United States Patent Office

2,792,342

Patented May 14, 1957

2,792,342

ELECTROWINNING OF COPPER

Sidney B. Tuwiner, Baldwin, N. Y., assignor to Phelps Dodge Corporation, New York, N. Y., a corporation of New York

Application January 26, 1956, Serial No. 561,407

14 Claims. (Cl. 204—108)

This invention relates to electrowinning of copper.

To recover refined copper from precipitated or cement copper, shotted blister copper, copper-rich alloys, copper-rich matte or from ores or concentrates containing chalcocite, it is advantageous to have a process which comprises the leaching of such materials with an acid sulfate solution followed by the electrowinning of the copper as cathodes. Two methods of leaching such copper-containing materials with acid sulfate solutions are known. In one of these methods the copper and acid are brought in contact with air, the oxygen of which converts the metallic copper and sulfuric acid into dissolved copper sulfate. In the other method a dissolved oxidizing agent—commonly, ferric sulfate—is employed to convert the metallic copper into the sulfate. The reactions which occur in these two operations are represented respectively by the following equations:

$$Cu+H_2SO_4+\tfrac{1}{2}O_2\rightarrow CuSO_4+H_2O$$

$$Cu+Fe_2(SO_4)_3\rightarrow CuSO_4+2FeSO_4$$

In the electrowinning of copper these reactions are caused to be reversed by the expenditure of electrical energy. In the first mentioned process the electrolysis comprises the deposition of refined metallic copper at the cathode while generating oxygen at the anode. This serves to regenerate the solution by removal of the copper and restoring an equivalent quantity of sulfuric acid for further leaching. In the second mentioned process copper is deposited at the cathode as in the first process but the anode reaction reoxidizes the ferrous sulfate back to ferric sulfate, thereby regenerating the composition to that prevailing prior to leaching.

In either of these two processes the solution may be recycled indefinitely but for the accumulation of impurities, or but for side reactions which may occur and which may alter the composition of the solutions from that which is most desirable for the process.

A principle object of my invention is the recovery at minimum expenditure of electrical energy of copper of high purity in compact physical form from scrap materials containing metallic copper, from copper-rich alloys, from shotted blister copper, from copper-rich matte, chalcocite, or from ores, concentrates, or other similar materials, containing copper. I achieve this by means of a cyclic process in which ferric sulfate, the leaching reagent, is regenerated to ferrous sulfate at the anode with a current efficiency equal to that of the cathode copper deposition.

I have discovered that by a combination of electrolyte composition, temperature, anode material and structure, and current density, I can so conduct the process of electrolytic deposition and regeneration that the cell voltage remains below the minimum for the generation at the anodes of oxygen and sulphuric acid. Also, in the practice of my process the expenditure of electrical energy for the copper electrowinning may be reduced to less than one-half that which has heretofore been required in commercial practice and more than twice the production rate

of cathode copper per unit of cell volume may be obtained.

Known commercial processes for copper electrowinning are operated at relatively low current densities of 10 or 12 amps./sq. ft. of cathode area at low cathode current efficiencies of 70 or 75%, and at high cell voltages of two volts or more. Materials heretofore used for anode construction include antimonial lead, complex cast copper alloys such as "Chilex" and high silicon cast irons. Each of these materials resists corrosion by the formation of a protective film at the surface of the anodes during operation. The electrical resistance of this film is responsible for the relatively high cell voltage obtained when using anodes composed of these materials.

I have discovered that a corrosion resistant metal, such as austenitic stainless steel, may be used for the construction of insoluble anodes in the electrowinning of copper and better results are obtained provided that the wetted surface area of the anodes within its peripheral dimensions be extended, preferably by the use of a grid so that the area of the surface exposed to the electrolyte solution is substantially greater than the area of a planar surface having the same peripheral dimensions. Preferably the effective wetted area of each anode should be at least two times the area of a planar surface enclosed by a corresponding periphery. That is, the anode may be in the form of a grid, preferably a foraminous grid, and preferably the effective wetted area of the anode when submerged should be more than two times what the effective wetted area would be if the anode were not in the form of a grid but had flat planar surfaces and the same peripheral dimensions. The electrolyte, in addition to the usual components, such as copper sulfate, and sulfates of other metals in the material being leached, should contain at least 20 gms./l. of total iron as ferric and ferrous sulfate.

The electrolyte temperature in the electrowinning cells should exceed 110° F. and should be preferably within the range of 135–165° F. The circulation of electrolyte should be such as to maintain a concentration of iron as ferric at less than 25 gms. per liter in the solution leaving the electrowinning tank. Preferably, the concentration of iron, as ferric sulfate, in the electrolyte entering the electrowinning tank should be no greater than 10 gms./l. Cell voltage should be from 0.85 to 1.2 volts. This will suffice to generate the required minimum of current while avoiding the liberation of oxygen at the anodes and the corrosion of them. Cathode current density may be in the range of 10 to 25 amps./sq. ft. but preferably should be in the range of 15 to 20 amps./sq. ft.

I prefer to operate the cells in electrowinning tanks similar to those used in standard multiple system copper refining. As anodes I prefer to use an assembly made of two closely spaced layers of stainless steel screen held by, or fastened to, one or more copper bars which support the screens mechanically and join them electrically. A suitable screen material is mesh screen made from 0.081 inch diameter austenitic stainless steel wire, woven to have six square openings per linear inch, viz, thirty-six per square inch.

As one example illustrating the method of my invention, five cathodes consisting of copper starting sheets 16 inches wide and 16 inches immersed depth were hung in a rectangular stainless steel tank having a capacity of 35 gallons with a spacing of 4 inches. Between each two of the cathodes were hung anodes consisting of two layers of 6 mesh, Type 316 austenitic stainless steel wire mesh. Both anodes and cathodes were joined to supporting copper bars which rested upon triangular bus bars, the anodes resting on a bus bar at one side, the cathodes resting on a bus bar on the other. The bus bars were connected electrically with a generator which furnished a current of 275 amperes. Liquor was circulated at the rate of ½ gal.