MINERALOGY OF THE EPITAXIAL COPPER SULFIDE COATING ON SPHALERITE

by

Ali Mohamad Ghazi

A THESIS

Presented to the Faculty of
The Graduate College in the University of Nebraska
In Partial Fulfillment of Requirements
For the Degree of Master of Science

Major: Geology

Under the Supervision of Professor R. J. Goble

Lincoln, Nebraska

December, 1983

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

DEDICATION

I would like to dedicate this thesis to two very important people in my life: my father Mohamad Ali Ghazi and my mother Meehan Nassiri. I thank them for their emotional and financial support throughout my life and, in particular, the past eight years.

ACKNOWLEDGEMENT

I would like to thank Dr. R. J. Goble for suggesting this project and for his assistance and supervision throughout the course of the project. I would also like to thank the faculty of the University of Nebraska Geology Department for their instruction and encouragement over the past five years. I am also indebted to Dr. D. L. Johnson, Professor of Mechanical Engineering, University of Nebraska, for his helpful suggestions concerning my flotation Cell. Thanks also to Dr. R. B. Nelson for reviewing the manuscript and serving on my thesis committee. Finally, thanks to Mrs. Ruth Ford for her helpful instructions in the library research part of this project.

ABSTRACT

Two methods were used for synthesizing geerite ($Cu_{1.6}S$) or the geerite structure. Standard evacuated silica tube techniques were used unsuccessfully to synthesize geerite from its elemental constituents. Synthetic copper sulfide samples of composition $Cu_{1.5}S$ and $Cu_{1.6}S$ and $Cu_{1.75}S$ were studied by the x-ray powder method, reflection ore microscope and a scanning electron microscope. Digenite invariably appeared in all final synthesized products at room temperature. The external morphology of the crystals of digenite was irrationally related to the quenching temperature, varying from high temperature irregularly shaped crystals to low temperature well-formed octahedrons and modified octahedrons resembling "hexagonal-like" plates, as indicated by Donnay (1958).

The principle of the leaching of synthetic copper sulfide of composition $Cu_{1.75}S$ was investigated by using ferric sulfate solution in the concentration range ($1.0X10^{-5}M$), ($1.0X10^{-3}M$), ($1.0X10^{-2}M$) and ($1.0X10^{-1}M$). Leaching of synthetic copper sulfide resulted in mineralogical and structural changes from digenite (Di) to blue-remaining covellite (Bc) to normal covellite (Cv). At constant concentrations of ferric sulfate solution for a set period of time, smaller sized particles were more readily dissolved and hence modified. The rate of dissolution of synthetic digenite was also directly related to the strength of the leaching solution, as well as to the exposure time. These synthetic specimens developed a structure similar to the pseudocubic structure of geerite. X-ray powder patterns of leached synthetic digenite strongly resembeled those of sphalerite and blue-remaining covellite.

Flotation was conducted in two types of experiments using a modified Hallimond microflotation cell with ($\frac{25 \text{ mg}}{1000 \text{ ml}}$) potassium ethyl xanthate as a collector. First the behavior of unleached, leached and normal covellite were studied. The results showed that unleached digenite is most readily floatable, followed by leached digenite and normal covellite. The unfloated residues from these flotations were examined and identified as normal covellite. The naturally occurring covellite showed only small recoveries, even when floated for up to thirty minutes. Secondly, the effects of the Cu(II) ion on the flotation of cubic ZnS in the absence of any collectors was also studied. Better recoveries were obtained when the sample was exposed in regular tap water rather than distilled water. The flotation of naturally occurring pure cubic sphalerite of both light and dark color (low and high iron content, respectively) was greatly enhanced by the absorption of the traces of the Cu(II) ion. The cupric ion gave a rather thick coating of a deep blue color over the entire sphalerite surface.

CHAPTER (I) - INTRODUCTION

Zinc occurs naturally as sulfides in the form of sphalerite, wurtzite (ZnS) and marmatite $Zn(S{:}FeS)_x$. In the majority of commercially important deposits, the zinc sulfides are associated with copper or lead sulfides, sometimes in binary mixtures and, commonly, together with pyrite (FeS_2) and pyrrhotite ($Fe_{1-x}S$) in ternary or more complex mixtures. Hence, the process of flotation of zinc sulfides is primarily concerned with the problem of separating these zinc sulfide minerals from copper, iron and lead sulfides.

Flotation is a process of mineral concentration based on the adhesion of some particles of a pulp to air bubbles while other particles adhere to water. That is, it depends upon the relative "wettability" of minerals. In practice, air is bubbled through a mineral mixture, adheres to the less wettable minerals and floats them off (Berry and Mason 1959). Other related processes include greased-deck concentration, in which separation is based on selective adhesion of some grains to organic liquids with adhesion of other grains to water. In froth flotation, adhesion is affected between gas bubbles and small particles in such a way that the specific gravity of the mineral-air association is less than that of pulp. The mineral particles and air bubbles rise in the pulp to produce a froth which is recovered (Gaudin 1939).

Flotation reagents are those organic and inorganic substances added to the pulp to modify or control the chemical conditions of the pulp and so enhance the selectivity of the process. In general, flotation reagents are classified as follows: "Frothers" are reagents used to promote the formation of bubbles and froth. The ability to lower the surface tension is characteristic of all frothers. "Collectors" are those substances that promote the adherance of air bubbles to the mineral grain and enable the mineral to be held at the air-water interface and, in the presence of the frothers, to form a mineralized froth. Collectors are two main types: (1) liquid hydrocarbon and (2) water soluable compounds. Comprising a hydrocarbon radical linked to a chemically active group (Gaudin 1957), as shown in figure 46, the structure of collectors has two ends: a reactive end which is attached to mineral particles, and a repellent end which produces the oily coating (table 14). "Conditioners" (modifying agents) are those substances that modify the surface of a mineral particle. They may act as "activators", "depressants" or "pH regulators" (see table 15). "Activators" are conditioners that affect the surface of a mineral particle in such a way as to make it easy for the collector's atoms to become attached. "Depressants" have the opposite effects.

In flotation, zinc sulfides demonstrate two remarkable behaviors. First, they respond poorly to thiol collectors, compounds containing a -SH group in combination with radicals. That is, they are not floated at all by short chain homologous of xanthates. On the other hand, the zinc sulfides are very weakly floatable with longer chain xanthates. Secondly, they can be activated toward flotation by thiol compounds after treatment with copper or other heavy metal solutions.

Selective zinc sulfide flotation is primarily based upon these features. Generally, copper and lead sulfides can be floated away from zinc sulfides under either strongly or mildly alkaline conditions (Ralston & Healy 1980). However, copper and in particular copper sulfate solution is the most widely used activating reagent (Baldwin et al. 1979). After activation with copper sulfate, the zinc sulfide can be floated away from other sulfide minerals. This step again takes place under a moderately alkaline condition (Ralston & Healy 1980). Previous flotation studies of the metal ion activation of zinc sulfide have often given inconclusive results due to the presence of metal ions impurities (Gaudin 1929, Gaudin et al. 1957, Gaudin et al. 1959, Fuerstenau et al. 1974, Baldwin et al. 1979, Ralston & Healy 1980).

Due to the action of the collectors alone, there are cases where zinc sulfides are found to float to a significant extent and to introduce an unacceptable contamination of lead and copper concentration. This flotability has been widely ascribed to natural or inadvertant activation of the sphalerite by heavy metal cation (Gaudin 1929, Gaudin et al. 1957, Sutherland et al. 1955).

If a copper salt such as copper sulfate is added to an alkaline or neutral sphalerite pulp and conditioned with the mineral for a few minutes the mineral changes in flotational behavior in such a way that the mineral can now be adhered to more effectively by the collector. In dealing with relatively coarse particles, the change is striking and can be described as representing an abrupt change from a nonfloating to a floating condition (Taylor & Warren 1979). However, if instead of being coarse, the material is relatively fine, the transition from unactivated behavior is more gradual, but again, change in flotability is striking.

The action of copper and similar salts on natural sphalerite has long been known. A. F. Rogers (1911) found visible blue-black coatings to be formed on sphalerite upon prolonged treatment with hot, strong copper sulfate solutions. Lack of reaction between the coating and silver nitrate ($AgNO_3$) solution was interpreted as proving the coating to be covellite (CuS), formed according to the reaction

$$ZnS + Cu^{++} \rightleftharpoons CuS + Zn^{++} \quad (1)$$

which proceeds from left to right and is in accordance with the solubility products of sphalerite ($K_{sp}=10^{-3}$) and cupric sulfide ($K_{sp}=10^{-44}$) (Gaudin 1929). Reaction (1) is in agreement with the data of Baldwin, et al. (1979). They showed that the changes in concentration of copper and zinc in a solution during activation of sphalerite (ZnS) by Cu^{++} solution confirm the formation of one monolayer of copper sulfide. The data from three separate tests showed that the final state corresponds to a Cu:Zn ratio of 1.0, 1.0 and 0.94, i.e. to stoichiometric replacement of Zn by Cu. This suggests the formation of a layer of covellite (CuS). However, the physical properties shown by the Cu-activated sphalerite are not, in fact, shown by covellite. In 1930, J. Ralston and his co-workers showed that covellite is not naturally floatable and that even the addition of collectors such as xanthates do not make it particularly floatable.

Covellite is distinguished from the similar blue-remaining covellite (blaubleibend covellite) by its behavior in immersion liquids, appearing blue when immersed in air, violet-blue in water, red-orange in methylene iodide, and scarlet in bromonaphthelene (Baldwin et al. 1979). Blue-remaining covellite ($Cu_{1+x}S$) distinguished by "remaining blue" under oil immersion (Shuey 1975), is an oxidation product of digenite (Cu_9S_5) or djurleite ($Cu_{1.96}S$). Baldwin et al. (1979) found that ZnS activated with one monolayer of copper retained the same green color in all liquids, suggesting that the material produced may be blue-remaining covellite. However, according to them, the composition of products of their experiments does not correspond to that of blue-remaining covellite.

R. J. Goble (Personal Communication, 1982) has suggested that the material which coats sphalerite may in fact be geerite ($Cu_{1.6}S$) or have the geerite structure. Geerite is a newly described copper sulfide, described by Goble & Robinson (1980). Natural geerite occurs as a thin, blue, iridescent coating on the (110) cleavage of sphalerite, where it was first discovered. X-ray patterns from geerite are very similar to those of sphalerite, suggesting strong structural similarities. Artificially leached anilite ($Cu_{1.75}S$) remains in the geerite structure to compositions approximately approaching covellite (CuS), (Goble 1981). Upon immersion in oil, geerite shows no color change. The flotability of geerite is not known.

The goal of this research is three-fold: (1) synthesis of geerite from its elemental constituents using evacuated rigid silica tube techniques. A second possible synthesis technique relies on the leaching of copper from synthesized copper sulfides to produce materials having the geerite structure; (2) upon the successful completion of one of the two synthetic techniques the study of flotation of the geerite or materials with the geerite structure will be conducted. At the same time, study of the flotational behavior of synthesized geerite will also be conducted; (3) the final purpose of this research is to identify the coating produced on sphalerite upon activation in dilute copper sulfate solution in the flotation process.

(CHAPTER (II) - FLOTABILITY AND HYDROPHOBIC PROPERTIES OF SPHALERITE

A) Some Properties of Zinc Sulfides

Sphalerite is the principal ore of zinc. It occurs in nature in numerous polymorphs. The two most important of them are hexagonal (wurtzite) and cubic (sphalerite or zinc blend). The former is a high temperature (1290^{o} K) form which is metastable at normal temperatures. Many specimens are mixtures of the two, with the cubic type predominating. In both sphalerite and wurtzite, each zinc atom is tetrahedrally coordinated to four sulfur atoms. Sphalerite has a face centered cubic arrangement of Zn whereas wurtzite possesses hexagonal close packing of Zn.

B) Associated Minerals

In both wurtzite and sphalerite, replacement of the zinc by other cations such as Mn^{2+}, Cd^{2+}, Fe^{2+}, and Cu^{2+} is common. In the case of Fe^{2+} this replacement results in large increases in the cell volume. Sphalerites that contain a relatively high concentration of iron are loosely called marmatite. Zinc sulfides are most commonly associated with lead sulfide (galena, PbS) and are present in hydrothermal deposits at various temperatures. There are also several other minerals such as tennantite ($Cu_{12}As_4S_{13}$), tetrahedrite ($Cu_{12}Sb_4S_{13}$) and chalcopyrite ($CuFeS_2$) which are structural derivatives of cubic zinc sulfide (sphalerite).

C) Structure and Bonding

Table 1 outlines both the major structures and other characteristics of cubic and hexagonal zinc sulfides. The sulfur atoms are close packed. Each sulfur atom is tetrahedrally coordinated by zinc. In the cubic type the Zn and S atoms are each on face centered cubic lattices, displaced from each other in the $[111]$ direction. The two polymorphs of ZnS differ from each other only in stacking sequence. However, it has been suggested, (Shuey 1975), that transformation from one type to the other is possible by introducing stacking fault.

In a purely ionic model, ZnS would consist of Zn^{2+} with a full 3d shell and S^{2-} with a full 3P shell. The S-S distance is larger than ionic diameter of sulfur atoms (3.68Å). Therefore, S-S covalence may be neglected. On the other hand, the Zn-S distance is distinctly less than the sum of the octahedral radii (2.580Å).

D) Flotation

Although those workers who have studied the flotation properties of zinc sulfides have generally assumed their samples to be pure cubic (sphalerite) and have not been able to distinguish between the hexagonal and cubic forms, it must be borne in mind that in flotation several properties of wurtzite will differ from those of sphalerite, i.e. the solubility product and free energy of formation (see table 1).

E) Flotability and Hydrophobic Properties of Sphalerites

A large number of previous investigators have considered the flotation properties of sphalerites, both with and without activation by metal ions. In each

Table-1 Properties of zinc sulfides.

PROPERTY	SPHALERITE	WŪRTZITE
crystal structure	cubic	hexagonal
lattice constants	a= 5.4060 Å	a= 3.820 Å c=6.260 Å
cell content	z=4	z=2
cleavage	$\{110\}$ perfect	$\{11\bar{2}0\}$ easy
hardness	3.5 – 4	3.5 – 4
density	4.096	4.089
Zn–S distance	2.35	2.25
Zn – Zn distance	3.85	3.81
free energy of formation	–198.5 kj/mole	–187.0 kj/mole
solubility product	2.57×10^{-26}	5.92×10^{-25}
band gap	3.7 ev	—

case they have conducted experiments with and without the addition of thiol collectors, (Gaudin 1929, Wark & Cox 1934, Clifford 1971).

F) Flotability With Xanthate (Without Activators)

It has been established that the short chain xanthates have little or no ability to collect sphalerite. This was clearly observed by Gaudin (1929), who established the exact flotability of sphalerite with ethylxanthate. He conducted experiments on a specially copper-free coarse crystalline sphalerite which had been deslimed in copper-free water. Under these circumstances he demonstrated that the flotability of sphalerite when using amylxanthate as collector was found to be smaller (although it was larger than ethylxanthate) and complete flotation of sphalerite was only obtained when Gaudin used heptylxanthate as collector. Recently, Clifford (1971) has shown that at the optimum pH (3.5) about $7.0\text{X}10^{-2}$ moles of potassium-ethylxanthate per liter of solution is required before an appreciable recovery of sphalerite is obtained. On the other hand, he also found no differences in response of the sphalerite (0.3% iron) and marmatite (8.8% iron) to flotation.

G) Activation Studies

In geological application, the action of copper sulfate and similar salts on sphalerite has long been known. Some experiments have been reported as far back as the early part of this century. Rogers (1911) found a blue-black coating formed on the surface of sphalerite upon prolonged treatment of the mineral with hot-strong copper sulfate solution. This observation was confirmed by other investigators.

The reaction between zinc sulfide and cupric ions is by no means unique. A large number of heavy metal ions such as lead, silver and cadmium have also been found to be effective collectors (Ralston & Healy 1980). In general, those cations whose sulfides are less soluble than zinc sulfide are effective activators (Sutherland & Wark 1955). There are two exceptions to this generalization: Ti^+ with a more soluble sulfide and Sn^{4+} with less soluble sulfide (Sutherland & Wark 1955).

Maust & Richardson (1975) showed that the activating ability of Ti and Sn can be correlated to their surface state energy at the sphalerite surface. According to their work, this surface state energy is a measure of electronegativity of the Ti^+ and Sn^{4+} relative to that of Zn. One can easily correlate this with the respective sulfides of these compounds. Surface state energy and solubility product cannot be thought of as two independent parameters. Therefore, the insolubility of these sulfides relative to that of sphalerite can in general be taken as the principle factor in the ability of cations to activate sphalerite. This principle has been proposed by a number of authors, including Sutherland & Wark (1955), Cook (1950) and Toshiiaki (1961).

H) Activation by Copper Salt

In flotation, copper sulfate is universally used for the activation of sphalerite and, to some extent, for the activation of other minerals (Bushell et al. 1961).

The copper-activated surface readily adsorbs standard collectors such as the xanthates and dialkyldithio phosphate whereas untreated zinc sulfides do not. The activation of sphalerite with copper sulfate has long been thought as a chemical reaction of the following form:

$$ZnS + Cu^{++} \rightleftharpoons CuS + Zn^{++} \quad (1)$$

Early experimentation (Gaudin et al. 1959), Ralston et al. (1930) showed that the reaction seemed to be stopped by the coating of insoluble copper sulfide. Rogers (1911) found visible blue-black coatings to be formed on sphalerite upon prolonged treatment with hot, strong copper solutions. The lack of reaction between the coating and silver nitrate ($AgNO_3$) solution was interpreted as proving the coating to be covellite (CuS), formed according to reaction (I). This assumption was confirmed by Cook (1950), who found a stochiometric replacement of Zn^{++} by Cu^{++} after 50 days reaction at about (100° C). Cook also suggested that the recovered, covellite-coated sphalerite is the product of the continuing replacement of Zn^{++} by Cu^{++} rather than diffusion of Cu^{++} throughout the sphalerite lattice.

Gaudin et al. (1959) found the ratio of the quantity of zinc released into solution to the quantity of copper taken up to be 0.8 and 0.96 in two separate experiments. Pomianowski, et al. (1961) showed that the ratio was between 0.8 and 1.0 unless the sample was heavily oxidized, in which case it was somewhat higher than 1.0. More recently Baldwin et al. (1979) showed that in three separate tests the final state corresponds to a Cu:Zn ratio of 1.0, 1.0 and 0.94, i.e., to stochiometric replacement of Zn by Cu. Cook (1950) found the ratio to be unity in experiments in which massive amounts of reaction product were formed. Thus, the observed behavior is reasonably close to the value of unity to be expected on the basis of equation (1).

For the kinetics of activation of sphalerite by copper, there is a continuing reaction that does not appear to reach a steady state. However, there is general agreement (Gaudin et al. 1959 and Toshiaki 1961) that the resuts of the reaction during the first thirty minutes to one hour are limited to the formation of a few nominal monolayers. Both Bushell et al. (1961) and Pomianowski et al. (1975) found the amount of copper abstracted by sphalerite to decrease as the iron content of the sample increased. Bushell and his colleagues also found that the abstraction of copper was lower when oxygen was present in the solution than when it was absent. Accordingly, they suggested that iron present in the lattice of sphalerite reacted to form ferric hydroxide which was the direct cause of inhibition of the reaction with cupric ions. On the other hand, Pomianowski et al. (1975) and Baldwin et al. (1979) found in separate experiments that the oxygen concentration of the solution had no effect.

I) Product of Activation

There have been a number of attempts at direct identification of the product of reaction. Although copper sulfate solution has long been used as the activating reagent for sphalerite, Cook (1950) reacted sphalerite with a solution of cupric chloride at about 100° C for 50 days, observing a thick blue-black coating, which x-ray analysis showed to be covellite. Sato (1957), using electron diffraction spectrometry, obtained only diffuse diffraction patterns from both thick and thin layers of product and was not able to draw precise conclusions as to whether or not this layer was indeed covellite. Other attempts to produce this layer have been made, the earliest being Gaudin (1929) and Ralston et al. (1930).

The ESCA (Electron Spectroscopy for Chemical Analysis) of copper-activated sphalerite, as determined by Clifford et al. (1961), showed only copper (I) to be present. On the other hand, Story & Pratt (1982) are currently applying Electron Spin Resonance Spectroscopy (ESR) to the problem. They have obtained results strongly indicative of copper (II) from artificial samples. Frost et al. (1972) and Clifford et al. (1961) consider two important factors as having caused these inconsistent results. First, the instrumental technique and experimental methods used all have important limitations. Although ESCA is a very strong and sensitive technique for the detection and identification of surface species, the experiment cannot be carried out under wet conditions. The analytical operations are carried out under dry, high pressure conditions which are much different than those found in flotation experiments. Furthermore, as shown by Frost et al. (1972), copper (II) compounds are susceptible to photoreduction in the source of the instrument and copper (I) compounds to surface oxidation. Thus, surface oxidation to copper (II) is likely to be present. Likewise, because ESR Spectroscopy is insensitive to copper (I) compounds, Story & Pratt (1982) have not conclusively shown this to be the only or even prime form in which the copper occurs.

Second, copper sulfide (II) is not stable under conditions of normal pressure (Jellinek 1968). He also states that covellite (CuS) is diamagnetic and hence can have no simple divalent copper. In sulfides, this preference of copper for the monovalent rather than the divalent state is perhaps responsible for the presence of Cu^+ in $CuFeS_2$ and probably also in $CuCr_2S_4$ (Jellinek 1968). Regarding the structural characteristics of Cu^+ when found in coordination with sulfur atoms Jellinek (1968) observes:

> --- One might expect that Cu^+ with a full 3d shell ($3d^{10}$) configuration to prefer a tetrahedral coordination by sulfur. Indeed, Cu usually is situated in tetrahedral holes of a close packed sulfur lattice. Frequently, it is however, not in the center of these holes but displaced towards a face or an edge of the surrounding sulfur tetrahedron, approaching triangular or linear coordination. With each tetrahedron several equivalent displacement are possible

Berry (1954) and Berry et al. (1962) determined that these structural ambiguities give rise to various possible Cu positions within sulfur tetrahedron at high temperatures and to complicated superstructures at low temperatures. An analysis of the structure of covellite (Berry 1954) suggests that those copper ions (one-third of all) which are surrounded by sulfur ions in triangular coordination are divalent, and that those which are tetrahedrally coordinated to sulfur are monovalent. However, the Cu-Cu distance (3.18Å) and the presence of diamagnetism indicate some bonding between copper ions. Thus, copper sulfides are likely to have intermediate valencies.

At high temperatures the Cu^+ ions can easily move from one possible position to another. This causes the ionic conductivity. Jellinek (1968) described the electronic configuration of Cu^+. He concluded that the occurrence of an irregular rather than regular tetrahedral coordination of Cu^+ may possibly be ascribed to (excited) configurations from d^{10} to $d^9\ (dS)^1$ or $d^8(dS)^2$ where (dS) stands for hybrid orbitals. There are two such hybrid orbitals which are degenerate in the free ion in sulfides; one of these can be stabilized by lowering the symmetry of the cation environment. In an extreme case the distortion will lead to either triangular or a linear coordination.

The above consideration together with what is known about the structure of covellite (Berry 1954) suggest that copper possibly occurs at the surface of sphalerite in two forms: as cupric sulfide with an unknown composition, which for the purpose of this work, is designated as $Cu^{2+}S^{2-}$ and as covellite (CuS). These two compounds are in turn formed under two separate sets of conditions, at different rates and mechanisms shown by the reaction below (Gaudin et al. 1959), (Baldwin et al. 1979):

$$ZnS + Cu^{2+} \rightleftharpoons Cu^{2+}S^{2-} + Zn^{2+} \quad (1)$$

$$2Cu^{2+} + 2S^{-} \rightleftharpoons 2CuS \qquad (2)$$

The net product of the above reactions is in proportions that vary with the extent of the overall reaction (Gaudin 1957):

$$Cu^{2+} + ZnS \rightleftharpoons CuS + Zn^{2+} \qquad (3)$$

It has been found (Gaudin et al. 1959, Bushell 1961, Baldwin et al. 1979, Story et al. 1982) that the initial stage of the reaction involves simple exchange between Cu^{2+} and Zn^{2+}. The resulting cupric sulfide is an unstable form and there is a strong tendency for the Cu to be reduced to Cu^{2+} as in reaction (1) and (2).

Reaction (2) requires that the lattice of the sulfide ions be rearranged into a complex configuration. A major structural rearrangement (Reaction 2) is apparently required to stabilize the intermediate copper sulfide compound. For instance, the S-S distance in sphalerite is 2.76 (Å), whereas in covellite, the same distance is only 2.05(Å) (Gaudin et al. 1957). This arrangement will certainly produce or require an appreciable activation energy. Most of the above authors postulated that activation starts with the reaction (1) until a number of layers of $Cu^{2+}S^{2-}$ are formed at the surface. These speculations are in agreement with kinetic studies which indicate that the activation takes place in two distinct stages.

J) Calculation of Cu^{++} Uptake

An indication of how much Cu^{2+} is required to form a monolayer can be obtained from the crystal structure of sphalerite. The amount of copper absorbed is in turn based on the calculation of the specific surface area of the (110) cleavage plane of sphalerite, assuming reaction (1):

$$ZnS + Cu^{2+} \rightleftharpoons Cu^{2+}S^{2-} + Zn^{2+}$$

This reaction goes toward completion and all the copper ions in solution have gone into mineral.

The crushed sphalerite surface is composed entirely of dodecahedral cleavage faces (110) (see figure 1). A dodecahedral has two cationic sites per unit surface area of (5.42) X (7.66)A or two sites for every $41.6(\mathring{A})^2$ (Guadin 1957). If it is assumed that two surface zinc atoms (represented by clotted and crossed areas) are replaced by two copper atoms, the possible copper uptake is one per $20.8(\mathring{A})^2$. Using this assumption of densest packing, there is only one copper-ion for each $10.4(\mathring{A})^2$. On the other hand, the specific area of the same cleavage plane of sphalerite (110) has been measured utilizing the (BTE) method (Braunaver et al. 1938) with krypton as a measuring gas. Applying this method, the calculated specific surface area varies with the grain size. For instance, (-150/+200 mesh) sphalerite has a specific area of $698cm^2/gm$, where as (-65/+100 mesh) has a value which ranges between $368cm^2/gm$ and $370cm^2/gm$, Gaudin (1957).

In the case of (-65/+100 mesh) sphalerite, knowing the required area for densest packing (one copper ion for each 10.4 square angstrom) and the specific surface area, one can calculate the number of copper atoms required to form a dense monolayer (a film of mineral one molecule thick) or molecular layer for each gram of sphalerite.

Fig_1

The (110) plane of sphalerite. Unit area; $5.42 \times 7.66 = 41.6$ Å^2. Sulfur atoms: S , and zinc atoms are designated as follow:

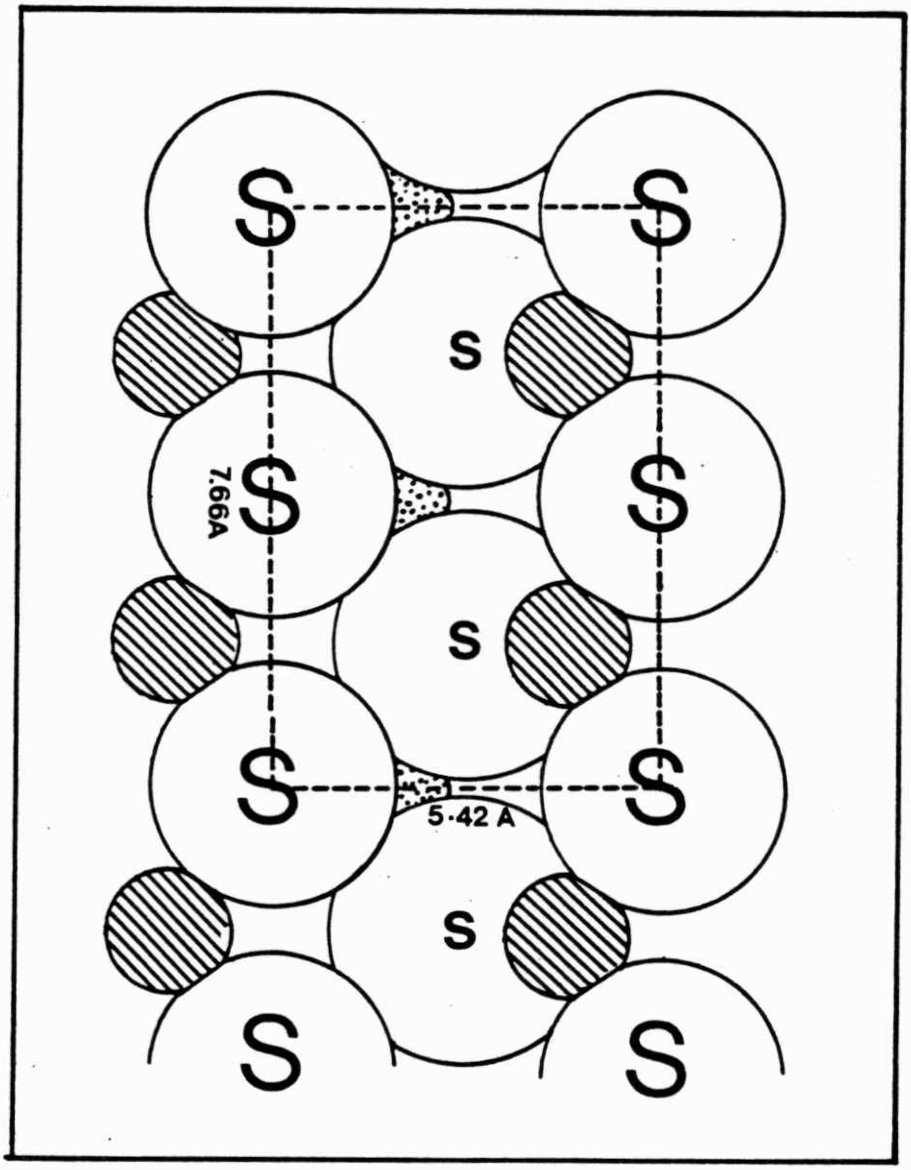
first layer [upper]

▨ **Zn**

second layer [lower]

░ **Zn**

[Gaudin, A. M., *et al.*, 1959]


S
S
s
S
S
7.66A
s
S
S
5·42 A
s
S
S

From the following calculations:

$$\text{Number of Cu atoms} = \frac{370 \ \frac{\text{cm}^2}{\text{gram}}}{10.4\text{Å}^2 \text{X}10^{-16} \ \frac{\text{cm}^2}{\text{Å}}} = 3.53\text{X}10^{+17}$$

Utilizing Avagadro's number ($6.023\text{X}10^{23}$) and the molecular weight of copper sulfate, this represents:

$$\text{Gram copper ion} = \frac{(3.53\text{X}10^{+17})\,(249.649)}{6.023\text{X}10^{23}} = 1.466\text{X}10^{-4}$$

The above value shows that the quantity of copper ion which is taken by only one zinc atom in a given surface area of (65/100 mesh) sphalerite. However, as is shown in figure 2, a dodecahedral cleavage face of sphalerite has two cationic positions. This in turn requires exactly double the amount of copper ions, calculated above. Therefore, on the basis of this calculation, the amount of copper ions needed to form a dense monolayer of copper per gram of sphalerite is approximately $3.0\text{X}10^{-4g}$/g or 0.3mg/g (micromole) of mineral. Gaudin et al. (1959) give an extensive list of copper abstracted per gram of sphalerite (65/100 mesh) from solutions containing excess Cu^{++} as a function of time of agitation at room temperature. Table 2 and figure 2 (after Guadin et al. 1959) illustrates the rate of copper abstraction by sphalerite.

K) Kinetics of Activation

Several investigators have made studies of the rate of reaction between zinc sulfides and cupric ion and have discussed the mechanism of the process on the

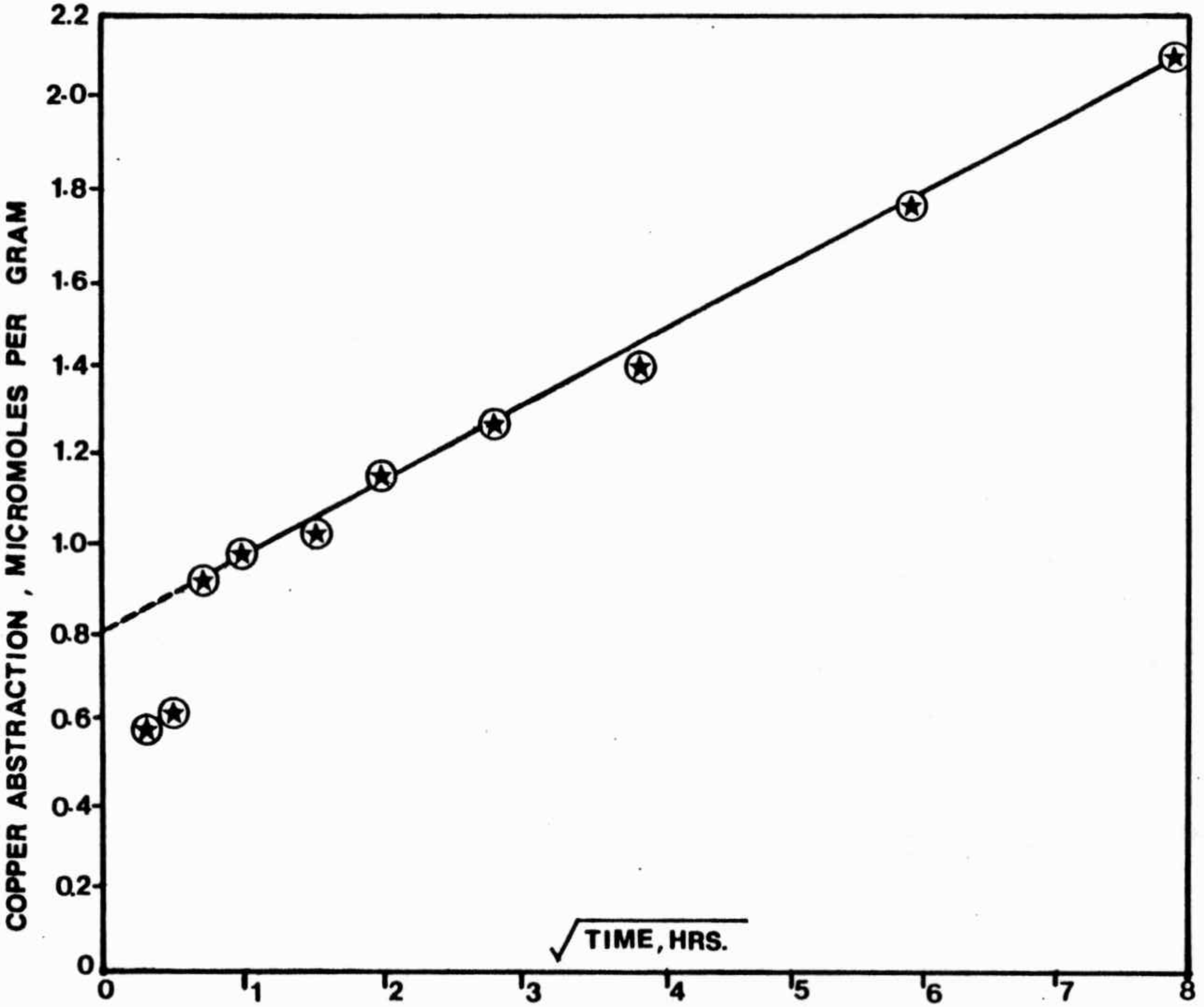


Fig_2 The copper abstraction by sphalerite as a function of the square root of the contact time, (Gaudin, A.M., et al., 1959).

TIME	ABSTRACTION MICROMOLES/GRAM
5 min	0.58
15 min	0.61
30 min	0.94
1 hr	0.98
2 hrs	1.04
4 hrs	1.17
8 hrs	1.26
16 hrs	1.42
32 hrs	1.73
63 hrs	2.14

Table—2 Data to the figure— ,
copper abstraction by sphalerite.

basis of analysis of the kinetics of reaction. Pomianowski et al. (1975), states that the second stage continues until equilibrium is reached, but there is no direct evidence that the uptake of copper ever ceases. This is true as long as cupric ion is present in solution. In fact, as is shown in table 2 (after Gaudin et al. 1959), copper was still being abstracted from solution after 63 hours.

For the first stage of reaction, several authors found the rate of uptake of copper to be a strong one, a function of the concentration of copper added to the system (Gaudin et al 1959). They also discovered that the reaction involving this stage obeys the first order of kinetics which is:

$$\frac{dq}{dt} = kA\,(Cu^{2+})$$

where K is constant. A is the surface area of the solid and q is the quantity of copper absorbed.

In the previous section, it was shown that 0.3 micromole of copper ion is required to form a monolayer on one gram of (-65/+100 mesh) sphalerite. However, table 2 (after Guadin et al. 1959) shows that the amount of copper involved in rapid uptake is 0.58 micromoles, almost exactly double the amount calculated. It is Gaudin's suggestion that Cu^{2+} immediately replaces the surface zinc atoms, designated as crossed areas in figure 1. Almost immediately after the first layer is replaced, partly buried zinc atoms, designated by dotted areas in figure 1, become involved in ionic exchange. At this time the total uptake of copper ions is about 0.60 micromoles per gram of sphalerite. However, by looking at figure 1 we see that another layer of zinc must be invovled in the first stage of reaction. Gaudin et al. (1959) suggest that once the reaction reaches this point, the second stage of reaction starts. They concluded that the second stage of reaction follows a parabolic law:

$$q^2 = kt + b$$

As it is shown in figure 2, Gaudin et al. have been able to construct a straight line by plotting the quantity of Cu^{2+} uptake by sphalerite versus the square root of time.

In the formation of copper sulfide film on sphalerite, it may be assumed that the large sulfur ions are practically devoid of movement while the small ions of copper and zinc with radius of 0.70 and 0.74Å, respectively, diffuse from lattice defect to lattice defect (Gaudin et al. 1959). This movement of cations within the lattice takes place in two opposite directions: zinc ions move outward whereas copper ions diffuse move inward. Nevertheless, the two diffusions must be equal so that the net result will be equal to the rate of growth of copper film on sphalerite. The equation: $\frac{dq}{dt} = kA\,(Cu^{2+})$ reveals the outcome of this movement, where, if dq is the thickness of the film of copper and t is the time, the rate of growth of thickness in the film is $\frac{dq}{dt}$.

L) <u>Mechanism</u>

The above discussion shows the present knowledge of the kinetics of the reaction between Cu^{2+} and zinc sulfide to be sketchy, incomplete and in many respects uncertain. Nevertheless, it is considered important to treat the matter in this work and consider the most obvious mechanisms involved.

It is clear that the overall reaction is effectively an ion exchange (equation 2). As previously discussed, the reaction takes place in two separate stages, the first being more rapid than the second.

Essentially, for the first stage two alternative mechanisms can be envisaged—firstly, adsorption takes place, followed by ion exchange and desorption:

$$ZnS + Cu^{2+} \rightleftharpoons ZnSCu^{2+} \rightleftharpoons CuS + Zn^{2+}$$

Secondly, diffusion of cations throughout the lattice is followed by surface nucleated precipitation. Available data, particularly on the influence of pH do not allow these mechanism to be distinguished. However, it is clear that the second stage of the reaction is one in which the progress of the exchange is progressively inhibited by the accumulation of the products. Gaudin et al (1959) stated that Zn^{2+} ions would diffuse inward. These diffusion mechanisms are consistent with the observed quadratic relationship between the density of absorption and time, but do not prove the mechanism. Firstly, it is entirely qualitative; nor would it be easy to make it more quantitative by the use of known values for diffusion coefficient data for cations. These data are invariably determined for single-crystals, and hence, would not be applicable to the type of indefinite structures that the CuS forms at the surface of zinc sulfides. Secondly, it is not certain that the rate of reaction shows the correct dependence on the concentration of Cu^{2+}. Finally, one may perhaps wonder whether it is realistic to consider a linear increase in resistance of Zn ions as due to diffusion occurring during the course of accumulation of a few monolayers of copper sulfide. However, it is possible that the transition between the first and second stages of the process marks a change of the surface layer from $Cu^{2+}S^{2-}$ with a poorly developed structure to a surface layer with the definite structure of covellite.

CHAPTER (III) - SYNTHESIS OF COPPER SULFIDES

Synthetic copper sulfides of different composition have been used for many years by numerous investigators to study the complex copper-sulfur system. Most synthetic materials are produced from nearly 100% copper and sulfur. Therefore, the final products are generally devoid of any impurities, a quality which enables them to be used in conjunction with naturally occurring minerals as a reliable source for detailed studies. Early experiments with synthetic copper sulfides were conducted primarily to investigate phase relations between different compounds as well as related thermodynamic and electrochemical properties, etc. Due to the high purities of the samples, they have also been used for crystallographic studies and subsequent identification of crystal structures.

One of the goals of this investigation was slightly different than those mentioned above in the sense that the author was primarily interested in the synthesis of geerite or material having the geerite structure. Two methods were used for the synthesis of geerite. Standard evacuated silica tube techniques were used to attempt to synthesize geerite from its elemental constitutents. Starting compositions of $Cu_{1.5}S$, $Cu_{1.6}S$ and $Cu_{1.75}S$ were used. A second possible synthesis technique relied on the leaching of copper from copper-rich synthetic materials. These synthetic samples were treated with an acidic solution of ferric sulfate, $Fe_2(SO4)_3\ XH_2O$, using the method of Goble (1980).

Leaching of copper sulfides results in mineralogical as well as crystallographic changes in these sulfide minerals. The prime reason for this phase of the investigation was to produce the pseudocubic structure of geerite

($Cu_{1.6}S$), a structure which x-ray studies suggest to be similar to that of sphalerite (Goble 1980). Subsequent to production of the above structure, flotation studies were conducted to reveal the flotability of the pseudocubic copper sulfide.

A) Starting Material and Method of Characterization

Mixtures of copper (99.999% purity) and sulfur (99.993% purity) were used in the synthesis of copper sulfides. These were produced by keeping mixtures of copper and sulfur of compositions $Cu_{1.75}S$, $Cu_{1.6}S$ and $Cu_{1.5}S$ at fixed temperatures for various periods of time. The technique employed involves the use of evacuated silica tubes. The final products were quenched in cold water and thus reached room temperature in a matter of a few seconds. The materials were identified at room temperature by the x-ray powder method using a 114.6mm diameter Gandolfi camera. A set of polished sections of each synthetic product was prepared for further optical studies of the materials. Upon the completion of the x-ray and optical identification of the final products, several single crystals were selectively chosen using a 40X power binocular microscope. Scanning electron microscope photographs of the crystals were then taken using a Cambridge S4 scanning electron microscope.

B) Experiments

All synthesizing experiments were carried out in evacuated silica glass tubes. For each run, depending on the quantity of charge, a segment of tubing was cut to between 8 and 10 inches in length, and separated into two segments using a small hot oxy-gas flame from a welding torch (Moh & Taylor 1971). This was accomplished by slowly rotating the tube over the flame, and at the same time pushing the two ends inward to avoid possible necking of the tube. After the walls collapsed as a result of the melting, the tube was slowly twisted and separated. The two segments were then quenched in cold water. Next, weighed samples of the desired Cu-S composition were carefully placed into the tubes. The capillaries were then gently shaken for better mixing. A short piece of silica rod of smaller diameter was next inserted into each tube over the charge to reduce the free space within the tube as well as to protect the fine powdered charge during evacuation and sealing. The loaded tube was then connected to a vacuum pump. A wet cloth was wrapped around the bottom and top ends of the tube to protect fingers from burning and the charge from heat, the vacuum pump switch cycled on and off rapidly several times to clear air from the charge. If the pump had been allowed to run too long at first, some of the powdered charge and silica rod would have been pulled up from the silica tube. After this period of cycling on-off, the pump was left on to produce a vacuum of approximately 0.02 mmHg. The tube was then sealed using the oxy-gas flame.

The tubes were placed in furnaces at temperatures regulated to $\pm 5^{\circ}C$. The outside walls of the tubes were at a pressure of 1.0 atmosphere; no external supporting pressure medium was employed. The vapor pressure inside a tube containing a mixture of copper and sulfur is low (Morimoto & Kullerud 1963), reaching 22 mmHg at $550^{\circ}C$ (Kushida 1952); at $600^{\circ}C$ sulfur cannot be distinguished as a phase over Cu_9S_5 crystals (Morimoto & Kullerud 1963). X-ray results show that homogeneous digenite was produced from samples of composition $Cu_{1.5}S$, $Cu_{1.6}S$ and $Cu_{1.75}S$, which were heated between 600-700°C for period of times ranging from two to five days. On the other hand, x-ray as well as optical examinations of those samples which spent less time in the furnace show the presence of a mixture of covellite and blaubeibender covellite (blue-remaining covellite).

C) Quenched Procedure

The samples heated at elevated temperatures were quenched by dropping the temperature to that of the room as quickly as possible. The silica tubes were withdrawn from the furnace with a long hollow silica tube of larger diameter and plunged into water. Thus, room temperature was reached in a matter of a few seconds.

D) Polished Sections of Synthetic Copper Sulfides

Selected grains of synthetic copper sulfide were picked up under a binocular microscope (40X objective). A large number of 15mm-long silica tubes of 3mm I.D. X 4mm O.D. were cut and one end sealed using strips of ordinary clear scotch tape. The selected samples were placed at the bottom of these sealed tubes. The samples were rotated to obtain the desired orientation, and a mixture of epoxy and hardening agent in 5:1 ratio by weight poured over them. They were allowed to harden for periods of 24-48 hours. Upon the solidification of the mixture, the samples were hand-polished on a sequence of polishing paper with grit ranging from 15 microns to 0.25 microns in size. Next, a diamond paste wheel with a grit size of 0.25 microns was used to obtain the best possible final polish. Polished sections of each sample were examined using a Nikon petrographic microscope and selected areas were photographed using a Zeiss ore microscope. Estimates were made of the relative abundance of minerals present and the textural relationships. Two of the minerals, digenite and anilite, are similar in appearance under reflected light and could not be positively identified by use of petrographic microscopes. Two others, blue-remaining covellite and normal covellite, were easily identified using oil immersion, normal covellite appearing orange-red and blue-remaining covellite appearing blue.

E) Previous Work

Phase relations in the Cu-S system at low temperatures is complex. In earlier studies of the Cu-S system, Diurle (1958) and Roseboom (1966) confirmed that four phases were stable at room temperatures. They were chalcocite (Cu_2S), djurleite ($Cu_{1.97}S$), digenite-type and covellite (CuS). Roseboom (1969) indicated that the digenite-type phase is stable in the composition range: $Cu_{1.765}S$ - $Cu_{1.79}S$ at room temperature. He also reported that the Cu-poor composition for this phase is not affected by temperature while the Cu-rich component changes to $Cu_{1.83}S$ at 83^oC. This temperature is that at which the digenite-type phase inverts to a high temperature form. (Morimoto & Kullerud 1963) reported three polymorphs in the digenite-type field, high temperature, low temperature and a transitional form. Morimoto & Koto (1970) refer to the latter as a metastable form. Roseboom (1966), in a study of the digenite-type x-ray pattern discovered anomalous displacements of weak lines with change in composition. However, he was able to index the strong lines of the powder pattern on the basis of cubic symmetry using a cell edge of about 5.56Å. He suggested two possible explanations for these anomolies: (1) the presence of a transitional polymorph, and (2) deviation from cubic symmetry. By studying the x-ray patterns of this form of digenite four hours after synthesis and again four years later, he eliminated the possibility of the presence of the metastable phase. Therefore, he assumed a pseudocubic symmetry for the digenite-type phase (Morimoto & Koto 1970). Morimoto et al. (1969) reported a new naturally occurring copper sulfide compound, anilite. X-ray identification of the mineral showed that it has a composition of $Cu_{1.75}S$. Anilite of composition $Cu_{1.75}S$ is very close to the copper-poor end of the digenite solid solution phase. This mineral has also been shown as having about the same compositional range as digenite. On grinding, anilite easily changes to the metastable (transitional) digenite type.

Moh (1964) outlined a stability field in the Cu-S phase diagram in which a peculiar mineral could exist in the presence of vapor only below 157±3°C. It forms slight solid solution with both covellite (CuS) and digenite (Cu_9S_5). The solid solution extends from about 67.5 to 68.5 weight percent of copper (see figure 3). This mineral, is known as blaubleibend or blaubleibender covellite (blue-remaining covellite), is distinguished from covellite by its behavior upon immersion in air, water, oil, methylene iodide and bromonaphthalene. It remains blue, while normal covellite appears blue, violet-blue, yellow-orange, orange-red and scarlet, respectively, when immersed in these media. In ores, blaubleibender covellite commonly occurs as a secondary product in oxidation, leaching or enrichment zones (Moh 1964). Yarrowite (Cu_9S_8) and spionkopite ($Cu_{39}S_{28}$) are two blaubleibender covellite which have been reported from Yarrow and Spionkop Creek areas of Southwestern Alberta, Canada (Goble 1980). They occur in replacement of other copper sulfides by selective removal of copper. Yarrowite also replaces spionkopite and copper-iron sulfides such as bornite.

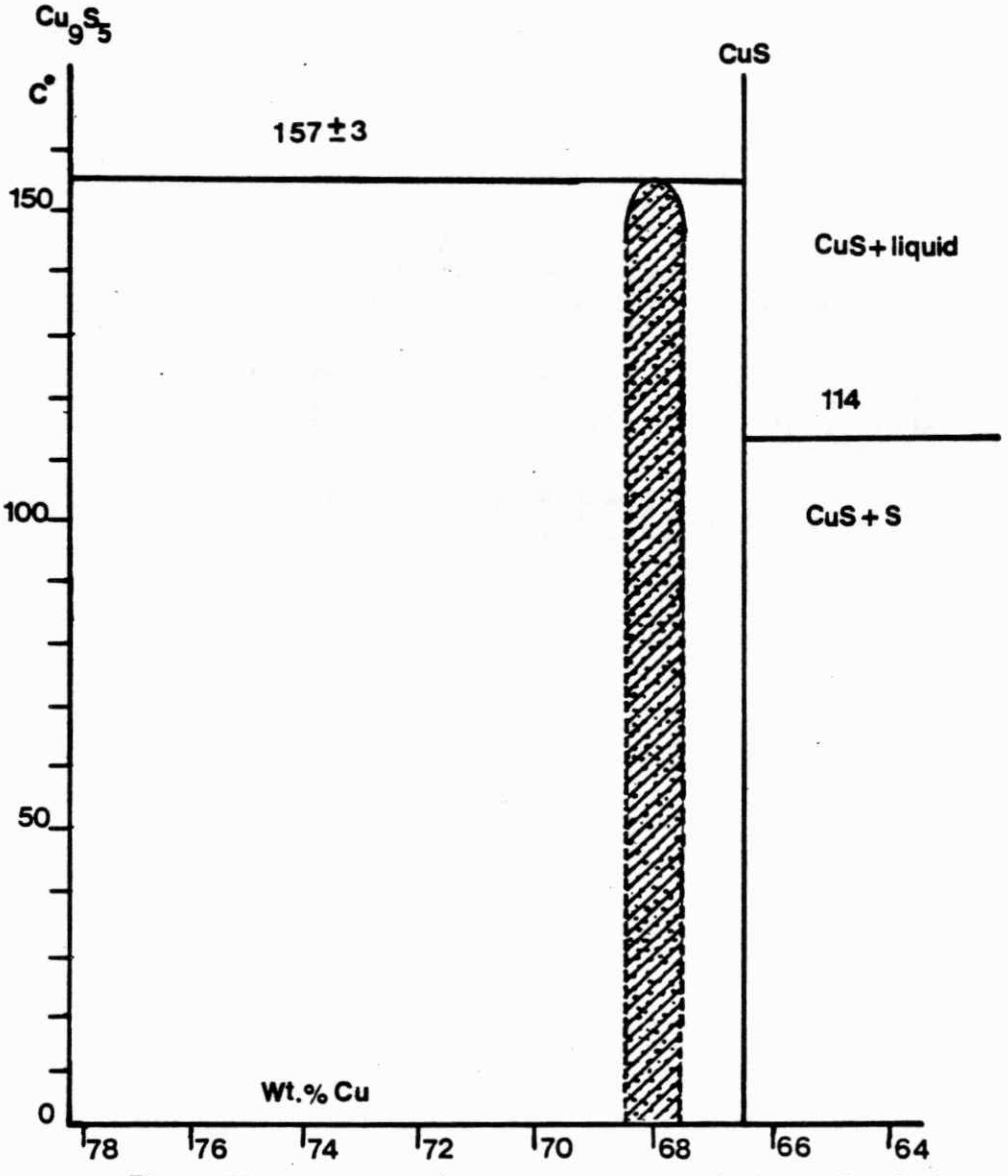


Fig_3 Phase relations at low temperatures in the region between Cu_9S_5 and CuS. Blaubleibender covellite contains from 67.5 to 68.5 Wt.% Cu and is stable below 157 ± 3 °C in the presence of vapor, (from Moh, G. H., 1964).

Geerite ($Cu_{1.6}S$) is the most recently discovered copper sulfide, identified and reported by Goble & Robinson (1980). It was first observed as thin black plates of iridescent coating on the (110) cleavage of sphalerite. In reflected light, geerite is bluish-white and weakly bireflectant with moderate anisotropism in yellow. It has a well-developed cubic subcell which resembles that of sphalerite.

Recently, Goble (1981) has divided the sulfides into three groups, based on sulfur close packing and composition (table 3). Group (1) minerals consist of those whose sulfur atoms have cubic close packing (geerite, anilite and digenite). Minerals of group (2) have hexagonal structures similar to that of covellite with close-packed sulfur layers interspersed with covalently bonded sulfur layers. Goble categorizes them as copper-deficient when compared with minerals of group (1). Djurleite and chalcocite are group (3) minerals which are copper-rich and characterized by approximately hexagonal close-packed sulfur layers.

F) Identification of Synthesized Samples

The products obtained from silica tube experiments were identified at room temperature by their microscopic physical appearance, optical properties in reflected light and x-ray patterns. A non-dispersive scanning electron microscope was also employed to reveal some of the microscopic external morphologies of several single and twin crystals at the termination of each experiment. Most synthetic products consisted of single crystals of 0.01 - 0.1 mm in size. In some specimen, larger crystals of about 0.5 mm in diameter were occasionally found. It was found that in the range of compositions studied in this investigation and under given conditions (Table 4), synthesis of geerite, directly from its elemental constituents was impossible. In fact the only four different phases, anilite or

TABLE 3: COMPOSITION, CRYSTALLOGRAPHY AND STABILITY OF THE EIGHT KNOWN COPPER SULFIDE MINERALS

**MINERAL NAME	COMPOSITION STRUCTURAL	COMPOSITION OBSERVED	CRYSTAL SYSTEM	SPACE GROUP	MAXIMUM THERMAL STABILITY (°C)*	REFERENCES
covelline	$Cu_{1.00}S$	$Cu_{1.00}S$	Hexagonal	$P6_c/mmc$	507	Berry (1954), Kullerud (1965), Potter (1977)
yarrowite	$Cu_{1.12}S$	$Cu_{1.0-1.2}S$	Hexagonal	$P\bar{3}m1$, $P3m1$ or $P321$	157	Moh (1964), Potter (1977), Goble (1980)
spionkopite	$Cu_{1.40}S$	$Cu_{1.3-1.5}S$	Hexagonal	$P\bar{3}m1$, $P3m1$ or $P321$	157	Moh (1964), Potter (1977), Goble (1980)
geerite	$Cu_{1.60}S$	$Cu_{1.5-1.6}S$	(Pseudocubic)	$(F\bar{4}3m)$	?	Goble & Robinson (1980)
anilite	$Cu_{1.75}S$	$Cu_{1.75-1.80}S$	Orthorhombic	Pnma	70	Morimoto et al. (1969), Morimoto & Koto (1970)
digenite	$Cu_{1.80}S$	$Cu_{1.75-1.80}S$	Cubic	Fd3m	83	Morimoto & Kullerud (1963), Roseboom (1966)
djurleite	$Cu_{1.97}S$	$Cu_{1.93-1.97}S$	Orthorhombic	Pmnm	93	Morimoto (1962), Roseboom (1966), Potter & Evans (1976)
chalcocite	$Cu_{2.00}S$	$Cu_{1.99-2.00}S$	Monoclinic	$P2_1/c$	103	Roseboom (1966), Evans (1971), Potter (1977)

*only low temperature forms are listed

**Pseudonyms: covelline covellite; yarrowite blaubleibend covelline I blue-remaining covelline; spionkopite blaubleibend covelline II blue-reamining covelline. Reproduced by permission of Goble, R. J., 1981.

digenite-type solid solution, covellite and "blaubleibend" (blue-remaining covellite) were found in the products synthesized in the composition range $Cu_{1.5}S$ to $Cu_{1.75}S$. The x-ray powder method and reflection microscope were not suitable for differentiation between co-existing anilite and digenite because anilite changes to the digenite-type solid solution upon grinding and polishing (Morimoto et al. 1969). However, since the second purpose of this stage of investigation was to produce a copper sulfide rich enough in copper so that it could later be artificially leached in ferric sulfate acidic media to produce the geerite structure, it was immaterial whether anilite or digenite was present. Normal covellite and blaubleibender covellite (blue-remaining covellite) were distinguished when the final synthetic product was viewed under reflected light using a Nikon ore microscope with an oil lens.

Several single crystals were selected individually from each synthetic sample. After observation under a binocular microscope, they were prepared for x-ray examination by mounting each single crystal on glass wool by means of "krazy glue" and nail polish. The results of x-ray examination, after careful measurements for d-spacing and relative intensity, , invariably indicated the existence of digenite as the major phase. Figure 4 shows a typical x-ray powder pattern from a digenite sample. Only one x-ray pattern showed the anilite-like pattern (see figure 6). However, the author believes that in almost all of the synthetic products, anilite and digenite are present but that due to their very close characteristics, it is very difficult to make a precise distinction between these two phases. Also, considering the purpose of this research, no further attempts were made to make such a distinction.

Fig—4

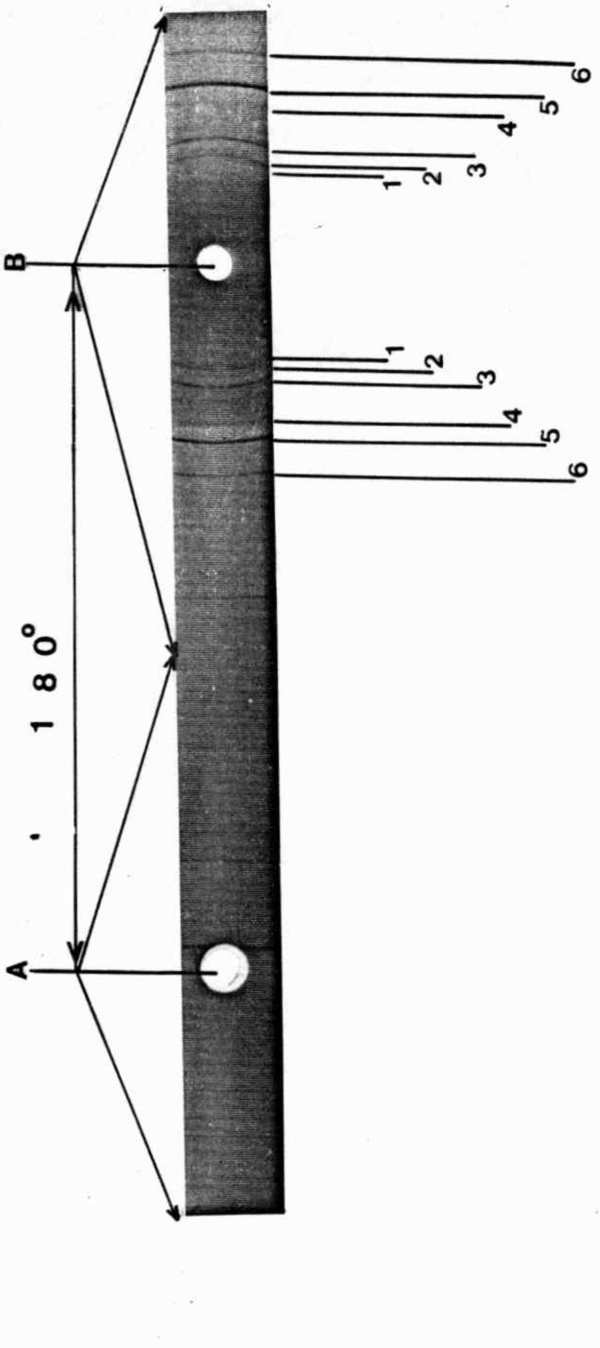
Illustration of x–ray powder pattern of the standard digenite obtained, using a 114.6 mm Gandolfi Camera, CuK_{α} radiation

[A] : back region [2θ> 90°]

[B] : front region [2θ< 90°]

LINE No.	CALCULATED ⊗			GHAZI 1983		POTTER 1976		COMPOSITION
	d[Å]	I/I°	hkl	d[Å]	I/I°	d[Å]	I/I°	
1	3.190	35	202	3.196	40	3.128	40	$Cu_{1.75}S$
2	3.020	14	113	3.048	20	3.076	30	
3	2.772	50	004	2.674	50	2.780	55	
4	2.158	12	124	2.175	15	2.173	35	
5	1.963	100	224	1.961	100	1.962	100	
6	1.674	24	206	1.664	20	1.674	15	

⊗ AFTER POTTER (1976).


B
A
180°
1
2
3
4
5
6
1
2
3
4
5
6

After determining d-spacings and relative intensities, the results were compared with a set of standards previously prepared by Dr. R. J. Goble. It was found that the most intense lines on the x-ray films matched those of Goble's standards. Figures 5 and 6 show two sets of data obtained in this study as compared to Goble's standards.

The results of the measurements were also compared with a set of JCPDS standard cards and with the data of earlier investigations (Potter 1976, Morimoto et al. 1969, Swanson et al. 1955). These comparisons also showed that the end product of each run was, without exception, digenite, anilite or a mixture of both minerals. Table 4 shows a tabulated result for all the experiments.

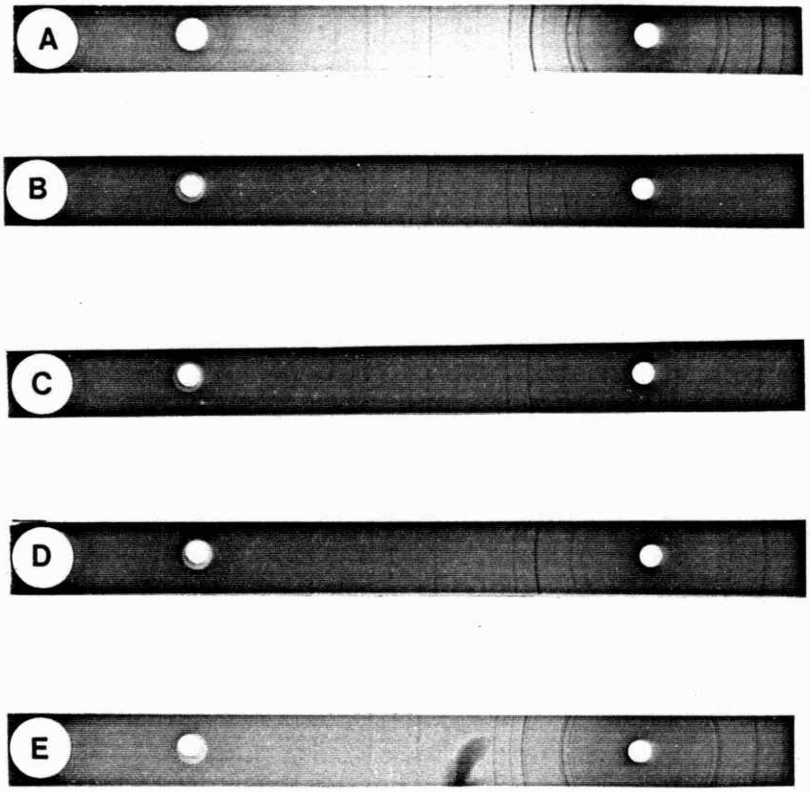
At the termination of each run, when samples were examined under a binocular microscope, the individual crystals were almost without exception coated with a thin, blue iridescent coating. Through reflected light observations, the coatings were identified as blue-remaining covellite or a mixture of that and normal covellite. The thickness of the coating was interpreted as being dependent on the original starting composition as well as on the heating and quenching temperatures.

The more copper-rich synthetic samples (CS2, CS3, CS10 and CS11) of composition ($Cu_{1.75}S$) were, after quenching at the temperatures outlined in table 4, found to be mixtures of digenite (Di), blue-remaining covellite (BC) and normal covellite. However, the final synthetic copper sulfide (CS2 and CS3) from the tubes which were quenched at low temperatures showed well-developed (figure 7), partially modified (figure 8), completely modified (figure 9), and twins or aggregates of octahedral crystals (figure 10).

Fig—5

Gandolfi x–ray powder patterns of five synthetic copper sulfides, prepared with CuK_α radiation

A – CS2
B – CS3
C – CS10
D – CS11
E – CS6


A
B
C
D
E

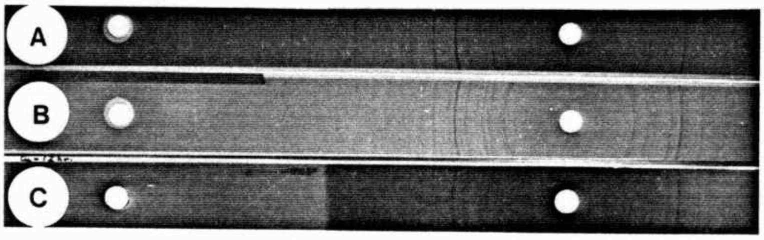
Fig– 6

A comparison of x–ray powder patterns obtained, using a 114.6 mm Gandolfi camera and filtered [Ni] CuK_{α} radiation.

{A} : digenite, sample: CS2 : $Cu_{1.75}S$

{B} : anilite, sample: CS1 : $Cu_{1.6}S$

{C} : Goble's standard anilite


A
B
C

Table—4 Results of synthetic experiments on the samples of the compositions: $Cu_{1.5}S$, $Cu_{1.6}S$ and $Cu_{1.75}S$.

SAMPLE NO.	COMPOSITION	INITIAL TEMP.(°C)	TIME HRS.	REDUCED TEMP. (°C)	TIME HRS.	QUENCHING TEMP. (°C)	RESULT	RADIATION TIME, HR.
CS1	$Cu_{1.60}S$	700	67	500	48	500	An, Cv, BC	7.5
CS2	$Cu_{1.75}S$	650	48	300	18	300	Di, Cv, BC	6
CS3	$Cu_{1.75}S$	700	72	300	18	300	Di, Cv, BC	6
CS4	$Cu_{1.60}S$	600	67	400	48	400	Di, Cv, BC	6
CS5	$Cu_{1.60}S$	650	72	400	48	400	Di, Cv, BC	5
CS6	$Cu_{1.50}S$	550	163	400	24	300	Di, Cv, BC	10
CS7	$Cu_{1.60}S$	700	48	300	48	300	Di, Cv, BC	6
CS8	$Cu_{1.60}S$	700	48	500	48	300	Di, Cv, BC	8
CS9	$Cu_{1.60}S$	500	48	400	48	300	Di, Cv, BC	8
CS10	$Cu_{1.75}S$	600	96	450	72	450	Di, Cv, BC	6
CS11	$Cu_{1.75}S$	700	72	500	48	400	Di, Cv, BC	7

The results were obtained using a 114.6 mm. Gandolfi camera, Nikon ore microscope, and a SEM, observed phases: Anilite [An], Digenite [Di], Covellite [Cv] and Blue—remaining Covellite [BC].

On the other hand, those samples (CS10 and CS11) which were quenched at higher temperatures, did not display such features; instead, the crystals were commonly fractured and possessed irregular shapes (see figure 11). These microscopic observations were then compared with those of previous workers and it was found that the results were in agreement. For instance, in one particular case, when crystals of sample CS2 were viewed under a binocular microscope, nearly all the crystals had a well-defined octahedral shape. SEM photographs, showing the shape of digenite crystals of those samples, were taken and compared with the description of Donnay & Kullerud (1958). They described the crystals of digenite as follows:

> the digenite "singl" crystals are always occur as octahedra, occasionally extremely malformed and frequently modified by small cube faces. Two opposite octahedral faces sometimes predominate over all other faces to such an extent that the crystal looks like a flat hexagonal plate. The crystals vary in size from 10 micron to 4 milimeter.

Figures 7 through 9 from samples, CS2 and CS3, respectively, clearly fit the above description, figure 9 showing the hexagonal-looking plate that is formed by the predominance of (A) faces over (B) faces. Furthermore, when polished sections of the above samples were photographed in reflected light, figures 12, 13, 14 and 15 were obtained. As is shown, the products of these runs were almost pure digenite. Digenite appears white to creamish-blue under reflected light and shows very little pleochroism (see figures 14 and 15).

The samples of $Cu_{1.6}S$ composition (CS1, CS4, CS5, CS7, CS8 and CS9) were also cooled down to their respective quenching temperatures (see table 4), at which they were then quenched. X-ray powder examinations revealed that digenite still existed as the primary phases. Figures 16, 17 and 18 clearly show

Fig. 7

S.E.M. Photograph of a perfectly formed octahedral crystal (sample CS2) with original Composition $Cu_{1.75}S$, Synthesized at 650°C and quenched at 300°C. Notice the patches of coatings on (A) faces.

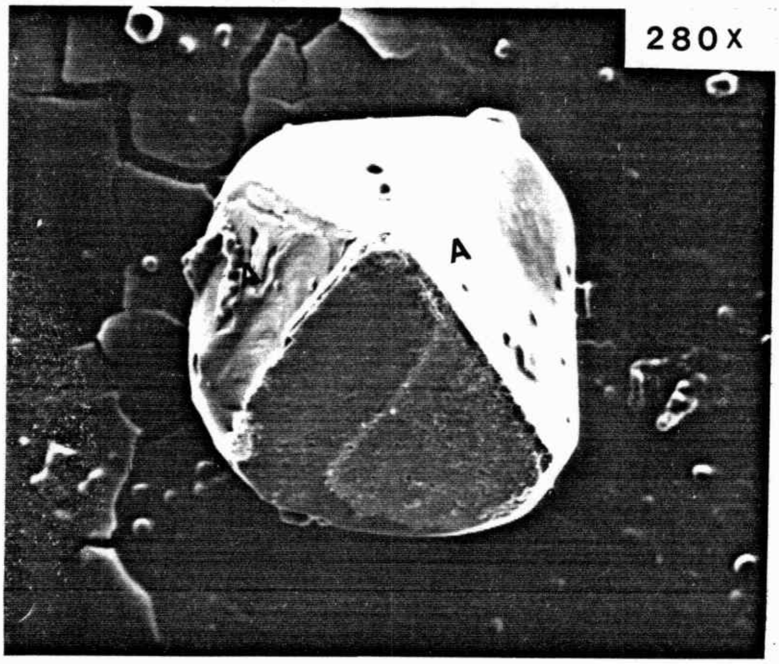

280X
A
A

Fig. 8

S.E.M. Photograph of a well crystallized octahedral crysta (sample CS3) with original Composition $Cu_{1.75}S$, heating temperature: 700°C, quenching temperature: 300°C. Note the relative dimensions of (AA') and (BB') faces.

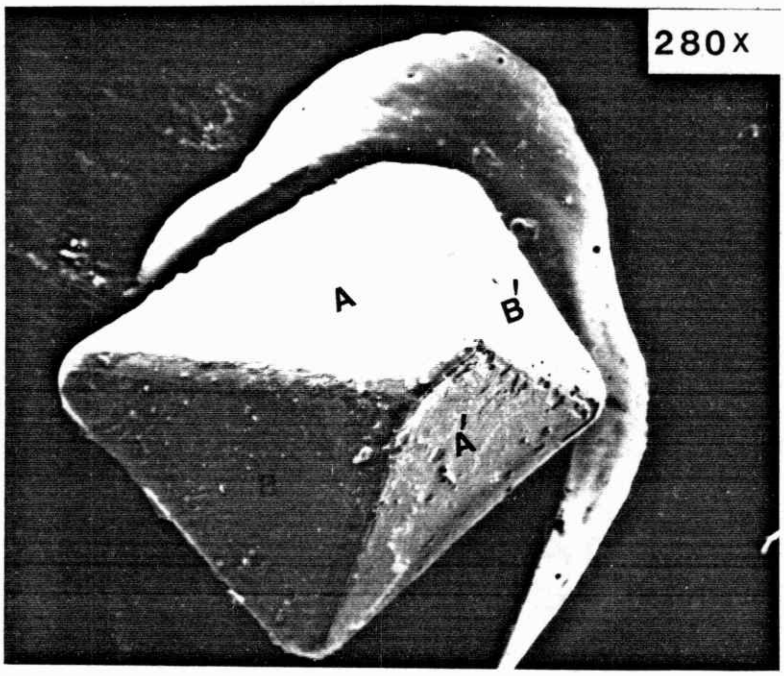

280X
A
B'
A'
B

Fig. 9

S.E.M. Photograph of another single crystal from sample CS2, showing "hexagonal-like" plate (described in text). (A) indicates one of the predominant faces. Crystal is laying on the matching predominate (A) face.

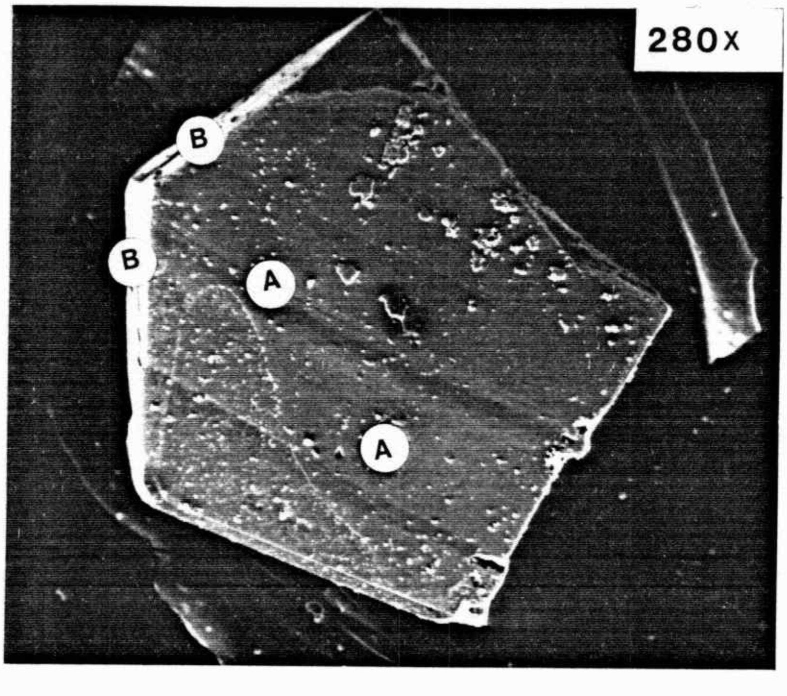

280X
B
B
A
A

Fig.10

S.E.M. Photograph of a well formed twin crystal of Digenite (Di), Sample CS3, Composition $Cu_{1.75}S$, Synthesized at 700°C. Photo shows two attached grains from an aggregate of crystals.

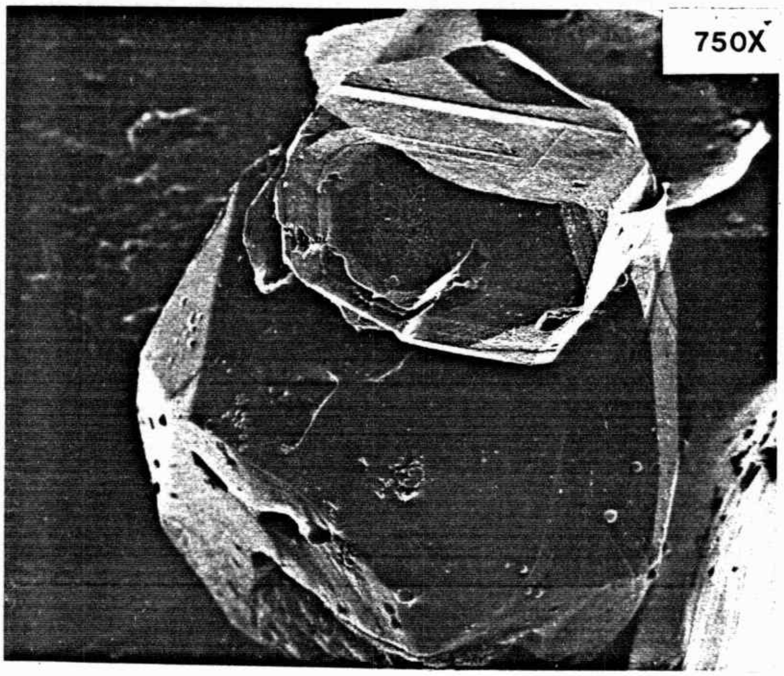

750X

Fig. 11

S.E.M. Photograph showing a single grain (sample CS11). Starting Composition $Cu_{1.75}S$, heating temperature: 700°C, quenched at 400°C. Note fractured shape of crystal compared to Fig. . Arrows point to conchoidal fractures.

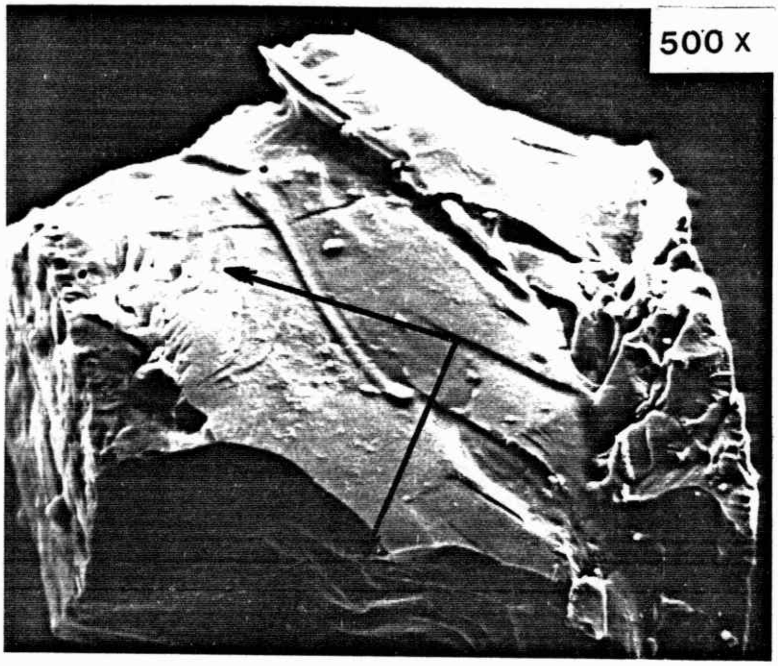

500 X

Fig. 12

Photomicrograph of sample CS3, (F-1/0-3) showing coexistence of Digenite (Di) and normal Covellite (Cv) (uncrossed nicols, poel light)

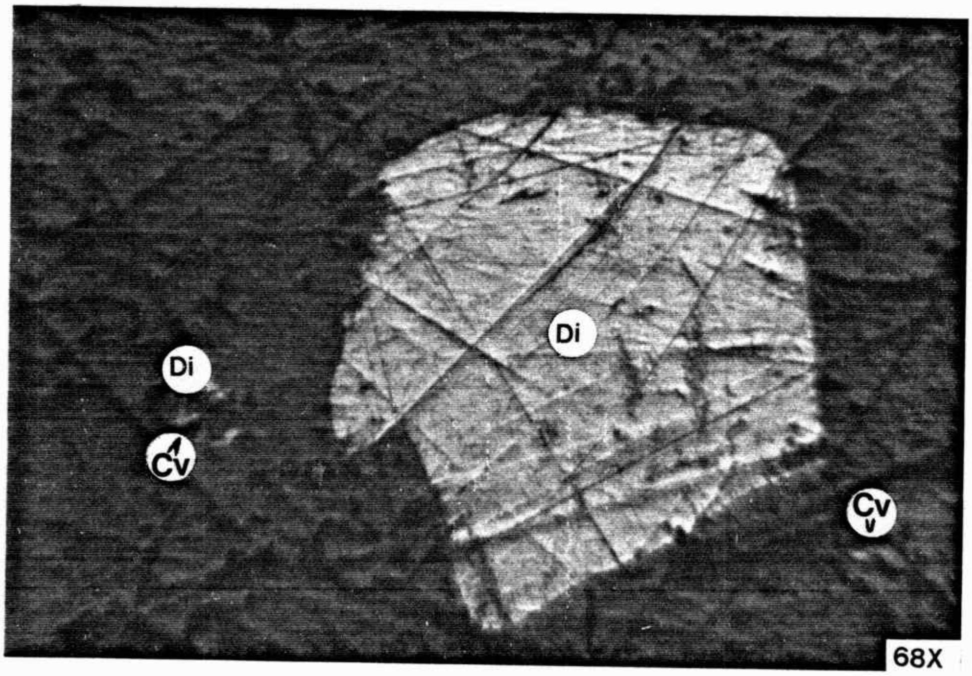
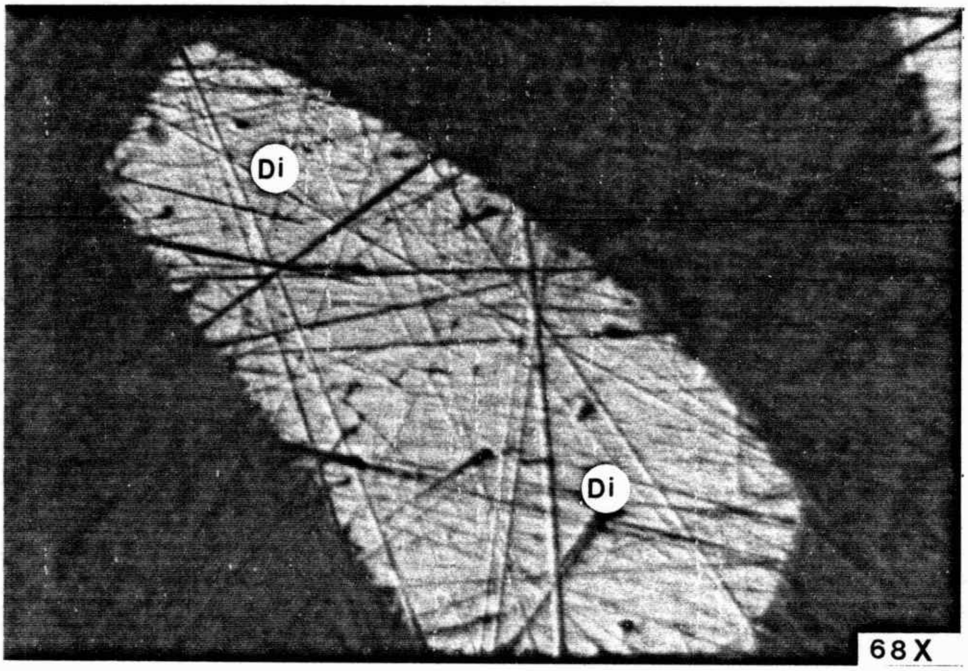

Di
Di
Cv
Cv
68X

Fig.13

Photomicrograph of a Digenite (Di) crystal (sample CS2) (uncrossed nicols, poel lens)

Fig.14

Photomicrograph of the above Digenite (Di) crystal, at slightly different orientation, showing a very weak to moderately weak pleochroism.


Di
Di
68X

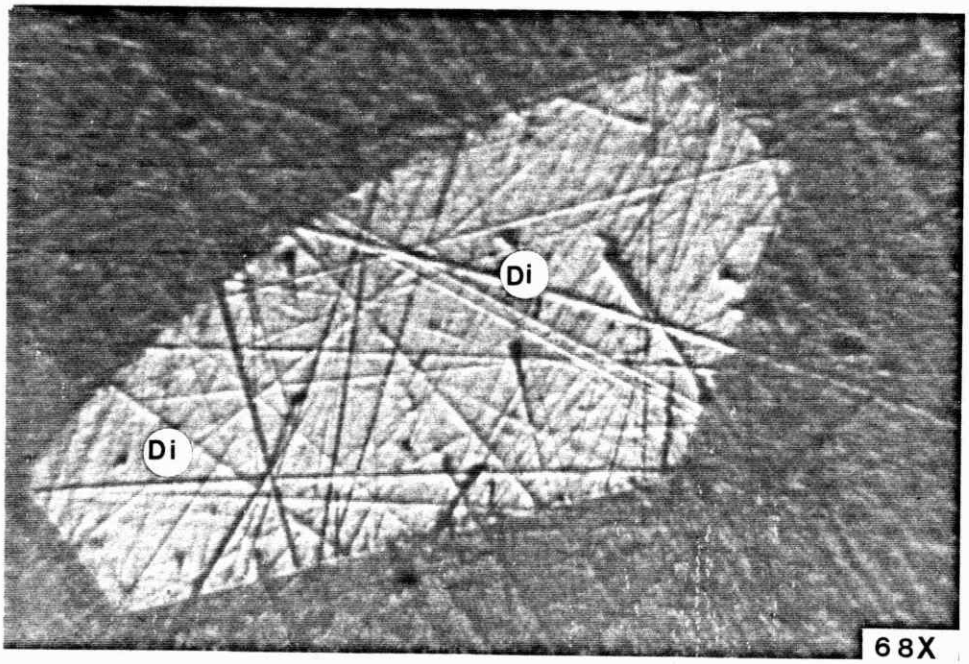

Di
Di
68X

Fig.15

Photomicrograph of a single Digenite (Di) Crystal from experiment CS11, showing blue patches of Blaubleibender Covellite (BC), (uncrossed nicols, oel lens).

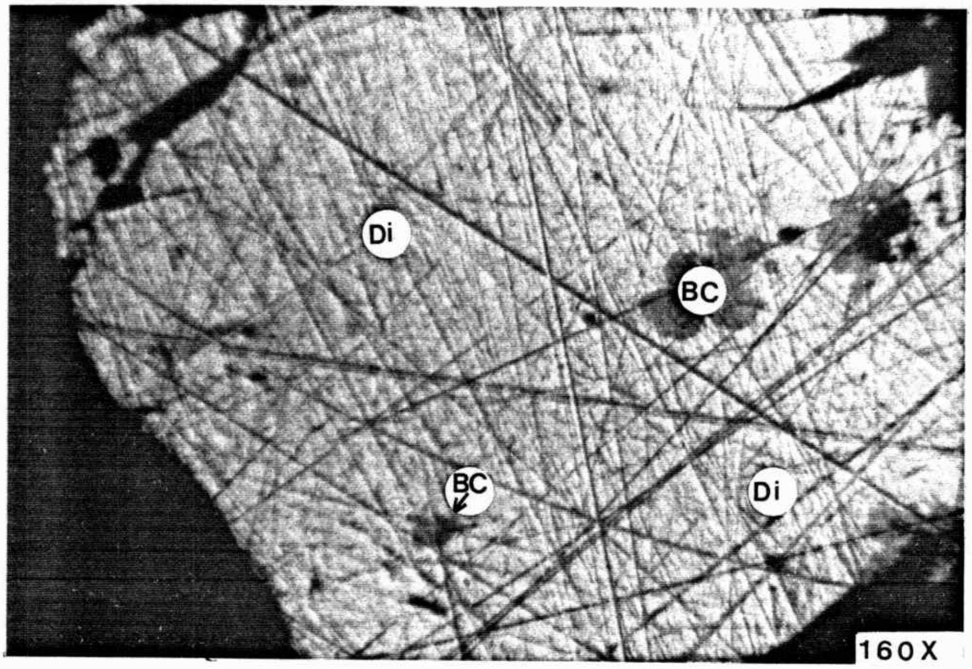

Di
BC
BC
Di
160X

Fig. 16

Photomicrograph of sample CS7, showing Digenite (Di)/Blue-remaining Covellite (BC) intergrown with patches of normal Covellite (BC), (uncrossed nicols, oel lens).

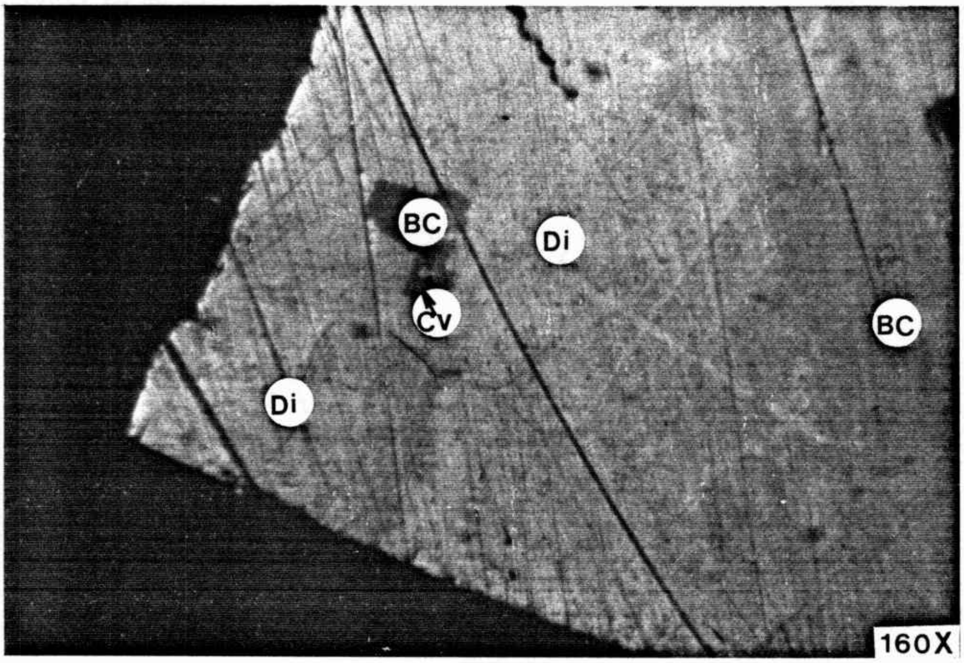

BC
Di
Cv
BC
Di
160X

Fig. 17

Photomicrograph of intergrown Digenite (Di)/Blue-remaining Covellite (BC). Minute quantity of normal Covellite is also present (orange-red) with in the blue color patches of Blaubleibender Covellite (BC), (uncrossed nicols, oel lens), (Sample CS8)

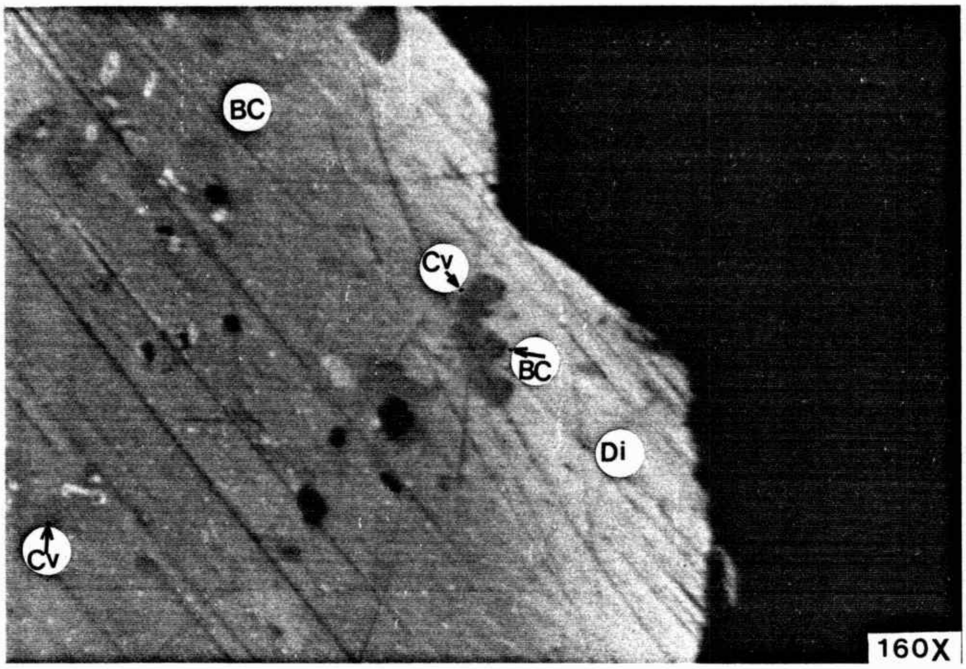

BC
Cv
BC
Di
Cv
160X

Fig.18

Photomicrograph of Digenite (Di)/Blue-remaining Covellite (BC) with veins of normal Covellite (Cv), (uncrossed nicols, poel lens), (sample CS9)

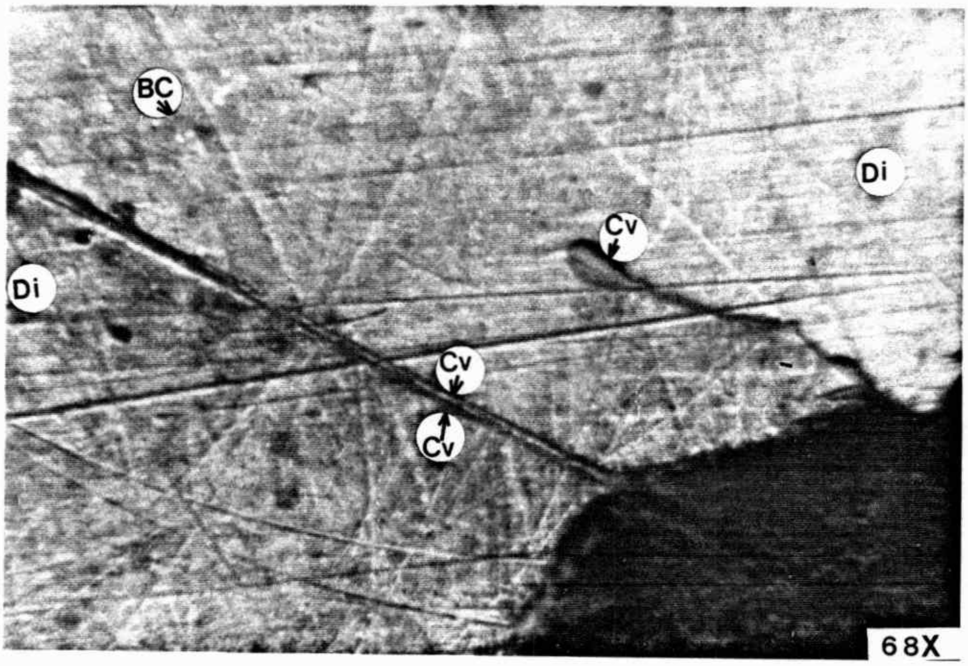
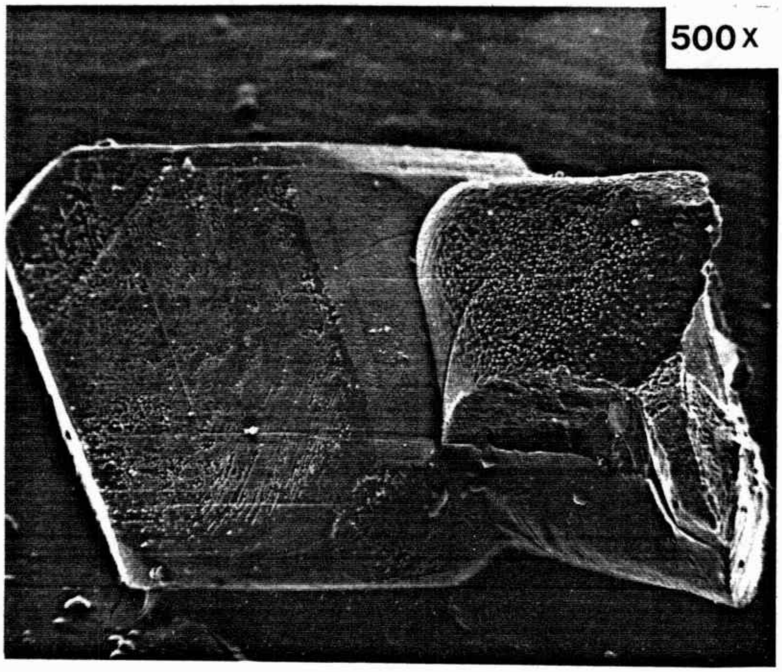

BC
Di
Cv
Di
Cv
Cv
68X

Fig. 19

S.E.M. Photograph of a well defined, partially fractured twin crystal of Digenite (sample CS8), starting composition: $Cu_{1.6}S$, note larger quantity of coatings on the crystal faces compared to figures


500 X

this, although the possibility of co-existence of digenite/anilite exists. However, when the samples were viewed under binocular microscope (40X), all the samples almost invariably had iridescent coatings that were of a darker blue than those previously observed in samples CS2, CS3, CS10 and CS11 (see figures 19 and 20).

It is the author's belief that the increase in color intensity primarily is a function of thickness of the coating which, in turn, can be thought of as caused by an increase in the quantities of co-existing covellite and blue-remaining covellite. In other words, this observation may be interpreted as a compositionally-dependent phenomenon. With regard to this assumption, it is now appropriate to further assume that as the ratio of Cu:S decreases, the thickness, and thus, the intensity of the color of the coating, increases.

In studying the crystals of $Cu_{1.5}S$ composition with the scanning electron microscope, similar morphological features to those of the $Cu_{1.75}S$ composition were observed. Figure 19 shows well-developed twin crystals of digenite, the heating temperature of which was reduced from 700°C to 500°C with the sample being quenched at 300°C.

In one sample (CS6) of composition $Cu_{1.5}S$, the digenite octahedral single crystals showed a coating having the most intense blue color. On the basis of previous assumption concerning the Cu:S ratio and its effect on the thickness of the coating and hence the appearance of the crystals, figures 20 and 21 clearly show the relative abundance of the blue colored minerals (blue-remaining covellite and normal covellite). However, the scanning electron microscope photographs of the coating showed the existence of several smaller-sized octahedral crystals embedded in the coating. This was interpreted as the net result from direct transformation of covellite and blue-remaining covellite to the digenite phase.

Figures 22 and 23 are SEM photographs which show the appearance of a coated octahedral crystal from this particular composition, and furthermore, figure 23 also shows a magnified octahedral crystal embedded in the blue coating.

G) Discussion

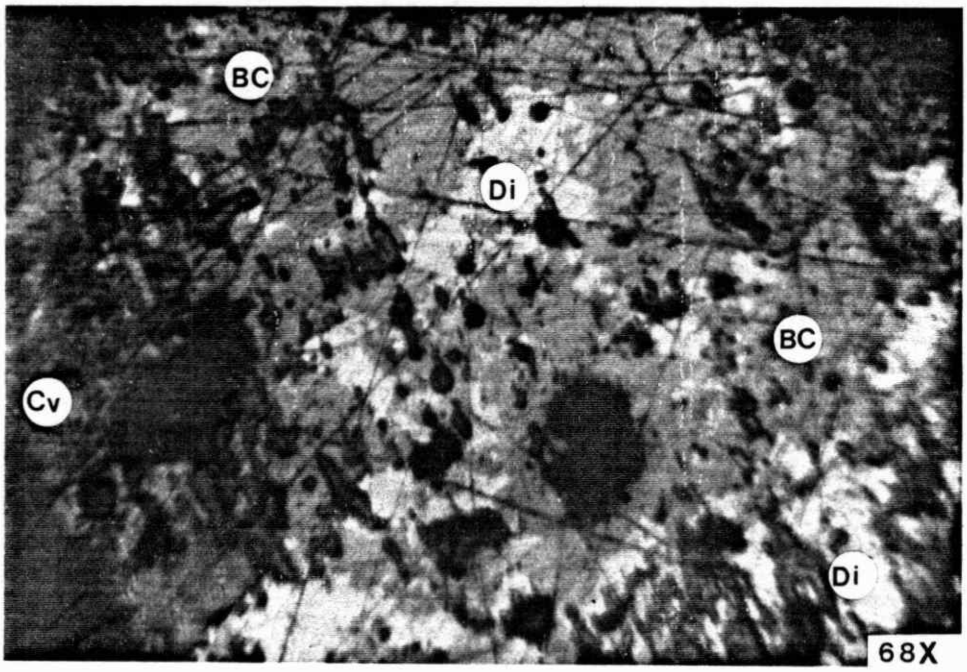
It was found that synthesis of geerite directly from its elemental constituents in the range of composition and conditions (see table 4) studied in this investigation was impossible. In other words the first stage of this work was not successful. This was interpreted to be either due to the rapid oxidation of synthesized copper sulfide, or simply to the fact that geerite is not a stable phase in this composition range and under these conditions. Furthermore it is clear from the data presented in table 4 that digenite is the most abundant phase in the composition range of $Cu_{1.5}S$ - $Cu_{1.75}S$. In fact, except for sample CS1, all the final products of each experiment were identified as digenite. This was confirmed by x-ray powder examination and reflected light and scanning electron microscopic observation. The results of each individual run showed complete agreement with previous works. The crystals of sample CS1, after quenching from a temperature of $500^{o}C$ and upon x-ray examination, produced a pattern which matched the Goble's anilite (see figure 6). However, subsequent x-ray powder examination of the same specimen, after it was ground in a laboratory ball mill revealed a pattern which was identical to that of digenite. This is in agreement with earlier workers (Morimoto et al. 1969), who found that anilite usually changed to a mixture of covellite and digenite upon grinding. However, in this experiment, the author was not able to identify any covellite reflection in the x-ray pattern obtained from ground anilite (CS1).

Fig. 20

Photomicrograph of a single crystal (sample CS6), showing relative aboundance of Blue-remaining Covellite (BC) and normal Covellite (Cv), Digenite (Di) is also present (lighter color areas), (uncrossed nicols, poel lens)

Fig. 21

Photomicrograph of enlarged portion of crystal, Fig. 20, immersed in oil, showing coexistence of three separate phases, Digenite (Di), Blue-remaining Covellite (BC) and normal Covellite (Cv), (uncrossed nicols, oel lens)


BC
Di
BC
Cv
Di
68X

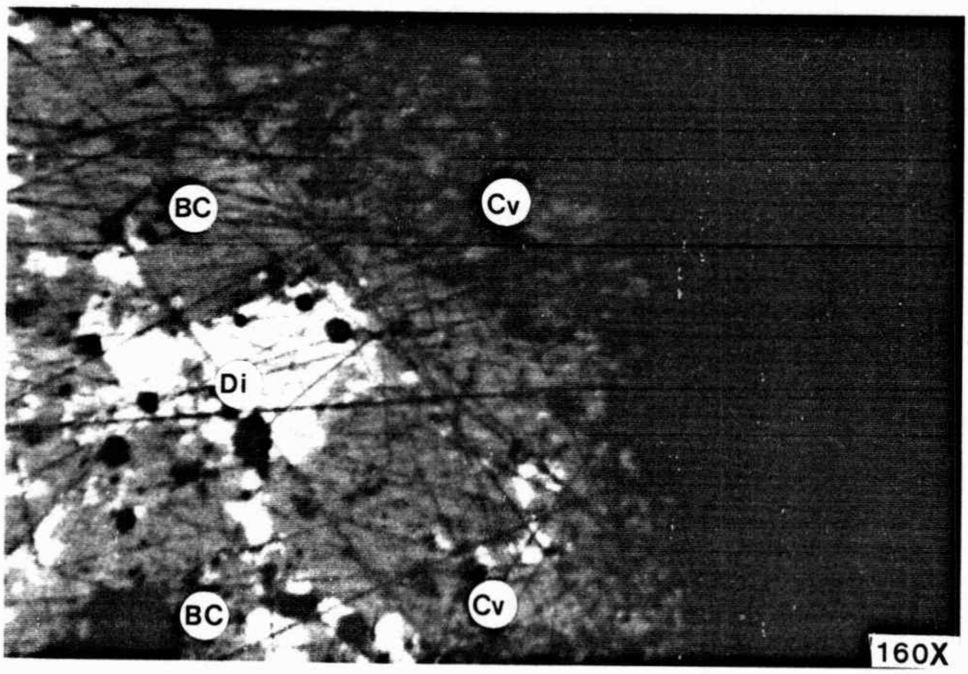
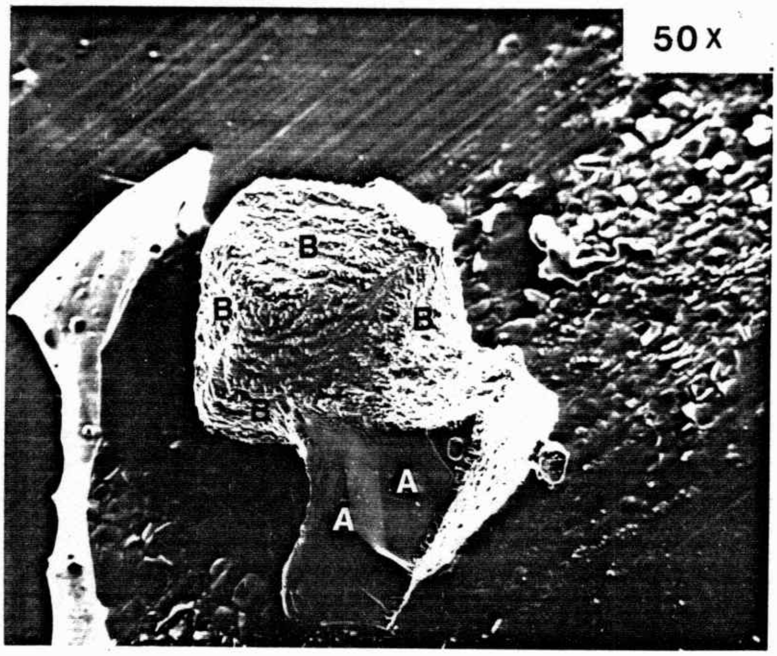

BC
Cv
Di
BC
Cv
160X

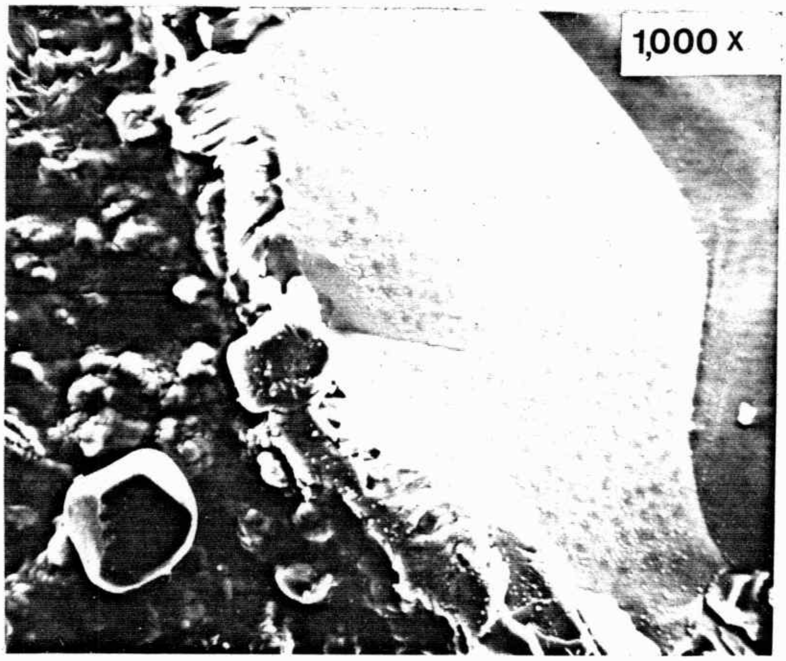
Fig. 22

S.E.M. Photograph (sample CS6), showing thickly coated twin octaheral crystal. Note, faces devoided of coating are black (A), coated faces (B) showed blue iridescent color.

Fig. **23**

S.E.M. Photograph of rectangle in figure . Arrow shows well developed octahedral crystal embedded in coating.


50 X
B
B
B
B
C
A
A


1,000 X

Most combinations of the phases in table 4 were described earlier by Roseboom (1966) and Yund & Kullerud (1966). They also reported the presence of anilite and digenite in all mixtures based on the superstructure reflections of both phases. However, in this report, it was impossible to distinguish the two co-existing phases of digenite and anilite by using a regular Gandolfi camera x-ray technique. In fact, only application of the single-crystal method on a natural specimen may disclose combinations of anilite and digenite.

CHAPTER (IV) - LEACHING OF COPPER SULFIDES

A) Procedure (Experimental Work)

A series of tests were run on ten selected single crystals from CS2 at room temperature, approximately 60°F. Results are listed in table 8. Ten individual single crystals were selected under the binocular microscope (40X), picked and after cleaning with distilled water, placed into ten 6.0mm glass tubes. Four separate batches of ferric sulfate solution of concentrations $1.0\text{X}10^{-5}$M, $1.0\text{X}10^{-3}$M, $1.0\text{X}10^{-2}$M and $1.0\text{X}10^{-1}$M were then prepared. The solution is acidic and usually contains some free acid. Leaching solution was added to each container. All glass tubes were kept at normal room temperatures (50-60°F) for a set period of time; experimental conditions are listed in table 5.

At the termination of each leaching period and upon the removal of the grains from solutions, they were washed with distilled water and prepared for x-ray powder examination. A Gandolfi camera with 114.6mm in diameter was used for the x-ray analysis.

Synthetic copper sulfide from experiment CS2 was chosen as the only source of material for this phase of investigation. The starting chemical composition, heating and quenching temperatures, period of heating, as well as the final identified phases are listed in table 4.

B) Characterization of Leached Samples

The experiments reported in this work consider only 1) the effect of particle size, 2) the effect of concentration of leaching solution, and 3) the mechanism of

Table_5 Data from leaching of synthetic $Cu_{1.75}S$

Run No	Sample No.	Leaching days/hrs	$Fe_2(SO4)_3 \cdot x\ H_2O$			Temp. (°F)	Sample Size (mm.)	X—ray Time, hr.	Crystal change	Remarks
			PH	Conc. (M)	Vol. (ml)					
1A	1	17h	5	10^{-5}	5	60	.5×.2×.3	5.5	NO	
2A	1	168h	5	10^{-5}	5	65	.5×.2×.3	6	NO	
1B	2	25h	5	10^{-5}	5	65	.1×.1×.1	5	NO	
2B	2	22d	5	10^{-5}	5	68	.1×.1×.1	6	NO	
3A	3	8d	5	10^{-5}	5	64	.05×.1×.1	6	NO	
3B	3	10d	5	10^{-5}	5	60	.05×.1×.1	8	NO	
4	8	48h	3	10^{-1}	5	66	.1×.1×.1	7	DIFFUSED	similar obtained pattern is shown in Fig— D
5	8	57h	3	10^{-1}	5	66	.1×.1×.1	8	DIFFUSED	
6	7	48h	4	10^{-3}	5	60	.5×.1×.2	5.5	NO	
7	9	48h	3	10^{-1}	5	65	.5×.5×.2	6	CHANGE	see Figs : B B
8	6	96h	4	10^{-2}	5	67	.1×.1×.1	6	CHANGE	
9	10	17h	3	10^{-1}	5	66	.1×.1×.1	7	CHANGE	
10	11	17d	5	10^{-3}	5	57	.1×.5×.1	7	CHANGE	
11	5	25d	5	10^{-5}	5	59	.1×.1×.2	7	NO	

Single crystals were selected from sample CS2 (table), all the x-ray patterns were prepared with a Gandolfi camera, using CuK_α radiation.

dissolution of digenite in ferric sulfate solution. However, there are other important factors, namely 1) the rate of reaction, 2) the effect of product, and 3) the effect of air and water upon digenite. Several of these factors have been revealed in detail by previous investigators (Sullivan 1929, Sullivan & Sweet 1929 and Sullivan 1930). Presently another sequence of investigations is being conducted to correlate the rate of change of digenite in various concentrations of ferric sulfate solution (Whiteside, L., in preparation). Therefore, no further attempts have been made to study the rate of this change.

C) The Effect of Particle Size

Most of the work described in this study was done on digenite single crystals in the size range of 50-200 microns, or approximately minus 65 to plus 200 mesh, measured using a set of Taylor standards screens. Experiments were performed at $\sim 60^{\circ}F$ on digenite crystals ranging from (-65) to (200) mesh to determine the effect of particle size on dissolution in acidified ferric sulfate solution. Samples 1, 2 and 3 of sizes 0.5X0.2X0.3, 0.1X0.1X0.1 and 0.05X0 - 05X0.1 microns respectively, were placed in $1.0X10^{-5}M$ ferric sulfate solution under conditions outlined in table 6. After a period of seventeen hours, all three samples were taken out and viewed under a binocular microscope. These observations showed no change in the external morphology of the crystals (table 7). The experiments were then repeated, allowing the crystals to leach for a period of 25 hours. Upon removal of the grains from solution, they were observed microscopically. No detectible modifications were found to be present (table 8).

When larger grains of digenite are leached in ferric sulfate solution, one might expect that as the leaching takes place, the particles would disintegrate and

Table—6 Tabulated results of the effects of particle size.

SAMPLE no.	LEACHING TIME DAYS—HRS.	SAMPLE SIZE (mm)	$Fe_2(SO_4)_3$ CONCE. (M)	TEMP. °F	VOL. ml.	REMARKS
1A	17 h	.5 x .2 x .3	10^{-5}	63	5	no change
2A	17 h	.1 x .1 x .1	10^{-5}	66	5	//
3A	17 h	.05 x .05 x .1	10^{-5}	64	5	//
1B	25 h	.5 x .2 x .3	10^{-5}	66	5	//
2B	25 h	.1 x .1 x .1	10^{-5}	66	5	//
3B	25 h	.05 x .05 x .1	10^{-5}	64	5	//
1C	7 d	.5 x .2 x .3	10^{-5}	61	5	small quantity of yellow color powder
2C	7 d	.1 x .1 x .1	10^{-5}	61	5	
3C	7 d	.05 x .05 x .1	10^{-5}	62	5	
1D	35 d	.5 x .2 x .3	10^{-5}	63	5	
2D	35 d	.1 x .1 x .1	10^{-5}	63	5	
3D	35 d	.05 x .05 x .1	10^{-5}	63	5	
1E	50 d	.5 x .2 x .3	10^{-5}	62	5	yellow powder, grains have definite outline but more porous
2E	50 d	.1 x .1 x .1	10^{-5}	62	5	
3E	50 d	.05 x .05 x .1	10^{-5}	62	5	

The results were obtained, using a binocular microscope 40X.

the residue becomes a powder. However, after leaching the particles for 35 days, the particles retained their original outline, but a minute quantity of yellow-orange powder was formed on the surface of the crystals (see table 10). It is this author's view that the sulfur left behind retains the original form of the mineral particles. After a period of 50 days, when the grains were viewed on a watch glass under a binocular microscope (40X), they still showed the original outline. Nevertheless, they were more porous than the starting materials, and a small quantity of alternating yellow-dark blue powdered material formed a ring on the outside of the grains (see table 11). This characteristic layering has been interpreted as sulfur (yellow) and mineral residue, perhaps covellite (dark blue).

D) <u>The Effect of Concentration of Leaching Solution</u>

Tests were made on single crystals of 0.1X0.1X0.1 micron size in solutions containing various concentrations of ferric sulfate. The results are given in table 12. The experiments were performed using ferric sulfate solutions of the following concentrations: 1.0×10^{-1}M, 1.0×10^{-2}M, 1.0×10^{-3}M and 1.0×10^{-5}M.

Single grains of digenite were picked and placed in 6mm glass tubes. After the addition of a volume of ferric sulfate solution of concentrations given above, and under the conditions outlined in table 12, the samples were then leached for 72 hours at $(60\text{-}65)^{\circ}$F. All the conditions were identical. At the termination of the experiments, the particles were removed from the solution, washed with distilled water and two sets of examinations conducted upon the leached crystals: 1) binocular microscope examinations, and 2) x-ray powder camera studies. The following observations were made: 1) A binocular microscope with 40X power

TABLE — 7

SAMPLE no.	LEACHING TIME DAYS—HRS.	SAMPLE SIZE — mm.	$Fe_2[SO_4]_3$ CONC. [M]	TEMP. °F	VOL. ml.	REMARKS
1A	17 HR	.5x.2x.3	10^{-5} M	60	5	NO CHANGE
2A	17 HR	.1x.1x.1	10^{-5} M	60	5	NO CHANGE
3A	17 HR	.05x.05x.1	10^{-5} M	60	5	NO CHANGE

THE EFFECTS OF PARTICLE SIZE [17HRS.] ON LEACHING OF COPPER SULFIDES.

TABLE—8

SAMPLE no.	LEACHING TIME DAYS—HRS.	SAMPLE SIZE — mm.	$Fe_2[SO_4]_3$ CONC. [M]	TEMP. °F	VOL. ml.	REMARKS
1B	25 HR	.5x.2x.3	10^{-5} M	60	5	NO CHANGE
2B	25 HR	.1x.1x.1	10^{-5} M	60	5	NO CHANGE
3B	25 HR	.05x.05x.1	10^{-5} M	60	5	NO CHANGE

THE EFFECTS OF PARTICLE SIZE, [25HRS.] ON LEACHING OF COPPER SULFIDES.

TABLE—9

SAMPLE no.	LEACHING TIME DAYS—HRS.	SAMPLE SIZE— mm.	$Fe_2[SO_4]_3$ CONC. [M]	TEMP. °F	VOL. ml.	REMARKS
1C	7D	.5x.2x.3	10^{-5} M	60	5	PRESENCE OF SMALL AMOUNT OF YELLOW POWDER.
2C	7D	.1x.1x.1	10^{-5} M	60	5	
3C	7D	.05x.05x.1	10^{-5} M	60	5	

THE EFFECTS OF PARTICLE SIZE, [7DAYS] ON LEACHING OF COPPER SULFIDES.

TABLE —10

SAMPLE no.	LEACHING TIME DAYS—HRS.	SAMPLE SIZE — mm.	$Fe_2[SO_4]_3$ CONC. [M]	TEMP. °F	VOL. ml.	REMARKS
1 D	35 D	.5x.2x.3	10^{-5} M	60	5	LARGER SAMPLE CONTAINED THE LARGEST AMOUNT OF THE POWDER.
2 D	35 D	.1x.1x.1	10^{-5} M	60	5	
3 D	35 D	.05x.05x.1	10^{-5} M	60	5	

THE EFFECTS OF PARTICLE SIZE, [35 DAYS] ON COPPER SULFIDES.

TABLE _11

SAMPLE no.	LEACHING TIME DAYS—HRS.	SAMPLE SIZE — mm.	$Fe_2[SO_4]_3$ CONC. [M]	TEMP. °F	VOL. ml.	REMARKS
1 E	50 D	.5 x .2 x .3	10^{-5} M	60	5	LEACHED GRAINS APPEARED MORE POROUS THAN THE ORIGINAL GRAINS
2 E	50 D	.1 x .1 x .1	10^{-5} M	60	5	
3 E	50 D	.05 x .05 x .1	10^{-5} M	60	5	

THE EFFECTS OF PARTICLE SIZE, [50DAYS] ON LEACHING OF COPPER SULFIDES.

TABLE_12

SAMPLE no.	LEACHING TIME DAYS–HRS.	SAMPLE SIZE – mm.	$Fe_2[SO_4]_3$ CONC. [M]	TEMP. °F	VOL. ml.	REMARKS
1D	72HR	0.1×0.1×0.1	10^{-5}M	60	5	NO CHANGE
2D	72HR	0.1×0.1×0.1	10^{-3}M	60	5	NO CHANGE
3D	72HR	0.1×0.1×0.1	10^{-2}M	60	5	YELLOW POWDER
4D	72HR	0.1×0.1×0.1	10^{-1}M	60	5	GRAINS MORE POROUS

THE EFFECTS OF CONCENTRATION ON LEACHING.

was employed to investigate the effects of concentration on crystal morphology. The corresponding data are given in table 11. It is evident that sample 1D and 2D, which were leached in the two weakest solutions (1.0X10^{-5}M and 1.0X10^{-3}M), showed absolutely no modification in the shape of crystal grains. Although sample 3D retained its original outline, very little yellow powder was formed on the surface of the particles. Sample 4D showed the most intense morphological modifications--to the extent that the crystals seemed to have higher porosity than the original materials. Furthermore, an alternating layer of yellow-dark blue material was also detected, resembling the one observed in the previous section. 2) Under given x-ray conditions, using a 114.6mm diameter Gandolfi camera, an x-ray pattern of each treated sample was produced. The results from x-ray runs were measured for d-spacing and intensity and the results then compared with a set of JCPDS standard cards and previously reported data (Morimoto et al. 1969, Potter 1976).

A sequence of visual comparisons were conducted between the original material, final leached products and several x-ray patterns from Goble's standards. Figures 24-30 illustrate the results of these observations.

Figures 24-27 show the final x-ray results versus those of the original patterns for samples 1D, 2D, 3D and 4D respectively. It is evident from these figures that the x-ray patterns of samples 1D and 2D which were leached in 1.0X10^{-5}M and 1.0X10^{-3}M ferric sulfate solution showed absolutely no deviation from the patterns of starting materials. Furthermore, d-spacing and relative intensity measurements also showed similar values to those obtained from the starting materials. On the other hand, when the x-ray pattern of leached sample 3D was compared with its unleached pattern, some noticeable modifications of the

Fig_24

Gandolfi x-ray powder pattern showing a comparison of unleached |vs.| leached pattern of sample CS2, leaching conditions outlined in table -

A_unleached

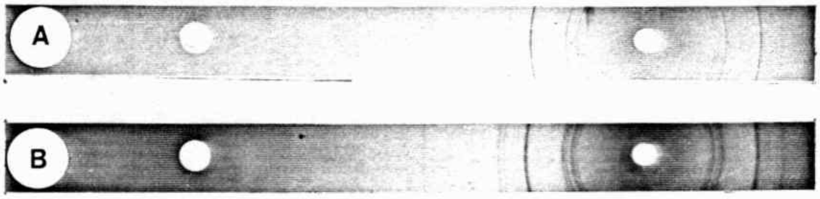
B_leache

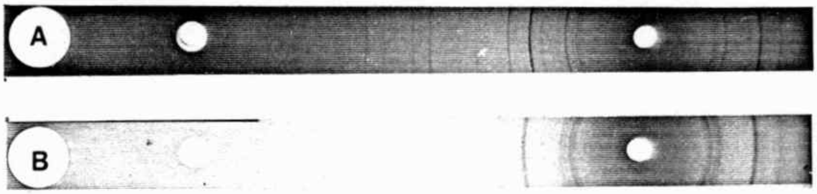
Fig_25

Gandolfi x-ray powder pattern showing a comparison of unleached |vs.| leached pattern of sample CS3.

A_unleached

B_leached


A
B


A
B

Fig—26

Gandolfi x-ray powder pattern of;

A— unleached CS10, $Cu_{1.75}S$

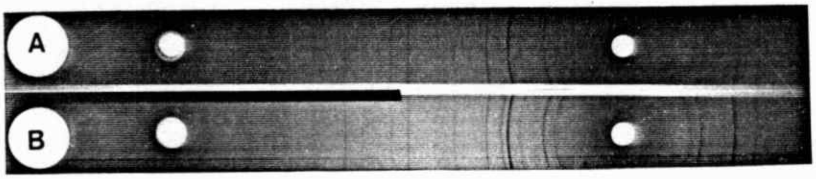
B— leached in 10^{-2} M $Fe_2(SO_4)_3$, 72 hours

Fig—27

Gandolfi x-ray powder pattern of;

A— unleached CS11, $Cu_{1.75}S$

B— leached in 10^{-1} M $Fe_2(SO_4)_3$, 72 hours


A
B


A
B

x-ray lines were present. As shown in figure 26B, lines were diffuse and difficult to measure accurately. However, similar reflections were observed when the same pattern was compared with that of blue-remaining covellite. Figure 28 is the comparison between x-ray results from leached and unleached sample 4D. The leached pattern obtained from this sample showed the most displacement of the lines. These lines were so completely diffused that they made any kind of measurement impossible. As one might expect, broadening in lines produced these diffusions. Nevertheless, when the x-ray pattern of leached samples 3D and 4D were compared with those of Goble's standards ($Cu_{1.2}S$ and sphalerite), obvious similarities were present; these are shown in figures 28, 29 and 30. Referring to the same figures, x-ray patterns B, C, D and E show the relative modifications of the reflection of all four samples, leached in ferric sulfate solution of different concentration. On the basis of figures 28 and 30, obvious similarities exist between the powder patterns of leached digenite samples (3D and 4D) in ($1.0X10^{-2}M$ and $1.0X10^{-1}M$) ferric sulfate solution and that of Goble's $Cu_{1.12}S$.

However, it is also apparent from figure 29 and 30 that the main lines of these x-ray films (3D and 4D) resemble the main reflections in the sphalerite pattern. When this is coupled with previous observations regarding the structural and compositional modifications of copper sulfides when leached with ferric sulfate (Goble 1981) it is reasonable to assume that these patterns belong to the geerite structure as obtained by Goble (1981). In fact, although x-ray patterns B and C in figure 30 are somewhat diffuse, the author believes that there is a better agreement between the lines on these two films and those in sphalerite pattern. This, in turn, means that the main lines in B and C resemble those x-ray patterns

Fig_28

A general comparison of x_ray patterns of the leached samples with Goble's $Cu_{1.12}S$ and unleached digenite pattern.

A_ digenite pattern

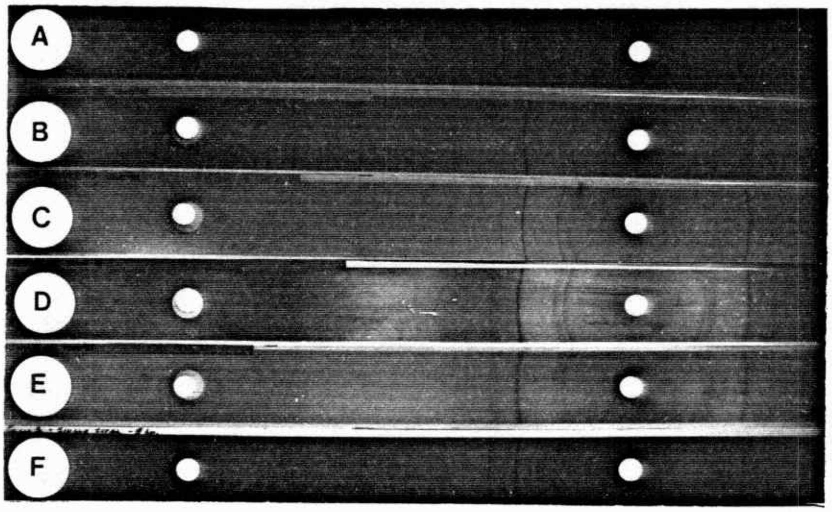
B_ $Cu_{1.75}S$, CS2 , $Fe_2(SO_4)_3$ 10^{-5} M

C_ $Cu_{1.75}S$, CS3 , $Fe_2(SO_4)_3$ 10^{-3} M

D_ $Cu_{1.75}S$, CS10 , $Fe_2(SO_4)_3$ 10^{-2} M

E_ $Cu_{1.75}S$, CS11 , $Fe_2(SO_4)_3$ 10^{-1} M

F_ Goble's $Cu_{1.12}S$ pattern


A
B
C
D
E
F

which are produceable from materials that have the crystal structure of sphalerite or are very similar to this structure.

Based on a study which used the X-ray precession method to investigate the artificial leaching of copper sulfides from anilite ($Cu_{1.75}S$) to spionkopite ($Cu_{1.40}S$) to yarrowite ($Cu_{1.12}S$) to covellite (CuS), Goble (1981) stated that the reciprocal lattice of leached anilite ($Cu_{1.75}S$) strongly resembles the reciprocal lattice of sphalerite. He observed anomalous displacement in the reflection of leached anilite when the x-ray patterns were compared with those obtained from the initial material. In fact, he states that:

> —— The reciprocal lattice of leached anilite does not, however, resemble the reciprocal lattice of covellite or the similar reciprocal lattice of yarrowite and spionkopite, as was expected from the observed replacement sequence in natural specimens. It does strongly resemble a geerite and sphalerite reciprocal lattice.

In the present investigation, Gandolfi-simulated powder patterns of the starting samples with the composition of $Cu_{1.75}S$ did not show the anilite reflections. Instead, characteristic digenite patterns were observed from these samples. However, again according to Goble's classification of copper sulfides, based upon the close packing of sulfur atoms (Goble 1981) geerite, anilite, and digenite belong to the same group. Therefore, as one might expect, leaching of copper sulfide with a $Cu_{1.75}S$ composition and digenite reflection pattern should give a result similar to that obtained from natural anilite.

E) Mechanism of Dissolution of Synthetic $Cu_{1.75}S$ in Ferric Sulfate

Several equations have been written for the decomposition of copper sulfides by ferric sulfate, and Sullivan (1929) discussed this mechanism in his report on the

Fig– 29

An overall comparison of all the leached samples with Goble's sphalerite and a digenite pattern.

A: digenite pattern

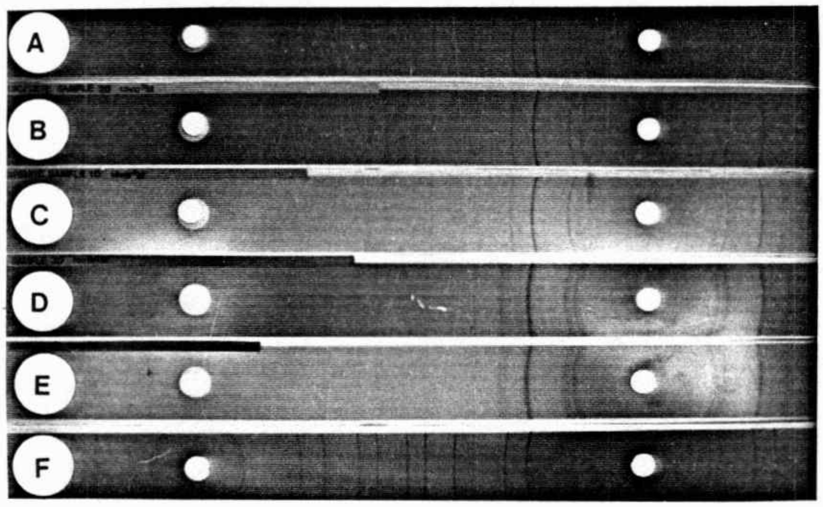
B: CS2 ; $Cu_{1.75}S$, 10^{-5}M $Fe_2(SO_4)_3$

C: CS3 ; $Cu_{1.75}S$, 10^{-3}M $Fe_2(SO_4)_3$

D: CS10 ; $Cu_{1.75}S$, 10^{-2}M $Fe_2(SO_4)_3$

E: CS11 ; $Cu_{1.75}S$, 10^{-1}M $Fe_2(SO_4)_3$

F: Goble's sphalerite


A
B
C
D
E
F

dissolution of chalcocite and covellite in ferric sulfate solution. He described the mechanism as following the reactions below:

a) chalcocite

$Cu_2S + Fe_2(SO4)_3 \longrightarrow 2FeSO4 + CuSO4 + CuS$ (1)

$CuS + Fe_2(SO4)_3 + H_2O + 30 \longrightarrow 2FeSO4 + CuSO4 + H_2SO4$ (2)

$XH_2SO4 + Cu_2S + 2Fe_2(SO4)_3 \longrightarrow 2CuSO4 \quad 4FeSO4 + S + XH_2SO4$ (3)

Equation (2) is also commonly written:

$Cu_2S + 2Fe_2(SO4)_3 + H_2O + 30 \longrightarrow 2CuSO4 + 4FeSO4 + H_2SO4$ (4)

However, the most common way of writing the reaction is:

$Cu_2S + Fe_2(SO4)_3 \longrightarrow CuSO4 + 2FeSO4 + CuS$ (5)

$CuS + Fe_2(SO4)_3 \longrightarrow CuSO4 + 2FeSO4 + S$ (6)

b) covellite

$Cu + Fe_2(SO4)_3 \longrightarrow CuSO4 + 2FeSO4 + S$ (7)

The most striking features of the above reactions are the formation of sulfuric acid (equation (4)) and the mineral covellite (equation (5)). According to equation (4), sulfuric acid is produced as a net result, after iron present in the solution has been completely oxidized. At this point a steady state condition is reached, where the ferric sulfate is reduced by sulfur dioxide and reoxidized simultaneously with oxidation of sulfur dioxide and the formation of sulfuric acid. On the other hand, equation (5) shows that covellite (CuS) is also formed as one of the net products of this reaction. This was confirmed by an examination of leached grains, which have a porous appearance under a microscope.

Considering the above reactions, and knowing that $Cu_{1.75}S$ is one of the intermediate compounds in the copper-sulfur system, in leaching with ferric

Fig_30

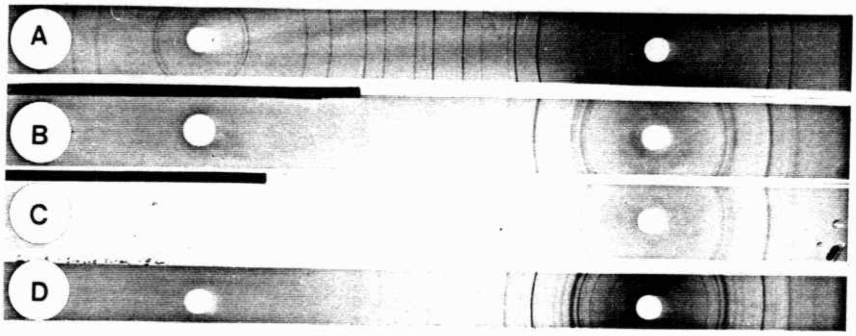
An overall comparison of the leached samples with Goble's sphalerite and $Cu_{1.12}S$ x-ray powder patterns.

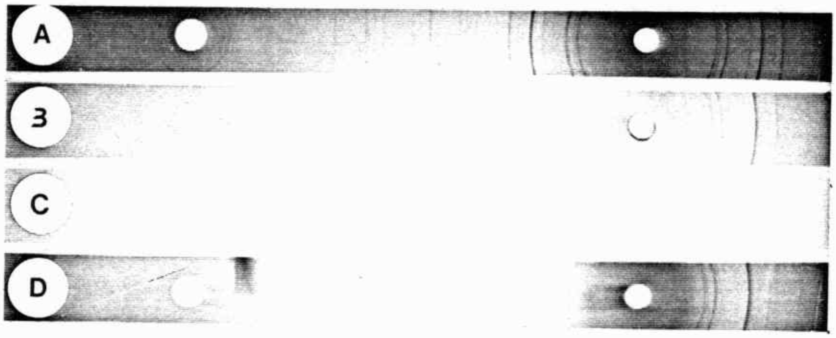
A _ Goble's sphalerite
B _ CS10
C _ CS11
D _ Goble's $Cu_{1.12}S$

Fig_31

Illustration of x-ray examination of sample 1D, leached in 1.0×10^{-2}M $Fe_2(SO_4)_3$ solution, time is outlined below.

A- original sample 1D
B- leached 12 hours
C- leached 24 hours
D- leached 36 hours


A
B
C
D


A
3
C
D

sulfate solution we can predict that the synthetic copper sulfide sample of composition $Cu_{1.75}S$ used in this experiment will follow the same mechanism.

It should be noted that equations (5) and (6) show a reduction of ferric iron to ferrous iron and the production of the element sulfur. Furthermore, it should be recalled that in the previous sections, the presence of yellow-powdered material was detected under a binocular microscope. Hence, as one might expect from equations (6) and (7), the yellow-powdered materials were indeed the element sulfur.

F) Discussion

Copper sulfide of composition $Cu_{1.75}S$ can be leached with ferric sulfate and the sulfides converted into the soluble sulfate. Simultaneously, with the removal of copper, ferric iron is reduced to ferrous iron.

Experiments described in this report showed that the rate of dissolution of similar sized samples (0.5X0.2X0.3mm), (0.1X0.1X0.1mm) and (0.05X0.05X0.1mm) was not the same in a solution containing a similar percentage of trivalent iron. However, the rate of removal of copper from these samples was not markedly different in 1.0×10^{-5}M solution.

The rate of removal of copper from synthetic copper sulfides was practically independent of the strength of the acidic solution for the first twelve hours when ferric iron concentration remained constant at 1.0×10^{-2}M. After a period of twelve hours, the structure of $Cu_{1.75}S$ samples had begun to change. Figure 31 shows a sequence of systematic structural modifications for periods of 12, 24, and 36 hours. From this figure it is obvious that the samples which have been leached for longer times show a more intense structural change.

When larger crystals of $Cu_{1.75}S$ samples were leached in ferric sulfate solution of $1.0X10^{-5}M$, they did not disintegrate but almost retained their original outlines. Apparently, the sulfur left behind retained the original form of the mineral particles. It is highly probable that artificial covellite is produced upon prolonged leaching of $Cu_{1.75}S$ with acidic ferric sulfate solution (Goble 1981).

The x-ray examinations of the final leached $Cu_{1.75}S$ samples in $1.0X10^{-1}M$, $1.0X10^{-2}M$ and $1.0X10^{-3}M$ ferric sulfate solution showed complete structural changes after periods of 17 and 96 hours, and 17 days respectively (see table 5). It was discovered that the material had a pattern approximately similar to those of sphalerite. However, due to broadening and extreme diffusion of the reflection lines, it was impossible to conduct any accurate measurements. These patterns, when they were compared with Goble's ($Cu_{1.12}S$) standard pattern, did show some degree of similarities. Figure 28 shows a general comparison of the patterns obtained from leached samples with that of $Cu_{1.12}S$. Furthermore, Goble (Personal Communication, 1983) suggested that these patterns are very similar to patterns that he had previously obtained from geerite ($Cu_{1.6}S$) and leached anilite. The similarity of the patterns of these phases was confirmed by further experiments using a precession camera (Goble & Robinson 1980). Hence, it is probable that the material produced has the geerite structure. Therefore, similar material was used in the flotation studies to determine the flotability of the geerite structure.

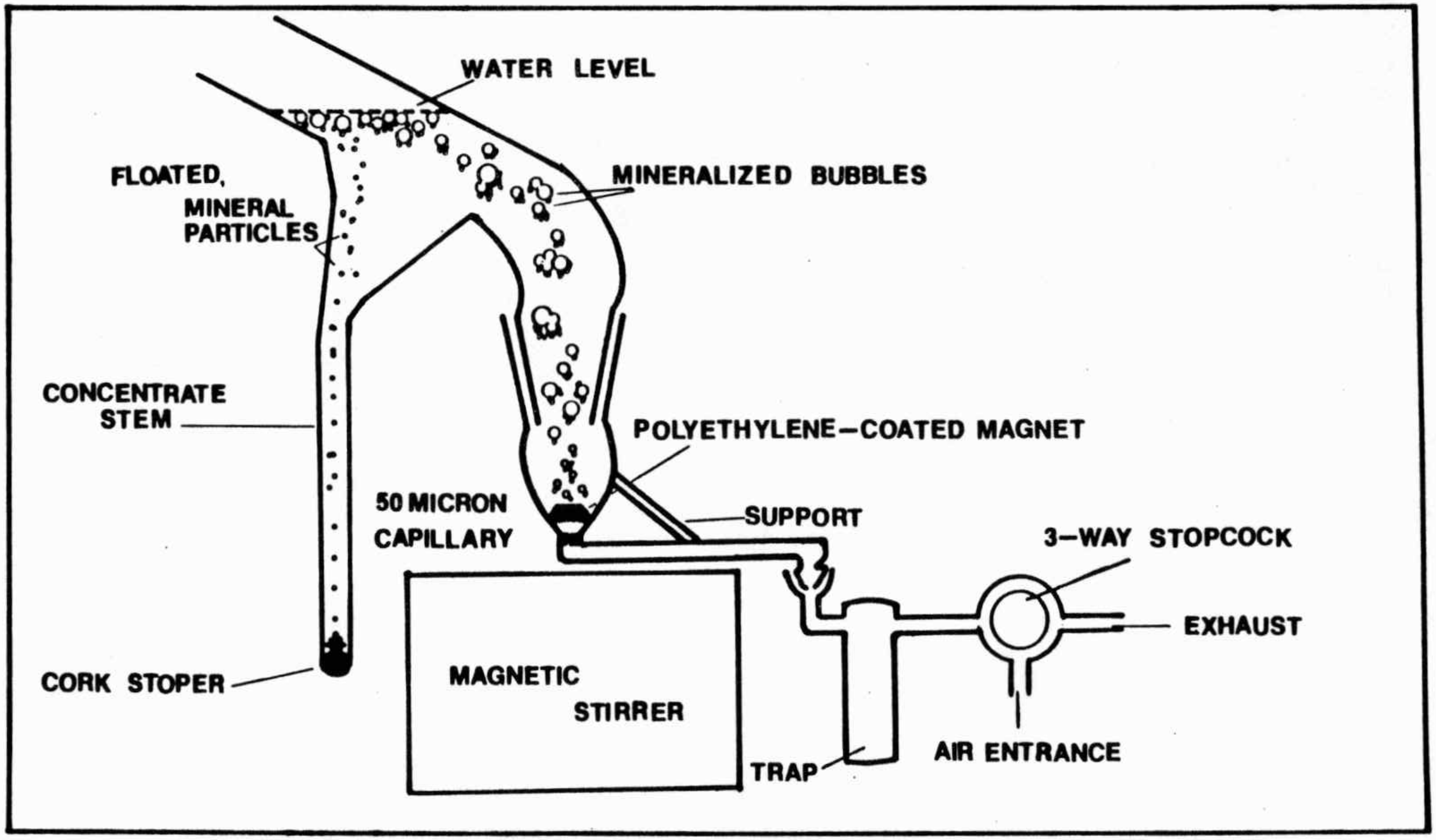
CHAPTER (V) - FLOTATION

A) Description of Flotation Cell

An improved laboratory flotation cell has been designed based on one developed by Hallimond (1944 & 1945). This improved cell can give reproductible results on 2 or 3 grams of sample of (-65/+100 mesh) charge (figure 32).

This flotation cell has three advantages: (1) samples of only 2 or 3 grams can be floated, (2) operating variables can be precisely controlled, and (3) neither the reagent concentration nor the amount of liquid changes during the course of experimentation. By changing reagents, but keeping the flotation time, gas flow rate and agitation intensity constant, the recovery of concentrate becomes a measure of the relative flotation rates under the different reagent conditions.

The final cell shown in figure 32 uses a glass capillary for gas inlet, a magnetic stirrer for agitation of the sample, and a ground glass joint for ease in handling. In addition, this cell has a solid glass tube to support the ground joint, the former making an angle of approximately 45° with the ground joint. This section of the cell does not play any role in the actual flotation process. The walls of the cell were made from a 29/42 pyrex-ground joint and have a steep angle so that the unfloated fine particles will always slide down and lie over the capillary tube at the bottom. The inside diameter of the capillary is 50 microns so that the cell can be clamped directly over the magnetic stirrer. A star-shaped polyethylene-coated magnet is used for better agitation. The cell can easily be removed from the gas flow system by means of a 12/5 ball and socket which is tied together by an ordinary laboratory clamp.



Fig—32 Modified Hallimond flotation cell in action.

Compressed air is used as the bubble production media. The air is introduced through a three-way stopcock so that the gas can be sent either to the exhaust or through a 50 micron capillary. Constant air flow through the cell is maintained by establishing a constant flow rate through the exhaust.

With the kind of arrangement described above, we can then vary any one of the following parameters while keeping the others constant: (1) reagent concentration, (2) conditioning time, (3) flotation time, (4) degree of agitation.

B) Flotation of Synthetic Copper Sulfide

Three different samples of previously synthesized copper sulfide of original composition $Cu_{1.75}S$ have been used for the flotation experiments. The samples were marked as (CS3), (CS10) and (CS11). The preparation conditions, along with other data, are outlined in table 4. In this and succeeding sections, the samples are designated as follows: (F-1/0-3), (F-2/0-10), and (F-3/0-11) respectively. The nature of the existing phases - determined by means of the x-ray powder method, reflection light microscope, and a scanning electron microscope - is also outlined in table 4. Furthermore, figure 5 shows the x-ray powder patterns obtained from the samples. When compared with the indexed digenite x-ray pattern (figure 5), it should be clear that these selected samples were digenite.

Samples (F-1/0-3) and (F-2/0-10) were treated with ferric sulfate solution prior to flotation experiments, whereas sample (F-3/0-11) was used only to reveal the flotability of unleached copper sulfide of $Cu_{1.75}S$ composition having a digenite x-ray pattern. In leaching, 0.3 grams (300 mg) of each sample (F-1/0-3) and (F-1/0-3) and (F-2/0-10) were slightly ground to obtain the desired grain size

(-65/+100 mesh), and then placed in 150 ml flasks. A volume of 25 ml of ferric sulfate solution of 1.0×10^{-1} molarity was then added to each flask, allowing the samples to leach for a period of seven days. Upon removal of the sample after the stated period of time, a series of experiments, similar to those previously described in the leaching section, were conducted on the leached samples. The outcome of these studies was in agreement with the earlier results.

B1) Flotation Procedure of Copper Sulfides

Experiments were carried out in a 200 ml modified Hallimond tube microflotation cell. The following steps were taken in preparation for subsequent flotation of each sample.

1) Previously leached samples of the weight (0.3 gram) and mesh-size (-60/+100) were washed with three percent hydrogen peroxide just prior to each run.

2) A sufficient amounts of K-ethylxanthate $(\frac{25\ \text{mg}}{1000\ \text{ml}})$ was combined with the charges to produce pulp with a total volume of 150 ml.

3) As is listed in appendix II and tables IIA, IIB, IIC and IID, the concentration of collecting reagent (potassium ethylxanthate), volumetric gas flow, volume of the pulp, and flotation time for all three experiments were kept constant unless otherwise stated.

4) The pulps were transferred to the microflotation cell and floated in the presence of compressed air.

5) Each experiment was run for a set period of 30 minutes.

6) Copper sulfide samples were allowed to build up in the concentrate stem and were then routinely removed at 5-minute intervals. The pulp volume was kept

constant by means of addition of the required amount of potassium ethylxanthate solution immediately after removal of the concentrates.

7) The concentrates were washed repeatedly with three percent hydrogen peroxide to remove the oily coating of potassium ethylxanthate formed during the flotation process. They were then washed with distilled water and dried at room temperature.

8) A 114.6mm Gandolfi camera was used for x-ray powder identification of the concentrates (floated material). All the unfloated charges of experiments (F-1/0-3) and (F-2/0-10) were routinely treated in the same manner.

Similar steps were taken in the preparation and in the flotation of unleached copper sulfide and normal covellite. However, as is indicated in appendix II, different quantitites of these samples were used as the initial charges for the flotation experiments.

B2) Discussion

Figures 33 and 34 are the two comparisons of the rate of flotation of examined copper sulfide samples. The x-ray results of the floated portion of sample (F-1/0-3) and (F-2/0-10) showed that the collected concentrates were essentially 100% leached digenite, having x-ray patterns similar to those obtained earlier in the leaching experiments.

However, on comparing the x-ray films obtained from unfloated residues with that of covellite, it was found that these residues were normal covellite. For further confirmation of this result, the unfloated samples were collected, washed, dried and observed under a binocular microscope (40X). The result of these observations were in agreement with the previously observed results of the

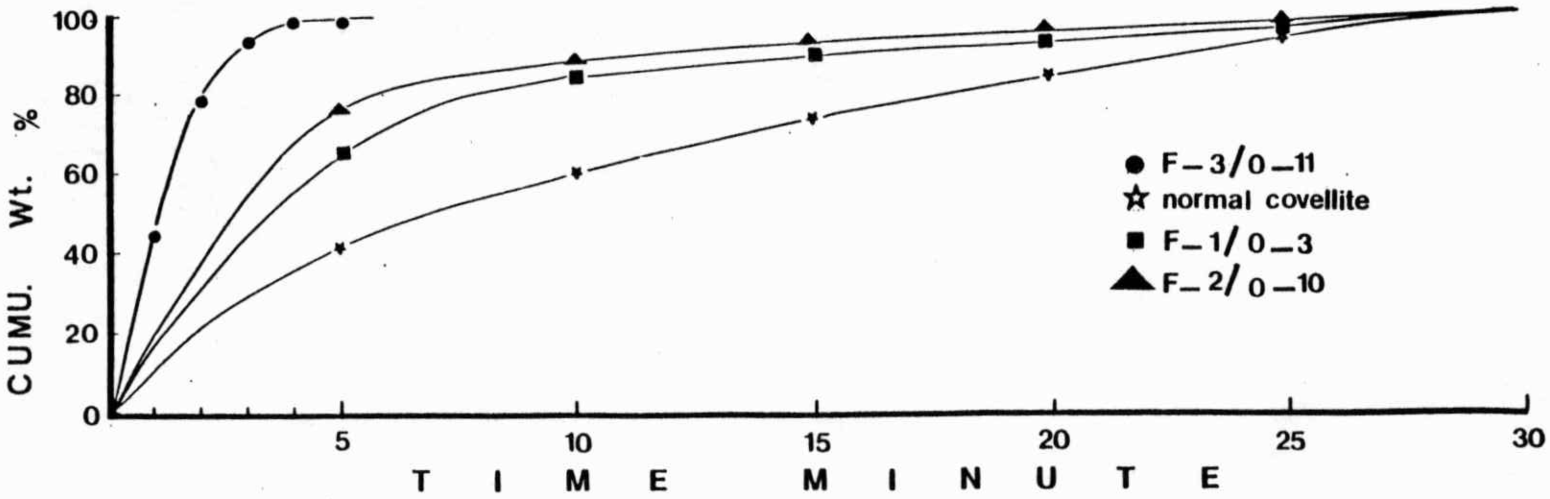


Fig.—33 An overall recovery of Copper Sulfides

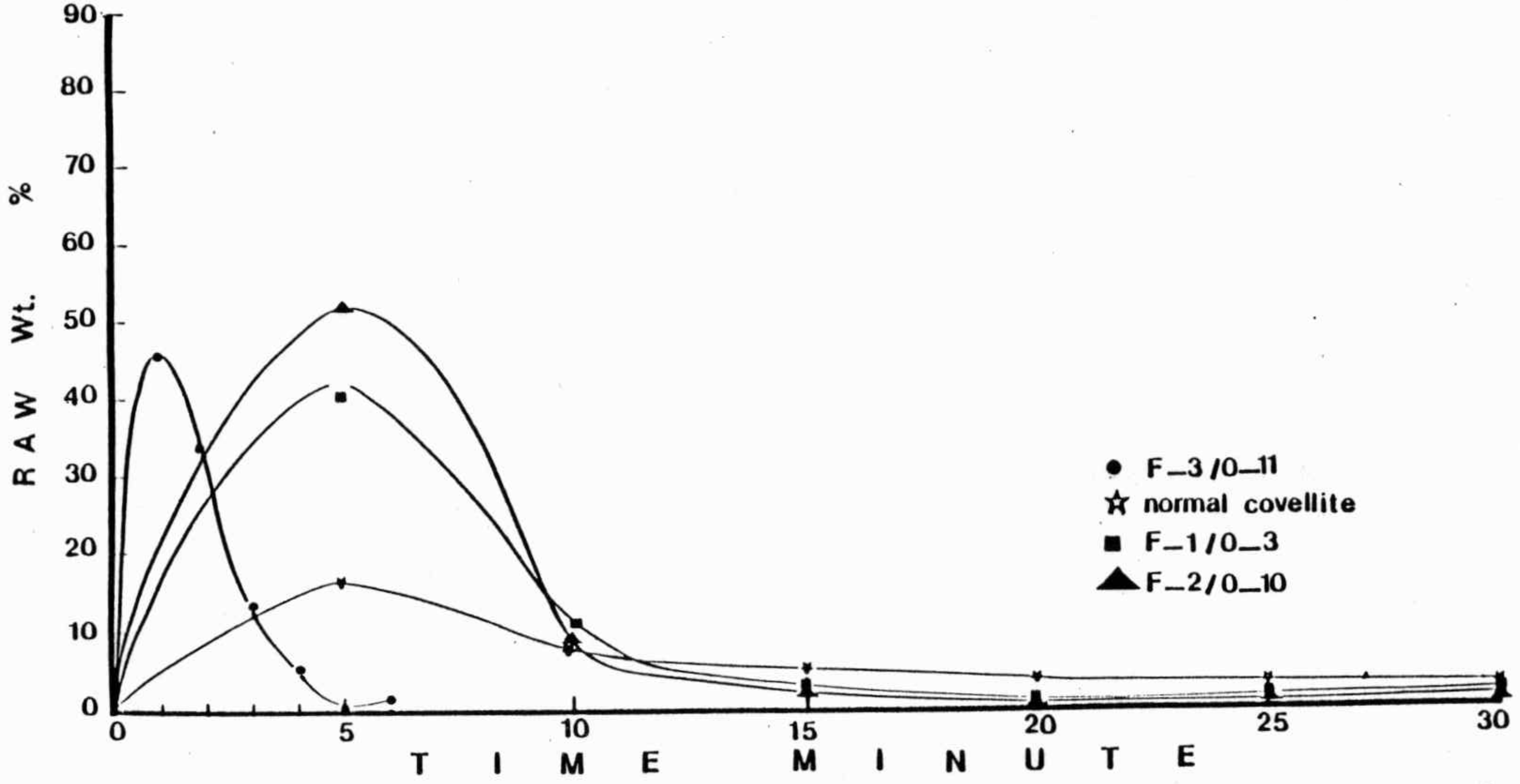


Fig.—34 A total comparison of different copper sulfide compound flotation recovery.

leaching experiments in which all the grains contained the yellow-powdered material. The latter also seemed to be more porous in appearance when they were compared with the floated materials.

Figure 33 shows the relative flotational behavior (cumulative weight percent) of normal covellite, unleached (F-3/0-11), and leached (F-1/0-3) and (F-2/0-10) for similar flotation tests in which the collector was potassium ethylxanthate. It should be noted here that all the cumulative weight percentage calculations are based on the total weights of floated samples which were collected at given intervals (see app. II). However, in the case of the unleached sample (F-3/0-11) in which the entire sample was recovered after a period of 5 minutes, the same calculations are based on the weight of the starting sample. Nevertheless, from the above figure, it is obvious that the unleached sample is by far the most floatable of all. In fact, as is shown by the flotation recovery rate in figure 33, the recovery of unleached copper-sulfide compound levels off at approximately 90%, i.e., the sample is not homogenous in its flotation behavior. This behavior could be accounted for by the co-existence of a minute quantity of normal covellite which is not floatable (Baldwin et al. 1979).

In contrast to the behavior of the unleached sample, the flotation rates for leached samples never reached the completion stage (see figure 33). These rates were reduced and the recovery curves had a totally different shape. Figure 33 also shows that the recoveries of these two leached samples took on a more gradual increase. In other words, even if one considers the flotation of the unleached sample to consist of two separate stages - i.e. 1) fast (where up to 90% recovery takes place), and 2) slow (during which complete recovery is achieved after a period of six minutes), it would still be very difficult if not impossible for one to distinguish these two stages, because of the flotational behaviors illustrated by the comparison of their recovery curves (Figure 33).

In Figure 34 the raw weight percentages flotation recovery have been compared. In this figure the recovery curve of three samples (F-1/0-3), (F-2/0-10) and (F-3/0-11) have approximately the same general shape. The similar convex character of these curves indicates time-dependent increases in the recovery rates of these samples. However, it is clear that the flotation for sample (F-3/0-11) is much greater and, as is shown, the corresponding curve has a narrow region of optimum flotability. On the other hand, those curves that represent the flotation recovery of leached copper sulfides, (F-1/0-3) and (F-2/0-10), have a wider range. This in turn means that the recovery of the samples were initially slow but increased with time. However, the author believes that even though the leached samples are not as flotable as the unleached sampels, they are indeed flotable and their recovery is a gradual one.

Appendix (II) and Figures 33 and 34 represent data and the corresponding rate of recovery of normal Covellite sample. In the author's view, the flotation recovery of Covellite shown in the above figures can be attributed to mainly mechanical entrainments caused by the cell rather than to the true flotation of normal Covellite. Another possible reason for this minute recovery might be the presence of some impurities in the starting Covellite sample. Yet another interesting point was discovered when an x-ray film was prepared of the unfloated residue of sample (F-1/0-3) and was subsequently compared with the Covellite x-ray pattern. It was found that the patterns obtained were identical. This confirms the results of earlier observation of leaching of the $Cu_{1.75}S$ compound;

these observations found Covellite to be the final leached product. When a copper sulfide sample of composition $Cu_{1.75}S$ was treated in acidic media of ferric sulfate solution. The most likely explanation for this lies in the structural and compositional modifications of digenite caused by this treatment. The above observations are also in complete agreement with result of previous studies (e.g. Baldwin et al. 1979). These studies not only found no evidence that Covellite is naturally flotable but discovered futhermore that even the addition of collectors such as xanthate does not necessarily make it particularly floatable.

In general, figures 33 and 34 represent the "flotation recovery of copper sulfides." Based on these figures and the data obtained, it can now be postulated that of these four compounds, "unleached digenite" ($Cu_{1.75}S$) has the best floatability. It is also evident that its recovery levels off at approximately 90%. The "leached digenite" ($Cu_{1.75}S$) sample, having the geerite-like structure, was also found to be floatable. On the other hand, the covellite sample was found to be completely unfloatable and only marginally floatable when subjected to mechanical entrainment.

C) Flotation of Sphalerite

C1) Experimental Sphalerite and Method

Two different samples of zinc sulfide, hand-picked from naturally occurring sphalerite and low in iron content, were selected from the University of Nebraska collection. For the purpose of this report they are designated as (ZnS-A) and (ZnS-B). Sample (A) had a lighter color than sample (B) due to lower iron content. The samples were washed, dried and subsequently ground in a laboratory-size ball mill to give a moderately fine-grained, yellow-light brown powder. The powders were sieved, using a set of Tylor laboratory sieves to obtain the following three sized samples:

1) ZnS (+60 mesh), used for binocular microscopic observations.

2) ZnS (-60/+100 mesh), used for flotation experiments as well as the x-ray powder examinations.

3) ZnS (+100 mesh), a fine powder, yellow to off white color (ZnS-A) and darker yellow (ZnS-B), used for x-ray fluorescent and x-ray powder diffraction purposes.

It is now appropriate to indicate that unless otherwise stated, all the experiments on the two samples of sphalerite in the following sections were conducted under similar conditions.

C2) X-Ray Fluorescent and X-Ray Diffraction Examinations

A fine powder (+100 mesh) of sphalerite was placed in a laboratory ball mill and ground gently to obtain a finer powder (-230/+325 mesh). The purpose of this step in the preparation of the sample was to produce the most homogeneous powder possible and avoid the possible preferred orientations of larger crystals. Upon the completion of this step, two grams of the samples were separately weighed to 0.0001 gram accuracy. They were mixed with one gram of boric acid and shaken for two minutes in an electric shaker. A pellet of these mixtures was then produced by means of a hydraulic press. These pellets were then subjected to x-ray fluorescent analysis.

The remainder of the powdered materials was used to prepare glass slide-type samples for x-ray powder analysis. A quartz standard was also used in x-ray powder diffraction examination for comparison and measurement of the accuracy of each run. The latter experiments were conducted using a Phillips diffractometer and Cu_k as the source of radiation (see figures 35 and 36).

C3) X-Ray Powder Camera Examinations

X-ray powder experiments were carried out on (-60/+100 mesh) sphalerite. A single crystal of each sample was selected and mounted on glass wool, and by using a Gandolfi camera, a set of x-ray film was produced from each sample. A comparison of measured d-spacing with JCDS standard cards and Goble's standard was indicative of pure sphalerite in both ZnS-A and ZnS-B.

C4) Flotation Experiments

The (-65/+100 mesh) segment of crushed sphalerite was washed with three percent hydrogen peroxide solution for a period of 18-24 hours to remove possible oily coatings on the surface. The samples were then washed repeatedly with distilled water and a magnetic stirrer was used as the agitating media for better results. After several periods of washing, the sphalerite samples were dried at room temperature.

The specific surface area of the product has been determined to be $370 Cm^2$/gram by the BTE (Brunauer-Emmet-Teller) technique which uses standard volumetric apparatus with krypton as absorbing gas (Gaudin 1957, Gaudin et al. 1959).

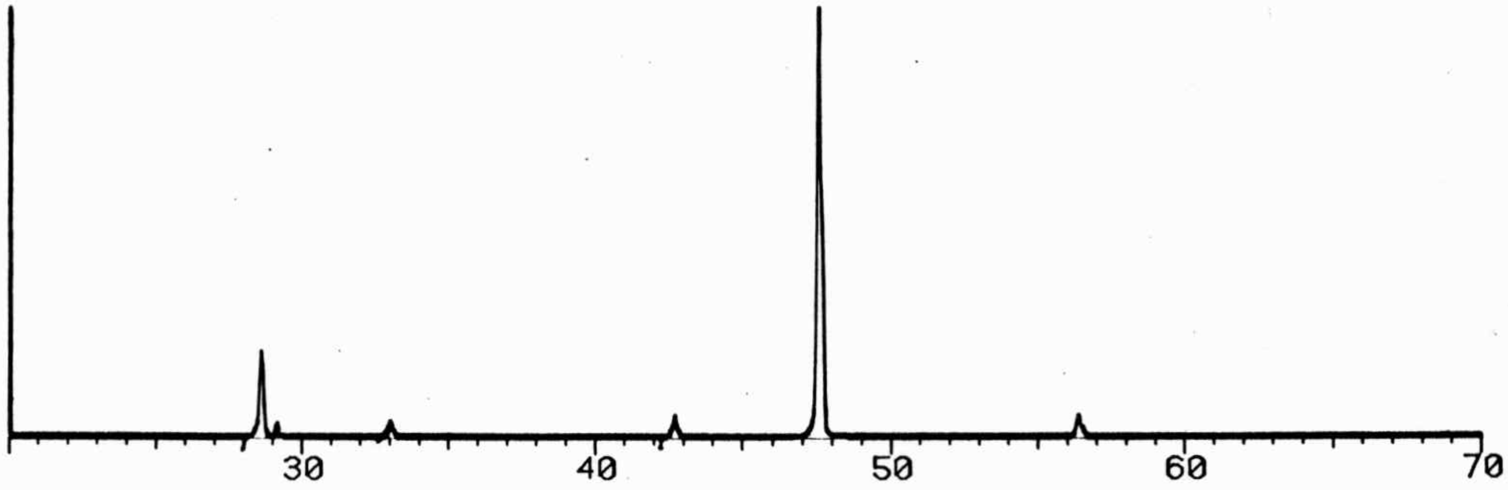


Fig –35 X – RAY DIFFRACTOMETER PATTERN OF SAMPLE ZnS – A.

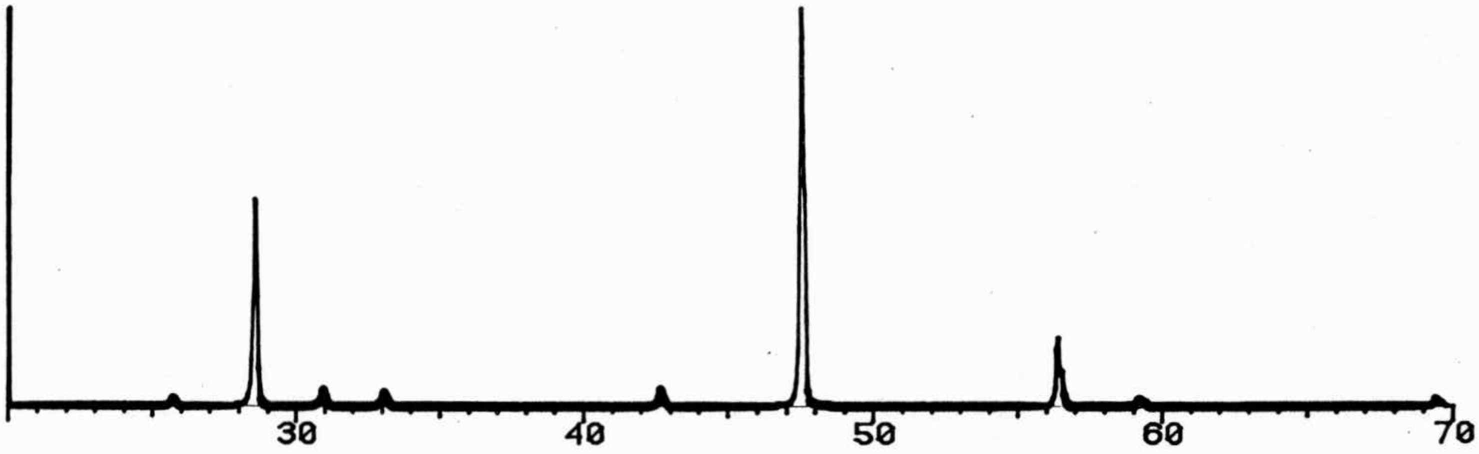


Fig_36 X_RAY DIFFRACTOMETER PATTERN OF SAMPLE ZnS_B.

Throughout the course of this investigation a copper sulfate of fixed concentration of 25 mg copper sulfate per 1000 ml of distilled water was utilized as the only activator. On the other hand, a solution of potassium ethylxanthate with concentration of 100 mg potassium ethylxanthate per liter of distilled water played the role of the collector.

C5) Effect of Copper Salts in Ordinary Tap Water on Sphalerite

For the experiment, 2.0 grams of (65/100 mesh) (ZnS-A) and (ZnS-B) weighed to 0.0001 gram were cleaned in hydrogen peroxide, placed in magnetic stirrer and washed with distilled water. The mixture was agitated in a 250 ml pyrex beaker for periods ranging from 5 to 60 minutes. The mixture was then filtered and the samples dried. The modified Hallimond microflotation cell was utilized for the flotation experiments.

The conditioned samples of sphalerite were placed in the flotation cell and a volume of 150 ml of fresh tap water was added. The materials in the concentrate stem were allowed to build up for 5 minutes and then collected from the stem at 5.0 minute intervals (see appendices III and IV). After the concentrate was collected, it was washed with distilled water, filtered, dried under regular laboratory conditions, and weighed to 0.0001 mg accuracy. The total volume of pulp was kept constant by adding the small volume of tap water required after each removal of concentrate. The volumetric gas flow rate was also kept constant unless otherwise specified.

C6) Effects of Copper Salts in Distilled Water on Sphalerite

After the completion of the experiments investigating the effects of copper salts on the flotation of ZnS in tap water, similar investigations were made using doubly distilled water. For this purpose a second 2.0 gram sample of sphalerite similar to that mentioned in the previous section was weighed and treated in the same manner. Total agitation time, volumetric gas flow, and volume of the pulp were kept constant as mentioned above; hence, the results are comparable.

These results have been compiled in appendices (III) and (IV) and represent flotation of recovery of the different sphalerite samples. Figures 40-42 are the corresponding, comparative graphical representations constructed on the basis of these results. The following discussion with regard to the flotational behavior of unactivated sphalerite in tap and distilled water is primarily based on the above values and diagrams.

1) In distilled and tap water, sphalerite acquires from contaminants (e.g., copper salts, Gaudin 1929) — a coating of copper sulfide having a thickness of a few atomic diameters. Thereafter, it is floatable.

2) It is evident that the distilled water and tap water in use contained copper salts in amounts large enough to affect the floatability of sphalerite.

3) However, the result shows that the floatability of sphalerite increases in tap water experiments. This is attributable to the fact that distilled water contains smaller amounts of dissolved copper salt.

C7) Flotation of Activated Sphalerite

Experiments were conducted in the modified Hallimond tube microflotation cell at room temperature according to the following procedures:

1) A sample of 2.0 grams of (-65/+100 mesh) sphalerite, washed in three percent hydrogen peroxide just prior to each set of tests, was weighed as the flotation sample.

2) The flotation samples were deslimed several times with distilled water.

3) 25 mg of K-ethylxanthate was combined with one liter of distilled water to yield the desired concentration.

4) An activating solution of $CuSO_4 \cdot 5H_2O$ was produced by mixing 25 mg of Cu^{++} and a liter of distilled water in a beaker.

5) The samples were activated for 30 minutes in Cu^{++} solution. After activation, the solution was decanted and the sphalerites conditioned for 5 minutes in potassium ethylxanthate solution.

6) The pulp was transferred to the microflotation cell and floated with compressed air.

The following operating variables can be controlled accurately in this particular type microflotation cell: 1) agitation intensity, 2) flotation time, 3) pulp volume, and 4) volumetric gas flow rate.

C8) Discussion

The sphalerite samples on which the flotation experiments have been conducted were found to be of a pure cubic polytype with low iron content. Both samples had a light yellow color, but sample (Zns-B) was darker in color, perhaps due to higher impurity content. However, when their x-ray powder pattern of the crystals were compared, no detectable differences were obtained. In fact, when

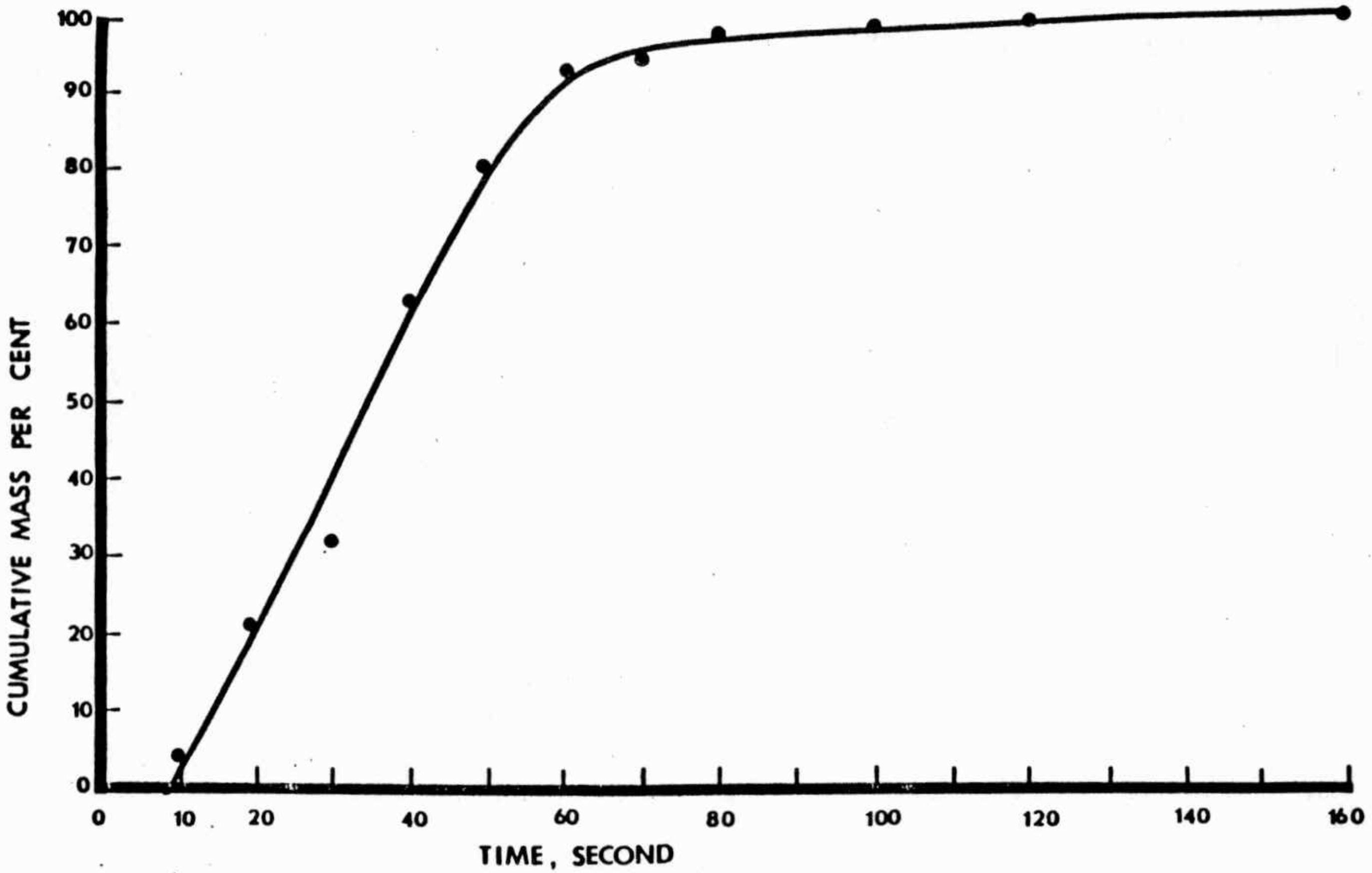


Fig.—37 Flotation recovery of activated ZnS-B

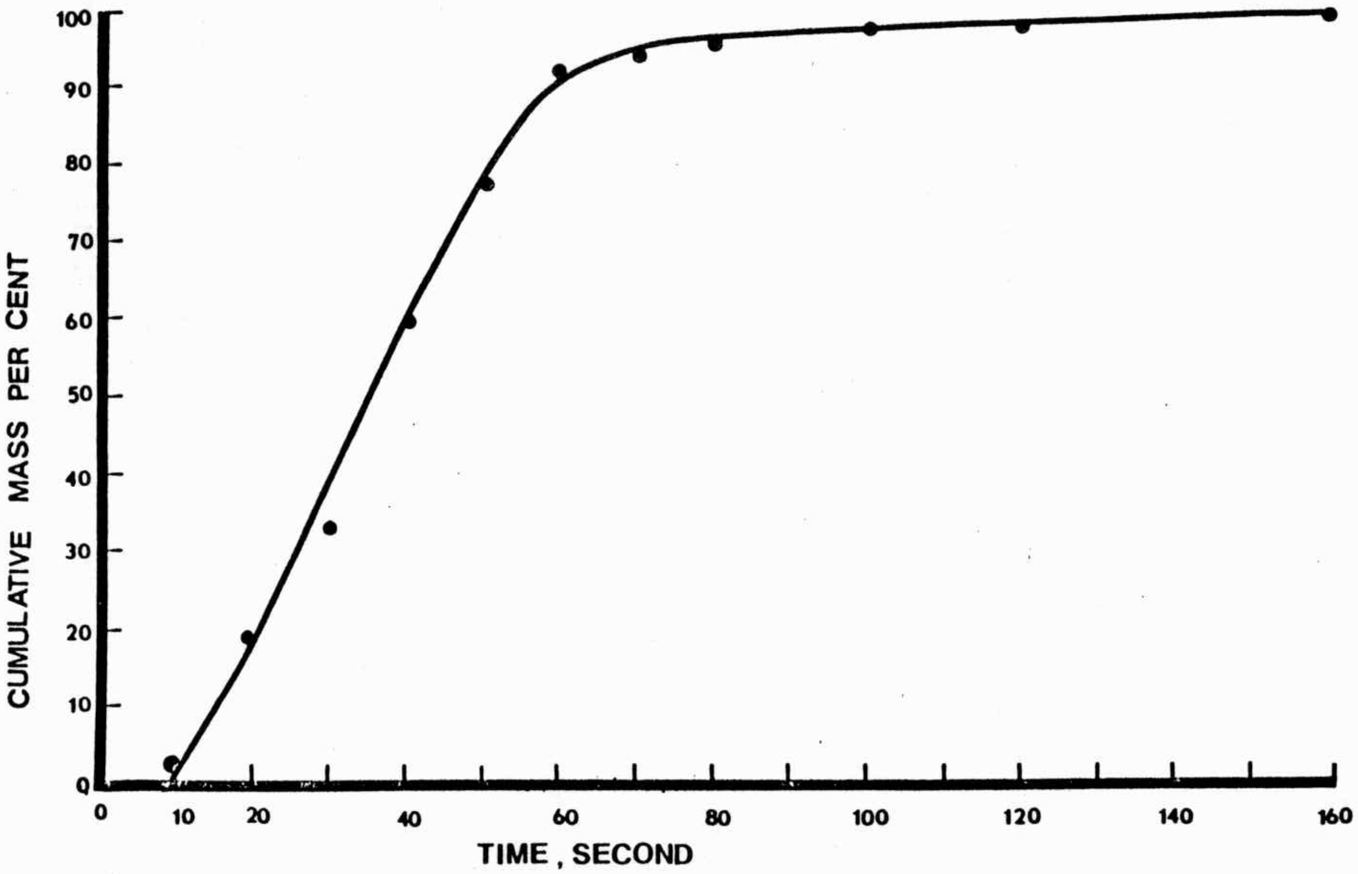


Fig.—38 Flotation recovery of activated ZnS-A

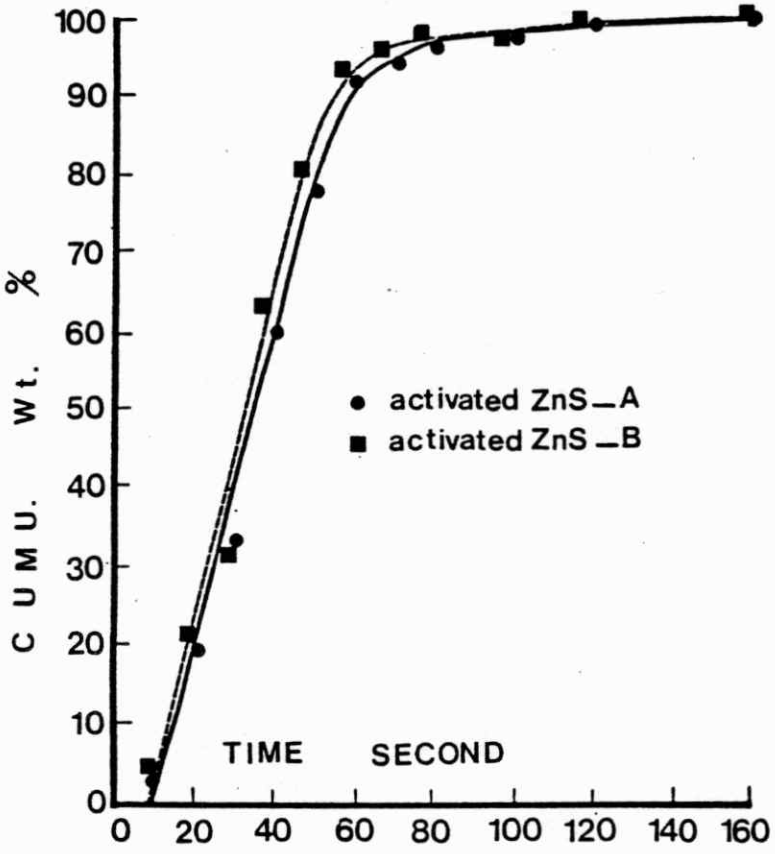


Fig.—39 A comparison of flotation recoveries of ZnS-A and ZnS-B the patterns were measured for d-spacing and their relative intensity, the results of these measurements were in complete agreement with those of JCPDS standard cards.

Three sets of flotation experiments were performed on both of the samples (Zns-A and ZnS-B), the results of which are tabulated in appendices III and IV. Also a set of cumulative and raw weight percent flotation recovery curves of sphalerite was prepared (see figures 37 and 38). Furthermore, figure 39-42 represent several comparisons of these recoveries of the activated and unactivated sphalerites.

It is now again appropriate to recall that all the preparation steps and flotation experiements for both samples were the same, hence, the results are totally comparable. In general, perhaps the most obvious and interesting observation was the effect of the color of the samples. As shown in all the corresponding figures, the sample ZnS-B (darker color) invariably had a higher flotation recovery, thus confirming the previous assumption concerning the higher impurity content of this particular sphalerite sample.

The effect of impurity, either in sample or in the water, was detected when the unactivated sphalerite of both batches was floated with pure, regular tap water. It was found that unactivated sphalerite had some "apparent" flotability (see figures 40 and 41). Baldwin et al. (1979) believe that those minute flotability results are probably mainly due to mechanical entrainment rather than to natural flotability. However, the author believes that some of these flotability behaviors should indeed be considered as being directly related to the composition of the sphalerite samples. Figures 40 and 41 illustrate the flotability of unactivated

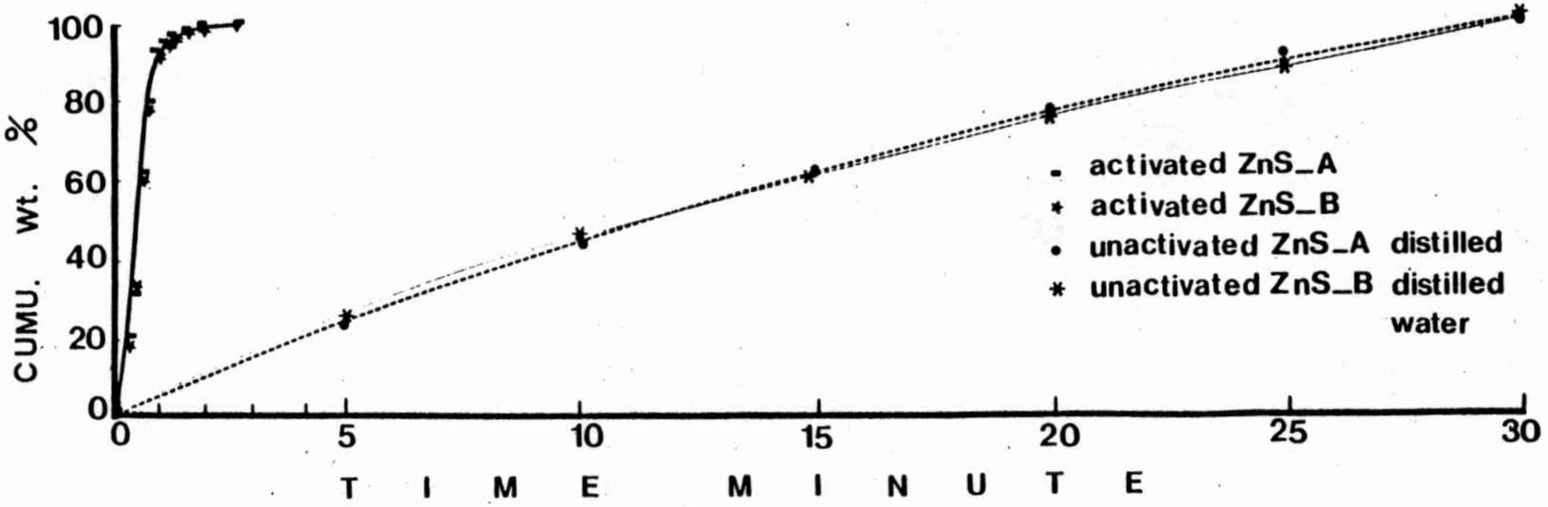


Fig.—40 Comparison of flotation recoveries of sphalerites, activated and unactivated in distilled water.

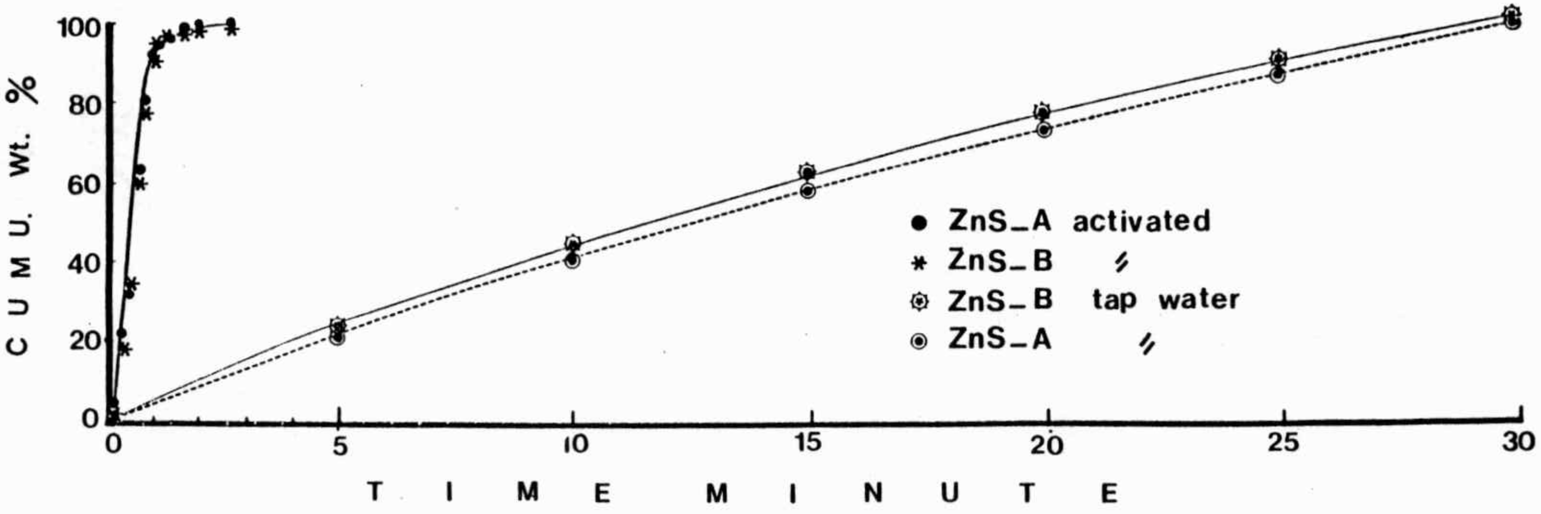


Fig.—4] Comparison of flotation recoveries of sphalerites, activated and unactivated in tap water.

sphalerites from both samples in distilled and tap water. They also compare these behaviors with those of activated sphalerite samples. Figure 42 shows another set of comparisons of the raw percent flotation recovery of all the sphalerites.

As shown in these figures, both samples of sphalerites (ZnS-A and ZnS-B) were somehow floatable. From the same figures it is also evident that the recoveries of two samples of sphalerite were slightly higher in tap water than in distilled water; this is perhaps indicative of a higher concentration of copper ion in tap water.

In view of the evidence obtained from the above observations, the following conclusions appear justified: 1) distilled and tap waters in use contained copper salt in amounts large enough to effect the flotability of sphalerite yet small enough to remain undetected by ordinary analysis, and furthermore, no trace of copper salt content was detected even with the x-ray analysis; and 2) differences in flotation properties of various native sphalerites are probably compositionally dependent in such a way that the darker color sample (ZnS-B) with higher impurity content, i.e. iron or other heavy base-metals, has better flotability and hence, a higher rate of recovery than the light color sphalerite sample (ZnS-A).

In connection with the finding that both distilled water and tap water had to be absolutely free of copper to be used in testing the flotability of sphalerite, it was established that washing the sphalerite sample with 150 ml of tap water increased the flotation recovery of unactivated sphalerite; unfortunately, no analytical measurements were made. However, it is very remarkable from a chemical standpoint that activation of the mineral should follow the presence of such minute amounts of copper salt.

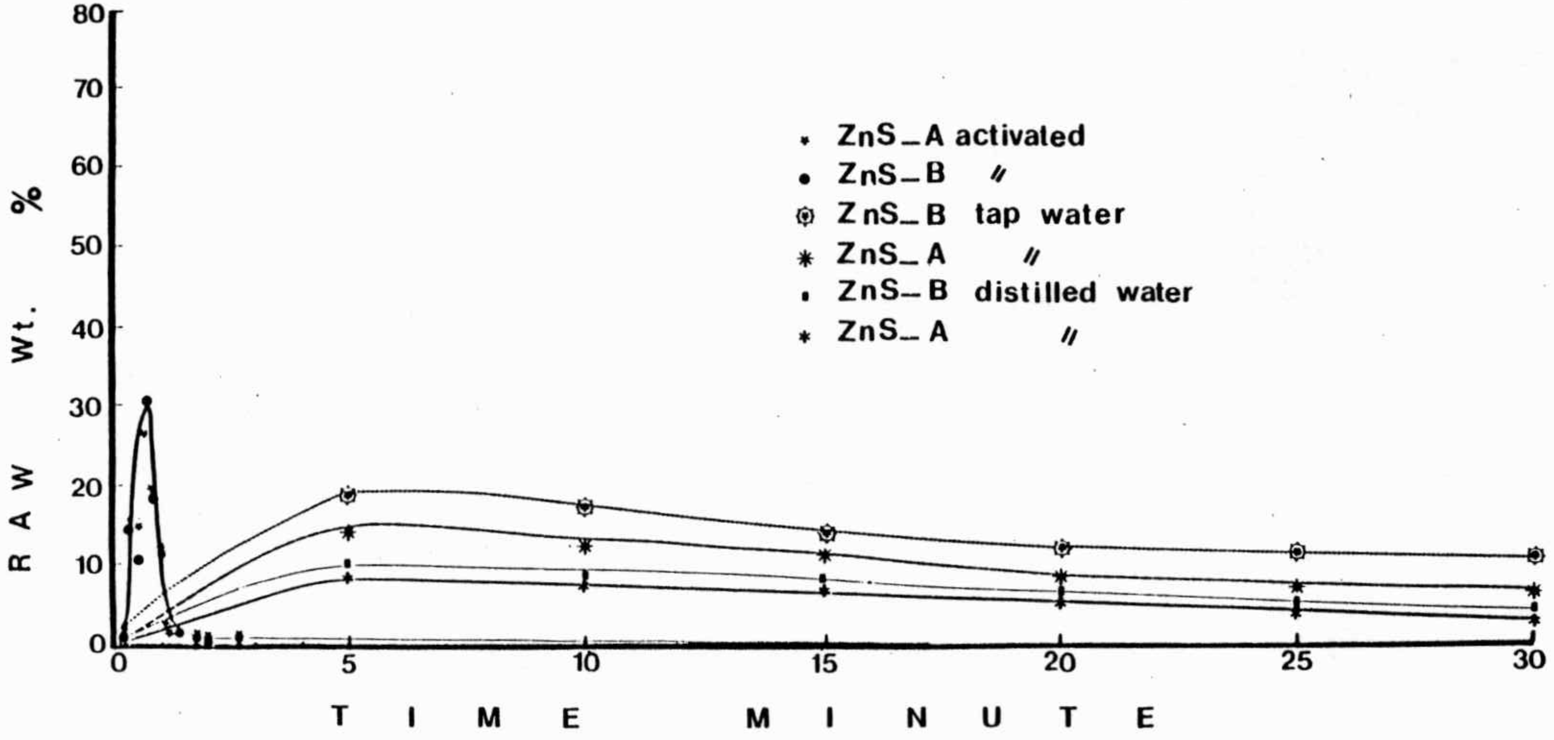


Fig.—42 A raw wt. % comparison of flotation recoveries of sphalerite samples.

Figures 37 and 38 show the complete recoveries of Cu-activated zinc sulfides. In both diagrams it is clear that recoveries level off at approximately 93% or after 60-70 seconds i.e. the sample is not entirely homogeneous in its flotation behavior. A comparison of the two flotation recoveries showed very little differences (see figure 39).

In flotation of activated samples, one general observation that was apparent was that after approximately 85-90% recovery, each rising gas bubble made contact with a progressively smaller amount of mineral and the complete recovery took place after a period of time about two times longer than that required for 85-90% recovery. Again, figures 38, 39, and in particular figure 40 illustrate the recovery an an overall comparison of the activated sphalerite samples. These diagrams show some apparent flotability of unactivated ZnS samples, a phenomenon that has been discussed above. Activation of sphalerites with copper sulfate solution dramatically increases the rate of apparent flotation by bubble attachment. Also, from the same comparative figures, it should be clear that there is a slight difference in the recoveries of activated/unactivated (ZnS-A) and (ZnS-B). It only became apparent as the research progressed that the batches of ZnS-A (light color) samples did indeed, without any exceptions, show a slight reduction in the flotation recovery.

However, it is not clear to the author whether these small differences are due to differences in impurity, (i.e., iron or other heavy metal contamination content of the sphalerite samples), particle size distribution, concentration of defects in the structure of sphalerites, or so on. In any case, the different batches of samples were treated in the same manner.

CHAPTER (VI) - SUMMARY AND CONCLUSIONS

X-ray, microscope and scanning electron microscope data together with numerous photomicrographs and several scanning electron microscope photographs show that the digenite is the most abundant phase obtained in the composition range of $Cu_{1.5}S$ — $Cu_{1.75}S$ during high temperature synthesis. In fact, on the basis of the data in table 4, except for sample CS1, all the products of each experiment were identified after careful study to be mixtures of digenite (Di), blue-remaining covellite (BC) and normal covellite (Cu), with digenite as the major constituent phase.

In the case of sample CS1, even though the optical photomicrographs showed the existence of both normal and blue-remaining covellite, the x-ray powder pattern of the sample suggested that the final synthesized product was anilite. This was supported by a comparison of the result obtained with Goble's anilite pattern and a previously determined digenite pattern. However, the same sample, upon being slightly ground in a laboratory ball mill, produced a pattern which matched that of digenite. This result confirms the observation of Morimoto et al. (1969) that anilite usually changes to a mixture of digenite, covellite and perhaps blue-remaining covellite upon grinding. The results of the synthesis experiments on this investigation also confirm and extend the observations of Roseboom (1966) and Yund & Kullerud (1966), who reported the presence of anilite and digenite in all mixtures based on the superstructure reflection of both phases.

In leaching, it was found that synthetic copper sulfide samples of the composition $Cu_{1.75}S$ can be leached in acidic media of natural ferric sulfate solution. The author believes that in the leaching process, the copper sulfides are converted into the soluble sulfate simultaneously with the dissolution of copper ions and the reduction of ferric ions to ferrous ions.

The effects of different factors upon the leaching of these copper sulfides have been studied for the effect of particle size upon the rate of dissolution of grains. Similar sized samples (0.5X0.3X0.2mm), (0.1X0.1X0.1mm) and (0.05X0.05X0.1mm) produced nearly the same result in dilute solution of $1.0X10^{-5}$ molarity when they were treated only for short periods of time (17 and 25 hours, and 7 days). However, as the leaching period increased, the finer particles had a faster rate of dissolution.

The rate of dissolution of synthetic copper sulfides was discovered to be practically independent of the strength of the acidic solution for the first twelve hours of leaching in $1.0X10^{-2}$M ferric sulfate solution. After this period x-ray examinations revealed that the structure had begun to change. Additional structural modifications were detected after periods of twenty-four and thirty-six hours. This result confirms the previous observations of R. J. Goble (1981) and C. Harlem and L. Whiteside (Personal Communication) in which they detected complete structural change after a period of twelve hours when they leached almost identical sized samples of natural digenite/anilite in $1.0X10^{-3}$M ferric sulfate solution. There is, however, one significant difference between their results with natural grains and more dilute solution and the results from this investigation using pure synthetic $Cu_{1.75}S$. They used natural specimens instead of synthetic samples throughout their leaching experiments; these are highly probable to have contained some impurities, e.g., those copper sulfide compounds whose structures are already similar to those of the leached materials. This difference probably makes it clear the need to study pure synthetic sample in parallel with natural minerals in order to separate the structural effects due to the lattice of the host mineral (anilite or digenite) from those due to that of the impurities (those materials with structure similar to leached samples).

The experiments on the effect of particle size showed that the fine-sized grains had faster rates of dissolution. When larger grains were leached in $1.0X10^{-5}$ M solution even up to a period of 50 days, they did not disintegrate but almost retained their original outline. Apparently, the sulfur left behind retained the original form of the mineral particles.

The effect of the concentration of ferric sulfate on leaching was also determined. X-ray examination of the final leached leach product, placed in $1.0X10^{-1}$M and $1.0X10^{-2}$M and $1.0X10^{-3}$M solution for periods of 17 and 96 hours and 17 days, respectively, showed complete changes in structure. It appeared that the final x-ray patterns resembled those of sphalerite. However, due to broadening and extreme diffusion no measurement of the reflection lines were made. X-ray films also show that the patterns obtained from leached samples resemble to some degree those of Goble's $Cu_{1.12}S$ standard pattern. Furthermore, it has now been confirmed, through different experiments using a precession camera method on a mineral with x-ray pattern similar to that of leached digenite that one particular reflection has the ideal structural composition of mineral geerite (Goble 1980). This reflection, according to Goble (1980), is that of the copper compound which belongs to group (1) of the copper sulfides where the ratio of Cu:S is the lowest with the structure nevertheless retaining cubic close-packing of sulfur atoms.

Flotation data on recovery rates of floated copper sulfide compounds are listed in the appendices II and also have been shown by two comparative diagrams (see figure 43 and 44). It is clear that the recovery of the unleached digenite sample (F-1/0-3) is the only one which reaches completion; this recovery is completed after a period of 6 minutes. At approximately 90% recovery the curve levels off, indicating some degree of variability in the flotation of the sample. It is not perfectly clear whether this flotation behavior is due to possible impurities, particle size, mechanical entrainment, etc.

From the author's point of view, this peculiar flotation behavior is primarily caused by the presence of non-floatable, co-existing phases, i.e., covellite, which is not floatable and which even with the addition of xanthate collectors does not become particularly floatable (Baldwin 1979). This finding is completely in accordance with the study detailed in previous chapters on the synthesis of copper sulfides. In that study, through optical observation under reflected light, normal covellite and blaubleibender covellite were almost invariably found to be present as separate phases. It is highly suggestive that even though covellite existed in such minute quantitites that it was not detectable by x-ray powder examination, its quantity was large enough to produce such obvious variability in the flotation behavior of the synthetic sample.

In contrast, leached samples behaved in such a way that they never reached the completion stage. The curves of recovery of the leached samples (F-2/0-10) and (F-3/0-11) have somewhat different shapes. These curves, when compared with those of the unleached sample (F-1/0-3) show a more gradual and uniform behavior. Recovery of unleached copper sulfide appears to take place via two separate and distinguishable stages. The first stage involves recoveries of up to 90% of the sample. The second stage, during which complete recovery is apparently achieved after 6 minutes, also takes place at a slower rate. Again, it should be clear to one that the recovery curves of the leached samples essentially represent the similar general characteristic of a faster rate being followed by a slower one.

Considering both the data obtained from flotations of all the copper sulfide compounds and the nature of the curves representing these results, the previous assumption concerning the flotational behavior of these copper compounds is confirmed. It is noteworthy that the similar convex character of these curves indicate increases in recovery rates which are time-dependent. Again, it must be clear that the flotation rates of sample (F-3/0-11) is much greater and as shown, the corresponding curves have a narrow region of optimum floatability. The results for unleached samples is noteworthy since they have wider ranges which fall nicely into place indicating the relative abundance of nonfloatable mineral constituents such as covellite. If this is the case, then the result is completely in line with the previous x-ray examination of the residue of the leached samples in which covellite was found to be the only existing phase. Here, the most likely explanation to consider is the structural and compositional modifications of the starting material (digenite) caused by the treatment in ferric sulfate solution.

Two different batches of sphalerite samples (ZnS-A and ZnS-B) were used for the purpose of examining the activated and unactivated sphalerite in different medias. The flotation of zinc sulfides was also brought about in the same manner

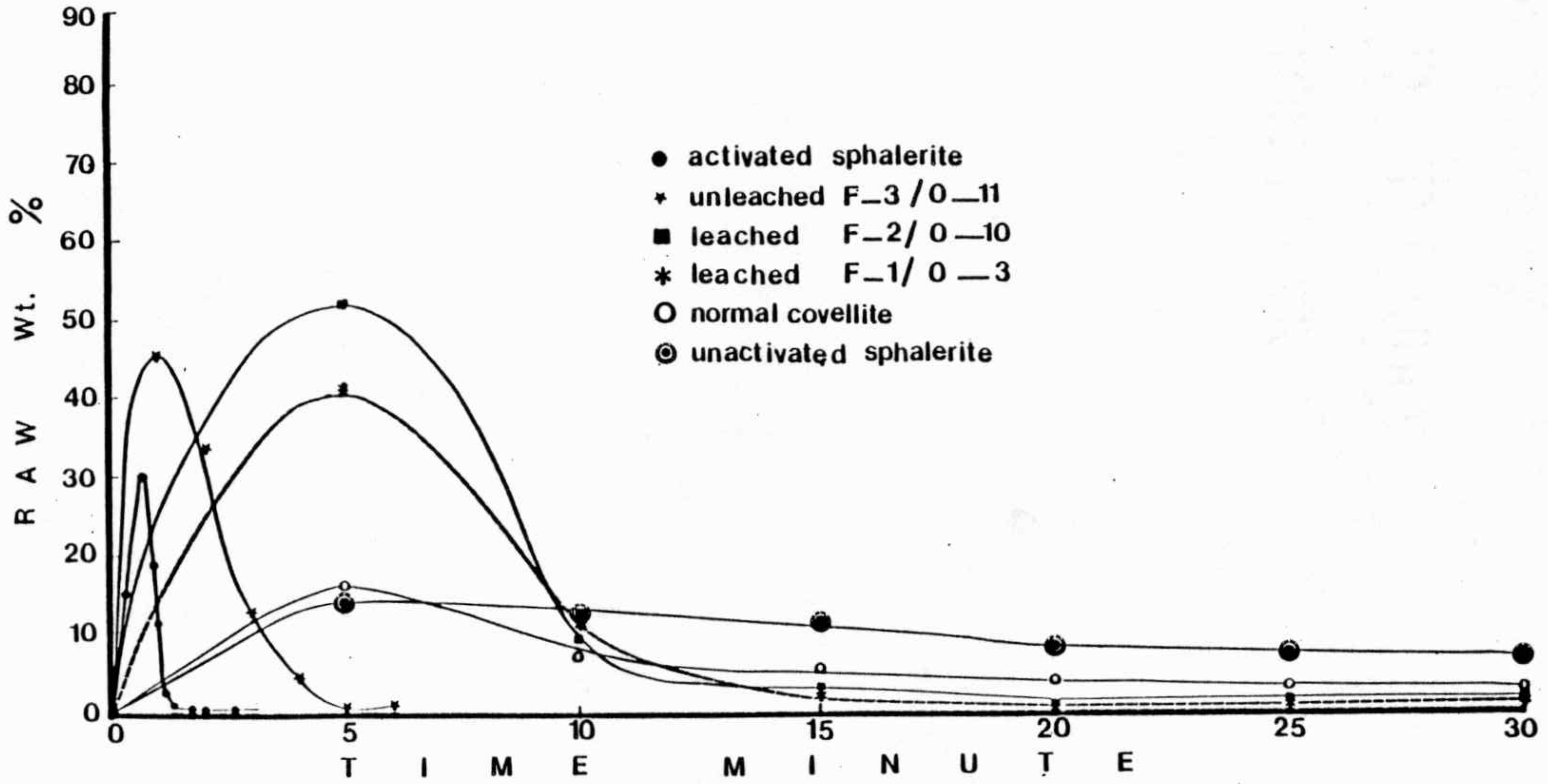


Fig.—43 A comparison of raw wt. % flotation recovery of the examined compounds.

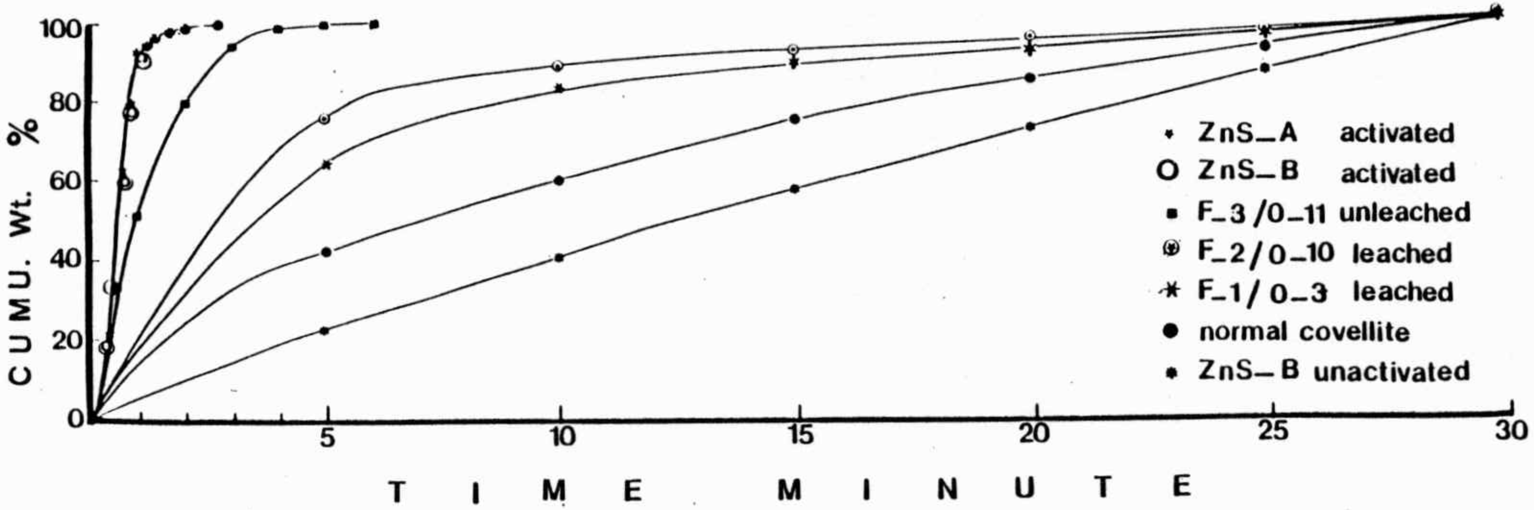


Fig.—44 A comparison of cumulative wt. % flotation recovery of the examined compounds.

as that of synthetic copper sulfides. A set of x-ray examinations was conducted on the sphalerite samples. A subsequent comparison of the obtained results with those of JCPDS standard cards showed that ZnS samples were cubic. However, as the research progressed, the two samples of sphalerite did indeed show differences in flotational behavior.

Sample ZnS-A appears light yellow, while sample ZnS-B possesses a darker yellow to brownish color. This is interpreted to be due to higher impurity contents of sample ZnS-B. Whether the impurities are hydrophilic or hydrophobic has an important impact on the flotational behavior of sphalerite samples, this is shown in figures 43 and 44.

It is noteworthy that the result of the above x-ray examinations of the samples also show entirely similar patterns. In other words, even though ZnS-B contains larger quantities of impurities, these are not large enough to produce differences detectable by x-ray powder examinations. No further systematic study concerning the precise chemical analysis of sphalerite samples was made. However, the greatest variations were easily detected, and invariably, of all the examined media, sample ZnS-B showed the highest rates of recovery. Perhaps these higher rates of recovery in the flotation of ZnS-B were caused by those impurities whose surface were already hydrophilic or were modified by conditioning in such a way to produce hydrophilic layers of insoluble materials on the surface of sphalerite.

The results of the recoveries of unactivated sphalerite samples in regular tap and distilled water make it clear that both samples are more readily floatable in the presence of tap water; this is interpreted as the result of higher percentages of tap water contaminants. Again, both samples are naturally floatable in distilled water. It thus becomes clear that the unactivated sphalerite has some "apparent" floatability.

It has been suggested (Baldwin et al. 1979), that these minute floatabilities are probably mainly due to mechanical entrainment rather than the natural floatability. However, the author believes that some of these floatabilities should indeed be considered as being directly related to the composition of the sphalerite samples.

After exposure of sphalerite samples in both tap and distilled water, it was discovered that both samples are somewhat floatable (see appendices III and IV). It should be clear that flotation in regular tap water led to higher rates of recoveries than exposure in distilled water. This observation can be interpreted as confirming the presence of a higher content of these contaminations, e.g., copper iron contents in tap water, the former acting as activators for sphalerite grains during the course of flotation.

In view of the evidence obtained from these observations and considering the earlier discussion on the composition of sphalerite samples, the following conclusions appear justified:

1) Distilled and tap water in use contained copper salt in amounts large enough to effect the floatability of sphalerites yet small enough to remain undetected by ordinary analysis (e.g., even an x-ray examination showed no trace of copper salt content).

2) Differences in flotation properties of various native sphalerites are perhaps directly related to the composition of the samples used. In the present

investigation, these differences were reflected by the differences of the color of the sphalerites in the following way: the sample with a darker color (ZnS-B), having presumably higher impurity contents, i.e., iron or any heavy base-metal, had better floatability and hence higher rates of recovery than the sample with lighter color (ZnS-A).

In connection with the finding that both distilled water and tap water had to be absolutely free of copper salts to be used in testing the floatability of sphalerites, it was established that washing sphalerite samples with 500 ml of tap water increased the rate of recovery of unactivated sphalerites; unfortunately, no further analytical measurement and x-ray examinations were conducted. However, that concentration of the mineral should follow the addition of such a minute amount of copper salt is highly remarkable from a chemical standpoint.

Prior to the flotation of activated sphalerite, several attempts were made to observe the results of the treatment of sphalerites in dilute copper sulfate solution. Even though no systematic procedure was pursued, the net results were in complete agreement with the work of previous investigators. After exposure of a sphalerite sample (ZnS-A) in a dilute copper sulfate solution $(\frac{25\text{ mg}}{1000\text{ ml}})$ for different lengths of time (5 minutes, 1 hour and 24 hours), the following observations were made which were also in complete agreement with those of earlier attempts.

First, it was found that, invariably, the color of all three samples had changed, in such an extent that they now could be very easily distingusihed from the unconditioned (uncoated) sphalerites. Secondly, an overall comparison of the coated samples made it apparent that the shorter the exposure time, the lighter the sample appeared to be. In other words, that sample which was treated only for five minutes had the lightest color. Furthermore, these color variations progressively increased with time to a point where the sample with 24 hours exposure time showed the darkest color. Several other similar results concerning the above observations have been achieved by large numbers of investigators. In fact, the action of copper sulfate on sphalerite has been reported as far back as 1911 by Rogers, who found a thin blue coating on sphalerite upon prolonged treatment of sphalerite in a hot copper sulfate solution. The results of the treatment of copper sulfate are also in complete agreement with those of Gaudin et al. (1959). He made several attempts to measure the rate of uptake of copper ion by sphalerite. Removal of an amount of copper sufficient to form a thin monolayer (which appears as a slight color change) takes place rapidly, but that a considerable increase in the time of contact is necessary to bring about a substantial thickening of coating.

The flotation experiment on the activated sphalerite samples (ZnS-A and ZnS-B) shows that the rate of recovery of the sample designated as ZnS-B again demonstrates higher flotation rates. This is in agreement with the previous observation, concerning the exposure and flotation of the same samples in regular and distilled water. As mentioned earlier, in the author's view, the overriding explanation for this behavior is that it is directly related to the higher concentration of impurities in sample ZnS-B.

Cu-activated sphalerite samples show complete recovery. It is clear that at approximately 93% recovery (which requires nearly 60-70 seconds), the recovery curves level off. In other words, the sphalerite samples also show some degree of variability in their flotation behaviors. It is noteworthy to recall that similar behavior was also previously observed in the flotation of unactivated copper sulfide. A comparison of the rate of recovery of both activated sphalerite samples and unleached digenite samples shows similar characteristics of flotation behavior.

Similar to unleached copper sulfide (F-3/0-11), the activated sphalerite also appeared to be floated via two separate stages. The first stage, which involves chemisorption of xanthate collectors, also takes place at a fast rate, while the second stage apparently involves the absorption of bulk-precipitated zinc xanthate on the hydrocarbon chains of previously absorbed xanthate species.

In studying flotation of the activated sphalerite sample, another behavior was also discovered. After approximately 85-90% recovery, each rising gas bubble made contact with progressively smaller amounts of mineral and the time required for complete recovery was about two times longer than that required for 85-90% recovery.

Finally, an overall comparison of all the floated samples show some apparent floatability for all unactivated sphalerite samples. Similar behavior was also observed in the flotation of natural covellite. These behaviors were interpreted to be functions of the amount of impurities, particle size, etc., as well as mechanical entrainments. The leached samples (F-1/0-3) and (F-2/0-10) were found to be floatable even though their flotation never reached completion. This was found to be directly caused by the presence of nonfloatable grains of covellite which were produced as a result of the leaching of synthetic copper sulfides in concentrated ferric sulfate solution. This presence was confirmed by x-ray powder examinations on the unfloated residue.

Furthermore, this finding is in complete agreement with that of Baldwin et al. (1979) who also found that covellite is not naturally floatable. The activation of sphalerite with copper sulfate solutions was found to dramatically increase the rate of apparent flotation with bubble attachment. In flotation, activated sphalerite samples appeared to be the most floatable, they were followed by unleached synthetic copper sulfides (F-3/0-11), leached copper sulfides (F-2/0-10), F-1/0-3), unactivated sphalerites and finally normal covellite.

The final products of all the synthesis experiments were identified as digenite or anilite together with covellite and blue-remaining covellite. In other words, the first phase of this investigation, an attempt to produce synthetic geerite directly from its elemental constituents, was not successful. There are two possible reasons for this failure, rapid oxidation of the final synthetic copper sulfide or the instability of geerite as a copper sulfide under the experimental conditions. However, the geerite structure was synthesized by leaching of synthetic digenite or acidic ferric sulfate solution.

In flotation with dilute potassium ethyl xanthate as a collector, leached synthetic copper sulfide with the geerite structure was found to be floatable. Using the same collecting agent under similar conditions, unleached synthetic digenite showed a more pronounced floatability whereas normal covellite was found to be totally nonfloatable. Unactivated sphalerite, in two separate experiments, showed some apparent floatabilities in both regular tap and distilled water. However, the floatability of sphalerite was greatly increased upon activation of samples in dilute copper sulfate solution.

Baldwin, et al. (1979) observed, in three separate experiments, a Cu:Zn ratios of 1.00, 1.00, and 0.94, corresponding to the final state of copper uptake by sphalerite. This corresponds to a stochiometric ratio of 1.00:1.00 replacement of Zn(99) in ZnS by Cu(II) from solution. However, the investigators were unable to determine the structure of this copper sulfide layer. Although this stochiometric replacement of Zn by Cu suggests the formation of a layer of covellite, the properties of activated sphalerite are not infact those shown by bulk normal covellite. Covellite show reflection pleochroism, appearing orange-red when immersed in oil. Sphalerite activated with one monolayer of copper sulfide does not display this pleochroism and retains its blue color upon immersion in oil. Furthermore as noted above covellite is not naturally floatable. Also in the flotation of leached copper sulfide, x-ray patterns of the unfloated residues were identical to those of normal covellite. Thus it seems unlikely that the sphalerite coating is covellite.

Even though leached and unleached digenite (the two other possible copper sulfide) showed obvious floatabilities, the latter appears to be an unlikely coating material, because of reported compositional ranges of $Cu_{1.65}S$ - $Cu_{1.79}S$ at room temperature (RaSeboome 1966). However, the compositional limits of leahed digenite are wider, (Goble 1981). Upon leaching of digenite in ferric sulfate solution. There is a structural change from digenite to geerite, with the material retaining geerite structure until the composition approaches that of covellite (Goble 1981). Therefore on the basis of composition it seems unlikely that the sphalerite coating is digenite. Material having geerite the geerite structure however, have the observered composition.

It seems clear that of the three possible copper sulfide (covellite, digenite and leached digenite) only material with the geerite structure satisfies all the above factors, optical properties, flotational behavior and compositional range. We must therefore conclude that the coating produced on sphalerite during activation with copper sulfate is material having the geerite structure. However, in as much as geerite has a composition of $Cu_{1.60}S$ it is unlikely that the material is geerite itself. Instead, it is a material form of Cu-S with a structure similar to that of geerite.

REFERENCES

Adams, N. K. (1941): The Physics and Chemistry of Surfaces. University Press, London, England.

Baldwin, D. A., Manton, J. M., Pratt, J. M. & Story, M. J. (1979): Studies on the Flotation of Sulfides. (I) The effect of Cu (II) ions on the flotation of zinc sulfides. Int. J. Min. Proc. 6, 173-192.

Berry, L. G. (1954): The Crystal Structure of Covellite, CuS and klockmantite, CuSe. Am. Mineral. 39, 1540-1546.

_______ & Mason, B. (1959): Mineralogy Concepts, Descriptions, Determinations. W. H. Freeman, San Francisco.

_______ & Thompson, R. M. (1962): X-ray powder data for ore minerals. In, The Peacock Atlas, Geol. Soc. Am., New York.

Brunauer, S., Emmett, P. H. & Teller, E. (1938): Absorption of gases in monomolecular layers. J. Am. Chem. Soc. 60, 309-319.

Bushell, C. H., Krauss, G. J. & Brown, G. (1961): Some reason for selectivity in copper activation of minerals. Can. Min. Metal. Bull. 54, 177-184.

Clifford, K. L. (1971): Mechanism of Flotation of Natural Sphalerite with Xanthates. Ph.D. Thesis, University of Utah.

Clifford, R. K., Purdy, K. C. & Miller, J. D. (1961): Characterization of sulfide mineral surfaces in froth flotation system using ESCH. App. of Int. Pheno. in Flotation Research, A.I.Ch.E., New York.

Cook, S. R. B. (1950): "Flotation". In Advances of Collidal Science. 3, 357-374.

Djurle, S. (1958): An x-ray study on the system CuS. Acta. Chem. Scan. 12, 1415-1426.

Donnay, G., Donnay, J. D. H. & Kullerud, G. (1958): Crystal and twin structure of digenite, Cu_9S_5. Am. Mineral. 43, 228-242.

Frost, D. C., Ishitani, A. E. McDowell, C.A. (1972): X-ray photoelectron spectroscopy of copper compounds. Molec. Phy. 24, No. 4, 861-877.

Fuerstenau, M. C., Clifford, K. L. & Kuln, M. C. (1974): The role of zinc xanthate precipitation in sphalerite flotation. Int. J. Min. Proc. 1, 307-318.

Fuerstenau, D. W., Metzger, P. H., and Seele, G. D. (1957): How to use this modified Hallimond tube for better flotation. Eng. Min. J. 158, 93-95.

Gaudin, A. M. (1929): Effect of xanthates, copper sulfate and cynides on flotation of sphalerite. Trans. Am. Inst. Min. Eng. 87, 417-428.

_______ (1939): Principle of Mineral Dressing. 1st ed., McGraw-Hill Book Co., New York.

_______ (1940): Mineral concentration by oil adhesion. In XV Century, Eng. Min. J. 141, 43-44.

_______ (1957): Flotation. 2nd ed. McGraw-Hill Book Co., New York.

_______ Fuerstenau & Mao, G. W. (1959): Activation and deactivation studies with Copper on sphalerite. Min. Eng. 11, 430-436.

Goble, R. J. (1980): Copper Sulfides from Alberta: Yarrowite Cu_9S_8 and Spionkopite $Cu_{39}S_{28}$ Can. Min. 18, 511-518.

_______ (1981): Leaching of Copper from anilite and production of a metastable sulfide structure. Can. Min. 19, 583-591.

Goble, R. J. & Robinson, G. (1980): Geerite $Cu_{1.6}S$. A new copper sulfide from Dekalb, Township, St. Lawrence County, New York. Can. Min. 18, 519-523.

Jellinek, F. (1968): "Sulfides", In Inorganic Sulfur Chemistry. G. Nickless, ed. Elsevier Publishing Co. London.

Leja, J. (1982): Surface Chemistry of Froth Flotation. Plenum Press, New York.

Maust, E. E. & Richardson, P. E. (1975): Electro Physical Consideration of the Activation of Sphalerite for Flotation. U.S. Bureau of Mines, Report of Investigation 8108.

Moh, G. H. (1964): Blaubleibender Covellite, Carnegie Inst. of Washington Year Book 63, 208-209.

_______ & Taylor, L. A. (1974): Laboratory techniques in experimental sulfide petralogy. Neuse Jahrb. Mineral. Mortsh., 450-459.

Morimoto, N. & Kullerud, G. (1963): Polymorphism in digenite. Am. Mineral. 48, 110-123.

_______ Koto, K., Shimozaki, K. & Yoshiki, K. (1969): Anilite Cu_7S_4 a new mineral. Am. Mineral. 54, 1256-1268.

_______ & Kotork. (1970): Phase relations of the CuS system at low temperature -stability of anilite. Am. Mineral. 55, 106-177.

Ralston, O. C. & Hunter, Wm. Cu. (1930): Activation of sphalerite for flotation. Trans. Am. Inst. Ming. Eng. 87, 401-416.

_______ King, C. R. & Tartaron, F. N. (1930): Copper sulfate as flotation activator for sphalerite. Trans. Am. Inst. Min. Eng. 87, 389-400.

Ralston, J. & Healy, T. W. (1980): Activation of zinc sulfide with Cu(II) and Pb(II): (I) Activation in weakly acidic media. Int. J. Min. Proc. 7, 175-201.

_______ & Healy, T. W. (1980): Activation of zinc sulfide with Cu (II) and Pb (II): (II) Activation in natural and weakly alkaline media. Int. J. Min. Proc. 7, 203-217.

Rogers, A. F. (1911): Quoted in Clark's data of geochemistry, 5th ed. Columbia School of Mines Quarterly Bull. 770, No. 32.

Roseboom, E. H. (1966): An investigation of the system CuS and some natural copper sulfides between 25°C and 700°C. Econ. Geol. 61, 641-672.

Pomianowaskii, A., Szczpa, J. Poling, G. W. & Leja, J. (1975): Influence of iron content in sphalerite — marmatite on copper ion activation in flotation. Paper presented at the 11th Int. Min. Proc. Cong. Cagliari.

Potter, R. W. & Evans, H. T. (1976): Definitive x-ray powder data for covellite, anilite and chalcocite. U.S.G.S. J. Res. 4, No. 2, 205-212.

Sato, R. (1957): "Electron Diffraction Investigation of Activation." Proceedings, International Congress on SurFace Activity, 2nd, London, V. 3, 349-353.

Shevy, R. T. (1975): Semiconducting Ore Minerals. Elsevier, Amsterdam.

Story, M. J. & Pratt, J. M. (1982): Test for relative importance of structural and electronic changes in determining the flotability of zinc sulfide. South African J. Chem. 4, 35.

Sullivan, J. D. & Sweet, A. J. (1929): factors governing removal of soluble copper from leached ores. U.S. Bureau of Mines. Tech. Paper 453.

_______ (1929): Chemistry of leaching of chalcocite, U.S. Bureau of Mines, Tech. Paper 473.

_______ (1930): Chemistry of leaching of covellite. U.S. Bureau of Mines, Tech. Paper 487.

Sutherland, K. L. & Wark, I. W. (1955): "Principle of Flotation." Australasian Institute of Mining and Metallurgy, Melbourn, 55 P.

Swanson, H. F. , Fuyat, R. K. & Ugrinic, G. M. (1955): Standard x-ray diffraction powder patterns. Nat. Bur. Stand. Circ. 4, 13-14.

Taggert, A. F., Taylor, T. C. & Knoll, A. F. (1930): Chemical reactions in flotation. Am. Inst. Min. Metall. Eng. 87, 217.

_______ (1945): Hand Book of Mineral Dressing, 2nd ed. John Wiley & Sons Inc. New York.

Toshiaki, Y. (1961): Experimental study of absorbtion and desorption of xanthat by sphalerite. Trans. Inst. Min. Metall. 652, 329-353.

Wark,I. W. & Cox, A. B. (1934): "Principle of Flotation Part I". Trans. AIME, vol. 112.

Wood, H. E. (1929): Early efforts in flotation of dry minerals. Eng. Min. J. 126, 571-573.

Yund,R. A. & Kullerud, G. (1966): Thermal Stability of assemblages in Cu. Fe. S system. J. Pet. 7, 454-488.

APPENDIX I

FLOTATION THEORY

HISTORIC VIEW

Flotation is a process for separating finely divided particles from each other. Usually, it is applied to the cleaning of solid fuels, or to beneficiation of nonmetallic minerals; but in a more general way it is also applied to the concentration of metallic ores.

Because of the early development of flotation under the strains of industrial need and empirical experimentation, flotation theory has lagged behind technological application, and even today flotation is practically more of an art than a science. In recent years, however, a number of noteworthy attempts have been made to discover the fundamental principle underlaying the process.

In fact, flotation is a specialized method of gravity concentration whereby certain minerals are rendered to a lower specific gravity than water by modification of their surfaces by chemical processes leading to attachment of air bubbles. The air bubbles so lighten the mineral particles that they are carried to the surface of the fluid and are removed as a concentrate. Associated and undesireable minerals, either by correct choice of a reagent or by addition of a specific reagent, remain hydrophile (air-avid) and are removed with the body of the fluid as a tailing product.

Bulk-oil, sink-float and froth are the descriptive adjectives which are commonly used for all the processes of concentration in which particles heavier than water are caused to rise in water itself. For instance, if some particles are retained in an oil layer, the process is referred to as bulk-oil flotation; if the particles are sunk within the pulp, forming a layer, the process is known as sink flotation; and if the particles are retained in a foamy layer several inches thick, the process referred to here is froth flotation.

History of Development

Although the earliest patent which may be considered as relating to the flotation process is that of Haynes in 1860, it is interesting to note that the Persians developed flotation procedures as early as the fifteenth century (Gaudin 1940). At least two of these procedures are of the "oiled-pulp knead" method by which water-wetted particles are freed in water from the oiled mass.

Haynes' recognition of the differences in wettability of various minerals by water and oil formed the basis for a number of "oil" flotation processes. During the next fifty years, flotation passed through three principle stages of development: 1) bulk-oil flotation, 2) sink flotation, and 3) froth flotation.

Bulk-oil flotation was based on the fact that minerals of metallic luster are preferentially wetted by oil in the presence of water and consequently pass into the interface between oil and water while the water-wetted gangue drops out. This process required large amounts of oil, usually about one part for each part of water (Taggert 1945).

Sink flotation, on the other hand, depended on the fact that when finely ground dry ore was gently brought into contact with still water, the metallic particles tended to float more than the gangue. This process was developed during the period of 1890-1915 (Wood 1928).

Introduction of Gas as a Buoyant Medium

The use of gas as a buoyant medium to lighten particles to the point of making them lighter than water was started as early as 1877 by the Bessel brothers (Gaudin 1957). Later, in 1902, Fromont in Itally and Ballot in Australia recognized gas bubbles as the ideal buoyant medium for carrying sulfide mineral particles to the surface of the pulp. Ballot's method of directly introducing gas involved the use of a beater or an impeller revolving in a pulp.

As the idea of reducing the amount of oil consumption in flotation processes increased, it became clear that not all the oily substances are similar in floative properties

Introduction of Organic Collectors

With the increase in acceptance of using soluble frothing agents during the period between 1915-1922, the term "collecting oils" gained remarkable popularity among the experts. These were then referred to as "the collectors." These collectors when applied to pulps provided an economical method of concentrating many of the sulfide ores. However, this method proved inapplicable to many complex ores such as those of Cu-Fe, Cu-pb-Zn-Fe, pb-Zn-Fe, Cu-Fe-Zn and Cu-Ni-Fe (Gaudin 1957), (Taggert 1945).

The need for treatment of such complex sulfide ores as well as the non-sulfide ores has inspired continual progress in the development of more selective reagent combinations. An important discovery was made by Keller in 1925 (Gaudin 1957).

In the late 1920's, diothio phosphate was introduced, these are xanthate's chief competitors for the collection of sulfides. Then amins and their related organic compounds capable of producing positively charged hydrocarbon-bearing ions were introduced for the flotation of other less important minerals such as silicates. This latter group of collectors are now referred to as cationic collectors (see table 13).

Introduction of Inorganic Reagents

The discovery of inorganic reagents in treating the sulfide ores dates back as far as 1913, when L. Bradford found the usefulness of copper sulfate in treating sphalerite, to increase its floatability (Gaudin 1957).

Alkaline circuits were introduced from about 1921 and have become standard in flotation of sulfide ores because of their great corrosion advantage over acid circuits. In 1912, Lowry and Greenway discovered the dichromates inhibit galena (Gaudin 1957). This in turn led to the discovery of the marked inhibiting property of limed pyrite and have made possible the use of effective selective agents such as sulfate, cynides and sulfides. Those processes of flotation which require the use of one of these agents are called selective flotation. In this process the selective agent promotes the flotation of one sulfide metal while it inhibits that of the other. At the other extreme from selective flotation is the widely used process of collective flotation, in which all metals are collected in one concentrate. This has also been called differential flotation.

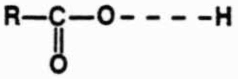
Flotation Reagents

Reagents are those substances added to the pulp to modify or control the chemical conditions and so enhance the selectivity of the process. Without them

TABLE – 13

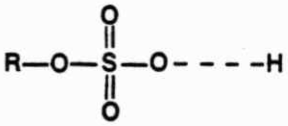
OXHYDRYL ANIONIC COLLECTORS

Carboxylates



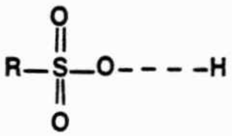
$R-\underset{\underset{O}{\|}}{C}-O----H$

Acid alkyl sulfates



$R-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O----H$

Sulfonates

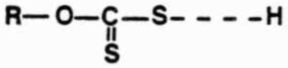


$R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O----H$

SULFHYDRYL ANIONIC COLLECTORS

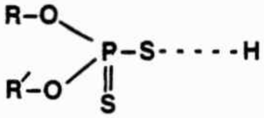
Thiols $R-S----H$

Thiolcarbonate (Xanthates)



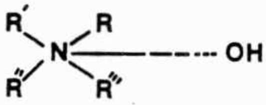
$R-O-\underset{\underset{S}{\|}}{C}-S----H$

Thiolphosphates



CATIONIC COLLECTORS

Amines



the process has limited applicability. Many substances so added serve dual purposes, but the simplest classification is as follows: frothers, collectors, activators, depressants and modifiers.

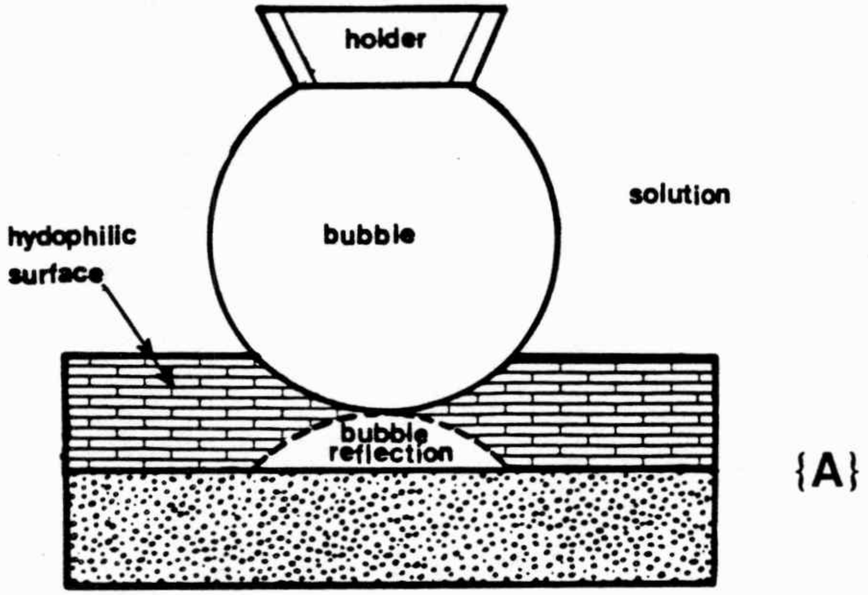
In froth flotation it is essential to create a large water-interfacial area, and frothing agents are used for this purpose. Collecting agents are the heart of the flotation processes since they are the reagents which produce the hydrophobic film on the mineral particle surface. Hydrophobic, as opposed to hydrophilic, refers to a hydrocarbon-like surface which is produced by collecting reagents which, in turn, make the minerals capable of adhering to gas bubbles and to enable them to be floated (see figure 45). Each collector molecule contains a polar and a non-polar group. When attached to the mineral particles, these molecules are so oriented that the non-polar or hydrocarbon group is extended outward (see figure 46). Such orientation results in the formation of hydrophobic film (hydrocarbon-like) on the mineral surface. Figure 46 shows the effect of a collector on the surface of galena (PbS).

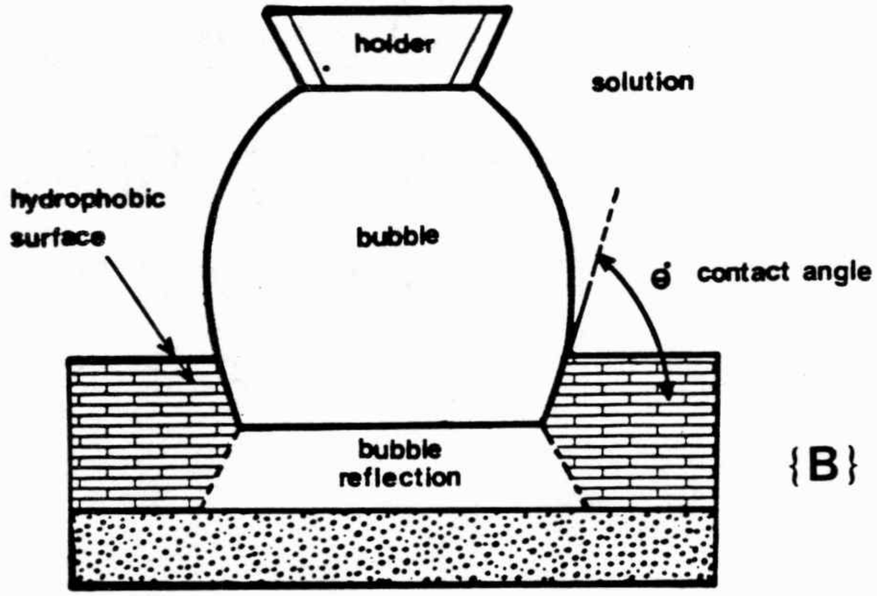
Some minerals do not respond to collection unless their surfaces are first modified by resurfacing or in some other manner. Reagents that form a bond between the mineral surface and the collector ions are known as activators. In a sense, depressants function in the converse manner; i.e., they so modify the chemical atmosphere or the ore pulp that collector ions either cannot attach themselves to the specified mineral surface or should they become attached cannot function as collectors.

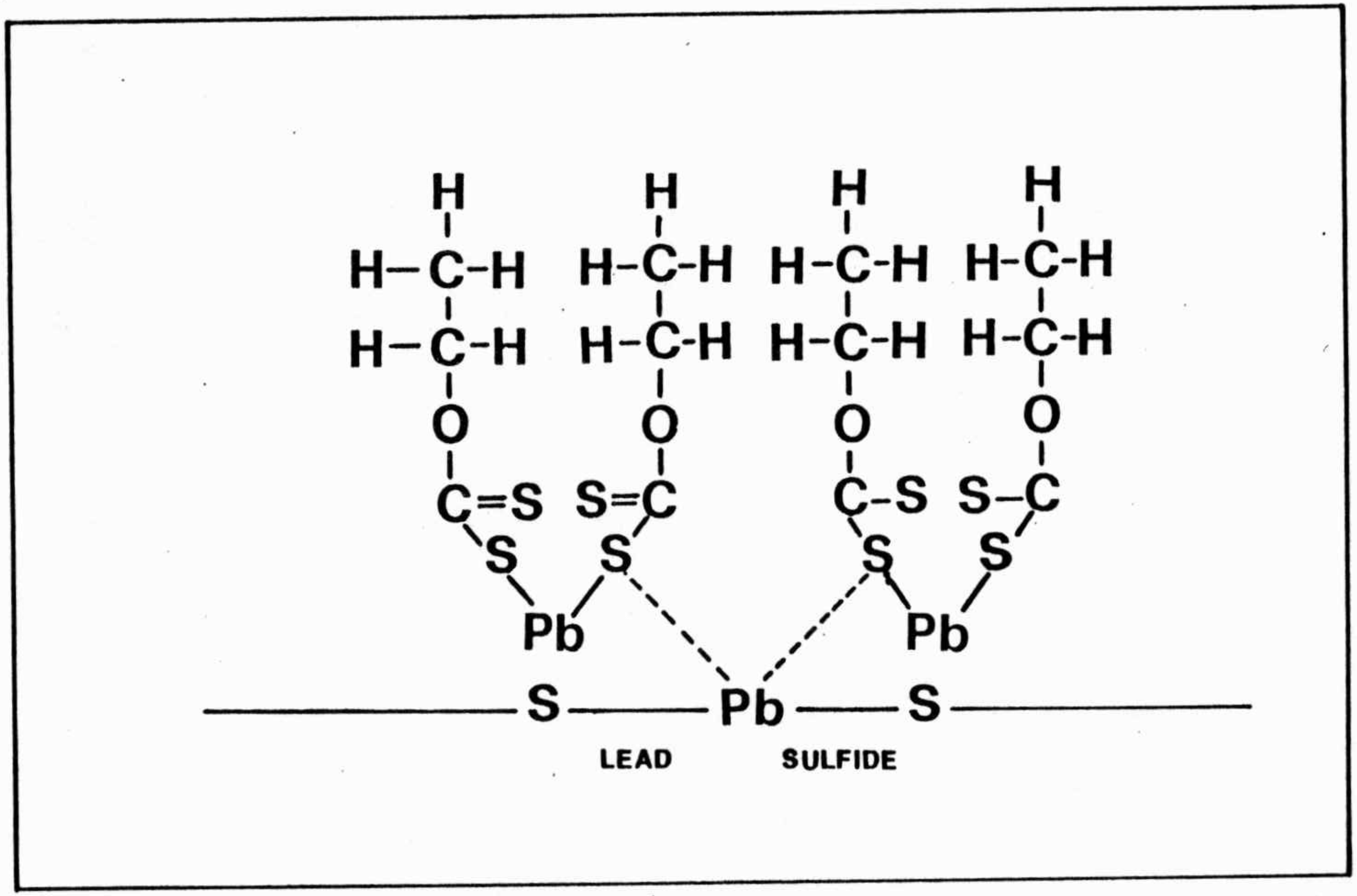
Fig – 45

A_ HYDROPHILIC SOLIDS. Spreading and no bubble attachment. Water wets the surface of solid completely, air bubbles are not able to pick up particles Typical of sphalerite, (modified after Cook, 1950).

B_ HYDROPHOBIC SOLIDS. Incomplete wetting, no spreading, bubble attachment depend on the degree of hydrophobicity. Typical of galena, (modified after Cook, 1950).


holder
bubble
solution
hydophilic surface
bubble reflection
{A}


holder
solution
hydrophobic surface
bubble
θ contact angle
bubble reflection
{B}



Fig—46 Illustration of a typical collector structure. (Taggert, A.F. 1945).

A) Frothers

The best way to describe frothers and their action is to consider a container partially full of pure liquid. If vigorously shaken, the entrapped air will rise as bubbles which, upon reaching atmospheric pressure at the surface of the liquid, collapse almost instantaneously. Now, if a minute quantity of frothing reagent is added to the liquid and shaken for an equal period of time, two obvious changes immediately appear. First, the life of the bubbles at the surface is greatly increased so that an appreciable depth of froth is formed. Second, the dispersion or state of subdivision of the individual bubbles is greatly increased, this being attributable to lower surface tension. The ability to lower the surface tension is characteristic of all frothers. Since most organic compounds can do the job at least to some degree, a large number of frothers are commercially available. However, using the paper frother is economically important. The frother must be low in cost, readily available and essentially free of collector properties. Table 14, modified after Taggert (1945), shows two commonly used frothers.

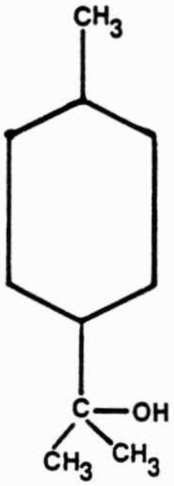
B) Collectors

Froth flotation of minerals is dependent upon their attachment to air bubbles, the net buoyancy resulting in their being rafted to the surface of the liquid pulp. Reagents called collecting agents or collectors, are added to the pulp for the purpose of creating surface conditions on the particles such that they become attachable to air bubbles; table 2 shows several common collectors.

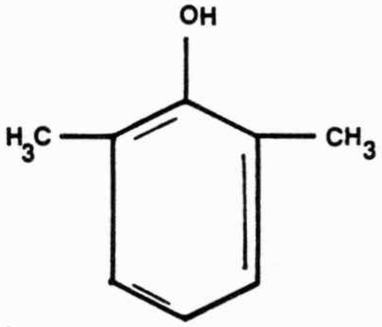
Much of the recent theory of collection is based upon experimental work employing the "Captive Bubble" method (Taggert et al. 1930). In this procedure a

TABLE-14 Two most widely used frothers.

PINE OIL



CRESYLIC ACID



clean mineral surface is immersed in an aqueous solution of the reagent to be tested, and an air bubble is presented to the mineral. Figures 45A and 45B show two entirely different modes of air bubble attachment to the mineral surface. As shown in figure 45B, θ represents the contact angle between galena surface and air bubble measured through a dilute potassium ethylexanthate solution. In the same figure, it is also evident that the contact angle (θ) is greater than zero and hence the mineral is floatable. In contrast, figure 45A illustrates lack of contact of air bubble at a sphalerite surface in dilute potassium ethylxanthate. Obviously, with $\theta = 0$, under this condition the mineral is not floatable.

Collectors are of two main types: 1) liquid hydrocarbons, and 2) water soluble compounds comprising a hydrocarbon radical linked to a chemically active group (Gaudin 1957).

In terms of liquid hydrocarbons, there are three classes of organic compounds—namely acid, base, and salts—which furnish most flotation collectors. Any organic acid consisting of one hydrocarbon chain attached to one anionic polar group is a possibility. Likewise, any organic base consisting of one hydrocarbon chain attached to one cationic polar group is also a possibility. Salts of organic acid and base are also suitable compounds. In fact, they actually are easier to use because of their greater solubilities (Taggert 1930).

However, it is claimed that certain minerals possess an inherent floatability (Gaudin 1940). This statement is definitely true with respect to naturally occurring hydrocarbons (which, being composed of non-polar hydrocarbons, would naturally be water repellent) and perhaps true of a few other substances such as:

soft coal, sulfur, graphite and a small group of sulfide minerals, of which molybdenite (MoS_2), orpiment (Sb_2S_3) and realgar (AsS) are the best known.

Most minerals do not become coated by natural hydrocarbon oil in water. When a droplet of the oil is pressed against them, it deforms itself just like a softly inflated rubber ball squeezed against a flat surface. When the exerting pressure is released, the droplet will regain a substantially spherical shape. If the specific gravity of the mineralized droplet is less than water, it floats away. However, if the droplet of oil is heavier than water, it will roll along a surface that is sufficiently sloping (Taggert 1945).

Collectors Action

The action of flotation collectors has been the subject of more exhaustive investigation than any other phase of flotation process and as a result, little doubt remains as to the outward orientation of the hydrocarbon portion of the collector molecule (Gaudin 1957).

Collecting agents in flotation are polar/non-polar substances and they function by creating a non-polar surface on the mineral to be floated. The nature of attractive forces between the polar portion of the collector and mineral surface has been the subject of study by numbers of investigators such as A. M. Gaudin, I. W. Wark, A. F. Taggert and many others. They proposed various theories involving attachment of collectors as an ion, a molecule, a monolayer and/or a multilayer. The two prevailing theories are the "chemical theory" and the "absorption theory." Taggert, A. F., has been the foremost defender of the "chemical theory." In 1934, he summarized his stand in the following statement:

> All dissolved reagents which, in flotation pulps, either by action on the to-be-floated or on the not-to-be-floated particles effect their flotability, function by reason of chemical reactions of well-recognized types between reagent and the particle affected.

The "chemical theory" postulates the formation of a metalloorganic compound layer on the surface of the mineral. Most of the work that is held to substantiate the chemical theory has been done through separation of zinc sulfide from lead and copper sulfides in the presence of xanthates. Xanthates have been generally used as collectors and are particularly useful in this type of work because of their ease of preparation, high purity and their high solubility. The xanthates are polar/non-polar substances, as is shown by the constitution of potassium ethylxanthate (C_2H_5OSSK) and sodium ethylxanthate (C_2H_5OSSNa).

Very insoluble metal xanthates are formed on the surface of the copper and lead sulfides. It is believed that those two sulfides are floatable because the resultant copper and lead xanthates are more insoluble than the original material whereas the zinc compound because of its higher solubility in the form of zinc xanthate is not floatable (Taggert 1945).

The second theory which has best been summarized by Gaudin (1939) states:

> All ions dissolved in a flotation pulp are absorbed at mineral surfaces. At each mineral surface, the absorption of each dissolved ion is specific, i.e., it depends on the dissolved ion and on a mineral: this specific ion absorption is also a function of the concentration of the dissolved ion under consideration and that of other dissolved ions. If and when a sufficient proportion of the mineral surface is covered by the collector ions, the particle becomes floatable . . .

An interesting pioneer work was carried out by Gaudin (1929) on compounds. Gaudin calculated the covering areas of certain collector ions, assuming them to be oriented on the mineral surface so that the polar ends are directed to the mineral, and the non-polar ends directed into the liquid phase. The covering area is taken to be the same as the maximum cross-sectional area of the ions projected on a plane normal to their length. By measuring the specific surface area using the BET method (Brunauer et al. 1938) and knowing the ratio of concentration, Gaudin was then able to calculate the quantity of reagent, its purity and the molecular weight of the reagent used.

Classification of Flotation Collectors

Collecting agents may be grouped into three classes according to their structure. These are: 1) anionic collectors, 2) cationic collectors, and 3) oily collectors or fatty acids. Table 13 shows a list of various groups of collectors.

1) Anionic Collectors

These are collectors in which the anion carries the water repellent hydrocarbon and reactive group known as anionic collectors. These collectors are, in turn, subdivided into two main categories which are based on the nature of the acidic hydrocarbon atom to the hydrocarbon chain. In the first category the acidic hydrogen is connected to the hydrocarbon chain through an oxygen atom (see table 13). In the case of salts of these acids, the equivalent metals are connected through the same oxygen to the hydrocarbon chain. In the second category of anionic collectors, the above connection is produced through a sulfur atom.

These two categories of anionic collectors may respectively be called oxyhydryl, and sulfhydryl compounds (see table 13). The former includes carboxylates, acid alkyl sulfates and sulfonates, whereas the latter includes mercaptanes, thiocarbonates (xanthates), dithiophosphate and many others (Gaudin 1957).

2) Cationic Collectors

Cationic collectors as shown in table 13 are those in which cations carry the aerophilic (water repellent) hydrocarbon and the reactive polar group. The functions and applications of these collectors are not too well known because they have been introduced recently and are difficult to obtain in high purity (Taggert 1945). In the cationic collectors, which are primarily represented by amines, the polar group is a nitrogen atom. A typical amine collector is shown in table 13.

3) Fatty Acids

The fatty acids or fatty acid soup are the most commonly used collectors for the basic non-sulfide minerals such as calcite ($CaCO_3$), hematite (Fe_2O_3), etc. Here it is appropriate to mention the fact that the silicate minerals which are generally acidic are floated by cationic amines. Both fatty acid and amine collectors have longer hydrocarbon chain lengths (12-13 carbons) than the sulfide mineral collectors. Table 13, modified after Gaudin (1957), shows classes of collectors.

C) Activators and Depressants

Activators are reagents that are added to the pulp to increase the flotability of certain minerals. The classic example of activation is the resurfacing of sphalerite with copper ions to permit collection with xanthate collectors. A clean sphalerite surface is not coated by xanthates which have alkyl group of less than six to eight carbon atoms (e.g., potassium ethylxanthate and sodium ethylxanthate). The introduction of a small quantity of copper ions under either acidic or alkaline conditions rapidly modifies the surface so that it will accept a short-chain xanthate. The mechanism of the process has been much discussed and the prevailing theory is that a monomolecular layer (monolayer) of copper is formed on the sphalerite (Gaudin 1957), (Gaudin et al. 1959).

Depression is the converse of activation, usually involving the addition of reagents to the pulp to prevent certain minerals from floating. The separation of galena, sphalerite and pyrite from one another is accomplished by judicious use of activators and depressants.

In general, activators and depressants are inorganic substances added to the pulp in order to modify the surface of mineral particles. In the case of activators, they are added in order to resurface the grains in such a way as to make them easy to be collected. On the other hand, depressants are used to obtain the opposite effect.

D) Modifiers

Since the object of flotation operation is to separate minrals from each other, it is desireable to regulate the action of collectors through the use of suitable additional agents called modifiers so as to obtain the most effective control.

Modifying agents may act as depressants, activators, pH regulators, dispersants, etc. A depressant is any reagent which inhibits or prevents the

Table-15 List of common modifiers.

MODIFIERS

A– p^H

Lime : CaO
Soda Ash : Na_2CO_3
Caustic Soda : NaOH
Acid : H_2SO_4 , HCl

B– RESURFACING

Catoinic : Ba , Ca , Cu , Pb , Zn , Ag

Anionic : SiO_3 , PO_4 , CN , CO_3 , S

Organic Colloids : dextrin , starch, etc

C– PRECIPITATION

Cationic : Ba , Ca

Anionic : CN , CO_3 , PO_4 , SO_3

Modified from FLOTATION FUNDEMENTALS. The Dow Chemical Company, 1958.

absorption of a collector by a mineral particle and, hence, prevents the flotation action. Activators, on the other hand, are those reagents that modify the surface of a mineral particle in such a way as to make it easy for the collector's atom to become attached. Depressants have the opposite effect. Frequently, several functions may be performed by a single compound; for example, soda ash (Na_2CO_3) may be an activator for pyrite (FeS_2) and a depressant for calcite ($CaCO_3$). Table 15 shows a brief classification of modifiers (modified after Taggert, 1945)

The Concept of Contact Angle

The term hydrophilic solid denotes a solid which is completely wetted by the bulk water phase (or an aqueous solution), while hydrophobic denotes a partial or incomplete wettability by water phase. Figures 43A and 43B show that wetting signifies an adhesion of a liquid phase to another phase (a solid or liquid) such that the cohesion of the spreading (wetting) is exceeded.

Theoretically, two phases are in contact along a two dimensional interface. Where three phases come together, a one dimensional line of contact is formed (see figures 47A, 47B and 48). The properties of this line are best expressed in terms of the angle formed by the joining surfaces in a plane perpendicular to the line (Gaudin 1957). The contact angle θ, measured through the liquid phase, between the solid surface and the tangent to the liquid surface at the three-phase contact, is often referred to as the degree of hydrophobicity.

Since air bubbles are one of the phases present along these lines, they are commonly referred to as bubble-particle contacts. They are the factors controlling the process of froth flotation.

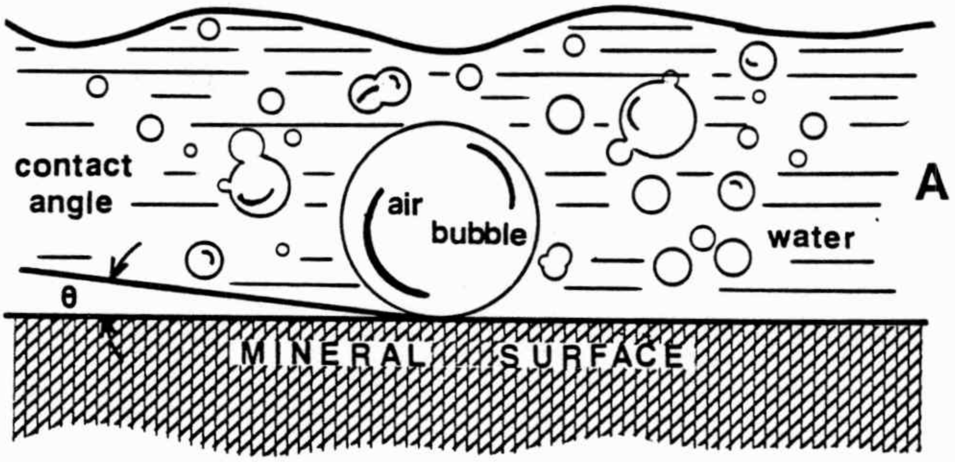
Fig_47

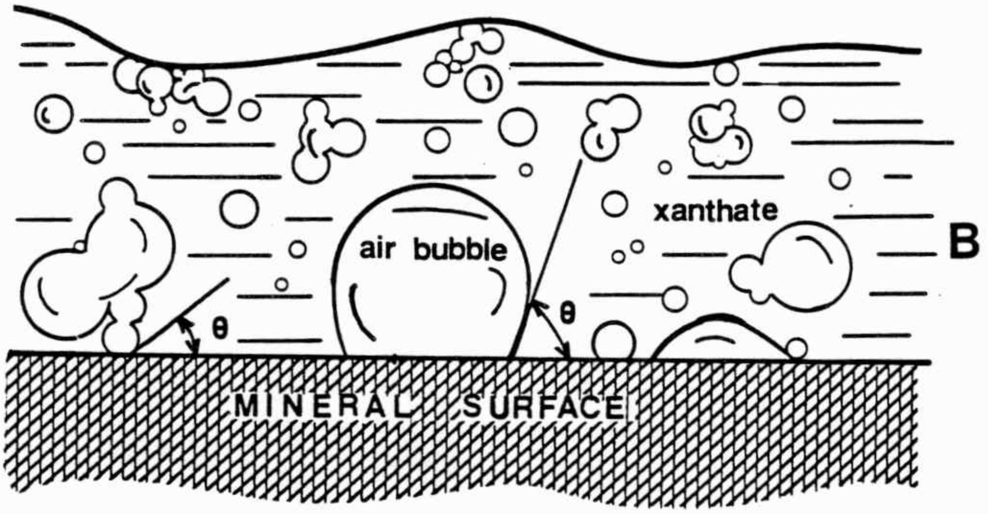
Illustrates air bubble_mineral surface contact with and without collector.

A_ Contact, without collector, [water]

B_ Contact, with collector, [xanthate]

It is evident that in the absence of the collector the air bubble makes only negligible contact with the mineral surface and hence flotation is impossible.


contact angle
θ
air bubble
water
MINERAL SURFACE
A


air bubble
xanthate
θ
θ
MINERAL SURFACE
B

A) Equilibrium Relations

When the three phases are in equilibrium, the surface and interfacial surface acting at equilibrium point (H) must be exactly balanced, as is shown by the equation below:

$$T_{SG} + T_{SL} + T_{LG} = 0 \quad (1)$$

T denotes the interfacial surface tension forces at the equilibrium point (H) (figure 45) and subscripts: SG, SL and LG denote the (solid-gas),(gas-liquid) and (liquid-gas) contacts respectively.

However, the basic relationship of the acting forces must be summed up vectorially:

$$T_{LG}\mathrm{Cos}\theta + T_{SL} + T_{SG} = 0 \quad (2)$$

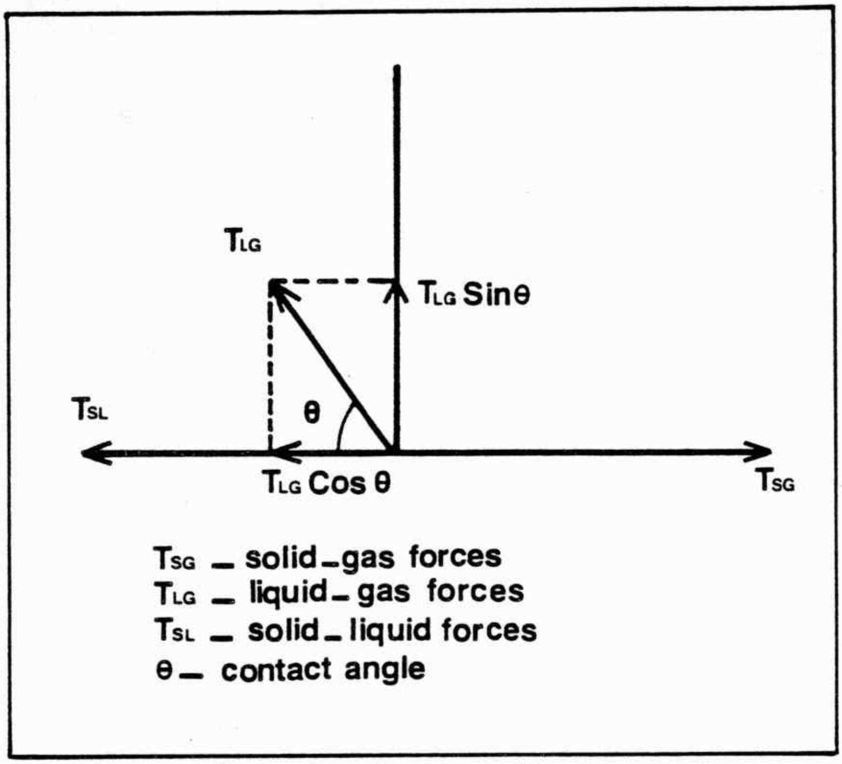
$$F_A = T_{LG}\mathrm{Sin}\theta \quad (3)$$

Scalar equations (2) and (3) represent the total forces acting at the triple point (H). The first team, called COSINE SCALAR, involves an evaluation of the work of adhesion. The lifting power of the submerged gas bubbles is provided through the second term (equation 3), also known as the SINE SCALAR. Equations (2) and (3) can be rearranged and written in terms of contact angle:

$$\mathrm{Cos}\theta = \frac{T_{SG} - T_{SL}}{T_{LG}} \quad (4)$$

$$F_A = -T_{LG}\mathrm{Sin} \quad (5)$$

F_A is referred to as the force of adhesion. The sine scalar does not exist unless a force directed vertically is assumed to exist. In equations (1) through (5), the T's represent surface and interfacial tensions and are most frequently expressed in dynes per centimeter. The force of adhesion (F_A) is also expressed in dynes per centimeter.



Fig–48 Illustrates forces acting at contact Point.

B) Thermodynamic Properties

The general thermodynamic condition for three phase contact is best defined by equation (6) (Gaudin 1957):

$$G = T_{SG} - (T_{SL} + T_{LG}) \quad (6)$$

where G is the free energy accompanying the replacement of a unit area of the solid/liquid interface by solid/gas interface. Combinations of equation (2) and (6) yields the following expression for the free energy change:

$$T_{LG}\text{Cos}\theta + T_{SL} - T_{SG} = 0 \quad (2)$$

$$T_{SG} = T_{LG}\text{Cos}\theta + T_{SL} \quad (7)$$

substituting in equation (6):

$$LG = T_{LG}\text{Cos}\theta + T/_{SL} - T/_{SL} - T_{LG} \quad (8)$$

$$G = T_{LG}\,(\text{Cos}\theta - 1) \quad (9)$$

C) Significance of Contact Angle

At the two extremes, the contact angles are zero and 180°. When the contact angle with a solid particle is zero (hydrophilic solids), this signifies that the mineral is completely wettable and no bubble attachment occurs (See figures 45A and 45B). In this case water wets the hydrophilic solid and the mineral particle cannot be picked up by air bubbles. This is better known as a non-floatability condition.

Conversely, a contact angle of 180 degrees would represent wetting of the mineral by air (i.e., that is the minerals are hydrophobic solids). However, it is known that no solids would give a contact angle greater than about 110 degrees (Gaudin 1957). When the degree of hydrophobicity is small, the angles formed by drops of water on the surface of the flat solids (or by bubbles attached to submerged solids) are also small $0<\theta \leq 90^{\circ}$. When the solid is hydrophobic, the contact angles are high 90° or even $\theta > 90^{\circ}$.

APPENDIX II

FLOTATION RESULT OF SYNTHETIC COPPER SULFIDES

TABLE 1

The rate of flotation of leached copper sulfide, sample: F-1/0-3, (CS 3)

Flotation Conditions

a) Constant volume: 150 ml, pH = 5
b) Constant gas flow rate
c) Constant K-ethyl xanthate concentration: $\frac{25\ \text{mg}}{1000\ \text{ml}}$
d) Flotation time: 30 minutes
e) Time intervals: 5 minutes

Characterization of starting leached sample and leaching conditions;

a) original Composition: $Cu_{1.75}S$
b) detected phases: digenite (di), blue-remaining covellite (BC) and normal covellite (Cv?).
c) leaching period: 48 hrs
d) concentration of $Fe_2(SO_4)_3 \cdot xH_2O$: 1.0×10^{-1} M
e) volume of leaching solution: 15 ml.

Initial weight = 0.3 gram (300 mg.)
Floated weight = 197.6 mg
Unfloated weight= 102.4 mg

TIME MIN.	RAW Wt.— mg	CUMULATIVE Wt.	RAW Wt. %	CUMULATIVE Wt. %
5	126.46	126.46	42.152	64.0
10	38.0	146.79	12.7	83.4
15	12.64	177.44	4.21	89.8
20	4.35	181.79	1.45	92.0
25	7.9	189.69	2.46	96.0
30	7.91	197.6	2.46	100.0

TABLE 2

The rate of flotation of leached synthetic copper sulfide,

Sample: F-2/0-10,(CS10)

Flotation Conditions

a) Constant volume: 150 ml., pH = 5

b) Constant gas flow rate

c) Constant K-ethyl xanthate concentration: $\frac{25 \text{ mg}}{1000 \text{ ml}}$

d) Flotation time: 30 minutes

e) Time intervals: 5 minutes

Characterization of starting leached sample and leaching conditions

a) original composition: $Cu_{1.75}S$

b) detected phases: digenite (di), blue-remaining covellite (BC), and normal covellite (CV)

c) leaching period: 48 hrs.

d) concentration of $Fe_2(SO_4)_3 \cdot xH_2O$: 1.0×10^{-1}M

e) volume of leaching solution: 15 ml.

Initial weight = 0.3g (300 mg)
Floated weight = 210.5mg
Unfloated weight= 89.5 mg

TIME MIN.	RAW Wt.– mg	CUMULATIVE Wt.	RAW Wt. %	CUMULATIVE Wt. %
5	157.87	157.87	52.62	75
10	27.37	185.24	9.123	88
15	10.52	195.76	3.50	93
20	4.21	199.97	1.4	95
25	5.26	205.23	1.75	97.5
30	5.27	210.5	1.75	100.0

TABLE 3

The rate of flotation of unleached synthetic copper sulfide,

Sample: F-3/0-11, (CS 11)

Flotation Conditions

a) Constant volume: 150 ml., pH = 5
b) Constant gas flow rate
c) Constant K-ethyl xanthate concentration: $\frac{25\text{ mg}}{1000\text{ ml}}$
d) Flotation time: 6.0 minutes
e) Time interval: 60 seconds

Characterization of starting sample

a) original composition: $Cu_{1.75}S$
b) observed phases: digenite (di), blue-remaining covellite (BC) and normal covellite (Cv)

Initial weight = 2.0 grams

TIME MIN.	RAW Wt.– mg	CUMULATIVE Wt.	RAW Wt. %	CUMULATIVE Wt. %
1	0.92	0.92	46.0	46.0
2	0.68	1.62	33.8	79.8
3	0.27	1.87	13.7	93.5
4	0.1	1.97	5.0	98.5
5	0.01	1.98	0.5	99
6	0.02	2.00	1.0	100.0

TABLE 4

The rate of flotation of normal covellite with composition CuS.

Flotation Conditions

a) Constant volume: 150 ml., PH = 5
b) Constant gas flow rate
c) Constant K-ethyl xanthate concentration : $\frac{25\text{ mg}}{1000\text{ ml}}$
d) flotation time: 30 minutes
e) Time interval: 5 minutes

Characterization of starting sample

a) Normal covellite: CuS, from mineral collection of Geology Department, University of Nebraska.

b) color: blue

c) size in mesh: -60/+100

Initial weight = 3.0 grams
Floated weight = 1.183 grams
Unfloated weight= 1.817 grams

TIME MIN.	R A W Wt.– mg	CUMULATIVE Wt.	R A W Wt. %	CUMULATIVE Wt. %
5	0.4968	0.4968	16.5	42
10	0.2130	0.7098	7.1	60
15	0.1656	0.8754	5.52	74
20	0.1242	0.9996	4.14	84.5
25	0.1004	1.1001	3.346	93
30	0.083	1.183	2.767	100

APPENDIX III

FLOTATION RESULTS OF SPHALERITE SAMPLE ZnS-A

TABLE 1

The rate of flotation of unactivated sphalerite (ZnS-A) in regular tap water.

Flotation Conditions

a) Constant volume: 150 ml

b) Constant gas flow rate

c) Constant concentration of K-ethyl xanthate: $\frac{25 \text{ mg}}{1000 \text{ ml}}$

d) Constant total flotation time: 30 minutes

e) Time intervals: 5 minutes

Initial weight = 2.0 grams

Floated weight = 0.83035 grams

Unfloated weight= 1.16965 grams

Time Min.	Raw Wt.	Raw Wt. %	Cumulative Wt.	Cumulative Wt. %	Vol. ml.	Size Mesh	Temp. °F	PH
5	0.19310	10.0	0.19310	23.25	150	65/100	55-60	5
10	0.17188	8.6	0.36498	43.95	150	65/100	55-60	5
15	0.15911	8.0	0.52409	63.11	150	65/100	55-60	5
20	0.11812	6.0	0.64221	77.35	150	65/100	55-60	5
25	0.10992	5.5	0.75213	90.5	150	65/100	55-60	5
30	0.07822	4.0	0.83035	100.0	150	65/100	55-60	5

TABLE 2

The rate of flotation of unactivated (ZnS-A) in distilled water.

Flotation Conditions

- a) Constant volume: 150 ml
- b) Constant gas flow rate
- c) Constant concentration of K-ethyl xanthate: $\frac{25 \text{ mg}}{1000 \text{ ml}}$
- d) Constant total flotation time: 30 minutes
- e) Time intervals: 5 minutes

Initial weight = 2.0 grams

Floated weight = 0.70246 grams

Unfloated weight= 1.2975 grams

Time Min.	Raw Wt.	Raw Wt. %	Cumulative Wt.	Cumulative Wt. %	Vol. ml.	Size Mesh	Temp. °F	PH
5	0.16789	8.5	0.16789	23.9	150	65/100	55-60	5
10	0.14698	7.5	0.31487	44.82	150	65/100	55-60	5
15	0.12508	6.5	0.43995	62.62	150	65/100	55-60	5
20	0.10644	5.5	0.54639	77.78	150	65/100	55-60	5
25	0.09708	5.0	0.54347	91.60	150	65/100	55-60	5
30	0.05899	3.0	0.70246	100.00	150	65/100	55-60	5

TABLE 3

The rate of flotation of activated sphalerite (ZnS-A)

Flotation Conditions

a) Constant volume: 150 ml

b) Constant gas flow rate

c) Constant concentration of K-ethyl xanthate: $\frac{25 \text{ mg}}{1000 \text{ ml}}$

d) Constant flotation time: 160 seconds

e) Time intervals: 10 seconds

f) Concentration of $CuSO_4 \cdot 5H_2O$: $\frac{100 \text{ mg}}{1000 \text{ ml}}$

g) Activation period: 30 minutes

h) Weight of starting material = 2.0 gram.

Time Sec.	Raw Wt. gram	Individual Raw %	Cumulative %	Volume ml	Temp ^oF	P^H	Size Mesh
10	0.06	3.0	3.0	150	60	5	65/100
20	0.33	16.5	19.5	150	60	5	65/100
30	0.28	14.0	33.5	150	60	5	65/100
40	0.53	26.5	60.0	150	60	5	65/100
50	0.36	18.0	78.0	150	60	5	65/100
60	0.28	14.0	92.0	150	60	5	65/100
70	0.06	3.0	95.0	150	60	5	65/100
80	0.04	2.0	97.0	150	60	5	65/100
100	0.02	1.0	98.0	150	60	5	65/100
120	0.02	1.0	99.0	150	60	5	65/100
160	0.02	1.0	100.0	150	60	5	65/100

APPENDIX IV

FLOTATION RESULTS OF SPHALERITE SAMPLE ZnS-B

TABLE 1

The rate of flotation of unactivated sphalerite (ZnS-B) in regular tap water.

Flotation Conditions

a) Constant volume: 150 ml

b) Constant gas flow rate

c) Constant concentration of K-ethyl xanthate: $\frac{25 \text{ mg}}{1000 \text{ ml}}$

d) Constant total flotation time: 30 minutes

e) Time intervals: 5 minutes

Initial weight = 2.0 grams

Floated weight = 1.74756 grams

Unfloated weight= 0.25244 grams

Time Min.	Raw Wt.	Raw Wt. %	Cumulative Wt.	Cumulative Wt. %	Vol. ml.	Size Mesh	Temp. °F	PH
5	0.38196	19.0	0.38196	21.8	150	65/100	55-60	5
10	0.34422	17.5	0.72678	41.6	150	65/100	55-60	5
15	0.27962	14.0	1.0064	57.6	150	65/100	55-60	5
20	0.25261	12.6	1.26501	72.4	150	65/100	55-60	5
25	0.24578	12.3	1.51079	86.5	150	65/100	55-60	5
30	0.23677	11.83	1.74756	100.0	150	65/100	55-60	5

TABLE 2

The rate of flotation of unactivated sphalerite (ZnS-B) in distilled water.

Flotation Conditions

a) Constant volume: 150 ml

b) Constant gas flow rate

c) Constant concentration of K-ethyl xanthate: $\frac{25 \text{ mg}}{1000 \text{ ml}}$

d) Constant total flotation time: 30 minutes

d) Time intervals: 5 minutes

Initial weight = 2.0 grams

Floated weight = 1.16676 grams

Unfloated weight= 1.83824 grams

Time Min.	Raw Wt.	Raw Wt. %	Cumu-lative Wt.	Cumu-lative Wt. %	Vol. ml.	Size Mesh	Temp. °F	PH
5	0.28514	14.25	0.28514	25.43	150	65/100	55-60	5
10	0.2480	12.4	0.53314	45.7	150	65/100	55-60	5
15	0.18283	9.14	0.71597	61.3	150	65/100	55-60	5
20	0.16182	8.09	0.87779	75.25	150	65/100	55-60	5
25	0.14899	7.44	1.02678	88.0	150	65/100	55-60	5
30	0.13998	7.0	1.16676	100.0	150	65/100	55-60	5