April 15, 1969 M. C. FUERSTENAU ET AL 3,438,494

FLOTATION METHOD FOR THE RECOVERY OF MINERALS

Filed July 25, 1966

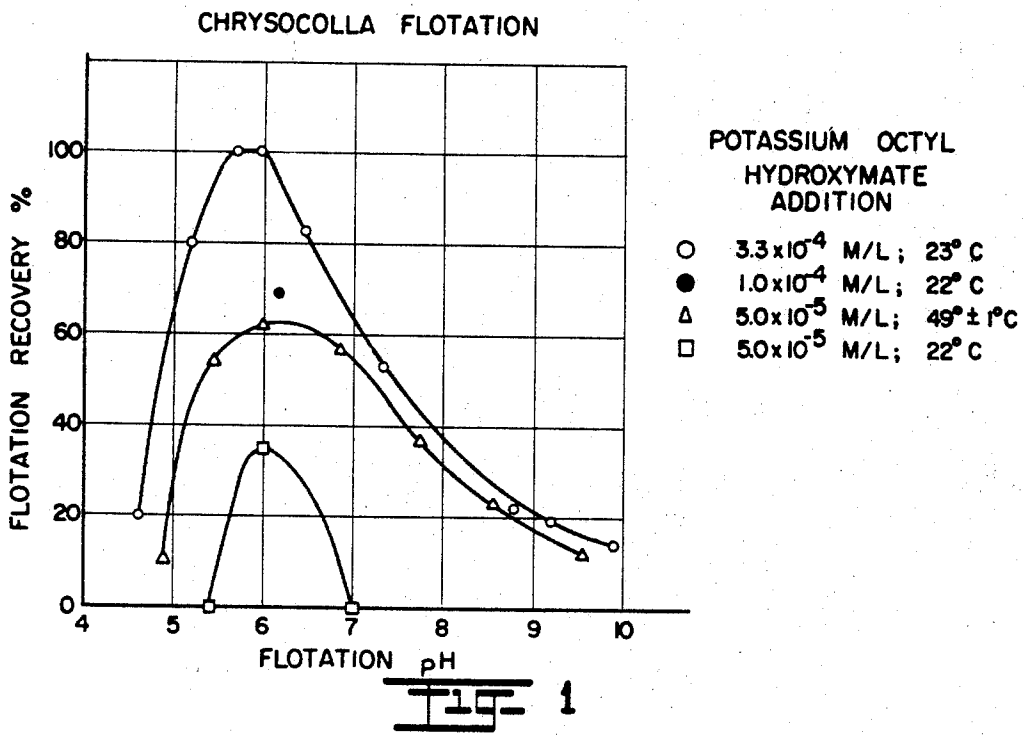


Fig. 1

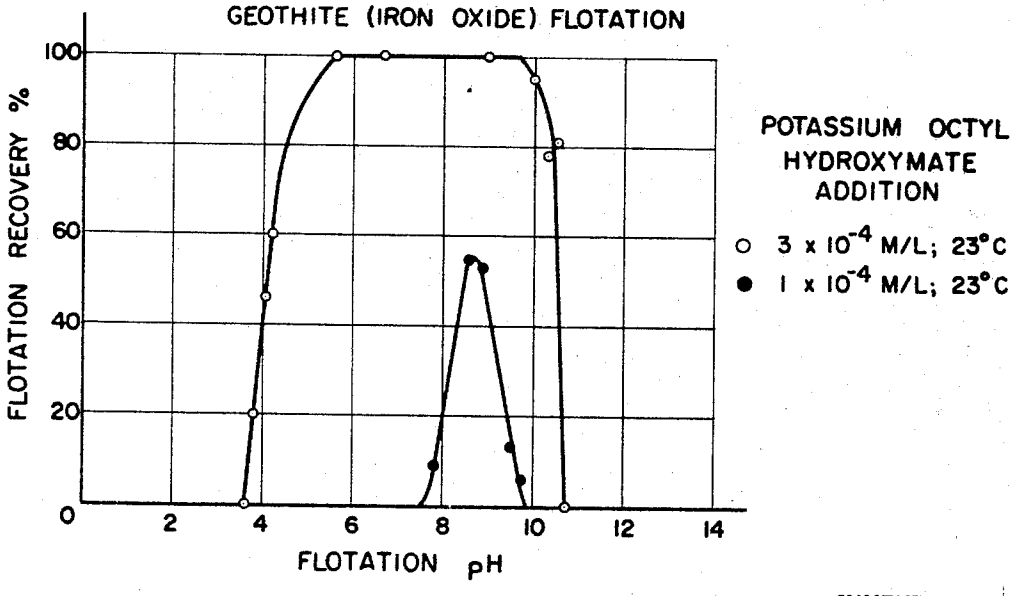


Fig. 2

INVENTOR.
MAURICE C. FUERSTENAU
HAL D. PETERSON

BY

Sheridan and Ross

ATTORNEYS

United States Patent Office 3,438,494
Patented Apr. 15, 1969

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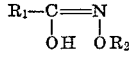
FLOTATION METHOD FOR THE RECOVERY OF MINERALS

Maurice C. Fuerstenau, Golden, and Hal D. Peterson, Boulder, Colo., assignors to Colorado School of Mines Foundation, Inc., Golden, Colo., a corporation of Colorado

Filed July 25, 1966, Ser. No. 567,734
Int. Cl. B03d 1/00
U.S. Cl. 209—166 9 Claims

ABSTRACT OF THE DISCLOSURE

A flotation method for recovering chrysocolla and iron oxide minerals from their ores which comprises adding to a water suspension of the finely divided ore at a pH at which the metal ions become hydroxylated, a chelating agent having the formula:



wherein R_1 is a member selected from the group consisting of aliphatic and aryl radicals having from five to ten carbon atoms and R_2 is a member selected from the group consisting of hydrogen and an alkali metal; adding a frothing agent; and recovering the floated mineral from the suspension.

This invention relates to a new flotation method for the recovery of minerals containing valuable metals.

The invention will be described specifically in connection with the flotation recovery of chrysocolla, a copper silicate bearing mineral, and also with the recovery of iron oxide minerals.

The flotation characteristics of the oxide copper minerals, malachite, azurite, and cuprite have not presented the difficulty for concentration as have those of the copper silicate, chrysocolla. The copper carbonates and oxides respond reasonably well to flotation with conventional collectors, whereas chrysocolla will not respond to flotation with fatty acids or xanthates under normal flotation conditions.

The prior art discloses that chelating agents can be used as collectors in flotation systems for various metals. Such chelating agents include ammonium nitrosophenylhydroxylamine for the flotation of cassiterite and dimethylglyoxime for the flotation of nickel oxide ores. It is disclosed in the prior art that oximes function well as collectors for chalcocite, malachite, azurite, and cuprite. Although the prior art indicates that the use of chelating compounds for the flotation of chrysocolla are a possibility, prior to this invention, no satisfactory chelating agent has been available which is effective for the flotation of this mineral.

While it is known that certain chelating agents will form insoluble complexes with cupric ion, they are not effective for the flotation of chrysocolla. Two examples of this phenomenon are dimethylglyoxime and benzoin α oxide. Experimentation showed that flotation could not be effected with dimethylglyoxime probably because the hydrocarbon chain is too short to render the surface hydrophobic. It was found that benzoin α oxide does function as a collector, but flotation can be obtained only over a narrow pH range (pH 7.3 to 7.4).

In order to promote flotation by the formation of insoluble complexes with chelating agents, the metal carried by the mineral sought to be collected should be one the ions of which in water suspension can be surface hydroxylated so that the metal-chelate can form. The water solubility constants of satisfactory chelating agents for the flotation of minerals containing valuable metals whose ions can be hydroxylated in water suspension must be

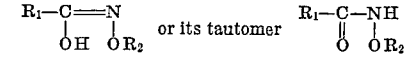
within a fairly well defined range which will promote flotation. It is well known that some organic metal chelating compounds offer a selectivity as to those metals with which they form insoluble complexes.

Accordingly, it is an object of this invention to provide a method for the flotation recovery of minerals containing valuable metals.

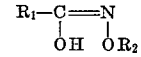
It is another object of this invention to provide a method for the flotation recovery of minerals containing valuable metals by the use of chelating agents.

It is another object of this invention to provide for the flotation recovery of minerals containing copper and iron, specifically, the copper mineral (chrysocolla), and iron oxide minerals, by the use of chelating agents.

In accordance with the invention, the above and other objects are accomplished by the use of flotation agents under certain pH conditions of a chelating agent having the formula:



wherein R_1 is an aliphatic or aryl group having from 5 to 10 atoms in the chain and R_2 is a member selected from the group consisting of hydrogen and alkali metal. The class of chelating agents will be designated hereinafter as:



The flotation of the mineral is achieved by adjusting the pH of a water suspension of a finely divided ore containing the mineral to a point at which the surface metal ions of the mineral become hydroxylated, at which point the selected chelating agent is added, followed by the addition of a conventional frothing agent, such as, an alcohol.

Compounds which have been found to be operative for the purpose of the invention are hydroxamic acids having an aryl group, or an aliphatic group with from 5 to 10 carbon atoms in the chain, and alkali metal salts of such hydroxamic acids. A preferred alkali metal salt is the potassium or sodium salt because of its favorable water solubility properties. Although the acids themselves are almost equally as effective as their alkali metal salts, their solubility is not quite as favorable as their alkali metal salts. It was found that when the number of carbons in the aliphatic compounds is less than 5, no flotation was obtained. When the number of carbons in the chain exceeds 10, the compound is too insoluble in water to produce effective flotation. The preferred frothing agents are alcohols and these compounds are conventionally used.

The invention will now be described with reference to the accompanying drawings in which FIGS. 1 and 2 are graphs respectively showing results obtained by the application of the invention to the flotation recovery of chrysocolla and iron oxide (goethite).

The chelating agent used for all of the examples was potassium octyl hydroxamate. This compound was prepared as follows: (1) 1.0 mole of KOH in 140 cc. of methanol was combined with 0.6 mole of hydroxylamine hydrochloride in 240 cc. of methanol at 40° C. (KCl precipitates under these conditions and to effect complete removal of KCl, the system was cooled to 10° C. and filtered, (2) a light methanol wash was then given the KCl cake, (3) the filtrate was agitated at room temperature and 0.33 mole of the methyl ester of the organic acid (i.e. methyl octanoate) was added, (4) agitation was maintained for a period up to 48 hours (over 90% conversion will occur in approximately 4 hours), (5) the potassium alkyl hydroxamate was filtered and then washed with methanol and (6) recrystallization was effected in methanol.

Example I.—Flotation recovery of Chrysocolla

Microflotation studies were conducted as well as experiments with the natural ore.

The chrysocolla used in the microflotation studies was from New Mexico and analyzed 20.8% copper. X-ray diffraction showed this material to be amorphous in character, but some faint lines of quartz were noted. A natural oxide copper from Utah was also used in the investigation. This ore contains malachite principally, but also contains chrysocolla and tenorite together with some sulfide copper. The sulfide copper comprises 15 to 20% of the total copper content of the ore.

Reagent grade n-amyl alcohol was used as the frother in the experiments with pure mineral, while MIBC was used in the work with the ore. The microflotation experiments were conducted with standard equipment and techniques using 3 gram charges of 48 x 150 mesh chrysocolla at ambient and elevated temperature.

Tests with the natural ore were conducted in accordance with the following procedure: (1) The ore was ground in a porcelain mill with porcelain balls with tap water at 60% solids and screened through 48 mesh, (2) the ground ore was deslimed by decanting until relatively free from slimes, (3) the pulp was heated to about 70° C. by bubbling steam into a Fagergren cell and the pH was adjusted to the desired value, (4) a given amount of potassium octyl hydroxamate and the frother were added to the cell and the pulp was conditioned for 3 minutes, (5) the pH was measured (termed flotation pH), and the temperature was measured (termed flotation temperature), and (6) the froth formed was collected until depleted.

Flotation tests were run with three constant additions of potassium octyl hydroxamate at two different temperatures and three pH values. The results of the tests are shown in the graph of FIG. 1 in which flotation recovery is plotted on the ordinate against flotation pH on the abscissa. The graph shows a marked effect of pH on recovery, with the most favorable pH value being about 6.

It can be seen that a recovery of 35% is obtained with 5×10^{-5} mole per liter at pH 6 at ambient temperature. Doubling the collector addition resulted in doubling the recovery under the same conditions. With an addition of 3.3×10^{-4} mole per liter, complete flotation was achieved at about pH 6 at ambient temperature and recovery was noted to decrease markedly above and below this value of pH.

When the pulp temperature was increased to 50° C., the maximal recovery of about 65% was obtained with an addition of 5×10^{-5} mole per liter of potassium octyl hydroxamate at pH 6 as compared to recovery of about 35% with the same pH and level of addition of collector at ambient temperature.

The experimental conditions for a favorable flotation response that evolved from the work with pure chrysocolla were also employed with the natural ore. Flotation recoveries of 58, 73 and 79% were obtained with 0.096, 0.41 and 2.4 lb. per ton of potassium octyl hydroxamate and 0.12 per ton amyl xanthate at elevated temperature and pH values between 5.8 and 6.5, and the grades of the concentrates were 31.3, 23.7 and 4.7% copper, respectively. Microscopic inspection of the tailings from the experiments in which the higher levels of addition of potassium octyl hydroxamate (e.g., 0.4 lb. per ton) were used, showed these products to be almost entirely free of malachite and chrysocolla.

It was found that the use of xanthate was unnecessary for the flotation of copper sulfide and that all four of the copper minerals present floated with the use of potassium octyl hydroxamate alone. Tests showed that the use of amyl xanthate alone resulted in flotation of only copper sulfide and tenorite.

Example II.—Flotation recovery of iron oxide

In the case of iron oxide flotation, microflotation experiments were conducted with 3 gram charges of goethite at ambient temperature using the apparatus and technique described in Example I. Goethite was selected for study because of the ease of obtaining pure samples and also because it has been previously shown that the flotation characteristics of the iron oxide minerals (hematite, magnetite and goethite) are similar. The results obtained with two levels of addition of potassium octyl hydroxamate are shown in FIG. 2. It can be seen that a maximal recovery of about 55% was obtained at about pH 8.6 with 1×10^{-4} mole per liter of potassium octyl hydroxamate. When 3×10^{-4} mole per liter of potassium octyl hydroxamate was used, complete flotation was obtained from about pH 5.6 to 9.6.

Experiments were also conducted with a natural ore containing about 12.5% iron as hematite and goethite. This ore was a tailings product from a spiral classifier, and as a result no further grinding or slime removal steps were necessary. Experimentally, 500 gram charges of this ore were conditioned with 2.3 liters of water at the natural pH of the system (pH 7.7) for three minutes with 0.2, 0.3, 0.4, and 0.5 lb. per ton of potassium octyl hydroxamate. Flotation recoveries of 52.8, 85.9, 90.6, and 92.4% were obtained with 0.2, 0.3, 0.4, and 0.5 lb. per ton of potassium octyl hydroxamate, respectively. Grades of the final concentrates were 69.5 and 68.4% iron when 0.3 and 0.4 lb. per ton of potassium octyl hydroxamate were added.

The above results graphically illustrate that the chelating agents of the invention are effective for the flotation of chrysocolla and iron oxide minerals as illustrated in the two examples.

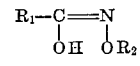
While the reason for the selective action of the chelating agents was not fully determined, it is believed to be due to the formation of an insoluble complex between the surface metal ions and the chelating agent. This complex is believed to be formed when the metal ions at the surface of the mineral are hydroxylated in water solution which establishes the required pH value. Flotation of the mineral is highly dependent upon the solubility properties of the chelating agent and this, in turn, is determined by the critical chain length of the aliphatic or aryl substituent of the hydroxamic acid and its alkali metal salts.

It is thus seen from the above examples and description that a method has been provided for the effective recovery of the mineral chrysocolla and iron oxide minerals. The method is relatively inexpensive, and can be readily adapted to commercial production.

It is to be understood that the description of the invention as set forth herein is for the purposes of explanation and illustration, and various modifications can be made within the scope of the appended claims without departing from the spirit of the invention.

We claim:

1. The method of recovering chrysocolla and iron oxide minerals from their ores by flotation which comprises: making a water suspension of the ore in finely divided form; adjusting the pH of the suspension to a point at which the surfaces of the metal ions of the mineral become hydroxylated; adding to the suspension to promote flotation a chelating agent having the formula:



wherein R_1 is a member selected from the group consisting of aliphatic and aryl radicals having from five to ten carbon atoms and R_2 is a member selected from the group consisting of hydrogen and an alkali metal; adding a frothing agent; and recovering the floated mineral from the suspension.

2. The method of claim 1 in which the temperature varies from about 22° C. to about 60° C.

3. The method of claim 1 in which said mineral is chrysocolla.

4. The method of claim 3 in which the pH varies from about 5 to about 10.

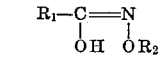
5. The method of claim 4 in which said chelating agent is potassium octyl hydroxamate.

6. The method of claim 1 in which said mineral is an iron bearing mineral and said pH varies from about 3 to about 11.

7. The method of claim 1 in which said chelating agent is a member selected from the group consisting of alkyl hydroxamic acids and alkali metal salts thereof in which the alkyl chain has from 5 to 10 carbon atoms.

8. The method of claim 7 in which said chelating agent is an alkali metal salt of an alkyl hydroxamic acid in which the alkyl chain has from 5 to 10 carbon atoms.

9. The method of flotation recovery from their ores of chrysocolla and iron oxide minerals the surface ions of which are hydroxylated in water suspension, which comprises: forming a water suspension of the ores in finely divided form; adjusting the pH of the suspension to the point where the surfaces of the minerals to be recovered are hydroxylated; and forming an insoluble complex between the hydroxylated surface metal ions and a chelating agent by adding to the suspension a chelating agent having the formula:



wherein R_1 is a member selected from the group consisting of aliphatic and aryl groups having from five to ten carbon atoms and R_2 is a member selected from the group consisting of hydrogen and alkali metal.

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FRANK W. LUTTER, *Primary Examiner.*

ROBERT HALPER, *Assistant Examiner.*