

1

2,981,603

**RECOVERY OF SELENIUM FROM ELECTROLYTIC  
COPPER REFINERY SLIMES****Sidney B. Tuwiner, Baldwin, N.Y., assignor to Phelps  
Dodge Corporation, New York, N.Y., a corporation  
of New York****No Drawing. Filed Aug. 26, 1957, Ser. No. 680,393****3 Claims. (Cl. 23—209)**

This invention relates broadly to an improved method for recovering selenium values from anode slimes produced in the electrolytic refining of copper and particularly to a method for recovering such values in the form of a sludge of elemental selenium of high purity which is readily convertible to electronics grade selenium.

In the electrolytic refining of copper an electrolytic cell is provided with an anode of impure copper, a cathode of substantially pure copper and an electrolyte composed of copper sulfate and sulfuric acid. When a direct electrical current is passed between the electrodes in such a cell the impure copper anode dissolves in the electrolyte and pure copper is plated onto the cathode. During the refining operation a sludge or slime is deposited in the bottom of the cell. This slime is composed of impurities from the copper anode including as a rule significant amounts of selenium, tellurium, copper, lead, silica, gold and silver and lesser amounts of nickel, tin, arsenic and antimony. The selenium and tellurium content of the anode slimes occurs chiefly in the form of the selenides and tellurides of copper and the noble metals. Various methods of recovering the selenium, tellurium and noble metal values of anode slimes have been employed.

One such method is described in U.S. Patent 2,378,824 to Betterton et al. In the Betterton et al. process anode slimes are treated to convert the selenium content to a water soluble form by admixing the slimes with sodium carbonate and water to form a thick slurry or paste and thereafter heating the resulting mixture at a temperature sufficient to drive off water and yield a baked but unfused mass. The baking operation is carried out at a temperature in the range from 800–850° F. for a period of two to three hours, the roasted product is leached with water, the resulting leach liquor acidified with sulfuric acid, and the dissolved selenium precipitated with sulfur dioxide gas. This process although satisfactory for laboratory scale operations such as those described in the specific examples in the Betterton et al. patent is uneconomic and inefficient particularly when applied to the recovery of selenium values from anode slimes on a commercial scale.

It is important for efficiency and economy in the roasting of anode slimes with soda ash in order to convert the selenium content of such slimes to a water soluble form that the roasting operation be conducted at as high a temperature as feasible in order to obtain substantially complete oxidation of the oxidizable constituents of the slimes in the shortest possible time. Fusion of the slimes-soda ash mass must be avoided however since it prevents access of oxidizing gases to all portions of the mixture thus causing incomplete oxidation and consequent reduction in selenium recovery efficiency. The roasting operation should, therefore, be conducted at a temperature close to but slightly below the temperature of incipient fusion of the slimes-soda ash mixture for maximum efficiency. The temperature of incipient fusion of suitable slimes-soda ash mixtures is generally about 887° F.,

2

which is above the roasting temperatures recommended by Betterton et al. The chemical reactions which take place during the roasting operation are highly exothermic and, if allowed to proceed uncontrolled, heat the mixture to incandescence with consequent fusion and loss of selenium values. It is necessary, therefore, except in relatively small scale operations, to provide means for the removal of large quantities of heat generated by the oxidation reactions during the roasting process in order to maintain the optimum roasting temperature. The anode slimes-soda ash roasting procedures currently employed in the art are not carried out at the most efficient roasting temperatures due to the fact that it is extremely difficult to maintain the roasting temperature within the desired range just below the temperature of incipient fusion by known techniques.

The Betterton et al. process is also disadvantageous if it is desired to recover selenium in a form which is readily convertible to elemental selenium sufficiently pure to meet the specifications of the electronics industry which, due to the increased use of selenium rectifiers, has developed a large demand for high grade selenium in recent years. The selenium sludge obtained by the roasting, leaching and precipitation techniques of the Betterton et al. process normally contains impurities such as tellurium which cannot be tolerated in electronics grade selenium and which are not removed from the selenium sludge by conventional distillation procedures.

Therefore, it is an object of the present invention to provide an improved method for the recovery of selenium values from anode slimes on a commercial scale which includes roasting such slimes with soda ash at a temperature close to but below the temperature of incipient fusion of the slimes-soda ash mixture in order to convert the selenium values to a soluble form in the most efficient and expeditious manner.

It is another object of the present invention to provide an improved method for the recovery of selenium values from anode slimes whereby the selenium is recovered in a form which can be converted to highly pure electronics grade selenium by a simple distillation operation.

It is a further object of the invention to provide an improved anode slimes roasting technique which prevents loss of selenium values due to localized fusion.

It is an additional object of the invention to provide a method of roasting anode slimes which eliminates loss of significant amounts of selenium, gold and silver due to dusting during the roasting operation.

It is a further object of the invention to provide an improved anode slimes roasting operation which assures substantially complete oxidation of the oxidizable constituents of the slimes in the shortest possible time without exceeding the temperature of incipient fusion.

It is a particular object of the invention to provide an improved roasting operation which assures maximum transformation of metallic selenides present in the anode slimes to water soluble alkali metal selenates while substantially avoiding the formation of alkali metal selenites.

It is a further object of the invention to provide a technique for removing tellurium and other impurities from a raw selenium-rich leach liquor obtained according to the invention prior to the precipitation of product selenium therefrom.

Briefly, these and other objects of the invention are attained by (1) performing a paste consisting of anode slimes, soda ash and water under controlled conditions to provide a macro-porous bed of micro-porous slimes-soda ash mixture in order to permit the circulation of air or other oxygen-containing gas through this material, (2) roasting the bed of preformed slimes-soda ash mixture at a temperature close to but below the temperature of incipient fusion of the mixture by circulating hot oxidiz-