Refining of blister copper

U. P. MULLICK

CRUDE blister produced in smelting process may contain impurities like Fe, S, O, Zn, Ni, As, Sb.

The average compositions of blisters from primary and secondary raw materials are given in Table I.

TABLE I Average compositions of blisters

Copper and impurities in blister	Percentage	
	Primary copper	Secondary copper
Cu	98·6 — 99·3	97·5 — 98·2
Fe	0·01 — 0·04	up to 0·05
Ni	0·005 — 0·6	0·3 — 1·0
S	0·05 — 0·1	—
Zn	0·01 — 0·05	up to 0·5
As	0·01 — 0·1	—
Sb	0·01 — 0·1	up to 0·3

Besides the above, blister copper may contain impurities like lead, selenium, tellurium, gold, silver and dissolved gases, which even present in minute quantities, may affect the mechanical properties, specially ductility. All impurities except the precious metals, also reduce the electrical conductivity.

Gold and silver contents, which may be 100 and 2000 grammes per ton respectively, are recovered during the refining process.

Commercial copper

Commercial copper as per USSR grading are in 5 grades : M_o, M_1, M_2, M_3, M_4.

Mr U. P. Mullick, President, Institute of Consulting Engineers, India Society of Engineers, Indian Interplanetary Society, Principal, Hope Johnstone and Son, Calcutta.

SYNOPSIS

The paper reviews the techniques of fire refining and electrolytic refining of blister copper.

The maximum impurities and minimum copper contents allowable are given in Table II.

Refining of copper

Refining processes

To obtain the commercial grades it is therefore necessary to refine the crude blister by refining processes. The two processes involved are (1) Fire refining process, and (2) Electrolytic process. The second process is normally taken up with the product of the first process.

Comparative merits of the two processes

Fire refining produces M_3 and M_4 grades, and is unable to recover bismusth and the precious metals.

Electrolytic refining however removes any gold and silver contained as impurities, and produces refined copper of highest purity. The capital outlay is higher, but this is fully compensated by the gold and silver recovered.

Due to high purity of copper obtained, a large proportion of refined copper is obtained electrolytically. To reduce refinery costs, crude blister is however first fire-refined, and then treated electrolytically.

Slabs and anodes

Crude blister in slabs is fire-refined, and then cast into anodes for electrolytic refining. The electrolytically refined copper may be treated to end-product as wire bars.

The waste of fire-refining, high in copper, is treated again with matte in converters.

Fire refining

Slabs of copper are charged into the furnace by means of a paddle mounted on the cab of an overhead E.O.T. crane. The paddle can take as much as 3·5 tons of

TABLE II Chemical compositions of commercial copper grades

Copper grade	Min. copper content	Maximum impurities %										
		Bi	Sb	As	Fe	Ni	Pb	Sn	S	O	Zn	Total
M_0	99·95	0·002	0·002	0·002	0·005	0·002	0·005	0·002	0·005	0·02	0·005	0·05
M_1	99·90	0·002	0·002	0·002	0·005	0·002	0·005	0·002	0·005	0·08	0·005	0·10
M_2	99·70	0·002	0·005	0·01	0·05	0·20	0·01	0·05	0·01	0·10	*	0·30
M_3	99·50	0·003	0·05	0·05	0·05	0·20	0·05	0·05	0·01	0·10	*	0·50
M_4	99·00	0·005	0·20	0·20	0·10	*	0·30	*	0·02	0·15	*	0·10

*denotes cases where particular impurity may be as high as difference between total impurity and sum of the remaining impurities.

copper slabs at a time. Molten copper blister is charged by means of an E.O.T. crane operated ladle or mixer truck of holding capacity up to 70 tons of copper.

After charging, the fire is raised to maximum. The copper rapidly melts. The impurities are oxidised by air-blown through-lined iron pipes 20 to 40 mm diameter inserted in molten copper. Oxidisation takes place at the surface of the rising air bubbles.

The equation for oxidisation of copper is :

$$4\ Cu + O_2 = 2\ Cu_2O$$

Cu_2O quickly spreads out throughout the molten metal. The general equation for oxidation of the impurities is :

$$M + Cu_2O = MO + 2\ Cu + Q\ Kcal$$
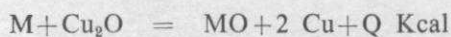
The oxides of the impurities float up to the surface, forming slag. Much of the remaining impurities are withdrawn by skimming of the slag.

The equilibrium in oxidation is reached when the dissociation pressure of Cu_2O and of the impurities are equal :

$$pO_2\ (Cu_2O) = pO_2\ (M.O)$$

The dissociation pressure of Cu_2O is given below :

TABLE III Dissociation pressure of Cu_2O

Temp. °C	...	P
1084	...	10^{-6} atm
1200	...	10^{-4} atm

The dissociation pressure of oxides of impurities increase with decreasing concentration of the impurities in the copper, and with increasing concentration of the oxides in the slag :

$$pO_2\ (M.O) = k.\ \frac{a^2\ (M.O)}{a^2\ (M)}$$

Sequence of oxidability

The sequence of oxidation of the impurities depends not only on oxidation of Cu_2O, but also on the presence of other impurities in the molten bath. This is expressed as :

$$M' + M''O = M'O + M''$$

Roughly oxidability has been found to vary with decreasing affinity for oxygen, and the metals of the impurities oxide in the following order :

Al, Si, Mn, Zn, Sn, Fe, Ni, As, Sb, Pb, Bi.

In a refining process the impurities in reality burn out simultaneously at different rates. This rate depends not only on affinity for oxygen, but also on concentration ratios, slagging ability rate of oxidation, volatility, etc.

The sulphur present in the copper is oxidised as :

$$Cu_2S + 2\ Cu_2O = 6\ Cu + SO_2$$
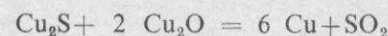
Fire-refining fails to remove the precious metals, because they have affinity to oxygen. Bismuth, selenium and tellurium are not eliminated and persist in the fire-refined copper as Cu_2Se, Cu_2Te, etc.

Poling of copper

After the metal in the bath is skimmed clean, the green

pole is inserted in the bath to agitate the metal and drive out the sulphur held in solution as well the dissolved sulphides and the other gases. This poling down operation leaves up to 12% Cu_2O.

A second operation of poling is also done to improve plasticity of the metal. Here, coke or charcoal is spread on the bath surface. The pole is then inserted in the bath to reduce Cu_2O to Cu, under equation :

$$4\ Cu_2O + CH_4 = CO_2 + 2H_2O + 8Cu$$

Gas rises to the surface, and Cu_2O is reduced to a trace content of 0.3-0.5%.

The slag is skimmed off prior to poling.

After the poling is completed the copper is ready for casting.

Reverbatory furnace

The reverberatory furnace in which fire refining is conducted is similar in design to the reverberatory furnace used for smelting of copper ore. The sizes are in capacities up to 400 tons of copper. The furnace length is 12 to 15 metres, width 5 meters and depth about one metre.

The hearth is constructed of silica or magnesite bricks encased in cast iron plates, and set up on pillars. This prevents leakage. The hearth bottom in acid furnace is fritted with a mixture of finely divided quartz and copper mill-scale. The basic furnace used for the purpose employs magnesite, limestone, quartz and iron mill-scale.

The walls of magnesite or high alumina fire bricks are also faced with cast iron plates on the outside and stiffened with I beams. The charging holes have lifting doors. The roof is of arch type made with silica bricks.

Fuel

Fuel used is either fuel oil, natural gas or pulverised coal. Large furnaces are fired with both fuel and air in a preset ratio. Fuel consumption is 10-11% of the charge weight.

Time

It takes 12 to 16 hours to refine a charge of blister copper, the operation involved being charging, melting, oxidising poling, and casting in the serial order.

Draw off

The metal is drawn off the side or end of the furnace through tapping slot. During working the slot is closed with a plug of fireclay. During casting, the plug is sawed off from the top sufficiently for the fire refined copper to flow over the edge to a launder or ladle. The metal is then cast into anodes for use in electrolytic process. The size of an anode is 914 mm ×914 m×998 overall height to hanger support.

Casting machines

There are several types of casting machines, one type being Walker Wheel. The moulds of cast iron or copper are located on the circumference of a wheel turned slowly by a motor. The moulds on Walker Wheel are brought under the furnace ladle. They are stopped, automatically filled and moved on for bringing the next mould under the ladle, and so on. Water is sprayed to cool the cast anodes and mould. After transfer to a boost filled with running water, the anodes cool off to room temperature and then stacked away.

Slag

The slag from fire refining in acid furnace contains 15-40% SiO_2, 5-10% Fe as silicates and ferrites and oxides of zinc, nickel, etc. The copper content of slag is 35-45% remainder as metal drops.

The slag from fire refining in basic furnace contains 50-75% copper, and usually not over 5-10% SiO_2.

The slag is treated again in small blast furnace for secondary production of matte and waste slag. It is also used in converters with the matte.

Electrolytic refining

The copper anodes from fire refining are placed in a tank filled with solution of copper sulphate to which is added some sulphuric acid as electrolyte. The cathodes are pure copper starting sheets suspended between the anodes. Anodes are connected to the positive and cathodes to negative terminals of the source of current. On passing of the current through the electrolyte, the anode is dissolved, anode copper passes into solution and the copper ions discharge at the cathodes forming deposits of the pure metal.

Anodes and cathodes

Anodes are usually 40-50 mm thick and 250-320 kg in weight.

Starting sheets are usually made by depositing copper on rolled and stretched copper blanks in an electrolytic bath. The blanks are first coated with a mixture of graphite and oil, to allow the sheets of copper deposit to be readily stripped from the blank. The blank is held 24 hours in the bath and the sheets then stripped and removed are 0.2-0.3 mm thick.

Starting sheets are 30-50 mm wider and longer than the anodes. The anodes and cathodes are hung by lugs from copper bars which also conduct the current.

Tanks

The refining tanks have sizes determined by the number of plates used. Typical sizes are 3 to 5 metres long, 1 to 1.1 metre wide (12 to 13 cm wider than the starting sheets) and 1 to 1.3 metres deep.

The tanks are made of either wood or concrete, and are set on reinforced concrete piers high enough to permit inspection of bottom for leaks and repair. The

tank and piers are separated by glass or porcelain insulation to prevent current leakage.

Walls of the tanks are lagged either by P. V. C. sheets or lead sheets to protect from scouring action of the acid in electrolyte.

Tanks may be gauged in cascades of upto 40 to 50, or more, for economy in floor space and labour requirements.

Current density

As current density or current per unit area at the anode increases, the petential at anode rises due to polarisation. This is because the copper ions are produced at the anode at a higher rate than they are released into solution through slow diffusion.

Silver precipitating

Silver dissolution is prevented by adding some Na Cl, to the electrolyte. The silver is precipitated as Ag Cl.

Impurities

The impurities of sulphur, selenium and tellurium are present in the copper as compounds like Cu_2R, (where $R=S$, or Se, or Te) pass into the slime.

The impurities do not deposit at the cathode, being of lower discharge potential than copper and remain dissolved in solution. These are Zn, Fe, Bi, As, Ni, Sn, Sb of anode copper.

Voltage

The total voltage and various voltages required for operation of a copper refining electrolytic tank, according to A. Grayev and O. Yesin, are given below :

TABLE IV Approximate requirement in voltage for electrolytic copper refining

Resistance	Voltage drop	
	V	%
Electrolyte	0·23850	80·5
Counter emf.	0·01597	5·3
Anode slime	0·02025	6·7
Cathode and anode	0·00337	1·1
Contacts	0·01829	6·4
Total	0·29638	100·0

Current density

The optimum current density for various % of copper content of anode is as given under :

TABLE V Optimum current density for different copper contents of anode

Copper content of anode %	Optimum current density A/sqm.
98–99	100–120
99·5 –99·8	200–400

Anodes and starting sheets are placed in the electrolytic tank by overhead crane. The anodes are left in the tank for 25 to 30 days, till they are fully dissolved depending on their weight and refining condition.

Scrap

Average anode produces about 15% of its weight as scrap. The scrap anodes taken from the tank are washed and sent back to anode furnace for remelting.

Slime

Slime produced by dissolution of anode settles at the bottom of the tank mostly and also remains partly dissolved in the electrolyte. At end of run, the accumulated slime is flushed into a launder, which takes it to a slime tank. Here coarse pieces of metallic copper are removed, and the slime is then pumped for recovery of precious metals.

TABLE VI Average composition of slime (%)

Slime	Cu	Pb	Bi	Sb	As	Ag	Au	Se	Te
Settled	14·3	2·4	0·5	5·5	2·7	35·0	0·6	5·7	2·7
Suspended	0·6	2·8	0·5	48·5	17·8	0·04	—	—	—

Nodules on starting sheets

Due to dense deposit formation of copper on starting sheets, irregularities of surface appears with fast formation of nodules. This formation is usually prevented by adding surface active materials like joiner's glue, gelatine, tannin or wood pulp waste.

Cathode

The cathodes are drawn every 5 to 12 days. They are removed by overhead crane, taken to a wash box, where they are cleaned by spraying hot water. They are then either fire refined in reverberatories, or in induction furnaces.

References

Sevryukov, N. Kuzmin, B. and Chelishchev, Y. : General Metallurgy, Translation from Russian by B. Kuznetsov, Moscow, The metallurgy of non-ferrous metals, pp. 176-190.

APPENDIX

In the Indian Copper Corporation Ltd, Maubhandar Plants near Mosaboni Mines and Ghatsila, 35 004 dry tonnes of concentrates of an average value of 25·965% copper were produced in 1967.

During this period 8 718 tonnes of fire refined copper were produced from concentrates. The overall recovery from ore to refined copper was 92·122%.

In the electrolytic refinery, 5 112 tonnes of wire bars were produced in 1967.

Average selling prices for 1967 have been :

Fire refined copper ingots   Rs. 6 856·63 per tonne
Electrolytic copper wire bars Rs. 7 416·70 per tonne

The overall operating cost to produce one tonne of electrolytic copper wire bar in 1967 has been Rs. 5 656·0.

Total power requirements have been 50 691 343 kWh.

In the expansion programme for the Flash Smelter Project, the design for the plant has come from Finland (Indian Copper Corporation Ltd. Directors' Report for the year ended 31-3-1967).

Discussions

Mr L. N. Misra (Khetri Copper Project) : We would like to know the best and most economical method of melting the cathode to produce electrolytic tough pitch copper, under Indian conditions.

Mr U. P. Mullick (Author) : Cathodes being pure copper starting sheets, suspended between the anodes, are drawn every 5 to 12 days. A longer run offers no advantage due to the formation of nodules causing short circuits which in turn reduce current efficiency.

The cathodes are removed by an overhead crane and taken to a wash box. Then they are either fire-refined in reverberatories or in induction electric furnaces.

The starting sheets are made by depositing copper on rolled and stretched copper blanks in an electrolytic bath. After thorough cleaning and prior to depositing, the blanks are coated with a mixture of graphite and oil. This is for the purpose of allowing the sheets of copper deposit to be readily stripped from the blanks. After 24 hours, the blanks are withdrawn and one sheet from each side is removed, 0·2 to 0·3 mm thick.

As for anodes, they are left in the electrolytic tank for 25 to 30 days, until they are fully dissolved, depending upon their weight and the refining conditions. Average anode copper produces about 15 per cent of its weight in scrap. The scrap anodes are drawn from the tank, washed and sent back to the anode furnace for re-melting.