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PROCESS FOR CONCENTRATING OXIDIZED ORES BY MEANS OF FROTH FLOTATION

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This invention relates to the concentration of ores and more particularly to the froth flotation concentration of oxidized base metal ores, that is, ores having a valuable base metal constituent which exists in chemical combination with oxygen.

The invention contemplates the use, as pulp conditioning reagents, of complex hydrolyzable polyacids and, more specifically, relates to the use of isopolyacids, or the salts thereof of a certain group of metals whose normal salts or acids, when incorporated in an acid, neutral, or slightly alkaline solution, are known to form complex isopolyacids.

Sulphide minerals generally are easily amenable and readily lend themselves to concentration by froth flotation through the use, as flotation reagents, of organic thio-derivatives such as the xanthates. Oxidized minerals, however, have been found to be quite refractory to xanthate flotation and attempts at the froth flotation of oxidized values have been, on the whole, not very satisfactory.

Now, according to The Chemistry of the Inorganic Complex Compounds, by Dr. Robert Schwarz, translated by L. W. Bass, Ph. D.; Wiley, 1923, polyacids are complex compounds formed from weak acids. According to the same authority, an isopolyacid is a polyacid in which the position of at least one of the oxygen atoms is occupied by an acid radical of the same chemical nature, while a heteropolyacid is a polyacid in which the position of at least one of the oxy atoms is occupied by an acid radical of a different chemical nature. Certain heteropolyacids, for instance, phosphomolybdic acid and phosphotungstic acid, have been employed in the flotation of oxidized chrome ores, namely, in the patent to Arnold No. 2,082,817, and have shown some success.

It is an object of this invention to provide an improvement in the recovery and grade of concentrate in the froth flotation of oxidized base metals through the employment, as conditioning agents, of a group of complex chemical compounds coming within the class of polyacids, and comprising certain compounds from the group known as isopolyacids.

It is discovered, as a part of this invention, that conditioning of an ore pulp containing oxidized base metal values in the presence of one or more isopolyacids of metals from the group comprising tin, tungsten, vanadium, molybdenum and germanium, and then subjecting the pulp to froth flotation by the addition of conventional frothing and collecting reagents, renders these oxidized values readily amenable to flotation in a concentrate of rich grade. The activating effect of these isopolyacids is believed to be due to the fact that, after hydrolysis has taken place, semicolloidal, high molecular systems are adsorbed on the surface of the ore particles, thus forming a polar film which allows the combination with the collector.

Additions of reagents to the ore pulp in order to insure the presence therein of the desired isopolyacids may be made in several ways. In one instance a salt of an isopolyacid of the metals from the group heretofore mentioned, may be added directly to the pulp, thereby insuring the presence of the isopolyacid or its salt in the pulp.

In another instance, the normal salt or the normal acid of metals from the group mentioned, may be introduced to the acid, neutral, or slightly alkaline pulp and, when so introduced, will form in solution, the isopolyacid of the particular metal used.

Jander and Jahr in Kolloid. Beihefte, Band 41, pages 1–58, have proven that when the normal salts or acids of the metals, tin, vanadium, molybdenum, tungsten and germanium, are dissolved in acid, neutral or slightly alkaline solutions, they do not behave as do other metals but clearly form their respective complex isopolyacids. Therefore, in order to insure the presence in the pulp of the desired isopolyacid, all that is neecssary is to introduce into the pulp, while it is in acid, neutral or slightly alkaline condition, a normal salt or normal acid of a metal from the group aforementioned. According to an embodiment of the invention, at least one isopolyacid of a metal of the group mentioned is caused to exist in the pulp.

There will be hydrolysis which can be strengthened by means of weak acid or alkaline reagents. Then there must be allowed sufficient time, which can only be determined empirically, for the oxidized values to become thoroughly conditioned by the isopolyacid reagent. Then flotation of the thus conditioned oxidized values is effected in known manner, preferably with the addition of gangue depressing agents, a collector and a frothing agent. The pulp temperature, the concentration of hydrogen ions, and the duration of treatment are to be determined in each instance for the particular ore.

Proceeding in this manner, it will be possible to activate the useful minerals of oxidized base metal ores, so that froth flotation of the same can be carried out with beneficial results. According to the invention it will thus be possible to concentrate economically, by flotation, with satisfactory recovery such ores as oxidized chrome ore (chromic iron), manganese ore (pyrolusite), cobalt ore (heterogenite), copper ore (cuprite, chrysocolla), uranite (pitch blende), titanic ore (rutile), tin ore (cassiterite), wolfram ore (scheelite), vanadium ore (descloisite), a. s. o.

The working of this process is set forth by the following examples, which, of course, are not meant to be limiting in any way.

1. A chromic ore (chromic iron with basic serpentine gangue) is wet crushed to 100 mesh (U. S. A. standard). After thickening to a ratio of 1:2, the pulp is brought into a suitable conditioning tank and slightly alkalized with sodium carbonate, whereupon 0.5 kg. of ammonium molybdate is added. This salt has the formula: $(NH_4)_6Mo_7O_{24}.4H_2O$ and is therefore an isopolyacid salt. (See Treatise on Chemistry, Roscoe & Schorlemmer, MacMillan & Co., London, 1913, vol. 2, The Metals, page 1068.) After conditioning for 40 minutes, there are added 2.0 kg. of water glass (28° Bé.) as a gangue depressing agent, 1.0 kg. oleic acid and 0.2 kg. phosphocresylic acid per ton of pulp. Finally, 5 minutes oiling and floating with 0.02 kg. pine oil, a frothing agent. As a result there is obtained a concentrate showing 58 to 60% chromic oxide with more than 90% recovery.

2. An oxidized manganese ore (pyrolusite with silicate gangue) is wet crushed to minus 65 mesh (U. S. A. standard) and conditioned. To the pulp is then added 0.1 kg. of sodium stannate and 0.3 kg. sodium vanadate per ton of pulp. Since the pH of the pulp will naturally be not more than slightly alkaline, the addition of these normal salts will cause the formation in solution of the isopolyacids of tin and vanadium, as previously described. After a suitable conditioning period the pulp is treated with 2.5 kg. quebracho bark, in order to depress the gangue. Finally, floating is done at 35° C., (95° F.) with 0.75 kg. of stearic acid and 0.05 kg. of amyl xanthate, as collectors, and 0.03 kg. terpin oil, as a frothing agent.

3. A tin ore cassiterite (with schist gangue) is wet crushed to minus 65 mesh (U. S. A. standard). After thickening, 0.02 kg. of sulphuric acid and 0.6 kg. of tungstic acid per ton of pulp are added. In solution in this pulp the tungstic acid will naturally form the isopolyacid of tungsten as hereinbefore shown. After 25 minutes conditioning in the presence of the isopolyacid of tungsten at 30° C. (86° F.) floating ensues in the usual way with 1.2 kg. of sodium palmitate and 0.03 kg. of cresol to the ton.

Thus, in the first example, a salt of the isopolyacid of molybdenum is added directly to the ore pulp and the pulp conditioned in the presence of this isopolyacid. In the second example, the normal salts of tin and of vanadium are added to the pulp, resulting in the formation, in solution, of the isopolyacids of these two metals so that the pulp is conditioned in their presence. Example 3 shows the addition to the pulp of tungstic acid which, in solution, forms the isopolyacid of tungsten as the advantageous conditioning agent.

The invention, therefore, has several aspects and may be accomplished in divers manner. An isopolyacid salt of at least one of the metals chosen from the group consisting of tin, tungsten, vanadium, germanium and molybdenum, may be added to the pulp, or there may be introduced into the pulp a normal salt or acid of at least one of these metals. In any event, in an acid, neutral, or slightly alkaline pulp, there ensues the formation of the isopolyacid of the metal. Conditioning of the pulp in the presence of these isopolyacids, results in thorough activation of the oxidized base metal values so that they may be subsequently recovered in a flotation concentrate of high grade, through the use of relatively small amounts of normal gangue depressing, collecting and frothing agents.

What I claim is:

1. In the concentration by froth flotation of ores containing oxidized base metals, the method which comprises subjecting a pulp containing such ores to conditioning in the presence of an isopolyacid of a metal chosen from the group consisting of tin, tungsten, vanadium, germanium, and molybdenum, and thereafter subjecting the pulp to froth flotation to obtain a concentrate rich in oxidized values.

2. In the concentration by froth flotation of ores containing oxidized base metals, the method which comprises subjecting a pulp containing such ores to conditioning in the presence of an isopolyacid of molybdenum, and thereafter subjecting the pulp to froth flotation to obtain a concentrate rich in oxidized values.

3. In the concentration by froth flotation of ores containing oxidized base metals, the method which comprises subjecting a pulp containing such ores to conditioning in the presence of an isopolyacid of tin, and thereafter subjecting the pulp to froth flotation to obtain a concentrate rich in oxidized values.

4. In the concentration by froth flotation of ores containing oxidized base metals, the method which comprises subjecting a pulp containing such ores to conditioning in the presence of an isopolyacid of tungsten, and thereafter subjecting the pulp to froth flotation to obtain a concentrate rich in oxidized values.

5. In the concentration by froth flotation of ores containing oxidized base metals, the method which comprises adding to an acid, neutral or slightly alkaline pulp containing such ores, a reagent chosen from the group consisting of stannic acid, tungstic acid, vanadic acid, germanic acid, molybdic acid and their salts, conditioning the thus treated pulp, and thereafter subjecting the pulp to froth flotation to obtain a concentrate rich in oxidized values.

6. In the concentration by froth flotation of ores containing oxidized base metals, the method which comprises adding molybdic acid or a salt thereof to an acid, neutral or slightly alkaline pulp containing such ores, conditioning the thus treated pulp, and thereafter subjecting the pulp to froth flotation to obtain a concentrate rich in oxidized values.

7. In the concentration by froth flotation of ores containing oxidized base metals, the method which comprises adding stannic acid or a salt thereof to an acid, neutral or slightly alkaline pulp containing such ores, conditioning the thus treated pulp, and thereafter subjecting the pulp to froth flotation to obtain a concentrate rich in oxidized values.

8. In the concentration by froth flotation of ores containing oxidized base metals, the method which comprises adding tungstic acid or a salt thereof to an acid, neutral or slightly alkaline pulp containing such ores, conditioning the thus treated pulp, and thereafter subjecting the pulp to froth flotation to obtain a concentrate rich in oxidized values.

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