FLOTATION OF SULFIDE MINERALS WITH ALKYL PYRIDINIUM SALTS

by

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I. INTRODUCTION

1.1 General

Froth flotation refers to a wet process for separating ground mineral particles into two or more products. The process involves physiochemical treatment of the ore pulp to create conditions that are favorable for the attachment of desired mineral particles to air bubbles. The air bubbles then carry the mineral particles to the surface of the pulp where they form a stable froth that can be skimmed off. For the case of copper minerals, this method of concentration makes it economically feasible to recover minerals from an ore containing as little as 0.5% Cu (Tatsch, 1975).

A variety of chemical reagents are used for this process, including collectors to improve adherence of the mineral to air bubbles. The most common collectors for sulfide mineral flotation are xanthates. First discovered in 1822 (Zeise, 1822), no commercial application for xanthates was found until after 1900 when the rubber industry used them in the curing and vulcanization of rubber. It was not until 1923 that Cornelius H. Keller discovered that xanthates could be used as collectors for sulfide minerals. The high collection efficiency and low cost of xanthates have made them the standard of comparison

among sulfide mineral collectors to date (Dow Chemical Co., 1976). More than 5.2 million pounds of xanthates were consumed in U.S. froth flotation plants in 1960 to treat over 105 million tons of ore and produce nearly 4 million tons of copper concentrate (Merrill and Pennington, 1962).

It is estimated that as much as 90% of the world's primary copper originates in sulfide ores, which are separated by froth flotation (Biswas and Davenport, 1976). As reported in Mineral Facts and Problems (1980), the average annual growth rate in world demand for copper is projected to be 3.9% for the period 1978-2000. This increase in demand will compel mining companies to consider mining lower grade deposits (Tatsch, 1975) which will, in turn, necessitate improvements in flotation technology.

It is the purpose of the proposed investigation to evaluate cetyl pyridinium chloride (CpCl) as a collector for sulfide minerals and to compare batch flotation results with those obtained using xanthates. It is also proposed to investigate the mechanisms by which CpCl adsorbs on the surfaces of sulfide minerals.

1.2 Literature Review

1.2.1 Flotation of Sulfide Minerals

The first froth flotation process in the United States was installed by James M. Hyde in 1911 at Basin, Montana. Oleic acid was used as both frother and collector, and the zinc ore pulp was heated to assist in the oiling of the mineral particles. This process yielded a zinc concentrate assaying 49.0% Zn with 90.2% recovery (Rickard, 1912). Early froth flotation practice with copper sulfide ores was not nearly as successful, however. Later, it was discovered that cresylic acid and crude turpentine were more suitable for froth flotation of ores containing chalcopyrite (Truscott, 1923). Further improvements were made by using coal tar as a collector in place of cresylic acid (Gahl, 1917). Wood creosotes, pine oil, kerosene and eucalyptus oil were also tried, but it was not until after 1925 that the first water-soluble, non-oily collectors were used in mill practice (Chapman, 1936). These collectors were very-soluble organic salts known as xanthates, named for the Greek word "xanthos", meaning yellow. Their adoption was immediate and widespread.

For many years, the mechanisms of mineral collection have been the object of considerable speculation. Bains (1915) suggested that static electricity generated by

agitation and friction was responsible for mineral particles sticking to air bubbles. Fahrenwald (1916) and Anderson (1916) opposed this idea and it was abandoned. A more modern idea was presented by Langmuir (1921), as well as by Taggart and Gaudin (1923), suggesting that collectors formed monolayers on mineral surfaces by an adsorption process. Taggart et al. (1934) suggested an ion-exchange mechanism between the ions on the mineral surface and the collector ions in solution, proposing that collectors are adsorbed as ions, rather than as molecules. Because mineral surfaces conditioned with xanthate became hydrophobic, it was apparent that the polar group of the collector was attached to the surface with the non-polar group projecting toward the solution phase. Taggart (1934) showed that the polar group of the xanthate ions was bonded to the metal cations on the mineral surface, forming a metal-xanthate. On the other hand, the 'electrochemical' theory suggests that a hydrophobic layer is produced on the mineral surface by two independent simultaneous electro-chemical processes (Woods, 1972). The anodic reaction produces the hydrophobic species (e.g., dixanthogen or metal xanthate) while the cathodic reaction involves the reduction of oxygen. Gould et al. (1972) showed that dixanthogen is formed on the surface of a sulfide mineral when the rest potential of the sulfide mineral-oxygen-xanthate system is above the reversible potential for the xanthate-dixanthogen couple. When the

rest potential is below the reversible potential, metal xanthate is formed.

Sulman (1930) and Gaudin (1932) also reported that some sulfide minerals such as chalcopyrite and galena were floatable without using collectors. This led some researchers to believe that some sulfide minerals were naturally hydrophobic. However, Taggart et al. (1934), as well as Sutherland and Wark (1955), contended that the observed natural hydrophobicity was due either to contamination of the samples by oily substances or to the use of frothers with collecting abilities. On the other hand, Plaksin (1949) suggested that adsorption of molecular oxygen aided dehydration of sulfide minerals and was responsible for the apparent hydrophobicity. Lepetic (1974) later used this theory to explain the collectorless flotation of chalcopyrite that had been dry-ground.

Ravitz and Porter (1933) showed that galena cleaned of its surface oxidation products floated completely with a frother alone in an oxygen-free atmosphere. Fuerstenau and Sabacky (1981) reported similar results with clean samples of galena, pyrite and chalcopyrite. Yoon (1981) used Na_2S as a cleaning agent to remove oxidation products from sulfide mineral surfaces and achieved flotation without collectors. Various other cleaning agents were also used, including pyridine. Good flotation results were obtained with several types of sulfide ores using pyridine as a

surface-cleaning agent, but the amounts required for flotation were prohibitive. It was later found that when long chain alkyl pyridinium salts were used, flotation could be achieved with significantly less reagent consumption. However, it was not known whether the pyridinium salts cleaned the mineral surfaces of their oxidation products or adsorbed as collectors.

Alkyl pyridinium salts are sometimes used as cationic collectors for the flotation of oxide minerals. Adsorption of alkyl pyridinium salts on quartz has been reported by Skrylev and Sviridov (1980) as well as Harrop (1977), with Langmuir-type isotherms reported in both cases. Flotation of fluorite and barite was studied by Baldauf (1977) using dodecyl pyridinium bromide as a collector, although the results were poor in comparison with oleic acid. Russian researchers Sviridov and Gomzikov (1977) have also used cetyl pyridinium chloride as a collector in ion flotation, achieving separation of Cu, Co and Ni complexes from an electroplating circuit effluent.

1.2.2 Classification of Adsorption Isotherms

Adsorption isotherms are useful tools in diagnosing the adsorption mechanisms involved in mineral-collector interactions. Early attempts to classify adsorption

isotherms were made by Ostwald and deIzaguirre (1922) and Brunauer (1944). Modifications and improvements of these classification systems are given by Giles et al. (1960) and are shown in Figure 1.1. This system divides experimentally obtained isotherms into four main classes according to their initial slope, and further divides them into sub-groups based on the shape of the upper portion of the curves. The four main classes are named S ("S shaped"), L ("Langmuir" type), H ("high affinity"), and C ("constant partition") isotherms.

In the case of S curves, adsorption becomes easier as the concentration increases. L-shaped curves indicate that as initial substrate sites are filled, adsorption proceeds with increasing difficulty. This seems to indicate that there is no strong competition for substrate sites. The H curves are described as a special case of the L curves, where the solute has such a high affinity for the substrate that in dilute solutions, there is no measurable amount of solute remaining in solution. Thus, the initial slope of the isotherm is vertical. C curves are observed for 1) a porous substrate with flexible molecules, 2) a solute with higher affinity for the substrate than for the solvent, and 3) solutes with penetrating power either by molecular geometry or by condition (2).

Sub-group classification is based on the shape of the upper portion of the curves. Isotherms in group 1 indicate

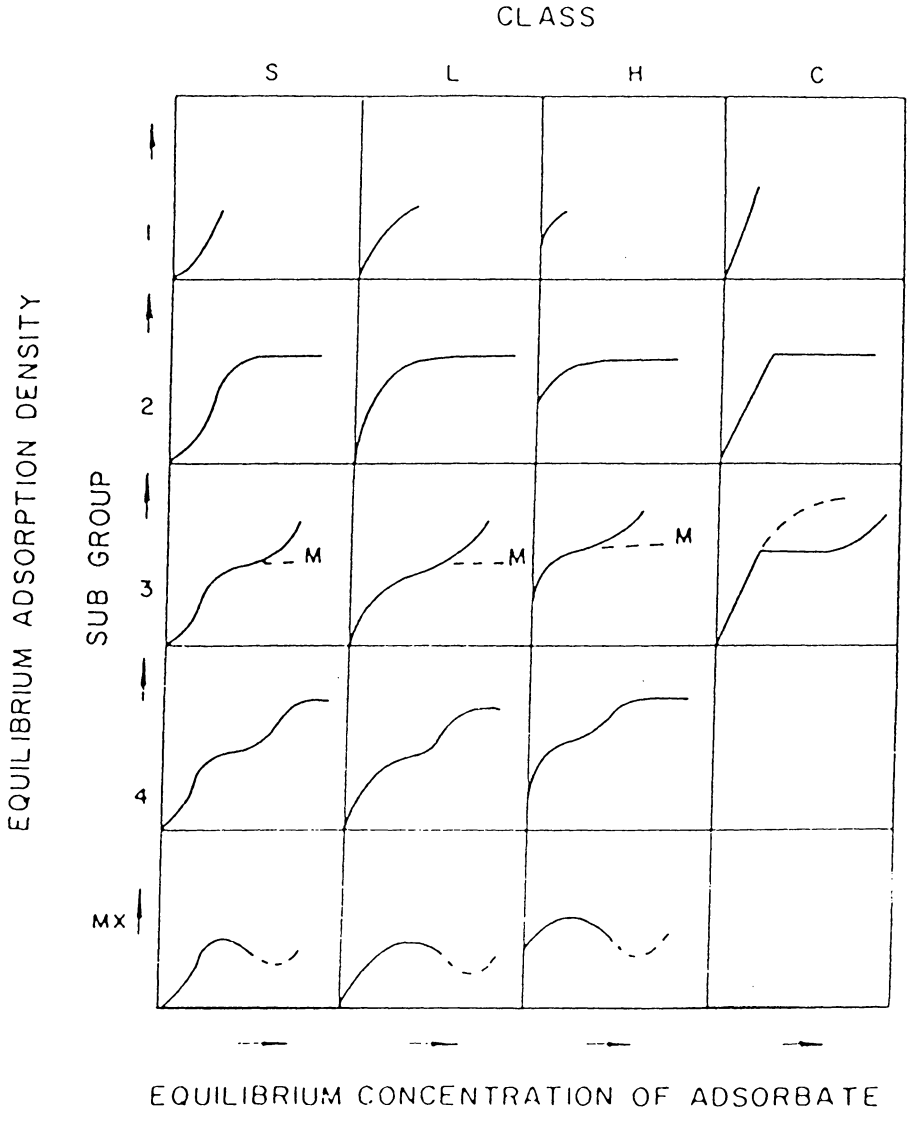


Figure 1.1 Adsorption Isotherm Classification (after Giles et al., 1960)

that surface saturation has not been reached. Plateau regions in group 2 represent a degree of surface saturation, conveniently referred to as a "monolayer". However, this in no way implies a close-packed layer of molecules. It is important to realize that the layer may contain both solvent and solute molecules, or may be made up of clusters of molecules adsorbed on the most active sites. "Step functions", as shown in sub-groups 3 and 4, are attributed to the development of fresh surfaces on which additional adsorption can occur.

1.3 Objectives

The objectives of this work were: 1) to test alkyl pyridinium salts as collectors for the flotation of chalcopyrite and galena ores, and 2) to study the mechanisms involved. Batch flotation tests were conducted on several ore samples and the results obtained with alkyl pyridinium salts were compared with those obtained using xanthates as collectors. This work involved studies on the effect of pH, the effect of collector dosages and the flotation kinetics. The flotation kinetic studies were conducted using a specially designed micro-flotation cell.

In order to better understand the mechanisms, the following work was done: i) electrophoretic mobility

measurements to study the electrical properties of chalcopyrite and quartz particles in solution at different pH and collector concentrations, ii) determination of the isotherms for the adsorption of alkyl pyridinium ions on chalcopyrite and quartz surfaces, which gave insight into the nature of the adsorption mechanisms, and iii) electrochemical studies to determine whether the adsorption of alkyl pyridinium ions is controlled by electrochemical mechanisms.

Success in the present work could establish that alkyl pyridinium salts can be used as an alternative to conventional flotation reagents in the sulfide flotation industry today. It may also contribute to the better understanding of the flotation mechanisms of sulfide minerals in general.

II. EXPERIMENTAL

2.1 Materials

2.1.1 Ore Samples

a. Falconbridge Copper Ore: Approximately one hundred pounds of copper ore was received from Falconbridge Copper Limited in October, 1980. The flotation feed was prepared in February, 1981, by crushing approximately 20lb of the ore to -20 mesh and splitting it into 500 g lots. These samples were stored in a freezer to minimize possible surface oxidation of sulfide minerals.

The ore assayed 4% Cu which was present as chalcopyrite. The chalcopyrite was finely disseminated in quartz which was the major gangue mineral present. The ore also contained 0.012 oz/ton Au and 0.33 oz/ton Ag.

b. Texasgulf Copper-Zinc Ore: A two hundred pound sample of Kidd Creek Type A ore was taken from the rod mill feed on November 27, 1978. The sample was stored upon receipt without taking any precautions to prevent surface oxidation. The flotation feed (-20 mesh) was prepared in February, 1981, by using a laboratory jaw crusher, hammer mill and disc pulverizer. The sample was riffled into 500 g lots and

stored in a freezer to minimize oxidation.

The ore assayed 2.1% Cu, 0.1% Pb, 6.4% Zn, 11.8% Fe and 1.2 oz/ton Ag. The major metallic minerals of the ore were pyrite, sphalerite, chalcopyrite and galena. Silver was present as native grains with subordinate acanthite. Quartz was the major gangue mineral present and smaller quantities of talc, pyrrhotite, siderite and cassiterite were also found.

c. St. Joe Minerals Lead Ore: This ore was obtained in September, 1980, and was ground to -20 mesh upon receipt. The ground sample was riffled into 500 g lots and stored in a freezer. The ore assayed 2.8% Pb. The major metallic mineral present was galena, although minor amounts of other sulfide minerals were also present. The major gangue minerals were calcite and dolomite .

2.1.2 Pure Minerals

Lump specimens of relatively pure Transvaal chalcopyrite were purchased from Ward Scientific Co. for investigations other than batch flotation. The specimens were initially broken with a hammer and large pieces of contaminant quartz were removed with tweezers. The

chalcopyrite was ground with a ceramic mortar and pestle to -65 mesh. This material contained some fine grains of quartz which were removed with a Franz Isodynamic Separator. The -65+100 mesh fraction was retained for use in micro-flotation and electrochemical studies.

A -65+100 mesh quartz sample was prepared similarly. The -100+200 mesh fraction of each mineral was separately wet-ground for four hours with a mechanical agate mortar and pestle. The material was filtered with a Buchner funnel aided by suction, and stored in a vacuum dessicator over silica gel. This material was used for adsorption studies. To remove iron contamination from the wet-ground quartz, the sample was cleaned with hydrochloric acid. The acid was decanted and the powder was thoroughly washed with double-distilled water and filtered. This procedure was repeated until the pH of the filtrate was neutral, indicating complete removal of the acid.

The chalcopyrite sample used for electrophoretic mobility measurements was a pure sample purchased from Ward Scientific Co., previously sized to -65+100 mesh. The sample was stored for four years without taking any precautions to prevent surface oxidation. The chalcopyrite was prepared by wet-grinding approximately 5 g using a mechanical agate mortar and pestle. The -3 micron fraction was obtained by sedimentation and stored in a flask. The quartz samples used for electrophoretic mobility

measurements were prepared in the same manner.

2.1.3 Chemicals

Commercial grade sodium iso-propyl xanthate (NaIpX) and potassium amyl xanthate (KAX) from American Cyanamid were used for flotation tests. Laboratory grade cetyl pyridinium chloride (CpCl), dodecyl pyridinium chloride (DpCl) and ethyl pyridinium bromide (EpBr) were purchased from Pfaltz and Bauer, Inc., and used in flotation tests. Other collectors used included laboratory grade dodecyl amine hydrochloride (DAHCl) from Kodak Chemicals and reagent grade n-dodecyl mercaptan (nDM) from Pennwalt Co., Inc. Dowfroth 250 was used as frother for all batch flotation tests and reagent grade $CuSO_4$ was used as an activator for sphalerite flotation.

For electrophoretic mobility measurements, adsorption studies and micro-flotation tests, the commercial grade xanthates were purified by following the procedures described by Rao (1971). Pyridinium salts and DAHCl were used for these experiments without further purification.

Blacksburg tap water was used for all batch flotation tests. All other tests were conducted with double-distilled water to prevent interference from trace quantities of contaminants. The double-distilled water

was prepared in the following manner: tap water was distilled with a Barnstead Model A1011 Still and stored in a Nalgene container. The distilled water was then pumped through a Corning Model LD-5 Demineralizer and finally distilled in an all-glass, Corning Mega-Pure Still, Model 3512, and stored in a Pyrex bottle.

2.2 Equipment

2.2.1 Flotation Machine

All batch flotation tests were conducted with a Denver Model D-12 laboratory flotation machine with rectangular stainless steel flotation cells (4 liter and 2 liter volumes).

2.2.2 Electrophoresis Apparatus

Electrophoretic mobility measurements were determined by using a Rank Brothers Particle Micro-Electrophoresis Apparatus, Mark II. A flat cell made of fused silica was used for all measurements. A pair of platinum electrodes fit into ground glass joints on both ends of the cell, as shown in Figure 2.1. The cell was immersed in a

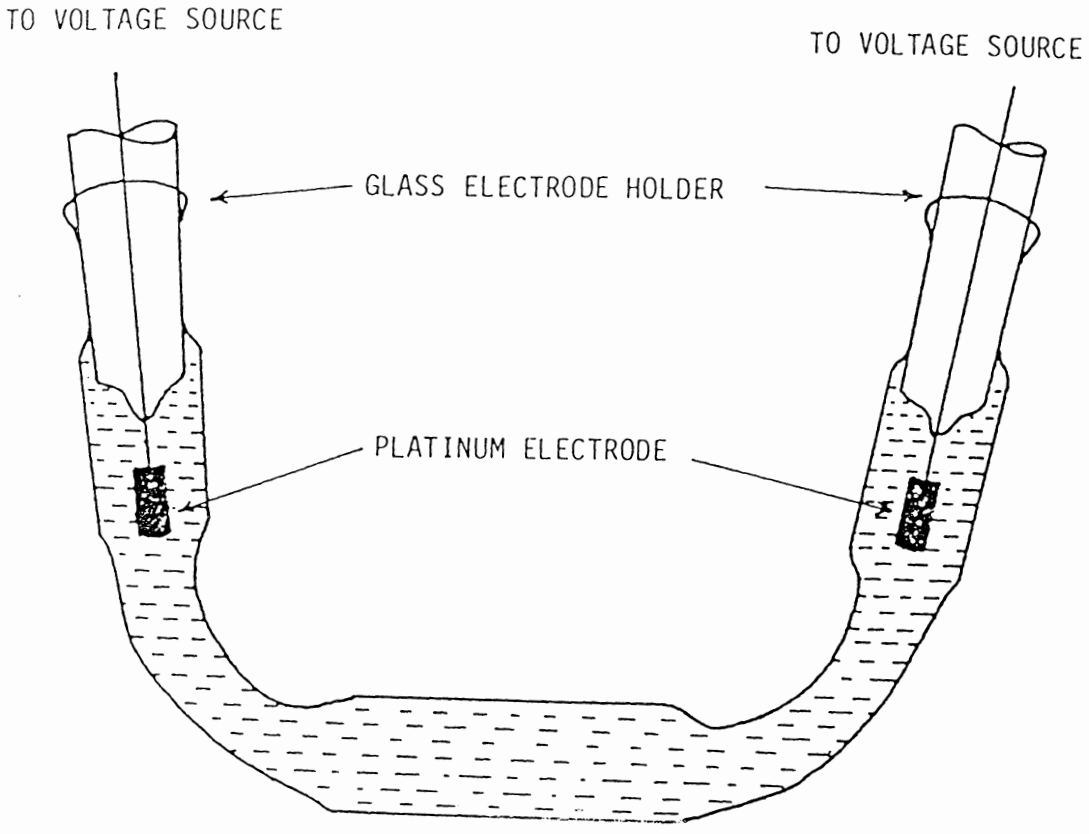


Figure 2.1 Flat Cell Used for Microelectrophoresis

thermostatic bath that was maintained at 25 + 1°C.

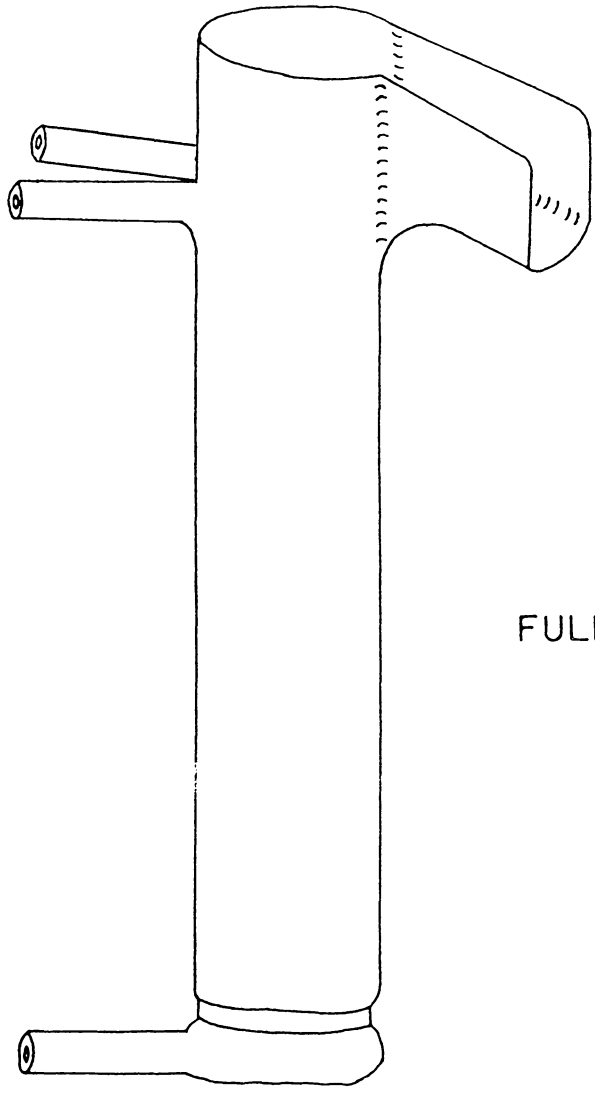
Determination of equipment parameters pertinent to calculations of ζ-potential are detailed in Appendix I.

2.2.3 Micro-Flotation

Pure mineral samples were floated in a Pyrex cell as shown in Figure 2.2. The sample suspension was stirred by means of a magnetic stirrer, Sybron Nuova II, and a Teflon-coated magnetic stirring bar. Air was supplied to the cell by means of a diaphragm pump, Universal Electric Co. Model LR126405. The air flow rate was controlled by means of a Gilmont Micrometer Capillary Valve. The entire apparatus is shown schematically in Figure 2.3.

2.2.4 UV-VIS Spectrophotometer

For adsorption studies, the concentration of alkyl pyridinium ions was determined using a Varian DMS 90 UV-VIS Spectrophotometer. This instrument has capabilities for determining absorbance at both fixed and scanning wavelengths. In the scanning wavelength mode, absorbance was recorded with a Hewlett Packard 7015B X-Y Recorder, while absorbance was recorded in the fixed wavelength mode



FULL SCALE

Figure 2.2 Micro-Flotation Cell

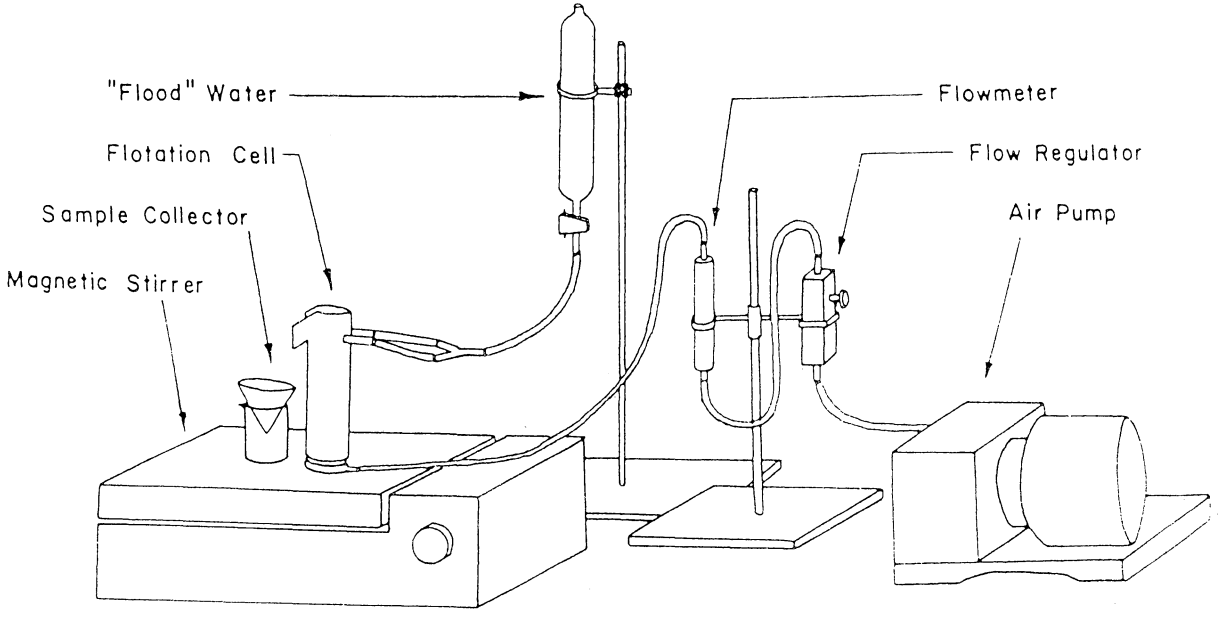


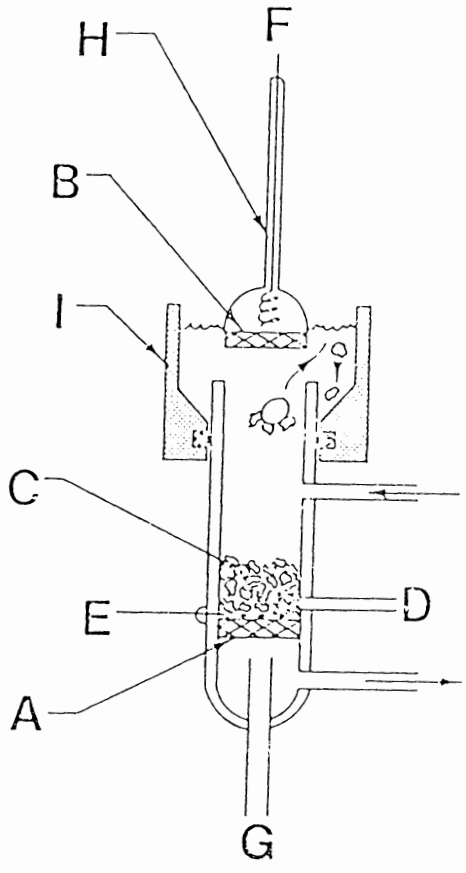
Figure 2.3 Micro-Flotation Assembly

by an LED readout.

2.2.5 Electrochemical Apparatus

The electrochemical studies were conducted by Dr. P. E. Richardson at the Avondale Research Center, U.S. Bureau of Mines. Essentially four major pieces of equipment were used: 1) a potentiostat (EG&G Princeton Applied Research Model 371), 2) a programmer (EG&G Princeton Applied Research Model 175), 3) a fast-scanning UV-VIS Spectrophotometer (Hewlett Packard 8450A), and 4) an electrochemical cell as shown in Figure 2.4.

The electrochemical flotation cell was designed to be able to conduct cyclic voltammetry, flotation and adsorption studies concurrently. It is made of Pyrex with a gas inlet tube (G) at the bottom. A platinum wire (E), which is in contact with a bed of mineral particles (C), serves as a working electrode. A calomel electrode is used as a reference electrode through a Luggin capillary (D), and a platinum wire (F) is used as the counter electrode. The counter electrode is located behind a glass frit (B). When recording voltammograms, the frit is pressed against the particle bed, and it is raised when the particles are floated while the applied potential remains unchanged. During voltammetric analysis, the sample solution can be



A- Glass frit
P- Glass frit
C- Mineral particle bed
D- Luggin capillary
E-- Platinum wire-working electrode
F- Platinum wire counter electrode
G- Gas inlet
H- Plunger assembly
I- Catch pan for floated particles

Figure 2.4 Electrochemical Cell

circulated to the spectrophotometer via inlet and outlet ports located above and below the particle bed. The ports are located in these positions in order to ensure thorough circulation of the sample solution. The cell assembly is approximately 10 cm high.

2.3 Procedure

2.3.1 Batch Flotation

All batch flotation tests were conducted using 500 g ore samples. The samples were ground in a porcelain laboratory ball mill (16.7 cm x 19.8 cm) with 300 ml of tap water and 7.5 kg of steel balls (1.7 cm to 2.5 cm in diameter) for a desired period of time. The comminuted slurry was transferred to a rectangular stainless steel flotation cell (4 l volume) which was then mounted on the flotation machine. The remaining volume was then filled to one inch below the cell overflow lip and the appropriate reagents were added. The pulp was then conditioned for a desired period of time at 1200 rpm. For cleaning operations, either 4 l or 2 l flotation cells were used, depending on the volume of the pulp to be treated, at impeller speeds of 1200 or 900, respectively. Froth products were skimmed off manually into stainless steel pans

for 4 minutes for each flotation stage. All flotation products were dewatered with a vacuum filter, dried, weighed and subsequently assayed using a plasma emission spectrometer, Spectraspan IV. The assaying procedure is described in detail in Appendix IV.

a. Falconbridge Copper Ore: For flotation tests conducted with Falconbridge copper ore, a 60-minute grinding time was used to achieve liberation of sulfide minerals. An arbitrary conditioning time of 10 minutes was employed after appropriate reagents were added. Froth products obtained after rougher and scavenger flotation were combined, followed by two cleaner flotation stages. No pH adjustments were made in any of the flotation tests conducted on this ore.

b. Texasgulf Copper-Zinc Ore: The ore samples were ground for 70 minutes (Figure 2.5) since fine grinding was necessary to liberate sphalerite. The ground ore pulp was aerated in the flotation cell at 1200 rpm for 7 minutes after the addition of a volume of dissolved SO_2. This procedure was adopted to help supress sphalerite during chalcopyrite flotation (Wills, 1982). After the aerative conditioning, the air valve was closed and a desired volume

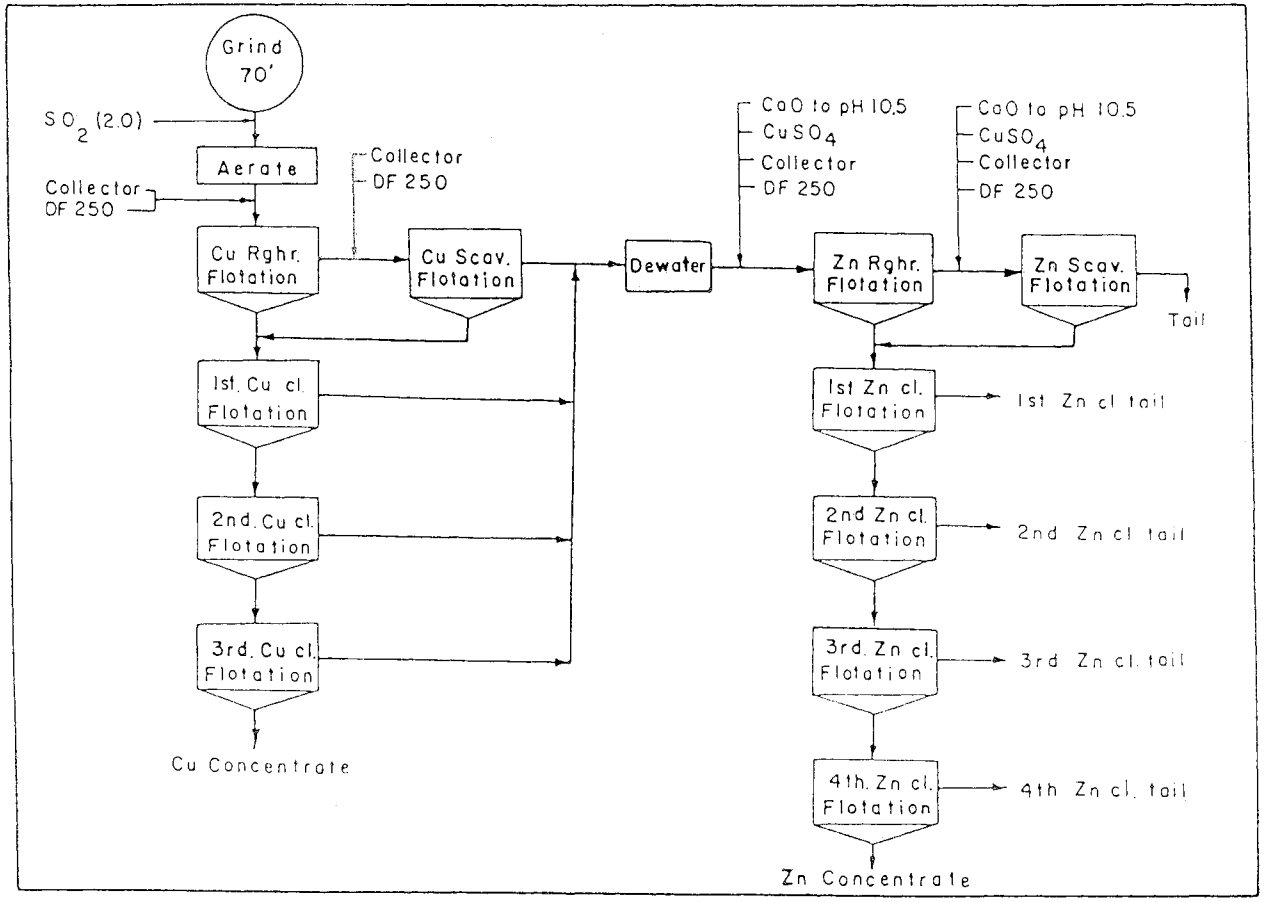


Figure 2.5 Laboratory Flowsheet for the Flotation Tests Conducted on Texasgulf Type 'A' Ore

of collector solution was added and conditioned for 10 minutes. After recovering the rougher flotation product, additional collector solution was added to the pulp for scavenger flotation, conditioned for 10 minutes and floated again. Both the rougher and scavenger flotation products were combined and cleaned three times. The tailings from the cleaner flotation stages were combined in a bucket and allowed to settle until enough clear water could be removed to leave approximately 3 l of slurry in the bucket. This procedure was necessary to ensure that all material excluding the copper concentrate could be transferred to a 4 l flotation cell for sphalerite flotation. The pH of the pulp was adjusted to 10.5 with lime prior to adding $CuSO_4$ to activate the sphalerite and conditioned for 5 minutes. Collector was then added to the pulp and another 10 minutes of conditioning time followed. Frother was added prior to flotation and conditioned for 2 minutes. Rougher, scavenger and 4 cleaner flotation stages were conducted, each for 4 minutes. In some of the tests conducted with this ore, the zinc flotation step was omitted.

c. Kinetics of Batch Flotation: Flotation kinetics were investigated with Texasgulf ore in the following manner: a 500 g sample was prepared as previously described, using a constant dosage of collector. Separate froth products were

removed continuously after ½, 1, 1½, 2, 3, 4, and 5 minutes of flotation. Each product was filtered, dried and assayed in the same manner as previously described.

d. St. Joe Lead Ore : Each sample was ground for 30 minutes. The comminuted slurry was transferred to a flotation cell and the pH was adjusted with CaO or HCl to a desired value. In each test, the same amount of collector and conditioning time (10 minutes) were employed to study the effect of pH. The rougher concentrate was cleaned twice as shown in Figure 2.6.

Another series of flotation tests was conducted at a constant pH by varying dosages of collector. This procedure is shown in Figure 2.7.

2.3.2 Electrophoresis

The electrophoretic mobility of both chalcopyrite and quartz were measured. The size of the mineral particles used for these experiments was -3 microns which had been obtained by sedimentation. The settling time was determined using Stokes' equation. A stock suspension of each mineral was obtained in this manner and stored in a flask.

Twenty-five ml portions of the stock suspension were

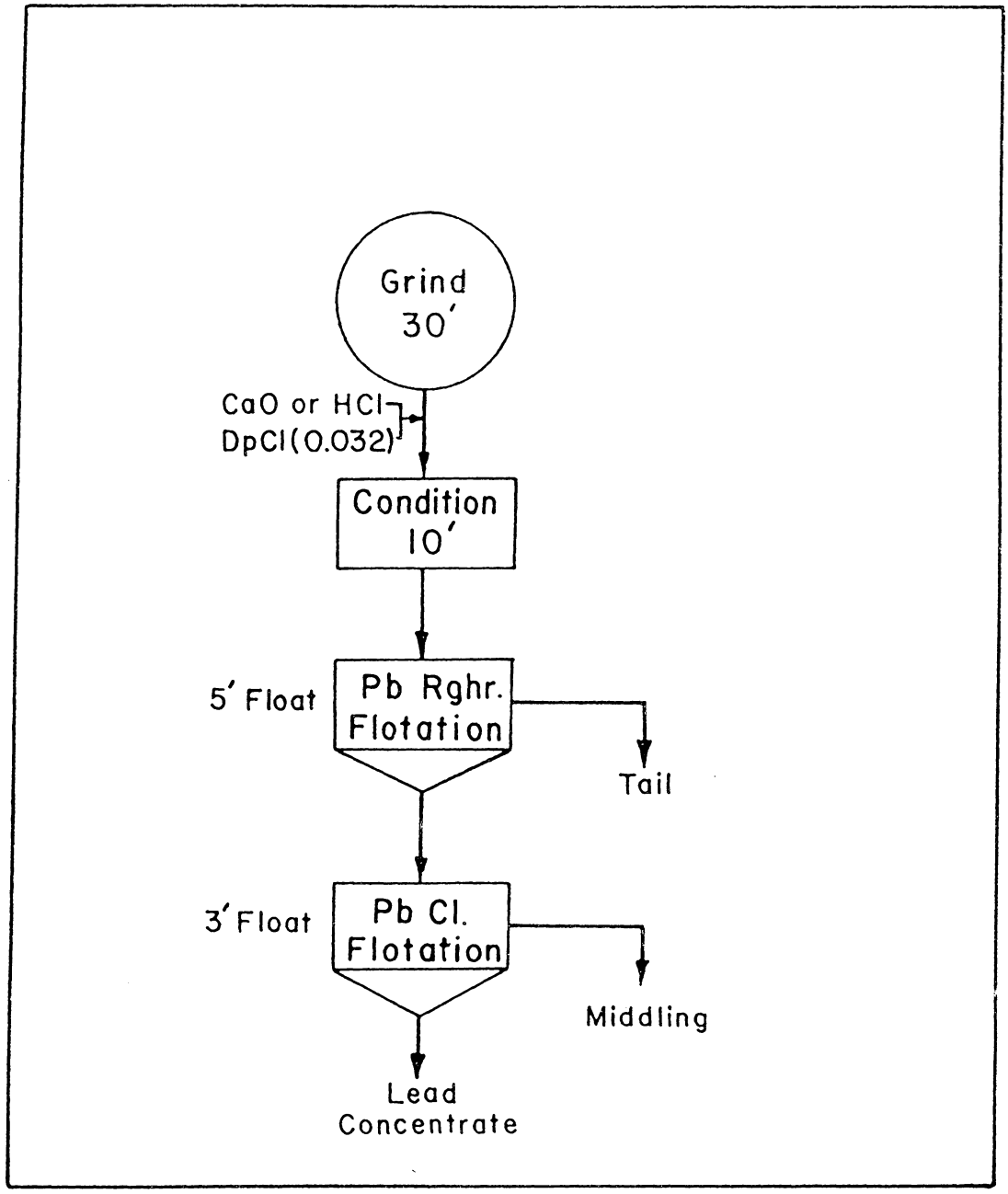


Figure 2.6 Laboratory Flowsheet for the Flotation of St. Joe Lead Ore as a Function of pH

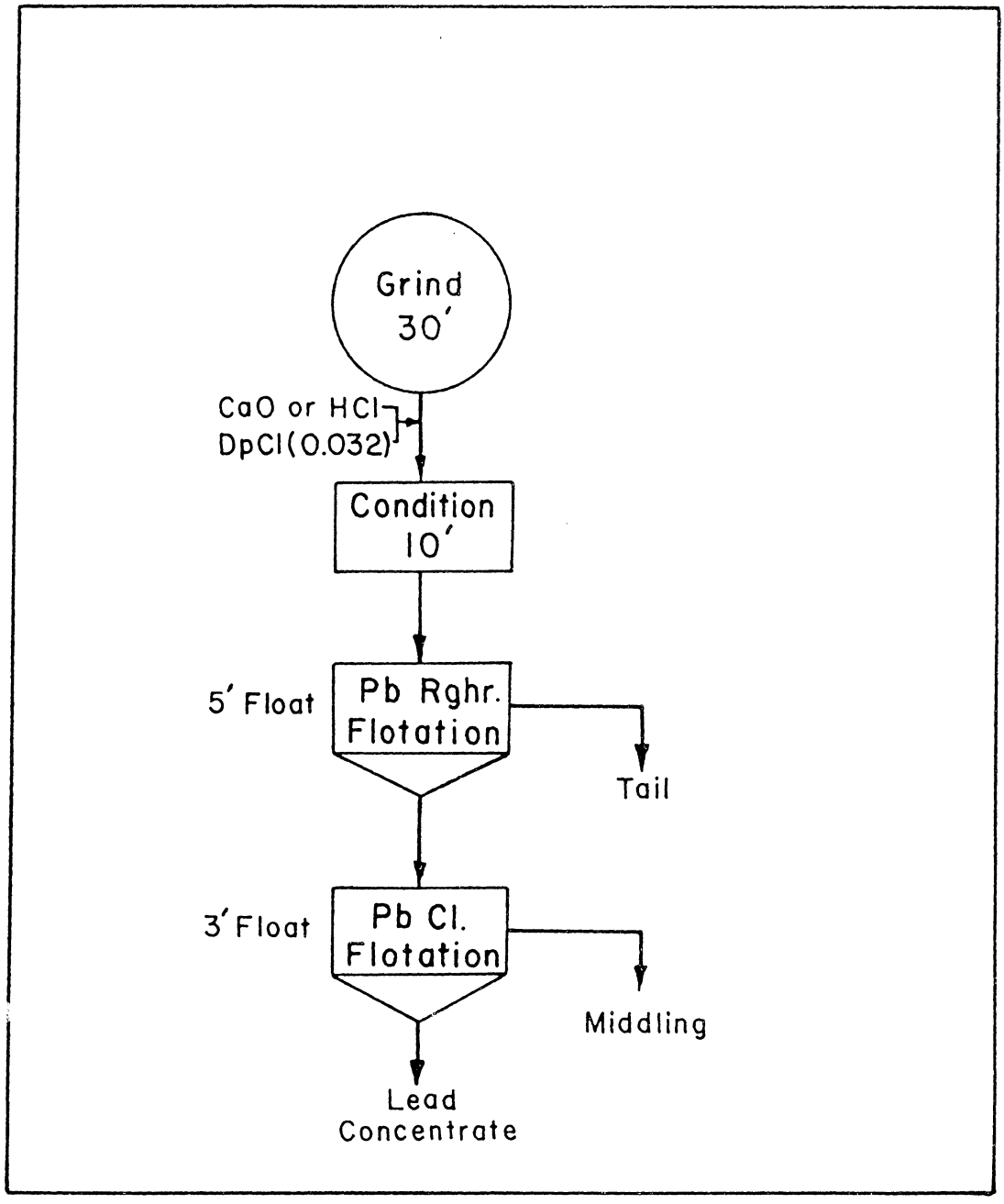


Figure 2.7 Laboratory Flowsheet for the Flotation of St. Joe Lead Ore as a Function of Collector Addition

transferred to beakers and the pH was adjusted between 2 and 11 by adding NaOH or HCl solution. The suspensions were conditioned for 30 minutes by agitation with a magnetic stirrer prior to electrophoretic mobility measurements. The pH was checked at the end of this conditioning time.

A portion of the suspension was then transferred to the flat cell and immersed in the thermostatic bath at 25 + 1°C. The platinum electrodes were placed in the cell and twelve measurements were taken at each stationary level, six in each direction, and then averaged.

When the mobility was measured in the presence of collector, the pH's of both the mineral suspension and the collector solution were adjusted to 7.0 + 0.1 prior to mixing the two.

2.3.3 Micro-Flotation

Micro-flotation tests were conducted on a -65+100 mesh chalcopyrite sample. When the sample was freshly prepared, it was completely floatable without a collector. Therefore, it was necessary to oxidize the sample to reduce its natural hydrophobicity. This was accomplished by oxidizing the sample in double-distilled water and aerating the suspension in a Buchner funnel with a glass frit. A total of 96 hours of aeration was necessary before the natural hydrophobicity

was completely supressed, as indicated by a blank flotation test.

In each test, approximately one gram of chalcopyrite was placed in the flotation cell. The remaining volume was filled with a collector solution and conditioned for 15 minutes with a magnetic stirrer. After conditioning, air was introduced into the bottom of the cell by means of a diaphragm pump to start the flotation. To remove floated mineral particles at each time interval, a gentle stream of double-distilled water was fed into the top of the cell. As the material overflowed the cell lip, it was retained on filter paper that was inserted into a beaker. Continuous samples were collected after 20, 40, 60, 90, 120, 180 and 240 seconds. Samples were then dried and weighed to determine the flotation recovery.

The same procedure was employed for the flotation of a pure quartz sample (-65+100).

Micro-flotation tests were also conducted on mixtures of pure chalcopyrite and quartz samples; one gram of each of the minerals was used. After the floated products were filtered and dried, the grade of each product was determined by separating the quartz and chalcopyrite using a Franz Isodynamic separator.

2.3.4 Adsorption Studies

Adsorption isotherms were established at pH 4.6, 7.0 and 11.0 using buffer solutions. The composition of each buffer solution was as follows:

pH 4.6: 0.5 M CH_3COOH + 0.5 M CH_3COONa

pH 7.0: 0.025 M KH_2PO_4 + 0.025 M Na_2HPO_4

pH 11.0: 0.025 M $NaHCO_3$ + 0.023 M NaOH.

The adsorption measurements were conducted using 100 ml Erlenmeyer flasks. In each flask, one gram of fine-ground pure mineral sample and 50 ml of collector solution, prepared in a buffer solution, were combined and agitated for 60 minutes with a mechanical shaker. A blank sample was also prepared in the same manner using 50 ml of buffer solution with no collector. After the agitation, each sample was centrifuged and the supernatant solution was analyzed for alkyl pyridinium ions using a UV-VIS spectrophometer. The absorbance was measured at 258 nm using fused silica cuvettes at a slit width of 0.5 nm. The reference solution for each sample was the same buffer solution that had been used for adsorption measurements. Care was taken to measure the absorbance of the blank test because the filtrate of the chalcopyrite suspension gave a considerable background absorbance, presumably due to the

copper complexes derived from chalcopyrite.

Calibration curves were constructed by measuring the absorbance of solutions of known CpCl concentrations at 258 nm. Beer's Law was obeyed to 2 x 10^{-4} moles/liter. The standard solutions used in constructing the calibration curves were also prepared in buffer solutions.

2.3.5 Electrochemical Studies

Twenty ml of 0.05 M sodium tetraborate purged with nitrogen was combined with 0.82 g of chalcopyrite in the electrochemical flotation cell. The voltammetric sweep was started at the rest potential in the cathodic direction to -0.7 V at a rate of 1 mV/sec. The return sweep was continued to a potential of 0.0 V. During the cyclic voltammetry, spectral changes were also recorded during both the cathodic and anodic sweeps.

The sample was returned to open-circuit and 1 ml of 4.5 x 10^{-5} moles/l CpCl was added to the top of the cell with a syringe. The absorbance of the solution was then measured at 258 nm. After adding more CpCl to bring the total addition to 8.8 x 10^{-5} moles/l, another cyclic voltammogram was constructed again beginning the sweep in the cathodic direction to a potential of -0.7 V. The anodic sweep was continued to the anodic limit of 0.47 V. Absorption

spectra were also collected during this cyclic voltammetry measurement.

III. EXPERIMENTAL RESULTS

3.1 Batch Flotation

3.1.1 Batch Flotation Tests for Falconbridge Ore

The results of flotation tests conducted with Falconbridge copper ore are presented in Figure 3.1; metallurgical balance sheets are presented in Appendix III. The flotation tests were conducted with no pH adjustment of the ore pulp, which is referred to as the 'natural pH'. The pH's of all the flotation tests conducted with this ore varied between 6.9 and 7.2, as measured prior to the addition of collector.

A notable feature of this ore was that chalcopyrite floated well without collector, as shown in Figure 3.1. Using only a frother, a high grade concentrate (32.8% Cu) was obtained with 89.7% recovery. In fact, when using 0.48 lb/ton NaIpX, a significantly lower grade concentrate was obtained with only a slight improvement in recovery.

Results obtained with 0.48 lb/ton CpCl were superior to those obtained using the same amount of NaIpX. At 0.56 lb/ton of CpCl, further improvements were made, the final concentrate assaying 29.8% Cu with 94.5% recovery.

Despite the natural hydrophobicity exhibited by the Falconbridge ore, the results suggest that CpCl may be a

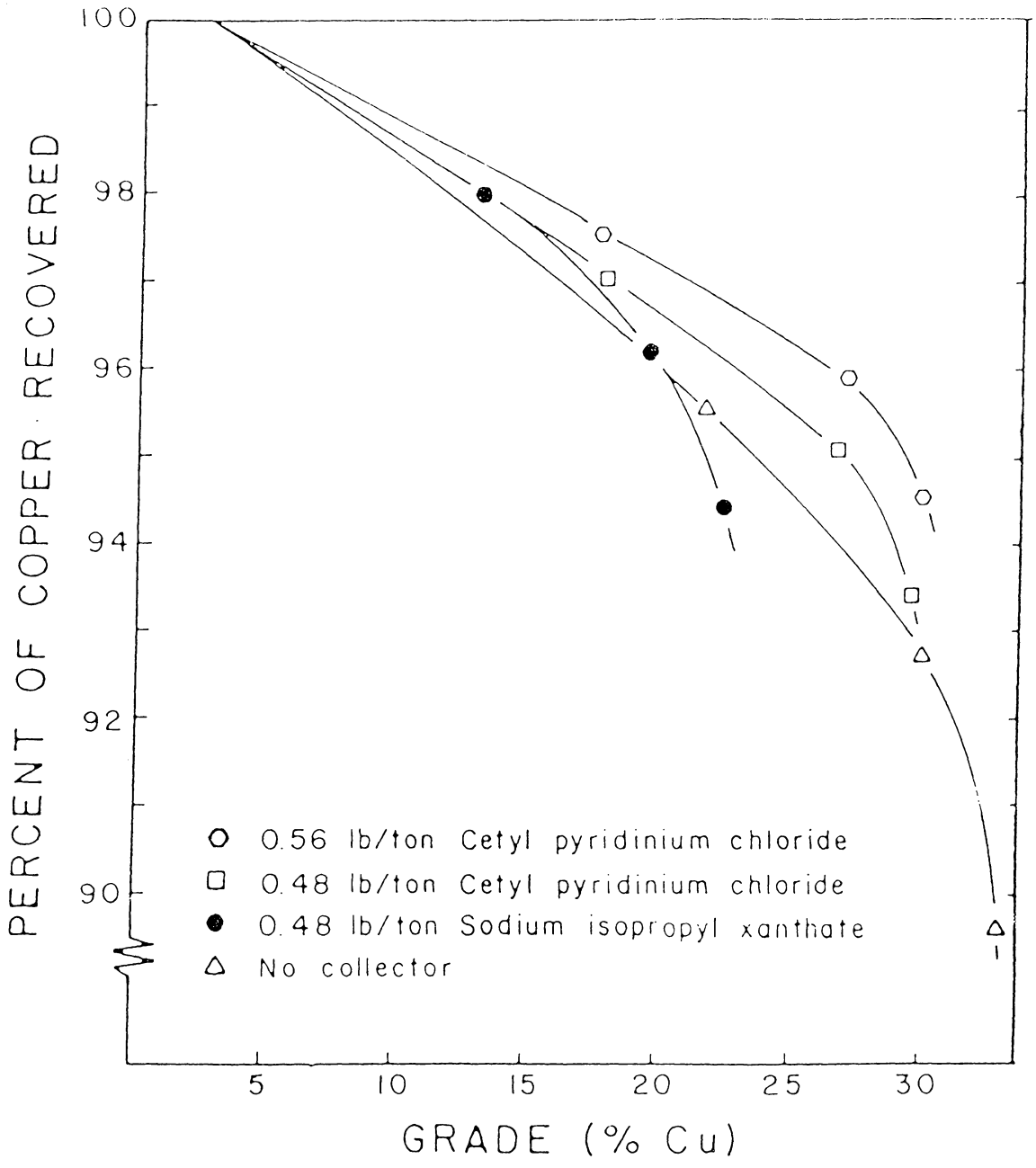


Figure 3.1 Results of Flotation Tests Conducted on Falconbridge Copper Ore Using Cetyl Pyridinium Chloride and Sodium Isopropyl Xanthate as Collectors

more powerful and also a more selective collector for chalcopyrite flotation.

3.1.2 Copper Flotation with Texasgulf Ore

a. Effect of pH: Flotation tests were conducted as a function of pH using 0.06 lb/ton of CpCl as collector. The pH was adjusted by using CaO and HCl as the pH regulators.

The results are given in Figure 3.2 in which both the recovery and the grade of the final copper concentrates are given as a function of pH. At pH 6.0, a copper concentrate assaying 22.5% Cu was obtained with 79.1% recovery. As the pH was increased, there was no immediate change in the grade of the final copper concentrate, but a decrease in grade was observed at pH's higher than about 8.0. The recovery increased with increasing pH and decreased at pH's higher than 9.5.

The natural pH of this ore pulp varied between 7.0 and 7.4, which corresponded approximately to the pH region at which the highest grade concentrate was obtained while maintaining reasonably high recoveries. For this reason, it was decided that flotation tests investigating the effect of collector additions would be carried out at the natural pH of the pulp.

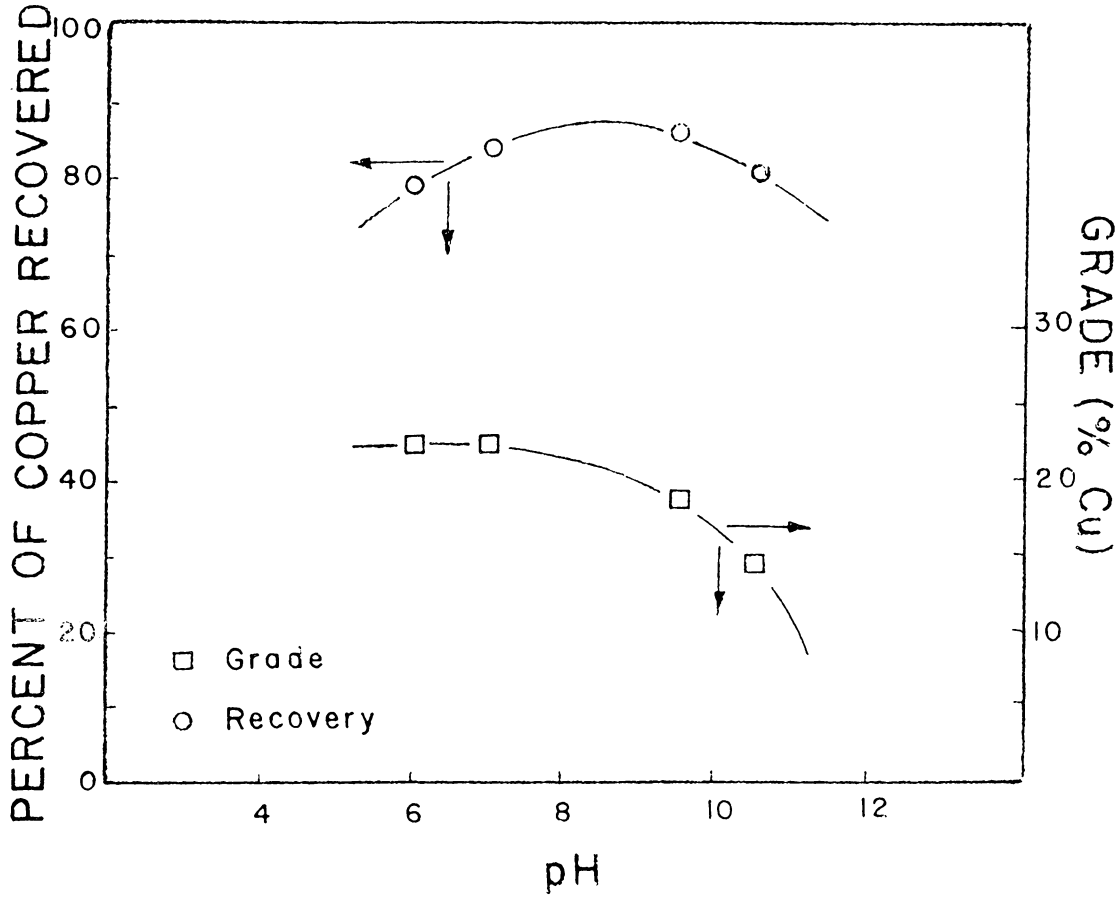


Figure 3.2 Results of Copper Flotation Tests Conducted on Texasgulf Type 'A' Ore Plotted as a Function of pH Using 0.06 lb/ton of Cetyl Pyridinium Chloride

b. Effect of Collector Dosage: Figure 3.3 gives the results of the batch flotation tests conducted by using varying amounts of CpCl and NaIpX as collectors. At a low collector dosage of 0.02 lb/ton, CpCl gave a much higher grade concentrate than NaIpX (32.6% Cu vs. 22.4% Cu) after the same number of cleaning stages, but NaIpX gave a higher recovery (71.9% vs. 63.1%). As the collector dosage was increased, the concentrate grades obtained using CpCl decreased but remained higher than those obtained using NaIpX. Recoveries increased with both collectors as the dosage was increased, and at 0.10 lb/ton, CpCl gave a considerably higher recovery than NaIpX (89.6% vs. 85.8%).

These results again suggest that CpCl is a more selective and more powerful collector than NaIpX for chalcopyrite flotation, even though NaIpX is regarded as one of the most selective collectors for sulfide flotation.

A less selective but more powerful xanthate is potassium amyl xanthate (KAX). Therefore, a series of batch flotation tests were conducted using CpCl and KAX for comparison, and the results are presented in Figure 3.4. Again, these tests were made at the natural pH of the pulp. At a collector dosage of 0.02 lb/ton, CpCl gave a substantially higher grade concentrate than KAX (32.6% Cu vs. 12.5% Cu), but KAX gave a much higher recovery (91.8% vs. 63.1%). As the collector dosage was increased to 0.06

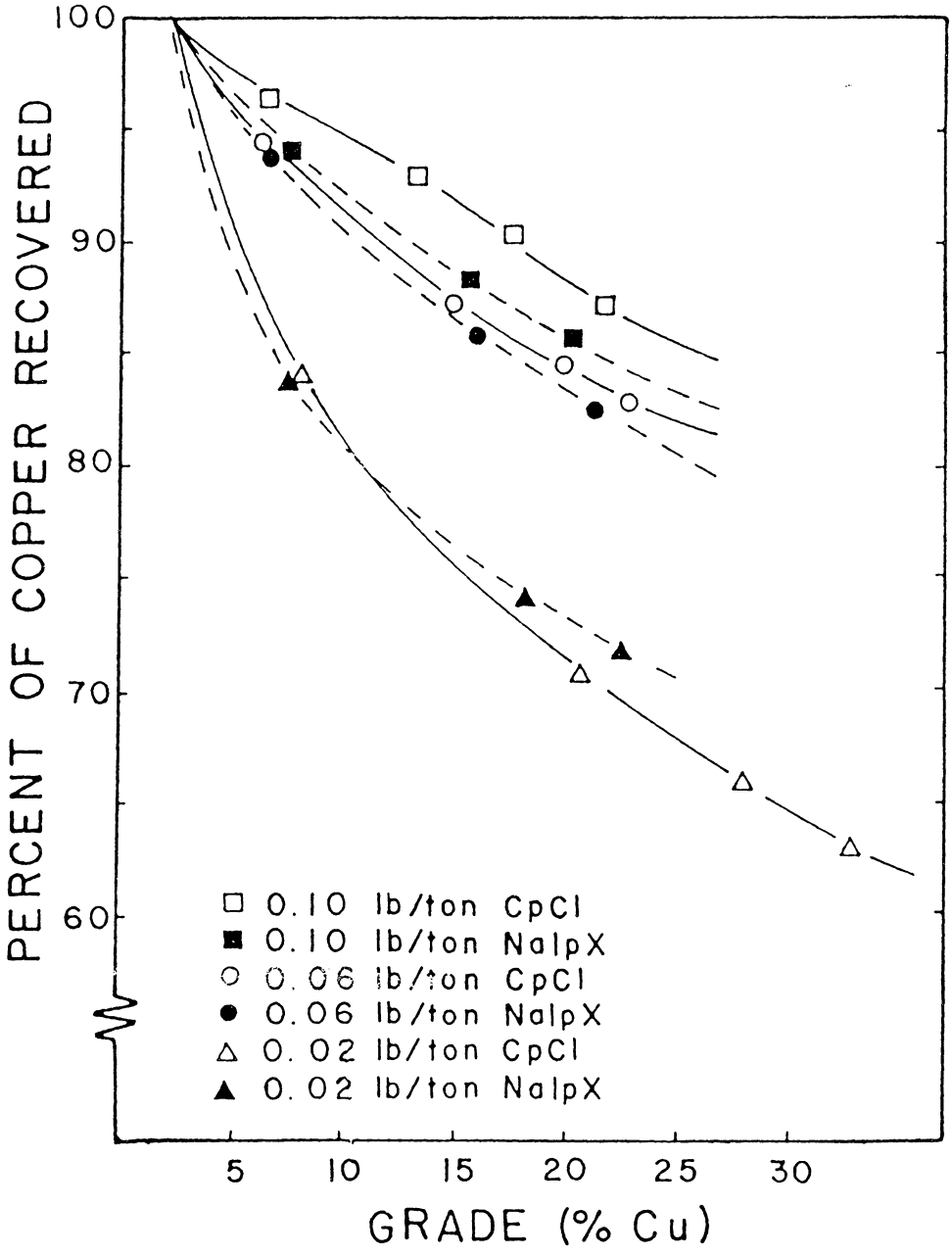


Figure 3.3 Results of Copper Flotation Tests Conducted on Texasgulf Type 'A' Ore Using Different Amounts of Cetyl Pyridinium Chloride and Sodium Iso-Propyl Xanthate

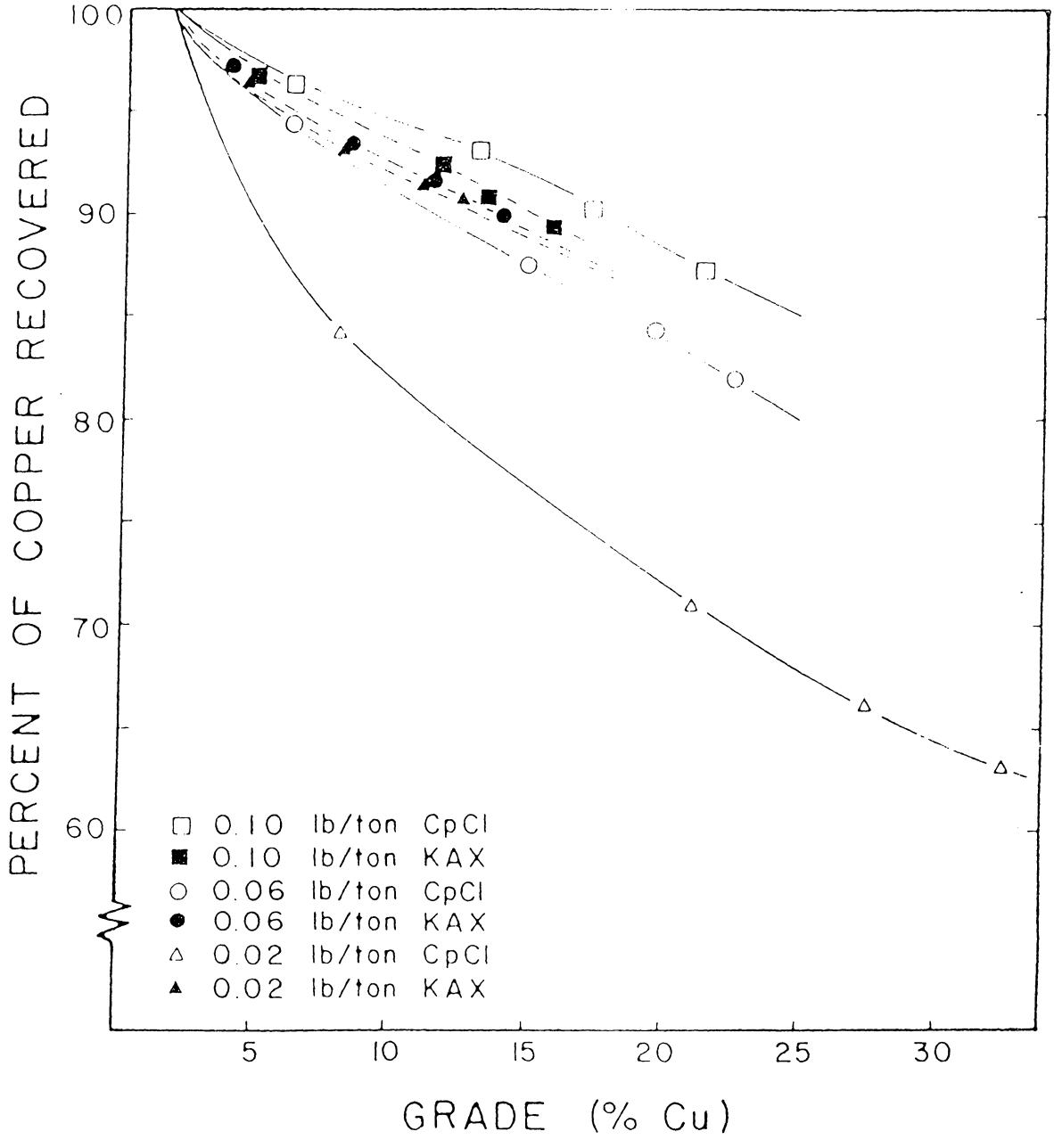


Figure 3.4 Results of Copper Flotation Tests Conducted on Texasgulf Type 'A' Ore Using Different Amounts of Cetyl Pyridinium Chloride and Potassium Amyl Xanthate

lb/ton, the grade of the concentrate obtained with CpCl was reduced to 22.5% Cu, but the recovery was increased to 88.2%. With the same dosage of KAX, no significant change in either grade or recovery was observed in comparison with that of the lower dosage. However, at 0.10 lb/ton, CpCl gave better results in both recovery and grade, as the curve lies above that for KAX. These tests demonstrated that CpCl is undoubtedly a more selective collector than KAX at all reagent dosages investigated and at the same time, is a more powerful collector at higher dosages.

c. Effect of Various Collectors: Figure 3.5 shows the results of the flotation tests conducted on Texasgulf Type A ore using various collectors. In each test, 0.06 lb/ton of collector was used with no pH adjustment. The highest grade concentrate in these tests was obtained with CpCl (22.5% Cu) with a recovery of 82.0%. NaIpX gave a concentrate assaying 21.1% Cu with the same recovery. KAX gave the highest recovery of all the collectors (90.0%), but after the same number of cleaning stages the concentrate assayed only 14.0% Cu. At higher collector dosages, CpCl is expected to give the best flotation results all around. Two other cationic collectors were also tested; n-dodecyl mercaptan (nDM) and dodecyl amine hydrochloride (DAHCl). As shown in Figure 3.5, CpCl gave better flotation results than either of these

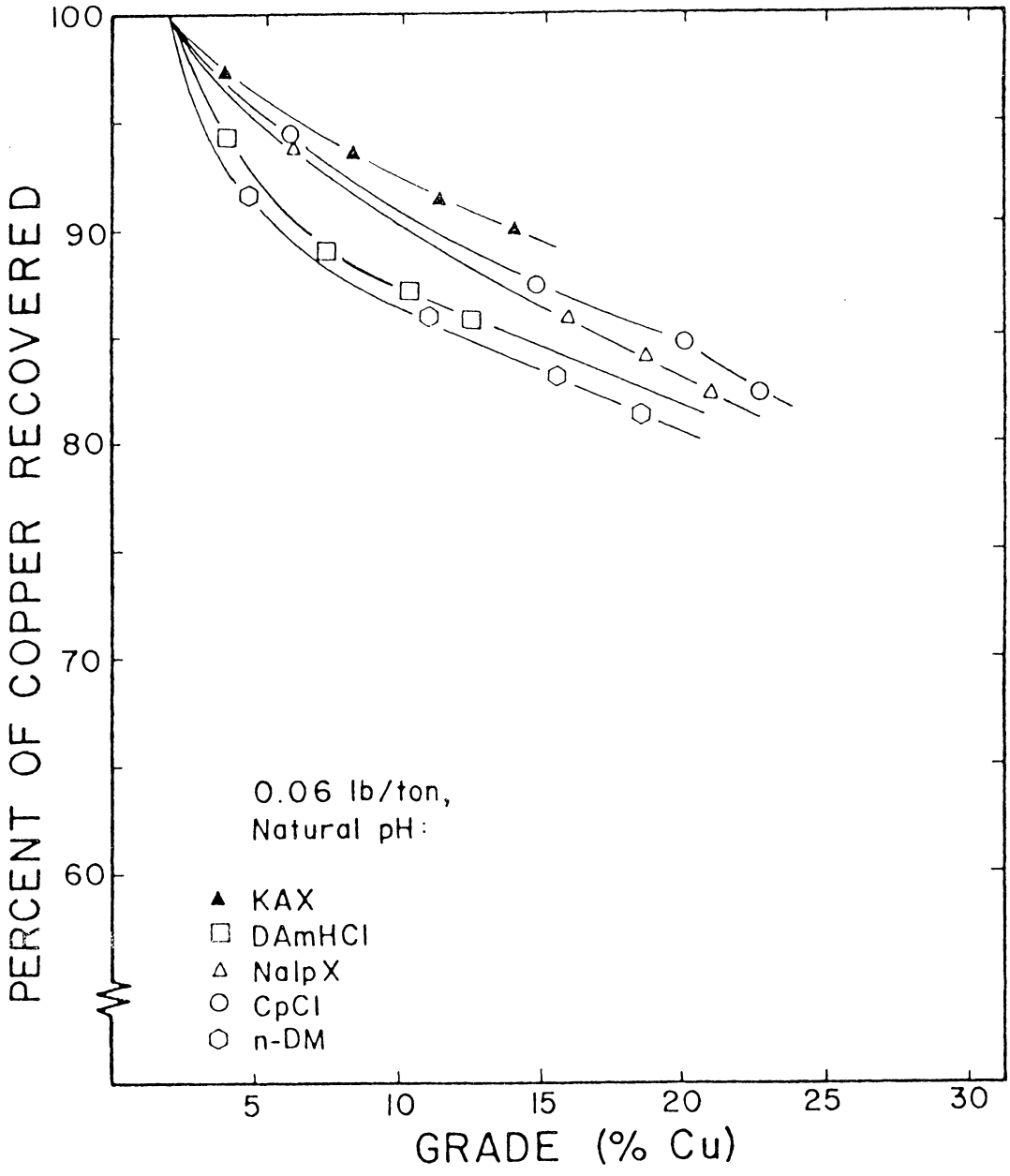


Figure 3.5 Results of Copper Flotation Tests Conducted on Texasgulf Type 'A' Ore Using 0.06 lb/ton of Various Collectors

collectors.

These tests again suggest that CpCl is a more selective collector for chalcopyrite flotation than either NaIpX or KAX. At higher collector dosages, CpCl is also a more powerful collector than either of the xanthates tested, as shown in Figures 3.3 and 3.4.

d. Effect of Hydrocarbon Chain Length: Flotation tests were conducted using alkyl pyridinium salts of various hydrocarbon chain lengths. All the tests were conducted with no pH adjustments, using 0.06 lb/ton of collector. The results, shown in Figure 3.6, demonstrate that the flotation results were significantly affected by the hydrocarbon chain lengths of the collectors. With ethyl pyridinium bromide (EpBr), a final concentrate assaying 17.6% Cu was obtained with a recovery of only 67.5%. With DpCl, the grade of the concentrate was increased to 21.0% Cu with a recovery of 73.7%. The best results were obtained with CpCl, the final concentrate assaying 22.5% Cu with a recovery of 82.0%.

It is rather surprising that an increase in the hydrocarbon chain length resulted in improvements in both recovery and grade. Typically, a longer hydrocarbon chain collector gives a higher recovery but a lower grade.

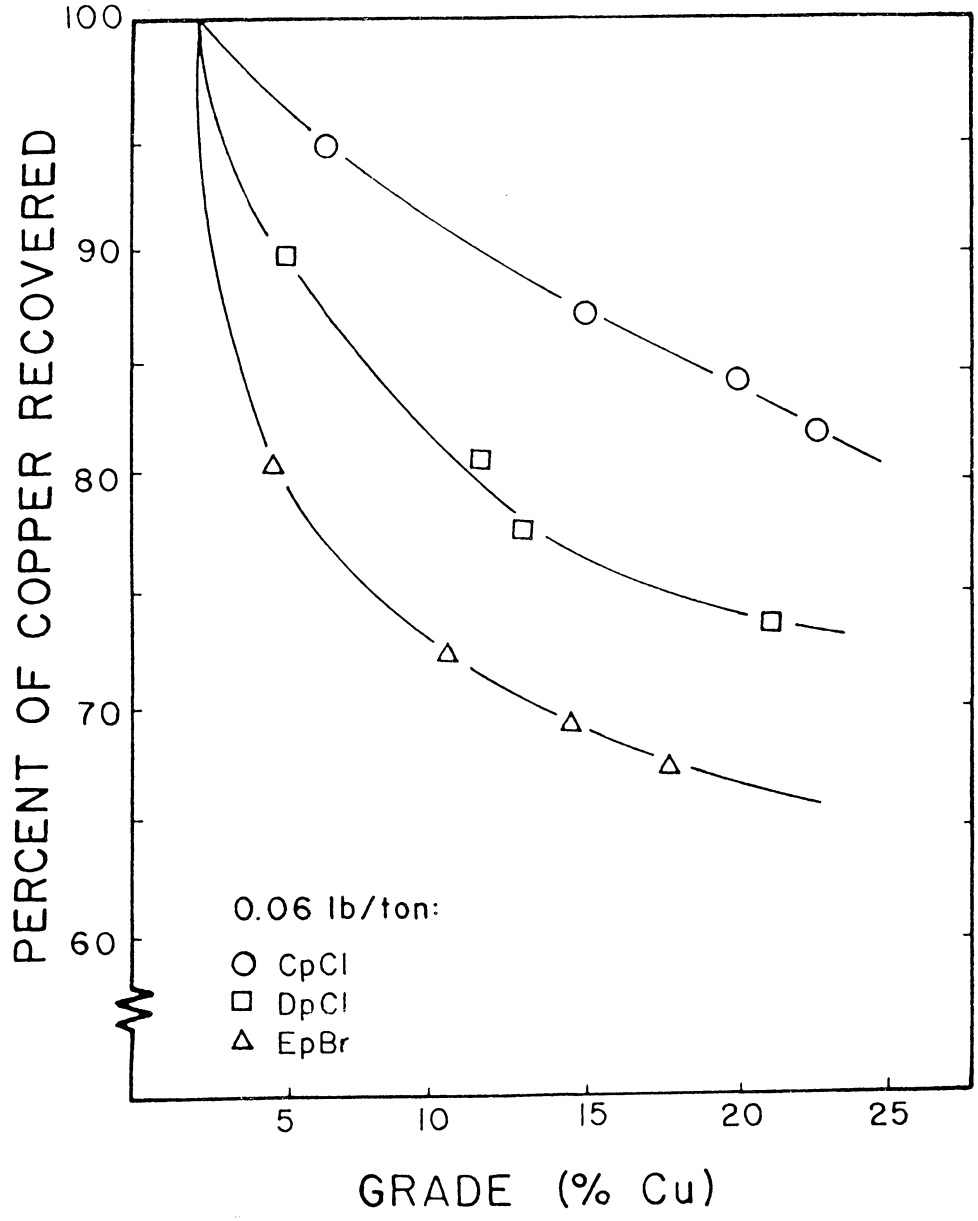


Figure 3.6 Results of Copper Flotation Tests Conducted on Texasgulf Type 'A' Ore Using 0.06 lb/ton of Alkyl Pyridinium Salts of Various Hydrocarbon Chain Lengths

3.1.3 Zinc Flotation with Texasgulf Ore

Sphalerite flotation tests were conducted on the chalcopyrite flotation tailings. Table I shows the results obtained using 0.06 lb/ton CpCl for chalcopyrite flotation and 0.16 lb/ton CpCl for sphalerite flotation. Both the grade and recovery of the copper flotation were satisfactory, while the grade of the zinc concentrate was relatively poor (39.3% Zn). An encouraging aspect of this flotation test was that the copper concentrate assayed only 4.6% Zn, which amounted to a loss of only 4.7% of the zinc into the copper concentrate. In another test using NaIpX as the collector and otherwise identical experimental conditions, the zinc loss into the copper concentrate amounted to 12.4% with the copper concentrate assaying 8.7% Zn. This may be yet another indication that CpCl is a more selective collector than NaIpX.

In an effort to improve the sphalerite flotation, a series of flotation tests was conducted using varying amounts of $CuSO_4$ and CpCl additions fixed at 0.16 lb/ton. To insure a constant feed assay for zinc flotation, a standard chalcopyrite flotation procedure was adopted prior to sphalerite flotation. The results of these tests are given in Figure 3.7. In constructing the recovery vs. grade curves, the Zn recoveries were calculated without considering the zinc lost in the copper concentrate. It is

Table I. Results of Chalcopyrite and Sphalerite Flotation Test Conducted on Texasgulf Type 'A' Ore

Test Tim - 8

Products	Weight (%)	Assays (%) Cu	Zn	Distribution (%) Cu	Zn
Cu Conc	5.85	26.86	4.55	80.0	4.7
Zn Conc	12.44	2.21	39.32	14.0	86.9
3rd Cl. Tls.	1.59	0.98	10.03	0.8	2.8
2nd Cl. Tls.	4.31	0.55	2.16	1.2	1.7
1st Cl. Tls.	19.79	0.22	0.79	1.2	0.6
Ro. Tls.	56.02	0.10	0.33	2.7	3.3
Feed	100.00	1.96	5.63	100.0	100.0

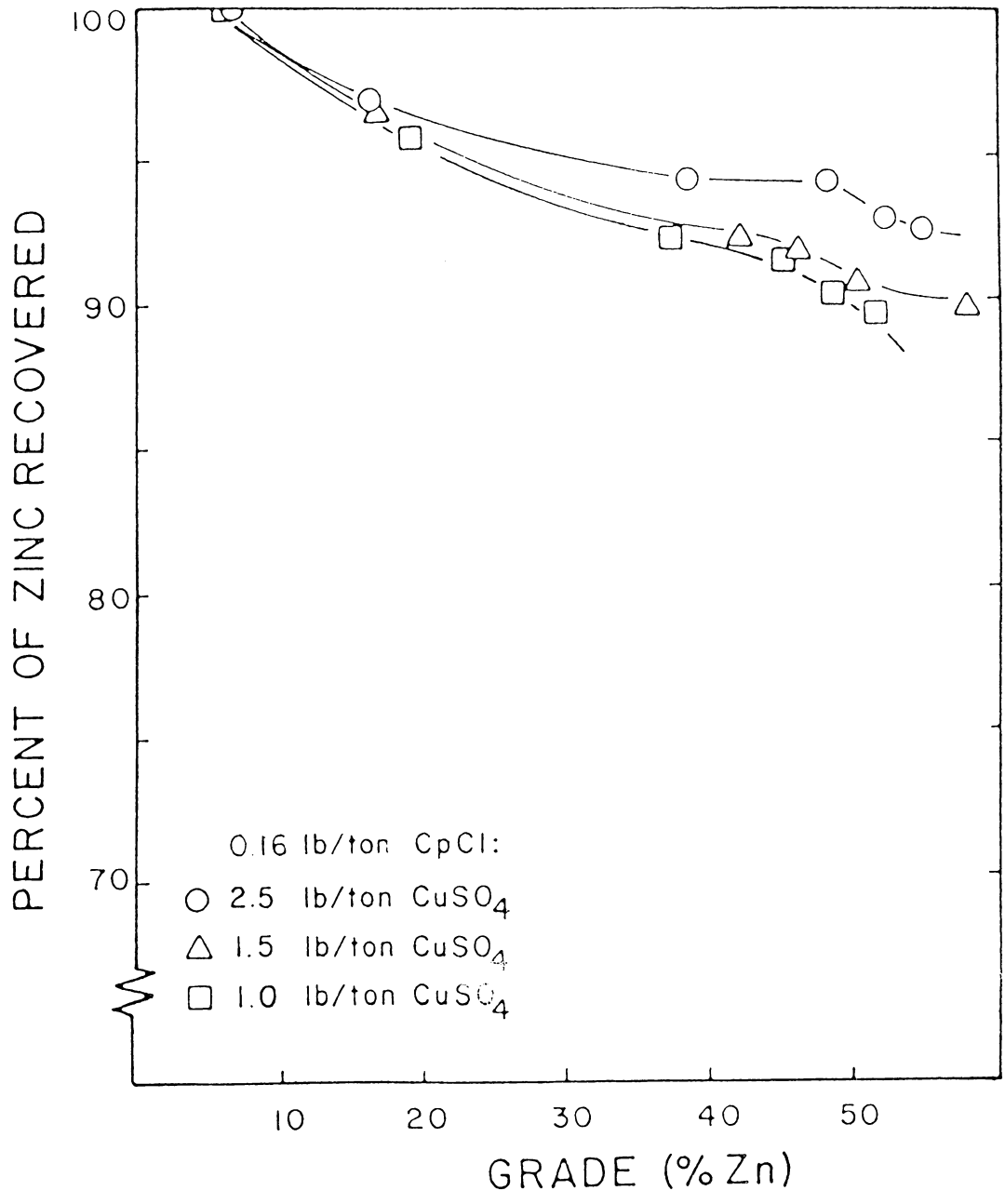


Figure 3.7 Results of Sphalerite Flotation Tests Conducted on Texasgulf Type 'A' Ore Using Varying Amounts of Copper Sulfate and 0.16 lb/ton of Cetyl Pyridinium Chloride

apparent from Figure 3.7 that both recovery and grade were improved as the $CuSO_4$ dosage was increased. The best results were obtained using 2.5 lb/ton $CuSO_4$, the zinc concentrate assaying 54.8% Zn with 85.3% recovery.

Another series of tests was conducted using 2.5 lb/ton $CuSO_4$ and varying amounts of collectors; both CpCl and NaIpX were used for comparison. The recovery vs. grade curves shown in Figure 3.8 show that at 0.08 lb/ton of collector addition, NaIpX gave slightly better flotation results. However, when the collector dosage was increased to 0.16 lb/ton, CpCl gave significantly better results than NaIpX. The final concentrate assayed 54.8% Zn with a recovery of 85.3%.

3.1.4 St. Joe Mineral Corp. Lead Ore

A series of flotation tests on St. Joe lead ore was conducted using 0.032 lb/ton dodecyl pyridinium chloride (DpCl) at various pH's. The pH adjustments were made with either CaO or HCl. Figure 3.9 shows the results of the flotation tests. The best results in terms of both grade and recovery were obtained at approximately pH 9.0. Similar tests were conducted using CpCl and NaIpX, and no significant improvements in grade or recovery were obtained. The results of these tests were poor in comparison with

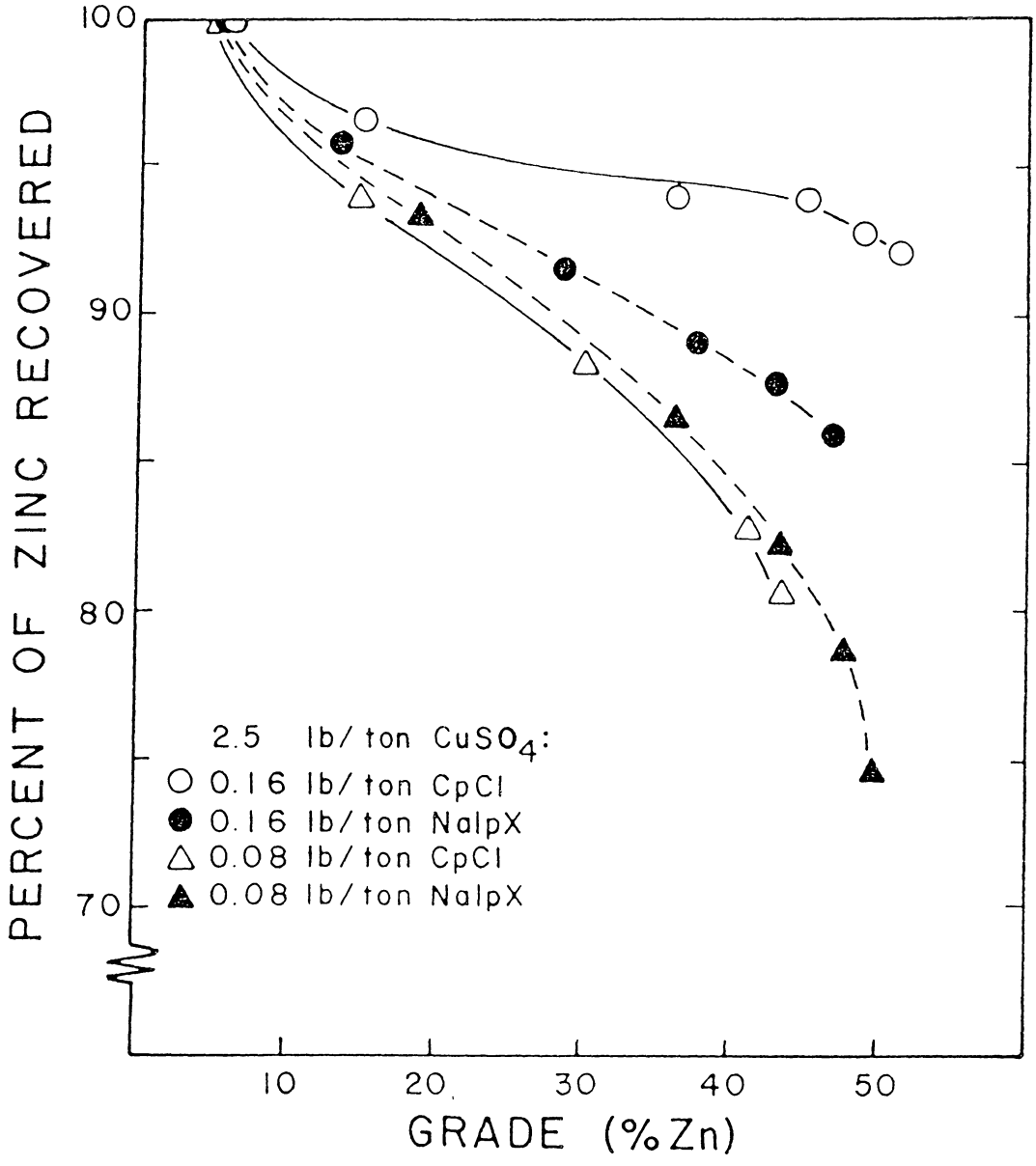


Figure 3.8 Results of Sphalerite Flotation Tests Conducted on Texasgulf Type 'A' Ore Using Varying Amounts of Cetyl Pyridinium Chloride and Sodium Iso-Propyl Xanthate and 2.5 lb/ton of Copper Sulfate

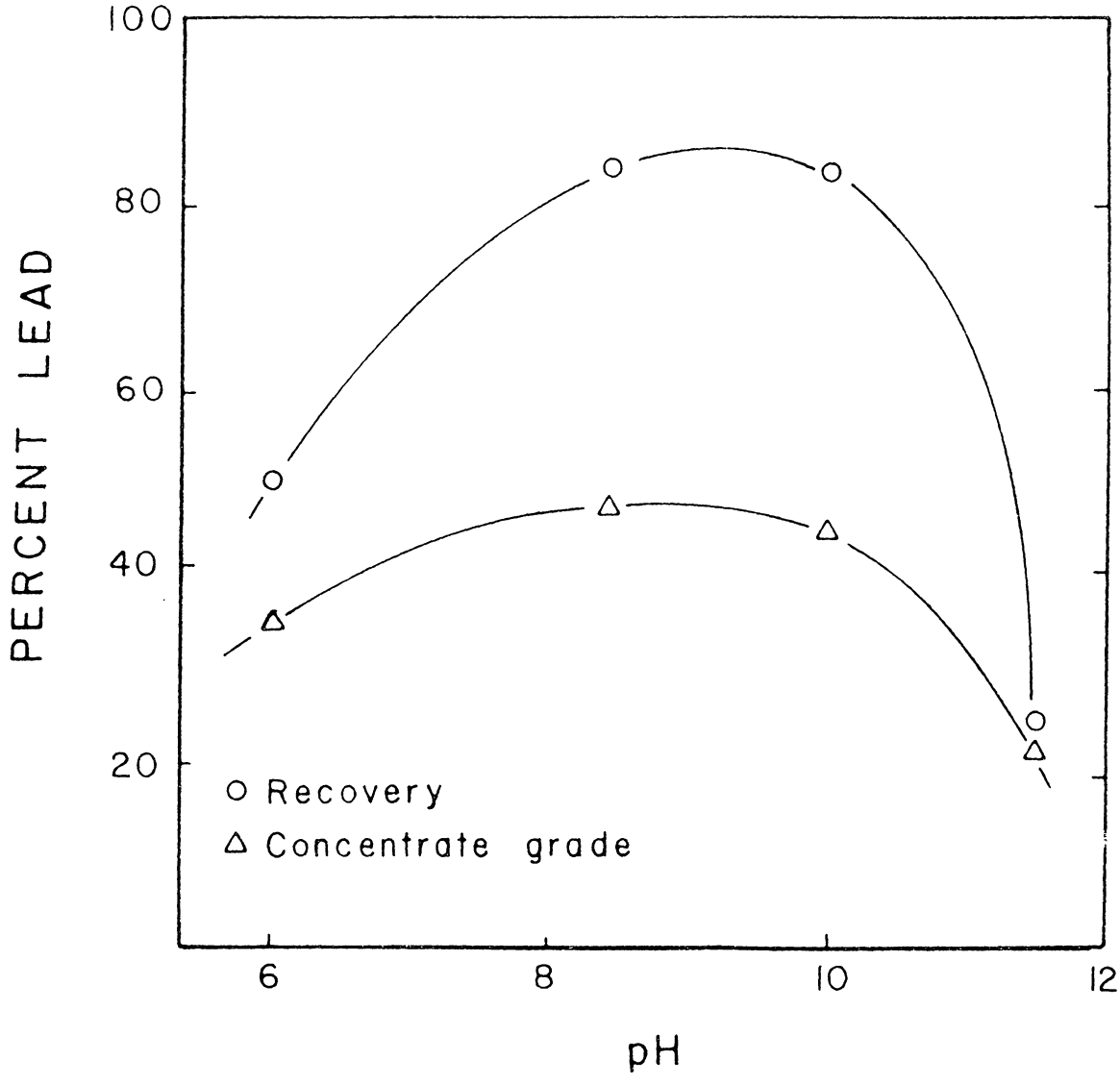


Figure 3.9 Results of Galena Flotation Tests Conducted on St. Joe Lead Ore as a Function of pH

those obtained in chalcopyrite and sphalerite flotation, probably due to oxidation of the ore sample.

3.1.5 Batch Flotation Kinetics

Kinetics of flotation was studied on Texasgulf copper ore using 0.05 lb/ton of CpCl and NaIpX as collectors. Results are given in Figure 3.10, in which the copper recovery is plotted as a function of time. It shows that, at a given time, more chalcopyrite is floated with CpCl than with NaIpX. For example, 83.0% of the copper was recovered after 5 minutes of flotation with CpCl, whereas only 64.5% of the copper was recovered after the same flotation time with NaIpX.

Figure 3.11 shows the results of similar tests in which the flotation kinetics were studied using varying amounts of CpCl and NaIpX. At a low collector dosage of 0.0048 lb/ton, CpCl gave slightly faster flotation kinetics than NaIpX; after 5 minutes of flotation, more copper was recovered with CpCl than with NaIpX (59.8% vs. 51.6%). As the collector dosage was increased to 0.048 lb/ton, flotation kinetics with CpCl were substantially faster than when NaIpX was used; after 5 minutes of flotation, CpCl gave 82.2% copper recovery and NaIpX gave only 62.3% recovery. Further increasing the collector dosage to 4.8 lb/ton, which is

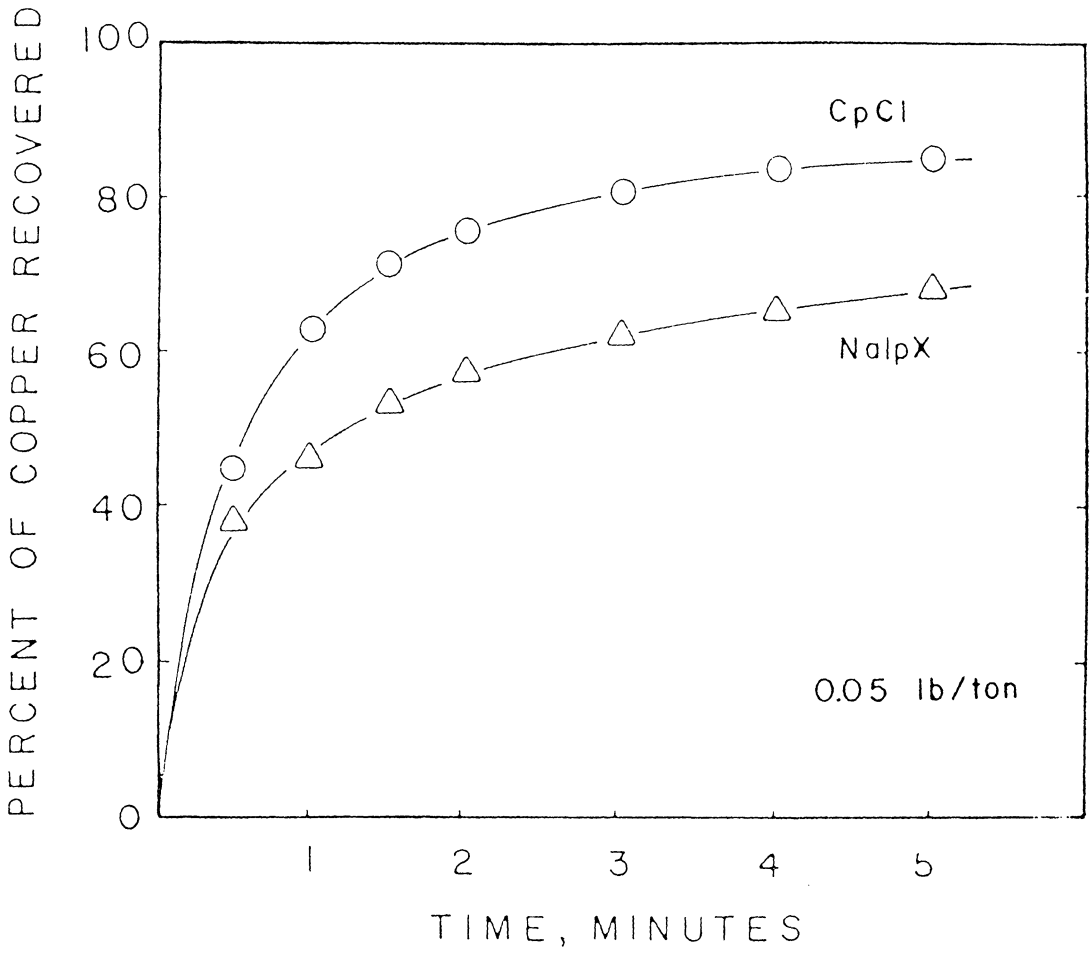


Figure 3.10 Comparison of the Flotation Rates in the Batch Flotation Tests Conducted on Texasgulf Type 'A' Ore Using 0.05 lb/ton of Cetyl Pyridinium Chloride and Potassium Amyl Xanthate

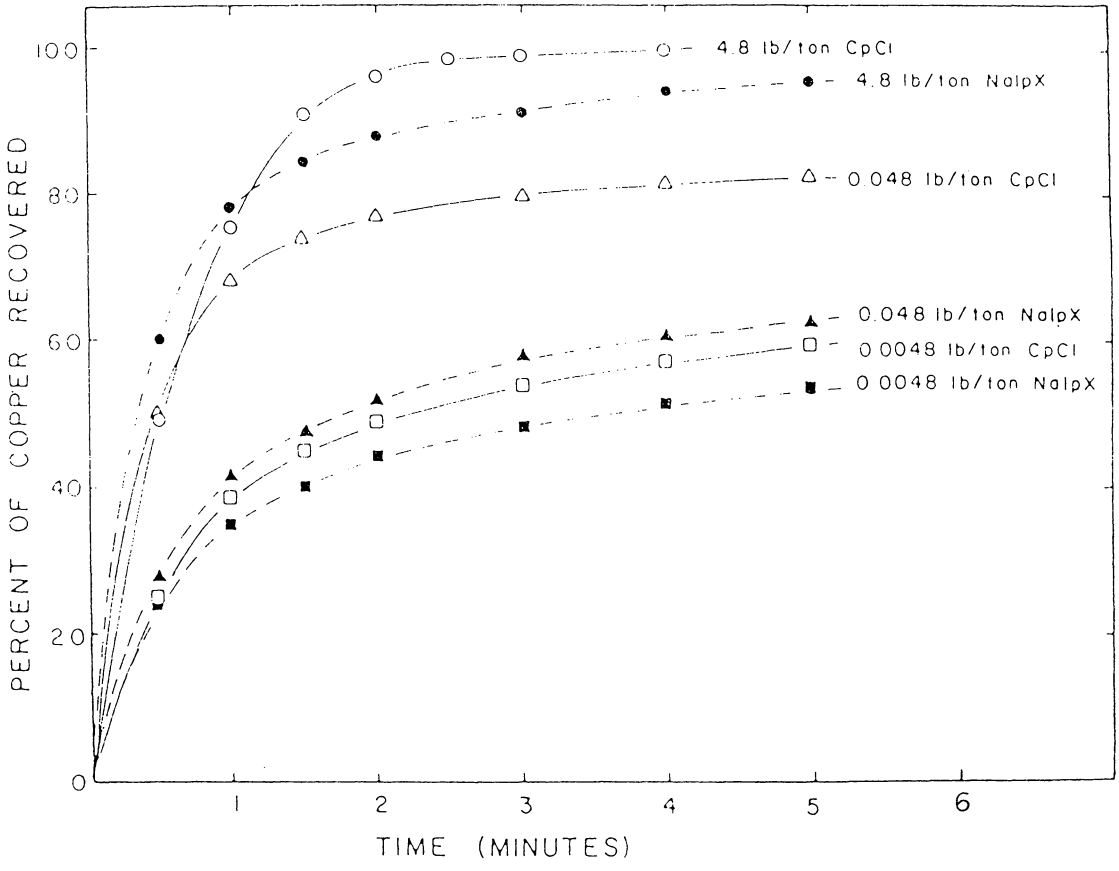


Figure 3.11 The Rates of Chalcopyrite Flotation in Batch Flotation Tests Conducted on Texasgulf Type 'A' Ore Using Cetyl Pyridinium Chloride and Sodium Isopropyl Xanthate as Collectors at Various Reagent Additions

undoubtedly an excessive amount for both collectors, the difference in kinetics is much reduced. Nevertheless, the results shown in Figure 3.11 demonstrate that CpCl offers significantly faster flotation kinetics than NaIpX.

To represent the grade of flotation products obtained in kinetics tests, Figures 3.12 and 3.13 were constructed. The cumulative grade of the flotation products was plotted against the collector dosage so that the grade after a given flotation time could be determined. When CpCl was used as a collector (Figure 3.12), the grade of the froth product was maximum at 0.048 lb/ton. With NaIpX, the maximum grades were obtained over a wider range of collector additions (Figure 3.13). At higher dosages, the use of CpCl resulted in low grade concentrates. As a result, cleaning stages were essential when relatively large amounts of CpCl were used. However, at collector dosages less than 0.048 lb/ton, CpCl gave a higher grade flotation product than NaIpX, as well as better recovery (Figure 3.11).

A more detailed evaluation of the flotation kinetics is included in the discussion section.

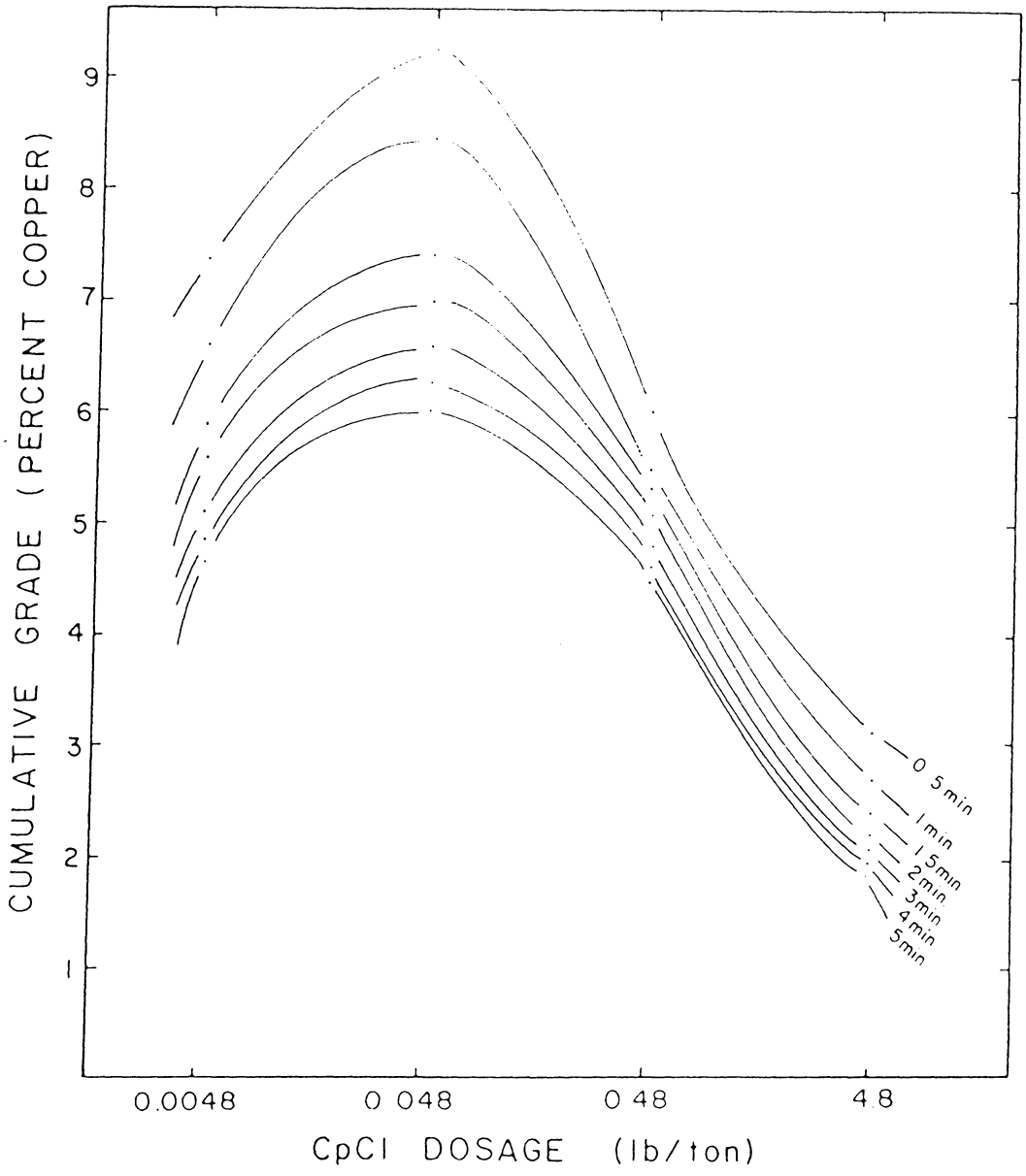


Figure 3.12 Changes in Grades of Flotation Concentrates as a Function of Cetyl Pyridinium Chloride Addition and Flotation Time

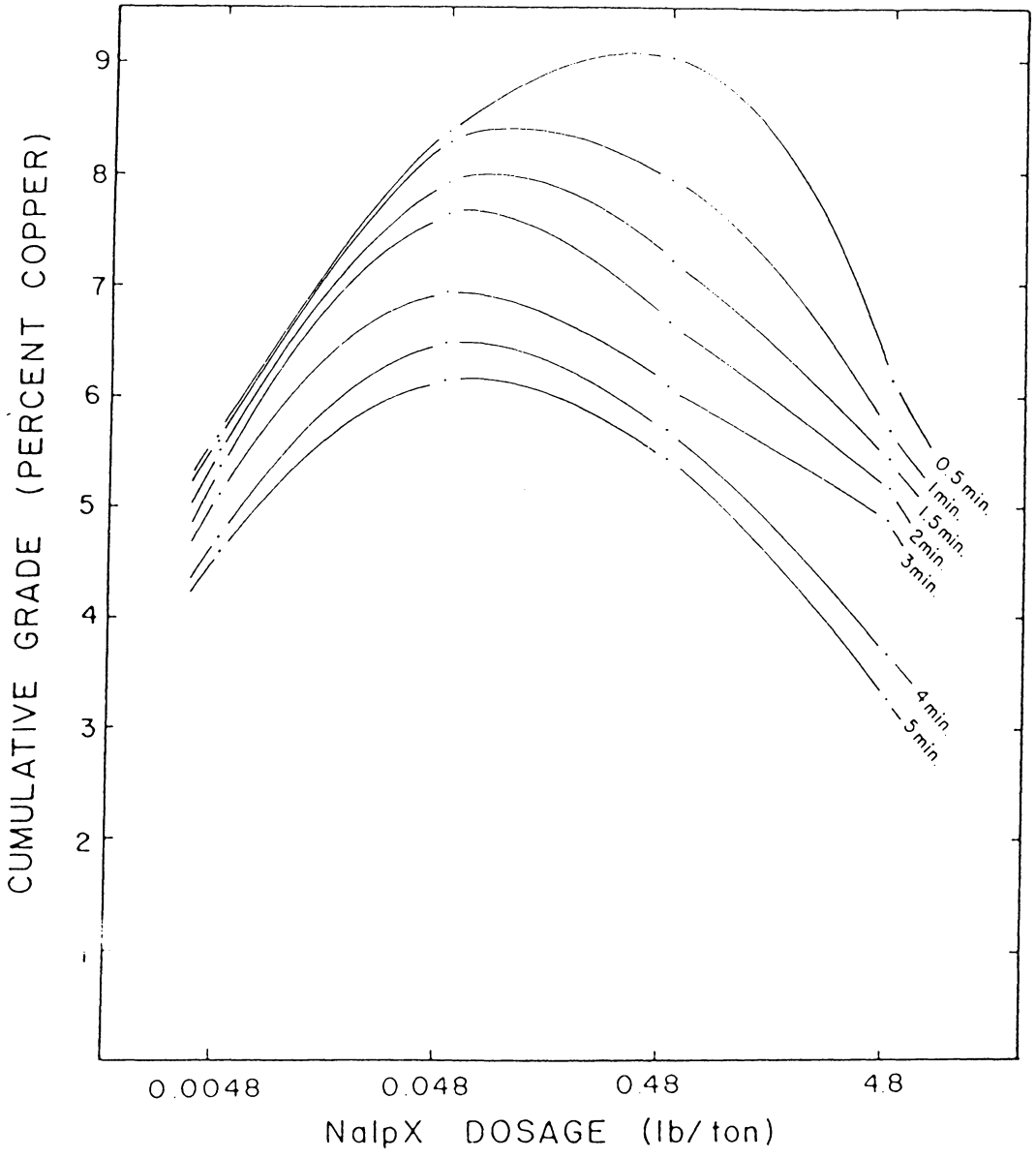


Figure 3.13 Changes in Grades of Flotation Concentrates as a Function of Sodium Isopropyl Xanthate Addition and Flotation Time

3.2 Electrophoresis

3.2.1 Effect of pH

Figure 3.14 shows the results of electrophoretic mobility measurements conducted on chalcopyrite and quartz in the absence of supporting electrolytes. From the mobilities measured, the ζ-potentials were calculated using the Smoluchowski equation (1914):

$$\mu = \frac{\zeta \varepsilon}{4\pi\eta} \qquad [3.1]$$

where μ is the electrophoretic mobility, ζ is the zeta potential, ε is the dielectric constant and η is the viscosity of the medium. The Smoluchowski equation has been shown to be valid for an arbitrary shape (Henry, 1931; Morrison, 1970) and is frequently assumed. Quartz was included in these measurements because it represents the major gangue mineral in the ore samples used for batch flotation tests. Both quartz and chalcopyrite exhibit a negative ζ-potential in the neutral pH region where the flotation tests were conducted. Chalcopyrite is slightly more negative than quartz between pH 4.5 and 7.3, while quartz becomes more negative than chalcopyrite above pH 7.3.

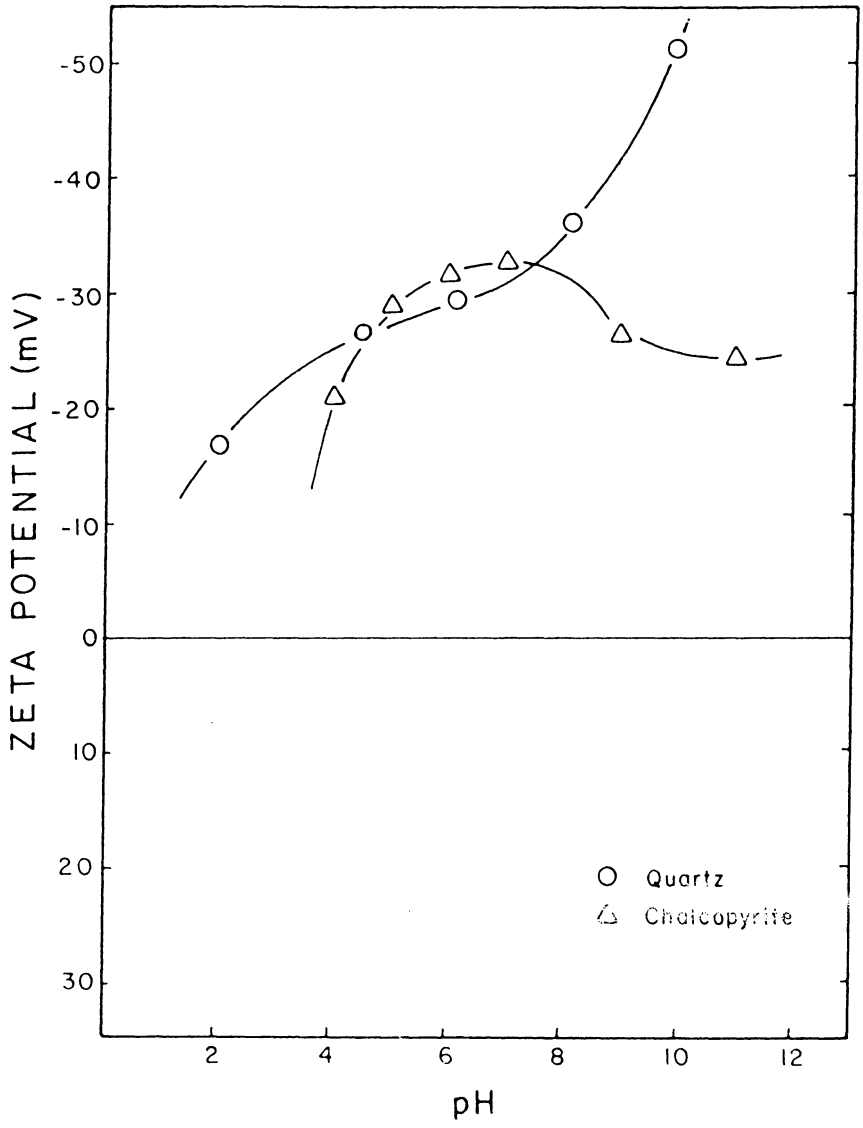


Figure 3.14 Zeta - Potential of Chalcopyrite and Quartz as a Function of pH

3.2.2 Effect of Concentration

Figure 3.15 shows the results of the electrophoretic mobility measurements conducted on chalcopyrite at pH 7.0 + 0.1 as a function of collector concentration. At low collector concentrations, the ζ-potential remains negative, but as the collector concentration is increased, the ζ--potential is modified depending on the collector type and concentration. In general, the ζ-potential becomes more positive in the presence of cationic collectors such as alkyl pyridinium salts and DAHCl, and tends to become negative in the presence of anionic surfactants such as NaIpX and KAX.

In the presence of longer chain cationic collectors, i.e., $c<12$, the ζ-potential is reversed from negative to positive at higher collector concentrations. This charge reversal occurs at lower concentrations with longer hydrocarbon chains. In the case of xanthates, the ζ--potential tends to become more negative at higher collector concentrations.

Note in Figure 3.15 that the ζ-potential of chalcopyrite is reversed at approximately 10^{-4} and 10^{-5} in the presence of DpCl and DAHCl ,respectively, indicating that DpCl has a higher affinity for the chalcopyrite surface

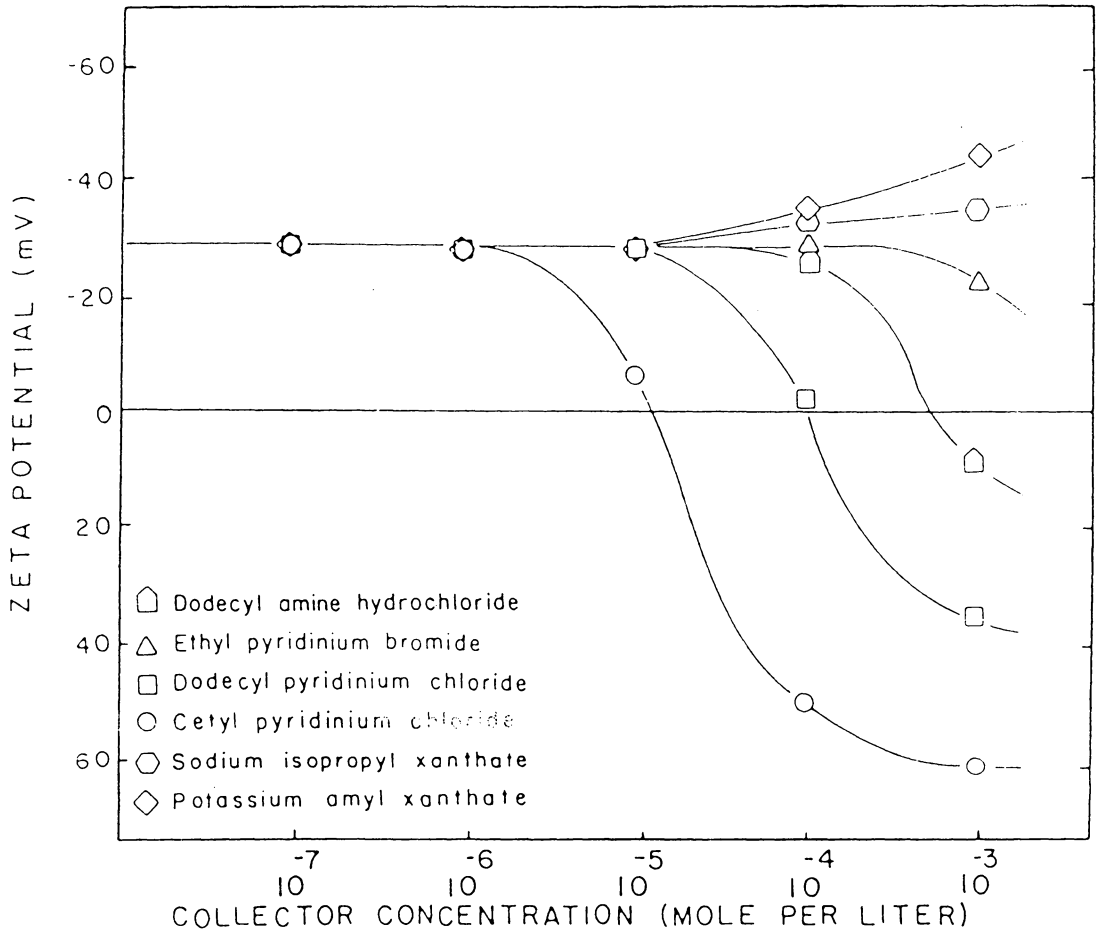


Figure 3.15 Zeta-Potential of Chalcopyrite at pH 7.0 as a Function of Alkyl Pyridinium Salts, Alkyl Xanthates, and Alkyl Amines of Varying Hydrocarbon Chain Lengths

than DAHCl. Since the two reagents have the same hydrocarbon chain length, it may be suggested that the polar group of the DpCl adsorbs on chalcopyrite more strongly than DAHCl. This may explain the flotation results shown in Figure 3.5, in which DpCl gave better results than DAHCl.

Figure 3.16 shows the results of electrophoretic mobility measurements conducted on quartz as a function of the cationic collector concentration at pH 7.0 + 0.1. As in the case with chalcopyrite (Figure 3.15), the ζ-potential remains negative at low collector concentrations, but the negative ζ-potential is steadily reduced with increasing collector concentrations. With further increases in collector concentration, the ζ-potential is reversed and becomes positive. Of the two alkyl pyridinium collectors tested, CpCl induces the charge reversal at a lower collector concentration than DpCl due to its longer hydrocarbon chain. DAHCl also reverses the ζ-potential of quartz, but at a much higher concentration (10^{-3}).

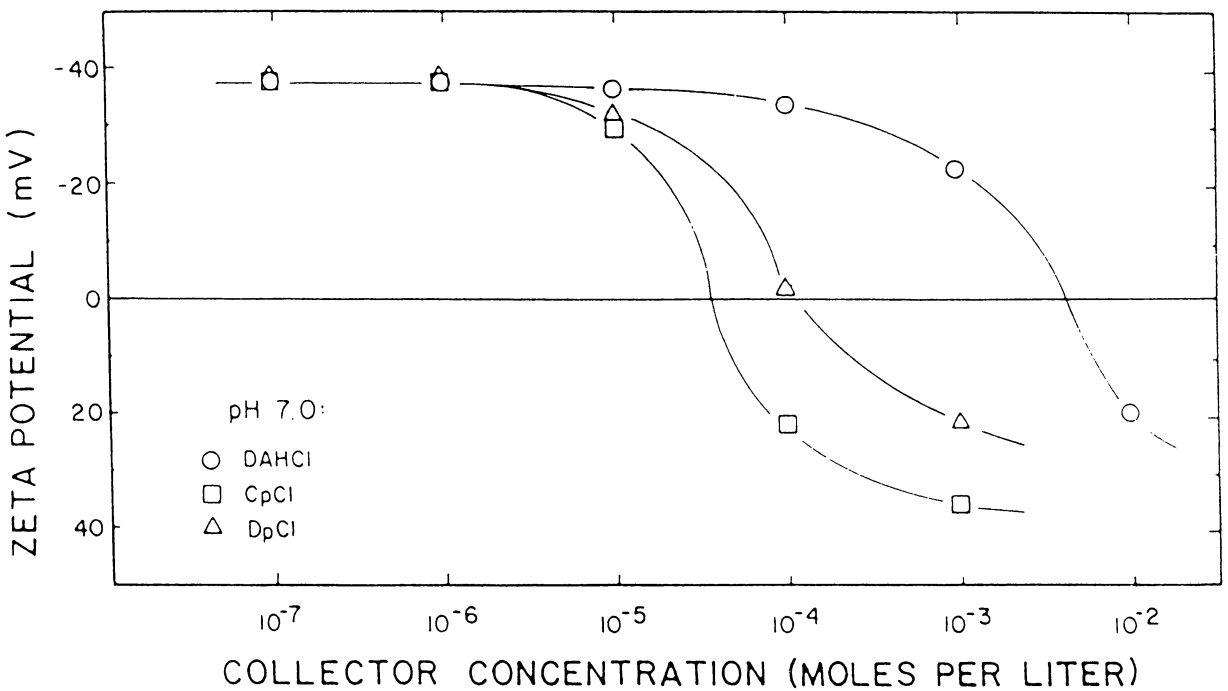


Figure 3.16 Zeta-Potential of Quartz at pH 7.0 as a Function of Alkyl Pyridinium Salts and Alkyl Amines

3.3 Micro Flotation

3.3.1 With Individual Minerals

Flotation kinetic studies were made on a pure chalcopyrite sample using a micro-flotation cell; the results are given in Figure 3.17. At a low collector concentration of 1×10^{-6} moles/liter, CpCl gave marginally better flotation kinetics than NaIpX. However, at 5×10^{-6} moles/liter, CpCl exhibited significantly better flotation kinetics than NaIpX; after five minutes of flotation, 90.5% of the chalcopyrite floated with CpCl, while only 66.4% was floated with NaIpX. At 1×10^{-5} moles/liter, the difference in kinetics became less dramatic.

The results given in Figure 3.17 show similar trends to those of the batch flotation tests (Figures 3.10 and 3.11). The advantages of using CpCl rather than NaIpX are marginal at low collector additions and become more pronounced at intermediate dosages.

A more detailed analysis of flotation kinetics for this pure mineral system is included in the discussion section.

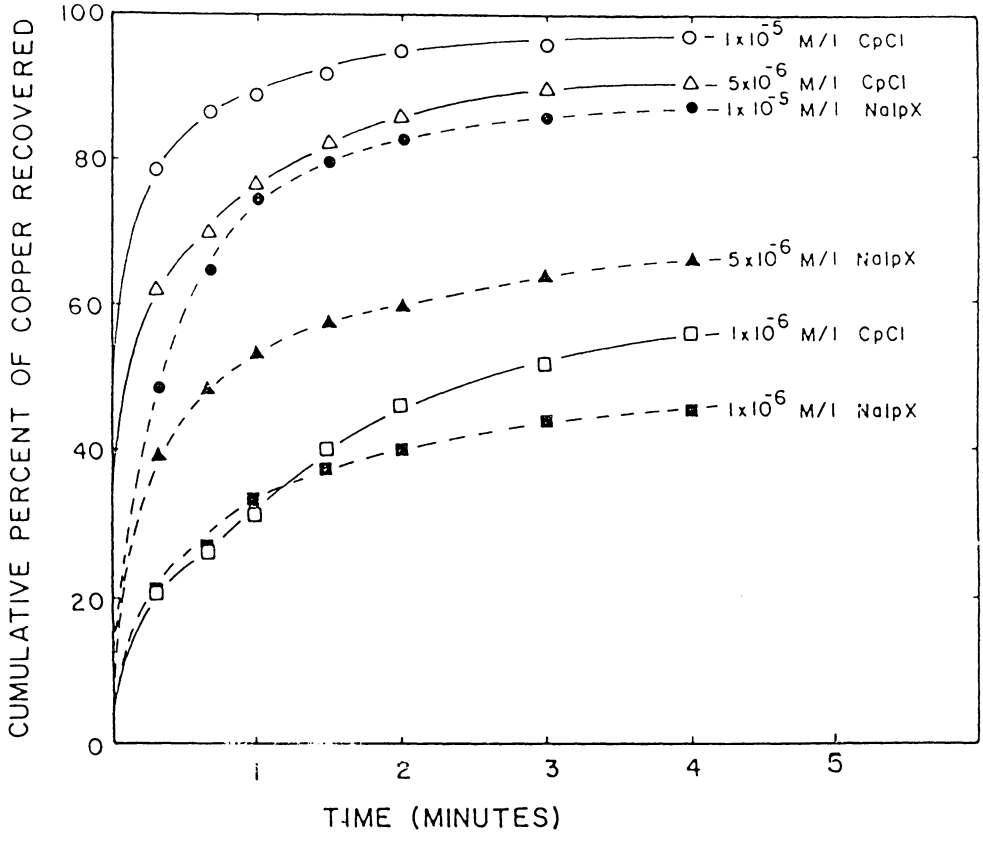


Figure 3.17 Results of Micro-Flotation Tests Conducted on Chalcopyrite Using Varying Amounts of Cetyl Pyridinium Chloride and Sodium Isopropyl Xanthate as Collectors

3.3.2 With a Mixture of Chalcopyrite and Quartz

Figure 3.18 shows the results of the micro-flotation tests conducted on a mixture of quartz and chalcopyrite samples using CpCl as a collector. At a collector concentration of 1×10^{-7} moles/liter, a four minute flotation time gave a 60.0% chalcopyrite recovery and virtually no flotation of quartz. Increasing the collector concentration to 1×10^{-6} moles /liter resulted in an improved recovery of 82.2% of the chalcopyrite after four minutes of flotation, with less than 1.5% of the quartz in the froth product again after four minutes of flotation. However, a further increase in collector concentration (to 1×10^{-5} moles/liter) gave flotation of both quartz and chalcopyrite; after four minutes of flotation, 82.6% of the chalcopyrite and 72.4% of the quartz were recovered.

3.4 Adsorption of CpCl on Chalcopyrite and Quartz

Figure 3.19 shows the isotherms for the adsorption of CpCl on chalcopyrite and quartz at pH 4.6, 7.0 and 11.0 at ambient temperature. In the case with chalcopyrite, the initial slopes of the isotherms are vertical, indicating that when small amounts of CpCl are added, the adsorption is complete and no measurable amounts of collector remain in

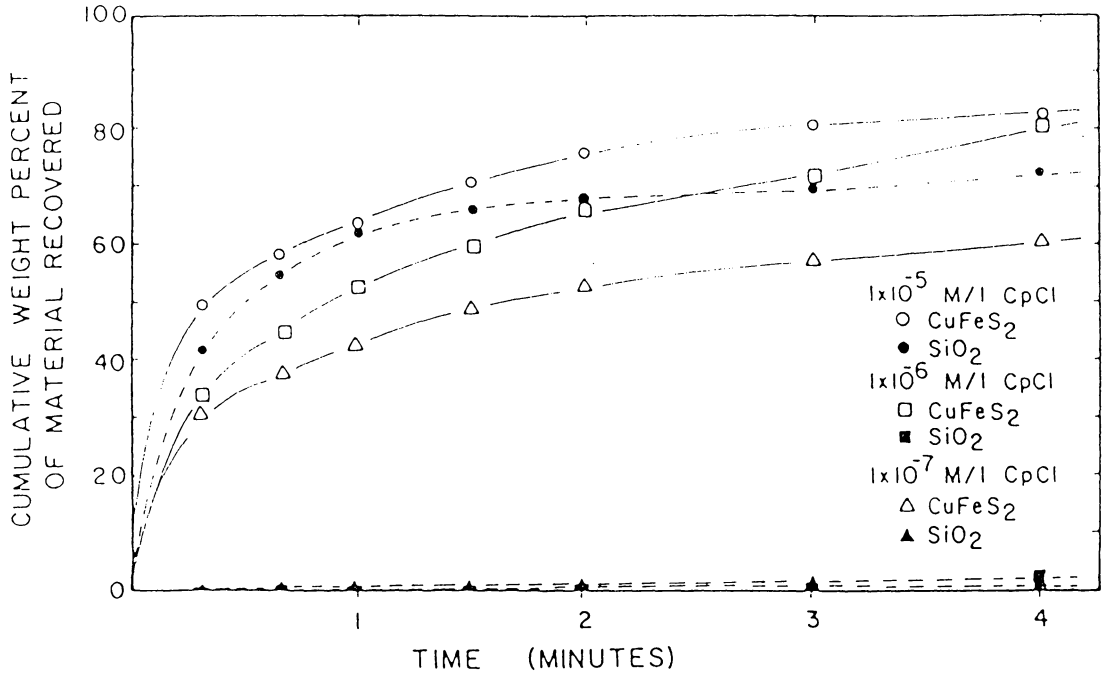


Figure 3.18 Results of Micro-Flotation Tests Conducted on a Mixture of Chalcopyrite and Quartz Using Varying Amounts of Cetyl Pyridinium Chloride as Collector

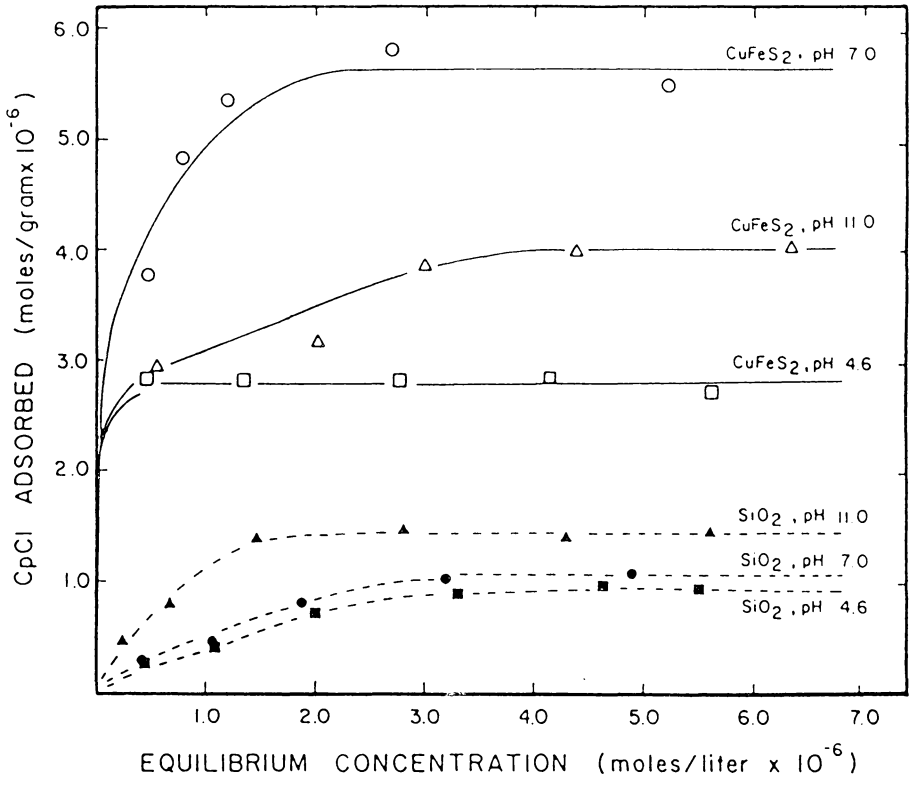


Figure 3.19 Adsorption of Cetyl Pyridinium Chloride on Chalcopyrite and Quartz as a Function of Equilibrium Concentration at pH 4.6, 7.0 and 11.0

solution. Following Giles' classification (Figure 1.1), these isotherms (Figure 3.19) belong to the H-2 type which is characteristic of strong chemisorption. Of the three pH's tested, the adsorption density is maximum at pH 7.0 and minimum at pH 4.6. These results conform to batch flotation results obtained at various pH's (see Figure 3.2).

For the CpCl/quartz system, the initial slopes of the adsorption isotherms are significantly less than those obtained with chalcopyrite, indicating much weaker adsorption. Unlike the CpCl/chalcopyrite system, the adsorption was maximum at pH 11.0, and reduced with decreasing pH. Since the ζ-potential of quartz is increasing with increasing pH (Figure 3.14), this might be an indication that the adsorption mechanism is controlled by the coulombic attraction force. Note also that the adsorption densities are much less on quartz than on chalcopyrite, which may be another indication that the pyridinium ions adsorb more strongly on chalcopyrite.

In Figure 3.19, the adsorption densities are given in terms of moles/g instead of moles/cm^2, since there were uncertainties in the surface area measurements. The BET surface area of chalcopyrite, determined by N_2 adsorption, varied depending on the degassing temperature; after degassing at 120°C, the specific surface area was 0.6 m^2/g, while it was only 0.1 m^2/g after degassing at 60°C. Since the samples degassed at 120°C showed elemental sulfur

deposited at the main manifold of the BET apparatus, possibly due to the decomposition of the sample, 0.01 m^2/g is probably a more realistic value for the specific surface area of chalcopyrite. However, at this temperature, the removal of physically adsorbed water may not have been complete. The specific surface area of quartz is probably more certain; after degassing at 120°C, a value of 0.1 m^2/g was obtained.

Plateau regions were observed for both mineral/collector systems. For the CpCl/quartz system, the greatest adsorption occurred at pH 11.0 and less adsorption occurred as the pH decreased. For the CpCl/chalcopyrite system, maximum adsorption occurred at pH 7.0 and less at pH's 4.6 and 11.0. Note that the adsorption of CpCl on quartz was significantly less than on chalcopyrite, regardless of the pH.

A more detailed analysis of adsorption isotherms and their relevance to classifying adsorption phenomena is included in the discussion section.

3.5 Electrochemical Studies

The cyclic voltammograms of chalcopyrite in a nitrogen purged borate solution are shown in Figure 3.20. In the absence of collector, the sweep started at the rest

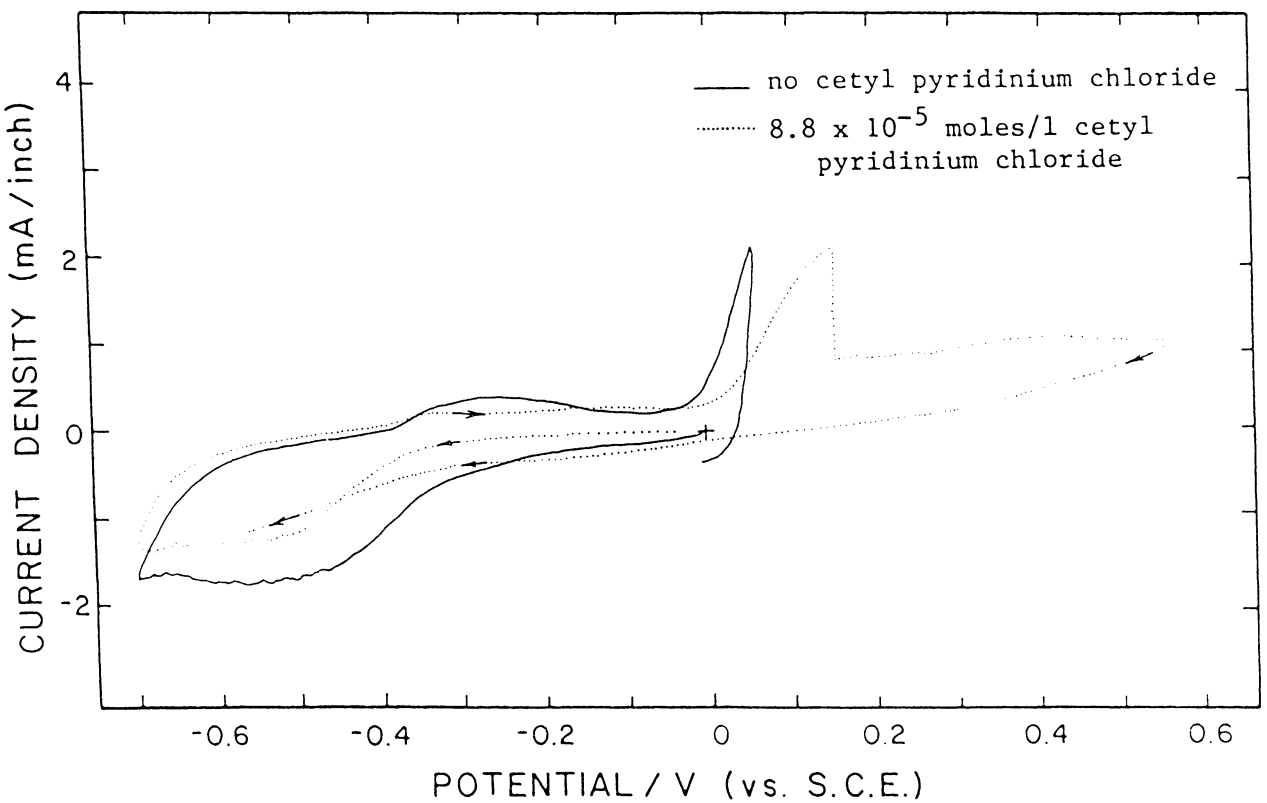


Figure 3.20 Voltammograms of Chalcopyrite Obtained in 0.5 moles/l Sodium Borate Solution

potential in the cathodic direction. A relatively large cathodic current at E<-0.3 V indicates reducible oxidation products on the surface. These may have been formed by prior air oxidation, electrochemical corrosion, or by the reduction of $CuFeS_2$. On the return anodic sweep there was a well-defined oxidation peak centered at -0.25 V and a well-defined dissolution wave near 0.0 V.

The sample was returned to open circuit potential (+0.008 V), and 4.5×10^{-5} moles/liter CpCl was added while the solution was being circulated through the mineral bed and the spectrophotometer. Figure 3.21 shows the change in absorbance at 258 nm as a function of time. The initial rise in absorbance at 62 seconds was due to the injection of CpCl. After about 15 seconds, the absorbance started declining rapidly, indicating the adsorption of cetyl pyridinium ions on chalcopyrite. Note that before the CpCl injection, the supernatant solution exhibited a relative absorbance (approximately 0.165) at 258 nm, most likely due to the species derived from the chalcopyrite surface and present in the aqueous phase. Note also that the absorbance falls below the base line, i.e., 0.165 absorbance, with the increasing time of adsorption. This may indicate that the adsorption process involves the following steps: i) a complex formation between the pyridinium ion and the species derived from the chalcopyrite surface, and ii) the subsequent transportation of the complex formed to the

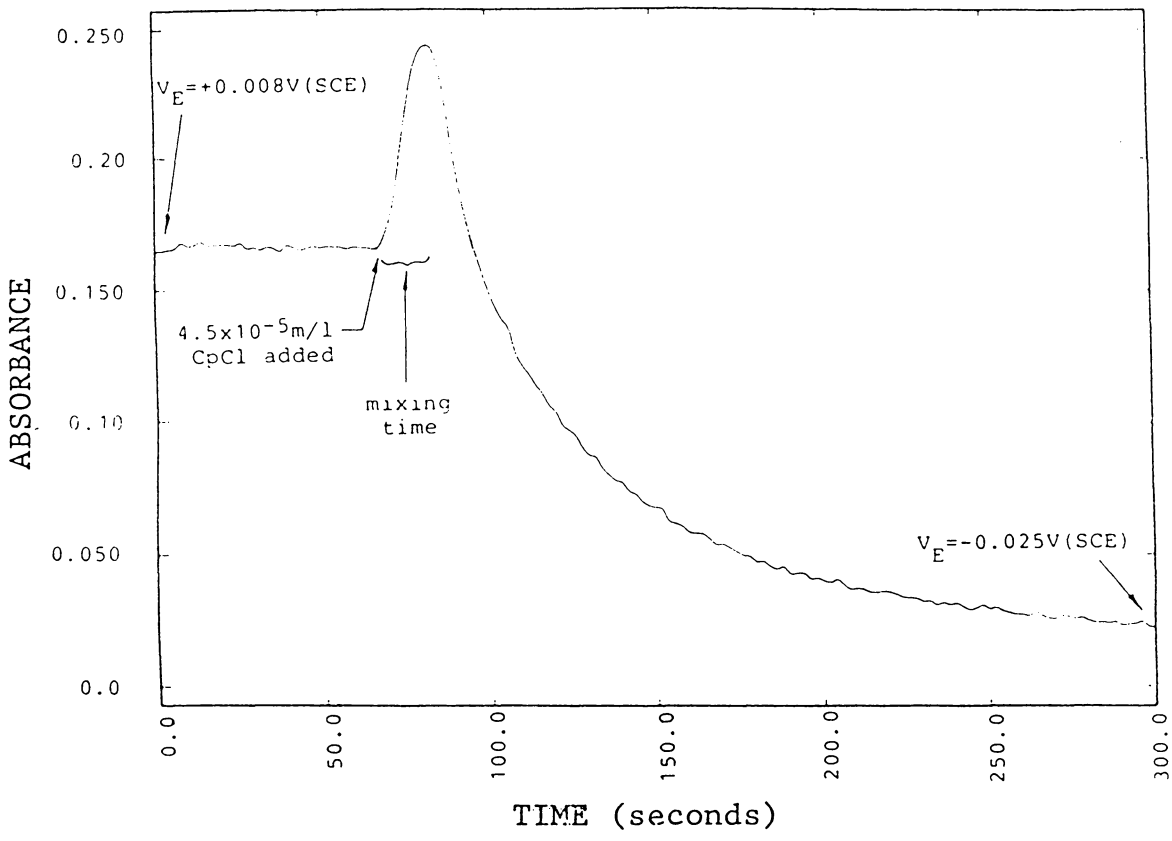


Figure 3.21 UV Absorbance as a Function of Time at 258 nm to Monitor the Changes in the Cetyl Pyridinium Ion Concentration during its Adsorption on Chalcopyrite after the First Injection

surface for adsorption.

Five minutes after the first addition of CpCl, more reagent was added to bring the total added to 8.8×10^{-5} moles/liter, while monitoring the CpCl concentration at 258 nm. As shown in Figure 3.22, the CpCl uptake was much slower.

Five minutes after the second addition, the potential of the chalcopyrite electrode was changed from the rest potential (-0.035 V) to -0.7 V at a slow sweep rate (1 mV/sec). Figure 3.23 shows the spectra at various potentials. From -0.035 V to -0.46 V, the concentration decreased slightly, probably by slow chemical reaction or adsorption, not by any electrochemical reaction. If an electrochemical reaction had occurred, the concentration changes would have been much greater, as is usually the case with xanthate (Walker and Richardson, 1982). An anodic sweep from -0.7 V to -0.03 V did not change the concentration either, confirming that CpCl adsorption on chalcopyrite is not controlled by an electrochemical mechanism.

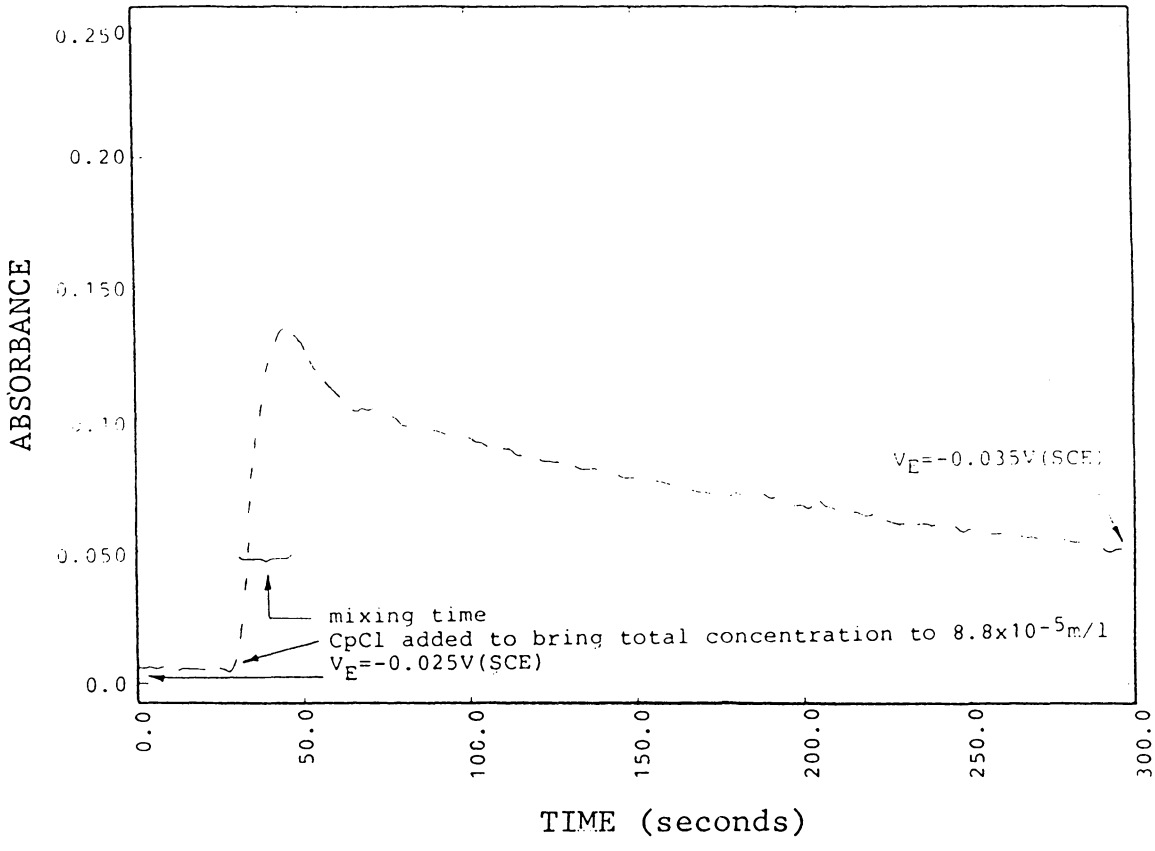


Figure 3.22 UV Absorbance as a Function of Time at 258 nm to Monitor the Changes in the Cetyl Pyridinium Ion Concentration during its Adsorption on Chalcopyrite after the Second Injection.

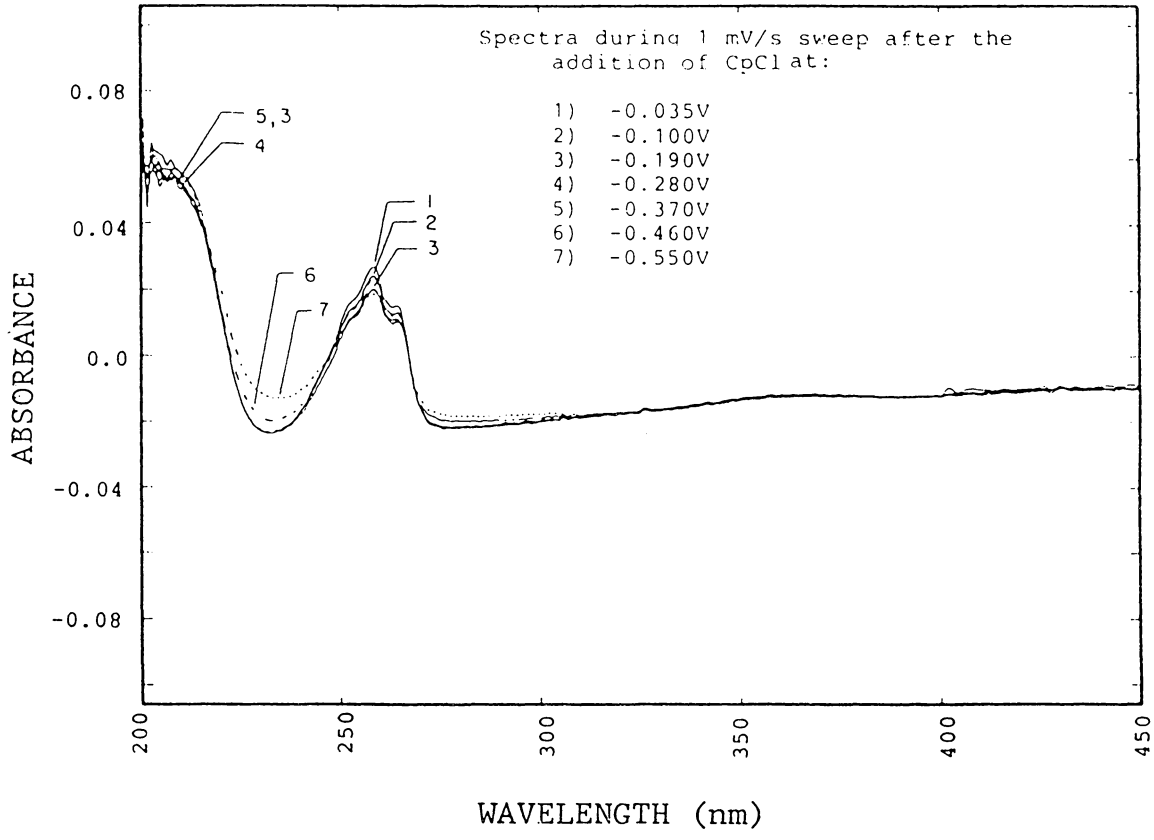


Figure 3.23 UV Spectra Recorded During the Cathodic Potential Sweep at 1 mV/sec Sweep Rate

IV. DISCUSSION

4.1 General

The role of sodium sulfide and pyridine in collectorless flotation is recognized to be that of surface-cleaning agents. They may remove hydrophyllic oxidation products from the surface, thus exposing unoxidized surfaces that might be naturally hydrophobic (Yoon, 1980). With this in mind, one may suspect that long chain alkyl pyridinium salts could also act as surface cleaning agents. However, electrophoretic mobility measurements conducted in the presence of alkyl pyridinium salts (Figures 3.15 and 3.17) show that these cationic surfactants actually adsorb on the sulfide mineral surfaces, as indicated by the reduction in the ζ-potential with increasing concentrations. Therefore, the role of long chain alkyl pyridinium salts is likely that of a collector which renders a mineral hydrophobic by an adsorption mechanism.

The general shape of the ζ-potential vs. collector concentration curves for alkyl pyridinium salts (Figure 3.15) are similar to those obtained for the quartz/dodecyl ammonium acetate (DAA) system (Gaudin and Fuerstenau, 1955; Smith and Akhtar, 1976). In this system, it is considered that the concentration of aminium ions (RNH^+) is higher in

the vicinity of the quartz surface than in the bulk solution. When the amine concentration near the surface reaches a critical value, the adsorption is enhanced by the hydrophobic bonding force between hydrocarbon chains.

Wakamatsu and Fuerstenau (1966) used the Stern-Grahame model of the electrical double layer theory, and determined the contribution for hydrocarbon chain association to the adsorption process as follows:

$$\Delta G^{o}_{CH_2} = n\phi \qquad [4.1]$$

in which $\Delta G^{o}_{CH_2}$ represents the free energy contribution due to association of hydrocarbon chains to the total free energy of adsorption (ΔG^{o}_{ads}), n the number of CH_2 groups in an alkyl chain, and ϕ is the free energy change for removing one mole of CH_2 groups from water to the adsorbed layer on a solid surface. Wakamatsu and Fuerstenau (1966) have evaluated ϕ to be -1.0RT (approximately 0.06 kcal/mole of CH_2 groups).

Equation 4.1 suggests that the longer the hydrocarbon chain, i.e. the greater the value of n, the greater the value of $\Delta G^{o}_{CH_2}$ and hence ΔG^{o}_{ads}. This may offer an explanation for the results obtained in the present work. As shown in Figure 3.15, the charge reversal occurs at progressively lower concentrations as the chain length of the alkyl pyridinium collector is increased from 2 to 18.

Similar results were reported for the quartz/amine system by Somosundaran (1964) and Somosundaran, Healy and Fuerstenau (1964).

To fully explain the complexity of the collector adsorption process, Raghavan and Fuerstenau (1975) split ΔG_{ads} as follows:

$$\Delta G^{o}_{ads} = \Delta G^{o}_{elec} + \Delta G^{o}_{chem} + \Delta G^{o}_{CH_2} + \Delta G^{o}_{solv} + \ldots \quad [4.2]$$

in which ΔG^{o}_{elec} is the electrostatic contribution to the total free energy, ΔG^{o}_{chem} represents the free energy due to the formation of covalent bonds with the surface and ΔG^{o}_{solv} essentially represents the entropic contribution to the total free energy. The electrical contribution, ΔG^{o}_{elec}, can be readily determined by the following equation (Palmer and Fuerstenau, 1975):

$$\Delta G^{o}_{elec} = zF\zeta \quad [4.3]$$

where z is the valence of the collector ion including the sign, F is Faraday's constant and ζ is the zeta potential.

In the present flotation system, e.g., Texasgulf ore, the major mineralization includes quartz, sphalerite, chalcopyrite, pyrite and chlorite, all of which are likely to be negatively charged at the flotation pH. Yet, only chalcopyrite was found to float when long chain alkyl

pyridinium salts were used as collectors. It is not that chalcopyrite is more negative than the other minerals present in this ore. As shown in Figure 3.14, the ζ-potential difference between chalcopyrite and quartz is too small at pH 7.0 to explain the remarkable selectivity obtained throughout the present work.

One might suspect that the selectivity is brought about by the modification of the quartz surface in the presence of heavy metal ions derived from chalcopyrite. For example, the coating of silicious gangue by Cu^{2+} ions may make the quartz surface positively charged, and prevent the alkyl pyridinium ions from adsorbing. In order to test this possability, electrophoretic measurements were made on quartz particles suspended in double-distilled water that had been contacted with a chalcopyrite powder for one hour. At pH 6.1, the ζ-potential thus measured was -25.3mV, while that of the quartz particles suspended in pure double-distilled water at the same pH was -24.9mV. The total copper concentration in the chalcopyrite contacted water was found to be 1.4×10^{-5} moles/l. Apparently, at this low concentration, the surface charge of quartz was not modified significantly.

The most striking demonstration of the selectivity of CpCl has been observed in the micro-flotation tests. When using small amounts of reagents (less than 10^{-7} moles/l), only chalcopyrite floated even after prolonged flotation

time (see Figure 3.18). This may be due to the possibility that CpCl adsorbs more strongly on chalcopyrite than on quartz.

The adsorption isotherms established at pH 4.6, 7.0 and 11.0 (Figure 3.19) indeed show that CpCl adsorbs more strongly on chalcopyrite than on quartz; the initial slopes of the isotherms are much steeper for chalcopyrite than for quartz at all three pH's investigated. In fact, the slopes are vertical, which is typical of the 'high affinity' type of adsorption (Giles et al., 1960).

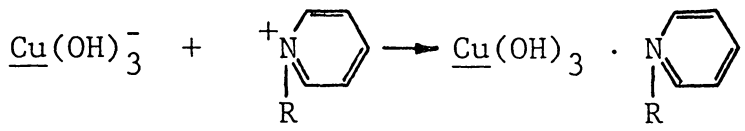
In view of equation 4.2, it may therefore be suggested that ΔG^{o}_{chem} is operating for the adsorption of alkyl pyridinium ions on chalcopyrite. It might further be suggested that these collectors are possibly copper-specific in view of the fact that ZnS can be floated by these collectors only after copper activation.

4.2 Possible Adsorption Mechanisms

On the basis of the foregoing discussions, three possible adsorption mechanisms will be considered in this section.

Firstly, the adsorption of alkyl pyridinium ions may occur via complex-formation with a copper hydroxo-complex,

such as $Cu(OH)_3^-$, as follows:

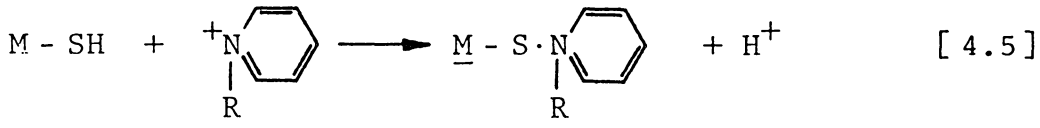


[4.4]

The underscored symbol refers to the species present at the surface of chalcopyrite. However, one might consider that the pyridinium ion complexes with $Cu(OH)_3^-$ (aq) and the resulting complex is subsequently transported to the surface. Evidence for this may have been given in Figure 3.21, and discussed in Section 3.5.

The above mechanism represented by Equation [4.4] suggests that the adsorption is favored at pH's where the $Cu(OH)_3^-$ species is abundant. Since the concentration is likely to increase with increasing pH, the adsorption would be more favorable at higher pH. This may explain the relatively low adsorption density of CpCl on chalcopyrite at pH 4.6 (Figure 3.19) and the lower recoveries obtained at acidic pH. However, with this mechanism, it is difficult to explain the seemingly copper-specific behavior of CpCl during flotation, since the pyridinium ion is not shown to be within the coordination shape of copper.

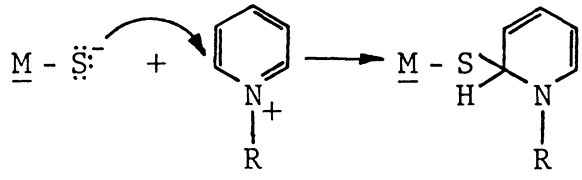
Secondly, the alkyl pyridinium ions may react with the sulfide ions on the surface of chalcopyrite as follows:



[4.5]

in which M represents the surface metal ion. This mechanism suggests that the pH should decrease during adsorption. This has been confirmed in an experiment, in which a volume of CpCl solution (1×10^{-4} moles/l) adjusted to pH 7.2 was injected into a chalcopyrite suspension at the same pH. After five minutes of conditioning, the pH dropped to 6.7. Equation [4.5] suggests that an acidic pH is favorable for the adsorption of the alkyl pyridinium ions, as has been observed in the present work. Equation [4.5] may also help explain the selectivity of CpCl for chalcopyrite over silicious gangue, but fails to explain the observed selectivity in the presence of other sulfide minerals.

Finally, the adsorption of alkyl pyridinium ions may involve nucleophilic reactions as follows:



[4.6]

in which M refers to the surface metal ion. Since nitrogen is more electronegative than carbon, the electrons around the neighboring carbon are pulled more toward the nitrogen, leaving the nitrogen vulnerable to nucleophilic attack. The

surface sulfide ion having unshared electron pairs is considered as the nucleophile.

The mechanisms considered in this discussion may be helpful in explaining the possible chemisorption, or 'high affinity' adsorption, of alkyl pyridinium ions on chalcopyrite. However, they fail to explain the selectivity among sulfide minerals, which requires further investigation.

4.3 Flotation Kinetics

The most general method to quantify flotation kinetics has been to assimilate the flotation process with chemical reactions. In doing so, a rate expression can be formulated in the form;

$$\text{rate} = -\frac{dc}{dt} = kc \qquad [4.7]$$

where k is the flotation rate constant, c is the floatable mineral concentration and n is the order of the kinetics. Constants k and n can be evaluated empirically by plotting the experimental flotation rate, $\frac{dc}{dt}$, vs. c according to the logarithmic form of the rate equation;

$$-\log (\text{rate}) = \log k + n \log c. \qquad [4.8]$$

In order to express flotation rates with techniques derived for chemical kinetics, modifications of the rate equation are necessary. When considering flotation processes, it is more meaningful to refer to recovery (R) rather than concentration, thus a value of 100-R can be substituted for c in the rate equation. To account for apparently floatable material that remains in the flotation cell after prolonged flotation times, Morris (1952) and Bushell (1962) developed another modification of the

flotation rate equation. The apparently floatable portion can be graphically determined by plotting the amount of material recovered vs. time, as shown in Figures 3.10 and 3.11. Each curve levels off after long flotation times and the apparently floatable portion is 100-R, designated as R_t. Therefore, a more realistic rate expression for flotation systems is:

$$-\log (\text{rate}) = \log k + n \log (100-R-R_t). \quad [4.9]$$

By plotting log $(100-R-R_t)$ vs. - log (rate), values for n and k can be determined graphically, with n as the slope of the plot and k as the intercept. Plots for batch flotation kinetics data are presented in this manner in Figure 4.1, which indicates that linear plots were obtained. Values for n and k are shown in Table II. Similarly, micro-flotation kinetics data is shown in Figure 4.2 while tabulated values of n and k are presented in Table III.

The most notable result of the flotation kinetics tests is that the order of the rate equation, n, is significantly higher for CpCl than for NaIpX. The difference in the order of flotation kinetics is more significant for the batch flotation tests. This is most likely due to the small amount of sample that was used in micro-flotation tests. In each of the flotation tests conducted, the flotation kinetics were determined to be

between a first and a second order process. Several authors (Arbiter and Harris, 1962; Mika and Fuerstenau, 1969) have reported that flotation is basically a first order process, while Arbiter (1951) has reported that a second order relation can also be applied under certain conditions.

According to Schuhmann (1942) the rate of flotation of particles of average size x is given by:

$$\frac{dR}{dt} = P_c P_a c(x) VF \qquad [4.10]$$

where R is the concentration of particles in the froth, P_c is the probability of a collision between a particle and a gas bubble, P_a is the probability of adhesion of the particle and bubble after collision, c(x) is the concentration of particles of average size x in the cell, V is the pulp volume in the cell and F is a factor to account for the stability of the froth. Laskowski and Iskra (1970) have proposed a generalized expression for the probability of flotation, P, in the following form:

$$P = P_c P_a P_s \qquad [4.11]$$

where P_s is the probability that a stable bubble-particle aggregate will form, and P_c and P_a have the same meaning as in Equation [4.10]. In this form, particle flotation can be

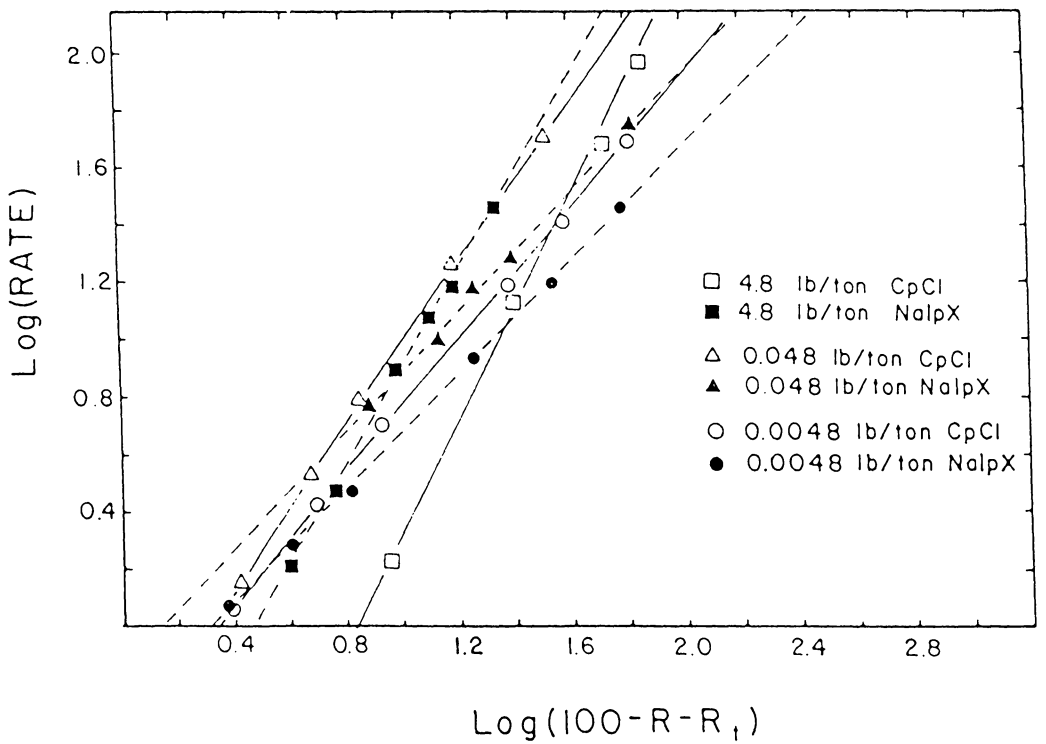


Figure 4.1 Log (Rate) vs. Log (100-R-R_t) Plots for the Laboratory Flotation Tests Conducted on Texasgulf Type 'A' Ore with Cetyl Pyridinium Chloride and Sodium Isopropyl Xanthate Used as Collectors

Table II. Rate Equation Parameters for Batch Flotation Conducted with Cetyl Pyridinium Chloride and Sodium Iso-Propyl Xanthate

Dosage (lb/ton)	Reagent	n	k
.0048	CpCl	1.178	-.415
.0048	NaIpX	1.061	-.388
.048	CpCl	1.474	-.482
.048	NaIpX	1.151	-.288
4.8	CpCl	1.963	-1.629
4.8	NaIpX	1.731	-.834

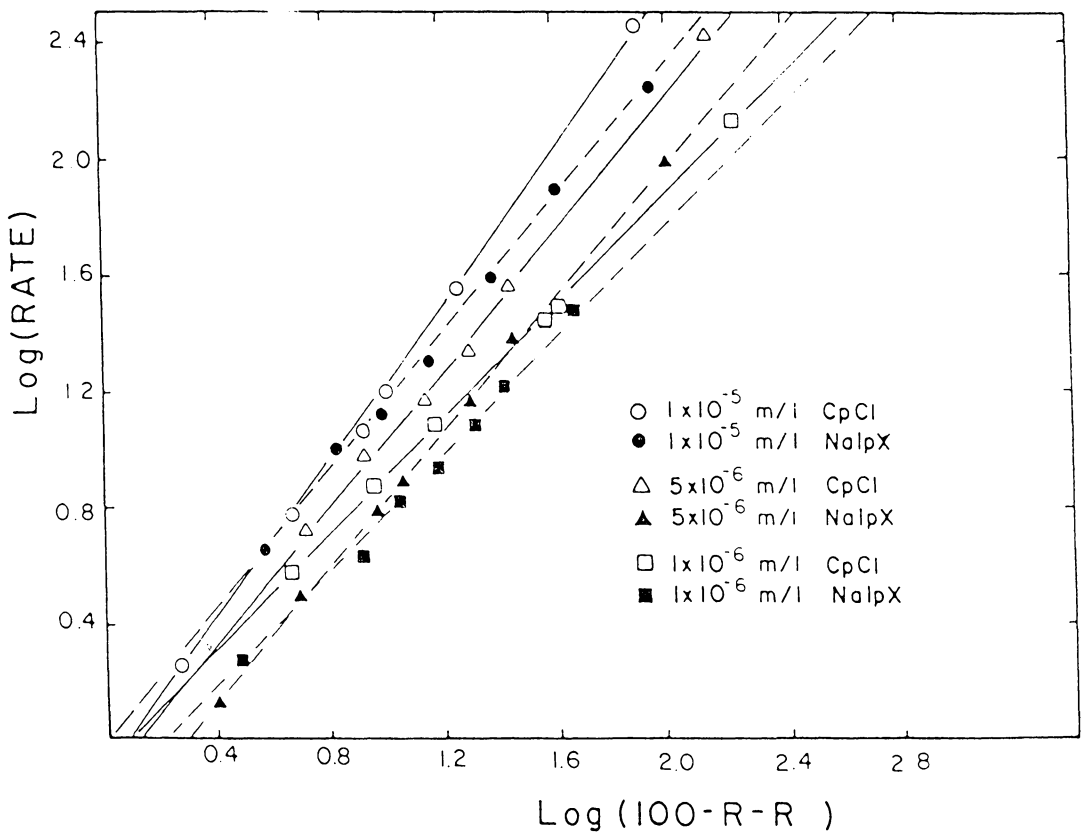


Figure 4.2 Log (Rate) vs. Log (100-R-R_t) Plots for the Micro-Flotation Tests Conducted with Cetyl Pyridinium Chloride and Sodium Isopropyl Xanthate Used as Collectors

Table III. Rate Equation Parameters for Micro-Flotation Conducted with Cetyl Pyridinium Chloride and Sodium Iso-Propyl Xanthate

Concentration (moles/l)	Reagent	n	k	r^2
1×10^{-5}	CpCl	1.381	-0.180	0.9999
1×10^{-5}	NaIpX	1.186	-0.041	0.9986
5×10^{-6}	CpCl	1.247	-0.184	0.9872
5×10^{-6}	NaIpX	1.166	-0.346	0.9995
1×10^{-6}	CpCl	1.137	-0.266	0.9976
1×10^{-6}	NaIpX	1.026	-0.259	0.9967

divided into three stages: i) bubble-particle collision, ii) thinning and rupture of the wetting film, and iii) formation of a stable bubble-particle aggregate that can withstand disruptive forces in the flotation cell (Laskowski, 1974). The wetting film behaves as though there was an excess pressure acting normal to the film and opposing further film thinning. This excess pressure is termed the disjoining pressure, Π, by Derjauguin and Dulchin (1960). Disjoining pressure is believed to result from three types of interactive forces at the interface:

$$\Pi = \Pi_{\text{van der Waals}} + \Pi_{\text{hydration}} + \Pi_{\text{electric}} \qquad [4.12]$$

in which $\Pi_{\text{van der Waals}}$ refers to the van der Waals force for the attraction of water molecules to the solid surface, $\Pi_{\text{hydration}}$ represents the hydration energy of the solid which is mainly due to H-bonding, and Π_{elec} is due to the interaction of the double layers around the particle and the bubble. Laskowski and Kitchener (1969) suggested that hydrophobicity occurs when $\Pi_{\text{hydration}}$ and Π_{electric} become small because dispersion forces such as $\Pi_{\text{van der Waals}}$ are always smaller than the van der Waals cohesive forces between water molecules. Usually, $\Pi_{\text{hydration}}$ is reduced by the adsorption of collector species which present hydrocarbon tails toward the aqueous phase and, thus, prevent the water molecules from forming H-bonds with the

surface.

In the sulfide flotation systems using xanthates as collectors, $\Pi_{electric}$ appears to be positive and hinders the flotation process. As shown in Figure 3.15, xanthate coated chalcopyrite tends to become more negative. If a bubble is also negative, which has been recently found to be the case with the bubbles generated using Dowfroth M150 (Yoon, 1982), there must be an electrostatic repulsive force operating against the bubble-particle adhesion. Unlike $\Pi_{van\ der\ Waals}$ and $\Pi_{hydration}$, $\Pi_{electric}$ is essentially a long-range force operating over a distance ranging from a few hundred to a few thousand Angstroms, and thus controlls the initial step of the bubble-particle adhesion process. Many researchers consider this to be the rate-determining step and, therefore, it is critical in determining the flotation kinetics (Blake and Kitchener, 1972).

The flotation of chalcopyrite with CpCl, on the other hand, presents a different picture. As shown in Figure 3.15, the negative ζ-potential of chalcopyrite is reduced with increasing CpCl concentration and eventually becomes positive with further increases. If the bubbles remain negative despite the presence of the cationic surfactant CpCl, the probability of bubble-particle adhesion would certainly be more favorable than the case of using a xanthate as collector. The superior flotation kinetics,

demonstrated consistently in the present work, is probably a direct manifestation of this effect.

During flotation, a bubble and a particle collide as a first step toward adhesion. If the conditions are favorable, a stable contact angle will form. This process must be completed within a very short period of time, in the range of milli-seconds, in actual flotation. Otherwise, the bubble-particle adhesion will not result in the formation of a stable contact angle and no flotation will be possible.

Schumann (1942) first considered that the role of flotation reagents, particularly that of a collector, was to reduce the minimum time of contact required for the bubble-particle adhesion, which was referred to as the 'induction time'. It was related to the Arrehnius type of kinetic equation:

$$\tau = \tau_o \exp\left[-\frac{E}{kT}\right] \qquad [4.13]$$

in which τ is the induction time, τ_o is an empirical constant, E is the activation energy for the bubble-particle adhesion, and k and T are the usual constants.

Rao (1974) suggested that the role of collectors in flotation is to reduce the energy barrier, E, by reducing the ζ-potential. It has been shown in the present work that CpCl reduces the ζ-potential of chalcopyrite while

NaIpX makes it become more negative. This may be another explanation for the better results obtained with CpCl in comparison with those obtained using NaIpX, particularly in flotation rates.

V. SUMMARY AND CONCLUSIONS

The major findings of the present work may be summarized as follows:

1. Batch flotation experiments conducted on a copper-zinc ore, from Texasgulf Mines Ltd., have shown that CpCl can be used as a collector for sulfide minerals with improved recovery and selectivity as compared to the results obtained using conventional collectors such as xanthates. selectivity has been shown at all reagent levels tested, while the improvements in recoveries have been obtained at relatively higher dosages.
2. The most pronounced advantage of using CpCl as a collector has been found to be in the improved flotation kinetics. Kinetic studies made in both batch and micro-flotation tests have shown that the rates of chalcopyrite flotation cannot be described by either first-order or second-order equations. However, analysis of the kinetic data on the basis of an n-th order rate equation has shown that both the order (n) and the rate constant (k) are higher when using CpCl as a collector than when using NaIpX.

   The improved kinetics of the CpCl flotation may be attributed to the reduction in the

ζ-potential when adsorption of cetyl pyridinium ions occurs on the negatively charged chalcopyrite surface. This is quite unlike the case where xanthates are used as collectors, in which the negative ζ-potential has not been reduced upon adsorption of collector. A reduced ζ-potential minimizes the electrostatic component, $\Pi_{electric}$, of the disjoining pressure and expedites the film-thinning process. It is considered that $\Pi_{electric}$, which is essentially a long-range long-range force, is operating during the initial stages of the bubble-particle attachment process and is most critical in determining the flotation rate.

3. Micro-flotation tests have been conducted on an artificial mixture of chalcopyrite and quartz. It has been found that when using small amounts of CpCl, only chalcopyrite floated selectively. This may indicate that CpCl adsorbs preferentially on chalcopyrite, which in turn suggests that CpCl adsorbs more strongly on chalcopyrite.
4. The adsorption of CpCl on both chalcopyrite and quartz has been measured. The isotherms established at pH 4.6, 7.0 and 11.0 are of the Langmuir-type for both minerals. However, the initial slopes of the isotherms are vertical for chalcopyrite while

those for quartz are much lower. This may be an indication that CpCl adsorbs more strongly on chalcopyrite, which may account for the selective flotation observed throughout the present work.

5. The preferential adsorption of cetyl pyridinium ions on chalcopyrite cannot be explained by the differences in the ζ-potentials of the two minerals. They are of the same sign and approximately the same magnitude at the neutral pH where most of the flotation tests were made. It has also been determined that the ζ-potential of quartz is not significantly modified in the presence of heavy metal ions derived from chalcopyrite under the experimental conditions employed in the present work.

Therefore, the selective flotation can only be explained by the difference in the affinity of cetyl pyridinium ions toward the chalcopyrite and the minerals, such as quartz. Several possible mechanisms have been proposed to account for the 'high affinity' type of adsorption for the CpCl-chalcopyrite system.

VI. INDUSTRIAL IMPLICATIONS

Several advantages of using CpCl rather than conventional xanthates as a collector for sulfide mineral flotation may be suggested on the basis of information derived from the present work.

Higher selectivity and higher recovery of sulfide minerals may be achieved by using CpCl as a collector. An improved selectivity is particularly desired when treating a complex sulfide ore containing more than one valuable mineral to be recovered. For example, a xanthate flotation on Texasgulf Cu-Zn ore resulted in a significant loss of sphalerite in the copper concentrate. The use of a more selective collector, such as CpCl, reduced the loss substantially. One might be concerned about the increased cost of using the new reagent, but a small improvement in recovery often results in a significant increase in profits.

As a collector, CpCl gives faster flotation kinetics than conventional xanthates. This will increase the throughput of a flotation plant for a given volume of flotation cells.

Xanthates are relatively inexpensive reagents at a cost of approximately 0.85 $/lb. Although CpCl is not yet mass produced, the synthesis procedure is quite simple. Expert opinions estimate that commercial grade CpCl can be produced

at a cost of $1.00 - $1.10 per pound (American Cyanamid, 1982). Even though this cost is slightly higher than that of xanthates, the advantages afforded by using CpCl would be expected to offset the marginal additional cost.

VII. RECOMMENDATIONS FOR FURTHER STUDY

Based upon the experience and information obtained during the course of the present work, additional research in the following areas is suggested:

1. An investigation of the effect of CpCl on the induction time required for bubble-particle adhesion may be warranted. This will provide fundamental information regarding the kinetics of flotation and the collector adsorption mechanism.
2. A thorough batch flotation investigation, utilizing a wide variety of sulfide ores, is necessary to consolidate the findings of the present work.
3. Flotation experiments exploiting the possible synergistic effects of using a combination of CpCl and xanthate may be fruitful.
4. A continuous flotation experiment on a pilot scale on the basis of the present investigation will provide useful information for engineering purposes.
5. An investigation using alkyl pyridinium salts synthesized with the hydrocarbon chain attached to a carbon in the ring structure may be fruitful. This will free the lone pair of electrons of the nitrogen, which might be donated to a metal,

such as as copper, in forming a coordination bond.

6. In order to better understand the adsorption mechanisms, it may be useful to conduct spectroscopic analysis of the CpCl species adsorbed on chalcopyrite. An infrared analysis using the ATR technique would be suitable for this purpose. Also, determination of the heat of adsorption may be helpful in understanding the nature of the bonding.

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Appendix I

Determination of Electrophoresis Instrument Variables

Determination of the eyepiece graticule - A stage micrometer was used to determine the distance measured by the eyepiece graticule. The distance was determined to be 70 microns.

Determination of the stationary levels - The positions of the stationary levels were found using Komagata's Equation:

$$\frac{s}{d} = 0.500 - 0.0833 + \frac{32}{\pi s}\frac{d}{h}^{\frac{1}{2}} \quad *$$

where s is the distance from the cell wall, d is the cell width and h is the cell height. Substituting the appropriate values for d and h, s was calculated. Once the cell holder had been secured in the bath and the cell walls had been located, the eyepiece was focused a distance s from the cell walls and measurements were made.

Determination of the interelectrode distance - The interelectrode distance, l, was determined by calculating the cross-sectional area of the cell, A, and measuring the resistance, R, of the cell using a solution of known specific conductance, K. Using the relation :

$$l = RKA$$

the interelectrode distance was calculated.

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*Operating Instructions and Manual for the Particle Micro-Electrophoresis Apparatus Mark II, Rank Brothers, High Street, Bottisham, Cambridge C8590A England.

Appendix II

Spectrophotometer Calibration Curves

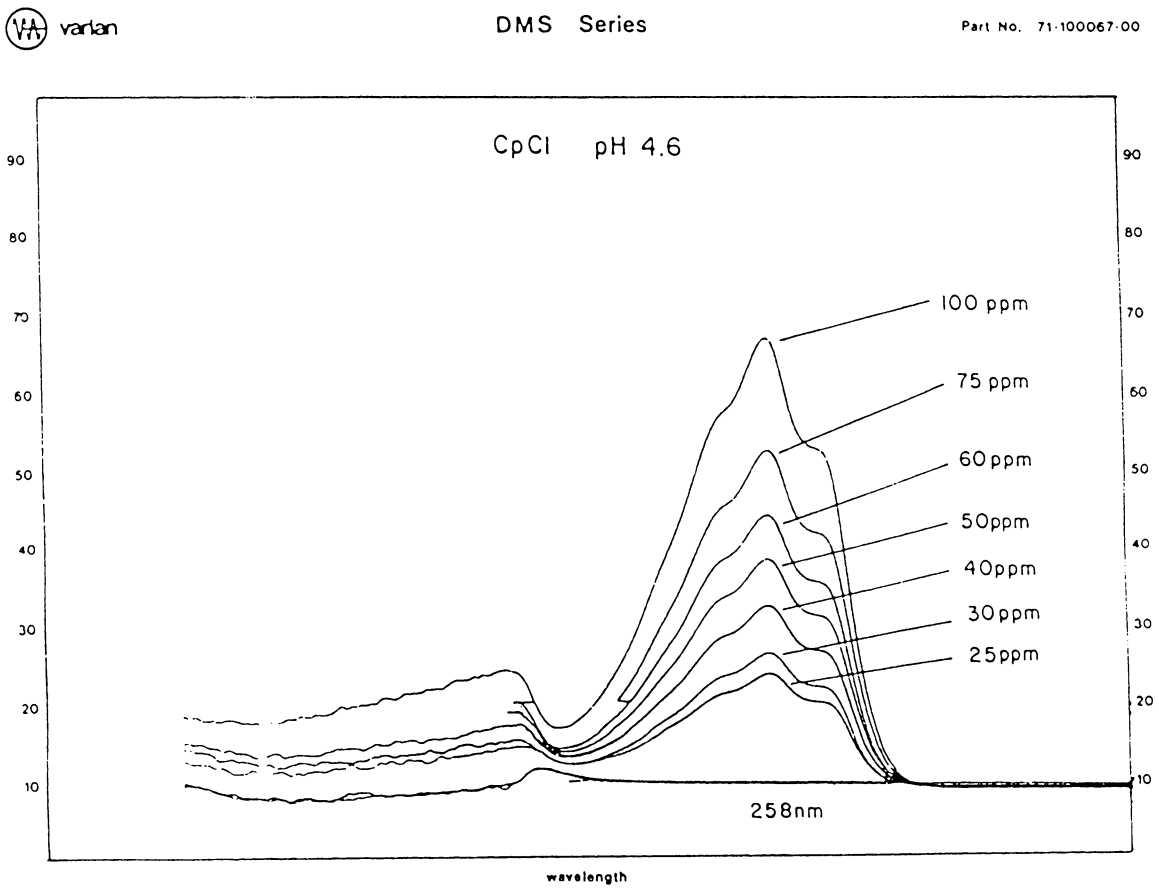

Figure 1. Absorbance Spectra for CpCl in pH 4.6 Buffer.

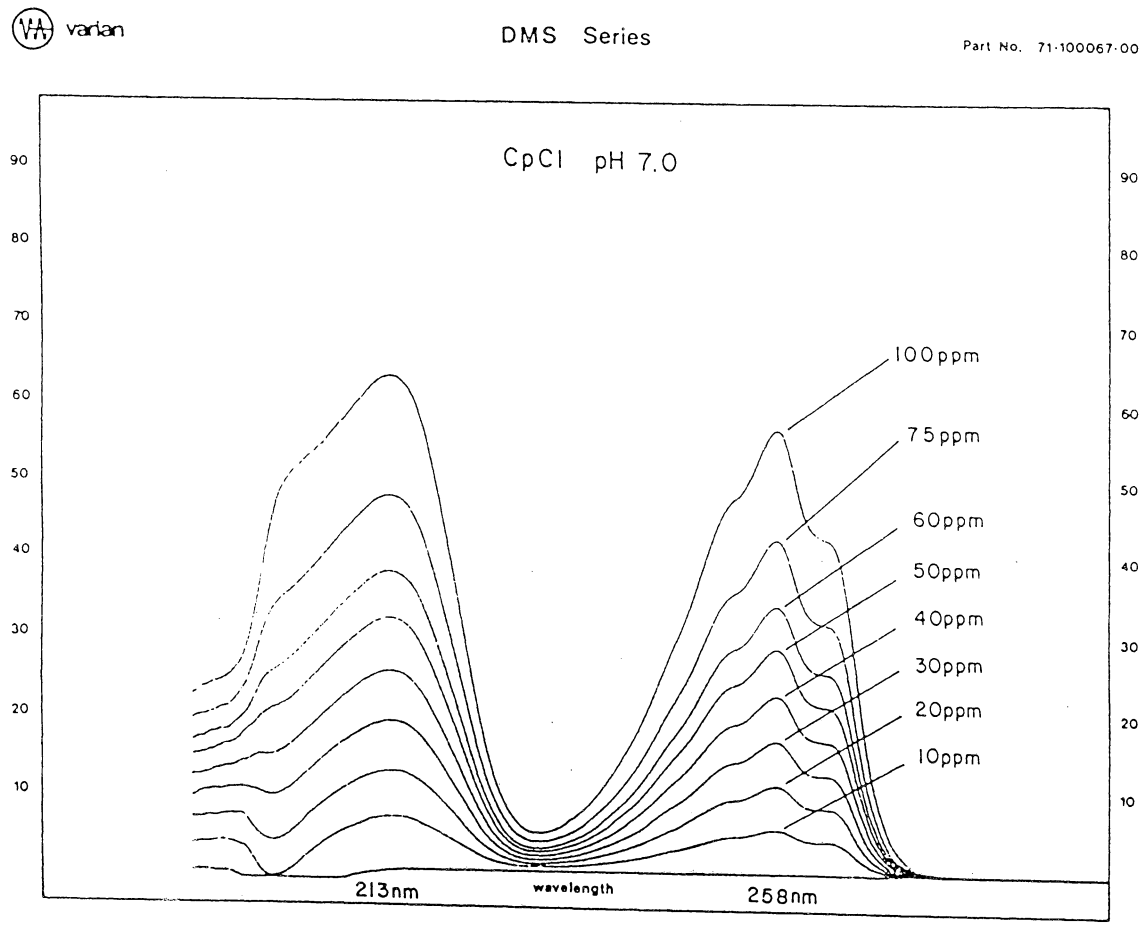

Figure 2. Absorbance Spectra for CpCl in pH 7.0 Buffer.

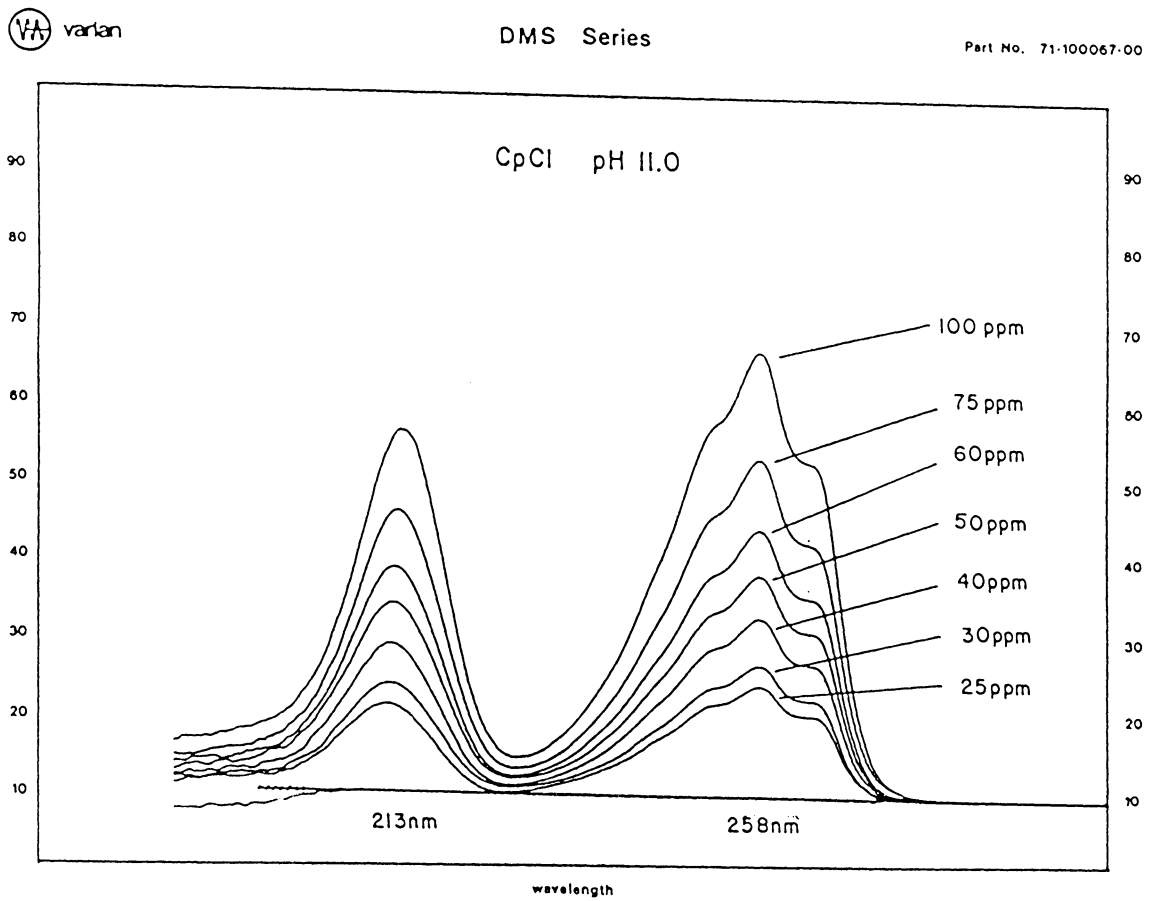

Figure 3. Absorbance Spectra for CpCl in pH 11.0 Buffer.

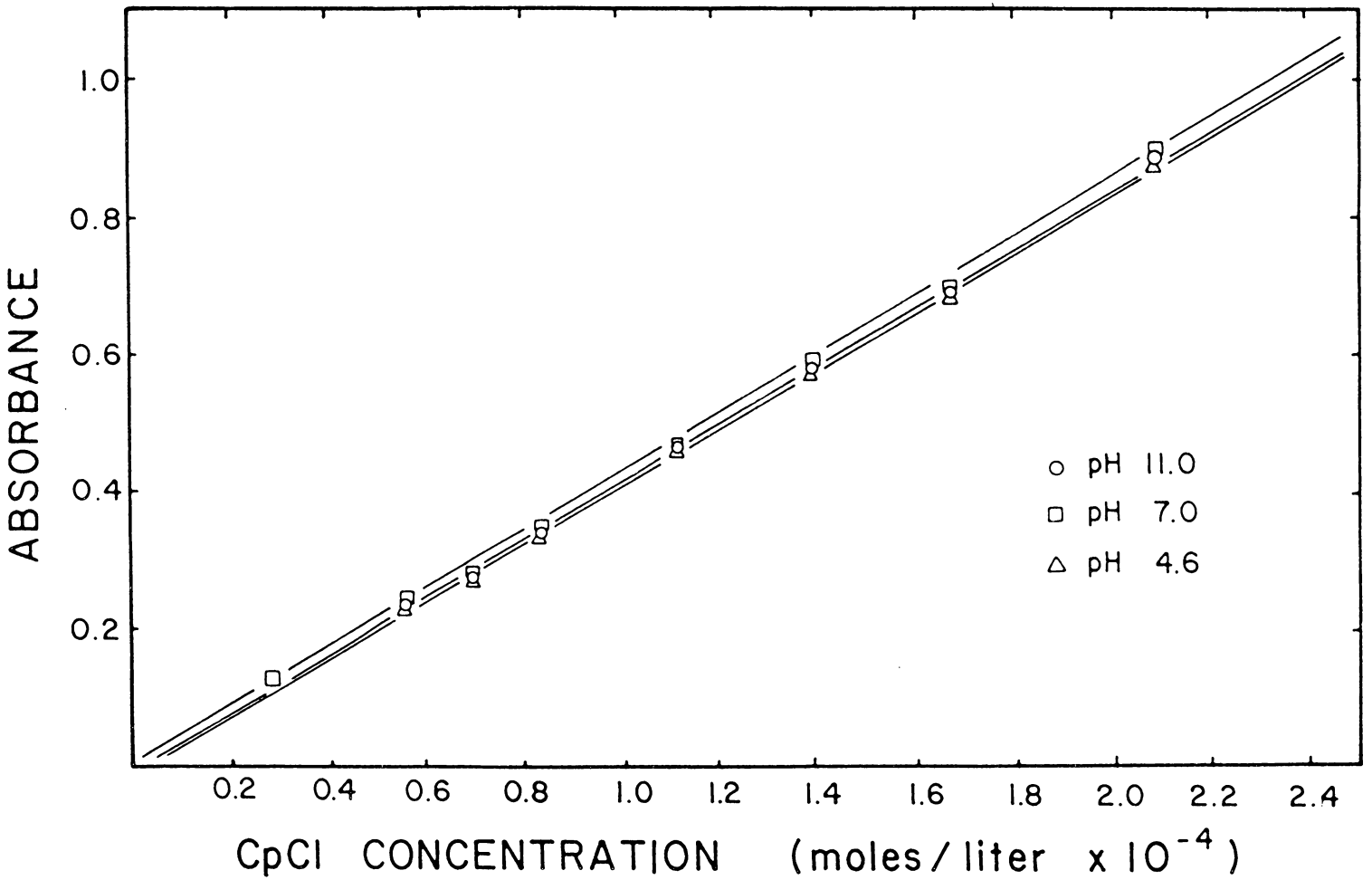

Figure 4 Calibration Curves for Determining the Concentration of Cetyl Pyridinium Ions Ions in Solution from Absorbance at 258nm.

Appendix III

Flotation Metallurgical Balance Sheets

0.48 lb/ton CpCl natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	13.2	13.2	29.42	29.42	93.4	93.4
2nd CLR Tail	1.6	14.8	4.41	26.71	1.7	95.1
1st CLR Tail	8.0	22.8	.99	17.63	1.9	97.0
Tail	77.2	100.0	.16	4.14	3.0	100.0
Feed	100.0		4.14		100.0	

0.48 lb/ton NaIpX natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	16.9	16.9	22.35	22.35	94.5	94.5
2nd CLR Tail	2.8	19.7	2.50	19.54	1.7	96.2
1st CLR Tail	10.4	30.1	.66	13.03	1.7	97.9
Tail	69.9	100.0	.12	4.00	2.1	100.0
Feed	100.0		4.00		100.0	

0.56 lb/ton CpCl natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	13.3	13.3	29.90	29.90	94.4	94.4
2nd CLR Tail	1.7	15.1	3.56	26.85	1.5	95.9
1st CLR Tail	8.5	23.6	.79	17.46	1.6	97.5
Tail	76.4	100.0	.14	4.22	2.5	100.0
Feed	100.0		4.22		100.0	

no collector natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	12.6	12.6	32.83	32.83	89.8	89.8
2nd CLR Tail	1.6	14.2	8.49	30.10	2.9	92.8
1st CLR Tail	6.3	20.6	2.01	21.44	2.8	95.5
Tail	79.4	100.0	.26	4.62	4.5	100.0
Feed	100.0		4.62		100.0	

0.06 lb/ton CpCl pH 6.0

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	6.6	6.6	22.52	22.52	79.2	79.2
3rd CLR Tail	2.6	9.1	4.37	17.41	6.0	85.2
2nd CLR Tail	5.0	14.1	1.85	11.92	4.9	90.1
1st CLR Tail	19.9	34.0	.53	5.26	5.6	95.8
Tail	66.0	100.0	.12	1.87	4.2	100.0
Feed	100.0		1.87		100.0	

0.06 lb/ton CpCl pH 9.5

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	8.7	8.7	18.93	18.93	86.2	86.2
3rd CLR Tail	1.1	9.8	2.89	17.13	1.7	87.9
2nd CLR Tail	2.3	12.1	1.83	14.19	2.2	90.1
1st CLR Tail	16.1	28.3	.68	6.49	5.7	95.9
Tail	71.7	100.0	.11	1.91	4.1	100.0
Feed	100.0		1.91		100.0	

0.06 lb/ton CpCl pH 10.5

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	10.9	10.9	14.18	14.18	80.5	80.5
3rd CLR Tail	9.6	20.5	.92	8.00	4.6	85.0
2nd CLR Tail	12.6	33.1	.68	5.21	4.4	89.5
1st CLR Tail	30.4	63.5	.50	2.96	7.9	97.3
Tail	36.5	100.0	.14	1.93	2.7	100.0
Feed	100.0		1.93		100.0	

0.02 lb/ton KAX natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	13.8	13.8	12.54	12.54	91.1	91.1
3rd CLR Tail	2.3	16.1	.92	10.87	1.1	92.2
2nd CLR Tail	4.0	20.1	.63	8.84	1.3	93.5
1st CLR Tail	18.9	39.0	.36	4.73	3.6	97.1
Tail	61.0	100.0	.09	1.90	2.9	100.0
Feed	100.0		1.90		100.0	

0.06 lb/ton KAX natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	12.3	12.3	14.21	14.21	90.0	90.0
3rd CLR Tail	3.2	15.5	.88	11.48	1.4	91.5
2nd CLR Tail	5.8	21.3	.67	8.55	2.0	93.5
1st CLR Tail	25.6	46.9	.29	4.04	3.8	97.3
Tail	53.1	100.0	.10	1.95	2.7	100.0
Feed	100.0		1.95		100.0	

0.10 lb/ton KAX natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	11.2	11.2	15.70	15.70	89.3	89.3
3rd CLR Tail	2.1	13.3	1.42	13.42	1.5	90.8
2nd CLR Tail	3.0	16.3	1.16	11.18	1.8	92.6
1st CLR Tail	21.5	37.8	.39	5.04	4.3	96.8
Tail	62.2	100.0	.10	1.97	3.2	100.0
Feed	100.0		1.97		100.0	

0.02 lb/ton CpCl natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	4.4	4.4	32.55	32.55	63.0	63.0
3rd CLR Tail	.9	5.3	7.23	28.04	3.0	66.1
2nd CLR Tail	2.4	7.7	4.49	20.72	4.8	70.8
1st CLR Tail	15.7	23.4	1.90	8.10	13.2	84.1
Tail	76.6	100.0	.47	2.26	15.9	100.0
Feed	100.0		2.26		100.0	

0.06 lb/ton CpCl natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	7.0	7.0	22.49	22.49	81.9	81.9
3rd CLR Tail	1.2	8.2	4.15	19.86	2.5	84.4
2nd CLR Tail	3.1	11.3	1.80	14.95	2.9	87.3
1st CLR Tail	17.5	28.8	.79	6.33	7.2	94.5
Tail	71.2	100.0	.15	1.93	5.5	100.0
Feed	100.0		1.93		100.0	

0.10 lb/ton CpCl natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	8.9	8.9	21.45	21.45	87.3	87.3
3rd CLR Tail	2.5	11.4	2.71	17.36	3.1	90.3
2nd CLR Tail	4.2	15.6	1.42	13.04	2.7	93.1
1st CLR Tail	17.8	33.4	.40	6.30	3.3	96.3
Tail	66.6	100.0	.12	2.19	3.7	100.0
Feed	100.0		2.19		100.0	

0.02 lb/ton NaIpX natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	6.1	6.1	22.40	22.40	71.9	71.9
2nd CLR Tail	1.8	7.9	2.44	17.95	2.2	74.2
1st CLR Tail	13.6	21.6	1.32	7.42	9.4	83.6
Tail	78.4	100.0	.40	1.91	16.4	100.0
Feed	100.0		1.91		100.0	

0.06 lb/ton NaIpX natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	7.3	7.3	21.22	21.22	82.5	82.5
2nd CLR Tail	2.9	10.2	2.31	15.91	3.5	86.1
1st CLR Tail	16.2	26.4	.89	6.68	7.7	93.7
Tail	73.6	100.0	.16	1.88	6.3	100.0
Feed	100.0		1.88		100.0	

0.10 lb/ton NaIpX natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	8.3	8.3	19.91	19.91	85.7	85.7
2nd CLR Tail	2.8	11.1	1.94	15.43	2.8	88.5
1st CLR Tail	14.3	25.4	.77	7.18	5.7	94.2
Tail	74.6	100.0	.15	1.93	5.8	100.0
Feed	100.0		1.93		100.0	

0.06 lb/ton DAHCl natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	13.8	13.8	12.36	12.36	85.8	85.8
3rd CLR Tail	3.2	17.0	.94	10.20	1.5	87.4
2nd CLR Tail	6.5	23.4	.49	7.52	1.6	89.0
1st CLR Tail	24.1	47.6	.45	3.93	5.5	94.4
Tail	52.4	100.0	.21	1.98	5.6	100.0
Feed	100.0		1.98		100.0	

0.06 lb/ton nDM natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	9.6	9.6	15.04	15.04	76.9	76.9
3rd CLR Tail	2.1	11.7	.65	12.45	.7	77.6
2nd CLR Tail	5.9	17.6	.49	8.43	1.5	79.2
1st CLR Tail	20.3	37.9	.54	4.20	5.9	85.1
Tail	62.1	100.0	.45	1.87	14.9	100.0
Feed	100.0		1.87		100.0	

0.06 lb/ton DpCl natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	6.9	6.9	21.00	21.00	73.7	73.7
3rd CLR Tail	5.0	11.9	1.53	12.77	3.9	77.7
2nd CLR Tail	1.7	13.6	3.87	11.63	3.4	81.1
1st CLR Tail	21.7	35.4	.78	4.97	8.7	89.8
Tail	64.6	100.0	.31	1.96	10.2	100.0
Feed	100.0		1.96		100.0	

0.06 lb/ton EpBr natural pH

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Cu Ind	Cum	DISTRIBUTION Ind	Cum
Concentrate	7.6	7.6	17.64	17.64	67.6	67.6
3rd CLR Tail	1.9	9.5	2.08	14.54	2.0	69.6
2nd CLR Tail	4.3	13.8	1.30	10.44	2.8	72.4
1st CLR Tail	21.2	35.0	.79	4.60	8.4	80.8
Tail	65.0	100.0	.59	1.99	19.2	100.0
Feed	100.0		1.99		100.0	

0.16 lb/ton CpCl 1.0 lb/ton $CuSO_4$ pH 10.5

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Zn Ind	Cum	DISTRIBUTION Ind	Cum
Cu Conc	7.1	-	8.78	-	10.4	-
Zn Conc	9.3	9.3	51.11	51.11	80.2	80.2
4th CLR Tail	0.4	9.7	4.77	49.03	0.4	80.6
3rd CLR Tail	0.9	10.6	8.31	45.46	1.3	81.9
2nd CLR Tail	2.7	13.3	1.31	36.83	0.6	82.5
1st CLR Tail	13.5	27.8	1.30	18.27	2.9	85.4
Tail	66.1	92.9	0.38	5.72	4.2	89.6
Feed	100.0		5.72		100.0	

0.16 lb/ton CpCl 1.5 lb/ton $CuSO_4$ pH 10.5

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Zn Ind	Cum	DISTRIBUTION Ind	Cum
Cu Conc	5.9	-	4.55	-	4.7	-
Zn Conc	12.4	12.4	39.32	39.32	86.9	86.9
3rd CLR Tail	1.6	14.0	10.03	36.10	0.8	87.7
2nd CLR Tail	4.3	18.3	2.16	28.11	1.2	88.9
1st CLR Tail	19.8	38.1	0.79	13.65	0.6	89.5
Tail	56.0	94.1	0.33	5.63	5.8	95.3
Feed	100.0		5.63		100.0	

0.16 lb/ton CpCl 2.5 lb/ton $CuSO_4$ pH 10.5

PRODUCT	WEIGHT PERCENTS		ASSAY, %Zn		DISTRIBUTION	
	Ind	Cum	Ind	Cum	Ind	Cum
Cu Conc	6.7	-	6.82	-	7.4	-
Zn Conc	9.6	9.6	54.84	54.84	85.3	85.3
4th CLR Tail	0.5	10.1	4.75	48.79	0.4	85.7
3rd CLR Tail	1.0	11.1	7.27	48.19	1.2	86.9
2nd CLR Tail	2.8	13.9	0.90	38.38	0.1	87.0
1st CLR Tail	20.7	34.6	0.81	15.31	2.7	89.7
Tail	58.7	92.3	0.30	5.69	2.9	92.6
Feed	100.0		5.69		100.0	

0.08 lb/ton CpCl 2.5 lb/ton $CuSO_4$ pH 10.5

PRODUCT	WEIGHT PERCENTS		ASSAY, %Zn		DISTRIBUTION	
	Ind	Cum	Ind	Cum	Ind	Cum
Cu Conc	8.4	-	8.67	-	12.7	-
Zn Conc	6.9	6.9	54.00	54.00	65.1	65.1
4th CLR Tail	0.7	7.6	27.56	51.56	3.4	68.5
3rd CLR Tail	1.2	8.8	16.24	46.75	3.4	71.9
2nd CLR Tail	2.2	11.0	9.39	39.28	3.6	75.5
1st CLR Tail	11.9	22.9	2.91	20.38	6.0	81.5
Tail	68.7	91.6	0.48	5.45	5.8	87.3
Feed	100.0		5.45		100.0	

0.24 lb/ton CpCl 2.5 lb/ton $CuSO_4$ pH 10.5

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAYS, %Zn Ind	Cum	DISTRIBUTION Ind	Cum
Cu Conc	6.8	-	6.58	-	7.3	-
Zn Conc	9.9	9.9	48.28	48.28	82.8	82.8
4th CLR Tail	0.7	10.6	8.49	45.65	1.0	83.8
3rd CLR Tail	1.2	11.8	4.84	41.50	1.0	84.8
2nd CLR Tail	3.4	15.2	2.67	32.62	1.1	86.3
1st CLR Tail	17.3	32.5	0.91	15.74	2.7	89.0
Tail	60.7	93.2	0.35	5.62	3.7	92.7
Feed	100.0		5.62		100.0	

0.08 lb/ton CpCl 2.5 lb/ton $CuSO_4$ pH 10.5

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAYS, %Zn Ind	Cum	DISTRIBUTION Ind	Cum
Cu Conc	7.4	-	5.48	-	7.32	-
Zn Conc	8.8	8.8	47.00	47.00	74.71	74.71
4th CLR Tail	0.7	9.5	15.93	44.71	2.01	76.72
3rd CLR Tail	1.3	10.8	10.05	40.54	2.36	79.08
2nd CLR Tail	3.1	13.9	4.88	32.59	2.73	81.81
1st CLR Tail	16.2	30.1	1.78	16.01	5.21	87.02
Tail	62.5	92.6	0.05	5.54	5.66	92.68
Feed	100.0		5.54		100.00	

0.24 lb/ton NaIpX 2.5 lb/ton $CuSO_4$ pH 10.5

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Zn Ind	Cum	DISTRIBUTION Ind	Cum
Cu Conc	5.5	-	4.56	-	6.2	-
Zn Conc	10.1	10.1	30.76	30.76	76.9	76.9
4th CLR Tail	1.1	11.2	8.83	28.04	2.4	79.3
3rd CLR Tail	2.2	13.4	4.95	24.25	2.7	82.0
2nd CLR Tail	4.2	17.7	2.34	18.92	2.4	84.4
1st CLR Tail	16.6	34.3	1.03	10.20	4.2	88.6
Tail	60.2	94.5	0.34	5.00	5.2	93.8
Feed	100.0		5.00		100.0	

0.16 lb/ton NaIpX 2.5 lb/ton $CuSO_4$ pH 10.5

PRODUCT	WEIGHT PERCENTS Ind	Cum	ASSAY, %Zn Ind	Cum	DISTRIBUTION Ind	Cum
Cu Conc	7.9	-	6.31	-	12.4	-
Zn Conc	8.5	8.5	**33.30**	33.00	70.2	70.2
4th CLR Tail	0.9	9.4	9.04	30.98	2.0	72.2
3rd CLR Tail	1.5	10.9	4.53	27.34	1.7	73.9
2nd CLR Tail	3.9	14.8	3.16	20.97	3.1	77.0
1st CLR Tail	18.8	33.6	1.17	9.89	5.5	82.5
Tail	58.5	92.1	0.36	4.84	5.1	87.6
Feed	100.0		4.84		100.0	

Appendix IV

Assaying Procedure

All glassware used throughout sample assaying procedures was cleaned in Micro cleaning solution, thoroughly rinsed with tap water and finally rinsed with distilled water.

One-half to two grams of each flotation product, depending on the expected metal content, was riffled out and accurately weighed in seperate 150ml beakers. Ten ml each of concentrated HCl and HNO_3 was added to each beaker and placed on a hotplate. A watchglass was placed on each beaker to reflux the evaporated solution and continually wash down the sides of the beaker . Sufficient heat was applied to maintain a slight boiling condition and the samples were evaporated almost to dryness. The sides of each beaker were rinsed with hot double distilled water to prevent precipitation of metal ions.

The samples were then allowed to cool and filtered through Whatman number 2 filter paper into appropriate volumetric flasks. The remaining volumes were filled with double distilled water. Samples were further diluted according to their respective metal concentrations to fit within the range of calibration standards.

The metal content of each sample was determined with a Spectraspan IV Plasma Emission Spectrometer. The wavelenghts used for each metal were as follows:

Cu 3247.54 Angstroms

Zn 2025.51 Angstroms.

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FLOTATION OF SULFIDE MINERALS WITH ALKYL PYRIDINIUM SALTS

by

John George Groppo, Jr.

(ABSTRACT)

Long chain alkyl pyridinium salts have been used as collectors for the flotation of chalcopyrite and copper-activeted sphalerite. For the ores tested in this study, these reagents have demonstrated improved selectivity and recovery in comparison to conventional xanthates. The best flotation results, in terms of both grade and recovery, were achieved with cetyl pyridinium chloride (CpCl). A distinct advantage of using CpCl instead of a conventional xanthate, such as sodium isopropyl xanthate (NaIpX), is that the kinetics of flotation are much faster. This may be explained by the reduction in the negative ζ-potential of the sulfide mineral upon adsorption of cetyl pyridinium ions, which, in turn, minimizes the electrostatic component of the disjoining pressure of the wetting film.

CpCl has also demonstrated a remarkable selectivity despite the fact that both chalcopyrite and the silicious gangue minerals present in the ore are negatively charged. This may be explained by the premise that cetyl pyridinium

ions adsorb more strongly on chalcopyrite than on the gangue. Analysis of the adsorption isotherms established for chalcopyrite and quartz supports this view. Several possible mechanisms have been suggested to explain the 'high affinity' type of adsorption observed in the CpCl-chalcopyrite system.