FROTH FLOTATION CONCENTRATION OF AZURITE AND MALACHITE IN ALKALINE EARTH GANGUE MATERIALS

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Major professor

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FROTH FLOTATION CONCENTRATION
OF AZURITE AND MALACHITE
IN ALKALINE EARTH GANGUE MATERIALS

by

PHILIP ALFRED LENTON

A THESIS

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THESIS

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INTRODUCTION

In Alaska, Arizona, and other sections of the North American continent there exist comparatively large quantities of copper carbonate ores. The copper exists as malachite ($CuCO_3 \cdot Cu(OH)_2$) and azurite ($2CuCO_3 \cdot Cu(OH)_2$). Unfortunately, there is present in the ores a large amount of impurities which consist principally of dolomite ($CaCO_3 \cdot MgCO_3$) and calcite ($CaCO_3$). Some of the ores, however, also contain large quantities of silica and some copper in the form of chrysocolla ($CuSiO_3 \cdot 2H_2O$). The separation of the copper carbonate minerals from the alkaline earth gangue materials by froth flotation was undertaken as a research problem.

Froth flotation has been used quite successfully for some time in the separation of precious metal minerals from gangue. However, the flotation of these copper carbonates has not, to the author's knowledge, been placed on a commercial basis because of the excessive amounts of reagents required for the separation.

The literature was reviewed in an attempt to find a new collecting reagent and to investigate the work already done on copper carbonate ores. Flotation tests were run and data collected by the use of a flotation cell built of Lucite in the Chemical Engineering Laboratories of Michigan State College. The separation of malachite and azurite from dolomite and calcite in synthetic mixtures containing 1% of the copper mineral was successfully completed, employing xanthates as collecting agents. Many less successful runs were made using various collecting agents. In addition, tests were carried out using naturally occurring ores from Alaska and Arizona.

The data presented herein have not completely solved this problem, but certainly the conclusions which can be reached from the results will prove very valuable to future work on this and similar research.

HISTORY

Although chalcocite (Cu_2S) has been successfully separated from gangue for some time by froth flotation, the separation of oxidized copper minerals has not been satisfactorily accomplished. Taggart (4) lists three general methods attempted in the flotation of oxidized base-metal minerals. These are: (1) sulphide-filming processes; (2) solution and precipitation as sulphide or metal; and (3) selective oxide-flotation. The first method, although suitable in some cases, is not satisfactory in the case of most copper carbonate ores. A variation of the second method was used with oxidized copper ores in Arizona. (3) The ores were leached with sulfuric acid and the copper was recovered by electrodeposition. The third method, that of selective flotation of the oxidized copper mineral, has been used on Katanga ores containing malachite and azurite. (3)

Several attempts have been made to separate malachite and azurite from gangue by selective flotation. DeWitt and von Batchelder (8) achieved some success in separating azurite and malachite from a siliceous gangue, using oximes as flotation reagents. The experiments were carried out with synthetic mixtures containing slightly less than 1% of the copper mineral. Recoveries were recorded as high as 97.7%, with the concentrate reaching about 34% copper in the case of malachite. Lower values were recorded for azurite. The pH of the solution was kept in the range of 4.0 - 5.0.

With regard to the separation of malachite and azurite from synthetic mixtures containing calcite, Gaudin and Martin (12) contributed much. The mixtures that they worked with contained 10 grams of the copper mineral to 40 grams of the calcite or, in other words, 20% of their ore was mineral. Experiments with fatty acids as collecting agents showed that, although the malachite and azurite floated, a separation from the calcite was not possible because the calcite also floated equally as well.

Results obtained by these authors using various xanthates as collectors were presented and proved to be much more satisfactory. Practically complete recovery of malachite and almost complete separation from calcite were obtained using potassium iso-amyl xanthate as the collecting agent. The concentration of the reagent necessary for this separation was three pounds per ton of ore. Results obtained by the use of mercaptans and other organic hydrosulphides as collectors were also fairly good.

In a later paper, Gaudin and Anderson (11) continued this work. Many new collectors were unsuccessfully tried. The effect of pH upon the separation of malachite from calcite was shown and, according to their results, the recovery changed considerably with a change in pH. When inorganic reagents were added before adding the collector, a depression of the malachite resulted. However, the addition of lead or zinc nitrate improved the separation remarkably. A good separation was obtainable using two pounds per ton of potassium secondary butyl carbinol xanthate as a collector after first conditioning with the lead or zinc nitrate.

THEORY

Although the term flotation would lead one to believe that the separations depend upon the densities of the various particles, this is certainly not the case in froth flotation. The fact is true, of course, that gravity separations are still in use, but, since 1912, (5) differential froth flotation has increased in importance until it is now used in the concentration of practically all minerals.

Several steps are involved in the froth flotation process. They are as follows: (1) the ore is crushed to a state where the mineral particles are free of the gangue material; (2) the crushed ore is suspended in water which contains various reagents, and these reagents, together with agitation and air, cause the mineral particles to cling to the rising stabilized air bubbles; (3) the bubbles, lined with the minerals, are then floated from the surface and the concentrated mineral may then be either further concentrated by the same process or it may be suitably treated as such for the recovery of the metal.(7)

The four functional reagents used in froth flotation are defined by Wark (5) thus:

"A frother is a substance (generally organic) which, when dissolved in water, enables it to form a more or less stable froth with air.

"A collector for any mineral is a substance (generally organic) which induces it to float at the air-water interface and, in the presence of a frother, to form a more or less stable mineralized froth.

"An activator for any mineral is a substance (generally inorganic) the addition of which induces flotation in the presence of some collector that otherwise is without effect on the mineral.

"A depressant for any mineral is a substance (generally inorganic) the addition of which prevents a collector from functioning as such for that mineral."

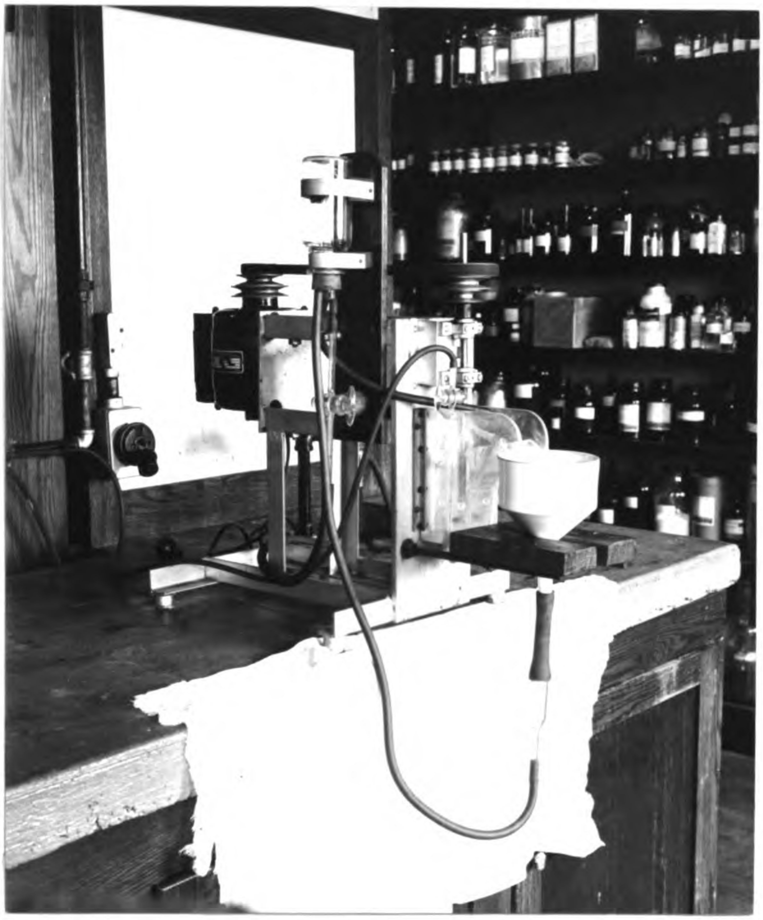
Frothers are almost entirely organic compounds whose molecules each contain one polar group and one non-polar group. These frothers act upon the gas-liquid interface, not at the surface of solids. They should not ionize appreciably as this would give them collecting properties. (Proper control of flotation processes is difficult if the frothers collect also.) Several investigators have showed that the frothing power of a reagent is related to the lowering of surface tension when that reagent is added to water. For example, DeWitt and Makens (9) found that the frothing agent with the most negative slope on a surface tension-molar concentration curve was the most efficient frother.

Collecting agents are similar to frothers in that they are also heteropolar, but collectors should be ionized to a greater extent. Furthermore, the polar part of collectors should have a specific affinity for specific minerals whereas the polar part of frothers should have affinity for water only. (2) The purpose of the collector is to cover the mineral at least partially with an organic compound. Two opposing theories have been presented to explain the mechanism of this film formation. Taggart and his collaborators believe that this film is an insoluble precipitate. This may result either from double decomposition at and with mineral surface atoms or by adsorption at the mineral interface from saturated solutions of difficultly soluble substances. The opposing adsorption theory adopted by Wark (5) suggests that the collector ions are merely adsorbed at the mineral surface. The adsorption is dependent upon the degree of insolubility of the compound formed by the cation of the mineral surface and the anion of the collector.

Both of these contentions are supported by experimental data, and it would not be surprising if there were cases where one was applicable and other cases where the opposite theory was true. At any rate, the result is essentially the same in either manner of formation. The film that is formed has non-polar groups projecting away from the mineral. These non-polar groups will, of course, seek out the non-polar air in preference to the polar water, with the result that the mineral particles adhere to the air bubbles. In other words, "the object of coating a mineral with an insoluble or tenacious organic film is to give it the property of exhibiting a finite contact angle in the presence of air--i.e., to make it possible for the air to displace the water partially from the coated mineral surface in order to make the mineral particle surface less easily wetted by water." (7)

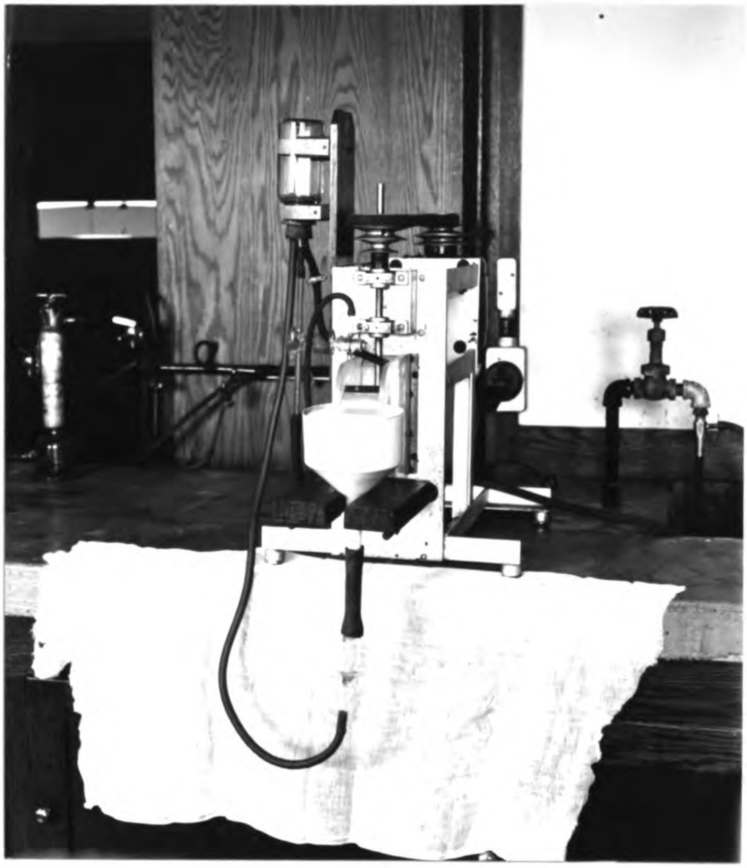
As in the case of the frothers, in a homologous series of collectors, the one possessing the most negative slope of the surface tension-concentration curves will be the most effective.

A word of explanation might be added here with regard to a few of the other terms used in this paper. "Heads" refers to the charge into a flotation cell. "Concentrate" refers to the material collected in the overflow and the solids remaining in the liquid are called "tails". The percentage recovery refers to the fraction of the total mineral in the heads that was present in the concentrate.



APPARATUS

SIDE VIEW



APPARATUS

FRONT VIEW

PROCEDURE

All minerals and ores used in the research were first crushed to size in a small Chipmunk jaw crusher. After crushing, the material was sized, using a standard set of screens. A Denver screen shaker was used in the sizing in most cases although some screening was done by hand. The portion passing through the 40 mesh screen but remaining on the 60 mesh screen was taken for experimentation almost exclusively.

The copper minerals, ores, and the concentrates from the flotation runs were analyzed for copper using the method of Park.(13) The samples were dissolved in concentrated nitric acid. The solution was aided by the use of two or three drops of concentrated hydrochloric acid which did not affect the analysis appreciably. After treatment with ammonium hydroxide and ammonium bifluoride, potassium iodide was added and the iodine liberated was titrated with .1 N sodium thiosulfate solution. The latter was prepared according to Willard and Furman.(6) In the case of the larger concentrates, aliquot portions were taken for analysis after the samples were dissolved.

The flotation runs were carried out in a flotation cell constructed of the transparent Lucite so that the material in the cell could be observed. The cell, 100 gram capacity, was built of one-fourth inch Lucite sheets glued together by a special acetone-Lucite cement. (14) The material in the cell was agitated by a stainless steel impeller driven by a one-sixth horsepower electric motor. An air compressor introduced air through the bottom of the cell. The air line, in addition to stop cocks for control, also contained a calcium chloride tower packed with glass wool to remove any oil from the compressor. The froth overflow, at the front of the cell, was sloping and a baffle was placed before it to prevent particles from being pushed over by the action of the stirrer. A small outlet was made in the bottom of the cell for the removal of the tails after a run.

The froth overflowed into a Buchner funnel and the filtrate was removed by a vacuum created by a water aspirator. This filtrate was drawn up into a small reservoir and, from time to time, the vacuum was released and the filtrate was returned to the cell. In this way, although the level in the cell was not constant, re-use of the froth water was possible and no make up water was necessary.

In preparation for a test, the impeller and the air were started, the ore was placed in the cell followed by water, and then the accurately weighed collector, in solution, was added. Unless otherwise indicated, there was, in all runs, an agitation period of three minutes. A frother, pine oil, was used in most of the tests and this was put in the cell by dipping a small wire into the pine oil and then dipping the wire into the water in the cell. After three minutes, more water was added and the air was increased so that the froth overflowed into the funnel. The froth was collected for six minutes, after which time the material on the filter paper was dried, first by the vacuum from the water aspirator and then in an electric oven at 100° C. for twenty to sixty minutes. The drying time depended on the size of the concentrate. After drying, the concentrate was weighed and analyzed for copper. The concentration of copper and the percentage recovery could then be calculated.

After some runs a sample of the solution remaining in the cell was taken and the pH was measured with a Beckman pH meter. After all runs the tails were removed and inspected visually, sometimes with the aid of a microscope.

In the first series of tests an effort was made to find a suitable collector to separate azurite from dolomite. The runs were made on synthetic mixtures containing ninety-nine grams of dolomite and one gram of azurite. For the more successful collectors, the xanthates, various graphs were prepared showing the effect of the concentration of the collector upon recovery and concentration. The most successful collector, potassium n-decyl xanthate, was also used in runs separating malachite from dolomite, malachite from calcite, and azurite from calcite, where the copper mineral was 1% of the mixture.

Several experimental runs were made on an ore from Alaska using potassium n-decyl xanthate as the collector. Among these were some dilution runs, showing the effect of diluting the ore with dolomite. Other more successful runs were made by first "desliming" the ore. Before flotation the ore was washed in a beaker and the liquid was decanted. This process was repeated several times until the liquid seemed to be free of any green color. In some cases the washings were analyzed for copper also. Less successful runs were made on fine Alaskan ore after a similar "washing" operation.

Runs were made on an ore from Arizona using potassium n-decyl xanthate as a collector on the washed ore.

An unsuccessful attempt was made to float the Alaskan ore in an acid circuit using salicylaldoxime as a collecting agent. Sulfuric acid was used for acidification.

The xanthates used in this research were prepared by the methods suggested by Foster. (10) The lower xanthates were made by first dissolving potassium hydroxide in the alcohol to form the alcoholate and then allowing the alcoholate to react with excess carbon disulfide. The yellow precipitate was filtered, washed, and recrystallized from mixtures of acetone and benzene. In the preparation of potassium n-decyl xanthate, a saturated solution of potassium hydroxide was added to the alcohol and the carbon disulfide was added to the mixture in an ice bath. Constant agitation was provided and the precipitate formed was purified by recrystallization.

DATA

SOURCE OF MINERALS

DOLOMITE

Obtained from the Inland Stone and Lime Company at Manistique, Michigan.

CALCITE

Obtained from the Michigan Alkali Company. This limestone probably came from the region of Alpena, Michigan.

AZURITE

Obtained from the Ward Natural Science Company. Found by analysis to contain 45.6% Cu.

MALACHITE

Obtained from the Ward Natural Science Company. Found by analysis to contain 52.65% Cu.

ALASKAN ORE

Obtained from the Kennecott Copper Company by courtesy of E. T. Stannard. Contains azurite and malachite with apparently traces of chrysocolla. Found by analysis to contain 9.38% Cu. Calcite and dolomite present in large quantities.

ARIZONA ORE

Obtained from the Phelps Dodge Company by courtesy of F. Kohlhaas. Contains malachite as the predominate copper mineral but also contains fairly large amounts of chrysocolla and traces of other copper minerals. Found by analysis to contain 3.94% Cu. Silica present in large quantity.

The following runs were made on a synthetic mixture of one gram of azurite and ninety-nine grams of dolomite. The collectors were all used at a concentration of two pounds per ton.

TABLE 1

COLLECTOR	FROTHER	% RECOVERY	% CONCENTRATION OF MINERAL
Benzyl Amidoxime	Pine Oil	2.04	.47
Malonic Hydroxamic Acid	" "	3.75	.64
Sodium Pectate	" "	3.30	.91
Reagent * 425	" "	2.12	1.81
Oleic Acid	None	23.1	.59
Aceto Hydroxamic Acid	Pine Oil	11.9	.83
Diphenyl ** Thio Carbazone	" "	4.40	8.83

* Sample furnished by the American Cyanamid Company.

** Dissolved in ethyl alcohol instead of water.

TABLE 1 (Cont.)

COLLECTOR	FROTHER	% RECOVERY	% CONCENTRATION OF MINERAL
Oleic * Acid	Pine Oil	20.8	.55
Salicyl-aldoxime	" "	7.65	1.28
Propion Hydroxamic Acid	" "	2.42	.89
Propion Amide	" "	3.40	.69
Trimethyl Cetyl Ammonium Bromide	" "	Negligible	
Trimethyl Benzyl Ammonium Hydroxide	" "	No analysis--recovery poor	
Duprex-20 **	" "	" "	" "

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* The acid was mixed with 2.6 m.l. of kerosene.

** A methylated pectin furnished by General Foods Company through the courtesy of Dr. Kramer.

The following runs were made on a synthetic mixture of one gram of azurite and ninety-nine grams of dolomite. The collectors were used at a concentration of two pounds per ton. The frother was pine oil.

TABLE 2

COLLECTOR	SODIUM TETRA-PHOSPHATE	% RECOVERY	% CONCENTRATION OF MINERAL
Amyl * Xanthate	None	48.0	6.65
	.087 gm. **	3.57	.81
	.102 gm. ***	20.9	5.67
Potassium n-Heptyl Xanthate	None	87.9	17.3
	.113 gm. ***	87.5	24.9

* Sample from the American Cyanamid Company.

** The sodium tetra-phosphate was added and the mixture was agitated for one minute before the collector was added.

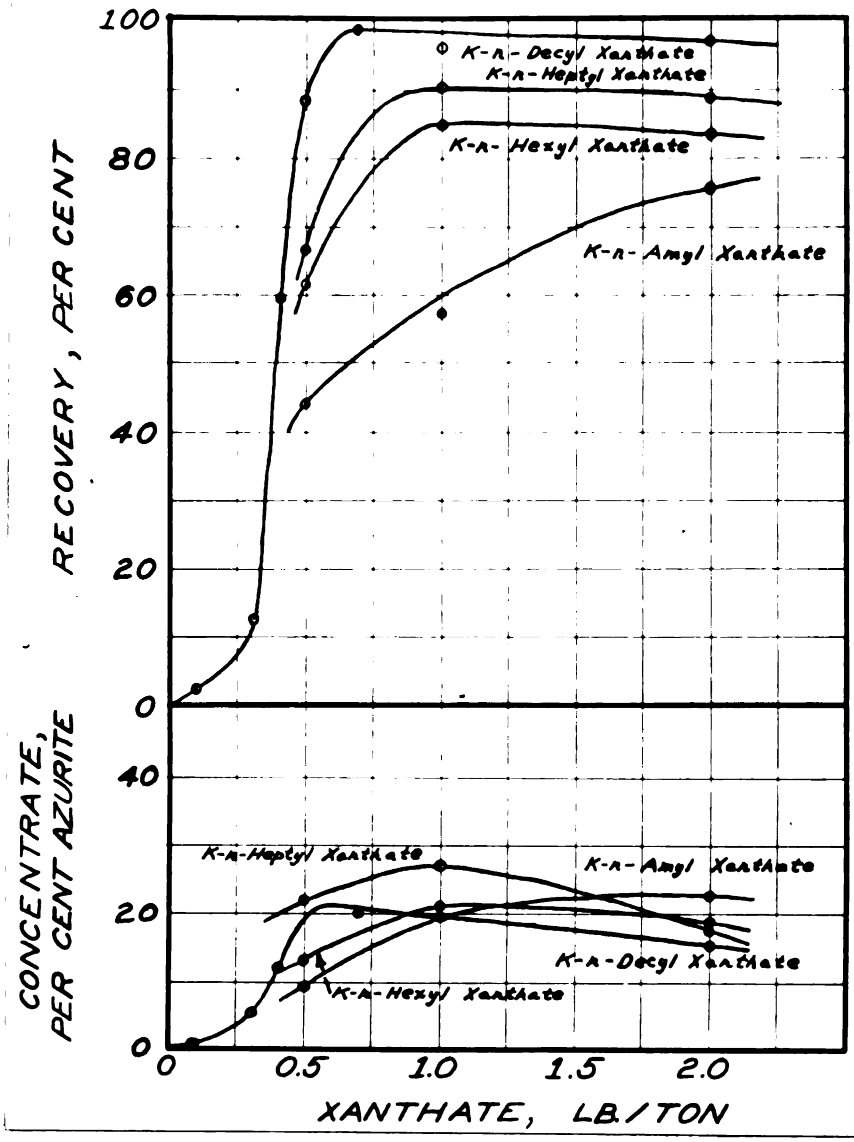
*** The collector was added and the mixture was agitated for three minutes before the sodium tetraphosphate was added.

The use of sodium silicate and Reagent 712 (American Cyanamid Company) as depressants was also tried with no success.

The following runs were made on a synthetic mixture of one gram of azurite and ninety-nine grams of dolomite. The frother used was pine oil.

TABLE 3

COLLECTOR	CONCENTRATION OF COLLECTOR	% RECOVERY	% CONCENTRATION OF MINERAL
Potassium n-Amyl Xanthate	.5 #/ton	44.0	9.40
	1.0 "	57.3	19.4
	2.0 "	75.2	22.6
Potassium n-Hexyl Xanthate	.5 #/ton	61.7	13.0
	1.0 "	85.0	21.5
	2.0 "	83.5	18.7
Potassium n-Heptyl Xanthate	.5 #/ton	66.6	22.4
	1.0 "	90.1	27.1
	2.0 "	87.9	17.3
Potassium n-Decyl Xanthate	.1 #/ton	2.98	.88
	.3 "	12.1	5.63
	.4 "	59.6	12.2
	.5 "	88.5	22.1
	.7 "	98.5	19.9
	1.0 "	96.1	19.5
	2.0 "	97.1	15.1

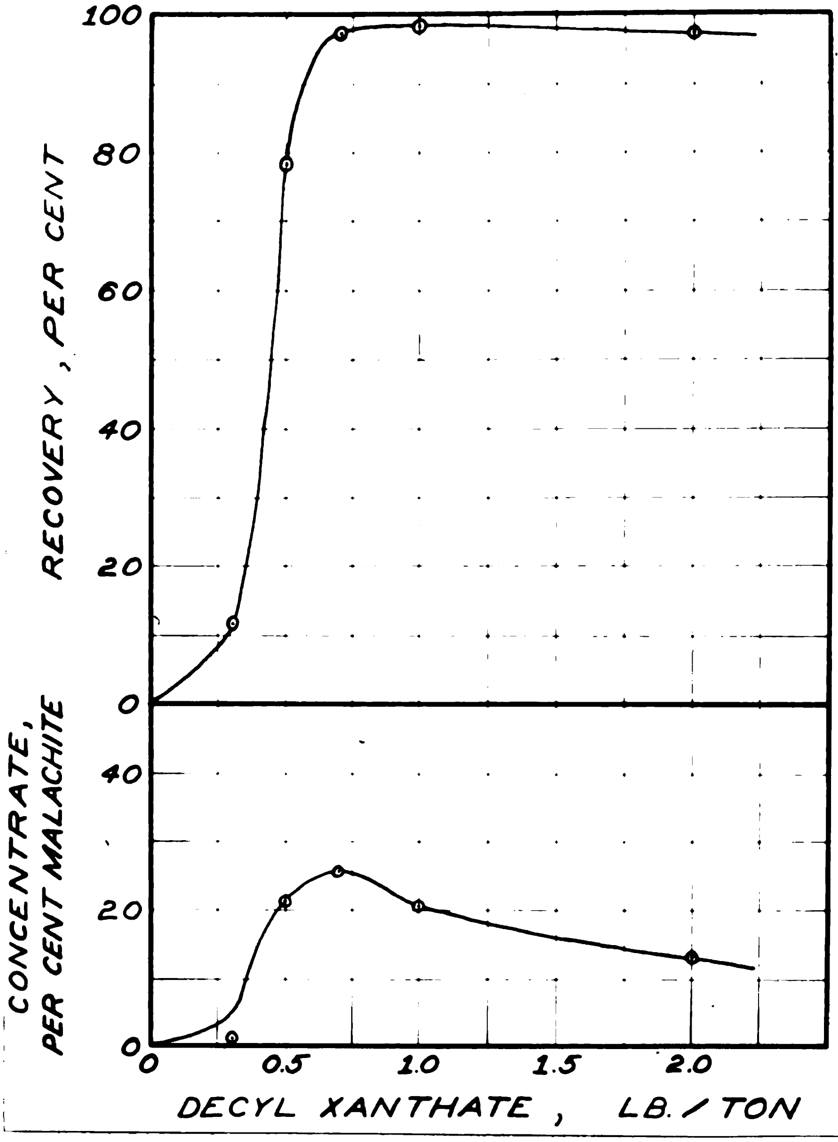


Graph 1.--Flotation of azurite from azurite-dolomite mixtures with normal potassium xanthates.

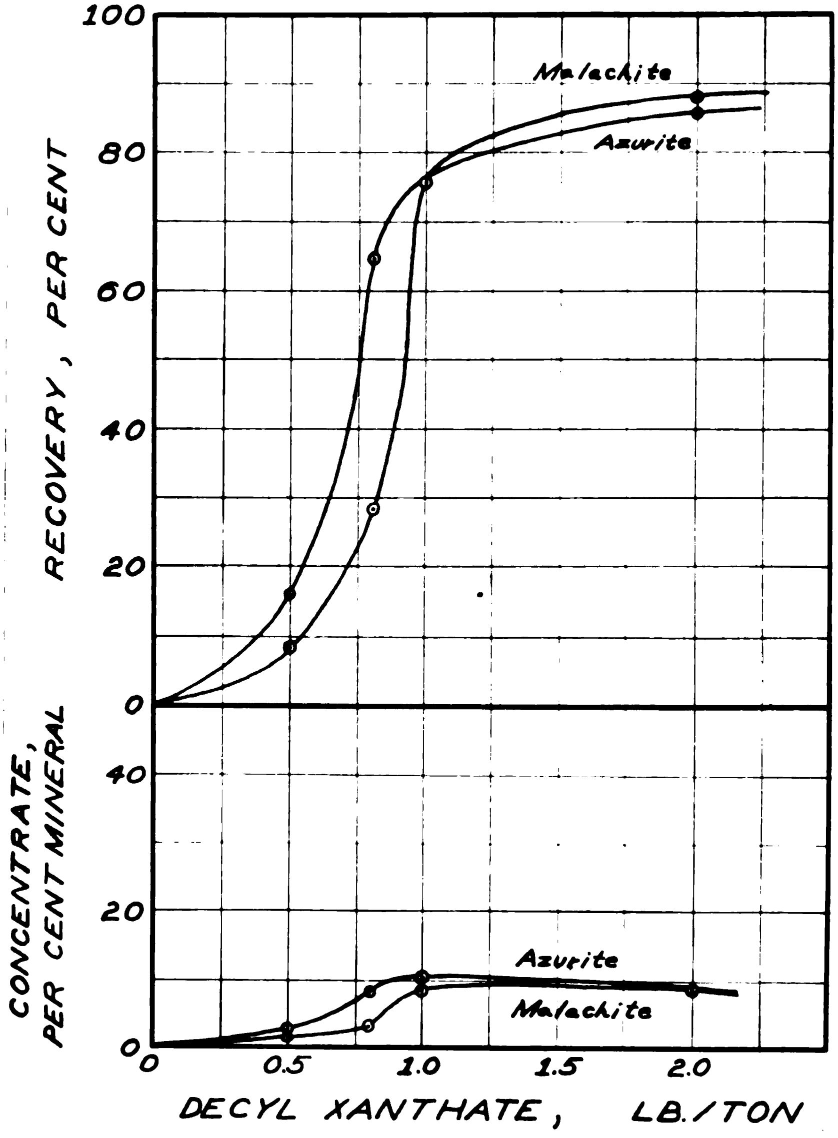
The following runs were made on the synthetic mixtures as indicated, using potassium n-decyl xanthate as the collector. Pine oil was used as the frother.

TABLE 4

MIXTURE	CONCENTRATION OF COLLECTOR	% RECOVERY	% CONCENTRATION OF MINERAL
Malachite- Dolomite	.3 #/ton	11.7	1.24
	.5 "	78.3	21.4
	.7 "	97.3	25.8
	1.0 "	98.3	20.4
	2.0 "	97.3	13.5
Malachite- Calcite	.5 #/ton	8.60	1.76
	.7 "	28.0	3.70
	1.0 "	75.8	8.55
	2.0 "	87.7	8.40
Azurite- Calcite	.5 #/ton	16.0	2.16
	.7 "	67.3	8.20
	1.0 "	76.1	10.5
	2.0 "	85.7	8.75



Graph 2.--Flotation of malachite from malachite-dolomite mixtures with potassium n-decyl xanthate.

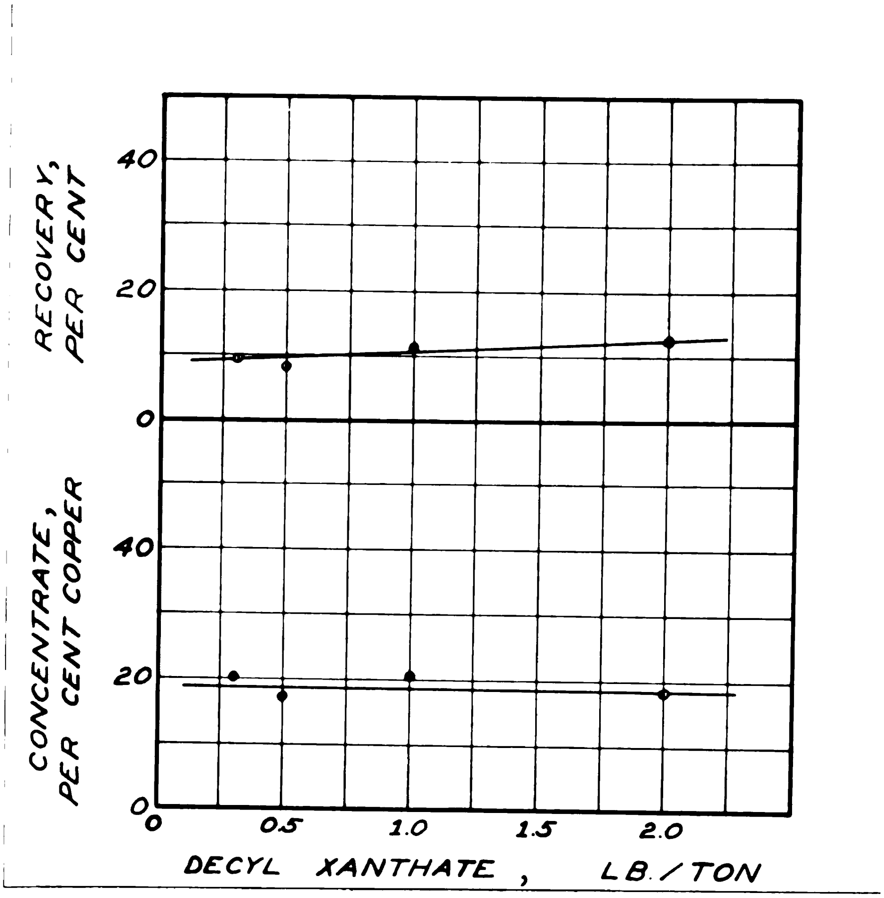


Graph 3.--Flotation of azurite and malachite from calcite mixtures using potassium n-decyl xanthate as a collector.

The following runs were made on one hundred gram samples of the Alaskan ore. The collector used was potassium n-decyl xanthate and the frother was pine oil.

TABLE 5

CONCENTRATION OF COLLECTOR	% RECOVERY	% CONCENTRATION OF COPPER
.3 #/ton	9.23	20.2
.5 "	8.08	17.2
1.0 "	11.5	20.4
2.0 "	12.6	18.1



Graph 4.--Flotation of copper minerals from an Alaskan ore using potassium n-decyl xanthate as a collector.

A run was conducted on one hundred grams of the Alaskan ore which was less than 100 mesh. The collector was potassium n-decyl xanthate at a concentration of one pound per ton. Pine oil was the frother.

% RECOVERY	% CONCENTRATION OF COPPER
29.2 *	14.7

* This is making the assumption that this ore had the same original analysis as the 40-60 ore.

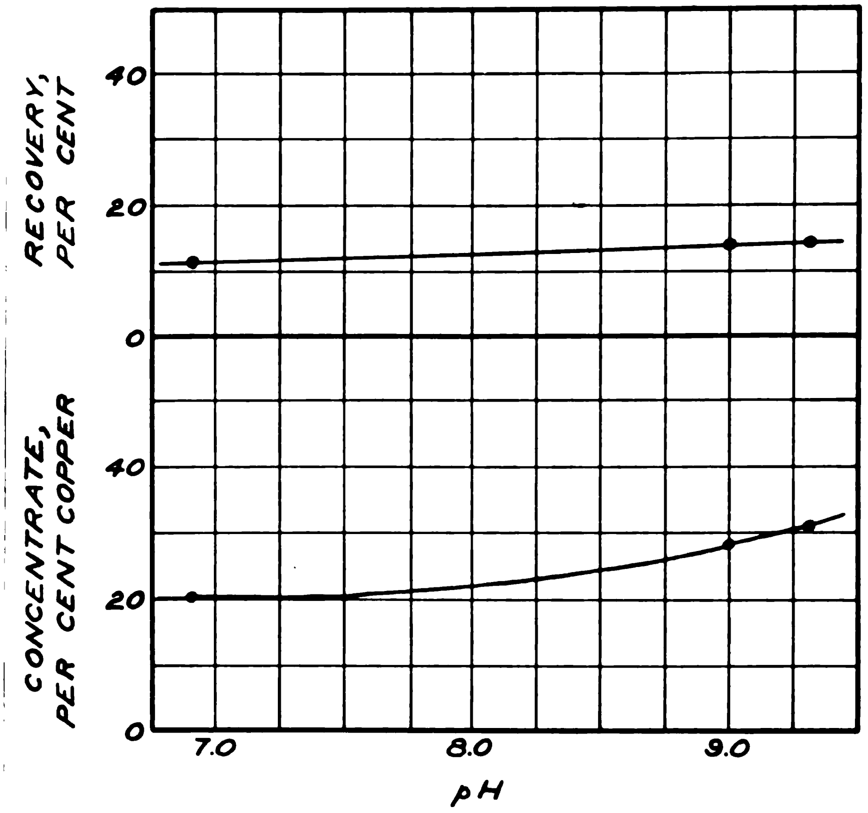
pH Values of Solutions

Material	Avg. pH
Azurite-Dolomite	8.0
Malachite-Dolomite	"
Azurite-Calcite	8.0
Malachite-Calcite	"
Alaskan Ore	6.9
Arizona Ore	8.1

The following runs were made on one hundred gram samples of the Alaskan ore. The collector was potassium n-decyl xanthate at a concentration of one pound per ton. The frother was pine oil. Sodium carbonate solution was used to regulate the pH.

TABLE 6

SODIUM CARBONATE	pH	% RECOVERY	% CONCENTRATION OF COPPER
None	6.9	11.5	20.4
1.25 gms.	9.0	14.0	28.1
2.50 gms.	9.3	14.2	31.0



Graph 5.--Effect of pH on the flotation of an Alaskan ore with potassium n-decyl xanthate as a collector.

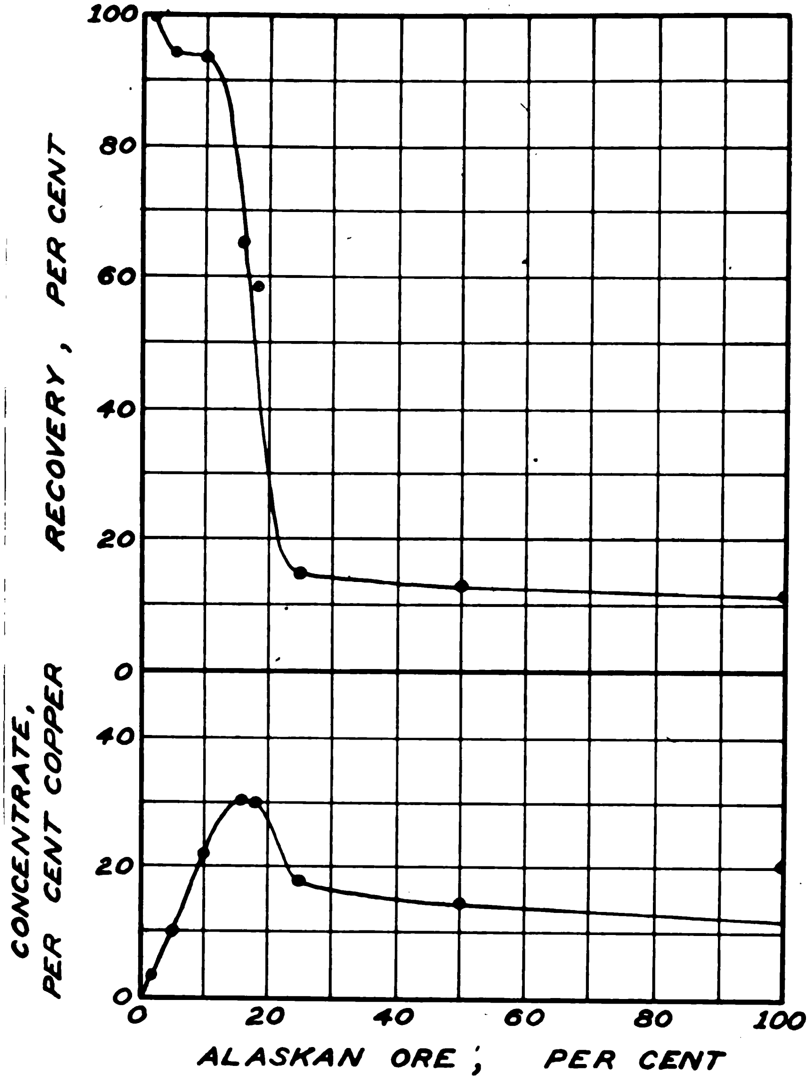
The following results were obtained using mixtures of the Alaskan ore and dolomite as indicated. Pine oil was used as a frother and the collector was potassium n-decyl xanthate at a concentration of one pound per ton of material.

TABLE 7

% ALASKAN ORE	% RECOVERY	% CONCENTRATION OF COPPER
100	11.5	20.4
50	12.9	14.8
25	15.1	17.7
18	58.5	30.0
16	65.2	30.5
10	93.5	21.8
5	94.2	10.0
2	100.0	3.53

A run using a saturated dolomite solution instead of water as the flotation medium gave the following results. The heads was one hundred grams of the ore.

% RECOVERY	% CONCENTRATION OF COPPER
10.2	25.1



Graph 6.--Flotation of copper minerals from Alaskan ore-dolomite mixtures using potassium n-decyl xanthate at a concentration of one pound per ton of mixture as a collector.

The following run was made on one hundred grams of the Alaskan ore, using pine oil as a frother and salicylaldoxime as the collector. The concentration of the collector was two pounds per ton of ore. Before addition of the collector the solution was made acid by the addition of three milliliters of concentrated sulfuric acid.

pH	% RECOVERY	% CONCENTRATION OF COPPER
4.8	2.82	5.45

Runs using propionhydroxamic acid as a collector at pH values of 3.8 and 5.4 also gave poor results.

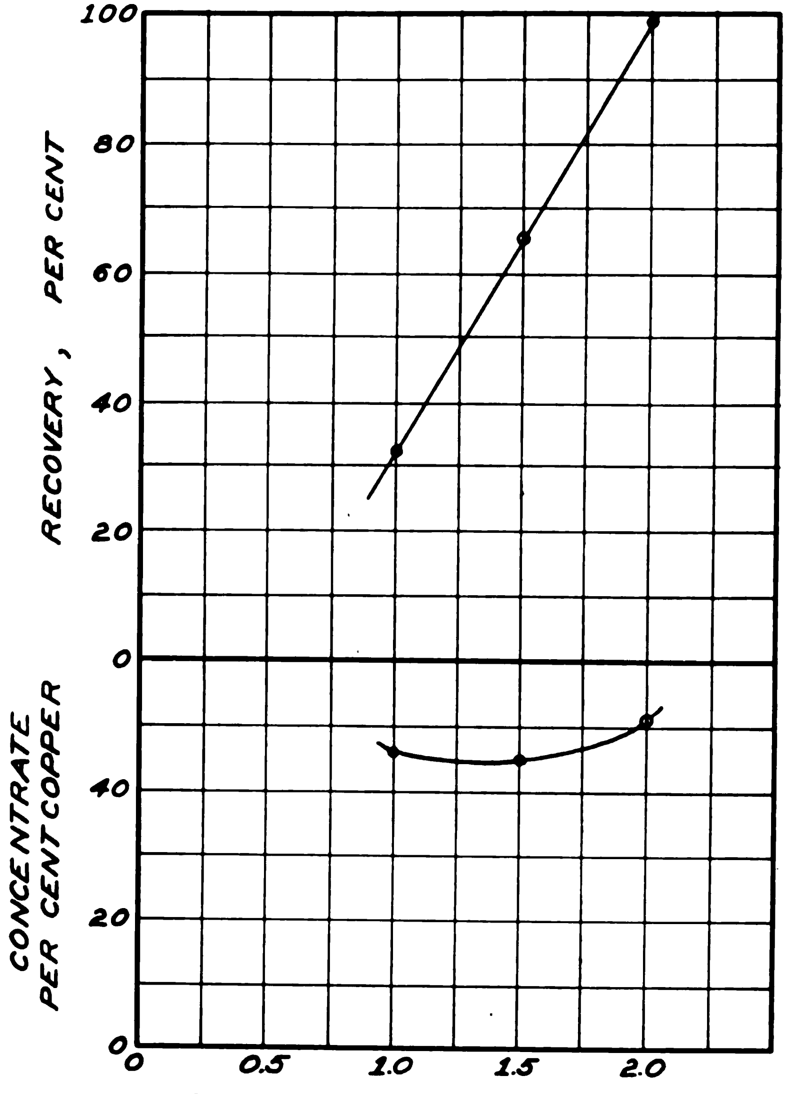
The following results were obtained from one hundred gram samples of Alaskan ore which were "deslimed" before flotation. The frother was pine oil and the collector was potassium n-decyl xanthate.

TABLE 8

CONCENTRATION OF COLLECTOR	% RECOVERY	% CONCENTRATION OF COPPER
1.0 #/ton	32.4	46.4
1.5 "	65.3	44.4
2.0 " *	98.6 **	51.4

* An analysis of the slimes washed out showed that they contained 2.3% of the original copper. The total of more than 100% copper is due to the method of sampling.

** This run was repeated with the same result.

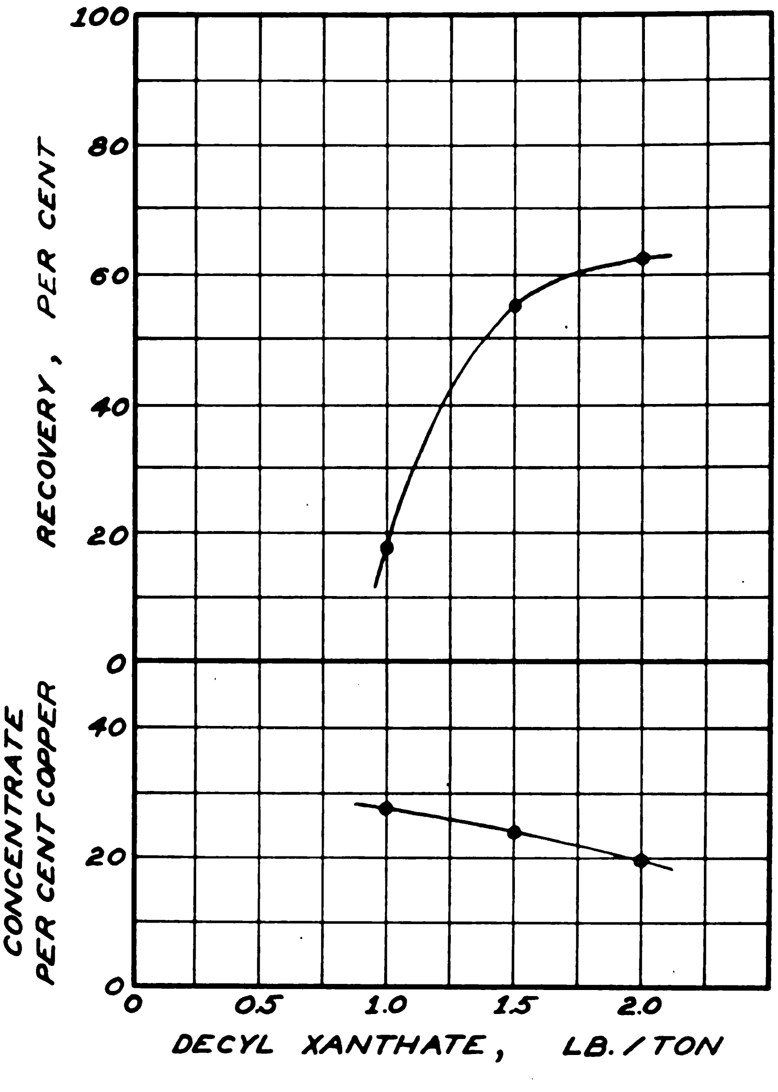


Graph 7.--Flotation of copper minerals from a deslimed Alaskan ore with potassium n-decyl xanthate as a collector.

The following results were obtained from one hundred gram samples of Arizona ore which were "deslimed" before flotation. The frother was α terpineol and the collector was potassium n-decyl xanthate.

TABLE 9

CONCENTRATION OF COLLECTOR	% RECOVERY	% CONCENTRATION OF COPPER
1.0 #/ton	17.8	27.5
1.5 "	55.0	24.0
2.0 "	62.2	19.7



Graph 8.--Flotation of copper minerals from a deslimed Arizona ore with potassium n-decyl xanthate as a collector.

One hundred grams of the Alaskan ore which was less than 60 mesh were "deslimed" by washing. The slimes were analyzed for copper.

WEIGHT OF COPPER--------------.465 gms.

A flotation run was carried out on the deslimed ore, using pine oil as the frother and using potassium n-decyl xanthate as the collector at a concentration of two pounds per ton. The concentrate was analyzed.

WEIGHT OF COPPER-------------2.31 gms.
CONCENTRATION OF COPPER-----12.0 %

Additional collector was added to the tails, the amount being equivalent to one pound per ton. The mixture was agitated for two minutes and flotation was then conducted for two minutes. This concentrate was also analyzed.

WEIGHT OF COPPER-------------3.62 gms.
CONCENTRATION OF COPPER-----24.6 %

A visual inspection of these tails showed only traces of copper mineral present.

One hundred grams of the Alaskan ore which was less than 60 mesh were "deslimed" in another manner. The material was placed in the cell with water and the mixture was agitated with air and the stirrer for ten minutes. The slimes were allowed to overflow and were collected and analyzed.

WEIGHT OF COPPER-------------3.16 gms.
CONCENTRATION OF COPPER------7.8 %

A flotation run was carried out on the deslimed ore, using pine oil as the frother and using potassium n-decyl xanthate as the collector at a concentration of two pounds per ton. The concentrate was analyzed.

WEIGHT OF COPPER-------------4.15 gms.
CONCENTRATION OF COPPER-----20.2 %

Visual inspection of the tails showed only traces of copper and this seemed to be the copper silicate.

DISCUSSION

This research was begun primarily in an effort to find a new collector to separate copper carbonate minerals from alkaline earth gangue such as calcium carbonate. In this search, compounds which, on a theoretical basis, would be good collectors for this separation were tested. According to accepted theory, such a compound should ionize and form an insoluble copper salt. This insoluble copper compound should be more insoluble than the copper mineral so that the copper ions from the mineral would form an insoluble coating with the collector ions at the mineral surface. As soon as this is accomplished, the copper mineral would, in all probability, float. However, since there is involved also a separation from the gangue material, the problem becomes more difficult.

Assuming the gangue to be calcium carbonate, if the calcium salt of the collector is also insoluble, then the same statements mentioned above could apply equally as well to the calcium carbonate with the result that the gangue would also float. The question of how much of the gangue would float in comparison with the copper mineral might conceivably depend upon the relative solubilities of the calcium and copper salts of the collector. At any rate, it would seem as though the ideal collector would form a soluble salt with the calcium and an insoluble salt with the copper in order to achieve separation.

With this end in view a search was made through Beilstein's "Handbuch der Organischen Chemie." (1) Several compounds were listed which showed possibilities but most of these were either difficult to prepare or else the preparation was expensive both with regard to time and from an economical viewpoint. For this reason, it was decided to first experiment with chemicals readily available in the laboratory.

The first experiments were conducted on synthetic mixtures of known composition because the data obtained could then be applied to various natural ores much more readily than could data obtained from a particular natural ore. The copper content of these mixtures was very low, with the view in mind that if successful separation could be accomplished with such a low copper content, then the separation would be even easier with an ore of higher copper content. This latter assumption later proved to be untrue.

The data presented in Table 1 illustrate the ineffectiveness of most compounds as collectors. When the oleic acid was used, the flotation was increased considerably but the concentration of the azurite in the concentrate was much less than the concentration in the original mixture, which indicated that the dolomite floated more easily than the azurite. As a matter of fact, the fatty acids have been used to float calcium carbonate on a commercial basis. Although no data were taken, the use of sodium silicate to depress the calcium carbonate, using oleic acid as the collector, was found to be of no value here.

The results from a run using amyl xanthate (Table 2) were quite an improvement over previous results. An attempt to use sodium tetra phosphate as a depressant succeeded in depressing both azurite and dolomite. The fact that the results depended greatly upon when the phosphate was added, as shown in the second and third amyl xanthate runs, was very interesting.

The xanthate run mentioned above suggested that perhaps higher xanthates might prove to be quite successful. The potassium salts of four different xanthates were prepared and these compounds were used as collectors. The data are presented in Table 3. In order to effectively compare these collectors, the percentage recovery of azurite was plotted against the concentration of the collector and the percentage of azurite in the concentrate was also plotted against the concentration of the collector (Graph 1). In the case of the three lowest xanthates the curves were not extended below a concentration of .5 pound of collector per ton. The recovery, as can be seen, was dropping rapidly at this point and the lower parts of the curves were not considered to be important. It is safe to assume that the lower parts of the recovery curves for these xanthates would be similar in shape to that of the potassium n-decyl xanthate curve.

The above data do not quite agree with Gaudin and Martin who found potassium n-amyl xanthate to be a better collector than either potassium n-hexyl xanthate or potassium n-heptyl xanthate in the separation of malachite from calcite. (12) However, when they plotted the percentage recovery against the millimoles of collector per liter they likewise found that the collectors with the longer chains provided better recovery. The fact that the activity of the reagent increases with increase in the hydrocarbon chain is in accordance with Traube's rule.

Gaudin and Martin (12) have shown that the iso-xanthates are better collectors than the n-xanthates. It is quite possible, then, that a xanthate formed from a higher branched alcohol would prove even more effective than the n-decyl xanthate.

The data presented in Table 4 and the curve on Graph 2 show that the flotation of azurite and the flotation of malachite are very similar. The azurite seems to show a slightly better recovery. According to the results of these data, the use of potassium n-decyl xanthate as a collector at a concentration of .7 pound per ton would effectively provide a separation of the copper minerals from dolomite if the original concentration of the mineral was 1% of the mixture.

The separation from calcite was not nearly as successful. This is shown in Table 4 and Graph 3. It can be seen that a higher concentration of the collector would be necessary for satisfactory separation. However, it was noted that the calcite seemed quite impure, containing apparently much iron and organic material which may have affected the flotation. Runs in which a more pure sample of calcite were used might prove more successful. Just why the two recoveries vary so when the concentration is .7 pound per ton is difficult to explain. This may, of course, be due to experimental error but the malachite run was rechecked and the results were identical with those of the original run.

After the malachite and azurite were successfully separated from synthetic gangue, an attempt was made to float these minerals away from a similar gangue existing in an actual ore. The results are given in Table 5 and depicted on Graph 4. (In the case of the natural ores, it should be noted that the concentration of the copper, instead of the copper mineral, in the concentrate is given in the results.) Such low recoveries would not, of course, be allowable in commercial practice. The recovery curve is slowly increasing and a complete recovery could probably be attained if enough collector were provided. The curve shown is, no doubt, the lower part of the familiar S curve. A run made on the ore passing through a 100 mesh screen was shown to provide a better recovery but was accompanied by a loss in concentration (page 32).

Since Gaudin and Anderson (11) claim better recoveries of malachite in a more basic solution, it was thought that a rise in the pH of the solution might produce better results. The data presented in Table 6 and Graph 5 show that the recovery is improved only slightly, but that the concentration of copper is improved considerably by an increase in pH. Runs taken at a pH of 10 or 11 might give fairly good results.

The fact should be noted that one hundred grams of Alaskan ore contained about 9.4 grams of copper whereas the synthetic mixtures previously employed contained approximately .5 of a gram of copper. The difference in the results of the tests upon the natural ore and the synthetic mixture was thought to be due to the fact that much more mineral surface had to be covered for complete recovery and hence more collector was needed with the Alaskan ore. In order to prove this, data were compiled from runs using mixtures of the Alaskan ore and dolomite. This data is presented in Table 7 and Graph 6. There is practically no improvement in recovery until the concentration of the ore is decreased to 25%. However, at a concentration of 10% the recovery is almost complete. The range between 10% and 25% is, then, a critical range where a slight change in the concentration of the ore would produce a large change in the recovery. If the concentration of the collector had been two pounds per ton instead of one pound per ton, the curve would undoubtedly have been shifted to the right.

It was thought at first to be possible that it was the dolomite in solution which was causing the increased recoveries. The run presented at the bottom of page 35 shows that this theory was wrong.

Because of the fact that DeWitt had been successful in separating malachite and azurite from siliceous gangue using salicylaldoxime as a collector in acid circuits, (8) this reagent was employed here also in an acid circuit. The results (page 37) were very poor.

In all of the runs made, a green slime formed at the surface of the liquid in the cell. In the case of the Alaskan ore this slime was excessive. Because of the fact that this slime was probably due to very fine particles that had adhered to the larger particles during screening, it seemed possible that perhaps these fine particles were responsible for the low recoveries. This is entirely plausible, because fine particles present an extremely large surface area, and flotation is, of course, a surface phenomenon. With a given concentration of collector, if the amount of copper in the heads is sufficiently small, there may be enough collector present to coat the slimes and to also coat the larger copper particles to provide good recoveries. If, however, the concentration of the copper in the heads is much higher, with consequent increase in fines, the collector may be in sufficient quantity to coat or partially coat the slimes, but the larger particles, containing most of the copper, would remain uncoated by collector ions. According to this theory, if enough collector were added, all of the copper mineral could be floated, or, if the fines were removed, a much smaller amount of collector would be necessary for good recoveries.

Some of the Alaskan ore was washed in an effort to deslime it and runs were performed on the washed ore. The data are presented in Table 8 and Graph 7. The remarkable results seem to justify the previously mentioned theory. The concentration of copper in the concentrate indicates that the concentrate obtained in the run where two pounds of the collector per ton were used was practically pure copper mineral with only a trace of gangue remaining. In addition, the recovery was practically complete.

This method of washing the ore has a disadvantage in that a small part of the copper mineral is lost in the washing. In addition to the very fine copper mineral particles, a few larger particles were also lost. Of course, the high concentration of copper in the concentrates is probably due to the fact that many of the fine gangue particles were washed out also, leaving only the heavier particles that were not easily mechanically carried over by the stirrer and the air.

In Table 9 and Graph 8 are presented the results of runs made on a similarly washed Arizona ore. The frother used here was α terpineol because the pine oil failed to provide a strong froth. The lower results obtained with this ore are not surprising. Although a quantitative analysis of the ore was not made, a microscopic visual analysis showed that the bulk of the copper mineral was malachite but that a considerable amount of chrysocolla, ($CuSiO_3 \cdot 2H_2O$), was also present in the ore. This copper silicate mineral is not floated by the potassium n-decyl xanthate collector. A visual inspection of the tails from the run where two pounds of the collector were used per ton, showed no traces of malachite. It may be assumed that at this concentration of the collector, all, or practically all, of the malachite has been removed. This assumption is borne out by the shape of the recovery curve. At a concentration of two pounds per ton the curve is beginning to flatten, indicating only a small increase in recovery with a large increase in the amount of collector. In other words, any collector present in excess of that needed to float the malachite has little effect upon the copper silicate remaining.

Runs made on washed samples of Alaskan ore less than 60 mesh produced results far less effective. The percentage recovery could not be calculated because an analysis of the heads was not made in this case. The data on page 42 show that considerable copper was lost in the washing operation. The addition of more collector to the tails of the first run increased the recovery remarkably. On page 43 is shown data resulting from a different desliming operation. The large amount of copper lost in the desliming would prevent the use of this method.

The great decrease in recovery when working with the finer ore is probably due to either one or both of two reasons. First, the finer ore contained much more slimes and these slimes were not all washed out; or second, disregarding the slimes or extremely fine particles, the fact that the particles were of smaller size increased the surface area and hence more collector would have been required for complete recovery.

Some of the results in this paper have been reproduced with surprising accuracy. Most of the points on the recovery curves seemed to fall on the curves but some of the concentration curves were not nearly as smooth and the points seemed more doubtful. Although an attempt was made to have most of the variables constant during the various runs, some of these undoubtedly varied somewhat. The liquid level in the cell, the amount of water added to the cell, the supply of air to the cell, and the amount of frother added are four variables which were not strictly controlled. It is easily seen that whereas these variables might not appreciably affect the recovery, they could cause larger errors in the concentration of copper of the concentrate. The temperature of the solutions was not controlled but tests from time to time showed it to be 18-20° C., or, in other words, there was not enough difference to cause appreciable errors. The pH for a series of runs remained fairly constant, as shown by repeated tests.

CONCLUSIONS

A collecting agent has been found which makes possible the successful separation of malachite and azurite from dolomite and calcite in synthetic mixtures.

From mixtures of dolomite and azurite containing 1% azurite, a recovery of 98.5% with a concentration of azurite equal to 19.9% has been attained using .7 pound of potassium n-decyl xanthate per ton of mixture as the collector. Using the same collector on a similar mixture of dolomite and malachite, the recovery was 97.3% with a concentration of malachite equal to 25.8%.

From mixtures of calcite and azurite containing 1% azurite, a recovery of 85.7% with a concentration of 8.75% azurite has been obtained, using as a collector the potassium n-decyl xanthate at a concentration of two pounds per ton. The same collector gave a recovery of 87.7% and a concentration of 8.4% of malachite from a calcite-malachite mixture.

By the use of potassium n-decyl xanthate as a collector, following a desliming or washing process, the copper minerals have been removed from natural ores. Using the collector at a concentration of two pounds per ton of ore upon an Alaskan ore, recoveries of 98.6% have been obtained. The concentration of copper in the concentrate was 51.4%.

Tests upon an Arizona ore containing malachite and chrysocolla have indicated that all of the malachite can be removed using two pounds of the collector per ton of ore, leaving some copper in the tails as chrysocolla.

Many data have been obtained and many graphs have been prepared which should aid further investigation upon this problem in particular and upon flotation in general.

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