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FLOTATION PROCESS

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6 Claims. (Cl. 209—166)

The present invention relates to flotation, and more particularly to the recovery of desired minerals from ores containing the same by application of froth flotation methods.

Froth-flotation is roughly based on the fact that the surface of a given mineral to be recovered can be rendered, by the action of so-called collectors, more or less water repellent, i. e. aerophil, and a mineral-air complex, the specific gravity of which is lower than that of the pulp, is thus formed with the air bubbles introduced into the pulp.

Although the usual gangue minerals (with a few exceptions like talc, graphite, etc.) when pure, are naturally more hydrophilic than the valuable metal bearing ones, they are easily floated after activation with metallic cations. Thus, quartz and most other silicates may be activated by very small amounts of iron, copper, zinc, lead, nickel, tin, titanium, barium and some other cations, and calcite by barium, copper, iron, and lead salts when floated with fatty acid or fatty alcohol collectors at pH values varying with each activating ion. Since in almost every pulp there are soluble metallic salts present such as dissolved iron from the ball-mill, or copper, zinc, or iron sulfates from the oxidation of sulfide-minerals, the gangue is always more or less activated and tends to concentrate in the flotation froth.

It will be seen therefore that in the flotation of ores, chemical and physical control shall be directed, first, toward increasing the floatability of the wanted minerals and, second, toward minimizing any flotation tendency exhibited by the unwanted gangue minerals contained in the admixture.

The present invention has the second of these objectives in view and, for the accomplishment of the same, it proposes to add to the flotation pulp relatively small amounts of certain organic compounds, which will be described presently, that react with the extraneous metal cations present so as to prevent the activation and flotation of unwanted gangue minerals by the agency of such cations.

Broadly, the invention embraces the addition to a flotation pulp of an organic reagent able to form very stable, water soluble, or insoluble but hydrophilic, inner complexes (chelate compounds) with the extraneous metallic cations in solution or adsorbed on the mineral particles, whereby such ions are prevented or inhibited from exerting an activating effect on the gangue particles.

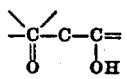
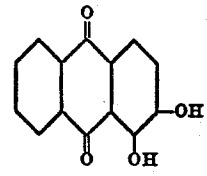
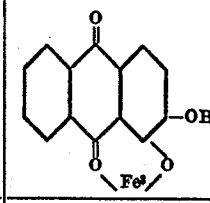
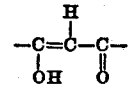
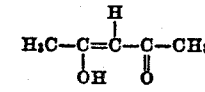
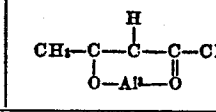
These specific organic reagents must possess in their molecule certain groups capable of uniting with metals through the replacement of the acidic hydrogen, the metal in the resultant compounds being held in position by a primary or electro-valence, and, on the other hand, other groups being capable of combining with metals through the coordination bond, that is, without the replacement of hydrogen. If these two functional groups are both attached to one single organic radical in the proper relative position such as to satisfy the Baeyer strain theory, a cyclic structure will be formed which is known as an inner complex or chelate compound. The metal atom in these four-, five- or six-membered rings is most frequently attached to a nitrogen, oxygen or a sulfur atom by electro-valence (salt formation), and it completes the cycle through coordinate valence linking it to another functional group containing nitrogen, oxygen or sulfur.

But, in order to fulfill the aim of disactivating or depressing the gangue by removal of the free or adsorbed metallic ions acting as actual or potential activators according to the present invention, the formed iner complexes or chelate compounds with said cations have to be water soluble or hydrophilic.

Thus, the present invention discloses the use of organic compounds capable of forming definite soluble or hydrophilic inner complexes with metallic ions in solution or adsorbed on the mineral particles, and thereby preventing such ions from exerting an activating influence on the gangue.

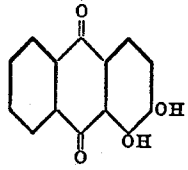
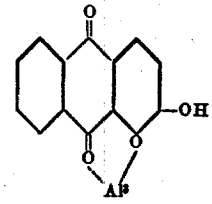
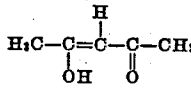
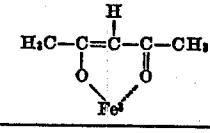
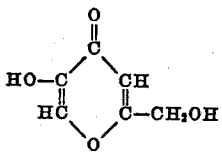
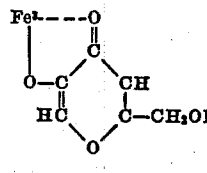
These chelating compounds may be classified by the nature and the relative position of the two functional groups, of which one is supplying the primary valence and the other the secondary valence in the formation of the chelate ring, i. e., by the reactive groupings. (Ref. H. M. Haendler and B. P. Geyer, J. Am. Chem. Soc. 60, 2813–1938.)

The object of this invention is a class of chelating compounds having an enolic or phenolic hydroxyl group supplying the primary valence by replacement of its hydrogen, and a (ketonic or quinonic) carbonyl group supplying the secondary valence in the formation of the chelate ring:

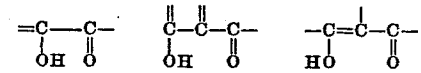
Structural characteristics			Example of—	
Salt forming group	Complex forming group	Reactive grouping	Chelate forming organic compound	Corresponding cyclic inner complex
Phenolic hydroxyl —OH	Carbonyl (quinonic) 		1.2 dihydroxy anthraquinone 	Iron complex 
Enolic hydroxyl —OH	Carbonyl —C=O	Enolized dicetones 	Enolized form of acetylacetone 	Aluminum complex 

In addition to these general conditions required to form a cyclic chelate compound, the latter must be water soluble or hydrophilic in order to fulfill the desired purpose. The structural features promoting water solubility or hydrophilic character for an organic compound are not yet completely understood (Refer, in H. Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, the chapter: "Constitution and physical properties of organic compounds" by Wallace R. Brode and John A. Leermakers).

In the following examples of soluble or hydrophilic inner-complexes, the features imparting water affinity are pointed out in addition to the chelate-forming structure:

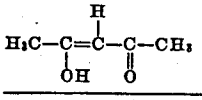
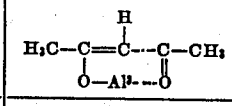
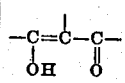
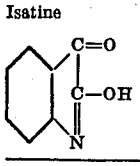
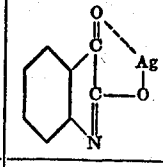
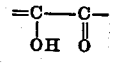
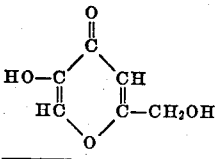
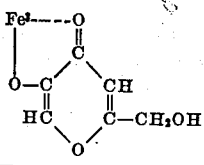
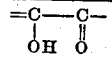
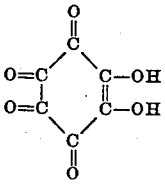
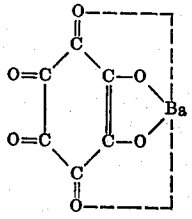
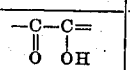
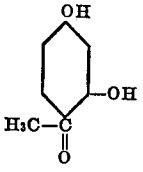
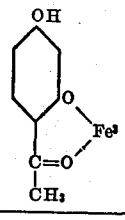
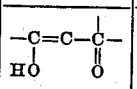
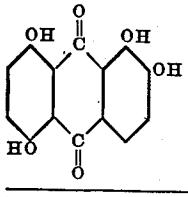
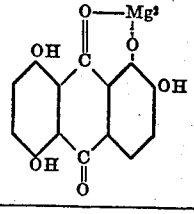
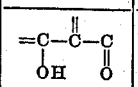
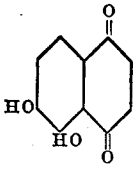
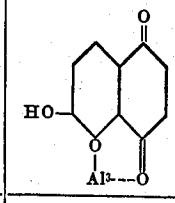
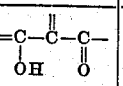
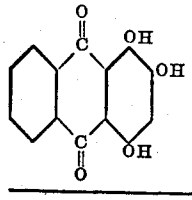
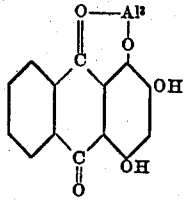
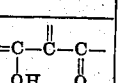
Example of—		Structural features			
Organic compound yielding soluble or hydrophilic chelates	Corresponding cyclic soluble or hydrophilic inner complex	Salt forming group	Complex forming group	Reactive grouping	Hydrophilic group or feature
Alizarin (1.2 dihydroxyanthraquinone) 		OH (α)	C=O		OH (β) and C=O
Acetylacetone 		—OH			Short carbon chain
Kojic acid 		—OH			Alcoholic hydroxyl —OH

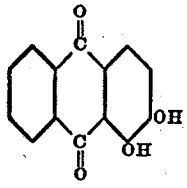
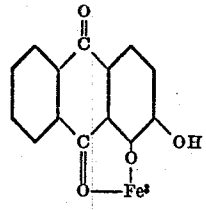
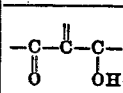
Among the reactive groupings yielding inner complexes (by combining in the proper relative position the salt-forming and complex-forming functions), the soluble or hydrophilic alpha and beta hydroxy-carbonyl compounds (enolized 1.3 dicetones and aromatic α hydroxy-quinones or cetones) are especially valuable as selective flotation modifiers for ores carrying iron or related metals. The reactive groupings of these compounds have the general formulas:



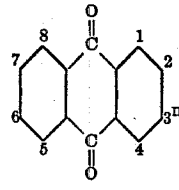
in which the hydroxyl group may be a phenolic or an enolized cetone function, but never an aliphatic alcohol function. Moreover, in order to insure water solubility or hydrophilic character, the aliphatic compounds ought to contain a short carbon chain (no more than 2C attached to any of the functional groups); while the aromatic (cyclic) compounds should have at least one additional solubility promoting hydroxyl-, carbonyl- or amino-group.

The following compounds are illustrative examples of the class of reagents which are the subject of this invention:

Examples of—		Structural features			
Organic α or β hydroxycarbonyl compound yielding soluble or hydrophilic chelates	Corresponding cyclic inner complex	Salt forming group	Complex forming group	Reactive grouping	Hydrophilic group or feature
Acetylacetone (enol) 		—OH	—C=O		2 carbon chains attached to functional groups.
Isatine 		—OH	—C=O		—N=
Kojic acid 		—OH	—C=O		—OH (alcohol)
Rhodizonic acid 		—OH	—C=O		—C=O, —C=O, —C=O
Dihydroxyacetophenone 		—OH	—C=O		—OH
Quinalizarine 		—OH	—C=O		—OH, —OH, —OH, —CO
Naphtazarin (5.6 dihydroxy 1.4 Naphtoquinone 		—OH	—C=O		—OH, —C=O
Purpurin 		—OH	—C=O		—OH, —OH, —C=O

Examples of—		Structural features			
Organic α or β hydroxycarbonyl compound yielding soluble or hydrophilic chelates	Corresponding cyclic inner complex	Salt forming group	Complex forming group	Reactive grouping	Hydrophilic group or feature
Alizarin 		—OH	—C=O		—OH, —C=O

It is evident that expensive laboratory products like rhodizonic acid (synthesis ref. G. Gutzeit Helv. Chem. Acta XII, 4 p. 725–727, 1929), which are selling for $10 per 1.0 gram, are economically unfit as flotation reagents. From a practical point of view (and unless cheaper procedures of manufacture are developed in the future) the polyhydroxyanthraquinones and polyhydroxynaphtoquinones with one phenol group in α (or 1) position to the quinonic oxygen atom, produced on a large scale as dyestuff intermediates or as dyes, are most suitable. They are generally marketed under trade names which do not disclose their chemical character:

Examples of some trade names of 1-polyhydroxyquinones	Chemical name  (anthraquinone formula)
Alizarin	1.2 dihydroxyanthraquinone
Anthrachrysone	1.3.5.7 tetrahydroxyanthraquinone
Anthrarufin	1.5 dihydroxyanthraquinone
Chrysazin	1.8 dihydroxyanthraquinone
Naphtazarin	5.6 dihydroxy-1.4 naphtoquinone
Purpurin	1.2.4 trihydroxyanthraquinone
Quinazarin	1.4 dihydroxyanthraquinone
Quinalizarin	1.2.5.8 tetrahydroxyanthraquinone
Etc.	Etc.

These quinones yield colored chelate compound which are hydrophilic in alkaline medium and soluble in acid medium.

The proper procedure for flotation of oxide ores following this invention is to add at first the organic gangue depressant, in amounts of 0.02–0.05 kg. per metric ton of ore, either as a slurry in water, or better in a saturated alkaline solution (sodium carbonate or caustic soda), and to condition (agitate) for several minutes. The pulp is then made alkaline, or if possible acid (generally with H_2SO_4), to a pH which varies with the nature of the ore, but should be below 4 if the gangue is mainly quartz. Hydrofluosilicic acid or sodium hydrofluosilicate is added as a dispersant (peptizer). For the flotation proper higher aliphatic alcohol sulfate or fatty acid sulfonates, with or without addition of a fatty acid, are used as collectors. A frother and/or mineral oil may be required to control the foam.

The following examples will further illustrate how the said invention may be carried out in practice, but the invention is not restricted to these examples.

Example I

A Norwegian iron ore (Dunderland) consisting mainly of crystalline hematite and magnetite with silica and biotite gangue was treated in a magnetic separator at 35 mesh to remove the magnetite, after which operation the product run 19% Fe. It was then ground to —65 mesh and conditioned by addition of the following reagents:

Alizarin paste 20%	0.03 kg. per ton	Condit. 10 min.
Sulfuric acid	3.0 kg. 60° Bé./ton	Condit. 5 min.
Sodium silicofluoride	0.3 kg./t.	Do.
Emulsion (10% duodecylsulfate, 20% sulfonated castor oil, 10% oleic acid, 60% water)	2.0 kg./t.	

Concentrates assaying 61.2% Fe were obtained with an iron recovery of 79.4%.

Example II

Table tailings from Stillwater chromite ore (Anaconda concentrator), representing 69.1% of the crude, with a gangue of heavy basic silicates (enstatite, bronzite, diopside, olivine, etc.) assaying 6.38% Cr_2O_3, were retabled after grinding to —35 mesh, yielding a secondary concentrate with 37.56% Cr_2O_3 (13.56% recov.) and middlings with 19.01% Cr_2O_3 (37.12% recov.). These middlings were floated as follows (reagents per 100 gr. charge):

Alizarine	1% solution from 20% paste.	0.15 cc.	Cond. 3 min.
Sulfuric acid 10% pH=3.6		0.8 cc.	Cond. 4 min.
Hydrofluosilicic acid 1.65%.		1.0 cc.	Cond. 2 min.
Wetanol (aliphatic alcohol sulfate).	1%	0.4 cc.	
Oleic acid		0.15 cc.	
Frother B–23 (American Cyanamid Co.).		0.02 cc.	

Results:

Product	Wgt. grs.	Percent Cr_2O_3	Recovery, percent
1st concentrate	8.0	36.90	15.91
2nd concentrate	7.0	28.91	10.90
3rd concentrate	19.5	22.37	23.52
Tails	63.0	7.49	49.68
Calc. heads	97.5	19.01	10.00

The tailings were scavenged under the same conditions, yielding a secondary concentrate with 14.92% Cr_2O_3 (38.23% rec.), a middling with 8.42% Cr_2O_3 (rec. 23.63%) and final tails with 3.72% (rec. 38.13%).

Example III

A "black sand" from Egypt, containing zircon (about 35%), ilmenite and magnetite (about 30%), monazite (10%), quartz and garnet (25%) was floated as follows:

Conditioning with purpurin (1.2.4 trihydroxy anthrachinone) 0.04 kg./t. Flotation of zircon in strongly acid medium (pH=3.3) using an emulsion of mineral oil in sodium lauryl sulfate. 91% recovery. Magnetic cleaning from ilmenite and magnetite.

Flotation of ilmenite by addition of sodium carbonate to a pH=5.5. Collector: oleic acid. Cleaning of the ilmenite concentrate at pH of 4–3.5. Recovery 83.2%.

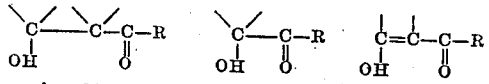
Example IV

A Swedish magnetite ore with 23% Fe was floated, using acetylacetone as the organic depressing agent for the silica gangue. The pH was 3.8, and hydrofluosilicic acid was used as the dispersant. The only collector was "Texapon," a high aliphatic alcohol sulfate. Concentrates with 67.3% Fe were produced, at a recovery of 88.7%.

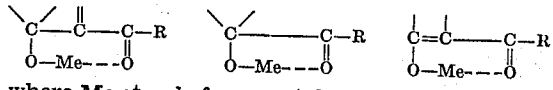
These examples show that the use, according to the present invention, of organic reagents accomplishing the purpose of gangue depression through complexing detrimental cations into a water soluble or hydrophilic chelate compound constitutes a marked advance in the art of froth flotation, and is highly advantageous in improving the selectivity of the collectors, thus improving the grade of concentrates and the recovery.

What is claimed is:

1. In the concentration by froth flotation of oxides of the heavy metals containing iron oxide as a significant constituent of the mineral to be concentrated and a siliceous gangue, said materials being substantially free from carbonaceous matter, using as a collector an aliphatic compound selected from the class of fatty acids, fatty alcohols, sulfated fatty acids, and sulfated alcohols, containing at least 9 carbon atoms in their molecules, and carrying out the flotation at a pH below 6, the step of adding first to the pulp a small amount of a non-collecting organic compound having one of the following schematic formulas

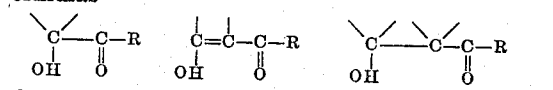


wherein OH stands for a group consisting of phenolic and enolic hydroxyl groups, C=O represents ketonic and quinonic carbonyl groups and R represents alkyl, alicyclic and aromatic radicals; said radicals, if aliphatic, having from one to four carbon atoms and said radicals, if aromatic, containing a solubilizing group included in the group consisting of hydroxyl, carbonyl and amino; this organic compound being adapted to react with the gangue activating cations of the pulp to yield a water soluble or hydrophilic chelate compound having the schematic formula

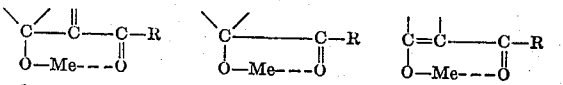


where Me stands for a metal atom (monovalent) replacing the hydrogen of the hydroxyl group by electron exchange and linked to the carbonyl oxygen by the coordinative bond.

2. In the concentration by froth flotation of oxides of the heavy metals containing iron oxide as a significant constituent of the mineral to be concentrated and a siliceous gangue, said materials being substantially free from carbonaceous matter, using as a collector an aliphatic compound selected from the class of fatty acids, fatty alcohols, sulfated fatty acids, and sulfated alcohols, containing at least 9 carbon atoms in their molecules, and carrying out the flotation at a pH below 6, the step of adding first to the pulp a small amount of a non-collecting organic compound having one of the following schematic formulas



where OH stands for a phenolic hydroxyl group, C=O stands for a quinonic carbonyl group and R stands for an aromatic radical containing a solubilizing group included in the group consisting of hydroxyl, carbonyl, amino; this organic compound being adapted to react with the gangue activating cations of the pulp to yield a water soluble or hydrophilic chelate compound having the schematic formula



where Me stands for a metal atom (monovalent) replacing the hydrogen of the hydroxyl group by electron exchange and linked to the carbonyl oxygen by the coordinative bond.

3. The process as claimed in claim 1, where the depressing organic compound is an alpha hydroxy benzoquinone.

4. The process as claimed in claim 1, where the depressing organic compound is an alpha hydroxy-diquinoyle.

5. The process as claimed in claim 1, where the depressing organic compound is an alpha hydroxy-naphtoquinone.

6. The process as claimed in claim 1, where the depressing organic compound is a basic polyhydroxy-anthraquinone, with one of the hydroxyl groups in alpha position.

GREGOIRE GUTZEIT.