

OPTIMUM CONDITIONS
FOR THE FLOTATION OF SPHALERITE

BY
ISO AMYL XANTHATE

submitted for the degree of

MASTER OF ARTS

by

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1942.

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In experimental investigation of the flotation of minerals, two techniques are in general use; the "contact angle" method as developed by Wark and Cox, and the direct flotation method, in which an experimental cell is used, operating on the same principle as those used commercially.

Using the second method, the behaviour of potassium ethyl xanthate as a collector of sphalerite has been investigated in this laboratory for the past several years. It was desired, however, to compile some data as to the behaviour of some other collectors with the same ore and under the same conditions. With this in view the present work was undertaken, using potassium iso-amyl xanthate as example.

The general opinion seems to be that pure sphalerite will not float unless activated. Gaudin(1) however, states that with collectors containing an alkyl group of five carbons or more, flotation is possible without activation and submits data indicating that with xanthates containing the ethyl, n-amyl and n-heptyl groups, collection of sphalerite increases in that order. He also finds a great variation of recovery of unactivated sphalerite at constant pH (6.5) using potassium n-amyl xanthate at concentrations ranging from zero to .6 lb./ton with a maximum of about 46% at the latter. C.R.M. del Guidice (2) quotes

and endorses Gaudin, Haynes and Haas, to the effect that using amyl xanthate, the maximum recovery of unactivated sphalerite comes in the pH range from 3.4 to 5.4, but does not state what recovery was obtained. Swainson and Anderson (3) however, express the belief that comparing various xanthates as collectors, their activity reaches a maximum at four carbon atoms and that for any number of carbons, the secondary compound is best, followed by iso- and normal. Their data are based on copper and lead ores however, not on sphalerite.

Wark and Cox (4) express the view, based on their measurements of contact angles, that in concentrations ~~up to~~ of 25mg./l., iso-amyl xanthate will not float unactivated sphalerite. In a later article (5) they state that in higher concentrations (up to 200 mg./l.), or in acid solution, (critical pH 5.5), contact is possible.

With regard to possible decomposition of the amyl xanthate in use, available data (6), (7) indicate extensive decomposition of ethyl xanthate in acid solution. Similar behaviour on the part of the amyl xanthate could be expected and was investigated in the course of the work.

EXPERIMENTAL

Materials

Two different samples of ore were used.

A. Source:

Dark in color and when ground fine retained this color. The exact composition was not determined, but rough analysis indicated approximately 1 % of copper in the ore. This would indicate that the ore was probably activated, at least partially.

B. Source: Ottawa County, Okla. Dark colored when in large pieces, but when broken up had a resinous appearance and when ground fine was creamy white in color. No copper could be detected.

Potassium iso-amyl xanthate was made by the usual method from C.P. i-amyl alcohol, carbon disulphide and potassium hydroxide. It was dissolved in acetone, crystallized twice from benzene, dried and stored over sulphuric acid in a desiccator.

Terpineol was used as frother in all tests, a stock solution of 250 mg./l. being made up and amounts from 10 to 25 ml. as required were placed in the cell along with the ore. The amount required varied considerably with the pH at which the test was made, strongly basic solutions requiring more terpineol.

Apparatus The ore was ground in a laboratory pebble mill with porcelain jar and flint pebbles. It was sized in an elutriator as described by Herd(8), the ore having a settling rate between 8 and 16 cm. per minute being used for all tests. The cell used for flotation tests was a modification of the design by Bennet (9), a pyrex fritted glass filter being sealed to a piece of pyrex tubing of the same diameter as the filter and 21 cm. long. A lip was formed at the top of the tube to provide for an overflow. Two pH meters were used; an industrial model Beckman with glass and calomel electrodes for measurement of pH; and a research model Beckman with platinum and calomel electrodes for titrations.

Flotation Tests

I Without Collector Gaudin (10) and Taggart, del Guidice and Ziehl (11), state that sphalerite has no native floatability, that is, it will not float in the presence of frother alone. In order to test the characteristics of the cell and also the ore, both ore samples were tested by the following method. To a weighed, dry sample of the ore in a beaker, about 200 ml. of water and 5 ml. of 3N ammonium acetate were added. pH was adjusted on the meter by additions of HCl or KOH as required. The water used in all tests and all solutions throughout this work was distilled, the only exception being elutriation of the ore. The

ammonium acetate was found necessary since without it pH drifted considerably during the test, and preliminary tests indicated that it had no appreciable effect on the flotability of the ore. This mixture was then placed in the cell, 10-25 ml. terpineol were added as needed and the volume was made up to 300 ml. Air was turned on and adjusted to a pressure of 34 cm. of mercury, which pressure seemed to work best with this cell.

The overflow was caught in a beaker and when the froth had become clean, the overflow was filtered through a weighed gooch crucible. The weight of heads was compared the the sample weight to give a measure of the recovery obtained, expressed as per cent. A large number of tests were made over a large pH range with ore A, the results of some of which are given in Table I. There is no regular variation with pH noticeable. Also, some factor not under control has a large effect on the recovery at any one pH.

A similar set of tests on Ore B gave an indication of regularity with pH, though not enough tests were made to make such a conclusion definite. Results of that set of tests are given in Table II and Fig. 1.

TABLE I

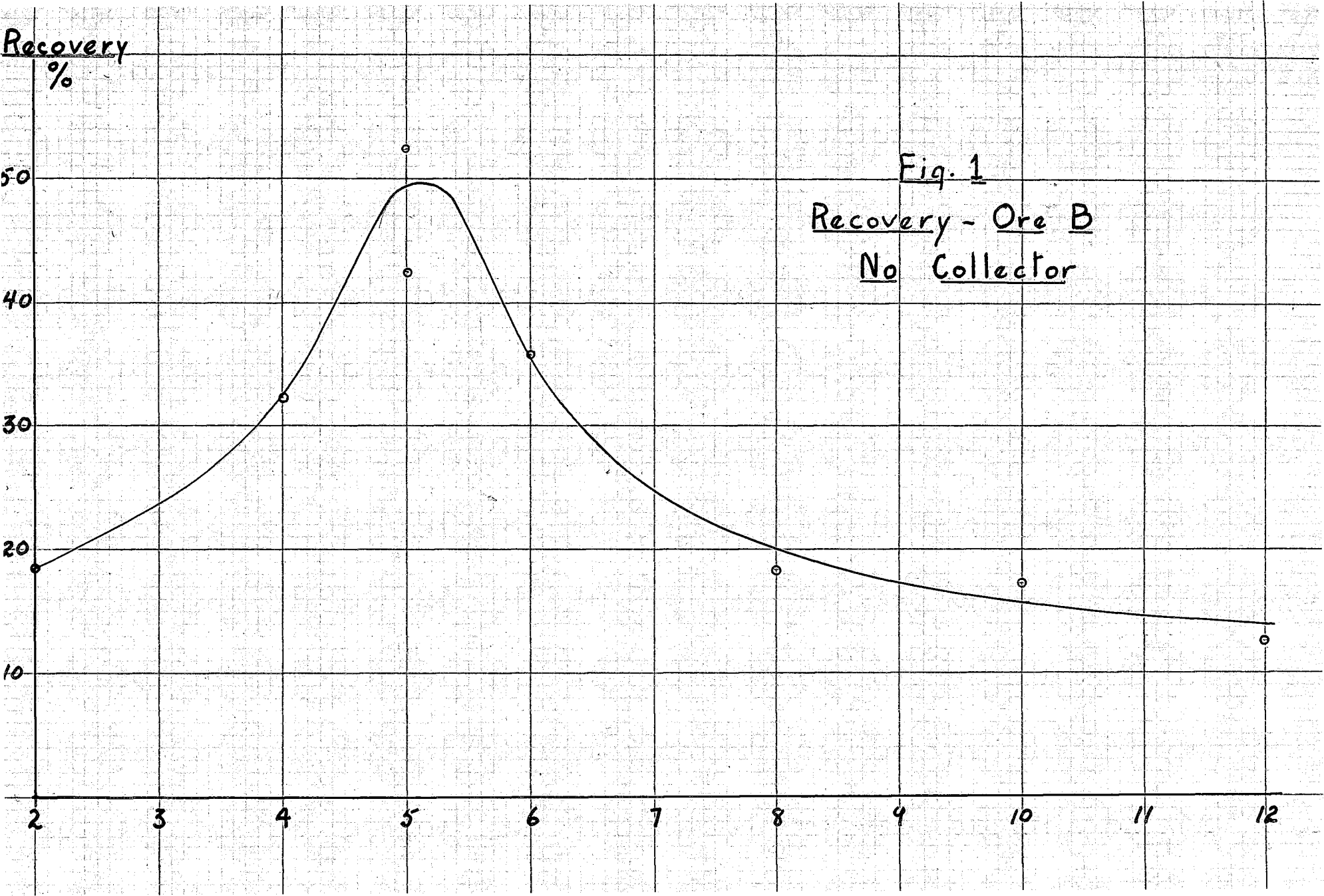
Recovery without collector - Ore #A

pH	sample weight	% recovery
2.2	5.001	.8 1.16
2.7	5.000	4.00
3.6	5.001	3.20
4.5	5.004	5.84
4.5	5.001	2.1
5.5	5.000	.8
7.5	5.001	.74
9.0	5.000	.96
10.9	5.000	1.2

TABLE II

Recovery without collector - Ore B

pH	sample weight	% recovery
2.0	5.00	18.4
4.0	do	32.2
5.0	do	52.4
5.0	do	44.6
6.0	do	35.9
8.0	do	18.2
10.0	do	17.2
12.0	do	12.6



II Constant pH - varying amounts of collector

This series of tests was conducted only with Ore A. Procedure was as outlined above, except that just before air was blown into the cell, a measured amount of a standardized solution of the xanthate was added, in volumes corresponding to the amounts of collector shown in the table. The ^{total} volume was 300 ml. in all cases. Results are shown for two complete series at pH 4 and 8.5 in table III and Fig. 2. Also shown are a few results obtained at pH 2.0 and 2.6, though these series are not complete. As soon as a froth head formed, when collection was good, the froth became very heavily mineralized. This formed a heavy cake on top of the cell which had to be scraped off. This behaviour was expected since it had been mentioned as a characteristic of amyl xanthate by Gaudin (12) and Ralston and Barker(13).

From the curves of Fig. 2., it is seen that in fairly acid solution, the collector is effective in very small quantities, about 1 mg. being all that is required to produce maximum recovery. In the basic range however, more collector is required, nearly 5 mg. being reached before the curve levels off.

Recovery
%

100

80

60

40

20

pH 4

pH 8.5

Fig 2

Recovery - Ore A
vs. Conc. Collector

mg. Collector

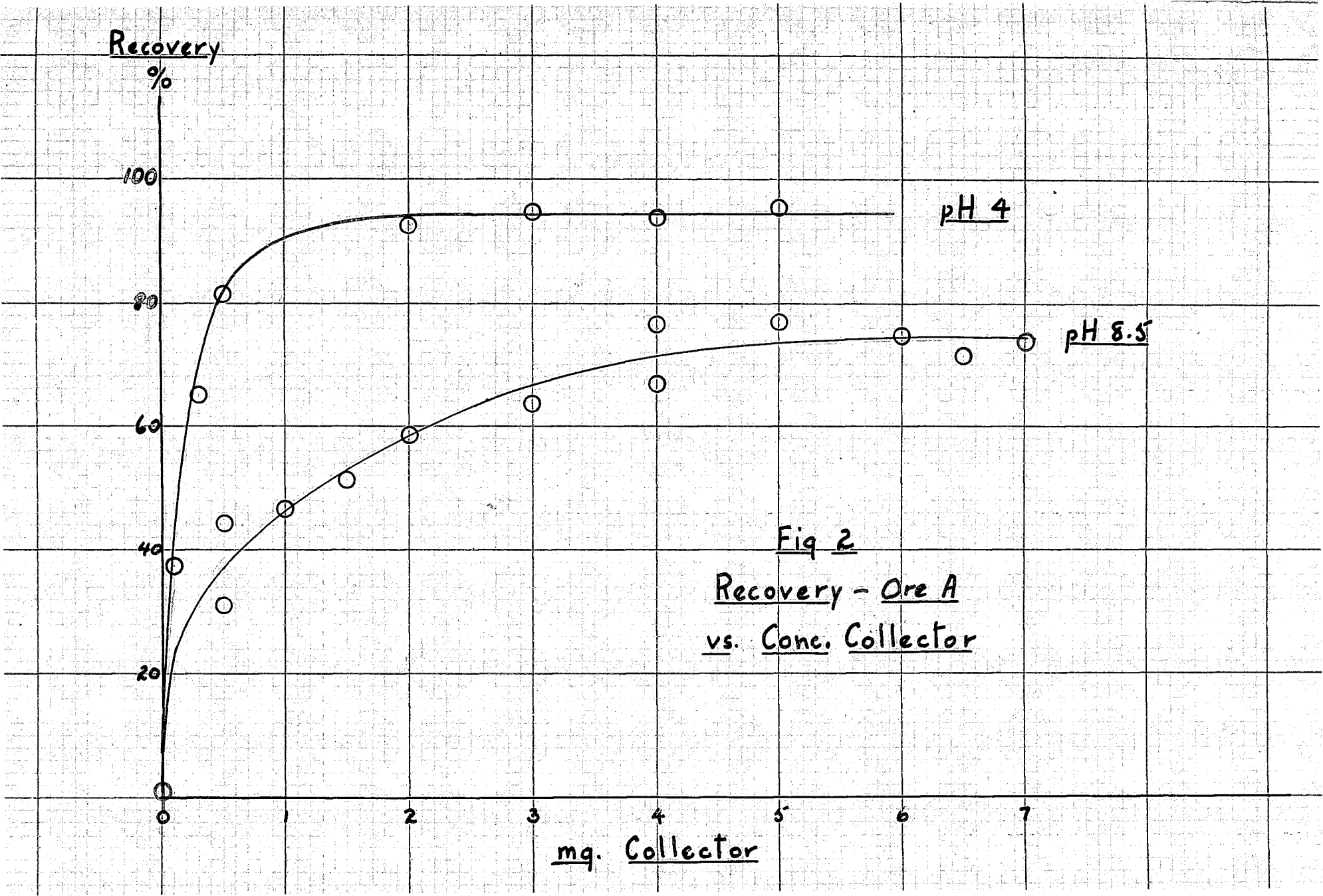


TABLE III

Collection of Ore A - varying amounts of collector

pH	sample	mg. coll.	% heads	pH	sample	mg. coll.	% heads
8.5	5.02	.5	31.2	4.0	5.00	.1	37.7
	5.02	.5	44.2			.3	65.0
	5.04	1.0	46.4			.5	81.5
	5.00	1.5	51.6			2.0	92.5
	5.03	2.0	58.2			3.0	94.5
	5.04	3.0	63.9			4.0	95.9
	5.04	4.0	66.9			5.0	95.4
	5.00	4.0	76.6	2.6	5.00	.65	91.0
	5.01	5.0	77.1			.70	92.3
	5.01	6.0	74.5	2.0	5.00	.35	90.7
	5.04	6.5	71.7			.35	88.9
	5.01	7.0	74.0				

III Constant Collector - Varying pH

This series was carried out on both ores. The collector was fixed at 5 mg. and was added immediately before blowing. All samples were 5 grams. Table IV and Fig. 3 give the results obtained with ore A.

Recovery

%

100

80

60

40

20

0

2

4

6

8

10

12

14

pH

Fig. 3

Recovery - Ore A

-vs- pH

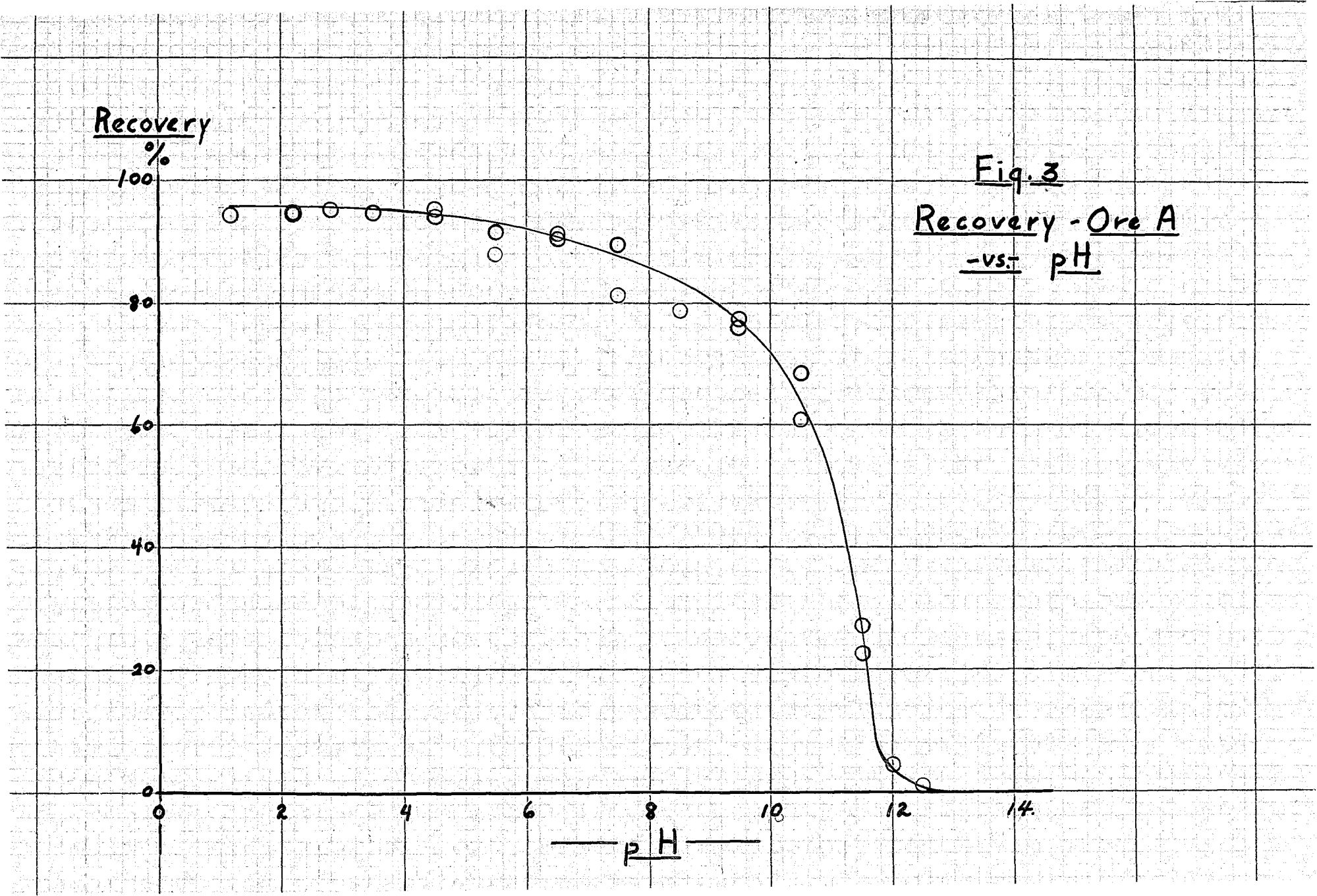


TABLE IV

Collection of Ore A - varying pH

pH	recovery	pH	recovery	pH	recovery
1-1.5	94.2	5.5	88.0	9.5	77.2
2-2.4	94.4	6.5	90.5	10.5	60.8
2.8	95.5	6.5	91.5	10.5	68.2
3.5	94.4	7.5	81.4	11.5	22.2
4.5	94.0	7.5	89.7	11.5	27.0
4.5	95.4	8.5	78.7	12.0	4.24
5.5	91.8	9.5	76.0	12.5	1.79

The following results for Ore B were obtained during the work on abstraction (see below). After treatment with the xanthate solution, which was filtered off, the ore was divided into approximately five gram samples. About 200 ml. of water was added to each and the pH was adjusted to that required. This was placed in the cell, terpineol added, the volume was made up to 300 ml. and the cell was blown. When the froth had cleared, both heads and tails were collected in weighed gooches and the sample weight was obtained by addition of the two weights. The first six results in the table are preliminary tests made on weighed samples and treated as shown, and indicated that this variation in technique (pre-washing with xanthate) has no appreciable effect on the flotation yield. Results in Table V and Fig.4.

TABLE V

Collection of Ore B - varying pH

pH wash	pH cell	sample	heads	%	treatment
---	3.0	5.000	4.974	99.5	5 mg. collector in cell
----	7.0	5.000	4.928	98.6	do
----	11.0	5.000	4.695	93.9	do
5.0	3.0	5.000	4.975	99.5	prewashed with 5 mg. coll.
7.0	7.0	5.000	4.967	99.3	do
11.0	11.0	5.000	4.750	95.0	do.
5.0	5.0	6.687	6.447	96.5	{ prewashed with 20 mg. xanthate -20 gr. ore
5.0	5.0	4.365	4.200	96.3	
5.0	5.0	5.322 5.245	5.243	98.5	do
5.0	5.0	5.999	5.967	99.2	do
5.0	3.0	3.189	3.152	98.8	do
5.0	3.0	4.864	4.754	97.8	do
5.0	7.0	5.487	5.202	95.0	do
5.0	7.0	5.717	5.520	96.6	do
8.0	8.0	4.315	4.212	97.6	do
12.0	12.0	4.970	3.684	74.1	do
12.0	9.0	6.644	6.344	95.4	do
---	12.0	5.000	3.742	74.3	5 mg. collector in cell
---	12.5	5.000	.441	8.8	do.

Another variation was made possible by the above technique. It will be noted that several of the samples were blown in the cell at a different pH to that at which they were treated with xanthate, but that this treat-

Recovery
%

100

80

60

40

20

Fig 4.

Recovery - Ore B

- vs. - pH

0

2

4

6

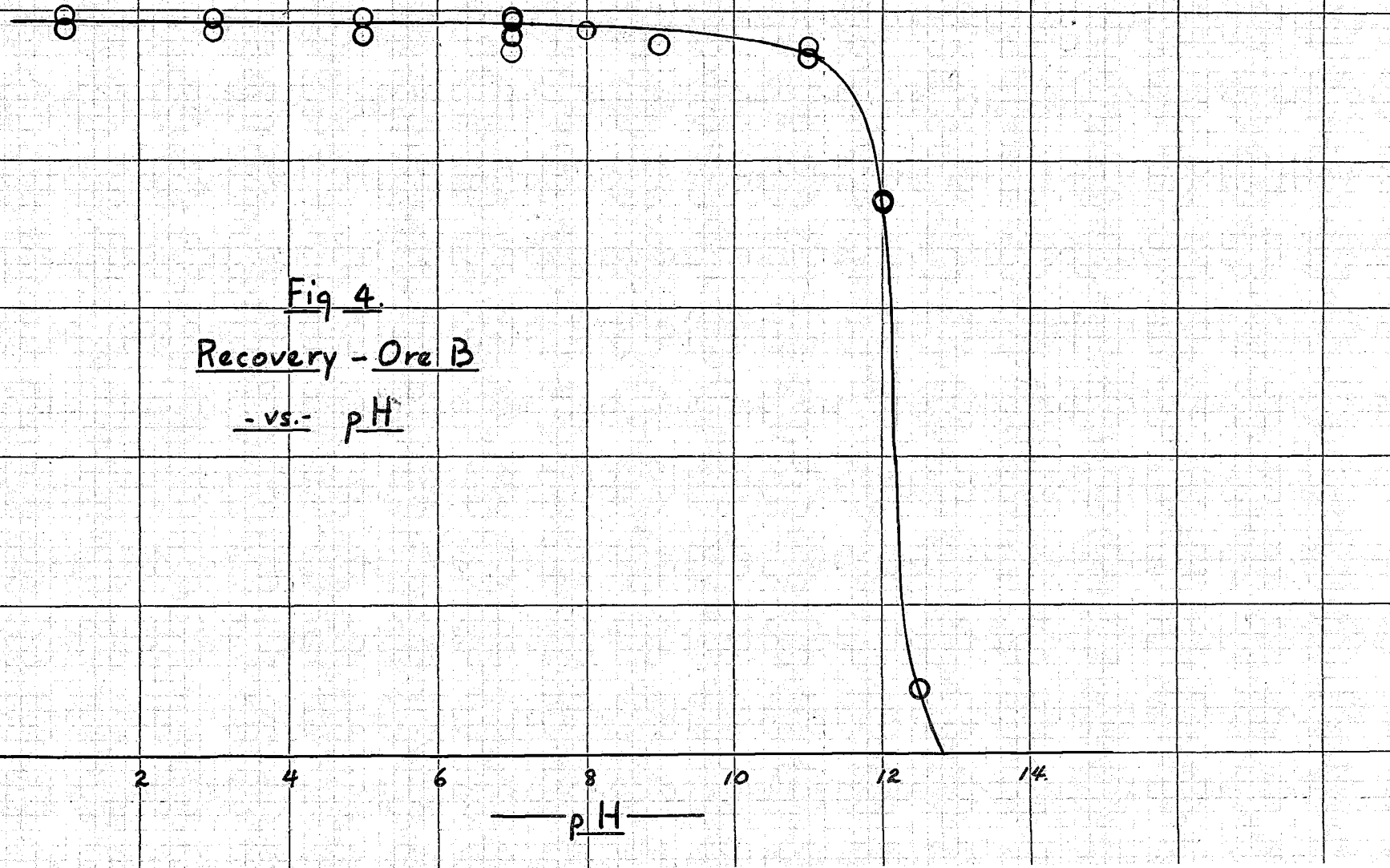
8

10

12

14

pH



ment seemingly has no effect, since the results agree within the experimental limits with the results of normal treatment. This would appear to indicate in a rather definite manner that whatever the controlling effect of pH is, it exercises that control during the reaction between the collector and the ore, and not at the attachment of the mineral to the air bubble.

Decomposition of Xanthate

As mentioned on page 2, decomposition of the amyl xanthate was expected in the acid range. Therefore it was rather surprising to find the collector behaving very efficiently as far up the pH scale as pH 1. (Fig. 3). The decomposition taking place was followed by a method similar to that applied to ethyl xanthate by Kemper (7). Samples of xanthate solution with buffer added, were adjusted to the desired pH, allowed to stand for 10 minutes, then returned to pH 6.5, which seemed to work best, and titrated electrometrically with standard iodine solution. The results are shown in Table VI and in graph form in Figure 5.

TABLE VI

Decomposition of Xanthate			
pH	mg. Xanthate orig.	final	% decomp.
1.6	.0099	.0004	96.0
2.0	.0099	.0004	96.0
2.0	.0108	.00051	95.3
2.4	.0108	.0005	95.3
2.5	.0104	.0005	95.2
2.75	.0099	.0005	94.8
3.0	.0099	.0018	81.8
3.0	.0099	.0021	79.8
3.25	.0099	.0036	63.7
3.5	.00507	.00308	39.2
3.9	.0099	.0081	18.2
4.5	.00507	.00493	2.76
5.0	.0114	.0112	1.75
5.5	.00507	.00507	—
6.0	.0114	.0114	—
6.6	.00507	.00507	—
7.0	.0114	.0114	—
9.0	.0105	.0105	—
12.0	.0108	.0108	—

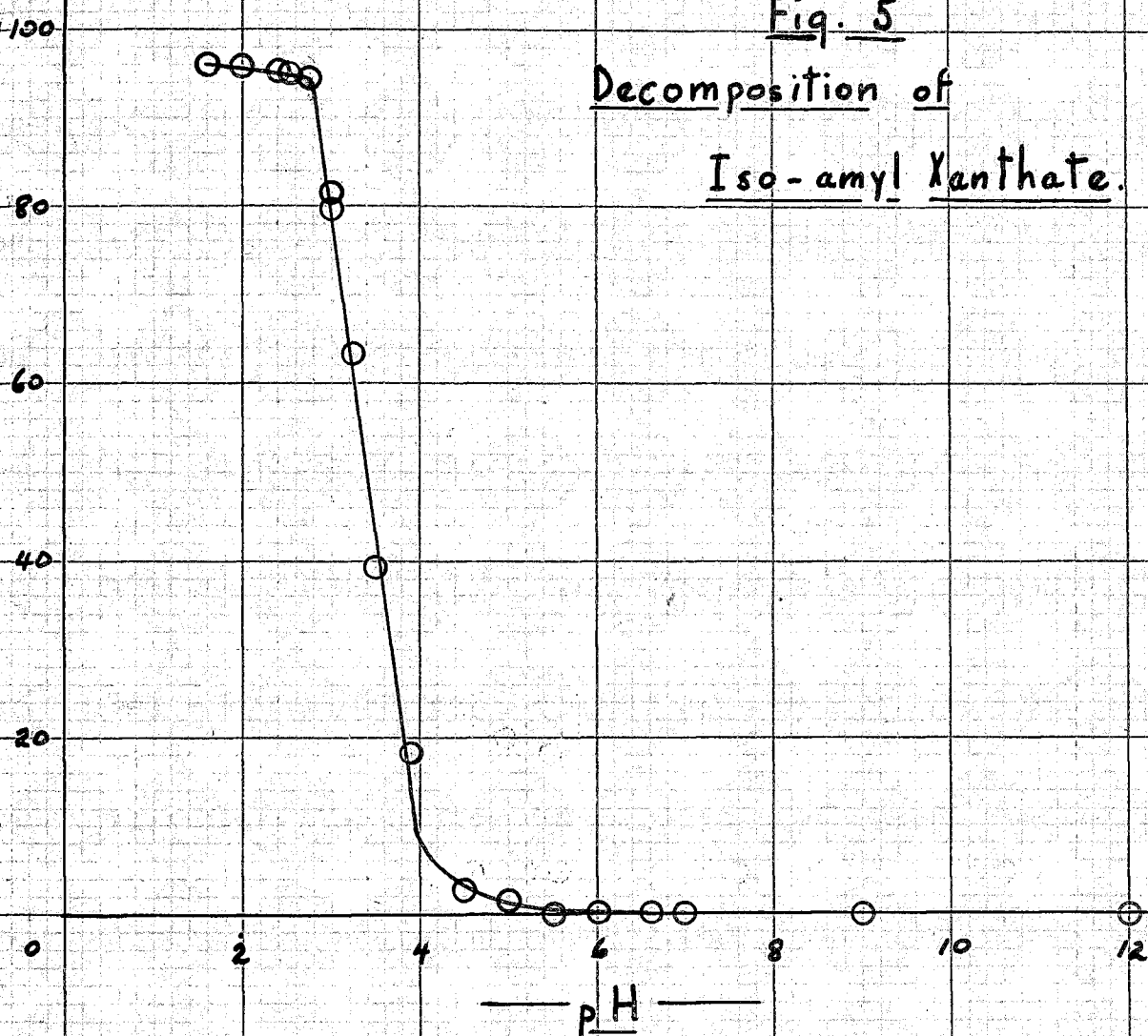
Effect of Decomposition

In an effort to find some reason for the high recovery in very strong acid pulp, the following var-

Fig. 5

Decomposition of

Iso-amyl Xanthate.



iations of flotation technique were introduced. 10 ml. (5 mg.) of the collector were diluted to about 200 ml., buffer was added and pH adjusted as required. This mixture was allowed to stand for 10 minutes, after which it was poured onto the ore sample in the cell. Terpineol was added and the cell was blown. This procedure, since it allows the collector to decompose as determined above before it comes in contact with the ore, should result in a diminution of recovery, provided the products of decomposition are inactive as collectors. A few tests were made with amyl alcohol in concentrations likely to be found, with no collection resulting, and carbon disulphide in small amounts has no collecting action. It will be seen from Table VII (a,b,c), that this is the case, indicating that any other possible products of decomposition have very little, if any, effect. Therefore, the high collection in the strong acid range, as indicated on Fig. 3, must be due to the action of the xanthate itself. Then for comparative purposes, knowing the amount of decomposition (from Fig. 5), another few tests were made adding the "effective" amount of collector present in the above tests. These are shown in Table VII (d,e). The collector was added immediately before blowing the cell.

TABLE VII

Effect of decomposition on recovery

	pH	2.5	3.0	3.5
a. Collector added (mg.)		5.0	5.0	5.0
b. Effective collector		.225	1.0	2.7
c. Collection (%)	1.	6.08	39.9	93.3
	2.	4.5	37.2	-----
d. Collector added		.225	1.0	2.7
e. Collection (%)		12.5	39.8	88.6

At the same time another few tests were made in which the ore and collector and water were allowed to stand at a definite pH for ten minutes before air was admitted. The results of two such tests were 94.6 % at pH 3 and 95.7 % at pH 2.5.

That is, allowing xanthate to stand for ten minutes in acid pH in the presence of the ore results in only a very slight reduction of recovery, nowhere near that to be expected if the xanthate were decomposed. Apparently, then, the ore coating, presumably zinc amyl xanthate is formed and remains, regardless of the pH.

Abstraction

In view of the fact that potassium i-amyl xanthate has been shown to be definitely effective in floating both samples of sphalerite used, an attempt was made to show that the ore "abstracted" the collector

from solution. In the following work ore sample B was used entirely.

Previous attempts have been made in this laboratory to measure abstraction with sphalerite and ethyl xanthate with no success(14), the difficulty being one of titration of the residual xanthate.

The general procedure followed was to stir the ore with an excess of xanthate in solution for 10 min. at the required pH. The liquid was then filtered off the ore and attempts were made to find either the amount of xanthate remaining on the ore or the amount remaining in the liquid. Filtrations were performed with the arrangement described by Kemper (7), except that the filter used was a pyrex fritted glass funnel of 10 cm. diameter. Several variations of procedure were tried as outlined below.

1. The filtrate was titrated electrometrically with standard iodine solution. This method, as found by other workers, gave results much too high, indicating either no abstraction, or indicating more reducing material in the filtrate than had been placed there originally in the form of xanthate. The end-point was not good, the potential tending to drift badly, making the titration very tedious and not very accurate.
2. The filtrate was titrated with iodine as before but using starch as indicator. This gave high results also, and had the further disadvantage that the dioxanth

thogen formed obscured the blue starch color.

3. The drifting of potential in(1.) above seemed to indicate that the reaction causing the interference was a slow one. This suggested the possibility of back-titration, carried out quickly, to remove the effect. This was tried by adding an excess of the iodine solution to the filtrate and then back-titrating with either sodium thiosulphate or sodium arsenite, again using starch indicator near the end-point. This, however, gave a very poor endpoint, the blue color returning for about five minutes after it had been first removed. Attempts were made to standardize the end-point (such as remaining clear after 2 minutes) but this was not dependable.

4. The next line of attack was to remove the xanthate from the ore and titrate it. After the original xanthate solution had been removed, the ore was stirred for 45 minutes in acetone. The acetone was then filtered off, diluted with water and titrated. Using starch, the acetone was found to decolorize the starch iodine complex, while electrometrically, the acetone caused the potential to drift so badly that an accurate end-point was impossible. Even after most of the acetone had been removed by evaporation under a vacuum, these effects remained.

5. It was noted that when zinc amyl xanthate was formed by addition of zinc chloride to potassium amyl

xanthate solution, it redissolved on addition of KOH. This suggested the possibility that the ore coating could be dissolved in KOH and then the resulting solution titrated. To this end an ore sample, after treatment with xanthate solution was washed thoroughly and then stirred for 5 hours in 2N KOH. Taylor and Knoll (6) state that under such conditions there is extensive decomposition of xanthate ion. One sample of xanthate solution was titrated after being in 2 N KOH for 5 hours. It showed a decomposition of 6 %, which could easily be allowed for in calculation of abstraction. The KOH solution was neutralized and titrated, and after correction by a blank titration, gave a result indicating some abstraction. However as a check on the removal of the coating, some of the ore was placed in the cell with water and terpeneol and blown. It was found to float just as well as it did before the KOH treatment. This was taken as an indication that the coating had not been removed. Further indication of the permanence of the coating was obtained in an attempt to reclaim some xanthate treated ore for further use. This ore was stirred for 10 hours in 2 N HCl, after which it was washed, thoroughly elutriated and dried. A sample was then placed in the cell with frother but no collector, when it was found to float approximately 40 % at pH 11.

The characteristic flocculated appearance of the pulp was noted, indicating that the floating was probably not just the result of cleaning.

These results seemed to indicate that removal of the xanthate layer, at any rate quantitatively, was not practical. It was then decided to return to a *more* indirect titration method.

6. Taylor and Knoll(6) have given a method used by them in a study of abstraction of ethyl Xanthate by gelena. Since this was the method used to obtain the results below it is given in detail.

A weighed sample of sized ore was placed in a beaker, a known amount of xanthate solution was added, and after the addition of a few drops of ammonium acetate buffer, pH was adjusted to that desired. The mixture (total volume about 50 ml.) was then stirred by motor for ten minutes. The xanthate was measured by volume of a solution which had been standardized by an iodine- starch titration. At the end of the ten minute period, the liquid was removed by suction in the apparatus referred to above(7). The ore was washed with about 100 ml. of distilled water and was then sucked as dry as possible. The filtrate, which was perfectly clear, was diluted to 500 ml. in a volumetric flask. 100 ml. portions were taken by pipette and treated as follows:

(a) titrated as it was with standard iodine solution.

(b) acidified (pH 5) and extracted with 2 20 ml. portions of toluene. This treatment removes ~~all~~ all xanthate as xanthic acid (soluble in toluene). The water solution remaining was then titrated after neutralization. The volume of iodine thus obtained was subtracted from that obtained in (a) as a correction for reducing substances present, other than xanthate. The resulting corrected volume was used to calculate the xanthate remaining in solution and thus gave a measure of the abstraction which had taken place.

In the first trial of this method, two more 100 ml. portions of the filtrate were treated as above except that titration was done electrometrically. Titration of (b), was very unsatisfactory and entirely undependable. The reason was not determined.

It was also found that by using very dilute iodine (about .3 grams per liter) and by adding, as recommended by Taylor and Knoll, 5 ml. of a .5 M solution of potassium sulphate solution, a very exact end-point could be obtained using potato starch. (Not soluble starch.). Dilution of the 100 ml. portion of filtrate to about 200 ml. before titration, so reduced the density of the di-xanthogen formed in the titration that its opalescent blue color did not interfere with the end-point blue.

Results obtained by this method are shown in Table VIII below. All at pH 6.0

TABLE VIII

Abstraction of i-amyl xanthate by sphalerite (B)

Test No.	Ore Wt.	Xanthate in mg.		Abstr.	Abstraction mg./gr.ore.
		Original	Final		
14	9.562	19.64	15.10	4.54	.475
15	6.473	20.48	18.02	2.46	.380
16	4.702	23.30	21.05	2.25	.477
17	5.391	23.30	21.68	1.62	.301
Average					.408

Tests no. 1 - 13 were those used in methods 1 to 5 described above. One test, (18) was run at pH 12.5 instead of pH 6 with the result that an abstraction of .227 mg./gr. was found. The reason for choosing these two values for pH will be found in Figs. 4 and 5. pH 6 is well in the range of maximum flotation, while it is not acid enough to cause decomposition. At pH 12.5 recovery has dropped off sharply. One would expect, then, less abstraction at pH 12.5. This expectation is borne out in the results above, though in view of the wide variation in results at pH 6, one value at 12.5 cannot be considered conclusive.

Discussion of abstraction results

Following the method applied by Herd (8) to galena, the calculations below were made. From Stokes Law, using the average rate of settling of the particles as 12 cm. per minute, the average radius is calculated to be

1.75×10^{-3} cm. To check this, a microscopic measurement of 560 particles was made, giving the frequency curve shown in Fig. 6., where one square unit equals 256 square μ m. Calculation of average area and radius from the frequency table by a method due to Thurstone(15) gave a value of 1.75×10^{-3} cm.

Area per cubic centimeter of particles is given by the relation: Area equals volume $\times \frac{3}{r}$ as 1715 sq.cm. Taking the density of sphalerite as 4 gm./cc. gives the area per gram of 428.7 sq. cm. Molecular volume of

$$\text{zinc sulphide} = \frac{97.38}{4 \times 6.03 \times 10^{23}} = 4.04 \times 10^{-25} \text{ c.c.}$$

Molecular diameter then is 5.43×10^{-8} cm. The number

$$\text{of molecules per sq. cm. area then is } \frac{1}{3.43 \times 10^{-16}}$$

$= .85 \times 10^{15}$. The number of xanthate ions then required for a unimolecular layer is 1.7×10^{15} .

From Table VIII, average abstraction per gram of ore is .408 mg. This corresponds to

$$\frac{.408 \times 6.03 \times 10^{23}}{.202 \times 10^5} = 1.22 \times 10^{18} \text{ xanthate ions.}$$

These are spread over an area of 428.7 sq. cm. The number of xanthate ions per square cm. then is

$$\frac{1.22 \times 10^{18}}{428.7} = 2.84 \times 10^{15}$$

Frequency

80

60

40

20

Fig. 6

Ore B

Distribution of Particles
According to Area.

0

1

3

5

7

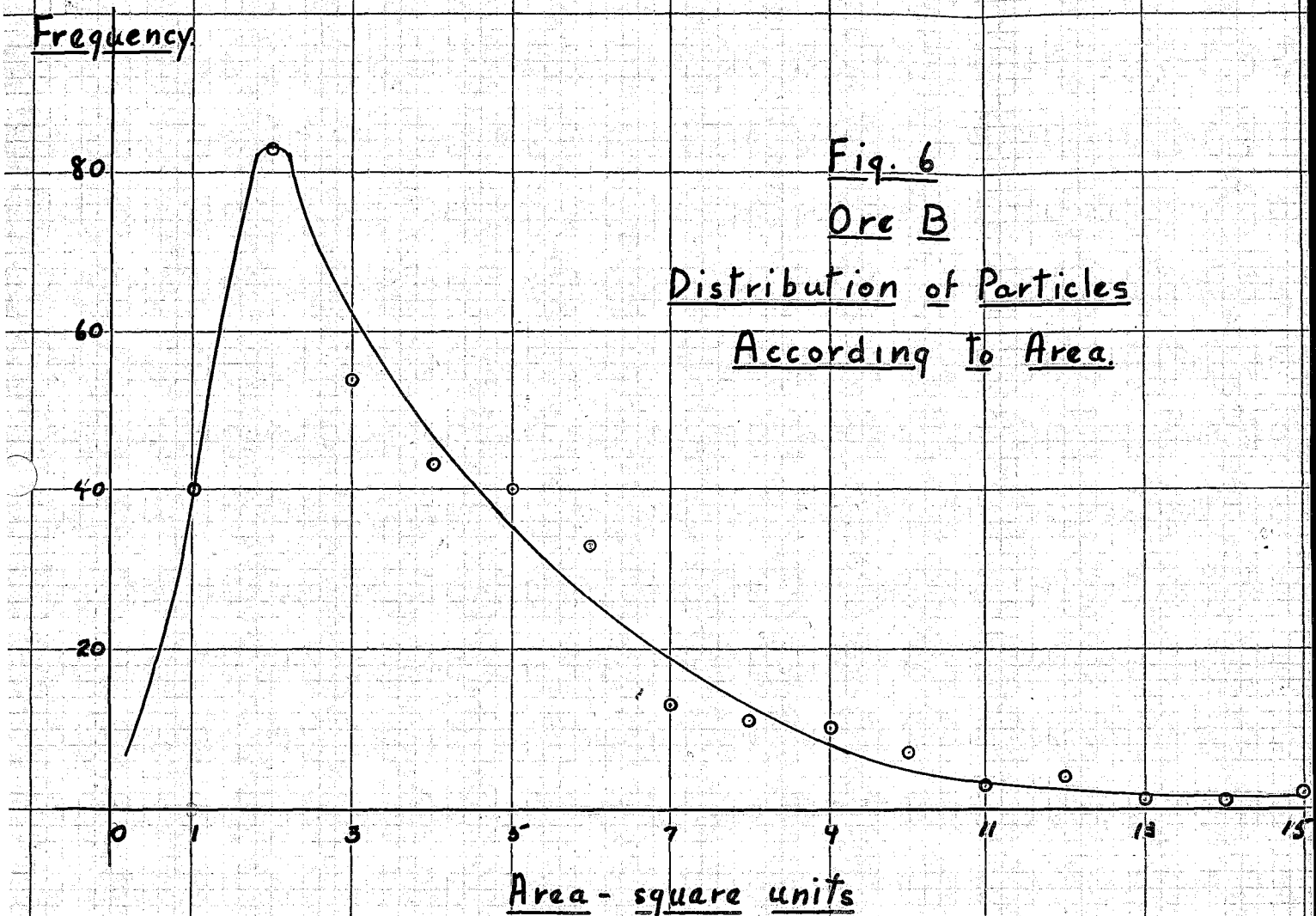
9

11

13

15

Area - square units



It is thus seen that the number of xanthate ions abstracted is sufficient to form a layer between one and two molecules thick. The calculations of area are probably largely in error, since the sphalerite particles are extremely irregular in shape, but the above result would seem to indicate a definite layer formation.

SUMMARY

1. Behaviour of two different samples of sphalerite with potassium iso amyl xanthate has been investigated, both with concentration of collector and pH as variables.
2. The decomposition of potassium iso amyl xanthate has been investigated.
3. Evidence is presented concerning the behaviour of the xanthate as a collector in strongly acid solution.
4. The problem of abstraction has been investigated and some results obtained.

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quoted in Stroud, "Educational Psychology" p 73.