Patented Dec. 8, 1942

2,304,197

UNITED STATES PATENT OFFICE

2,304,197

TIN RECOVERY PROCESS

William H. Osborn, New York, N. Y., assignor to Phelps Dodge Corporation, New York, N. Y., a corporation of New York

Application February 7, 1941, Serial No. 377,823

19 Claims. (Cl. 75—85)

This invention relates to the recovery of tin and more particularly to improvements in the procedures for the separation of tin from other metals commonly associated with it. In the description particular reference will be made to the recovery of tin from cassiterite ore or concentrates from Bolivia. However, the process as a whole and the various novel steps of the process are also applicable to the recovery or separation of tin from other ores or tin concentrates or from other sources and particularly sources in which tin is associated with a relatively large amount of iron and silicates.

Most ores and concentrates of tin, such as the concentrates produced in Bolivia, consist principally of the mineral cassiterite (a tin oxide having the formula SnO_2), oxides of iron such as hematite or combined iron silicates, and silica such as the mineral quartz or combined silicates. In addition to these principal constituents, there are generally the minerals of other metals such as arsenic, antimony, lead, bismuth, silver, etc., present in relatively minor proportions. When such concentrates are melted down by application of temperature and in the presence of just sufficient reducing agents, for example, solid carbonaceous matter such as coal or coke, or gaseous reducing agents such as carbon monoxide or hydrogen, the tin is first reduced to stannous oxide and combines with the silica to form a fluid stannous silicate of the generalized formula $(SnO)_x(SiO_2)_y$, and the ferric oxides are reduced to ferrous oxide to form ferrous silicates of the generalized formula $(FeO)_x(SiO_2)_y$. If reduction is carried further than the point at which these tin and iron silicates are formed, they will be reduced to metallic tin which will remain in equilibrium with the stannous silicates of the slag, and if carried far enough iron compounds will be reduced to metallic iron which will remain in equilibrium with the ferrous silicates of the slag. These equilibriums are such that when the ratio of iron to tin in the original ore or concentrates is relatively high, and it is desired to reduce the amount of tin in the slags to a point where the slag may be discarded without excessive loss of tin, it is necessary to reduce to metal, along with the tin, a certain proportion of the iron. The proportion of iron reduced with tin increases rapidly as the ratio of iron to tin in the original ore or concentrates increases.

If lime is added to the ore or concentrate to be smelted, it has the effect of increasing the ratio between metallic tin and tin combined as a silicate so that lower commercial slags can be produced by the addition of lime, but the proportion of iron reduced with the tin to metal remains roughly the same.

Thus, in order to produce tin free or relatively free from iron in the reduction of low grade tin concentrates, it is necessary to limit the reduction to a point where excessive amounts of tin will remain in the slag.

In order to meet this problem, previous commercial practice in the smelting of tin ores has been to first reduce the ore by smelting with carbonaceous matter only to a point where metallic tin relatively free of iron is separated from the molten bath, leaving a slag which contains too much tin to allow its rejection. This slag is then generally separated from the reduced tin metal by skimming and further reduced with additional carbonaceous matter to a point where a commercial grade of slag has been produced through the reduction of iron as well as tin to metal. The iron-tin-alloy known as "hardhead" thus produced is then generally re-smelted with fresh cassiterite concentrates and through the chemical reaction:

$$SnO_2+2Fe \rightarrow Sn+2FeO$$

the iron in the metal is oxidized by the tin oxide in the fresh charge and returned to slag.

This method of smelting tin concentrates becomes practical when the grade of concentrates is relatively high—say, 50% tin or better—but even at best, requires an expensive rehandling and recycling of slag and hardhead materials.

When the grade of concentrates is low—say, from 45 or 50% tin down to 10% tin—this method or reducing tin becomes increasingly impractical as the proportion of the total tin which can be reduced from the slag without reduction of iron with it becomes less and less.

In order to avoid this difficulty, various schemes have been proposed whereby the tin is separated from the iron by making use of the fact that stannous sulfide is volatile at elevated temperatures at which iron sulfide is not volatile. Tin oxide such as cassiterite SnO_2 may be turned to stannous sulfide by contact with sulfur in sufficient quantities to carry out the reaction:

$$SnO_2+2S \rightarrow SnS+SO_2$$

or by reaction with carbon and sulfur according to the simplified equation:

$$SnO_2+C+S \rightarrow SnS+CO_2$$

Previous methods of carrying out this sulfidation have contemplated and practiced the sulfidation