THE SURFACE CHEMISTRY OF FLOTATION

by

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CHAPTER I

HISTORICAL AND INTRODUCTORY

Flotation is a process of ore concentration in which the ore minerals are separated into two or more products. One product, usually containing worthless minerals, is termed tailings; the other products, containing the valuable minerals in a more concentrated state, are termed concentrates.

In modern flotation, air is generated in, or introduced into a pulp of finely-ground ore suspended in water, which contains small amounts of various reagents. Because of the presence of froth-forming reagents, a zone of rising froth forms at the upper surface of the pulp, and flows over the lip of the containing vessel. The minerals in the ore-pulp are mechanically carried into this froth zone to a greater or less extent. Certain minerals show a greater tendency than others to be carried into the froth by the air bubbles rising through the pulp; and, once in the froth, to rise with it. These minerals eventually reach the upper surface of the froth, overflow with it, and are removed as concentrate. Other minerals either do not enter the froth; or, if they do enter, tend to settle out and fall back into the pulp. To do this, their effective downward velocity in the froth must be greater than the effective upward velocity with which the froth is rising. These minerals eventually remain

suspended in the pulp and are removed as tailings. The density of a given mineral does not determine whether the mineral will become concentrate or tailing.

Early flotation processes, which have become obsolete, are bulk-oil flotation, and skin-flotation.

The first practical process of flotation was the bulk-oil process, introduced by William Haynes in 1860 (Brit. Pat. 488/1860) and modified by Carrie J. Everson (U.S.Pat. 348,157 --1885). The Elmore process, typical of bulk-oil flotation, consisted in treating ore with water and large quantities of oil; selective adsorption of certain minerals in the oil phase, or at the oil-water interface; and removal of the mineral-containing oil after it had risen to the surface of the water.

Skin-flotation consisted of retention of selected mineral particles in a thin layer at a free water surface. Apparatus for this process is described by Macquisten (U.S.Pat. 865,194-5/1907) and Wood (U.S.Pat. 1,088,050/1915) (28.6.1)

Gas as a buoyant medium was introduced by Delprat in 1902 (U.S.Pat 735,071/1903; Brit.Pat. 26,279/1902) and by Potter in 1904 (U.S.Pat. 776,145/1904). The Potter-Delprat Process involved chemical generation of gas by the reaction of acid with sulfides and carbonates contained in the ore. This process marks the beginning of froth flotation as now practiced.

Air was first introduced directly into the pulp by

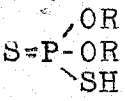
Sulman, Picard and Ballot in 1906 (U.S.Pat. 835,120/1906). With the use of air instead of oil as a buoyant medium, it was found that the quantity of oil could be materially reduced without affecting performance.

In 1909 Greenway, Sulman and Higgins (U.S.Pat. 962,678/1909) recommended the use of soluble frothing agents, such as pine oil. The quantities of such agents which were required, were of the order of less than one pound per ton of ore. This patent marks the recognition of frothing agents; although the frothers used also had collecting power, as defined below.

During the period from 1915 to 1922, certain non-frothing reagents, having the property of collecting desired minerals into the froth, were introduced.

In 1921, Perkins (U.S.Pat 1,364,304/1921) differentiated between the frothing and the collecting functions of a reagent. He showed that certain non-oleaginous organic compounds, containing trivalent nitrogen or divalent sulfur, specifically thiocarbanilid, or other thioamido, or thiourea compounds, had the property of increasing the tendency of a mineral to adhere to the air phase, and be collected in the froth. Compounds which have this property are now termed collectors. The action by which the air-adhering tendency is increased, is termed collection. The compounds introduced by Perkins had no frothing properties, and were designed to be used in conjunction with known reagents which would cause a froth to form.

Xanthates as collectors were patented in 1925 by Keller (U.S.Pat. 1,554,216/1925; Can.Pat. 247,547/1925), and dithiophosphates of the type formula:



R = hydrocarbon group

prepared from phosphorus pentasulfide and cresylic acid, were patented in 1926 by Whitworth (U.S.Pat. 1,593,232/1926)

The patent of Perkins in 1921 marks the beginning of a new flotation technique, which has been termed "chemical flotation", in contrast to the older "oil flotation".

This brief survey has indicated the stages in the development of frothing and collection, as practiced in modern flotation. Mention must be made, also, of the development of two other phases of flotation. These are activation and depression.

Activation of a specific mineral, or minerals, is accomplished by adding to the ore-pulp a reagent, termed an activator, which will cause the mineral, otherwise unaffected by a collector, to be collected into the froth. Depression is accomplished by adding a reagent, termed a depressor, which will cause the mineral, normally collected, to be depressed; that is, unaffected by the collector.

Schwarz in 1906 (U.S.Pat 807,501/1906) introduced alkali sulfides or polysulfides as activators for oxidized ores.

Copper sulfate, the most common activator for sphalerite, was discovered by Bradford in 1913.

Dichromates, as depressors for galena, were suggested by Lowry and Greenway in 1912 (Austral. Pat. 5,065/1912)

Oil flotation was usually carried out in an acid circuit, but with the advent of chemical flotation about 1921, alkaline circuits soon became common practice. The use of alkaline circuits led to the discovery of the depressing effect of lime on pyrite, and of cyanide on sphalerite by Sheridan and Griswold (U.S.Pats. 1,421,585/1922; 1,427,235/1922)

CHAPTER II

AN ANNOTATED BIBLIOGRAPHY OF EXPERIMENTAL AND THEORETICAL INVESTIGATIONS IN THE PHYSICAL CHEMISTRY OF FLOTATION

INTRODUCTORY

Flotation has developed largely as an art. Discoveries, in many cases, have been the result of trial and error. Until about 1928, very little fundamental experimental work was done, although several theories were advanced. Much of the experimental work carried on since has dealt with the extremely complex systems existing in a flotation cell treating natural ores. While such work has given definite information regarding treatment methods for a specific ore, it has thrown little light on the fundamental reactions taking place. Early experimenters often failed to realize the delicate nature of the reactions they dealt with, and the profound effect on flotation performance of almost intangible amounts of reagents. The fact that as small a quantity as 0.002 mgm. of potassium cyanide is sufficient to prevent a 6 sq. cm. area of pyrite from being floated; and a comparable amount of copper sulfate will cause sphalerite, otherwise unfloatable, to be floated; emphasize the necessity for extreme care in investigating the phenomena of flotation.

These facts must be carried in mind when considering the following experimental work, and the conclusions based upon it. This work is considered as it relates to the study of four fundamental chemical operations: froth formation, collection, depression, and activation.

FROTH FORMATION

A froth is a dispersion of a gas in a liquid, which forms when the gas-bubble walls are made capable of withstanding stresses. They are in this condition when the surface-tension of the liquid-gas interface, forming the bubble wall is capable of rapid change. If a capillary active substance is dissolved in water it will tend to concentrate in the froth (03.8.1) at the air-water interface, in agreement with the Gibb's equation relating the amount of adsorption of a substance at an interface to its effect on surface tension. If a film of such a solution is stretched, the concentration of the substance in the surface is decreased, and the surface tension of the film necessarily increases; thus setting up a force which will oppose the stretching force.

Frothing agents, as used in flotation, are capillary active substances which stabilize a froth in this way.

Langmuir's work (16.25.2)(~~17.25.2~~) suggests that oriented adsorption of a monomolecular film of a heteropolar frother such as amyl alcohol, will occur at the air-water interface, in such a way that the non-polar hydrocarbon group is oriented towards the gas phase.

Taggart and Gaudin (22.3.1) note the heteropolar character of molecules of the frothers used in flotation. Bartsch (24.25.1)(24.25.2) finds that hydrocarbons, chloroform, carbon tetrachloride and carbon disulfide have little

or no frothing, or foam stabilizing ability; but organic acids, alcohols, amines, aldehydes, ketones, etc. aid in the production and stability of foams. Each reagent has an optimum concentration for greatest foam stability. He notes that minerals also exert a stabilizing effect.

As a result of a statistical study of a large number of organic compounds, in which both the frothing effect, measured by a special apparatus, and flotation performance, are correlated to structure, Taggart, Taylor and Ince (30.3.3) state that the molecule of a non-collecting frother should contain one (and preferably one only) oxygen-bearing, water-avid group, such as:

$$-OH \qquad -\overset{\overset{O}{\|}}{C}-OH \qquad =C=O$$

at least a six carbon-atom chain, attached to the above group; and that the compound should have a solubility in water of about 1 gm. per litre.

Because the solubility of the compounds studied decreases with 'hydrocarbon loading', they suggest the hydrocarbon group is hydrophobic, while the rest of the molecule is hydrophilic, in line with Langmuir's treatment of partial solubility.

Frothing of solutions of an homologous series increases to a certain point, then decreases with increasing molecular weight; presumably because of the decreasing solubility of the higher members.

Gaudin (32.25.5) states that the presence in a frother of ionizable polar groups such as $-COOH$ or $-NH_2$ will

cause it to have collecting tendencies.

The modern conceptions of frothing have been summarized by del Giudice (34.6.3)

A device for testing the frothing properties of flotation reagents is described by Christmann (U.S.Pat. 1,866,296) 1932).

In practice, pine oil or cresylic acid are almost exclusively used as frothing agents. Little attention was paid to the development of new frothers until the work of Dean and Hersberger (35.3.1). They state that the ideal frother, in low concentrations, should form a copious but not too persistent froth; the froth should be independent of pH, added salts, and added collectors; and the frother should be non-collecting, but should emulsify and disperse insoluble collecting agents. By balancing polar and non-polar groups, and making use of the fact that a complex polar group will allow long chain hydrocarbon groups to be used without decreasing the solubility of the compound too greatly, they propose a list of compounds which should conform to the specified characteristics.

Recent frother patents are reviewed by Bassett (38.4.1)

COLLECTION

Definition of a Collector

Collectors are reagents, invariably organic, which react with a mineral in such a way that its tendency to adhere to air, in preference to water; hence its tendency to float, is increased.

Examples of Collectors

Examples of such reagents, commonly used, are:

Xanthates $S{:}C\begin{smallmatrix}\diagup OR\\ \diagdown SX\end{smallmatrix}$ R usually = C_2H_5, C_3H_7, C_4H_9, etc. X = Na or K

Dithiophosphates $S{:}P\begin{smallmatrix}\diagup OR\\ -OR\\ \diagdown SX\end{smallmatrix}$ R is usually $C_6H_4.CH_3$

Thiocarbanilid $S{:}C\begin{smallmatrix}\diagup NH.C_6H_5\\ \diagdown NH.C_6H_5\end{smallmatrix}$

Diazoaminobenzene $C_6H_5N{:}N.NH.C_6H_5$

Trimethylcetyl ammonium bromide $\begin{smallmatrix}CH_3\diagdown\\ CH_3\text{-}N\diagup\\ CH_3\diagup\end{smallmatrix}\begin{smallmatrix}\diagdown C_{16}H_{33}\\ \diagdown Br\end{smallmatrix}$

Structure of Collectors

The heteropolar nature of collector molecules was early recognized (24.3.1)(28.3.1). Taggart, Taylor and Ince (30.3.3), from a statistical study of the collecting index (an arbitrary measure of collecting effect, dependent on contact angle measurements) for a large number of organic compounds, reach the conclusion that the effectiveness of

a compound as a collector depends on the hydrocarbon group present in the molecule. From studies of the abstraction of a collector from solution by a mineral, they show that abstraction is dependent on the presence of a :S or similar group. They state that non-frothing collector molecules must contain divalent sulfur, trivalent nitrogen, or other multivalent negative element in the low valent state, and must have a hydrocarbon complex with 8 or more carbon atoms. The compound should have a solubility of 200 to 300 mgm. per litre in water, and probably possess the ability to form relatively insoluble base metal salts.

Preparation and Purification of Collectors and their Compounds

The methods of Foster (28.19.2) for the preparation of xanthates and other trithiocarbonates have been quoted by Gaudin (32.25.5). Foster's method has been modified by De Witt and Roper (32.1.1) in their preparation of a highly purified potassium ethyl xanthate.

Gaudin and Schumann (36.8.3) give methods for the preparation and purification of potassium n-amyl xanthate and cuprous n-amyl xanthate.

Chemical Reactions of Collectors

A study of the solubility and kinetics of decomposition of xanthic acids in water shows that decomposition is accelerated by hydrogen ions, and retarded by sulfate ions (18.25.1)

The kinetics of decomposition in organic liquids has also been studied (13.25.1). The decomposition is accelerated in liquids containing ·OH groups.

Alkali xanthates decompose in acid solution to form carbon disulfide and alcohol. If, however, the pH is not below 5, and the temperature is less than 5° C. (13.25.1), the stable, water-insoluble xanthic acid is formed.

In 1 to 2 normal alkaline solution, xanthate ion is decomposed (08.25.1), as evidenced by the composition of the insoluble cuprous salts precipitated from such a solution. It is probable that mono-, di-, or trithiocarbonates are formed. Taylor and Knoll (34.3.7) consider the most probable decomposition products of an aqueous solution of an alkali xanthate are either dixanthogen[1], or carbon disulfide and alcohol.

De Witt and Roper (32.1.1) state that the hydroxyl ion derived from hydrolysis cannot account for the observed pH change in solutions of potassium ethyl xanthate. Schaum, Siedler and Wagner (32.12.3) note very slight hydrolysis of 0.01 normal xanthate solutions at room temperature. The hydrolysis increases autocatalytically after 20 hours. They consider xanthates, at the concentrations used in flotation, are completely dissociated.

Taylor and Knoll investigated the stability of potassium ethyl xanthate solutions (34.3.7), and find that a

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1. Dixanthogen = $\left(S{:}C{<}^{OR}_{S}\right)_2$

water solution has a pH of 7.2. Conductivity measurements indicate ethyl xanthic acid is a strong acid.

Sodium or potassium ethyl xanthate, from a solution containing cupric ions, precipitates yellow cuprous xanthate[2] (1835.25.1)(08.25.2)(10.25.1)(31.1.1), and from a solution containing lead ions, precipitates white lead xanthate (34.3.7) as determined by analyzing the precipitates for base metals.

Taggart, del Giudice and Ziehl (34.3.6) state that ferrous salts, with xanthate ion, on oxidation, form a precipitate which is probably dixanthogen and ferric xanthate; that ferric salts, with ethyl xanthate ion, form ferric ethyl xanthate, as determined by analysis. They give a table of the reactions of collectors with heavy metal ions.

Physical Properties of Collectors and their Compounds

The solubility in water at 0° C. of sodium methyl and ethyl xanthates is reported to be 0.05 and 0.02 mol. per litre, respectively (18.25.1)

The surface tension of aqueous solutions of potassium ethyl xanthate has been measured by De Witt and associates (32.1.1)(35.1.1) who note that solutions of the isomeric forms of potassium ethyl xanthate have different surface tensions.

Taggart and co-workers mention the solubility of zinc ethyl xanthate is about 335 mgm. per litre (30.3.1); that of

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2. $2Cu^{++} + 4\left(S{:}C\begin{smallmatrix}\diagup OC_2H_5\\ \diagdown S\end{smallmatrix}\right)^{-} \rightarrow S{:}C\begin{smallmatrix}\diagup OC_2H_5\\ \diagdown SCu\end{smallmatrix} + \left(S{:}C\begin{smallmatrix}\diagup OC_2H_5\\ \diagdown S\end{smallmatrix}\right)_2$

lead ethyl xanthate is 0.2 mgm. per litre (32.8.1).

Weinig and Palmer (29.25.4) state that xanthates are more soluble than the corresponding sulfides.

Brighton, Burgener and Gross (32.6.2) find that the solubility of cupric and zinc n-amyl, and cupric ethyl xanthates is increased by increase in sodium cyanide concentration. They report the solubility in water of zinc n-amyl xanthate as 80 mgm. per litre; lead n-amyl xanthate as 30 mgm. per litre. They were unable, using colorimetric methods, to determine copper xanthates in water, or lead xanthate in sodium cyanide solution.

The relative solubilities of various metallic xanthates in water have been determined by Warren (33.5.1).

Gaudin (34.3.5A) gives solubilities for cuprous n-amyl xanthate in various organic solvents, as follows: acetone 16, diethyl ether 15, carbon disulfide 7.3, benzene 388, petroleum ether less than 1 mgm. per litre.

EFFECT OF VARIOUS REAGENTS ON RECOVERY IN FLOTATION TESTS AND PRACTICE

Small Scale Flotation Tests

The small scale flotation test is probably the oldest experimental technique used in studying flotation phenomena. Various devices have been described for this work; many manufacturers market miniature cells, taking a charge of 500 or 1000 grams, which are miniatures of their plant units. A 50 gram agitation type cell, with automatic froth overflow is described by Gates and Jacobsen (25.6.1), and has been modified by Hansen (32.6.5). This cell has received wide acceptance for use in experimental work.

A flotation test is usually carried out as follows: A weighed amount of ore is crushed to 4 to 20 mesh, and ground with water and certain reagents in a laboratory ball mill. The pulp is then transferred to the flotation cell, and water is added to give the desired ratio of ore to water. Frothing and other reagents may now be added, and the cell set in operation. The mineral rising into the froth is scraped off, or overflows, and is recovered as concentrate. Tailings and concentrate pulps are filtered, and their solid content dried, weighed, and assayed for various metals. The recovery of a given metal is reported as the percentage of that metal present in the charge, which is recovered in the concentrate.

More complete details of flotation testing methods and apparatus are described by Dietrich, Engel and Guggenheim (37.13.2).

For the results of flotation tests on a wide variety of natural ores, reference should be made to the publications "Investigations in Ore Dressing and Metallurgy" published annually by the Department of Mines, Ottawa, Canada.

Floatability of Pure Minerals (Inherent Floatability)

Although it has been shown repeatedly that clean minerals do not make contact with an air bubble under static conditions, it has not been conclusively demonstrated that minerals, under actual flotation conditions, have no inherent floatability. The conflicting conclusions reached by various workers depend, in part, therefore, upon their experimental approach to the subject of inherent floatability.

Investigators who have measured the contact angles developed by an air bubble on a mineral surface (30.3.1) (33.8.2)(34.3.2)(34.3.6) agree that no contact is developed if the mineral surface is clean.

Gaudin, (32.25.5), summing up the results attained in actual flotation practice, and in small scale tests, gives a table of inherent floatabilities of pure minerals. He considers that metals are the most floatable; then, in order of decreasing floatability: intermetallic compounds; sulfides of metals nearest sulfur in the periodic table; sulfides of metals furthest from sulfur in the periodic table; non-acid-

forming oxides of the metals nearest to the dividing line between metals and metalloids in the periodic table; and that the least floatable compounds are compound oxides, and oxides of the metals far removed from the dividing line between metals and non-metals in the periodic table. He states that graphite and sulfur have inherent floatability, and xanthates do not function as collectors with these minerals. Rey (35.17.1) substantially agrees with Gaudin in contending that sulfur, graphite, talc, and molybdenite will attach to an air bubble in the absence of any organic reagent.

Ravitz and Porter (34.3.1) report that they were able to float pure, unoxidized galena in a nitrogen atmosphere, in the absence of reagents, thus supporting the idea of inherent floatability. They state that air will displace water from a pure galena surface, in direct contradiction to the work of Taggart (30.3.1) and Wark and Cox (34.3.2)

Effect of Various Reagents on the Recovery of Minerals in the Presence of a Collector

Galena

Galena, when pure and unoxidized, according to Gaudin, (32.25.5) floats readily without a collector; a frother only being required. If the galena is oxidized, increasing amounts of collector are required to produce the same recovery, depending on the extent of oxidation. These observations are confirmed by other workers (34.3.1)

Kellermann and Bender (30.12.2) note that fresh xan-

thate solution barely floats galena, but becomes effective on standing, or on treatment with sulfuric acid, and conclude that flotation is effected by xanthate hydrolysis products.

Flotation tests made in a 50 gram cell (25.6.1) in the laboratories of the American Cyanamid Company (27.2.1) showed that pure, dry-ground galena gave equal recoveries with pine-oil and potassium ethyl xanthate; and with phosphocresylic reagent[1], but poorer recoveries with thiocarbanilid o-toluidine mixture (TT mixture), for the same reagent concentration.

Pyrite

Equal recoveries of pure pyrite are obtained with pine-oil-potassium ethyl xanthate, phosphocresylic reagent, and TT mixture, in the pH range 5.0 to 5.2 (27.2.1).

Gaudin (32.25.5) notes a poor recovery of pure pyrite with methyl quinoline, but better recovery of pyrite than chalcocite, when both minerals are present; due presumably to the activation of pyrite by copper ions derived from the chalcocite.

Pure, clean pyrite is easily floated, and oxidation inhibits flotation, according to Gaudin et al (28.19.1--Part 2). Gaudin notes, further (32.25.5) that pyrite is floated more readily by higher xanthates than by lower; and more readily by xanthates than by mercaptans. Using amyl xanthate as collector, Gaudin (29.10.1) found that the re-

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1. Probably $S{:}P\begin{matrix}O.C_6H_4.CH_3\\ O.C_6H_4.CH_3\\ SH\end{matrix}$

covery of pyrite was zero if the pH was above a critical value between 6.4 and 7.0.

Sphalerite

Most workers agree that potassium ethyl xanthate does not collect sphalerite until the mineral has been activated, by copper sulfate, for example (28.19.1)(30.3.5). Results of Buchanan and Christmann (27.2.1), who find high recoveries of pure sphalerite with various collectors, including potassium ethyl xanthate, are explained by assuming traces of copper sulfate were present while the tests were made.

Gaudin (32.25.5) considers pure sphalerite is one of the most difficult sulfides to float, and states that collectors with less than five carbon atoms in their hydrocarbon chain do not collect sphalerite, unless used in large amounts. The following list of collectors for pure sphalerite is given: di-iso-amyl ammonium di-iso amyl dithiocarbamate; xanthates higher than hexyl xanthate; trithiocarbonates higher than propyl trithiocarbonate; certain amines such as monoisoamylamine; and certain hydrazines such as phenylhydrazine.

Sphalerite recovery is an optimum at a certain pH for each collector studied (28.19.1). This has been explained (32.8.1) by assuming that the maximum recovery zones correspond to pH bands of maximum reaction velocity between collector and mineral.

Kraeber (30.25.2) finds that maximum recovery is attained at pH 6 to 7; and that the optimum pH decreases as

the iron content of the sphalerite increases.

Flotation tests made by Yamada and Naganuma (36.25.7) indicate that sphalerite is not floated at a pH above 7.6.

Chalcocite

Flotation tests made by Gaudin and Sorenson (28.19.1) show that the activity of collectors for chalcocite increases as the non-polar part of the molecule is made more complex, and that aliphatic sulfides and disulfides are more active than aromatic sulfides and disulfides, but that the converse is true for the hydrosulfides.

De Witt, Makens and Helz (35.1.1) correlate the surface tension of normal xanthate solutions, from ethyl to heptyl , to their collector activity, as referred to chalcocite and malachite.

Gaudin mentions methyl quinoline (32.25.5) and mono-isoamylamine (29.10.1) as collectors for chalcocite

Chalcopyrite

Gaudin (32.25.5) states pure chalcopyrite, if unoxidized, is readily floated, with a frother only.

The recovery of chalcopyrite decreases from 96% to 84.4% through the pH range 10.42 to 11.76, according to Yamada and associates (36.25.6)

Miscellaneous Sulfide Minerals

Yamada and associates (34.25.5) find that complete flotation of pyrrhotite is possible with camphor blue oil and coal tar in the pH range 4.6 to 5; but that floatability is negligible at a pH greater than 5.

Recent tests made by the same authors show that the recovery of arsenopyrite is decreased from 88% at a pH below 5 to zero above pH 5 (36.25.1); that enargite gives low recoveries above pH 6 (36.25.2); and that the optimum recovery of stibnite is attained in the pH range 4 to 6.5 (37.25.3). The recovery of marmatite is decreased from over 60% to 2% as the pH is increased from 5.7 to 12 (37.25.2)

Oxidized Minerals

The oxidized minerals which are considered, in particular, are azurite and malachite (basic copper carbonates), cerussite (lead carbonate) and anglesite (lead sulfate). In general, oxidized minerals are less readily floated than the sulfides.

Malachite and azurite (32.25.5) are collected by higher fatty acids and soaps, which separate the minerals from quartz, but not from calcite.

There is an optimum pH (28.19.1--T.P.9) for the flotation of cerussite, of 9.0 with potassium amyl xanthate, and 7.8 with thiocresol. Gaudin (32.25.5) states that cerussite and anglesite are floated by soaps; and may be separated from a siliceous gangue by fatty acids. Cerussite is collected by thionaphthol and by amyl xanthate, but not by methyl xanthate.

Plumbojarosite (32.25.5) can not be sulfidized, is not collected by ethyl or amyl xanthates, but is collected by n-octyl and n-lauryl xanthates if these reagents are used in large amounts.

Non-metallic minerals

Graphite and sulfur are readily floated. An instance is reported (24.19.1) of the flotation of sulfur with amyl alcohol as the only reagent. Gaudin (32.25.5) does not believe that xanthates exert any collecting action on sulfur or graphite. The recovery of sulfur is affected by the pH (30.6.1). A pH of 7.5 to 8.0 has been suggested as an optimum range.

In contrast to the view that graphite has inherent flotability is that of Wark and Cox (35.8.1) who find that a high concentration of frother (which has graphite collecting power) is required to float graphite. They note that certain frothers are ineffective as collectors, and conclude that graphite requires a collector, such as a xanthate, for flotation. Confirmatory work (37.8.1) in which it is found that amyl and ethyl xanthates increase the floatability of charcoal, leads Wark and Cox to conclude that the flotation of graphite, obtained in their previous work, was not due to metallic impurities in the graphite.

Although sulfur usually floats without a collector, Wark and Cox (35.8.1) show that the presence of a collector enhances its flotation.

Berl and associates (23.23.1)(24.12.1)(24.12.2)(24.12.3) have studied the flotation of various minerals, particularly artificially prepared silica, by the use of dyes, which, by adsorption on specific minerals, make them hydrophobic and cause the mineral to float.

The effect of soluble metal salts on quartz flotation has been investigated by Kraeber and Boppel (34.9.1), who advance the theory that a complex is formed between the salt cation and the oxygen of the mineral surface, and that the character of the complex and its flotation effect depend on the pH of the salt solution.

The flotation of non-metallics, particularly with regard to past and present practice, is extensively reviewed by Ralston (37.5.1). A bibliography containing 126 references to this phase of flotation is appended.

Specific Effects of Collectors on Minerals

Gaudin (34.3.5A) recapitulates the known effects of xanthates in increasing the floatability of minerals, as follows: They are without effect on silicates, silica and gangues generally; in small amount they increase the floatability of copper, lead, silver, iron, and mercury sulfides, and of elemental copper, silver and gold. They increase the floatability of zinc sulfides only when the mineral is first activated, as by copper sulfate. In large amounts they increase the floatability of oxidized lead and copper minerals; and of oxidized zinc minerals only when the xanthate contains a long-chain hydrocarbon group. Iron oxides and carbonates are not floated by xanthates. Sulfides of not typically metallic elements (stibnite, realgar, molybdenite) are not made to float markedly better by xanthate treatment.

Gaudin (32.25.5) notes the selective action of certain collectors for specific minerals, and gives the following list: Soaps collect the minerals of all di- and tri-valent metals, and minerals of certain monovalent metals such as silver. The lower xanthates collect copper, lead, iron, silver and mercury sulfides to the exclusion of the sulfides of zinc, calcium, barium and aluminium. Xanthates collect lead minerals in preference to copper or mercury minerals. Substituted dithiophosphates select copper minerals. Aliphatic mercaptans select copper, silver and mercury minerals.

Influence of Temperature on Floatability

Huber-Panu (31.9.1) states that each ore and method has an optimum flotation temperature between 23° and 40° C. As the temperature is increased the time of flotation is decreased, and the total recovery is increased up to a certain point. It is supposed that the decrease in recovery above this point is due to increased oxidation of the mineral, and increased solubility of the compounds formed at the mineral surface.

EXPERIMENTAL EVIDENCE FOR THE REACTION OF COLLECTORS WITH MINERALS

Changes in a Collector Solution in Contact with a Mineral

Considerable study has been made of the changes in a collector solution when it is brought into contact with a mineral. Experimental methods usually consist in agitating the solution with a known weight of sized mineral, for a given time, and determining, by analytical methods or surface tension measurements, any changes resulting in the collector solution. If a change in concentration of collector results, the collector is said to be abstracted by the mineral.

Abstraction, in general.

The first work dealing with abstraction of flotation reagents by minerals was probably that of Fahrenwald (21.25.1) who found, by measuring the surface tension of an oil-water emulsion or solution before and after bringing it into contact with minerals, that all minerals investigated abstracted oil from the emulsion or solution; that sulfides abstracted more than gangue minerals; and that, in general, the floatability of a treated mineral was proportional to the amount of oil abstracted. He noted that electrolytes affect the amount of oil abstracted. Taggart and Gaudin (22.3.1) made a similar study with confirmatory results.

Other workers (33.8.3)(32.8.1) have noted a close connection between the abstraction of a soluble collector by a mineral and the solubility of the salt of the collector and the metal contained in the mineral. When the metal salt is relatively soluble, concentrated collector solutions and long treatment are necessary to effect abstraction.

Rimskaya (37.16.1) has studied the wetting isotherms of pyrite in sodium oleate; malachite in heptylic acid; galena in butyl xanthate solutions, and interprets them as showing two parts, the first corresponding to gradual saturation of a unimolecular collector layer; the second to a saturated film, which shows the least wetting.

Abstraction by galena

Taggart, Taylor and Knoll (30.3.1) prove that there is a metathetical equivalence between the amounts of xanthate ion abstracted from solution by galena, and the oxidation products of galena appearing in solution. They were unable to detect sulfide ions in solution, and suggest the mechanism of abstraction is purely chemical: Lead sulfide is oxidized to lead sulfate, which reacts with xanthate ion to form insoluble lead xanthate. The fact that the xanthate abstraction is decreased by grinding and treating galena in the absence of air, and increases with the time of exposure of galena to moist air, is taken to confirm this mechanism. Taggart, Taylor and Ince (30.3.3) and Taylor and Knoll (34.3.7) continued this work and found that the potassium concentration was unchanged, and that no lead ion could be

detected in the solution after abstraction had taken place. The necessity for oxidation of galena to precede reaction with the collector is confirmed by Ralston et al (30.3.4) who found that galena ores, ground in the absence of oxygen, gave poor flotation results; and by Wilkinson (35.9.1) who states that partial oxidation of galena is essential, if xanthate is to be adsorbed. Berl, Schmitt and Schulz (33.12.1) note that oxidation of galena increases its collector requirements. In contrast to the above views is that of Ravitz and Porter (34.3.1) who floated galena in the absence of air, and consider oxidation products on the surface inhibit flotation, and are not essential for the flotation of galena with ethyl xanthate.

Gaudin and Wilkinson (33.8.5) state that galena abstracts dixanthogen from an aqueous suspension.

It has been shown (28.9.2) that the abstraction of capric acid from aqueous solution by galena follows the law:

$$\alpha = \beta c^{1/n}$$

α = weight abstracted

c = equilibrium concentration in solution

$\beta = 67$

$\frac{1}{n} = 0.5$

and was further noted that dry galena shows leas adsorptive power than wet galena.

Ince (30.3.2) notes that galena abstracts more thiocarbanilid than sphalerite does.

It has been shown that galena abstracts palmitate ion only from a solution of sodium palmitate, presumably to form insoluble lead palmitate (29.25.1)(29.15.1); and abstracts oleate ion from sodium oleate solution (34.3.6). Taggart (32.8.1) reviews the experimental work to date and notes that a-naphthylamine, potassium ethyl xanthate, mono- and di-phenyl thiourea, and p-thiocresol are abstracted by galena. Rimskaya (37.16.1) has studied the wetting isotherms of galena in butyl xanthate.

Abstraction by pyrite

It is stated (34.3.6) that pyrite abstracts only ethyl xanthate ion from a solution of potassium ethyl xanthate. Gaudin and Wilkinson (33.8.5) advance evidence to show that the xanthate, on abstraction, is changed to dixanthogen. Taggart (32.8.1) reviews the experimental work on abstraction and states that pyrite abstracts a-naphthylamine, potassium ethyl xanthate, mono- and diphenyl thiourea and p-thiocresol. Wark and Cox (38.3.1) were unable to determine the xanthate abstracted by cyanide-treated pyrite, because reducing ions were liberated by the alkali present. By an indirect method however, they show that the depressant reduced, and probably prevented xanthate abstraction.

Abstraction by sphalerite

The non-abstraction of ethyl xanthate by pure sphalerite has been noted by Taggart, Taylor and Knoll (30.3.1) and confirmed by others (30.3.7)(33.8.5), and is considered due to the high solubility of zinc ethyl xanthate (30.3.1)

Abstraction of ethyl xanthate ion by copper-activated sphalerite has been measured by Gaudin (30.3.7), who finds it to be greater than the abstraction by cyanide-treated copperized sphalerite. Taggart states (32.8.1) that during abstraction of collector by copperized sphalerite, sulfate ions appear in solution.

A very low abstraction of collector by cyanide-treated sphalerite was noted by Ince (30.3.2), who also found that pure sphalerite abstracts less thiocarbanilid than galena does.

According to Berl, Schmitt and Schulz (33.12.1), who determined the amount of collector required to make a mineral hydrophobic, as shown by the inversion of a benzene-in-water to a water-in-benzene emulsion, the oxidation of sphalerite decreases its collector requirement, by virtue of the high solubility of zinc sulfate.

Gaudin, Haynes and Haas (28.19.1 - T.P. 4) showed that certain amines which float sphalerite, do not form insoluble zinc salts or sulfides.

Abstraction by chalcocite

Chalcocite abstracts ethyl xanthate ion from a solution of potassium ethyl xanthate (34.3.6)

Abstraction by chalcopyrite

The abstraction by chalcopyrite of various collectors, including potassium ethyl xanthate, has been noted by Taggart (32.8.1). Gaudin and Schumann (36.8.3) found that chalcopyrite abstracts ethyl xanthate ion only, very rapidly,

from potassium ethyl xanthate solution, in quantity to form cuprous ethyl xanthate; and that hydroxyl, carbonate, sulfate, and reducing ions of the form $S_mO_n^{--}$ are thrown into solution, in total amount metathetically equivalent to the amount of xanthate ion abstracted.

Abstraction by sulfur and graphite

In contradiction to Gaudin (32.25.5), Wark and Cox (35.8.1) show that a wide variety of minerals, including sulfur, graphite, cerussite and gold, abstract xanthate from solution. The abstraction of ethyl and amyl xanthate from solution does not change the pH of the solution. In further work (37.8.1) they find that charcoal abstracts both anions and cations of potassium amyl and ethyl xanthates from solution; that more xanthate ion than potassium ion is abstracted; and that the difference is accounted for as an increase in the alkalinity of the solution. The abstraction of potassium ion probably takes place by exchange adsorption with hydrogen ions of the charcoal, and the increase in alkalinity by exchange adsorption of xanthate with hydroxyl ions.

Abstraction by miscellaneous minerals

Oxidized minerals (malachite) abstract xanthate ions from solution (32.25.5), and adsorption isotherms of ethyl and butyl xanthates on malachite are given by Shneerson (36.16.4)

The equivalence of the reaction[1] between cerussite and

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1. $PbCO_3 + 2EtX^- \rightarrow Pb(EtX)_2 + CO_3^{--}$

xanthate has been shown by Gaudin (34.3.5A) by titrating the carbonate formed. Wark and Cox (36.3.1) state that anglesite and cerussite abstract sodium sulfide in preference to xanthate.

Apatite removes palmitate ion from solution, as determined by surface tension measurements, presumably to form an insoluble calcium palmitate (29.25.1)(29.15.1). Cassiterite (29.25.1), which does not normally abstract palmitate ion, will abstract it from sodium palmitate solution after the mineral has been treated with calcium hydroxide.

Volkova et al (35.12.1) show that, in the flotation of talc by isovaleric acid, an exchange reaction occurs and magnesium passes into solution. Gaudin (32.25.5) states that certain silicates, activated by metal ions, abstract soap collectors from solution. Volkova and Zaporozhetz (35.12.2) find that, in the flotation of certain finely-powdered nonmetallic minerals with isoamyl alcohol, adsorption of alcohol, as evidenced by surface tension measurements, does not occur. Peetz (28.9.2) finds that quartz does not abstract capric acid from solution.

Changes in a Mineral in Contact With a Collector Solution

Physical nature of coating

Visible coatings formed by collectors on various minerals have been noted. It is stated that visible coatings are formed on malachite by treatment with xanthates (34.3.5A) on azurite by amyl xanthate (28.19.1), and on lead carbonate

by xanthates, mercaptans and thiophenols (32.25.5).

Fahrenwald (24.3.1) estimated the thickness of the oil film formed on sulfides in oil flotation was 10 to 100 molecules, but was greater if high concentrations of oil were used. The abstraction of various collectors by pyrite, malachite and galena (37.16.1) and copperized sphalerite (37.16.4), correlated to the amount of wetting, indicates that maximum floatability is attained when a monomolecular film is formed on the mineral surface.

Analysis of coatings on galena

When slightly oxidized galena, which has been treated with a xanthate, is leached with a solvent for lead xanthate, lead xanthate is obtained in the leach liquid (33.25.3 through 32.25.5). On longer treatment with xanthate, sulfur and unidentified oils are also leached from the surface (33.8.5). Gaudin (34.3.5A) believes that, on long treatment, the lead xanthate which forms first, decomposes to sulfur and oils (probably dixanthogen), since the amount of lead xanthate recovered decreases with the time of treatment while the amount of sulfur and oils increases. Lead xanthate is also leached from the surface of galena treated with dixanthogen (32.25.5)

Analysis of coatings on pyrite

Gaudin et al (34.3.5A) state that xanthates react with a pyrite surface to form ferric xanthate, which decomposes rapidly to sulfur and an oil. For the latter reason, it is not usually possible to extract ferric xanthate from the

mineral surface.

Analysis of coatings on chalcocite

Cuprous xanthate is extracted from the surface of chalcocite which has been treated with an alkali xanthate (34.3.5A). Gaudin and Schumann (36.8.3) leached xanthate-treated chalcocite with water, and with pyridine. Leaching with water had no effect on the floatability of the treated mineral. The pyridine extract contained cuprous xanthate, and probably small amounts of other substances. They conclude that the filming of chalcocite by xanthates is accompanied by reaction of part of the xanthate to form cuprous xanthate and other substances removable by organic solvents.

The coating formed by dixanthogen on chalcocite gives no tests for sulfur, dixanthogen, or oil, but shows the presence of various other products, presumably oxidation products of cuprous xanthate (34.3.5A)

Analysis of coatings on miscellaneous minerals

Base metal xanthates have been identified by Gaudin (34.3.5A) in the visible coatings formed by xanthates on malachite and cerussite. Covellite reacts with dixanthogen and alkali xanthates to form cuprous xanthate and sulfur. In the reaction with xanthates, dixanthogen is formed as an intermediate product, (34.3.5A), and may be extracted from the coating.

Wark and Cox (35.8.1) were unable to recover amyl xanthate from hot water or alcohol washings of treated graphite; but obtained an indication of xanthate by an

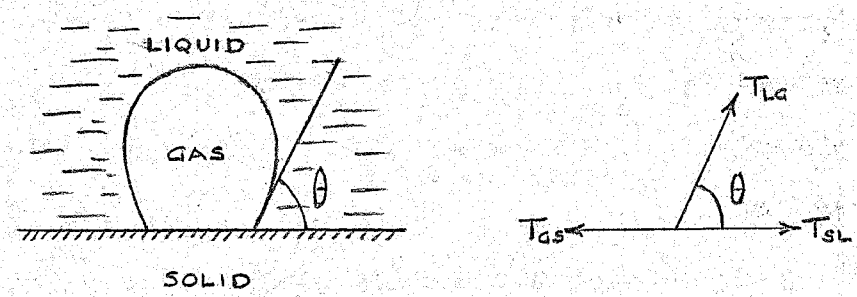
iodine titration of a suspension of treated graphite.

Taggart, del Giudice and Ziehl (34.3.6) consider the formation of dixanthogen on minerals treated with xanthate as noted by Gaudin (33.8.5)(34.3.5A) is not a significant factor in their flotation, since Wark and Cox (34.3.2) have shown that the characteristic contact angles for dixanthogen and xanthate are different, and that xanthate-treated galena gives the typical xanthate contact angle

CONTACT ANGLES AS A MEASURE OF FLOATABILITY

The Contact Angle

When a gas bubble is brought into contact with a solid surface in a liquid, the bubble may become attached to the solid, or may fail to make contact. If attachment occurs, a definite angle is subtended between the plane tangent to the bubble and the plane of the solid surface at any point along the line of three phase contact. This angle, measured



across the water phase, is called the contact angle.

Reinder's relates the contact angle to the interfacial tensions:

$$T_{gs} = T_{sl} + T_{lg}\cos\theta$$

T_{gs} = gas-solid interfacial tension

T_{sl} = solid-liquid " "

T_{lg} = liquid-gas " "

θ = contact angle

The "bubble machine", an apparatus for measuring contact angles, was introduced by Taggart, Taylor and Ince (30.3.3) and has been described in detail by del Giudice (36.6.1). A similar apparatus to that of Taggart is used

by Wark and Cox (36.6.2), who describe their machine, and give notes on the technique of operation.

Significance of the Contact Angle As a Measure of Floatability

Taggart and Beach (16.3.1) used Reinder's equation as a qualitative guide in expressing the relation between contact angles and flotation results.

Shepard (32.10.1) shows that the work to pull a bubble away from a solid surface is $T_{lg}(1 - \cos\theta)$, and that, as a close approximation, collectivity is directly proportional to the contact angle. Wark (32.22.1) gives the quantity $T_{lg}(1 - \cos\theta)$ as the free energy change ($-\Delta F$) associated with bubble adhesion.

Wark and Cox (32.22.1)(33.8.1), before using contact angle measurements as the major tool in their investigations of flotation, made a thorough study of the significance of the contact angle, from a mathematical, thermodynamic, and practical point of view. They show that the contact angle is directly proportional to the force of air-solid adhesion, and is the best measure of the adhesion of a bubble of air and a single solid particle.

del Giudice (34.6.3) reviews certain work on contact angles.

Valentiner (36.9.1) does not consider the contact angle is a measure of floatability, because the conditions under which it can be measured do not correspond to those in flo-

tation.

Effect of various factors on the contact angle

The following results have been obtained by Wark and Cox, from an extensive study of contact angles (33.8.3) (34.3.2)(35.8.1)(37.8.1)(38.3.1).

Clean surfaces of all the minerals examined, including galena, sphalerite, pyrite and pyrrhotite, do not develop contact with an air bubble, in pure water.

On treating the mineral with a xanthate solution, if it then makes contact with the air bubble, the magnitude of the contact angle is independent of the mineral[1]; but depends only upon the non-polar group in the collector molecule[2]. This is further evidence for the outward-orientation of this non-polar group at the mineral surface.

Certain sulfides make contact with air in the presence of any xanthate. Other sulfides and xanthates require activation before contact develops.

Whether any contact will develop between an air bubble

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1. Metallic copper, various sulfides, graphite, sulfur, and activated charcoal all show the same contact angle in a given xanthate solution.
2. For example: Diethyl dithiophosphate $\left(S=P\begin{smallmatrix}-OEt\\-OEt\\-S-\end{smallmatrix}\right)^-$ and ethyl xanthate $\left(S=C\begin{smallmatrix}-OEt\\-S-\end{smallmatrix}\right)^-$ give the same contact angle because they have the same non-polar group.

and a sulfide in a given xanthate solution, depends in general upon the solubility of the xanthate of the metal contained in the mineral.[1] Sulfides whose metal constituents form relatively soluble xanthates, and gangue minerals, do not show air-mineral contact in a xanthate solution.

In an homologous series of xanthates, the magnitude of the characteristic contact angle increases with the molecular weight of the xanthate.

For each mineral, in a given xanthate solution, there is a critical pH above which contact is impossible, and below which the full angle, characteristic of the xanthate, is obtained. For a concentration of 25 mgm. per litre of potassium ethyl xanthate, the critical pH values for galena and pyrite are about 10.2 and 10.5 respectively, at room temperature. As the concentration of a particular xanthate is increased; or if a more complex xanthate is used at the same concentration, the critical pH becomes higher.

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1. It was found, with the following collectors:

   (1) sodium diethyl dithiophosphate

   (2) potassium ethyl xanthate

   (3) sodium diethyl dithiocarbonate

   (4) Potassium isoamyl xanthate

   (5) potassium di-n-amyl dithiocarbamate

   arranged in order of decreasing solubility of their heavy metal salts, that chalcopyrite responds to all five; galena and pyrite respond to all except the first; sphalerite responds to the fifth only.

Anglesite responds to potassium ethyl xanthate best between pH 9 and 11; cerussite at a pH less than 9. In the presence of sodium carbonate, a higher xanthate concentration is necessary to produce contact with these minerals.

As the temperature is decreased from 35°C to 10°C, the critical pH for galena, pyrite and chalcopyrite, in the presence of ethyl xanthate only, becomes lower. The following values are given:

	Critical pH	
	35° C	10° C
Galena	10.8	9.7
Pyrite	10.7	10.0
Chalcopyrite	12.7	10.9

Hysteresis of Contact Angle

Sulman noted (20.25.1) that contact angles show hysteresis, and considered that flotation depends on this factor. Wark and Cox (34.3.2) however, believe that hysteresis of the contact angle is due to friction. They were able to eliminate it in their experiments, and conclude that it does not help flotation.

Time to Develop Contact

Freundlich, Enslin and Lindau (33.25.1)(33.25.2) have studied the rate of wetting of minerals. They note that zinc sulfide and copper sulfide are wetted slowly; lead sulfide and iron sulfide rapidly; and that oleic acid favors wetting.

Sven Nilsson (34.12.1) correlates floatability to in-

duction time (the time required, in contact angle measurements, for an air bubble to make contact with a mineral), and shows that collectors decrease this time, while depressors increase it. Wark and Cox (36.8.1) comment on this work, and show that the induction time depends on the concentration of collector solution.

Methods for measuring wetting hysteresis in powdered minerals and ores are described by Klyachko (37.12.1), who observes a possible correlation between floatability and differential wetting hysteresis of a given powder, before and after adsorption of a wetting agent.

Miscellaneous Contact Angle Investigations

Contact angle studies made by Wark and Cox (35.8.2) with amines and sulfide minerals show that the maximum contact angle is independent of the amine; that copper minerals and activated sphalerite respond most readily; pyrite least readily to an amine; and that hexylamine allows sphalerite to be floated away from galena. They state that contact angle measurements closely parallel flotation tests.

Mokrushin and Demenev (35.18.3) have measured contact angles on metal sulfide films formed on a solution of the metal salt (35.12.4). They conclude that wetting of the films is a temporary phenomenon, not explainable entirely by molecular orientation, but due also to ion adsorption from solution. They state that sulfide films adsorb anions preferentially.

Demeney (36.25.3) finds that xanthates do not change the wettability of sulfur films formed by hydrogen sulfide on ferric chloride, which is taken to indicate that there is little or no adsorption. He was unable to obtain the constancy of contact angle claimed by Wark and Cox.

ELECTRICAL EFFECTS IN FLOTATION

Charge on Minerals, Air Bubbles, and Oil Particles

It has been shown (14.25.1)(22.25.1)(24.25.3) that air bubbles and oil droplets in pure water carry an electric charge, that the number of free charges is very small (27.24.2), and that the origin of the charge is probably ionic rather than electrostatic.

Ince (30.3.2) shows that, in similar aqueous solutions, certain minerals are positively charged; others negatively.

Sven-Nilsson (32.25.6) states that air-mineral adhesion is good at high values of the potential measured by electro-capillary tests; poor at low values. The value of the potential at which the air-adhering tendency of the mineral changes varies with the mineral.

Potential of Mineral Electrodes

The potentials of galena, copperized sphalerite, and glass electrodes, against a calomel electrode, have been measured by Kamienski and Benis (37.16.5).

Effect of Reagents on Mineral Charge

Kamienski (32.25.1)(32.25.2) found that the potential of negative platinum, galena and graphite electrodes in potassium chloride solution becomes more negative; but that the potential of zinc is unchanged, on adding terpineol and

potassium ethyl xanthate to the electrolyte. This work was carried out to test the theory that wetting of the electrode will reduce its positive charge. He suggests that oil-sulfide adhesion is due to static phase-boundary potentials.

Bull (29.24.1) determined the potential developed by galena, and by quartz, carrying initial positive and negative charges respectively, on falling through solutions of metal salts. It is suggested that certain ions raise the charge on galena and prevent its collection.

Both lime and oleic acid reverse the charge on quartz, and potassium ethyl xanthate changes the sign on pyrite, according to Tikhonov (35.25.1).

The electro-kinetic potential of precipitated particles of metal ferrocyanides and sulfides increases during peptization (36.25.5).

THERMODYNAMICS OF FLOTATION

Heat of Wetting

The heat of wetting of silica was measured by Parks (02.25.1) and Edser (22.24.1). Fahrenwald (31.3.1) noted that the heat of wetting is an approximate measure of the adhesion of a mineral to water; and Wark (32.22.1) showed, from a thermodynamic treatment, that it is only a rough indication of the adhesive force, and that the contact angle is a better measure of this force. Recently (37.25.1) the heats of wetting by water, ethyl alcohol, and carbon tetrachloride, of powdered barium sulfate and potassium halides have been measured.

Surface Energy

Fahrenwald (31.3.1) has estimated the surface energy of quartz.

Displacement Pressure and Adhesion Tension

Bartell and associates (27.11.1)(27.25.1)(33.8.6) have developed a method for measuring the pressure of displacement of one liquid by another at the surface of a powdered solid, by which the liquid-solid adhesion tension may be evaluated. The adhesion tension of crude oils (28.11.1), various organic liquids and water (32.8.3) on silica have been determined by this method.

A relation between the interfacial angle and adhesion tension is given by Bartell and Bartell (34.1.1), which allows, from one determination of the adhesion tension or contact angle of a liquid on a solid, the calculation of the adhesion tension of the solid on water or on any liquid whose interfacial tension against water is known.

Bartell and Greager (32.8.3) found that the adhesion tension of various liquids on silica, carbon black, and calcium fluoride is a linear function of the absorbtion of the liquid by the solid, in those cases where liquid drops make zero contact angle on the solid; and that oil absorbtion is low if the adhesion tension is high, or if the contact angle is large. It is stated (32.11.2) that aqueous solutions which are most effective in displacing crude oil and benzene from silica are adsorbed on, or react chemically with the silica.

If the various liquids studied (33.8.6) are arranged in the order of increasing adhesion tension against silica, it is found that this series is the reverse of the series for carbon; and that, for any given liquid, the sum of the adhesion tension on silica and the adhesion tension on carbon is approximately constant.

The adhesion tension of liquids (34.8.2) against strongly hydrophilic solids is independent of the solid used. From this it is concluded that the solids are covered by an adsorbed water film.

Adhesion tension studies of stibnite (34.8.3) and

galena (35.8.3) indicate that the former changes slowly from a hydrophilic to an hydrophobic solid as it is subjected to successive limited oxidations, and that the latter is either an organophilic or hydrophilic solid, depending on whether it is first wetted by an organic liquid, or by water.

The rate of displacement of water by pine oil from mineral surfaces has been measured by Barsky and Falconer (31.22.1), following the method of Bartell (27.11.1)(27.25.1). They found that reagents which produce flotation cause the oil to displace the water, whereas depressants have the reverse effect. Wark (32.22.1) discussed this work and criticized the conclusions.

David and Curtis (32.11.1) have also studied wetting of minerals by water and organic compounds.

Contact Angle as a Thermodynamic Quantity

Wark (32.22.1) gives the following relationships:

$$-\Delta F = T_{lg}(1 - \cos\theta)$$

$$\Delta F = \Delta H - T\Delta S$$

$$\Delta S = \left(\frac{d(\Delta F)}{dT}\right)_p$$

T_{lg} = liquid-gas interfacial tension

θ = Contact angle

ΔH = heat of wetting

MISCELLANEOUS STUDIES OF WETTING

Agnes Pockels (33.12.2) noted that the readiness with which a solid is wet by water decreases after drying.

Metals and metalloids, crushed under water and then brought to the surface, exhibit certain water-repellent characteristics, according to Devaux (33.25.5)

Luyken and Bierbrauer (29.25.1) measured the wetting of minerals by the contact angle formed at a drop of solution on the mineral surface.

Bartell, in connection with his work on adhesion tension of liquids against solids, has determined the contact angle formed by liquid drops on solid surfaces (29.11.1) (32.8.3)(34.1.1)(35.8.3), and has studied the wetting characteristics of talc, waxes and resins (36.1.1) by this technique. He found that water and organic liquids form contact angles on talc, waxes and resins, and concluded that the surface tension of these solids is low. He states that solids which are soft and have a low surface tension are wetted less readily by liquids than hard solids of higher surface tension.

THEORIES OF COLLECTOR ACTION

Introductory

Several theories of collector action have been proposed. Most workers now agree that the collector or collector ion is removed from solution by the mineral, with consequent alteration of the mineral surface to make it more hydrophobic. The mechanism of the alteration is not agreed upon. It is thought to be either metathesis between negative ions of collector and positive ions from the mineral; or adsorption of an unspecified nature.

Chemical Theory

What has become known as the chemical theory of flotation was introduced by Taggart, Taylor and Knoll (30.3.1), and amplified in later papers by Taggart and his associates (32.8.1)(34.3.6). In the first paper the generalization is made that soluble collectors react with minerals by metathesis between mineral cations and collector anions; and that the formation of a water-repellent film on the mineral makes it floatable, while the formation of a water-avid film makes it non-floatable. It is further stipulated that the reaction of a xanthate with galena requires previous oxidation of the galena to form lead sulfate. This mechanism was verified by the stoichiometric balance between the xanthate ion abstracted by the galena and the ions, derived from galena, which

appear in solution; by the non-change in potassium ion concentration in solution; by the non-detection of sulfide ion in solution; by the recovery of lead xanthate from the surface of treated galena; and by the poor floatability of fresh galena.

Opponents of the chemical theory, however, have noted that the floatability of anglesite (natural lead sulfate) is less than the floatability of galena; that certain minerals such as gold (34.3.1)(33.8.3), sulfur and graphite (35.8.1)(37.8.1), which do not ionize in the usual sense, are collected by xanthates; and that xanthates are more soluble than the corresponding sulfides, rendering improbable the suggested reaction in which a sulfide is replaced by a xanthate. Taggart (34.3.6) does not believe that gold flotation disproves the chemical theory, as he was unable to float pure gold until it had been treated by a dissolving agent; presumably to provide gold ions required by the chemical theory. He explains the activating effect of sodium hydroxide on cassiterite, and of sulfides on oxides, as being due to similar effects.

Cox and Wark (33.8.2) contrasted the chemical theory to adsorption theories, and pointed out that a true chemical theory implies adsorption can only occur when the solution is saturated with respect to the adsorbed compound.

Gaudin (32.25.5)(34.3.5A) takes an intermediate stand. He believes that chemical reaction is responsible for the collection of some minerals, (e.g. azurite by amyl xanthate,

which forms a visible coat); that metathesis is the mechanism, at least in part, for collection of galena, chalcocite and covellite by xanthates; but that the original reaction is followed by decomposition or oxidation of the coating, so that the coat during flotation may or may not be base metal xanthate. He states that collection of sphalerite by phenyl hydrazine, and mono-isoamyl amine; and of chalcocite by mono-isoamylamine and methyl quinoline is not explainable on the basis of insoluble compound formation.

A mechanism for the flotation of pyrite, in accordance with the chemical theory, is stated by Taggart et al (34.3.6): Pyrite is oxidized to ferric sulfate; which, by metathesis with xanthate ion, forms ferric xanthate.

Adsorption Theory

Fahrenwald's early work dealing with oil flotation (24.3.1) led him to believe that the heteropolar oils used as reagents were adsorbed, possibly as oriented films, on the mineral surface, and that adsorption took place when the mineral particles and oil droplets carried unlike charges. As early as 1921, Ryskewitsch (21.25.2) stated, "the difference of adsorption on gangue minerals and metallic minerals is due to difference of structure. The space lattice of gangue minerals is made up of molecules; that of metallic minerals of atoms. The metallic minerals therefore have a residual valence or unbalanced static force at the surface which is responsible for adsorption".

Berl and associates (23.23.1)(24.12.1) were able to float quartz by the use of dyes, and conclude that adsorption of the dye at the mineral surface forms a hydrophobic coating which renders the mineral floatable. They state that there is no relation between the sign of the charge on a mineral and its floatability.

Gaudin (28.3.1) postulated that xanthates adsorbed at mineral surfaces to form non-Daltonian compounds. Schaum and associates (32.12.3) stated that collecting action is due to ionic adsorption. Bartell, Miller and Almy (33.1.1) discussed the application of the Gibb's adsorption theorem to solid-liquid interfaces.

Adsorption of the collector at a mineral surface is thought by Cox and Wark (33.8.2)(34.3.2) to result in a closely packed film, with the alkyl groups oriented outward.

Gaudin (34.3.5A) discussed the adsorption theory, and noted that there is doubt as to whether the adsorbed entity is xanthic acid or alkali xanthate molecules; xanthate ion; base metal xanthate molecule; or xanthate oxidation products. Adsorption theories, in general, have been criticized by Taggart and associates (34.3.6) as not explaining the unchanged potassium ion concentration, or the recovery of lead xanthate from treated minerals. Their conception of adsorption is based on the Gibb's equation.

De Boer and Custers (34.25.4) have attempted to calculate the energy of adsorption by considering it to be the sum of the van der Waal's and electrostatic forces. They

show that molecules with a high dipole moment are largely adsorbed electrostatically, while van der Waal's forces act, with the non-polar portion of the adsorbed molecule. Wark and Cox (35.8.1), on the basis of this work, consider that the unbalanced forces, particularly electrostatic forces, at solid surfaces, act either on dipoles or dissociated ions of the collector; since collectors have either a high dipole moment, or a high degree of dissociation. Specifically, on graphite, xanthate ion is adsorbed with a surrounding layer of potassium ions, and every second carbon atom of the graphite surface, carrying an unshared electron, should be able to adsorb a xanthate ion. They consider that the force binding ethyl xanthate ion to lead sulfide is stronger than that binding it to lead ethyl xanthate, and that the concentration of xanthate ions in equilibrium with such different surfaces must also be different.

Ostwald's Theory

Wolfgang Ostwald (32.12.1) introduced the concept of "linear" flotation, which involves a three-phase (air-water-mineral) linear contact; as contrasted to oil flotation, which involves only a two-phase (oil-mineral) contact. He states that film flotation uses diphilic collectors such as oleic acid, while "linear" flotation uses triphilic collectors. A triphilic collector contains a capillary active group, and groups with affinity for metal and for water respectively. He stated that ethyl dixanthogen is not a collec-

tor, because of the absence of a hydrophilic group, while carbanilid and thiourea lack capillary active groups.

Evidence in support of Ostwald's Theory is adduced by King (33.12.3) from observations with nickel dimethyl and diphenyl glyoximes and galena.

Ostwald's Theory is contradicted by photographic evidence (32.12.2) which shows that the mineral, as such, does not extend into the air phase. The compounds stated by Ostwald to be non-collectors, are collectors in alcoholic solution. Wark and Cox (33.8.4) have also criticized Ostwald's Theory.

Electrical Theories

Early explanations of flotation (15.25.2)(16.25.1)(17.25.1) considered that air-mineral adherence was due to different electrical charges on these phases. Gaudin (32.25.5) believes, however, that the early investigators confused the electrostatic charge on minerals with the charge due to the Helmholz double layer, which exists around air-bubbles, and notes that the existence of electrostatic charges on particles in an ore pulp presupposes the pulp is a dielectric, which is not the case.

Fahrenwald (24.3.1) believed that selective oiling of a mineral was the result of favorable electrical charges on the oil and on certain mineral particles, and that flotation could be controlled by regulating the charge. He correlated flocculation and peptization, as indications of the relative

charge carried by the particles, to flotation and depression respectively. Ridsdale Ellis (US Pat. 1,425,185) agrees with Fahrenwald, and considers the function of chemical reagents is to control the sign of the charge on particles. Previous correlation between flocculation and flotation had been noted by Sulman (20.25.1), Edser (22.24.1) and Bartsch (24.25.1). Ralston and Barker (31.22.3) commented on the effect of collectors on flocculation in practical flotation. Fahrenwald (31.22.4) advanced the facts that sphalerite is weakly peptized in water, strongly in dilute sodium cyanide; quartz is peptized in water; copper sulphate flocculates a sphalerite suspension in sodium cyanide as further evidence for the connection between flocculation and flotation, and between peptization and wetting.

Taggart, Taylor and Knoll (30.3.1) observed that particles in Brownian movement do not float; and noted that Brownian movement can be controlled by the presence of reagents. These workers could not explain certain of their results by the kinetic theory. Taggart, in a later review (32.8.1) however, offers an explanation for the previously observed effects of reagents on the Brownian movement, which is not in disagreement with kinetic theory.

Wark (32.22.1) believes that dispersion, as such, is no bar to flotation; but that the surface conditions which lead to dispersion also hinder flotation. Gaudin (32.25.5) takes the opposing view to Fahrenwald, Taggart, et al, and considers dispersion is necessary for flotation. He cites

the practical use of dispersing agents (such as sodium silicate) which produce cleaner concentrates and yield higher recoveries. In more recent work (34.3.6) Taggart concludes that flocculation is independent of flotation, but that particles in Brownian movement will not float because they are already wetted.

Tikhonov (35.25.1) noted that xanthate changes the sign of the charge on a mineral, but does not consider that electrostatic charges can account for all flotation phenomena. Recent work by Shneerson (36.16.4) shows that xanthates increase the rate of flocculation of malachite suspensions; and that flocculation is due to adsorption, and fixation of polar groups on the mineral.

Miscellaneous Theories

Volkova (35.12.3) has explained the flotation of asbestos and barite by assuming oriented coagulation of powder particles at a phase boundary.

Hel'd (35.16.1) distinguished three types of molecular attraction in flotation: (a) molecular adsorption (b) ionic adsorption, and (c) chemical reaction. He states that the type is determined by the properties of the collector, and the elements of the mineral crystal lattice.

Shvedov (36.16.2) advanced a modified chemical theory for the reaction of collectors with the products of semi-oxidation of minerals.

DEPRESSION

A depressor is a chemical, used either before, or in conjunction with a collector, to decrease the recovery of a specific mineral.

Acids and alkalis may be classed as depressors. Their action, however, has been considered under the heading of the effect of pH on collector action.

Sodium cyanide is used extensively to depress sphalerite. Soluble chromates are used to lower the recovery of galena; and lime is sometimes employed to depress pyrite.

EVIDENCE OF DEPRESSION OBTAINED FROM FLOTATION TESTS AND PRACTICE

Galena

The depressing effect of various cations (28.19.1-TP. 1) (29.8.1) on galena, which decreases through the series: Cr^3, Th^4, Al^3, Cu^2, Fe^3, Hg^2, Hg^1, Ag^1, Pb^2, Cd^2, Co^2, corresponds roughly to the insolubility of the sulfides formed by the cations. Gaudin (32.25.5) terms this class of depressant "toxic agents", because there is no evidence of chemical reaction between reagent and mineral.

Oxidized galena (32.25.5) is depressed by chromates, phosphates, tungstates, arsenates and arsenites. Compounds of lead with these anions are, in general, less soluble than either the oxidized coating on galena, or the lead salt of

the collector used.

Buchanan and Christmann (27.2.1) from flotation tests on pure galena specimens, using as collectors (1) pine oil and potassium ethyl xanthate (2) phosphocresylic reagent, and (3) thiocarbanilid-o-toluidine mixture; found that lime depressed galena with all three collectors, while sodium carbonate and cyanide were depressants only when using the third collector.

Trusov (35.16.2) found that galena is temporarily depressed by sodium hyposulfite, but not by sulfite or thiosulfate.

Pyrite

The depressant action on pyrite of lime (30.3.4) and of sodium cyanide (30.25.2) have been studied.

Buchanan and Christmann (27.2.1) found that lime strongly depresses pyrite at concentrations above 0.75 gm. per litre (pH 7.0 or higher); sodium carbonate up to 4 gm. per litre has little effect with the first two collectors; but at concentrations above 1 gm. per litre has a marked depressing action when used with the third collector; sodium cyanide is a strong depressant at concentrations greater than 1 gm. per litre for the first, and greater than 0.25 gm. per litre for the other collectors.

Brighton, Burgener and Gross (32.6.2) found that the depression of pyrite is proportional to the sodium cyanide concentration for a given size of particle. Smaller particles require a greater concentration of cyanide to effect the

same amount of depression.

Pure Sphalerite - depression by cyanide

Gaudin (30.3.7) found that sodium cyanide has no depressant action on unactivated sphalerite when reagents are used which collect unactivated sphalerite (e.g. amyl xanthate, thiocresol, amyl mercaptan). Wark and Cox (34.3.4) do not agree with Gaudin. According to Yamada (36.25.7) the effect of cyanide on the floatability of sphalerite is very slight.

Activated Sphalerite - depression by cyanide

Flotation of sphalerite, possibly unintentionally activated, was studied by Buchanan and Christmann (27.2.1), who found that sodium cyanide, at concentrations greater than 0.25 gms. per litre, is a strong depressant. If sphalerite is intentionally activated by copper sulfate, more cyanide is required to cause depression.

Gaudin (30.3.7) showed that cyanide completely depresses copper-activated sphalerite, by dissolving the copper sulfide coating and removing the copper ion from solution as undissociated $Cu(CN)_3^{--}$ ion.

The depression by cyanide of sphalerite is less than that of pyrite, according to Brighton, Burgener and Gross (32.6.2). pH as a factor in depression was recognized by Gaudin (29.10.1). Kraeber (30.25.2) has studied the influence of cyanide on the floatability of zinc minerals.

Recent work includes that of Mitrofonov and Arashkevich (36.16.1), and Mantsev (37.16.2). The latter found that

copper-activated sphalerite is completely depressed, as evidenced from wetting diagrams, by 0.005% sodium cyanide, when using potassium iso-amyl xanthate as collector.

Sphalerite - depression by reagents other than cyanide

Pallanch (28.3.2) showed that soluble sulfites depress sphalerite, but not galena. Trusov (35.16.2) found that sphalerite is slightly depressed by sodium hyposulfite, but strongly depressed by its decomposition products: sulfites and thiosulfates.

Hellstrand (US Pat 1,469,042 - 1923) has patented the use of sodium sulfide as a depressor for sphalerite. Sladkov (36.16.3), as a result of laboratory and plant tests on a lead-zinc-copper-iron-gold ore, considers sodium sulfide is a better sphalerite depressant than cyanide.

Buchanan and Christmann (27.2.1) found that lime depresses sphalerite strongly with the first, slightly with the second collector they studied; and that sodium carbonate depresses in the reverse order.

The depressant action of sodium carbonate and zinc sulfate has been investigated by Mitrofonov (36.16.1).

Mantsev (37.16.2), from a study of wetting diagrams, states that ferrocyanide does not depress activated zinc sulfide, and that ferricyanide is less effective than cyanide as a depressant. The action of ferricyanide is increased below pH 5, and decreased above pH 9.

Sphalerite is depressed by potassium dichromate (500 g. per ton of ore) at a pH above 5.45; by tannin (500 g. per

ton of ore) at a pH above 5.25; and by potassium permanganate (100 g. per ton of ore); but is not materially affected by zinc sulfate or sodium chloride (36.25.7)

Chalcocite

Tucker, Gates and Head (26.3.1) observed that chalcocite is depressed by cyanide in alkaline solution. According to Gaudin (32.25.5), chalcocite is depressed by thiosulfate, sulfite, sulfide, and ferro- and ferricyanide.

Chalcopyrite

Chalcopyrite is depressed by oxidizing agents, cyanide, sulfide, and lime (32.25.5), but not by hyposulfite, sulfite, or thiosulfate (35.16.2). Brighton, Burgener and Gross (32.6.2) however, state that sodium cyanide, up to 1 lb. per ton of ore, has no depressing effect. Recent work of Yamada and associates (36.25.6) indicates that 893 g. potassium cyanide per ton of ore, at pH 7.8, causes a sudden decrease in the floatability of chalcopyrite.

Miscellaneous minerals

The work of Yamada and associates on arsenopyrite (36.25.1), enargite (36.25.2), marmatite (37.25.2) and stibnite (37.25.3), indicates that arsenopyrite is depressed by copper sulfate below pH 5, and by sodium sulfite, potassium cyanide, zinc sulfate and tannin above about pH 5; that enargite is possibly depressed by cyanide in alkaline solution; that marmatite is depressed by zinc sulfate above pH 5.4, and is also depressed by tannin; that stibnite is depressed by copper sulfate in the pH range 3.5 to 7.0, and

by tannin in the range 6.2 to 7.2.

Gaudin states that cerussite is depressed by alkali chromates (32.25.5).

Belash (36.16.5) finds that sodium sulfide depresses molybdenum in partially oxidized sulfide ores of molybdenum.

Sulfidized malachite (37.16.2), as evidenced by wetting diagrams, is completely depressed by cyanide, but unaffected by ferro- and ferricyanides.

EXPERIMENTAL EVIDENCE FOR THE REACTION OF DEPRESSORS WITH MINERALS

Changes in a Solution of Depressor in Contact with a Mineral (Abstraction of Depressor)

Galena

Galena does not abstract cyanide ion from solution (32.6.2)

Pyrite

Pyrite abstracts cyanide in proportion to the soluble iron present, and to the exposed mineral surface (32.6.2)

Chalcopyrite

Chalcopyrite abstracts more cyanide than sphalerite, but less than pyrite (32.6.2)

Sphalerite

The abstraction of cyanide from solution by sphalerite is greater than that by galena (30.3.2), but less than that by pyrite (32.6.2), since sphalerite is dissolved by sodium cyanide (30.3.8). When sphalerite abstracts cyanide from solution, the concentration of sulfate ion in solution increases (30.3.1). The abstraction by copperized sphalerite is greater than by unactivated mineral (30.3.7).

Mokrushin and Villesova (35.18.2) found that copper sulfide films, formed on the surface of a copper sulfate solution, adsorb chloride ion from sodium chloride solution, and zinc ions from zinc sulfate solution. They believe that the latter ions are held as if a zinc atom had replaced a copper

atom in the crystal lattice; while chloride ions are held as if by true adsorption.

Changes in a Mineral in Contact with a Depressor Solution

Tucker and associates (25.3.1)(26.3.1) claim that cyanide produces a visible change on the mineral surfaces they investigated. Previous experiments (20.25.2), and later attempts to duplicate Tucker's findings (30.3.3)(30.3.7)(28.9.1) do not confirm the presence of visible coatings. Tucker and associates also claim to have analyzed the coating formed on sulfide minerals by lime and cyanide.

Gaudin (32.25.5) states that chromates produce a visible coating on oxidized, but not on fresh galena.

CONTACT ANGLE STUDIES OF DEPRESSION

The results of contact angle measurements, outlined below, are those of Wark and Cox (34.3.2)(34.3.3)(34.3.4)(36.3.1)(36.8.1)(37.8.1)(38.3.1), except where otherwise noted.

Depression by Cyanide

Galena

Cyanide, in the usual concentrations, does not affect air-galena contact with any of the collectors studied.

Pyrite - pure mineral

Cyanide lowers the critical pH for pyrite. As the pH is increased, the critical cyanide concentration for pyrite and chalcopyrite is decreased.

The cyanide concentration to prevent contact with pyrite and chalcopyrite, when using the following collectors:

1. sodium diethyl dithiophosphate
2. potassium ethyl xanthate
3. sodium diethyl dithiocarbamate
4. potassium isoamyl xanthate
5. potassium di-n-amyl dithiocarbamate

(arranged in order of decreasing solubility of their heavy metal salts), increases in the order 1 to 5.

The concentration of cyanide to depress pyrite and chalcopyrite decreases slightly as the temperature is raised from 10°C. to 35°C.

If trimethylcetyl ammonium bromide is used as collector, pyrite is not depressed by cyanide, but is depressed by copper sulfate used with cyanide; presumably by the effect of the cupricyanide ion.

Pyrite - in the presence of copper sulfate

If copper sulfate is also present, contact is similarly prevented by cyanide with all five collectors noted.

With ethyl xanthate, at a given pH, the cyanide concentration to prevent contact with pyrite is less when copper sulfate is present; but with chalcopyrite, is greater.

The concentration of sodium cyanide to prevent air-pyrite contact in the presence of copper sulfate and ethyl xanthate, increases rapidly with temperature to a maximum at about 35°- 40°C. It is suggested, therefore, that the best separation of sphalerite or chalcopyrite from pyrite is effected at a low temperature and low xanthate concentration.

Sphalerite - pure

Pure sphalerite responds to potassium di-n-amyl dithiocarbamate and makes contact with an air-bubble. If cyanide is added this response is prevented.

Mokrushin and Demenev (35.18.1) have found that potassium cyanide decreases the contact angle to zero at a zinc sulfide film on the surface of a liquid.

Sphalerite - activated by copper sulfate

Cyanide makes copper-activated sphalerite non-responsive, and prevents activation of pure sphalerite by copper compounds unless the copper ion concentration is in excess of the ratio

1Cu:3CN.

An increase in the pH improves the action of cyanide. Temperature has little effect on the concentration of cyanide required to depress copper-activated sphalerite.

When amyl xanthate is used as collector, in the presence of copper sulfate, and at a given pH, a greater concentration of cyanide is required to prevent contact, than when ethyl xanthate is used as the collector. The effect is greater if the pH is high.

Taggart and associates (34.3.6) noted that a sphalerit e particle, showing no contact in a xanthate-cyanide-copper sulfate solution containing cyanide in excess of 3CN:1Cu ratio, does not respond to xanthate after it is removed from the solution and washed.

If copper sulfate is present, the cyanide and/or alkali necessary to prevent contact with sphalerite is proportional to the copper sulfate present.

In the presence of a collector, less cyanide is required to prevent activation of fresh sphalerite, than to deactivate sphalerite that has been previously activated. The amounts approach each other as collectors are used in the order 5, 4, 3, 2, 1 in the series given. With diethyl dithiophosphate, the amounts are equal. This suggests that more cyanide is required to remove the copper xanthate, than to remove the copper-bearing activation film from sphalerite.

If trimethylcetyl ammonium bromide is used as a collector sphalerite is not depressed by cyanide, but is depressed by a

mixture of copper sulfate and sodium cyanide; presumably by the cupricyanide ion.

Chalcopyrite (see also Pyrite)

If copper sulfate is present, the amount of cyanide and alkali, used either alone or together, which is necessary to prevent contact on chalcopyrite, is proportional to the copper sulfate present. Temperature has little effect on the concentration of cyanide required to depress chalcopyrite in the presence of copper sulfate.

Mokrushin and Demenev (35.18.1) found that potassium cyanide decreases the contact angle to zero at a copper sulfide film on the surface of a liquid.

Miscellaneous minerals

Covellite is less sensitive to cyanide than is activated sphalerite.

Marmatite, christophite and sphalerite, in the presence of copper sulfate, are equally sensitive to cyanide and/or alkali. Pyrrhotite is not activated by copper sulfate in the same manner.

Graphite and charcoal are unaffected by sodium cyanide, with ethyl xanthate as collector.

Tinstone is depressed by a mixture of copper sulfate and sodium cyanide, using trimethylcetyl ammonium bromide as collector.

Arsenopyrite, like galena, is unaffected by cyanide in the absence of copper sulfate. In the presence of copper sulfate, the effect of cyanide is similar to its effect on pyrite.

The contact angle at films of bismuth sulfide formed on the surface of a liquid is decreased by potassium cyanide, and more strongly decreased by silver nitrate, according to Mokrushin and Demenev (35.18.1)

Depression by Sodium Sulfide

Sodium sulfide depresses sulfides. The concentration of sodium sulfide to prevent contact is a function of pH. HS^- ion is the effective depressant. There is a critical HS^- concentration for each mineral, just sufficient to prevent response to a given potassium ethyl xanthate concentration. The xanthate concentration does not greatly affect the critical HS^- concentration.

Copper sulfate influences the effect of sodium sulfide on chalcopyrite and galena, probably by removing the sulfide ion as copper sulfide.

If trimethylcetyl ammonium bromide is used as a collector sodium sulfide does not depress sphalerite or pyrite.

Depression by other Reagents

Copper sulfate depresses pure pyrite, under certain conditions, with sodium diethyl and potassium di-n-diamyl dithiocarbamates.

Silver nitrate reduces slightly the contact angle on films of copper sulfide and zinc sulfide on the surface of a liquid, according to Mokrushin and Demenev (35.18.1)

Depression in General

The amount of cyanide, at a given pH, to prevent contact with pure minerals, increases through the series pyrite, chalcopyrite, bornite, covellite, and chalcocite. If copper sulfate is also present, the order is pyrite, sphalerite, chalcopyrite. The resistance of a given mineral to depression by cyanide becomes greater as collectors are used which form more insoluble salts of the metal in the mineral.

The influence of cyanide on copper and iron minerals appears to depend only upon the cyanide ion concentration. There is a critical cyanide ion concentration for each mineral, just sufficient to prevent contact. The pH of the solution, if below the critical value (see Collectors - Effect of pH on Contact Angle) is important only so far as it controls the cyanide ion concentration. If the pH is above the critical value, contact is impossible, whether cyanide is present or not.

THEORIES OF DEPRESSOR ACTION

Depression by Cyanide

According to Ince (30.3.2), cyanide forms an insoluble metal cyanide on zinc and iron sulfides with the water-avid cyanogen groups outer-oriented. He states that no simple cyanide of lead is known, but this is not confirmed by handbooks.

A theory of depression has been advanced by Berl and Schmitt (30.12.3). Christmann (30.2.1) and Buchanan (31.22.3A) believe that complex cyanide ions are adsorbed by sphalerite, but may be replaced by copper. They also suggest (27.2.1) that pyrite is depressed by complex iron cyanides formed by the reaction of cyanide and soluble iron.

Fahrenwald (31.22.4) believes that depression involves peptization; and that cyanide forms a zinc cyanide film on sphalerite which does not react with the collector. The desirability of making electro-osmotic measurements on sphalerite in the presence of sodium cyanide, to determine if it becomes more polar, is suggested by Buchanan (31.22.4)

Taggart (32.8.1) contends that depressors react with mineral surfaces to form adherent salts which are less soluble than the salts of the collector with the metal in the mineral. Gaudin (32.25.5) states that the effect of cyanide on pyrite may consist of coating the mineral surface, or in the solution of an activating copper film. Brighton,

Burgener and Gross (32.6.2) conclude that cyanide prevents metallic xanthate formation on the surfaces of pyrite and sphalerite, either by forming a precipitate, a weak salt, or complex ion; or by dissolving an existing film of xanthate. Gaudin (30.3.7) states that depression of copper-activated sphalerite is due to solution of the copper-bearing coating to form undissociated $Cu(CN)_3^-$ ions.

Taggart and associates (34.3.6) advanced the theory that cyanide either dissolves the copper sulfide film on activated sphalerite or reacts with and removes the copper ion made available by oxidation. Because the concentration of cyanide to cause depression varies with the collector used, they state that removal of a copper sulfide film can not be the entire mechanism. They incline to the view that cyanide dissolves a film of cuprous xanthate from activated sphalerite but also forms an insoluble zinc cyanide coat on pure sphalerite. They also suggest that depression of pyrite by cyanide involves coating the mineral surface with a complex copper-iron cyanide, since depression, in contact angle measurements, appears to be related to cupricyanide ion concentration.

Wark and Cox (34.3.2) adduced evidence to prove that cyanide removes the copper compound formed on activated sphalerite, probably as a complex cuprocyanide; and that prevention of contact in cyanide solution is due to prevention of adsorption by the mineral of a film of collector, <u>not</u> due to formation of a cyanide film at the mineral surface. Their

recent work (38.3.1) indicates that the combination of copper sulfate and cyanide is a more effective pyrite depressor than either compound used alone, presumably by the action of a complex copper cyanide ion. The combination is particularly effective at low temperatures (10° C.)

Depression by Reagents other than Cyanide

Chromates

Gaudin (32.25.5) believes alkali chromates depress cerrussite and galena by coating them with lead chromate, which is less soluble than the existing coat on the mineral (e.g. lead carbonate). In this way they cause the mineral to resist the action of collectors. Taggart and associates (34.3.6) suggest a similar mechanism for the depression of galena by chromates, but postulate that the chromate may also oxidize an existing collector film.

Lime

Ralston (30.3.4) showed that pyrite reacts with lime to form soluble sulfides and thiosulfates, which are then oxidized to sulfates. He considers that the oxidation products cause depression. Gaudin (32.25.5) suggested that lime may dissolve pyrite to some extent; at the same time coating the mineral with effective depressants.

Sulfites

Pallanch (28.3.2) believes that sulfites depress sphalerite in the presence of galena by forming a zinc sulfite coating on the zinc but not on the lead mineral.

Miscellaneous Reagents

The action of reagents such as aluminium and chromium salts in inhibiting flotation is ascribed, by Gaudin (32.25.5) to hydrolysis of the reagent, with the formation of colloidal hydroxides which adhere indiscriminately to the mineral surfaces.

ACTIVATION

An activator is a reagent, used with a given mineral and collector to cause the mineral, otherwise unfloated, to be floated by the collector.

The most common example of this class of reagent is copper sulfate, used as an activator for sphalerite. Ethyl xanthate does not collect sphalerite until the mineral has been treated with an activator such as copper sulfate. In the separation of galena from sphalerite, galena is first floated away from cyanide-depressed sphalerite. Copper sulfate is then added to activate the sphalerite and allow it to be floated.

EVIDENCE OF ACTIVATION OBTAINED FROM FLOTATION TESTS AND PRACTICE

Pyrite

Although Gaudin (32.25.5) stated that pure pyrite is activated by soluble copper, contact angle measurements by Wark and Cox (38.3.1) indicate that, under no circumstances, is pure pyrite activated by copper sulfate.

Recovery of pyrite, which has been depressed by lime, sodium carbonate, or sodium cyanide, is enhanced by copper sulfate with ethyl xanthate, but not with TT mixture or phosphocresylic reagent as collectors (27.2.1). Depressed pyrite is apparently activated by soluble sulfides, or by an acid

circuit (32.25.5)

Sphalerite

The activation of sphalerite by copper sulfate has been studied by Buchanan and Christmann (27.2.1) and by Gaudin and associates (28.19.1--TP 1 & TP 7). The latter found that sphalerite is activated by salts of metals whose sulfides are less soluble in water than zinc sulfide (e.g. silver, copper, mercury, cadmium, and lead); that copper sulfate widens the pH zones of highest recovery; and, with certain collectors, also increases the recovery.

Ralston and Hunter (30.3.6) noted that cuprous and cupric salts are equally effective activators. They correlate the activating effect of a given metal ion to the position of the metal in the electromotive series. From copper to silver, activation decreases. Lead, cadmium and zinc are depressors. They also noted that copper oleates, resinates and xanthates, when added as such to a flotation pulp, are non-effective as activator-collectors.

Mitrofonov and Arashkevich (36.16.1) have studied the effect of copper sulfate on the floatability of sphalerite. In the presence of copper sulfate (500 g. $CuSO_4.5H_2O$ per ton of ore) sphalerite is completely recovered in the pH range 1.3 to 11.65 according to Yamada (36.25.7)

Miscellaneous sulfide minerals

Oxidized sulfide ores of molybdenum (36.16.5) are activated by treatment with copper sulfate followed by sodium sulfide. It is presumed that a copper sulfide coating is formed.

Marmatite is activated by copper sulfate in the pH range 2 to 11; by zinc sulfate if the pH is below 5. Above pH 5.4 zinc sulfate acts as a depressor (37.25.2)

Stibnite is activated by $PbO(Ac)_2$ in the pH range 6.5 to 6.8 (37.25.3)

Oxidized minerals

Malachite is activated by lead salts (28.19.1 - TP 9), cerussite by soluble sulfides (32.25.5), presumably by coating the mineral with lead sulfide.

Non-metallic minerals

Calcite, activated by copper and lead ions, will respond to soap collectors (34.6.3).

EXPERIMENTAL EVIDENCE FOR THE REACTION OF ACTIVATORS WITH MINERALS

Changes in a Solution of Activator in Contact with a Mineral (Abstraction of Activator)

Various investigators (25.6.1)(24.3.1)(26.5.1) have shown that copper sulfate is abstracted from solution by sphalerite. At the same time a coating of copper sulfide is formed on the mineral and the concentration of zinc ion in solution increases. The abstraction of copper sulfate by pure minerals (30.3.5) increases in the order: pyrite, chalcopyrite, schist, and sphalerite.

Ince (30.3.2) found that more copper sulfate is abstracted by cyanide-treated sphalerite than by the pure mineral.

The abstraction of metal ions from solution by silicates has been noted by Gaudin (32.25.5). Such metal-coated silicates are activated towards a soap collector if the metal coat forms an insoluble soap with the collector.

Changes in a Mineral in Contact with an Activator Solution

Rogers (11.25.1) and Tucker and Head (25.3.1) have observed visible coatings on copper sulfate-treated sphalerite, but Ince (30.3.2), Mitrofenoff (28.9.1) and Ralston, et al (30.3.5) were unable to duplicate their results. Gaudin (30.3.7) found that sphalerite reacts rapidly, at first, with cupric nitrate in acid solution to form a thin

coating of cupric sulfide, but that the rate decreases with the time of reaction. He noted (32.25.5) that the coating formed on sphalerite by the action of copper sulfate is visible if high temperatures are employed. A visible coating (32.25.5) is formed by sodium sulfide on cerussite. Although Wentworth (10.6.1) was unable to detect any surface alteration he found that the conductivity of sphalerite increased after treatment with copper sulfate.

It is generally considered (25.19.2)(26.3.1)(28.19.1--TP 7)(30.3.5)(30.3.6) that the coating formed by copper sulfate on sphalerite is cupric sulfide, sometimes referred to as covellite. Gaudin (30.3.7) stated that the coating has been shown to contain copper, and to be non-reactive toward silver nitrate. It is presumed to be covellite on the basis of the demonstrated reaction:

$$ZnS + Cu^{++} \rightarrow CuS + Zn^{++}$$

Taggart (32.8.1) takes an opposing view, apparently without presenting experimental evidence for the contention, that the coating consists of cuprous sulfide which is subsequently oxidized. Because natural covellite is difficult to float, Beck (34.25.1) suggests that the film formed is a mixture of cupric and cuprous sulfides and sulfur, rather than covellite, and that free sulfur is the activator. Kamenetzi (34.25.2) found that 0.01 N silver nitrate reacts with such mineral surfaces as chalcopyrite, pyrite, galena, covellite, orpiment, and sphalerite, to precipitate Ag_2S and throw sulfide into solution.

Ravitz and Wall (34.8.1), assuming that copper sulfate forms cupric sulfide on sphalerite, found the concentration of copper sulfate to give the best flotation recovery is that required to form a monomolecular film on the surface of the sphalerite. They noted that the abstraction from the solutions used in practice is in excess of this amount. On the basis of Zwicky's theory of mosaic crystal structure (29.25.3) (30.25.3)(33.13.1), they explain the fact that smaller particles require less copper sulfate than is required to form a monomolecular film, in order to effect the same flotation recovery as attained with large particles.

CONTACT ANGLE STUDIES OF ACTIVATION

The results of contact angle measurements, outlined below, are those of Wark and Cox (34.3.3)(34.3.4)(36.3.1)(36.8.2)(37.8.1)(38.3.1).

Copper sulfate activates sphalerite and activates galena above its critical pH. It is without effect on the response of pure pyrite, graphite, or charcoal, to potassium ethyl xanthate. Copper sulfate is a more effective activator for sphalerite in neutral cyanide-free solution than in an alkaline solution containing cyanide. Copper sulfate, in combination with cyanide, depresses, rather than activates pyrite.

Salts of such metals as platinum, gold, bismuth, mercury, silver, copper, cadmium, lead, cerium, antimony and arsenic, activate sphalerite, so that it will respond to potassium ethyl xanthate. Thallium and cobalt salts have a slight activating tendency, while salts of titanium and tin show none. In general, those metals which are effective activators form sulfides less soluble than zinc sulfide, while the non-effective metals form sulfides which are more soluble. However, thallium sulfide is reported more soluble, and stannous sulfide as less soluble than zinc sulfide. These metals are apparently exceptions to the generalization.

Sphalerite, depressed by sodium sulfide, may be activated by copper sulfide, if the copper sulfate is in stoichiometric excess of the sodium sulfide. Controlled concentrations

of sodium sulfide activate anglesite and cerussite, presumably by coating the minerals with a lead sulfide film, so that they will respond to a lower concentration of xanthate. Excess sodium sulfide, however, prevents response. In certain cases sodium phosphate may be substituted for sodium sulfide as an activator for these minerals.

THEORIES OF ACTIVATOR ACTION

All theories for the activation of sphalerite by copper sulfate are basically the same. They postulate the formation, on the sphalerite surface, of a copper-containing coat which will react with the collector, whereas the unaltered sphalerite surface does not react. The various theories differ as to the composition of the coating, and the mechanism by which it is formed.

Various theories have suggested, on the basis of the reaction:

$$ZnS + Cu^{++} \rightarrow CuS + Zn^{++}$$

that the coating is cupric sulfide. As pointed out by Ralston, King and Tartaron (30.3.5) however, the mineral covellite, which is cupric sulfide, is difficult to float.

Mitrofanoff (28.9.1) suggested the formation, in an alkaline copper sulfate solution containing cyanide, of a coating of hydrate, cyanide or carbonate, followed by the formation of the corresponding copper compounds, which react with xanthate to form insoluble copper xanthate.

Ince (30.3.2) advanced the theory that an insoluble cupric cyanide is formed at the surface of cyanide-treated sphalerite. Cyanide ion is thus removed, and frees the zinc of the mineral to react with the collector.

Taggart (32.8.1) contended that the cuprous sulfide coating first formed is oxidized and then reacts with xanthate

to form cuprous xanthate. The abstraction of xanthate ion, and liberation of sulfate ion is evidence for such a reaction. The activation of cyanide-treated sphalerite is thought to be effected by the decomposition of zinc cyanide, accompanied by the formation of soluble cuprocyanide ions. Taggart and associates (34.3.6) discuss activation in terms of the chemical theory.

Ralston, King and Tartaron (30.3.5) noted that the film formed by copper sulfate on sphalerite is probably different in nature from that on pyrite, because displaced zinc is soluble, while iron is insoluble in alkaline solutions. They consider that this difference may account for the fact that copper sulfate activates sphalerite to a greater extent than pyrite.

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3. Publications of the American Institute of Mining and Metallurgical Engineers
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6. Engineering and Mining Journal
7. Economic Geology
8. Journal of Physical Chemistry
9. Metall und Erz
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THE SURFACE CHEMISTRY OF FLOTATION

PART 2.

EXPERIMENTAL

The Solubility of Lead Ethyl Xanthate

and

The Flotation of Lead Sulfide

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THE SURFACE CHEMISTRY OF FLOTATION

PART 2. EXPERIMENTAL

The Solubility of Lead Ethyl Xanthate

and

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CONTENTS

ILLUSTRATIONS

THE SURFACE CHEMISTRY OF FLOTATION

PART II

INTRODUCTION TO EXPERIMENTAL WORK

Previous investigators have demonstrated that flotation of a solid is accomplished by maintaining or producing a hydrophobic coating on its surface, and that non-flotation results when the coating is hydrophilic. The mechanism by which the surface of a solid mineral becomes more hydrophobic after contact with a solution of a collector has not been satisfactorily explained. It is thought to be either chemical metathesis between entities derived from the mineral and the soluble collector; or adsorption of the collector, in whole or part, on the mineral surface. It has been shown that xanthate collectors are abstracted from solution by minerals if the basic constituent of the mineral forms a xanthate of low solubility, and are not abstracted if the xanthate has an appreciable solubility. It has also been shown that adhesion between an air-bubble and a xanthate-treated mineral surface is possible only below a critical pH value; more or less specific for a particular xanthate and mineral.

It is the purpose of the present investigation to determine the effect of pH on the solubility of certain base metal xanthates, and on the floatability of the corresponding xanthate-treated minerals, and to determine whether any correlation exists between this solubility and the floatability of

the mineral.

For the investigation, galena and potassium ethyl xanthate were selected as a typical mineral and collector, respectively.

PREPARATION OF MATERIALS, ETC.

The preparation and purification of the reagents used are described by R. F. Pearce.[1]

Mineral specimens used in flotation tests are described below:

Galena #1 Massive specimen of Sullivan galena obtained from Geology Dept., University of B.C.

Galena #2 Large specimen, visibly altered on the surface, and composed of 1/4" and larger cubes; obtained from Geology Dept., University of B.C.

Galena #3 Fine crystalline

Galena #4 Medium crystals, containing sphalerite and quartz.

Galena #5 Silver-Lead ore from St. Eugene Extension Mine. Massive, brittle, highly-lustrous specimen with no visible impurities. Obtained from B.C. Chamber of Mines, Vancouver.

All pH determinations were made with a Beckman glass-electrode pH meter.

1. The Surface Chemistry of Flotation. The Solubility of Zinc Ethyl Xanthate, R.F.Pearce, B.A.Sc. Thesis, University of British Columbia, 1938

SOLUBILITY OF LEAD ETHYL XANTHATE

Gravimetric Procedure

Procedure

Equivalent quantities of lead nitrate (0.2948 gms.) and potassium ethyl xanthate (0.2852) gms.) to form 0.4 gms. of lead ethyl xanthate were dissolved in separate 500 cc. portions of water. The solutions were mixed, and the mixture allowed to stand overnight, while the precipitate became completely flocculated.

This suspension of lead ethyl xanthate was filtered through asbestos on a weighed Gooch crucible, and the precipitate washed with 100 cc. water and 25 cc. ether. The crucible and contents were dried overnight at 80° C. then weighed to obtain the combined weight of precipitate and asbestos. The contents of the crucible was now transferred to 1000 cc. of distilled water and placed on a shaking machine overnight. This suspension was then filtered through asbestos on a weighed Gooch crucible, the precipitate dried, and its loss in weight determined.

A second preparation of lead ethyl xanthate was treated in the same way, but was extracted in the crucible with 1000 cc. of water instead of being transferred from the crucible and agitated with water.

Results

The pH of the lead xanthate suspension was 5.5 - 5.6. The loss in weight in the first procedure was 198 mgms; and

in the second was 120 mgms.

Conclusions

Experimental difficulties make this procedure useless as a method for determining the solubility of lead ethyl xanthate. The hydrophobic nature of the precipitate causes it to form a heavy scum on the surface of all suspensions, and to climb the walls of any vessel in which the preparation is placed, tending to cause loss of the material and leading to high results. Furthermore, the solubility of the asbestos used in the procedure is probably of the same order as that of the lead ethyl xanthate.

Colorimetric Procedure

Preparation of lead ethyl xanthate

Preliminary tests showed that a colorimetric procedure was suitable for determining lead in a saturated solution of lead ethyl xanthate. The following method was adopted for estimating the concentration of lead ions in equilibrium with solid lead ethyl xanthate in aqueous solution at various pH values.

Two solutions were prepared to contain 0.1474 gms. lead nitrate and 0.1454 gms. potassium ethyl xanthate respectively in 500 cc. of solution. This allowed 2% excess xanthate over the amount required to react with the lead nitrate and form 0.2 gms. of lead ethyl xanthate.

The lead nitrate solution was poured into the xanthate solution, contained in a litre flask, while shaking the latter.

The fine suspension of lead xanthate, which formed immediately, was then allowed to stand for two or three hours until it became flocculated and settled out, leaving a clear solution above the precipitate. In this condition, the precipitate showed no water-repelling tendency, and remained settled at the bottom of the flask. If the flask was agitated, however, the precipitate tended to concentrate as a dry scum at the free liquid surface, and to climb the walls of the flask.

The clear liquid above the precipitate was decanted off, the precipitate washed on to a paper filter, and washed on the filter with 1000 cc. of distilled water. At no time during the washing process, was the precipitate allowed to become completely dry.

Treatment of lead ethyl xanthate

After washing, the precipitate was transferred to a 1 litre rubber-stoppered bottle, about 900 cc. of distilled water added; then various amounts of either N/10 KOH or N/10 HCl to adjust the pH; and the total volume was made up to 1 litre. After a couple of minutes agitation, the initial pH of the preparation was measured, and the bottle and contents placed on a rotary shaking machine for a time interval varying from 16 hours up to several days. At intervals the bottle was removed from the shaking machine and the pH of the contents measured.

Determination of Pb^{++} concentration

When it was desired to measure the Pb^{++} concentration in the preparation, the bottle was removed from the shaker, and

the final pH reading was made. The contents of the bottle was filtered through asbestos on a Gooch crucible, and the filtrate placed in a 1 litre Pyrex beaker. After the addition of 2 cc. 6N HCl, the filtrate was slowly evaporated, without boiling, to a volume of 5 - 10 cc. Ammonia was added to the solution until it was slightly alkaline to litmus. The red color of the litmus was then brought back by adding glacial acetic acid and the solution was made up with distilled water to a measured volume of 100 cc. This solution was used as the unknown in the subsequent colorimetric comparisons.

Colorimetric comparisons for lead

Standard solutions were prepared by dissolving 2.2881 gms. $Pb(C_2H_3O_2)_2.3H_2O$ (lead acetate) in water and diluting to 500 cc. This solution (A) contained 2500 mgms. Pb^{++} per litre.

10 cc. of solution (A) were diluted to 500 cc. to prepare a solution (B) containing 50 mgms. Pb per litre.

100 cc. of solution (B) were diluted to 500 cc. to prepare a solution (C) containing 10 mgms. Pb per litre.

10 cc. of solution (B) were diluted to 500 cc. to prepare a solution (D) containing 1.0 mgms. Pb per litre.

When making a comparison with the colorimeter, 10 cc. of unknown solution was placed in one colorimeter cup, and 10 cc. of a suitable standard solution in the other; 4 drops of a saturated sodium sulfide solution were added to each cup, and the solutions stirred carefully.

The cups were now placed on the colorimeter and several

readings were taken, after which the cups were reversed, and a second set of readings obtained.

Fresh portions of standard and unknown were now placed in the cups, so that the cup formerly containing the standard solution contained the unknown, and a new series of readings was made.

These precautions were found to be essential in order to eliminate instrumental errors.

From the above readings an average value was obtained for the ratio of the depth of standard solution to the depth of unknown solution. This ratio was multiplied by the lead ion concentration in the standard solution to obtain the lead ion concentration in the unknown. The latter value, multiplied by 10, was taken to be the lead ion concentration in the original saturated lead xanthate solution.

The method is illustrated by the following example:

Unknown Solution No. 11

Unknown in Cup #1

	Depth - mm.		Depth - mm.
Standard on left	41.0	Unknown on right	36.0
" " "	40.8	" " "	36.0
" " "	40.8	" " "	36.0
" " "	41.1	" " "	36.0
" " right	40.8	" " left	36.0
" " "	40.3	" " "	36.0
" " "	40.1	" " "	36.0
" " "	40.6	" " "	36.0
Mean	40.7	Mean	36.0

Ratio: $\frac{\text{standard}}{\text{unknown}} = \frac{40.7}{36.0} = 1.131$

Unknown in Cup #2

	Depth - mm.		Depth - mm.
Standard on left	47.6	Unknown on right	43.0
" " "	48.3	" " "	43.0
" " "	47.7	" " "	43.0
" " "	48.4	" " "	43.0
" " right	47.8	" " left	43.0
" " "	47.8	" " "	43.0
" " "	47.7	" " "	43.0
" " "	47.3	" " "	43.0
Mean	47.8	Mean	43.0

Ratio: $\frac{\text{standard}}{\text{unknown}} = \frac{47.8}{43.0} = 1.111$

Mean Ratio = 1.12

Standard solution = 10.0 mgm. Pb per litre

Unknown solution = (1.12)(10.0) = 11.2 mgm. Pb per l.

Original solution = $\frac{(11.2)(100)}{1000}$ = 1.12 mgm. Pb per l.

Comparisons made between a particular unknown solution and different standard solutions gave comparable results. It was concluded that a correction for non-linear absorbtion, as required by Beer's Law, was outside the limits of experimental error. In most comparisons, the depth of one solution did not exceed twice the depth of the other.

A blank determination on the distilled water used in the analyses showed a concentration of 0.12 mgms. Pb per litre. It is felt that this value is probably too high, as it was determined during the early part of the work, before the colorimeter technique had become standardized. Subsequent values were not corrected for the Pb concentration of the water, because of the doubtful accuracy of the latter, and bacause it was more desirable to determine the trend of Pb concentra-

tion with pH, than to evaluate the absolute values of the Pb concentration.

Results and Conclusions

The results of this work are given in table 1 and plotted in Fig. 1. From these results it is concluded that:

(1) The concentration of lead ions in a solution which is in equilibrium with solid lead ethyl xanthate depends on the pH of the solution.

(2) The lead ion concentration has a minimum value of 0.15 mgm. Pb per litre at a pH of 8.0-8.2. This corresponds to a solubility of lead ethyl xanthate at this pH of 0.33 mgms. per litre. At pH values above or below 8.0 - 8.2, the lead ion concentration is greater.

(3) The solubility of lead ethyl xanthate in pure water, at a pH of 6.4 is 1.8 mgms. per litre.

(4) Lead ethyl xanthate, in the presence of water and hydrochloric acid, or potassium hydroxide, is slowly decomposed. This decomposition is accompanied by a decrease in pH in alkaline solutions, and an increase in acid solutions. The decomposition in the presence of potassium hydroxide is also accompanied by a darkening of the lead ethyl xanthate. This darkening is more rapid in the more concentrated alkaline solutions.

Note

Samples of lead ethyl xanthate for determinations 19 - 22 inclusive were prepared from equivalent quantities of reagents, allowing no excess xanthate. The lead concentrations obtained

for these samples, as tabulated in Table 1, are less than for comparable samples prepared with an excess of potassium ethyl xanthate. This is mentioned, inasmuch as it may have a bearing on the solubility figures obtained from the samples as prepared with excess xanthate. It is possible that excess xanthate ion may alter the lead xanthate surface in such a way that it will have a different solubility. To justify this assumption, further work is necessary.

TABLE 1.

LEAD CONCENTRATION AT VARIOUS pH VALUES IN SATURATED SOLUTIONS OF LEAD ETHYL XANTHATE

NO.	REAGENT ADDED PER LITRE	HRS	pH	HRS	pH	HRS	pH	HRS	pH	HRS	pH	FINAL TIME	FINAL pH	MGMS Pb PER LITRE @ FINAL pH
1	nil			18	6.90							41		0.885
2	"			18	6.75							41		0.648
3	"											50	6.38	0.892
4	"											50	6.47	0.831
5	1.0 cc N/10 KOH	0	8.8	26	8.95							44	8.61	0.928
6°	5.0 cc N/10 KOH	0	10.4	26	8.51							44	7.66	-
7	0.4 cc N/10 KOH											49	7.07	0.505
8°	10.0 cc N/10 KOH			44	9.77	73	9.25					91	9.24	-
9	1.0 cc N/10 HCl			47	4.30							65	4.33	5.27
10°	2.0 cc N/10 KOH			42	8.54	71	7.21	89	7.16			166	7.64	-
11°	1.3 cc N/10 KOH	1¼	9.41	51¼	9.11							70¼	8.85	1.08
12°	1.8 cc N/10 KOH	1¼	9.78	51¼	9.21	70¼	8.95	95	8.79	147	8.16	216	8.00	-
13°	1.0 cc N/10 KOH	¼	9.27	49½	8.93	68½	8.71					93½	8.54	0.620
14°	1.9 cc N/10 KOH	¼	9.63	49½	9.26	68½	9.11	93½	9.07	145½	8.94	214	8.80	-
15	0.2 cc N/10 HCl	0	4.80	48½	5.37							67½	5.51	1.31
16	0.6 cc N/10 KOH	0	8.43	2	7.89							20	7.95	<0.156
17	0.8 cc N/10 KOH	0	9.19	1¼	8.69	19¾	8.73					71¼	8.57	0.206
18	0.6 cc N/10 KOH	0	7.99	3	7.42							50	7.47	0.252
19	nil	¾	5.53	4¾	5.52							46¼	5.78	0.470
20	"	½	5.44	4½	5.47							46¼	5.69	0.528
21	"	¼	5.79	43	5.98							65¾	6.02	0.499
22	"	¼	5.88	43	6.11	65¾	6.16					90	6.26	0.528

° See Note on following page

NOTES RE TABLE 1.

No. 6 Yellowish initially; turned black after 24 hrs.

No. 8 Black after 24 hrs.

No. 10 Dark after 24 hrs.; blackening with longer time

No. 11 Very slightly dark after 48 hrs. Final filtrate and precipitate both fairly dark.

No. 12 Darkened after 48 hrs.

No. 13 Very slightly dark after 72 hrs. Filtrate and precipitate both slightly dark.

No. 14 Dark after 48 hrs.

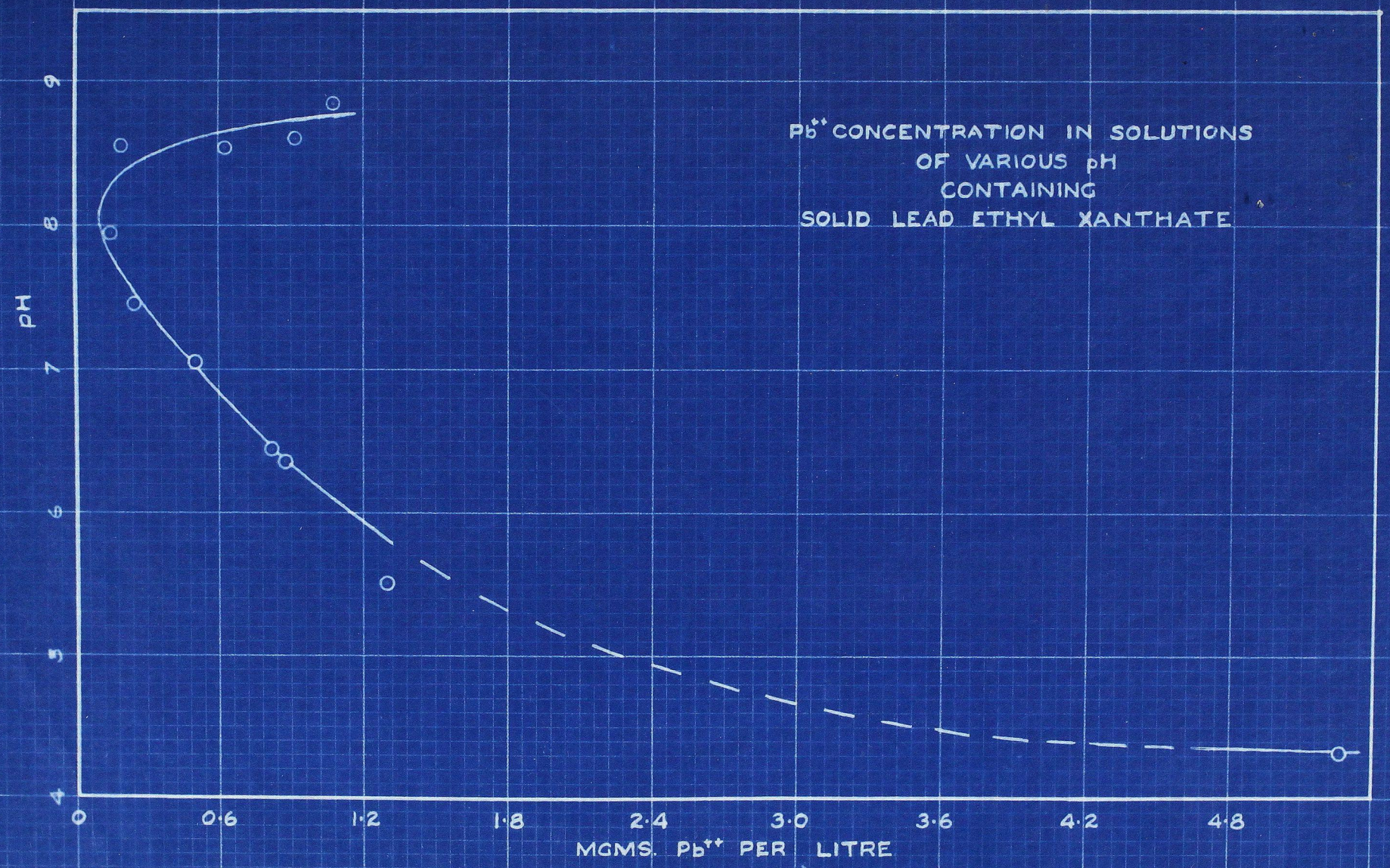
Pb^{++} CONCENTRATION IN SOLUTIONS
OF VARIOUS pH
CONTAINING
SOLID LEAD ETHYL XANTHATE
pH
9
8
7
6
5
4
0
0·6
1·2
1·8
2·4
3·0
3·6
4·2
4·8
MGMS. Pb^{++} PER LITRE

FIG. 1

SOLUBILITY OF CUPROUS ETHYL XANTHATE

Equivalent quantities of copper sulfate ($CuSO_4.5H_2O$) (13.4 gms.) and potassium ethyl xanthate (17.3 gms.) to react according to the equation:

$$2\ CuSO_4 + 4\ KEtX = 2CuEtX + (EtX)_2 + 2K_2SO_4$$

and form 10 gms. cuprous ethyl xanthate, were dissolved in water, and the solutions mixed. The precipitate was filtered and washed with water and with 95% ethyl alcohol, and stirred overnight in water.

The precipitate was again filtered, extracted with alcohol and ether, and dried at a low temperature.

0.1 gm. portions of dry cuprous ethyl xanthate, prepared as above, were agitated overnight with about 1 litre of water, then filtered; and the precipitate transferred to 1 litre bottles with 1000 cc. of distilled water, to give a solution having a pH of 7.1 - 7.4. These preparations were agitated for 21½ hours. At the end of this time the pH was 5.0 - 5.1. They were then filtered through filter paper and asbestos; but continued to pass through the filter as a cloudy liquid, probably an emulsion of dixanthogen.

2 cc. 6 N hydrochloric acid was added to the filtrate, which was then evaporated almost to dryness, made just alkaline with ammonia, and then boiled to expel excess ammonia. 2 cc. ammonium nitrate solution (100 gm. per litre) were added, and the solution was made up to a volume of 60 cc.

A colorimetric comparison was attempted between a 10 cc. portion of the above solution, and a 10 cc. portion of a standard copper sulfate solution, containing 4 gm. ammonium nitrate per litre, after adding 2 drops of potassium ferrocyanide solution (40 gms. per litre) to each. It was found, however, that insufficient color was developed to make this procedure feasible.

Further work on the solubility of cuprous ethyl xanthate was not attempted.

METHODS FOR MEASURING FLOATABILITY

If the premise is accepted that a solid is floatable when its surface is hydrophobic; and that it may possess this property to a greater or less extent; the question arises: How can this degree of water-repellence or floatability be measured? It has been determined previously in various ways. The floatability has been measured as the percentage of finely-ground solid recovered in a flotation froth, under particular conditions approximating those existing in industrial flotation cells. The extent to which a surface is hydrophobic has been measured by the magnitude of the contact angle between an air-bubble and the submerged solid surface; or between a water drop and the solid surface in air. To a lesser extent, the displacement pressure of water by air, and the heat of wetting of the surface have been used as measures of floatability.

The contact angle is probably the most fundamental measure of the state of a solid surface, and is a derivable function of the solid interfacial tension. However, the concentration of a finely - ground solid at a liquid-gas interface is a more direct measure of floatability. In the current work it was decided to use the latter method. It became necessary, therefore, to develop an apparatus to make small scale flotation tests, which would permit close control of as many as possible of the variables inherent in the process.

It was at first thought that some information might be obtained by allowing single air bubbles of known size to rise

through a pulp of mineral in water, and determining the concentration of mineral in the upper part of the pulp, as a function of the total interfacial area represented by the bubbles. No satisfactory method could be devised, however, to remove the concentrated solid before the air bubbles collapsed and allowed the solid to settle back into the pulp. In order to hold the water-repellent mineral above the pulp, it is necessary to maintain a froth zone in which the individual air bubbles are rising with a velocity greater than the effective downward velocity of the mineral particles. With this in mind, a pneumatic glass flotation cell (Fig. 2) was developed, which is believed to have certain advantages for the present work over existing types of laboratory cells. The all-glass construction facilitates cleaning, and minimizes contamination of the pulp by the material of the cell. In practice it is found necessary to clean the sintered plate after each run by forcing aqua regia through it, to remove small sulfide particles which tend to clog the pores. Air supply is easily regulated. Elimination of mechanical agitation, other than by the stream of air bubbles allows closer reproducibility of this variable than is possible when an impeller is used.

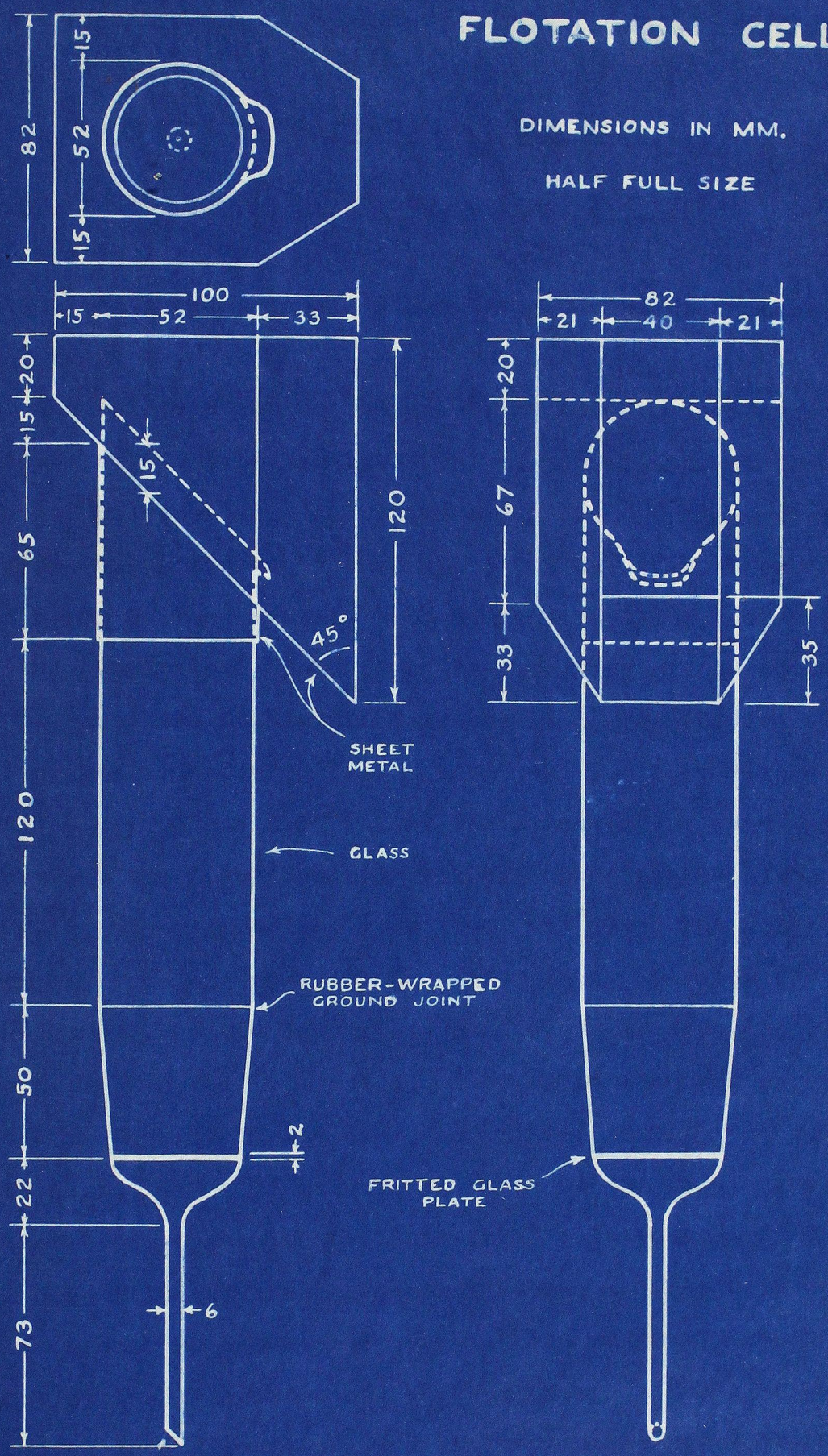
FLOTATION CELL
DIMENSIONS IN MM.
HALF FULL SIZE
82
15
52
15
100
15
52
33
20
15
65
120
15
45°
SHEET METAL
GLASS
120
RUBBER-WRAPPED GROUND JOINT
50
2
22
73
6
82
21
40
21
20
67
33
35
FRITTED GLASS PLATE

FIG. 2

FLOTATION WITHOUT REAGENTS

Procedure with precipitated PbS, galena, and silica

The cell was used first to study the flotation of synthetic lead sulfide in distilled water, using no frother or other reagents.

The cell was set up and provision made to introduce a constant stream of water (about 5 cc. per minute) at the top, to cause an overflow. Approximately 5 gram portions of lead sulfide were prepared by saturating 500 cc. of a water solution of 7 grams of lead nitrate with hydrogen sulfide gas, and washing the precipitate eight times by decanting off successive 500 cc. portions of distilled water. A 5 gram portion of lead sulfide was transferred to the cell, and the pulp volume made up to about 300 cc. Sufficient air pressure was maintained to prevent the liquid running through the sintered plate, but insufficient to cause any overflow. The pH of the pulp was taken, and the air pressure increased until overflow was just about to occur. The feed water was turned on, and the overflow collected for 10 minutes, after which the feed water was shut off, the air turned down, the volume of pulp and concentrate noted, and a pH measurement made on the pulp. The "concentrate" overflow, and the "tailings" pulp remaining in the cell were filtered through Gooch filters, and the weights of solid in each were measured. From these weights, the total weight of lead sulfide used, the percentage of this weight recovered in the overflow, and the percentage recovered per

unit volume of the overflow were calculated. The results of this series of runs are given in Table 2.

In the above tests a certain amount of pulp overflowed with the incipient froth. The pulp mechanically carried a definite weight of solid into the overflow. If the solid used is hydrophobic, the observed recovery should be greater than the mechanical recovery; and if hydrophilic, the observed recovery should be less. In order to calculate the mechanical recovery, it is assumed that, at any instant, the concentration of solid in the overflowing pulp is the same as in the body of the pulp. It is also assumed that the initial volume of pulp does not change. This implies that the feed water causes an overflow of a volume of pulp equal to that of the water added. Let A cc. be the constant volume pf pulp in the cell, and G gms. be the original weight of solids in the pulp. After n cc. of feed water has been added, an equal volume of concentrate, containing x gms. of solids has overflowed. After x gms. of solid has overflowed, the instantaneous concentration of solid in the pulp will be $\frac{G - x}{A}$ gms. per cc. If a volume dn cc. now overflows, it will contain dx gms., and the concentration of solid in the overflow will be $\frac{dx}{dn}$ gms. per cc. It has been assumed that these concentrations are equal. Therefore:

$$\frac{dx}{dn} = \frac{G - x}{A}$$

$$\int_0^x \frac{dx}{G - x} = \frac{1}{A}\int_0^n dn$$

$$\ln \frac{G}{G - x} = \frac{n}{A}$$

$$x = G\left(1 - \frac{1}{e^{n/A}}\right)$$

From this equation, the weight of solid (x gms.) overflowing "mechanically" has been calculated for the various tests, and the results tabulated in Table 2 and subsequent tables.

From the work with precipitated lead sulfide certain conclusions may be drawn. If all variables (pulp volume, air pressure, weight of solids, and volume of feed water added) are kept constant in a series of runs; the volume of overflow is necessarily constant, and the weight of solids recovered in the overflow is a reproducible figure. If the air pressure, initial pulp volume, and volume of feed water added are kept constant in a series of runs, but greater weights of solid are used in the cell, the pulp volume tends to increase during a run, and the final volume of overflow is less. At the same time the recovery increases, but the recovery per unit volume of overflow tends to remain fairly constant. The latter figure, because it tends to take care of slight unavoidable variations in overflow volume, has been used as the final figure in each run. The air pressure which must be applied to just cause the cell to overflow depends on the volume of pulp in the cell. A small pulp volume requires a high air pressure, and vice versa. At the same time, the total recovery, and the recovery per unit volume of overflow are increased by the use of a smaller pulp volume and a greater air pressure. In all cases, the

TABLE 2.

FLOTATION OF PRECIPITATED LEAD SULFIDE WITH NO REAGENTS

RUN NO.	WEIGHT--GMS. HEADS	WEIGHT--GMS. CONC.	PULP VOL.-CC. BEFORE	PULP VOL.-CC. AFTER	CONC. VOL. CC.	AIR PRESS. CMS.	PULP pH BEFORE	PULP pH AFTER	ACTUAL RECOVERY %	ACTUAL RECOVERY %/cc.	CALC. RECOVERY %	CALC. RECOVERY %/cc.	REMARKS
1	0.491	0.120	300	300	49	46.0			24.4		15.1	0.308	Preliminary run
2	5.128	0.318	325	-	45	47.0			6.2		12.9	0.287	" "
3A	4.837	0.342	300	-	27	48.7	7.1	-	7.07	0.262	8.69	0.322	" "
3B	4.496	0.298	-	325	26	48.7	-	6.7	6.16	0.237	7.75	0.298	" "
4	4.772	0.585	320	310	48	45.0	6.4	6.3	12.3	0.256	14.0	0.292	
5	4.849	0.545	300	300	44	45.0	6.1	6.1	11.2	0.252	13.6	0.309	
8	4.894	0.694	270	260	49	48.0	6.4	6.4	14.2	0.290	16.5	0.336	
9	4.836	0.564	340	340	49	41.9	6.1	6.4	11.7	0.237	13.5	0.276	
10	4.774	0.540	280	295	42	45.0	6.0	6.2	11.3	0.269	13.6	0.324	
11	4.640	0.588	280	280	44	46.3	6.0	6.2	12.6	0.286	14.6	0.332	
32	6.952	0.583	300	325	35	45.0	6.5	6.6	8.39	0.239	10.7	0.306	
33	5.914	0.558	300	305	35	45.0	6.7	6.7	9.44	0.269	11.0	0.314	
34	5.068	0.573	300	315	43	45.0	6.6	6.1	11.3	0.262	13.1	0.304	
35	3.868	0.520	300	310	45	45.0	6.8	6.9	13.4	0.299	13.8	0.307	

actual recovery is less than the calculated recovery per cc. of overflow. This indicates that, under the conditions of the experiment, precipitated lead sulfide shows no tendency to concentrate at the air-liquid interface; that is, it does not display any inherent floatability. This conclusion assumes, of course, that in the process of overflowing, there is no tendency at the overflow lip for the solid to be held back to a greater extent than the liquid.

In an endeavor to make this latter assumption unnecessary, parallel tests were made with lead sulfide, galena, and an hydrophilic material such as silica.

Preliminary tests on various silica samples, given in Table 3 showed that it was necessary to make comparisons between similarly sized materials. A water elutriator (Fig. 3) was built, and calibrated by the rising velocity of water produced at various stopcock settings. This apparatus gave velocities up to 26 cm. per minute, corresponding to the settling rate of a quartz particle of approximately 0.07 mm. diameter, or 200 mesh.

Galena, for use in subsequent tests, was prepared just before using by grinding 8 to 10 grms. of 1/4" mineral under distilled water in a carefully cleaned porcelain or agate mortar, and intermittently washing fine material into the elutriator until the entire portion had been transferred. Particles with a settling rate of 3.5 to 9 cm. per minute were then separated by the elutriator, and transferred at once to the flotation cell. Portions of an assay grade of powdered

TABLE 3.

FLOTATION OF MISCELLANEOUS SILICA SAMPLES WITH NO REAGENTS

RUN NO.	WEIGHT--GMS. HEADS	CONC.	PULP VOL.-CC. BEFORE	AFTER	CONC. VOL. CC.	AIR PRESS. CMS.	PULP pH BEFORE	AFTER	ACTUAL RECOVERY %	%/cc.	CALC. RECOVERY %	%/cc.	REMARKS
12	Incomplete - silica too fine												
13	4.984	0.164	300	285	53	45.0	7.2	7.3	3.30	0.0623	16.6	0.314	-100 mesh
14	4.930	0.405	300	290	47	44.4	6.6	6.7	8.24	0.174	14.7	0.313	Deslimed silica
15	4.921	0.294	300	295	46	44.0	6.7	7.1	5.97	0.132	14.3	0.311	" "

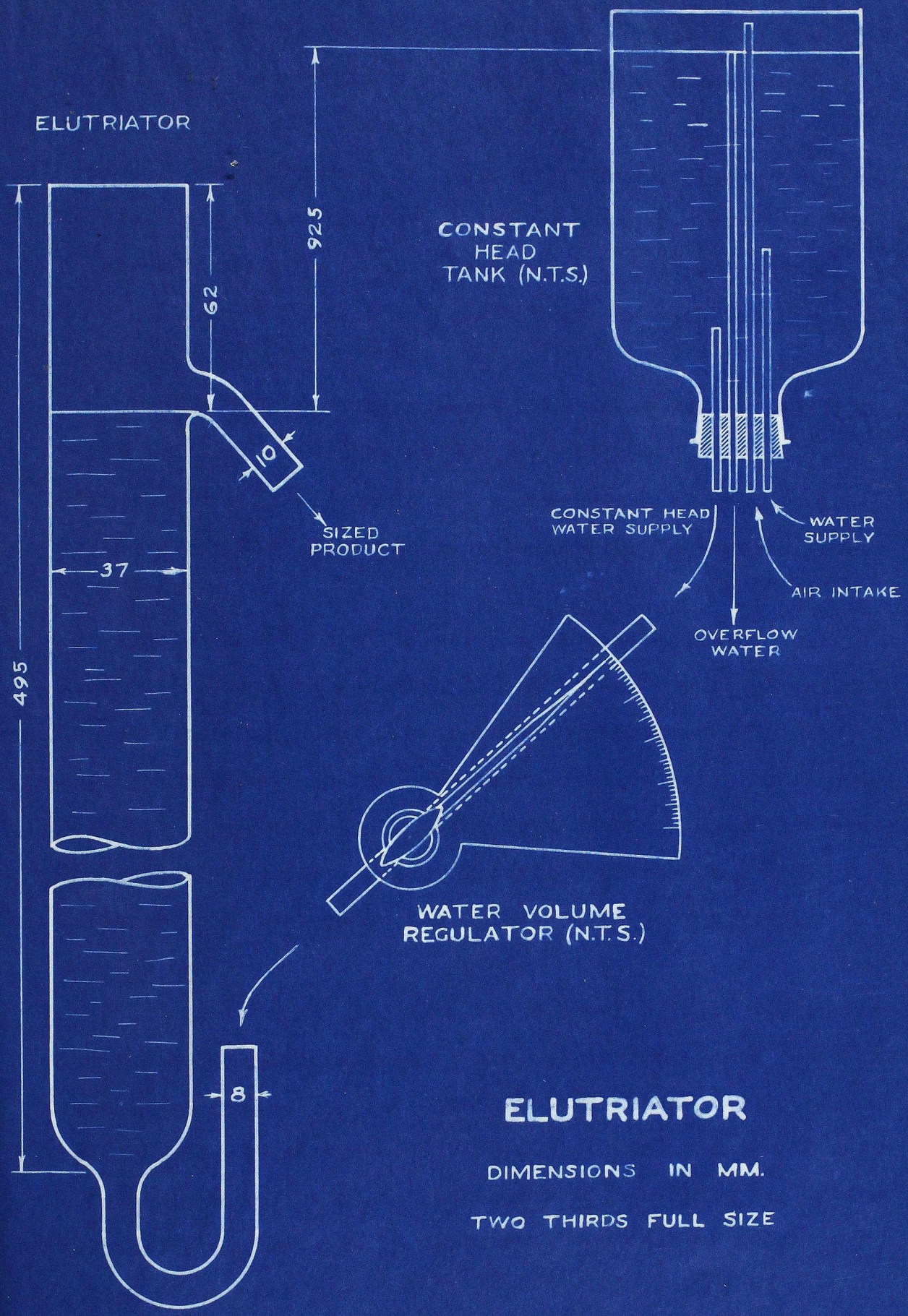
ELUTRIATOR
925
62
10
SIZED PRODUCT
37
495
8
CONSTANT HEAD TANK (N.T.S.)
CONSTANT HEAD WATER SUPPLY
WATER SUPPLY
AIR INTAKE
OVERFLOW WATER
WATER VOLUME REGULATOR (N.T.S.)
ELUTRIATOR
DIMENSIONS IN MM.
TWO THIRDS FULL SIZE

FIG. 3

silica were placed in the elutriator, and the fraction with a settling velocity in the range 3.5 - 9 cm. per minute was removed. This portion was digested in hydrochloric acid, washed free of ferric chloride, dried, and bottled until required. No attempt was made to size the precipitated lead sulfide, as it consisted of flocs which would break up when the suspension was agitated.

The results of tests made on the sized galena and silica, using the same procedure as followed for lead sulfide, are given in Table 4 and Table 5. A comparison of results is shown by the graph Fig. 4, in which only comparable results have been plotted.

Tables 6 to 8 are the results of miscellaneous runs on lead sulfide and silica with the addition of various reagents to the flotation pulp. The runs made with lead sulfide in a pulp containing 25 mgm. potassium ethyl xanthate per litre, over the pH range 3 to 10, show that xanthate slightly increases the actual recovery per cc. Insufficient work was done in this series to determine the effect of pH on recovery.

Conclusions

It may be concluded from these results that, within the limits of experimental error, the galena and silica particles investigated have the same floatability; hence, that this specimen of galena has no inherent floatability. It is also evident from Fig. 4 that the behavior of precipitated lead sulfide is not materially different from that of galena or silica.

TABLE 4.

FLOTATION OF SIZED GALENA WITH NO REAGENTS

RUN NO.	WEIGHT--GMS. HEADS	WEIGHT--GMS. CONC.	PULP VOL.-CC. BEFORE	PULP VOL.-CC. AFTER	CONC. VOL. CC.	AIR PRESS. CMS.	PULP pH BEFORE	PULP pH AFTER	ACTUAL RECOVERY %	ACTUAL RECOVERY %/cc.	CALC. RECOVERY %	CALC. RECOVERY %/cc.	REMARKS
16	7.362	0.726	300	295	47.0	45.0	7.1	6.9	9.87	0.210	14.5	0.309	#1 Galena
18	4.084	0.537	300	295	52.0	45.0	6.7	6.8	13.2	0.254	15.9	0.306	
19	2.879	2.300	300	295	50.0	45.0	6.0	6.3	79.9	1.60	15.5	0.310	Ether-washed galena
22	3.209	1.232	300	295	50.0	45.0	4.9	5.2	38.4	0.768	15.5	0.310	" " "
23	1.729	0.699	300	295	50.5	44.8	6.4	6.2	40.4	0.801	15.6	0.309	#2 " " "
24	2.774	0.330	290	290	50.5	45.0	5.8	5.8	11.9	0.264	16.0	0.317	#2 Galena
25	4.350	0.319	305	295	(57)	44.8	6.0	6.2	7.34	(0.129)	17.3	(0.304)	Conc. vol. estimated
26	4.518	0.598	300	295	53.0	45.0	5.9	5.9	13.2	0.250	16.3	0.308	
27	5.794	0.431	300	295	51.0	45.0	5.9	6.0	7.45	0.146	15.7	0.308	
29	4.458	0.271	300	290	51.5	45.0	6.1	6.1	6.06	0.118	16.0	0.310	

TABLE 5

FLOTATION OF SIZED SILICA WITH NO REAGENTS

RUN NO.	WEIGHT--GMS. HEADS	WEIGHT--GMS. CONC.	PULP VOL.-CC. BEFORE	PULP VOL.-CC. AFTER	CONC. VOL. CC.	AIR PRESS. CMS.	PULP pH BEFORE	PULP pH AFTER	ACTUAL RECOVERY %	ACTUAL RECOVERY %/cc.	CALC. RECOVERY %	CALC. RECOVERY %/cc.	REMARKS
17	7.085	0.614	300	295	45.0	45.0	6.9	6.9	8.67	0.193	14.0	0.311	
20	3.979	0.595	300	290	54.0	45.0	6.5	6.6	15.0	0.277	16.8	0.312	
21	4.968	0.697	300	295	53.0	45.0	6.7	6.6	14.0	0.264	16.3	0.308	
28	5.973	0.803	300	295	55.0	45.0	6.8	6.8	13.4	0.244	17.0	0.309	
30	4.576	0.590	300	295	54.0	45.0	6.9	6.9	12.9	0.239	16.7	0.310	
31	5.562	0.546	300	300	48.5	45.0	6.6	6.9	9.83	0.202	15.0	0.310	

TABLE 6.

FLOTATION OF PRECIPITATED LEAD SULFIDE WITH 25 mgm./l. POTASSIUM ETHYL XANTHATE AND pH CONTROLLING REAGENTS

RUN NO.	WEIGHT--GMS. HEADS	CONC.	PULP VOL.-CC. BEFORE	AFTER	CONC. VOL. CC.	AIR PRESS. CMS.	PULP pH BEFORE	AFTER	ACTUAL RECOVERY %	%/cc.	CALC. RECOVERY %	%/cc.	REMARKS
6	4.646	1.198	300	280	50	45	7.0	6.7	25.8	0.515	15.5	0.310	No reagents ex.KEtX
40	5.021	0.916	300	310	47	45	3.1	3.2	18.2	0.388	14.3	0.304	3 cc N/10 HCl
41	5.076	0.930	300	310	46	45	4.4	4.7	18.3	0.398	14.0	0.304	2 cc N/10 HCl
42	4.997	0.552	300	335	36	45	10.1	8.6	11.0	0.307	10.8	0.300	4 cc 0.13 N KOH
43	4.939	0.539	300	345	38	45	9.5	7.8	10.9	0.288	11.1	0.292	2 cc 0.13 N KOH
44	4.883	0.737	305	325	46	45	5.5	6.1	15.1	0.328	13.5	0.294	1 cc N/10 HCl

TABLE 7.

FLOTATION OF PRECIPITATED LEAD SULFIDE WITH ETHYL ALCOHOL

RUN NO.	WEIGHT--GMS. HEADS	CONC.	PULP VOL.-CC. BEFORE	AFTER	CONC. VOL. CC.	AIR PRESS. CMS.	PULP pH BEFORE	AFTER	ACTUAL RECOVERY %	%/cc.	CALC. RECOVERY %	%/cc.	REMARKS
7	4.761	0.538	300	280	61	45.0	6.6	6.7	11.3	0.185	18.5	0.304	333 mgm EtOH/l.
36	5.377	0.240	240	280	26	48.5	7.7	7.1	4.45	0.171	9.5	0.366	834 " "
37	4.452	0.224	250	265	34	48.5	6.7	7.0	5.02	0.148	12.5	0.368	800 " "
38	6.383	0.189	260	255	51	48.5	6.5	6.6	2.96	0.058	18.1	0.356	770 " "

TABLE 8.

FLOTATION OF SIZED SILICA WITH ETHYL ALCOHOL

39	4.939	0.408	250	200	97	48.5	7.25	7.20	0.085	0.0083	34.8	0.360

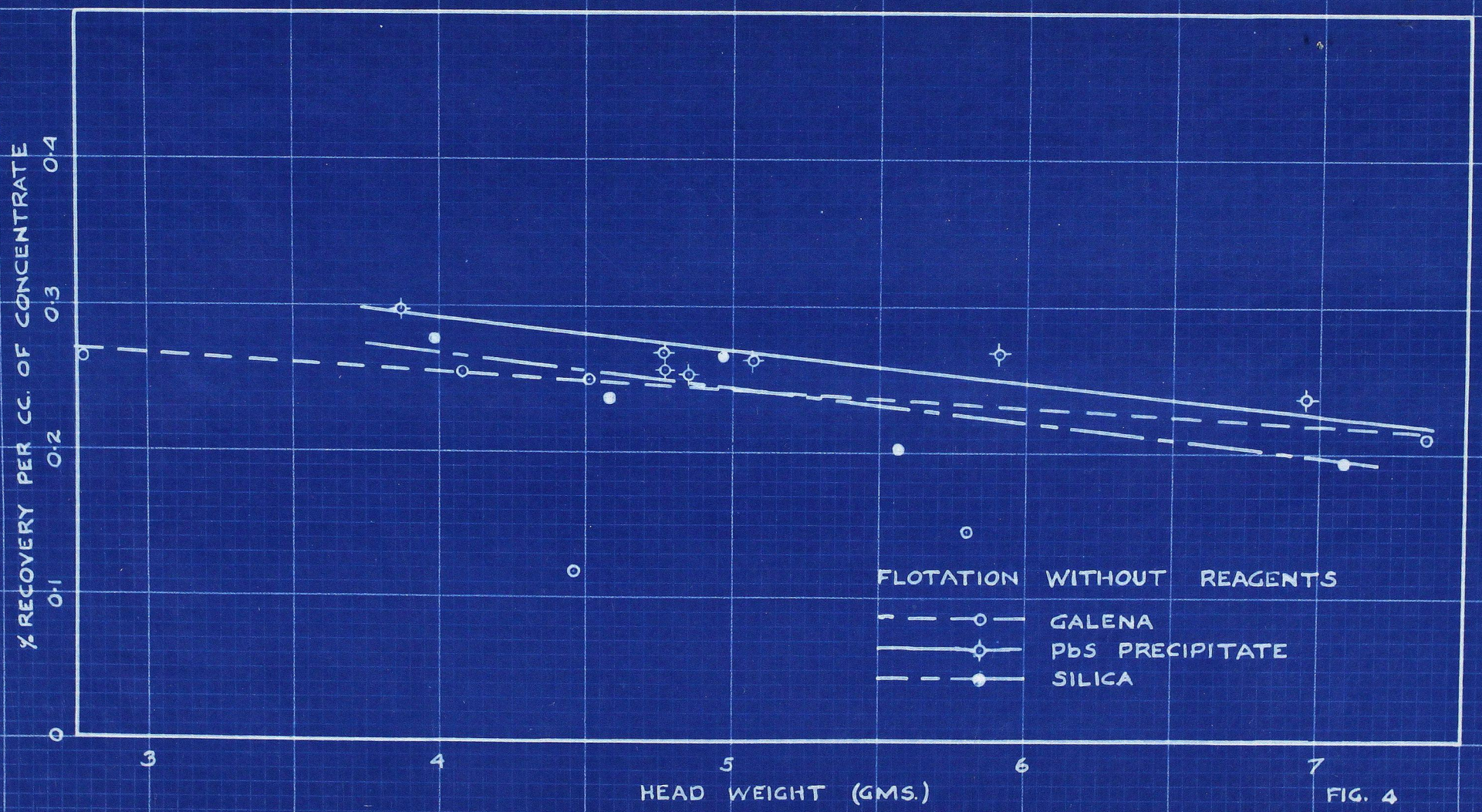
% RECOVERY PER CC. OF CONCENTRATE
0
0·1
0·2
0·3
0·4
3
4
5
6
7
HEAD WEIGHT (GMS.)
FLOTATION WITHOUT REAGENTS
GALENA
PbS PRECIPITATE
SILICA

FIG. 4

FLOTATION WITH TERPINEOL ALONE
(Inherent Floatability)

The runs with lead sulfide and silica, in which ethyl alcohol was used as a frothing agent (Tables 7 and 8) show that the frother materially decreases the recovery per cc. by decreasing the "mechanical recovery". While ethyl alcohol does not give a satisfactory flotation froth, the runs outlined in Tables 7 and 8 suggested the advantage of using a frothing agent to decrease to a minimum the mechanical recovery of an hydrophilic solid, while allowing maximum recovery, with small overflow of liquid, of a solid which is hydrophobic. The following tests were made using terpineol as a frother.

Procedure with precipitated lead sulfide

Approximately 5 gms. of precipitated lead sulfide in 150 cc. of pulp, containing 5.3 mgms. terpineol per litre was placed in the flotation cell, and air pressure applied sufficient to form a copious froth.

No trace of lead sulfide appeared in the froth.

Procedure with Galena #2 (Run No. 45)

All apparatus was carefully cleaned with chromic acid and distilled water.

A sample of Galena #2 was ground under distilled water, sized, and a 1.82 gm. portion, having a settling rate of 9 - 25 cm. per minute transferred to the flotation cell. The pulp volume was made up to 150 cc. and 3.5 cc. terpineol solution (1cc. = 0.25 mgm.) added to make the concentration of

terpineol 5.8 mgm. per litre.

In this solution, containing no acids or alkalis; and in the presence of hydrochloric acid or sodium hydroxide, over the pH range 3 to 11 there was no trace of galena in the froth.

Procedure with Galena #5 (Run No. 58)

All apparatus was carefully cleaned with chromic acid and distilled water.

A sample of Galena #5 was ground under distilled water, sized, and the portion having a settling rate of 9 - 25 cm. per minute transferred to the flotation cell. The pulp volume was made up to 250 cc. and 4 cc. terpineol solution (1 cc. = 0.25 mgm.) added to make the concentration of terpineol 4 mgms. per litre. Time was measured from the time of adding terpineol. Three five-minute concentrates were taken off, as shown below, with the addition of 4 cc. of terpineol solution before concentrates #2 and #3 were removed.

Run No. 58

Product	Weight (gms.)	pH Pulp	% Recovery
Concentrate #1 (1-6 min.)	1.042	4.04	36.8
" #2 (13-18 min.)	0.202	4.04-4.13	7.06
" #3 (30-35 min.)	0.092	4.13	3.24
Tails	1.503		52.9
Heads	2.839		100.0

Conclusions

Precipitated lead sulfide is not floated by terpineol alone.

Two samples of galena, both apparently pure specimens,

differ materially in their floatability with terpineol alone. Of the two samples studied under similar conditions, the first has no inherent floatability, while the second has an appreciable floatability.

The galena specimen showing no natural floatability, in view of earlier observations, yields lead ions to a greater extent than the other specimen, when placed in water.

Because of these conflicting results, no conclusion can be drawn at this time, as to the inherent floatability of galena. It is probable that the state of oxidation of the galena surface determines its floating characteristics with terpineol alone. As a tentative hypothesis it is suggested that the surface of a pure lead sulfide crystal(which might be obtained by grinding galena under oxygen-free water for contact angle measurements) may be non-floatable; but that adsorption of atmospheric oxygen may make such a surface floatable. If the adsorption continues to such a point that the surface becomes essentially one of lead sulfate, or lead oxide, the character of the mineral surface is again hydrophilic.

This hypothesis might be tested by preparing and floating galena in the presence of some inert gas, although elaborate precautions would be necessary to insure the purity of the lead sulfide surface, the total exclusion of oxygen, and the elimination of any possible contaminants.

FLOTATION OF XANTHATE-TREATED GALENA WITH TERPINEOL

Procedure

Galena was ground and sized as before, and the portion having a settling rate of 9 - 25 cm. per min. (35 - 50 microns measured particle size) was transferred at once to a beaker and carefully stirred for 4 min. with 250 cc. of potassium ethyl xanthate solution (25 mgm. per litre). The solution was poured off, and the mineral again treated for 4 min. with 250 cc. of fresh xanthate solution of the same concentration. This solution was poured off and the galena stirred for 4 min. with 250 cc. of distilled water, after which the wash water was decanted off, the galena transferred to the flotation cell, hydrochloric acid or potassium hydroxide added to control the pH, and the volume of pulp brought up to 250 cc. while maintaining a low pressure of air.

The pulp was air-agitated in the cell for 5 - 10 minutes, while initial pH readings were made at frequent intervals. 4 cc. of terpineol solution (250 mgm. per litre) was added to make the terpineol concentration in the pulp 4 mgm. per litre. The air pressure was brought up to 45 cm. of mercury, and the overflowing froth collected for 5 min. A fine stream of water (about 5 cc. per min.) was used to wash down the inside glass walls of the cell during the run, and to assist the froth to overflow. After the 5 min. period, the air pressure was lowered to stop the overflow; a series of pH measurements was made on the pulp remaining in the cell; and

the volume of pulp in the cell was noted. The concentrate and tailings pulps were filtered through Gooch crucibles; the crucibles were dried overnight at approximately 80° C., and weighed. The recovery was calculated as the percentage weight of total material recovered in the froth overflow.

The pH at the beginning and end of each run was obtained by plotting pH versus time, and interpolating.

Results

The results of this series of tests are given in Table 9 and Fig. 5. Runs numbered 45 - 56 were made on #2 Galena; runs #57 - #60 on No. 5 Galena.

Remarks

The xanthate solution, after it was used for treating No. 2 Galena, became quite cloudy; but remained practically clear with No. 5 Galena. It would appear that the former sample may have contained an appreciable amount of soluble lead compounds which reacted with the xanthate solution to form a suspension of lead ethyl xanthate. Subsequent tests (Runs 45 and 58) also showed that the two samples behaved differently in flotation.

In all runs made, the pH in alkaline solutions tended to drop; and in acid solutions, to rise during the course of the run. This change of pH with time is shown by Fig. 6 and Fig. 7. In only two cases (Runs 53 and 55) did the pH tend to reach a constant value of 7.4 - 7.5. The rate of change of pH with time appears to be greatest when the initial concentration of alkali is small. It is significant that this

TABLE 9.

FLOTATION OF SIZED GALENA WITH TERPINEOL

RUN NO.	WEIGHT-GMS. HEADS	WEIGHT-GMS. CONC.	PULP VOL.-CC. BEFORE	PULP VOL.-CC. AFTER	PULP pH BEFORE	PULP pH AFTER	RECOVERY %	REMARKS
46	3.218	2.978	250	255	5.73	5.63	92.5	
47	2.915	2.827	250	250	6.08	6.09	97.2	
48	4.023	nil	250	250	11.3	11.0	0	10 cc. 0.09 N - KOH
	4.023	3.696	250	250	10.0	9.23	91.9	10 cc. 0.09 N - KOH + 2 cc N/10 HCl
49	3.384	1.940	250	250	10.65	9.90	57.1	9.2 cc. 0.09 N - KOH
50	4.767	1.787	250	260	10.78	10.14	37.4	9.2 cc. 0.09 N - KOH
51	5.774	5.030	250	260	10.40	9.60	87.0	6 cc. 0.09 N - KOH
52	4.538	3.909	250	255	3.15	3.37	86.2	10 cc. N/10 HCl
53	3.620	3.233	250	260	9.05	7.70	89.3	3 cc. 0.09 N - KOH
54	2.178	2.146	210	215	2.24	2.27	98.7	20 cc. N/10 HCl
55	2.353	1.897	250	265	7.36	7.38	80.7	1.5 cc. 0.09 N - KOH. Added 1 cc extra terpineol soln at end.
57	3.578	3.578	250	250	2.48	2.52	100.0	4 cc. N/10 HCl; 7 min. conc. extra terpineol added.
59	6.263	1.564	250	250	10.84	10.42	25.0	9.5 cc. 0.09 N - KOH
60	4.848	3.476	250	250	10.43	9.96	71.7	9.0 cc. 0.09 N - KOH

NOTES RE TABLE 9.

Run #48 Measuring time from the addition of terpineol, there was no trace of galena in the froth at 7 min. (pH 10.91); but a small amount was visible at 8 min. (pH 10.82). At 11 min. 2 cc. N/10 HCl was added to reduce the pH to 10.0, and a concentrate was taken off during the interval between 14 and 19 min. The final pH observed at 14 min. was 9.23.

Run #49 As the pH continued to drop after the run was completed, more galena appeared in the froth.

In this run, the concentrate liquid was yellowish in color, but clear.

Run #54 An appreciable quantity of lead sulfide was recovered from the tailings filtrate by saturating it with hydrogen sulfide gas after the run was completed.

A microscopic examination of the unfloated galena in the tailings showed it to contain a considerable amount (30 to 50%) of a white, siliceous-appearing mineral.

Run #57 The pulp in the cell was free of galena at 5 min. The longer time and extra terpineol was used to cause the galena already in the froth at 5 min. to overflow.

A negligible amount of lead was detected in the tailings filtrate by saturating it with hydrogen sulfide.

Run #59 The tailings filtrate was very dark in color.

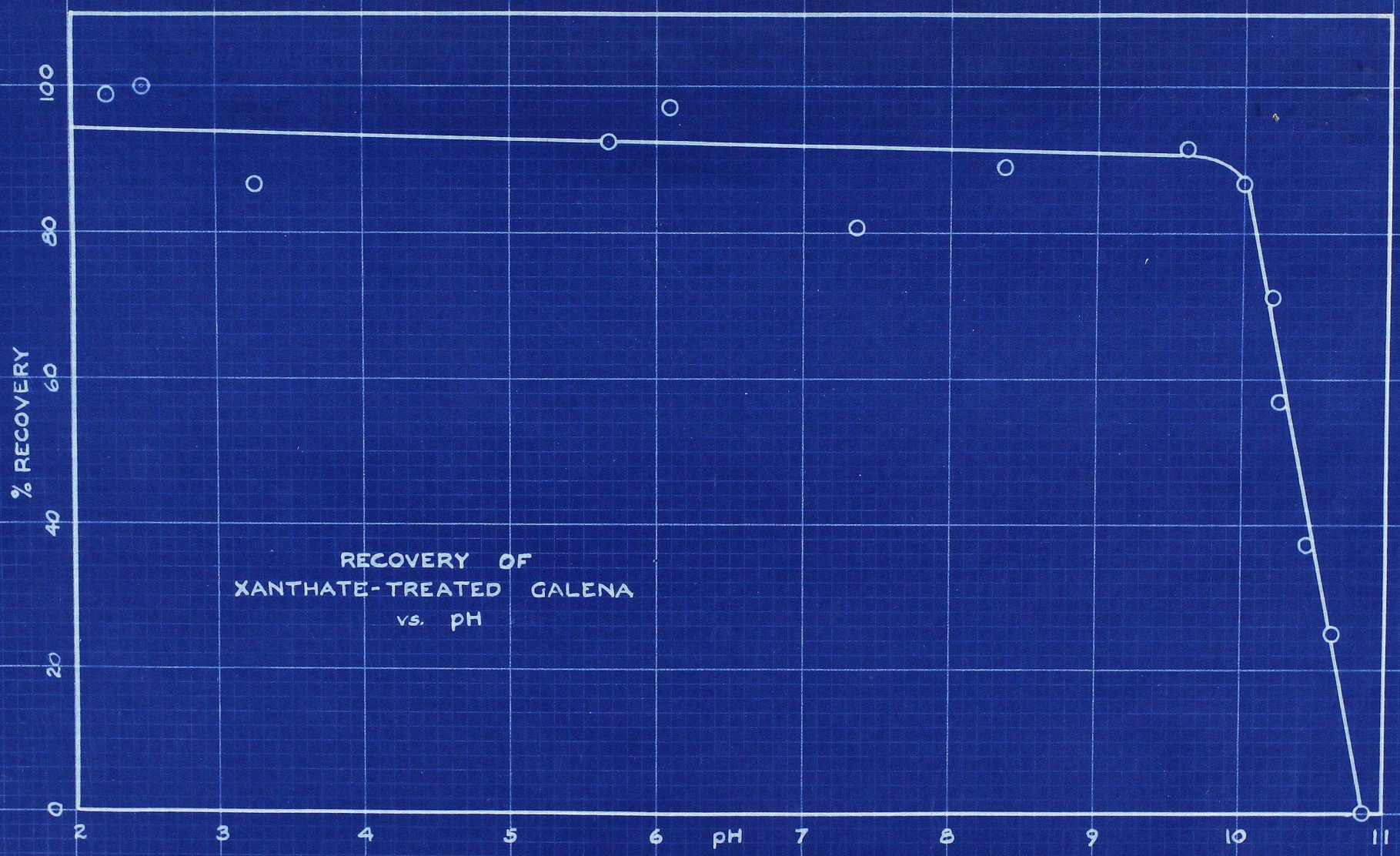
RECOVERY OF
XANTHATE-TREATED GALENA
vs. pH
% RECOVERY
0
20
40
60
80
100
2
3
4
5
6
pH
7
8
9
10
11

FIG. 5

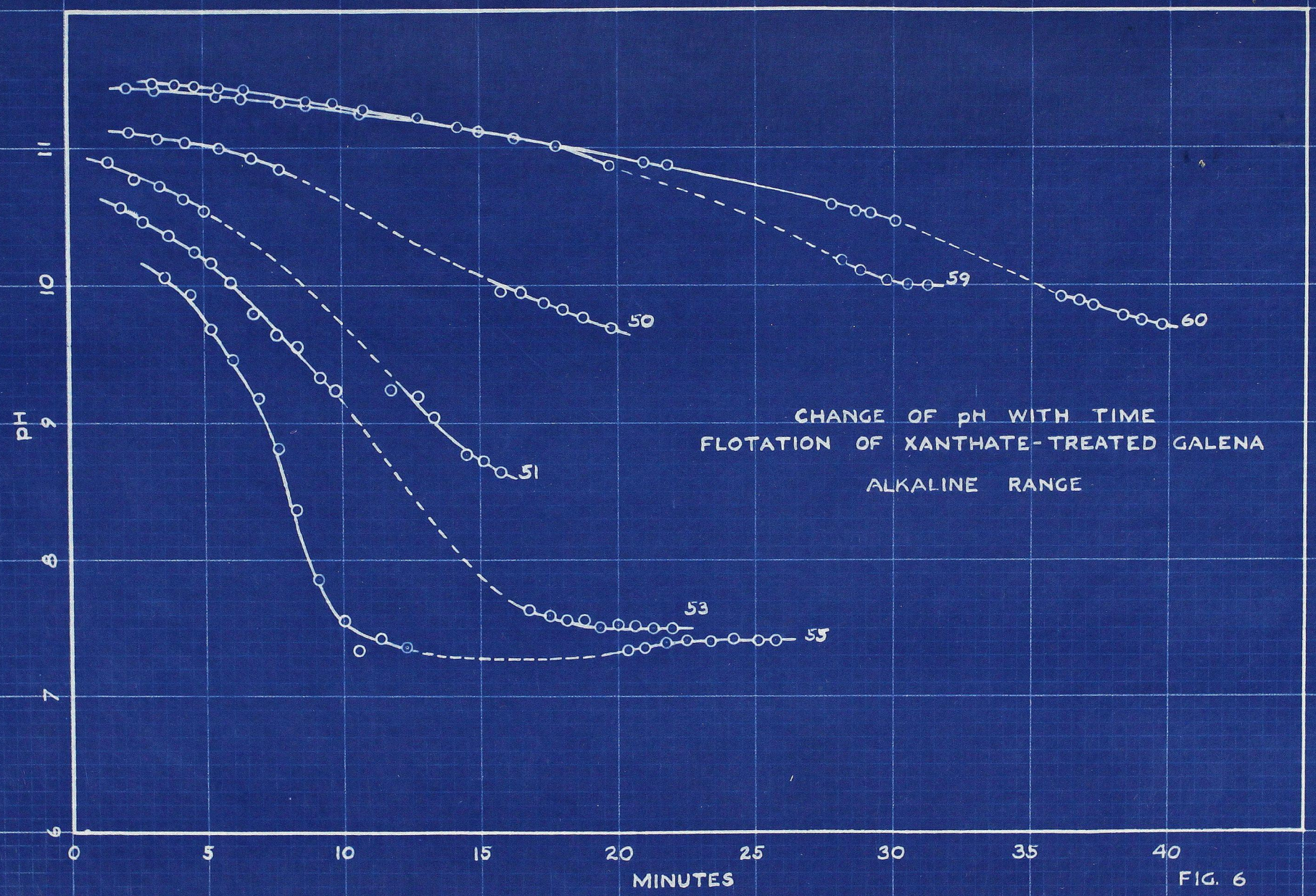
CHANGE OF pH WITH TIME
FLOTATION OF XANTHATE-TREATED GALENA
ALKALINE RANGE
pH
MINUTES
50
51
53
55
59
60
0
5
10
15
20
25
30
35
40
6
7
8
9
10
11

FIG. 6

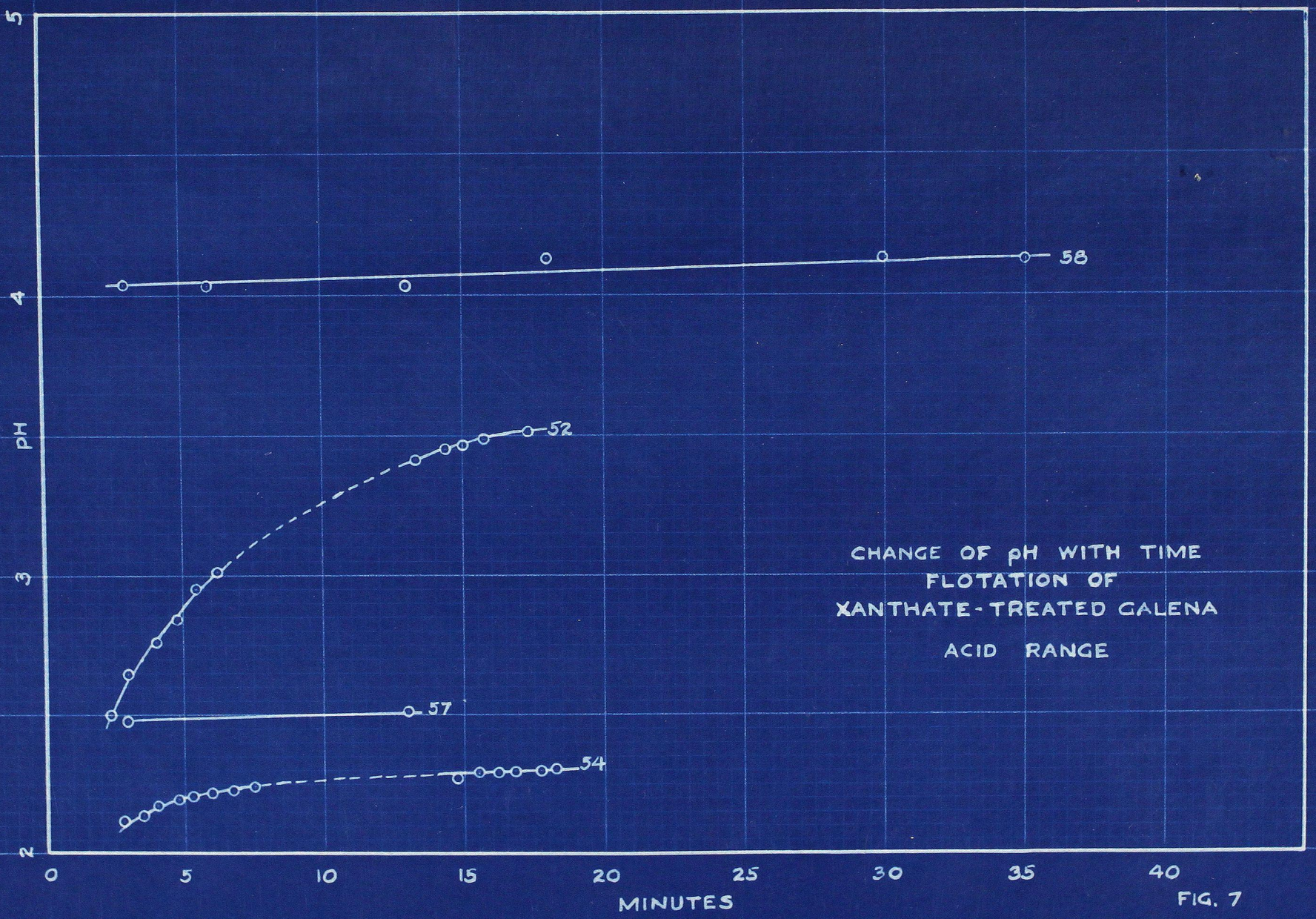
CHANGE OF pH WITH TIME
FLOTATION OF
XANTHATE-TREATED GALENA
ACID RANGE
pH
MINUTES
58
52
57
54
5
4
3
2
0
5
10
15
20
25
30
35
40

FIG. 7

change of pH is very similar to that observed with the lead xanthate suspensions used in determining the solubility of lead xanthate. The equilibrium pH of 7.4 - 7.5 may correspond with the pH associated with minimum lead xanthate solubility.

It is also noteworthy that the two points on the graph (Fig. 5) for runs 59 and 60, made with Galena #5, fall on the curve obtained for Galena #2.

Conclusions

The graph (Fig. 5) shows that complete, or almost complete recovery of galena is attained in the pH range 2.5 to 9.5 (approximate). Between pH 10.0 and 10.8 the recovery is a linear function of the pH, and becomes zero when the pH is 10.8 or higher. These findings substantially agree with those of Wark and Cox (34.3.2) obtained by contact angle measurements. These workers reported the critical pH of galena in a 25 mgm. per litre potassium ethyl xanthate solution as 10.1 - 10.3.

A FURTHER EFFECT OF pH

Procedure

A sample of Galena #2 was ground and sized as before, treated with potassium ethyl xanthate in the usual way, and transferred to the flotation cell with 10 cc. 0.09 N. KOH in a pulp volume of 245 cc. Time was measured from the time of transfer to the cell. At 8 min. 4 cc. terpineol solution was added to make the terpineol concentration in the pulp 4 mgms. per litre; and the air pressure was kept just below that necessary to produce overflow.

No collection of galena took place as the initial pH of 11.45 dropped to 11.2 over a period of 12 min.; but galena started to show in the froth about pH 11.15. At 16-19 min. 10 cc. 0.09 KOH was added to bring the pH from 11.1 up to 11.5; but the increase in pH did not appear to decrease the amount of galena in the froth.

Further additions of 0.09 N KOH were made as follows:

Time (min.)	cc. KOH added	pH before addition	pH after
43½	5	10.98	11.28
56½	10	10.96	11.45
69½	10	11.17	11.56

Throughout this time, no decrease in the amount of galena in the froth was observed.

At 75 min. 1 cc. terpineol solution (250 mgm. per litre) was added; the air pressure increased to 45 cm. of mercury, and a concentrate removed for 5 min.

Results

The results of this run are as follows:

Head weight:	2.521 gms.	Concentrate weight:	2.357 gms.
Pulp Volume:	Before run 275 cc.	After run 275 cc.	
Pulp pH:	" " 11.46	" " 11.42	
% Recovery:	93.4%		

Conclusions

It would appear that once galena is brought up into the froth, it is not depressed, or difficultly depressed by a pH above the critical value.

The time factor may, however, play some part. This could be checked by controlling the addition of alkali in such a way that the pH is always maintained above the point at which collection starts, and making the run over an extended time.

SUMMARY

The work undertaken in the present research is exploratory in nature. The aim has been to cover a fairly wide field, rather than to investigate fully some particular phase of that field, in the hope that the general findings will point the way to a more exacting investigation of the problems presented. Conclusions advanced at this time should be regarded, therefore, as suggestions for further work rather than as final, carefully checked statements.

1. The concentration of lead ions in equilibrium with a saturated solution of lead ethyl xanthate depends on the pH of the solution, and is a minimum at 0.15 mgms. per litre in the pH range 8.0 - 8.2.

2. A pneumatic glass flotation cell has been developed and found suitable for making measurements of floatability with samples of minerals weighing only a few grams.

3. A method for measuring the floatability of solid particles in the absence of reagents other than water has been investigated sufficiently to indicate that it has some merit, but requires more careful control of variables if it is required to yield quantitative results.

4. Some natural galenas may show inherent floatability; others do not.

5. A synthetic precipitated lead sulfide can not be floated with terpineol alone.

6. The recovery of galena treated with ethyl xanthate

and floated in the presence of terpineol is substantially complete in solutions of pH less than 9.5. The recovery is zero if the pH of the solution is 10.8 or higher.

7. A reaction of measurable rate takes place when lead xanthate, or xanthate-treated galena is placed in an aqueous acid or alkaline solution. The course of the reaction may be followed by the change in pH with time.

8. Xanthate-treated galena, once it is brought into the froth, is difficult or impossible to depress by an increase in the pH of the pulp above the critical pH for the mineral.

9. Some correlation may exist between the pH corresponding to minimum solubility of lead ethyl xanthate, and the equilibrium pH attained when xanthate-treated galena is placed in an alkaline solution of pH greater than the equilibrium value.