentrate is analyzed for chemical composition in accordance with GOST 15934.0-70-GOST 15934, 17-70, the copper content must not be lower than the one approved according to the plan.

Concentrate is supplied to the metallurgical shop via a belt conveyor system. To ensure the rhythmic operation of the workshop, the warehouse of the filtering and sagging department of the CEP must have a remainder of concentrates of at least 3000 tons.

Copper cake, zinc production, corresponds to TU 48-6-61-77, moisture content for copper cake should be no more than - 30%. Before being used in production, the cake is subjected to testing and chemical analysis for the content of copper and precious metals, the copper content must be at least 45%. Copper cake is delivered to the CEP in a special tank by road and, together with copper concentrate, is subjected to thickening, dehydration, filtration and drying.

Flotation gold concentrate corresponds to TU-48-16-6-75 and has the following chemical composition and moisture content:

Content				Humidity is not more,%
Gold, not less, g / t	Impurities no more,%			
	Arsenic	Antimony	Alumina	
20	2	0,3	10	6

Gold-bearing concentrate is supplied to the Refinery by road and is subject to control weighing and testing. Before feeding the gold-bearing concentrate for processing, it is mixed with copper concentrate in the FSO compartments.

Preparation for processing of the concentrate of the gold section is carried out similarly to the copper cake of zinc production, and the molybdenum cakes and sands of the copper enrichment plant (CEP) - to the gold-containing concentrate.

Flux limestone of the Mirabad deposit, for copper production, meets technical specifications TU-48-7-2-76, CaO content is not less than 48%, moisture content is 2.5%, particle size is up to 8 mm.

Limestone is delivered to the metallurgical shop in a batch in dump cars with the acceptance of the quantity and quality of the Quality Control Department. A batch is considered to be a daily supply of limestone. The irreducible stock of limestone in the workshop must be at least 200 tons. Quartz flux ore used for semerizing copper mattes, as well as in the charge of reflective smelting and EFP smelting, must comply with TU-48-07-26-76.

Before being used in the production of blister copper, fluxed quartz ore is analyzed for the content of components: alumina, silica and precious metals. The number of pieces less than the lower size limit of the established standard for the converter class is allowed no more than 10%.

Quartz flux ores are supplied by rail or road. Converter grade quartz fluxes are received in the silos of the crushing and charge section, and of the reflective class - in the compartments of the quartz crushing section.

Part of the converter grade quartz fluxes is unloaded to the flux ore warehouse. The irreducible stock of ore in the warehouse must be at least 20 thousand tons.

The chemical composition of quartz ore, the size of the classes and grades must meet the following requirements:

class and grade	Content, in%				
	silica, not less	alumina, no more	arsenic, no more	antimony, no more	size, mm
Reverberatory class, grade 2	65	10	0,7	0,2	0 - 6
Converter grade grade 2	65	10	0,7	0,2	6 – 35

The raw material for the production of anode copper is blister copper of our own production and partially imported copper from other plants, as well as the remains of the anodes of the copper electrolysis workshop. Imported blister copper, both in size and in chemical composition, must comply with the industry standard GOST - 48 - 33 - 72.

5. Finishing copper materials

Blister copper of our own production is transported to the anode furnaces by an electric bridge crane. Copper is transferred by metallurgical ladles in a molten state.

Imported blister copper from the warehouse of imported raw materials is supplied to the workshop by in-plant transport. The irreducible stock of imported blister copper must be at least 500 tons.

The anode residues of the copper electrolysis shop must be well washed from sludge and free from moisture residues. The remains of the anode scrap are transported to the workshop by in-plant transport to scoops on special trolleys. Anode residues should not accumulate in the shop.

The raw material for the production of copper ingots (wirebars) is cathode copper, recycled materials of wirebar processing and copper wire rod workshop and partially imported cathode copper. Cathode copper must comply with GOST 546 - 67 grade MO and chemical composition GOST 859-78.

Cathode copper should have a dense structure, should not be brittle and break from shock during overloading and transportation, and should be accepted by the Quality Control Department.

Imported cathode copper arrives at the plant in railway cars and is unloaded at the finished product warehouse.

All cathode copper and recycled materials are transported to the metallurgical shop on special trolleys.

The irreducible stock of cathode copper for the production of copper ingots must be at least 350 tons (the rate of one heat).

The raw material for the production of granules is the copper cathode of the regenerative baths, which corresponds to GOST 546-67 and partially recycled materials of the wirebar furnace.

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