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RECOVERY OF TELLURIUM

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This invention relates to recovery of tellurium from anode slimes produced in the electrolytic refining of copper.

Speaking generally regarding 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 comprising a solution of copper sulfate and sulfuric acid. When a direct electrical current is passed between the anode and cathode in such a cell the impure copper 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 s chiefly in the form of the selenides and tellurides of copper, silver and gold.

This invention provides a method for recovery of the tellurium from the anode slimes, and more particularly to the separation of tellurium from certain residual products formed in the practice of certain steps in the process of separating the selenium content from the anode slimes.

In one method I have employed in recovering metal values, and more particularly, selenium, from anode slimes (described in my copending patent application Serial No. 680,393), the slimes are mixed with sodium carbonate to form a paste which is extruded and formed into a macro-porous bed of micro-porous masses. The macro-porous bed is dried and roasted at a temperature near to, but below the fusion temperature of the dried mixture of slimes and sodium carbonate. As a result of the roasting operation the selenium is oxidized to water-soluble state, metallic copper is oxidized to cupric oxide and metallic tellurium is oxidized to tellurous oxide and other lesser metals present in the slimes, such as arsenic, lead, and silica, are oxidized. The roasted product is treated with water. This forms a liquor in which the water-soluble selenium is dissolved and a residue (herein for convenience called a "first" residue) containing gold and silver and oxides of the metals present in the slimes. This slurry is filtered. The filtrate contains the selenium. The "first" residue, just mentioned, contains the gold and silver and oxides of tellurium, copper and other metals in minor amounts. The filtrate may be treated to recover the selenium as described in my said patent application. The "first" residue containing the tellurium and other above mentioned metals in oxide form is treated, in accordance with the present invention, for the recovery of tellurium.

The residue just mentioned, which may be in the form of filter cake, contains, in addition to tellurium in oxide form, all of the metals contained in the slime from the electrolytic copper refinery excepting only selenium which has been removed by a selenium recovery process, such, for example, as mentioned above. These metals in the "first" residue would include copper, present in the form

of cupric oxide as a result of the oxidizing roast which is a part of the selenium extraction process; tellurium in the form of tellurous oxide; and minor amounts of arsenic, antimony, lead and silica as oxides; and also the precious metals, gold and silver.

The purpose of roasting the slimes-sodium carbonate mixture in the selenium recovery process mentioned above, is not only to convert the selenium in the slimes to the water-soluble state, but also to oxidize metallic copper to cupric oxide and tellurium to tellurous oxide. Both of these metals are thereby rendered acid-soluble.

In accordance with the process of this invention, the "first" residue containing tellurium oxide, copper oxide, gold and silver, and minor amounts of oxides of other metals present in the slimes, is digested with sulfuric acid. This converts the copper and tellurium into sulfates. Preferably, the process is conducted in such a way that sulfuric acid is added to a slurry of the telluruim and copper-bearing material with agitation at a temperature of at least 160° F. With sufficient acid the dissolution of copper and tellurium is substantially completed within a period of an hour. The product of this acid digestion is filtered and this separates the liquor containing copper and tellurium in the form of sulfates from the solid residue which contains the precious metals and other values. This residue is herein, for convenience of description, called the "second" residue. The precious metals and other metal values may be recovered from this second residue by known methods. The filtered liquor containing the copper and tellurium in sulfate form is then treated with metallic copper, to form a tellurium-copper cementation product, sometimes referred to herein as the "third" residue. Shotted blister copper, copper wire, and other forms of copper presenting a large or extended surface area are suitable for this purpose. Preferably, finely divided copper powder is used. Under suitable conditions of temperature and agitation it reacts within a period of one hour to reduce the tellurium content of the acid liquor substantially completely, while precipitating finely divided metallis tellurium as a copper-tellurium cementation product. Small amounts of metallic silver which are sometimes dissolved with the copper and tellurium are precipitated with the metallic tellurium, and the acidic liquor is a solution of copper sulfate, substantially free of metallic impurities, and therefore is suitable for the production of copper sulfate. Sufficient metallic copper is added to react at least with all the tellurium present.

The cementation product after filtration and separation from the sulfate liquor is then treated for the separation and recovery of tellurium from the gold, silver and copper values. The filter cake or residue from the filtration step is charged into a suitable furnace and subjected to a smelting operation using sodium carbonate as a flux. Sodium or potassium hydroxide, sodium or potassium nitrate, or alkali or alkali-yielding compounds or materials may be used as the fluxing material. By subjecting the tellurium cementation product and at least an equivalent amount of soda flux to a smelting operation at a temperature of approximately 2200° F. under oxidizing conditions, there is a separation of the charge into two slag layers. The top layer of slag (herein for convenience referred to as the tellurium-containing slag layer) is composed of sodium tellurite dissolved in an excess of flux with only minor amounts of other values. The bottom slag layer is rich in copper, as cuprous oxide, and precious metals and also contains most of the selenium which had not theretofore been extracted in the initial process directed to extraction of selenium from the anode slimes; the cuprous oxide slag acting as a collector for the precious metals and also selenium, if present in the charge. The two layers may be drawn off separately.