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By W. W. Simpson, I. L. Nichols, and J. L. Huiatt

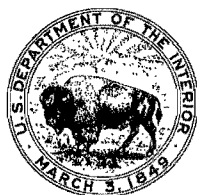


UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8787

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UNITED STATES DEPARTMENT OF THE INTERIOR

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CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	2
Experimental methods.....	2
Materials.....	2
Identification of potassium trithiocarbonate.....	3
Hallimond tube flotation.....	3
Bench-scale flotation.....	3
Results and Discussion.....	3
Solution analyses.....	3
Copper-molybdenum flotation.....	3
Hallimond tube flotation.....	4
Bench-scale flotation.....	6
Summary and conclusions.....	7
References.....	8

ILLUSTRATIONS

1. Thin-layer chromatograms of 1 μg each of KEX, KTTC, KEX-KTTC, and aged KEX.	4
2. Effect of KTTC concentration on floatability of chalcopyrite at pH 10.....	4
3. Effect of pH on chalcopyrite recovery using 10^{-3} mol/L KTTC as collector...	5
4. Effect of collector concentration on floatability of molybdenite at pH 10..	6

TABLES

1. Chalcopyrite and molybdenite flotation using variable KTTC concentrations and a constant KEX concentration of 10^{-5} mol/L.....	5
2. Flotation of copper ore using KEX and fuel oil No. 2.....	7
3. Flotation of copper ore using KTTC and fuel oil No. 2.....	7

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	mL/min	milliliter per minute
g	gram	min	minute
kg	kilogram	mol/L	mole per liter
kg/t	kilogram per metric ton	ppm	part per million
L	liter	pct	percent
μ g	microgram	rpm	revolution per minute
M Ω /cm	megohm per centimeter	wt pct	weight percent

EFFECT OF POTASSIUM ETHYLXANTHATE DEGRADATION ON FLOTATION OF CHALCOPYRITE AND MOLYBDENITE

By W. W. Simpson,¹ I. L. Nichols,² and J. L. Huiatt³

ABSTRACT

The Bureau of Mines conducted research to determine the effects of potassium trithiocarbonate (KTTC), a degradation product of potassium ethylxanthate (KEX), on flotation of chalcopyrite and molybdenite. Small amounts of KTTC were identified in fresh and aged solutions of KEX using thin-layer chromatography. Hallimond tube flotation tests on pure minerals showed that KTTC acts as a weak collector for chalcopyrite. Both KEX and KTTC tend to depress molybdenite, but the depression effect is easily overcome by addition of a small quantity of fuel oil. The results of the Hallimond tube tests were confirmed in batch flotation tests using a porphyry copper ore.

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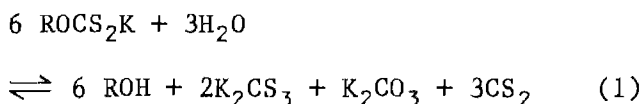
INTRODUCTION

The efficiency of many mineral separation processes, particularly froth flotation, often depends on the type of process water employed. New water suitable for processing is limited in the Western United States; consequently, process waste water is recycled whenever possible. Recycled water from sulfide mineral flotation contains residual flotation reagents, such as xanthate collectors, and chemicals produced by degradation of these reagents. The presence of these degradation products in recycled water interferes with mineral recovery.

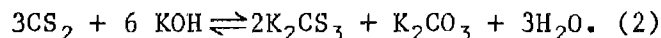
A portion of Bureau of Mines research programs on environmental technology involves process waste control. Therefore, an investigation was performed to determine effects of degradation products on sulfide mineral flotation separation and whether the degradation products should be removed from recycled water.

A review of literature indicated that the overall decomposition of the common collector potassium ethylxanthate, (KEX) yields ethanol and carbon disulfide. However, these are not the only products of KEX decomposition (5);⁴ experimental

evidence revealed that side reactions may occur to produce products such as potassium trithiocarbonate (KTTC) (1, 2, 5, 7). Klauditz (4) first reported the formation of KTTC by the hydrolysis of KEX in alkaline solutions. The reaction may be represented by the general equation



where R represents the alkyl group of the xanthate or alcohol. Rao (5) reported that carbon disulfide can undergo alkaline hydrolysis in aqueous streams to produce KTTC via the equation



Xanthate collector is continually added to a flotation; consequently, a small amount of KTTC will remain in the recycle water.

The purpose of this investigation is to verify the presence of KTTC in flotation water and to determine the effect KTTC has on the flotation of a copper-molybdenum sulfide system.

EXPERIMENTAL METHODS

MATERIALS

Pure molybdenite and chalcopyrite minerals, obtained from a commercial source, were used in the Hallimond tube flotation tests. The minerals were dry-ground to minus 65-mesh, purified by magnetic separation, and sized by screening. The minerals were stored in a freezer until used. The minus 65- plus 200-mesh size fraction was used in the test work. Chemical analyses indicated the molybdenite contained 58.5 pct Mo and the chalcopyrite contained 30.1 pct Cu.

A porphyry copper ore containing 0.27 pct Cu and 0.038 pct Mo was employed in

the bench-scale flotation tests. Petrographic analysis revealed chalcopyrite, pyrite, and molybdenite as the principal sulfide minerals. Quartz and potassium feldspars were the most abundant gangue minerals. Biotite and amphibole were present in smaller quantities. Run-of-mill ore was crushed and ground through minus 10-mesh, packaged in 750-g lots, and stored in a freezer to retard oxidation of sulfide surfaces.

Potassium ethylxanthate (KEX) was selected for this investigation, because it is a collector commonly used in industry. The KEX was purified by dissolving in a minimum amount of acetone and recrystallizing with petroleum ether. After recrystallization, the material was filtered, washed with petroleum ether, vacuum dried, and stored in a refrigerator.

⁴Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Potassium trithiocarbonate (KTTC) was purchased from Alfa Products, Inc.,⁵ Danvers, MA, and used without further purification. Fuel oil No. 2, methyl isobutyl carbinol (MIBC), and lime were used as received.

High-purity water with a resistivity of 2.3 M Ω /cm was used in the Hallimond tube flotation tests. Tapwater was used in bench-scale flotation tests.

IDENTIFICATION OF POTASSIUM TRITHIOCARBONATE

The separation and identification of KEX and KTTC were accomplished by thin-layer chromatography. Four spots containing 1 μ g each of fresh KEX, KTTC, a KEX-KTTC mixture, and aged KEX were placed at the origin of a 20- by 20-cm silica gel plate. The plate was placed in an eluting solvent containing 3 parts n-propanol, 1 part petroleum ether, and 1 part NH₄OH, and allowed to develop for 60 min. The plate was dried and sprayed with alcoholic silver nitrate to visualize the separated components. The R_f values (distance the compound traveled divided by the distance the solvent front traveled) were calculated, and rough estimates of the KTTC concentration were made.

HALLIMOND TUBE FLOTATION

One-gram samples of minus 65- plus 200-mesh fractions of pure chalcopyrite or

molybdenite were conditioned in a beaker for 3 min with the collector reagent at the flotation pH. The pH was adjusted using KOH or HCl. The sample was transferred to a modified Hallimond tube cell (3) and floated for 2 min using nitrogen gas at a flow rate of 70 mL/min. The flotation products were dried, weighed, and recoveries calculated.

BENCH-SCALE FLOTATION

The 750-g charges of minus 10-mesh porphyry copper ore were ground for 6 min at 60 pct solids in a laboratory ball mill to produce all minus 65-mesh material. The ball charge was 10 kg. The pulp was transferred to a Fagergren flotation cell, diluted to 25 pct solids, and the alkalinity was adjusted to pH 10 using 1.243 kg/t of lime. The pulp was conditioned for 3 min with either KEX and fuel oil No. 2 or KTTC and fuel oil No. 2. Reagent dosages, in kilograms per metric ton of ore, were 0.050, 0.030, and 0.050, respectively, for KEX, fuel oil No. 2, and KTTC. After 1 min conditioning with 0.024 kg/t MIBC frother, the pulp was floated for 4 min at an impeller speed of 2,000 rpm. The rougher concentrate and tailings were filtered, dried, weighed, and chemically analyzed, and the copper and molybdenum distributions were calculated.

RESULTS AND DISCUSSION

SOLUTION ANALYSES

Figure 1 shows thin-layer chromatograms of fresh KEX, KTTC, a mixture of KEX and KTTC, and aged KEX. The results showed the KTTC and KEX have R_f values of 0.23 and 0.98, respectively. The chromatograms also showed small amounts of KTTC present in fresh KEX solution, and slightly larger amounts present in aged KEX solution of pH 10. Densitometer measurements indicated about 0.5 to 1 pct of the new KEX was KTTC and about 2 to 2.5

pct of the aged KEX was KTTC. The increase in KTTC may be caused by the reaction of carbon disulfide and hydroxyl ion via equation 2. The chromatogram of the aged KEX also showed trace of another compound, which was not identified.

COPPER-MOLYBDENUM FLOTATION

The literature and the Bureau's experimental data indicated KTTC should exist in aqueous solutions. If the rate of addition of KEX to a flotation circuit exceeds the decomposition rate, a gradual buildup of KTTC should occur. The concentration of KTTC present in an aqueous process stream, assuming waste water is

⁵Reference to specific trade names or manufacturers does not imply endorsement by the Bureau of Mines.

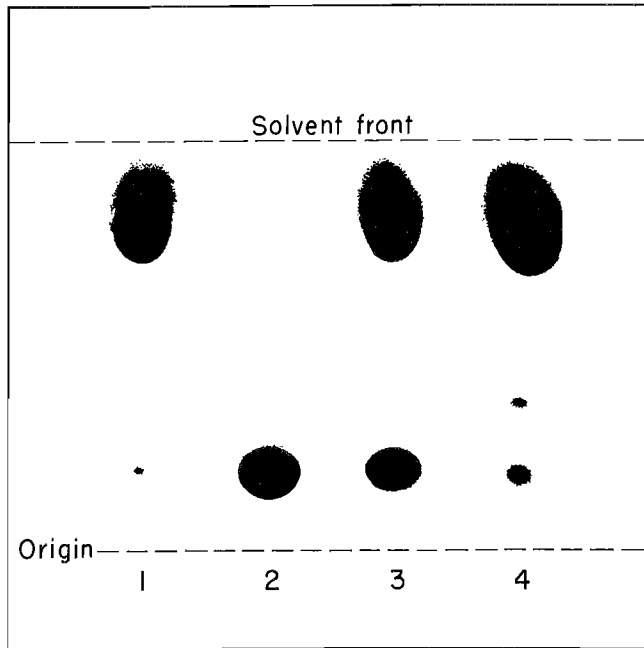


FIGURE 1. - Thin-layer chromatograms of $1 \mu\text{g}$ each of (1) KEX, (2) KTTC, (3) KEX-KTTC, and (4) aged KEX.

recycled, was estimated to be between 10^{-6} and 10^{-5} mol/L. The degree to which KTTC affects copper and molybdenum flotation recovery was investigated using Hallimond tube and bench-scale flotation.

Hallimond Tube Flotation

Hallimond tube tests were designed to study the effect of variable KTTC dosages on chalcopyrite flotation using a constant dosage of KEX. The flotation pH was maintained at pH 10. The KEX dosage was held constant at 10^{-5} mol/L, while the KTTC dosages were varied from 10^{-5} mol/L to 5×10^{-5} mol/L. These dosages were selected because they represent typical collector reagent dosages used in Hallimond tube flotation of sulfide type minerals. The results, listed in table 1, indicate that increasing KTTC dosages raised the chalcopyrite recovery from 50 to 75 pct.

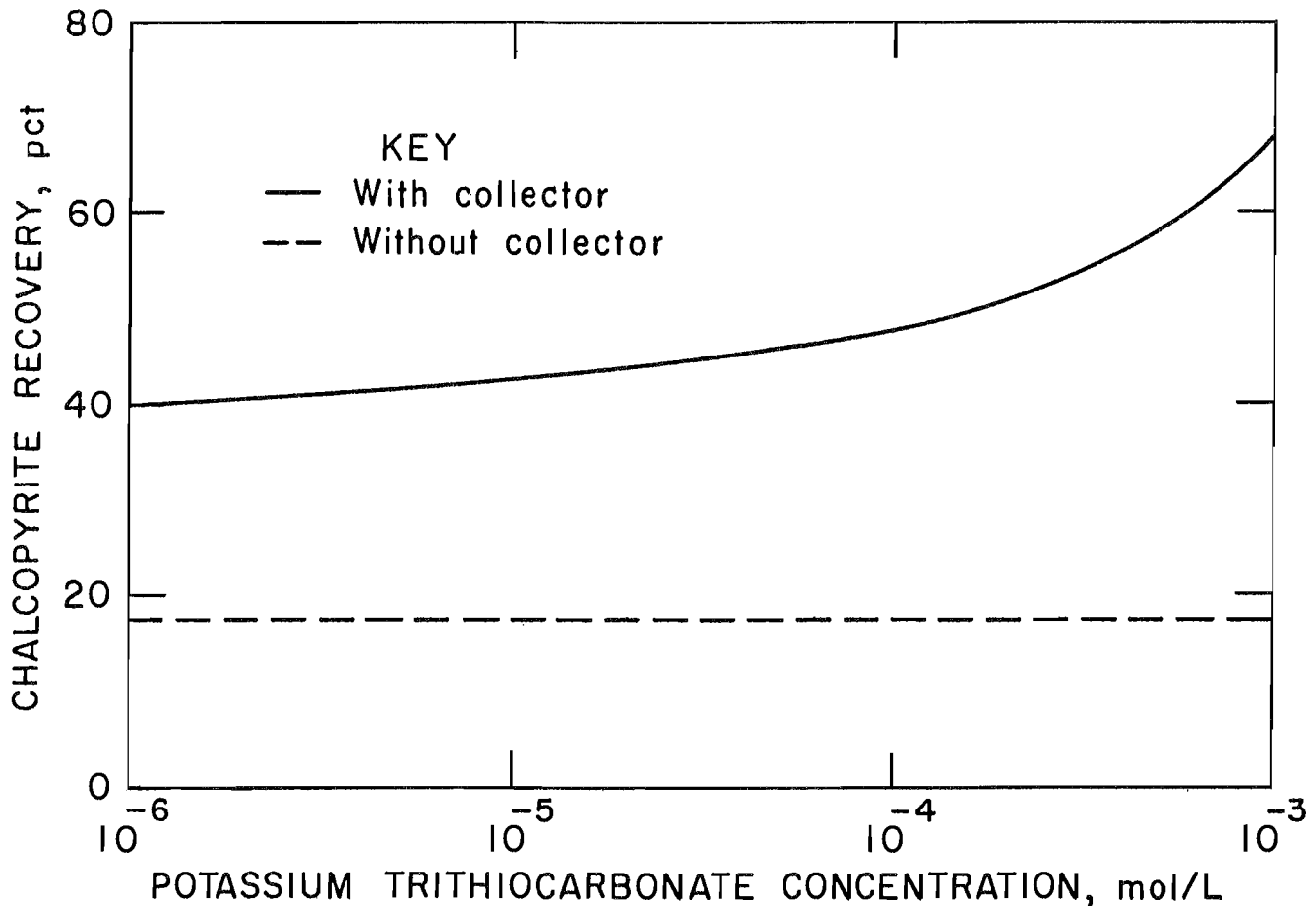


FIGURE 2. - Effect of KTTC concentration on floatability of chalcopyrite at pH 10.

The collecting ability of the KTTC is also demonstrated in figure 2. In figure 2, the plot of KTTC concentration versus chalcopyrite recovery shows a significant increase in recovery over that obtained when no KTTC was added. As little as 10^{-6} mol/L KTTC increased recovery from 17 pct (no collector) to 40 pct. A moderate increase in chalcopyrite recovery occurred when the KTTC dosage was increased from 10^{-4} to 10^{-3} mol/L.

Additional testing revealed chalcopyrite flotation using KTTC collector depended on solution pH. Flotation recovery versus pH is shown in figure 3. The curve shows recovery decreased from 50 pct at pH 2 to about 29 pct at pH 6.5, then increased to a maximum of 66 pct at pH 10. Above pH 10, the recovery dropped rapidly to a value of 10 pct.

The flotation response of molybdenite in the presence of KTTC, KEX, and fuel oil No. 2 was examined using the Hallimond tube flotation procedure. Table 1 shows that molybdenum flotation decreased

from 51 to 38 pct when the ratio of KTTC to KEX increased from 1:1 to 5:1. Note that the KEX concentration was constant at 10^{-5} mol/L while the KTTC varied from 10^{-5} to 5×10^{-5} mol/L. The flotation pH was 10. This concentration effect is illustrated further in figure 4. Without collector molybdenite recovery at pH 10 was constant at about 70 pct. When KEX or KTTC was added, recovery decreased. The KEX reduced recovery to 56 pct. Even as the collector dosage was increased

TABLE 1. - Chalcopyrite and molybdenite flotation using variable KTTC concentrations and a constant KEX concentration of 10^{-5} mol/L

Reagent concentration ratio ¹	Recovery, pct	
	Chalcopyrite	Molybdenite
1:1.....	50	51
2:1.....	66	51
3:1.....	68	51
4:1.....	73	48
5:1.....	75	38

¹KTTC:KEX.

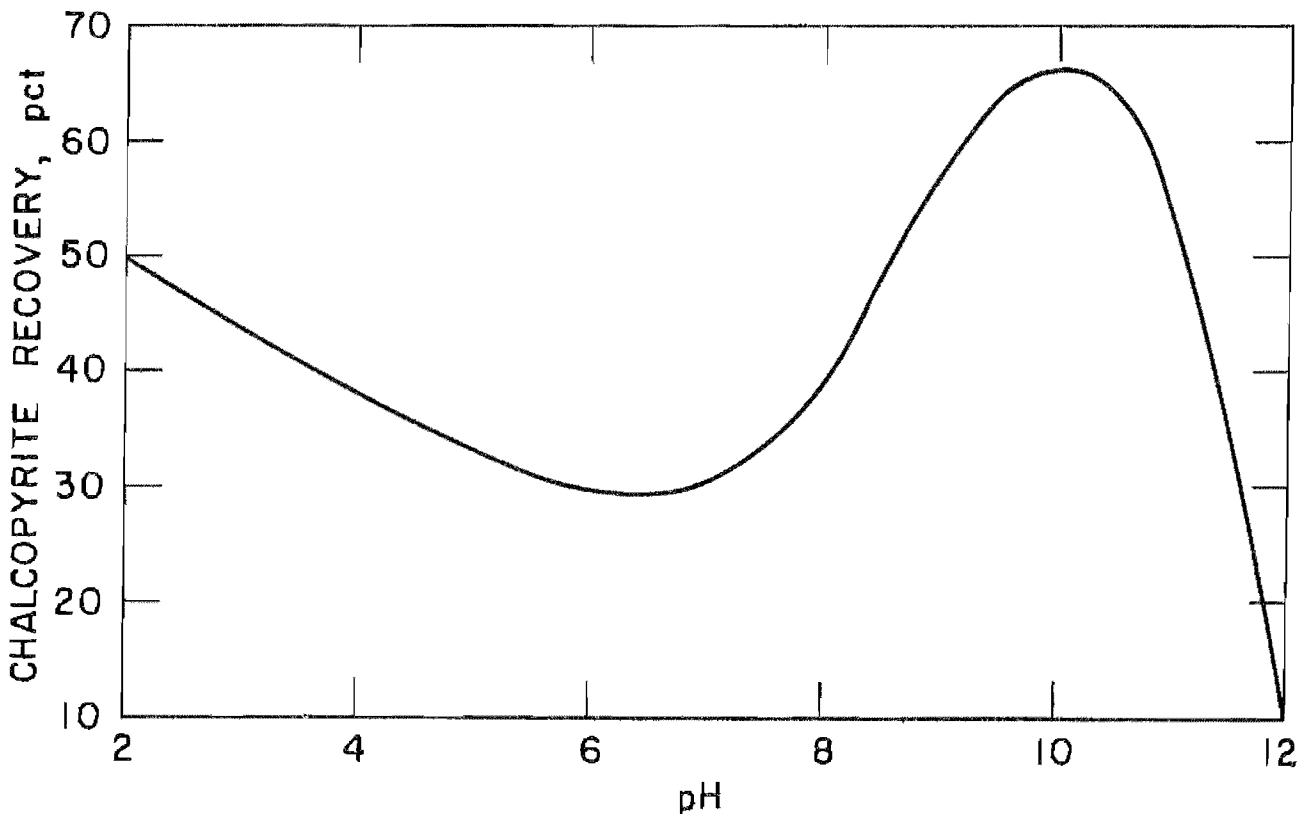


FIGURE 3. - Effect of pH on chalcopyrite recovery using 10^{-3} mol/L KTTC as collector.

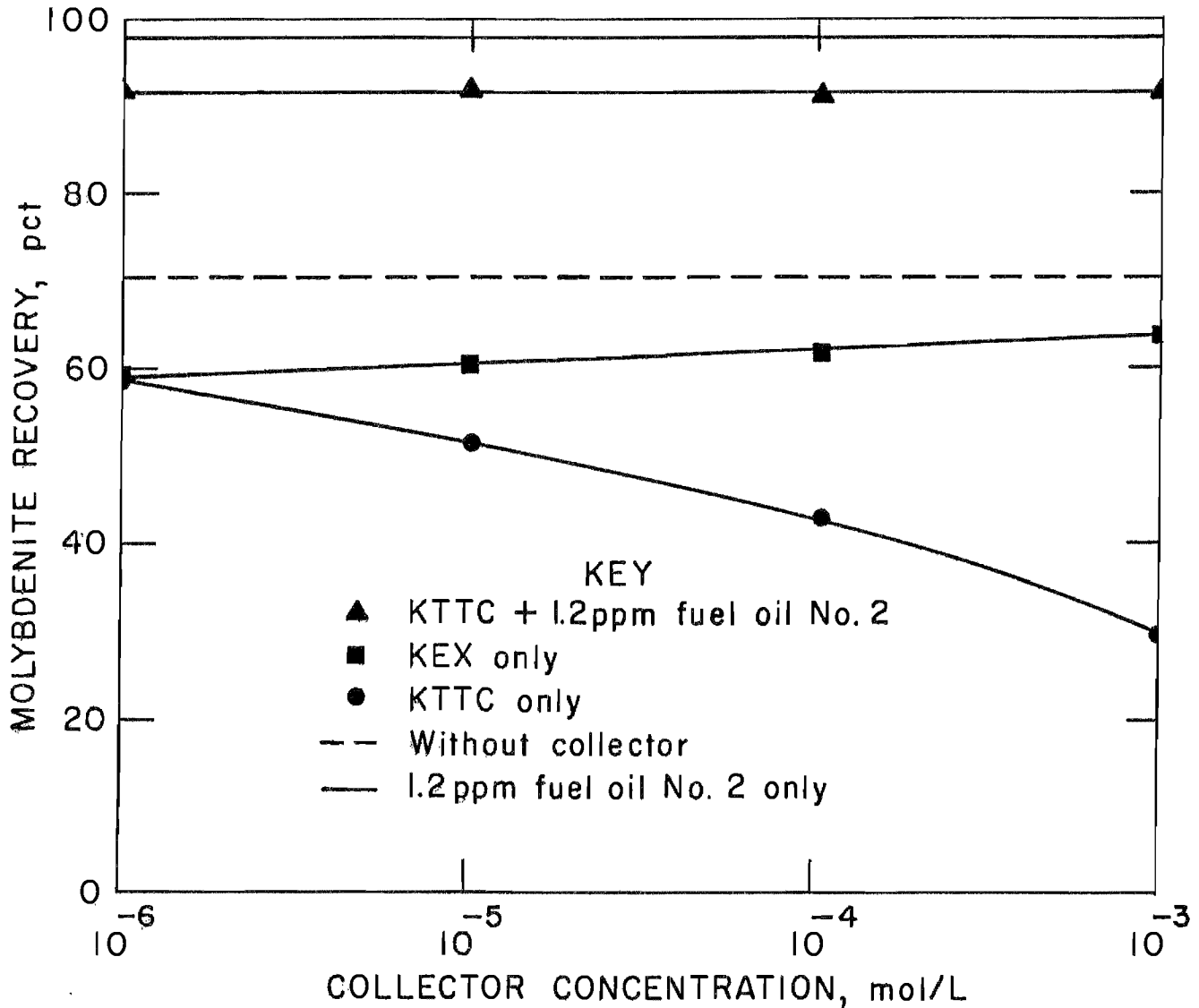


FIGURE 4. - Effect of collector concentration on floatability of molybdenite at pH 10.

four orders of magnitude, the recovery remained less than that of natural flotation. Increasing the dosage of KTTC from 10^{-6} to 10^{-3} mol/L caused the molybdenite recovery to drop from 58 to 29 pct. The presence of 1.2 ppm fuel oil apparently overrides any effect of KTTC and KEX, regardless of dosage, and causes molybdenite recovery to increase to 91 pct.

Bench-Scale Flotation

The recovery of copper and molybdenum from the porphyry copper ore was studied using typical industrial dosages of KEX, KTTC, and/or fuel oil. In one test

series the sample was floated using KEX and fuel oil No. 2. In another series KTTC and fuel oil No. 2 were used as collectors. The results of duplicate tests are listed in tables 2 and 3.

Flotation with KEX and fuel oil produced average copper and molybdenum recoveries of about 90 pct and 57 pct, respectively. Respective grades were 13.0 and 1.1 pct. These are normal bench-scale flotation results for this particular ore. Flotation with KTTC and fuel oil produced average copper and molybdenum recoveries of 67 and 55 pct. Respective grades were 14.6 and 1.8 pct.

TABLE 2. - Flotation of copper ore using KEX and fuel oil No. 2¹

Product	Wt pct	Assay, pct		Distribution, pct	
		Cu	Mo	Cu	Mo
Test 1:					
Rougher concentrate...	2.0	13.0	1.0	90.0	56.0
Rougher tailings.....	98.0	.03	.016	10.0	44.0
Calculated head....	100.0	.29	.036	100.0	100.0
Test 2:					
Rougher concentrate...	2.0	13.0	1.1	90.0	58.3
Rougher tailings.....	98.0	.03	.016	10.0	41.7
Calculated head....	100.0	.29	.038	100.0	100.0

¹Concentration, kg/t: KEX, 0.50; fuel oil No. 2, 0.030.

TABLE 3. - Flotation of copper ore using KTTC and fuel oil No. 2¹

Product	Wt pct	Assay, pct		Distribution, pct	
		Cu	Mo	Cu	Mo
Test 1:					
Rougher concentrate...	1.2	14.6	1.8	66.8	56.5
Rougher tailings.....	98.8	.089	.017	33.2	43.5
Calculated head....	100.0	.26	.038	100.0	100.0
Test 2:					
Rougher concentrate...	1.2	14.5	1.7	67.0	52.5
Rougher tailings.....	98.8	.088	.019	33.0	47.5
Calculated head....	100.0	.26	.039	100.0	100.0

¹Concentration, kg/t: KEX, 0.50; fuel oil No. 2, 0.030.

The results showed KTTC and KEX had no significant effect on molybdenum recovery from ore. Based on Hallimond tube test results (fig. 4) the collecting properties of fuel oil may override any depressing effect of either KTTC or KEX. Similar response could be expected in

bench-scale flotation of ore. The KTTC did not float copper as well as KEX; however, KTTC addition improved selectivity. This is seen when comparing the average grades of copper and molybdenum obtained by KTTC with the average grades obtained by KEX.

SUMMARY AND CONCLUSIONS

Using thin-layer chromatography KTTC was identified, and its presence in both fresh and aged solutions of KEX was established.

Hallimond tube flotation tests on chalcopyrite and molybdenite suggested that KTTC acts as a collector for chalcopyrite. The presence of small amounts of KTTC in combination with KEX resulted in improved recovery of chalcopyrite. This

effect was confirmed in flotation tests on porphyry copper ores. Under similar test conditions using pure molybdenite, the results showed that both KEX and KTTC act as depressants for molybdenite. This depression effect was overcome by small additions of fuel oil. The results of the Hallimond tube tests were verified in batch flotation tests on porphyry copper ore.

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