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[54] **FROTH FLOTATION METHOD FOR RECOVERY OF MINERALS**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 251,458, May 8, 1972, abandoned.

[52] **U.S. Cl.** **209/166**

[51] **Int. Cl.²** **B03D 1/02**

[58] **Field of Search** 209/166, 167

[56] **References Cited**

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Primary Examiner—Robert Halper

[57] **ABSTRACT**

An improved method in concentration of oxidic ores by froth flotation process which comprises subjecting an oxidic ore of a metal which in its highest valency state forms peroxy acid by the action of potentially higher inorganic peroxy compounds in the presence of an effective quantity of a flotation collector-frother, an alkyl mono olefine, diolefine or triolefine adducts of polyhydric alcohol, the indicated compounds provide selectivity and/or recovery of oxidic minerals of Ti, Zr, Ce, Th, V, Nb, Ta, Cr, W, and U, over silica and silicate gangue.

2 Claims, No Drawings

FROTH FLOTATION METHOD FOR RECOVERY OF MINERALS

This is a continuation-in-part of my prior application of Ser. No. 251,458 filed on May 8, 1972, now abandoned in favour of the present application.

RELATED APPLICATIONS

The prior art discloses the application of oxidizing agents in conjunction with fatty acids, ester of fatty acids, and various hydrocarbons of petroleum origin. U.S. Pat. No. 2,826,301 teaches the use of sodium peroxide and hydrogen peroxide as oxidizing agents for eliminating of reducing slimes; the proper flotation is done with fatty acids and kerosene for the concentration of phosphate ore. U.S. Pat. No. 1,966,649 teaches the use of alkali perborate, to passivate, i.e., to augment the wettability of accessory minerals in flotation of cryolite.

BRIEF SUMMARY OF THE INVENTION

This invention relates to the concentration of metal values from oxidic minerals and ores. Particularly, it relates to the use of alkyl olefine adducts of polyhydric alcohols and alkylpolyhydroxy compounds as flotation reagents with collecting and frothing properties to effect a separation of metal values in ores from silica, alkali and earth alkali aluminum silicates. The minerals and ores of which the metal values are to be floated out are pretreated with strong oxidizing agents of peroxy type which form metal peroxyacids or peroxy compounds at the surface of the mineral with the respective metal of the respective mineral, which peroxy compound presumably activate the double bond of the olefinic collector-frother, thus effecting a succesful flotation of the desired metal values from the mineral slurry. Among such ores and minerals, to the beneficiation of which this invention is particularly adopted, are the oxidic ores of titanium, zirconium, cerium, thorium, vanadium, niobium, tantalum, chromium, wolfram and uranium, i.e., the dioxide of titanium, zirconium and thorium, as well as the phosphates of cerium and the rare earths, the vanadates, niobates, tantalates, chromates, wolframates, and uranates minerals.

The object of this invention is to provide an improved process of beneficiating or concentrating oxidic ores.

Another object of the present invention is a beneficiation process effective economically to recover the heretofore said metallic values from silica and silicate gangue.

A still further object of this invention is to subject oxidic ores to froth flotation, thus collecting a concentrate having improved sales appeal both as to grade and purity.

One or more of the foregoing objects is achieved by the present invention.

Still further objects of this invention will be apparent upon a complete understanding of the invention as hereinafter more fully described.

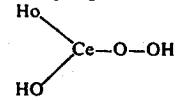
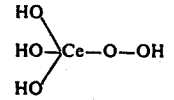
The present invention comprises a process for the beneficiation of minerals and ores of metals which in their highest oxidation states form metal peroxyacids, so that the metal at the mineral surface is peroxidized which state acts, presumably catalyticaly on the double carbon to carbon bond of the collector-frother, an unsaturated alkyl hydrocarbon, which as a π-bond compound presumably attaches the unsaturated collector-

frother to the mineral surface. Thus the process comprises comminuting the ore to substantially completely liberating the valuable mineral from the gangue; pretreating the comminuted ore with a chemical peroxidizing agent to modify at least a portion of the surface of the mineral which is to be floated by forming some metal peroxide, or peroxyacid, and subjecting the comminuted and pretreated surface modified ore or mineral to the beneficiation by froth flotation method in the presence of alkylolefine adduct of polyhydric alcohols, polyoxymethylene.

More particularly described, the present invention comprises contacting comminuted ore or minerals of the afore said metals with inorganic peroxidizing agents at the mineral surface provoking peroxidizing of metal at the mineral surface. The mineral particle from its surface act as a weak and slow acting oxidizing agent upon the double bond of said olefinic compounds binding the disposable π-bond of the double carbon to carbon bond to peroxy oxygen, which is charged. The double bond of the collector-frother is lost in formation of a kind of metal-oxy-hydrocarbon compound. Thus, the alkyl olefine adduct of polyhydric alcohols serve in this invention as collecting agents. In other words it is believed that peroxidation to effect a change in the surface oxidation-reduction potential of the ore particles, which particles are believed to exert by their acquired oxidation-reduction potential a change in the oxidation-reduction potential of the alkyl olefinic compounds, attacking the double carbon to carbon bond, compounding of metal(oxide) and unsaturated alkyl hydrocarbon compound, thus the olefine adduct of polyhydric alcohol serves in this invention as collecting agents.

While it is not desired to be bound by the theory here expressed, it is believed that treatment of the comminuted ore according to the process of this invention results either in actual chemical peroxidation of portions of the surface of the mineral of the metal which normally and naturally form peroxyacids, or alternatively, alters the oxidation-reduction potential of a portion of the surface of the metalliferous particle. Metals of the ore treated in accordance with the invention are rendered responsive to froth flotation, i.e., levitation from siliceous gangue and collection in a froth flotation process.

The metal peroxyacids which may appear in the froth flotation process of this invention of claimed and unclaimed metals in respective minerals are as follows:

Peroxyyttro acid	$Y_4O_9.nH_2O$
Peroxylanthanum acid	$La_4O_9.nH_2O$
Peroxysamarium acid	$Sm_4O_9.nH_2O$
Peroxycerium acid	$CeO_3.2H_2O$
Peroxymonocerous acid	
Peroxymonoceric acid	
Peroxymonotitanic acid	$(HO)_3Ti—O—OH$
Peroxymonozirconium acid	$(HO)_3Zr—O—OH$
Peroxymonohafnic acid	$(HO)_3Hf—O—OH$
Peroxythoric acid	$Th_2O_7.4H_2O$
Peroxydistannic acid	$H_2Sn_2O_7$
Peroxymonostannic acid	$HSnO_4$
Peroxyvanadic acid	$H_4V_2O_{11}$
Peroxyniobic acid	K_3NbO_8
Peroxytantalic acid	K_3TaO_8

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Perchromic acid	$K_3(Cr_2O_8)_n$
Perchromic acid	$K_3\ Cr_2O_{12}$
Peroxymolybdic acid	$HOOMoO_2OH$
Peroxymolybdic acid	H_2MoO_8
Peroxytungstic acid	$H_2W_2O_{11}$
Peroxyuranic acid	$UO_4.2H_2O$

The present invention embraces inorganic peroxidizing agents with a high oxidation-reduction potential. Appropriate agents to put in practice the present invention include: hydrogen peroxide, peroxycarbonate, peroxyborate, peroxynitric acid, peroxymonophosphoric acid, peroxydiphosphoric acid, peroxymonosulfuric acid, peroxydisulfuric acid and peroxydisulfates, and hypochlorous acid and hypochlorites as accelerators of peroxidizing process.

The amount of the peroxidizing reagents employed in the practice of the present invention may vary depending upon the nature of the ore, the conditioning time and the like operations. The peroxidizing agents of this invention are preferably employed in amounts ranging from 0.05 pound per ton of ore to about 0.2 pound per ton of ore treated.

The consumption of acid and alkali which are employed as auxiliary reagents to bring the pH values to the necessary concentration to fulfill the peroxidation in an acidic or alkaline media is low and never more than two pounds per ton of ore milled, so that the pH of the pulp of the mineral slurry is operative between 5 to 9, which depends on the electronegativity of the metal in the mineral to be floated, i.e., of the oxidation-reduction potential involved in the process. The time of contact of the peroxidizing agent and the ore may be varied between wide limits depending on the particular ore treated as well as the concentration of the agent.

The collector employed in this froth flotation process of my invention are neutral alkyl olefins or alkyldiolefine, or alkyl triolefine. Since the olefins are poor frothing agents or at least have no frothing properties at all, a frothing agent of alcohol type is needed to be added to develop a carrying froth. Preferably the collector is olefine, diolefine, or triolefine adduct of polyhydric alcohols, polyoxymethylene, with no more than six hydroxyl groups, i.e., two to six hydroxyl groups.

The collectors of the present invention which presumably function by the chemical reaction based on the activation of the double carbon to carbon bond of a olefine compound, i.e., the π-bond, by the action of a metal peroxyacid or simple peroxide formed at the very surface or portion of the surface of the mineral to be floated, forming thus with the metal atoms, exposed on the surface of mineral particles, presumably addition compounds, make that the process is operative.

It is obvious that the rest of the hydrocarbon compound or substituted hydrocarbon compound is oriented outward from the said particle. Thus, the attachment of these (nonionic) collector-frothers to the ore particle form a water repellent surface or barrier around at least a part of the surface of the ore particle and thereby facilitates the formation of froth when the ore slurry is agitated in the presence of air.

In view of the above outlined necessary characteristics of a good collector-frother, it would appear that it is necessary for the organic unsaturated compound of applicant's collector-frother to be of a particular size, i.e., have an upper and a lower size limit or chain length. It has been found that the olefinic part of the compound should contain about 8 carbon atoms or more and two to six hydroxyl groups in the adduct side chain attached to about 8 carbon atoms or more.

The upper limit on the size or number of carbons in the olefine, diolefine, or triolefine is determined primarely by the factors which necessitate to attach the metal in the mineral to be floated, i.e., the strength and scope of the bonding so to speak, and not to the solubility factor, for all these olefins are substantially water insoluble. In general, as the olefine, diolefine, or triolefine approaches 16 carbon atoms in length, they approach the technical limit of production of the same. Thus the upper limit of the adducts is at about 14 carbon atoms in which to maximum six carbon atoms is attached one hydroxyl group. Hence, the preferred olefinic, diolefinic, or triolefinic adducts of polyhydric alcohols, polyoxymethylene, contain from 10 to 22 carbon atoms, but those of 10 to 16 are normally satisfactory as collector-frothers for the olefinic series.

The preferred embodiments of collector-frothers in the olefine series are as follows:

Amylene adducts of glycerol, diglycerol, or hexantriol,
Octylene adduct of polyoxymethylene.

The preferred embodiments of collector-frothers in the diolefine series are:

Tetramethylallene adduct of polyoxymethylene.

The preferred embodiments of collector-frothers in the triolefine series are:

Hexatriene adducts of polyoxymethylene.

The method of making the various adducts is well known and described in the literature. Therefore, their method of preparation does not constitute a part of this invention.

In the use of my collector-frothers, based on the π-bond activity, to float the mineral values, the ore is crushed, milled and sized to at least about 60 to 100 mesh, which depends on the particular ore treated. Milling to finer sizes is preferable. The crushed and sized ore is pulped and as a mineral slurry is ready for treatment in the flotation equipment with the peroxidizing agent, which is always done prior to the addition of olefinic collector.

An excess of peroxidizing agents may be harmful for the collector which may oxidize to saturated hydrocarbon or split at the double bond. It is preferable to operate the flotation with fresh water after conditioning with peroxidizing agents, i.e., to cycloning the oxidized mineral slurry, followed by addition of fresh water. After peroxidizing of the mineral surface is accomplished the collector and auxiliary agents, if any are to be used, are added for further treatment in the flotation equipment. In the flotation cell the ore pulp is contacted with air to form a froth to achieve the desired separation of metal values from the gangue. In most cases it is advantageous to use a multiple stage flotation process to treat the underflow or partially metal values barren pulp to increase the degree of separation or to enhance the degree of recovery. Also, the use of varying amounts of emulsifiers, dispersants and depressants etc. in different stages may be used to advantage to obtain the highest yields and best separations.

Having disclosed the novel collector-frother of this invention as well as the handling of the ore, wherein the use of activation steps as is the peroxidizing, I have to say the final object of this invention is to provide a method for the flotation recovery of minerals containing oxides of: cerium, titanium, zirconium, thorium, vanadium, niobium, tantalum, chromium, wolfram, and uranium.

The above discussion illustrates my invention in a general way, but for a detailed illustration thereof the examples of flotation procedure are set forth below.

EXAMPLE 1

The activator-promoter used;
Peroxymonophosphoric acid.
The collector-frother used:
Tetramethylallene adduct of polyoxymethylene.
The purpose:
Recovery of descloizite and cuprodescloizite.

The quantity of the mineral treated was small, therefore, the flotation test was accomplished in a 50 grams flotation cell with 10 grams of descloizite, cuprodescloizite, and 40 grams of a mixture of quartz and silicate shist rock. The addition of reagents was done dropwise. This qualitative flotation test gave the float fraction, assaying 92 percent of descloizite, cuprodescloizite by microscopic count, in a concentrate weighing 11.2 grams.

EXAMPLE 2

The activator-promoter used:
Potassium peroxycarbonate and sodium hypochlorite.
The collector-frother used:
Amylene adduct of glycerol.
The purpose:
Recovery of rutile from siliceous ores.

500 grams of a rutile schist containing 7.8 percent of TiO_2 was ground wet at 60 percent solids by weight in a laboratory ball mill with one pound per ton of sulfuric acid to pass 80 mesh sieve. In the flotation machine 0.2 pound per ton of sodium peroxycarbonate and 0.1 pound per ton of sodium hypochlorite was added for peroxidizing of the rutile surface. After conditioning for five minutes, the sample was decanted. With fresh water, 0.2 pound per ton of amylene adduct of glycerol was added. The rougher concentrate was cleaned with used water and 0.05 pound per ton of the collector.

The results of this test were as follows:

Fraction	Weight (grm)	Assay TiO_2 percent	Distribution of TiO_2 percent
Concentrate	40.5	89.0	92.4
Tail, general + cleaner	459.0	0.65	7.6

EXAMPLE 3

The activator-promoter used;
Potassium peroxydiphosphate.
The collector-frother used:
Amylene adduct of hexantriol.
The purpose:
Recovery of scheelite.

500 grams of a lode scheelite with 3.3 percent WO_3 was ground wet at 60 percent solids by weight in a laboratory ball mill to pass 100 mesh sieve. In the flotation machine 0.3 pound per ton of sulfuric acid and 0,1 pound per ton of potassium peroxydiphosphate was added. Conditioned for five minutes, then the sample was decantated and the flotation accomplished with fresh water, and 0,1 pound per ton of amylene adduct of hexantriol was added. Conditioned for two minutes. The rougher concentrate was skimmed for five minutes. The rougher concentrate was cleaned with used water and 0.05 pound per ton of collector.

The results of this test were as follows:

Fraction	Weight (grams)	Assay WO_3 percent	Distribution of WO_3 percent
Concentrate	24.7	59.5	89.3
Tail, general + cleaner	474.0	0.38	10.7

EXAMPLE 4

The activator-promoter used:
Peroxynitric acid.
The collector-frother used:
Octylene adduct of polyoxymethylene.
The purpose:
Recovery of pyrochlore.

The quantity of pyrochlore mineral was small, therefore, the flotation test was accomplished in a 50 grams flotation cell with 10 grams of pyrochlore and 40 grams of a mixture of quartz and feldspar. The addition of the reagents was done dropwise. this qualitative flotation test gave the float fraction assaying 95 percent of pyrochlore by microscopic count, in a concentrate weighing 11 grams.

EXAMPLE 5

The activator-promoter used:
Ammonium peroxydisulfate.
The collector-frother used:
Amylene adduct of diglycerol.
The purpose:
Recovery of thoryanite.

The quantity of thoryanite mineral was small, therefore, the flotation test was accomplished in a 50 g flotation cell with 10 grams of thoryanite and 40 grams of a mixture of quartz and feldspar. The addition of the reagents was done dropwise. This qualitative flotation test gave the float fraction assaying 97 percent of thoryanite by microscopic count, in a concentrate weighing 11.3 grams.

The afore mentioned examples are presented to illustrate the specific embodiments of collector-frothers of the present invention and are not intended as a restriction on the scope of the invention briefly discused and claimed.

I claim:

1. An improved method of beneficiating ores selected from the group consisting of oxide ores and minerals of titanium, zirconium, cerium, thorium, vanadium niobium, tantalum, chromium, wolfram, and uranium, by froth flotation process to produce a froth concentrate of desired metal values which improvement comprises: effecting the froth flotation of the ore by treating the comminuted ore of the mineral slurry with inorganic peroxyacids or their alkali or ammonium salts, followed by an effective amount of a collector-frother of an alkyl mono-, di-, tri-olefin adduct of a glycerol, diglycerol, hexanetriol, polyoxymethylene or a mixture thereof having no more than six hydroxyl groups per molecule, said olefin having from 5 to 10 carbon atoms, said adduct having from 10 to 22 carbon atoms; and recovering a froth concentrate relatively rich in the desired metal values to leave the tailings relatively poor in desired metal values.

2. A method according to claim 1, wherein the peroxidizing agents are selected from the group consisting of peroxycarbonate, peroxyborate, peroxynitric acid, peroxymonophosphoric acid, peroxydiphoshoric acid,

peroxymonosulfuric acid, peroxydisulfuric acid, and in the presence of hypochlorous acid and hypochlorites as accelerator of the peroxidizing process.

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