

REFINING OF BLISTER COPPER (*)

U.P. Mullick
President, Institute of Consulting
Engineers, Calcutta

Crude blister produced in smelting furnace may contain impurities like Fe, S, O, Zn, Ni, As, Sb, which are present in traces in primary copper, and slightly higher in secondary copper. Percentage of copper in primary is 98.6-99.3, and in secondary 97.5-98.2. Gold and silver presence are in ranges of 100 and 2000 grammes per ton respectively.

Commercial grades of copper according to USSR practice, are in 5 ranges: M₀, M₁, M₂, M₃, M₄, with copper contents varying from 99.95%, 99.90%, 99.70%, 99.50% and 99.0% respectively. Fire refining produces M₃ and M₄ grades, Crude blister in slabs, is generally, to reduce costs, first fire refined and cast into anodes, and the anodes are then electrolytically refined to higher grades, and treated to end products as refined copper wire bars. The waste of fire refined blister copper, is high in copper, and this is re-treated with matte in converters.

Fire refining is conducted in reverberatory furnaces in capacities upto 400 tons of copper. Fuel used is either fuel oil, natural gas or pulverised coal, the fuel consumption being 10-11% of the charge weight, and time taken 12 to 16 hours for refining a charge of blister copper. The blister copper slabs are charged by EOT cranes 70 tons at a time. Air is blown through 20 to 40 mm diameter mined iron pipes.

The impurities are oxidized under equation $M + \frac{1}{2} Cu_2O = MO + \frac{1}{2} Cu + Q$ kcal. The dissociation pressure of Cu_2O varies from 10^{-6} atm. at $1084^\circ C$ to 10^{-4} atm. at $1200^\circ C$. The dissociation pressure of oxides of impurities increase with increasing concentration of the oxides in the slag, and decreasing concentration of impurities in Copper.

(*) Paper for presentation at the Symposium on "Recent Developments in Non-Ferrous Metals' Technology" - 4th to 7th December, 1968, Jamshedpur.

Not to be reproduced in any media (C) National Metallurgical Laboratory, Jamshedpur.

Again oxidability has been found to vary with decreasing affinity for oxygen. The metals of the impurities oxide in the following order: Al, S, Mn, Zn, Sn, Fe, Ni, As, Sb, Pb, Bi. Sulphur present in copper is oxidised as $\text{Cu}_2\text{S} + 2 \text{Cu}_2\text{O} = 6 \text{Cu} + \text{SO}_2$.

Fire refining fails to remove the precious metals, because they have affinity for oxygen. Thus Bi, Se, Te are not eliminated, remaining in fire refined copper as Cu_2Se , Cu_2Te etc.

In fire refining, the slag is skimmed off prior to poling. Of the two stages of poling, by green poling the metal is first agitated, and sulphur held in solution is driven off. Under second poling operation, coke and charcoal are used on surface of bath and Cu_2O is reduced to Cu, and thereby plasticity improved. After the draw off, casting machines of the Walker Wheel types are used to cast the anodes. The copper content of slag from fire refining in acid furnace is 35-45%, and in basic furnace 50-75%. In acid furnace slags contain 15-40% SiO_2 and 5-10% Fe, and in basic furnaces 5-10% only SiO_2 . The slag is retreated in small blast furnace for secondary production of matte and waste slag and in converter with the matte.

In electrolytic refining, the refining tanks used are of concrete or wood, and well insulated, and are 3 to 5 metres long, 1 to 1.1 metres wide, and 1 to 1.3 metres deep, and are oftened ganged in cascade formation. The anodes weigh 250-320 kg in weight, and are 40-50 mm thick, and are handled by cranes.

As current density at anode increases, the potential of anode rises due to polarisation. Nerst's equation for potential rise at anode is $E_{\text{Cu}} = E^{\circ} + \frac{RT}{nF} \ln a. \text{Cu}^{2+}$.

Silver dissolution is prevented by adding NaCl to electrolyte. The silver is precipitated as AgCl. The impurities of S, Se, Te present in Copper phases into slime. The impurities of anode copper, Zn, Fe, Bi, As, Ni, Tin, (Sn) Sb remain dissolved in solution.

Percentage of voltage drop due to resistance is 80.3% in electrolyte, 5.3% in counter e.m.f., 6.7% in anode slime, 1.1% in cathode and anode, and 6.4% in contacts. Optimum current density (A/Sq.m) is 100-120 for 98-99% purity copper, and 200-400 for 99.5-99.8% purity copper.

In the composition of slime, for settled and suspended slime, Cu is 14.3% in former, and 0.6% in latter, while Ag is as high as 35.0% in former and 0.04% only in latter. Again Sb and As are 5.5% and 2.7% in former, but as high as 48.5% and 17.8% in latter.

Nodule formations on starting sheets are prevented by adding surface acting materials to electrolyte, like joiners' glue, gelatine tannin, and wood pulp waste. Cathodes are drawn every 5 to 12 days, and cleaned by spraying hot water, and again fire refined.

/Ahmed