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Copper Sulfate as Flotation Activator for Sphalerite

By O. C. RALSTON, C. R. KING AND F. X. TARTARON
CLARKDALE, ARIZONA

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Copper Sulfate as Flotation Activator for Sphalerite

By O. C. RALSTON,* C. R. KING* AND F. X. TARTARON,* CLARKDALE, ARIZ.

(San Francisco Meeting, October, 1929)

THE use of copper sulfate for improving the flotation behavior of sphalerite is probably at least 15 years old. The original discovery of its activating influence is somewhat obscure. The story goes that in the mill at Mascot, Tenn., its favorable action was discovered by accident, early in 1914, as follows: The original laboratory test work on a sphalerite ore gave favorable flotation results, but after a mill had been built the flotation concentration of the ore was very unsatisfactory. In diagnosing the probable reasons, one fact pointed out was that the laboratory test machine had been constructed of bronze whereas the commercial machine allowed pulp to come in contact only with wood and iron. A plate of sheet copper was hung in the flotation machine and results immediately improved. At first fanciful explanations of electrolytic and electrostatic behavior were given credence, but when the copper plate was removed and a small amount of copper sulfate substituted in the pulp an even more favorable result was obtained. Toward the end of 1914 copper sulfate was also adopted in the acid flotation circuit of the Butte and Superior Copper Co. Just who is responsible for the original discovery the present writers do not know. It seems strange that in that era of flotation litigation this discovery was not patented.

While for pragmatic purposes it may be sufficient to know that the mere addition of copper compounds to a flotation pulp is sufficient to activate the flotation of the sphalerite, for scientific purposes it is quite desirable to know more about how the action takes place. It is the purpose of this paper to present certain evidence dealing with the mechanism of the beneficial effect.

The description of the effect as *activation* in contradistinction to *depression* is now common in both the English and German languages. It makes no assumptions as to whether the zinc sulfide surfaces have been filmed with copper compounds. In fact, the principal differences of opinion expressed in the literature deal with whether there is an actual formation of CuS (or even Cu_2S) on the surface of the sphalerite.

Activation of sphalerite takes place in alkaline, neutral or weakly acid solutions and whereas the present day flotation of sphalerite is usually in an alkaline solution, the early use of copper sulfate was in a sulfate solution.

*Of the Research Staff, United Verde Copper Co.

MICROSCOPIC EXAMINATION

Some of the first to use a microscope in studying surfaces of sphalerite particles when treated with reagents were Tucker and Head.¹ Large cleavage surfaces of pure minerals were covered in half by paraffin and were attached to the impeller of a flotation machine to be immersed with proper agitation in a flotation pulp containing copper sulfate. When the paraffin film was removed, the exposed surface was found to be coated with an unknown film. This gave credence to the theory that a film probably of copper sulfide had been formed.

On the other hand, Ince² says that despite intensive microscopic study of sulfide surfaces after treatment in solutions more concentrated than those used in practice, there were revealed no surface alterations visible at a surface magnification of 500. Also, S. I. and A. S. Mitrofenoff³ state that pure crystals of blende and pyrite lay in a 10 per cent. solution of copper sulfate solution without stirring for two months with no visible alteration of their surfaces.

The Mitrofenoffs noticed that if sodium carbonate were added to a dilute copper sulfate solution the blende, and to a less extent pyrite, became covered with spotty discolorations, or even radiating crystalline masses of high luster. In the presence of weak xanthate solutions, blade-shaped forms were seen on the blende grains in either acid or alkaline solutions. Therefore they formed the conclusions that the important film was cupric xanthate and their theory of activation includes primary formation of zinc hydrate, cyanide or carbonate film on the zinc sulfide surface followed by metathetic formation of the corresponding copper compounds followed by reaction with the xanthate solution to form insoluble copper xanthate. Without disputing their theory, it must be pointed out that copper sulfate has been used for an activator for many years before xanthates were adapted to flotation, and in the presence of almost every conceivable flotation oil or soluble collector.

While the work of Tucker and Head has been criticized by Taggart, Taylor and Ince⁴ in such a manner as to cast serious doubt on the character of their visible films, there is one bit of forgotten evidence in the literature which gives strong probability to the existence of a microscopically invisible film of copper sulfide on the activated sphalerite surface. This is provided by Wentworth⁵ who, in describing the old electrostatic

¹ E. L. Tucker and R. E. Head: Effect of Cyanogen Compounds on Floatability of Pure Sulfide Minerals. *Trans., A. I. M. E.* (1926) **73**, 354.

² C. R. Ince: A Study of Differential Flotation. *A. I. M. E. Tech. Paper* 195 (1929).

³ *Mineralnoje Syrjo* (1928) 246; through *Metall und Erz* (1928) **25**, 644.

⁴ A. F. Taggart, T. C. Taylor and C. R. Ince: Experiments with Flotation Reagents. *A. I. M. E. Tech. Paper* 204 (1929) 39.

⁵ H. A. Wentworth: Electrostatic Separation of Minerals in Ores. *Eng. & Min. Jnl.* (1910) **90**, 15.

concentrating or separating processes, pointed out that the electrostatic separators functioned because of differences in conductivity of mineral particles. Sphalerite has low conductivity, therefore minerals of higher conductivity, such as galena and pyrite, can be separated from it, leaving the sphalerite mixed with gangue minerals. If this remaining mixture is placed in a copper sulfate solution, washed, dried and concentrated on the same electrostatic separator, the sphalerite particles will function like good conductors and will separate from the gangue. They are not visibly altered, but apparently even an invisible film of the highly conductive copper sulfide is sufficient to make them function as good conductors. After long immersion, or several immersions, the blende particles grow distinctly brown; this, of course, is not evidence proving the existence of a film of copper sulfide because some other copper compound might have been involved. The evidence, at least, supports the inference that there is a film of some copper compound.

TYPICAL EFFECTS OF COPPER SULFATE

As an example of the beneficial effects of copper sulfate in the activation of sphalerite toward flotation, the series of results shown in Fig. 1 is of interest. These represent rougher tests on a sample of heavy pyritic

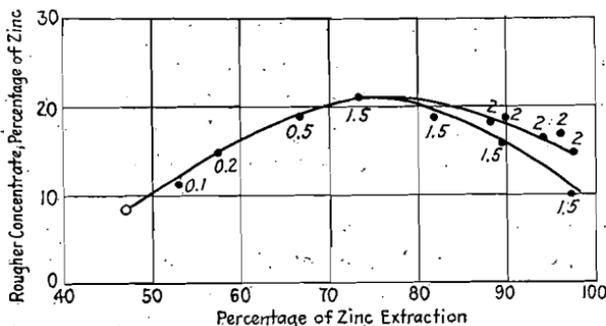


FIG. 1.—EFFECT OF COPPER SULFATE IN ROUGHING TESTS.

Amounts $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ given on diagram, in pounds per ton ore. Other reagents: 0.1 lb. pine oil; 0.1 lb. potassium amyl xanthate. Causticity: 0.25 lb. CaO per ton water.

ore from the United Verde Copper Co. mine at Jerome, Ariz. The particular sample in question contained about 5.6 per cent. zinc as marmatite, and was treated in a circuit made alkaline with lime, using pine oil as a frother and potassium amyl xanthate as a collector. As can be seen, in the blank test with no copper sulfate, less than 50 per cent. of the zinc was contained in a rougher concentrate, analyzing only 8.5 per cent. zinc. The addition of increasing amounts of copper sulfate increased both grade of rougher concentrate and extraction, until about 80 per cent. extraction was reached. For higher percentages of extraction the grade of the rougher concentrate fell off. The proportions of copper sulfate

used are expressed on the face of the diagram in pounds $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per ton of ore. It will be noticed that most of the beneficial effect is obtained by as little as 1 lb. blue vitriol per ton of ore, although slightly improved results are obtained with up to 2 pounds.

The fact that these results were obtained in a pulp made alkaline with lime suggests that the copper sulfate added is probably not present as copper sulfate but was converted to copper hydroxide before the activation of the sphalerite surfaces. With this in mind the following studies were undertaken.

Another sample of ore of the following analysis was used:

	PER CENT.		PER CENT.
Cu.....	3.03	MgO.....	0.43
Zn.....	5.85	Al_2O_3	0.84
Pb.....	0.121	SiO_2	13.29
Fe.....	34.00	S.....	40.75
CaO.....	1.18		

In this ore copper was present almost entirely as chalcopyrite and the zinc as marmatite, containing slightly over 60 per cent. zinc. The bulk of the ore consisted of pyrite and the total gangue present was only 15 per cent., of which a portion is the schist with which the ore deposit is associated.

CONSUMERS OF COPPER SULFATE

Modern flotation is carried on mainly in alkaline pulp, therefore when copper sulfate is added to it there are several possible consumers or precipitants of the copper, which may be tabulated as follows:

1. Soluble constituents of the water, such as lime, calcium bicarbonate, cyanide, etc.
2. Gangue minerals (in this ore the schist absorbs copper sulfate).
3. Sulfide minerals, which interact with the copper sulfate solution.
4. Finely ground metallic iron from grinding machinery.

Even if copper is precipitated as hydroxide or basic carbonate by the pulp solution, or by carbonates in the gangue, the resulting precipitate is not completely insoluble, but has a certain minute solubility. From the physicochemical tables of Landoldt-Börnstein and the solubility tables of Seidell, it was found that the solubility of cupric carbonate at 18°C . is 0.031 part per 100 parts water, whereas the bicarbonate is soluble to the extent of 0.041 part at 18°C . and the hydroxide, 0.000650 part at 18°C . The solubility of the basic carbonate of the copper is given as 0.00026 part per 100 c.c. water. Therefore, while copper may be precipitated almost entirely by constituents of the pulp the solution will always be saturated to the extent represented by these figures.

CONSUMPTION OF COPPER SULFATE IN NEUTRAL PULP

When grinding the ore in local water, the resulting pulp was not truly neutral but slightly alkaline, the water in it having a pH of 7.6. A series

of tests was run in which 2 lb. of blue vitriol, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, was added to each ton of ore, which had been ground until about 20 per cent. remained on a 300-mesh sieve and pulped with water until there were 4 tons of water for every ton of ore. Two liter batches of this pulp were agitated from 1 to 10 min., then immediately filtered and the remaining copper determined. A blank was also run on a filtered portion of water from grinding a batch of ore and to it was added copper sulfate, resulting in a precipitate, which was likewise filtered. In Table 1 are given essential data of this series of tests. As can be seen, 1.9 lb. of the 2.0 lb. of copper sulfate was precipitated by the water filtered away from the neutral pulp, and at the end of 5 min. practically all the copper in each charge had been used up. Therefore this series was disappointing as far as showing whether the copper sulfate or copper carbonate or hydroxide interact with the zinc sulfide in the ore.

TABLE 1.—*Consumption of Copper Sulfate in Neutral Pulp*

Time, Minutes	Temperature, Deg. F.	pH	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Consumed, Lb. per Ton
1	80	7.5	1.962
2	80	7.4	1.831
3	80	7.4	1.894
4	80	7.4	1.870
5	80	7.4	1.997
8	80	7.4	1.997
9	83	7.4	1.983
10	86	7.4	1.996
Blank	80	7.6	1.901

CONSUMPTION OF COPPER IN ACIDIFIED PULP

A series of tests was designed in which sufficient sulfuric acid was added to the pulp to keep copper sulfate in solution. The pH of the pulp was brought to about 6.0 with sulfuric acid and another series of tests was run using 2 lb. copper sulfate per ton of ore, as described above. The results of this series on the effect of time on consumption of copper sulfate are given in Table 2.

TABLE 2.—*Consumption of Copper Sulfate in Acidified Pulp*

Time, Minutes	pH	CuSO_4 Consumed, Lb. per Ton
Blank	6.4	0.185
2	6.0	1.793
15	6.0	1.922
45	6.2	1.775
90	6.2	1.950
120	6.4	1.950

In this case, it will be noted that the blank test showed a consumption of only 0.185 lb. of copper sulfate, so that the remaining copper sulfate as such was available for interaction on the sulfide and gangue minerals. In this case, after only 2 min. time of contact 90 per cent. of the copper sulfate had been used up, but even after 120 min. a very small amount of copper sulfate still remained in solution. The practical conclusion is that the consumption of copper sulfate by the ore in an acidified pulp is a very rapid reaction.

Since in all the above tests 2 lb. of bluestone had been used for each ton of ore, it was thought best to vary the amount of bluestone and to give a sufficient time of contact (30 min.) in another series of tests in acidified pulp, which are reported in Table 3. Here again, acid amounting to 4 lb. per ton ore brought the pH to 6.0, and amounts of copper sulfate varying from 5 to 150 lb. per ton of ore were applied in the solution.

TABLE 3.—*Consumption of Copper Sulfate in Acidified Pulp*

Temperature, Deg. F.	pH	CuSO ₄ Added, Lb. per Ton	CuSO ₄ Consumed, Lb. per Ton
83	6.0	5	5.0
83	6.0	8	8.0
83	6.2	15	15.0
83	6.2	25	25.0
83	6.2	50	50.0
83	6.0	75	67.5
...	6.0	100	82.1
83	6.0	150	90.0

In the 30-min. interval as much as 50 lb. of copper sulfate would be consumed completely and for greater quantities the consumption would be increased, but not all of the available copper sulfate was used up in 30 min. The copper sulfate consumption was increased at such a rate that it seemed to be approaching a maximum of about 100 lb. per ton of ore. The resulting solutions were found to contain both zinc and iron, so it could be concluded qualitatively that at least a portion of the copper sulfate had been used up on the sulfides of iron and zinc, probably with precipitation of a sulfide of copper and the passing into solution of zinc or of iron.

CONSUMPTION OF BASIC COPPER COMPOUNDS BY ORE

While the work in acidified pulp is interesting, it still does not approach the conditions reached in practice where neutral or alkaline pulps are involved. A method of analysis was therefore perfected for differentiating copper carbonate and hydroxide from freshly precipitated sulfides of copper. Pulp samples could be deaerated by means of a vacuum or by blowing nitrogen through them. An air-free ammonia solution was used

to leach out copper carbonate and copper hydroxide from such pulp. If air is excluded copper sulfide or metallic copper is not attacked by the ammonia solution.

A series of neutral pulp samples was prepared to which copper sulfate was added as above, with immediate precipitation of the basic carbonate of copper, and after various periods of agitation in closed bottles each was leached with air-free ammonia, whereby it was determined how much of the copper carbonate had interacted with the suspended ore, producing copper sulfide presumably as a film on the various sulfide minerals. The data of these tests are given in Table 4.

TABLE 4.—*Consumption of Copper Carbonate by Ore*

Time, Minutes	Temperature, Deg. F.	CuCO ₃ Consumed, Lb. per Ton
5	82	1.754
10	82	1.833
30	82	1.881
90	82	1.983

This table shows that of the copper corresponding to 2 lb. original copper sulfate per ton of ore, the equivalent 1.75 lb. is used up in 5 min. and practically all of it is gone in 90 min. Therefore, in spite of the low solubility of the carbonate and hydrate of copper, each can be quite rapidly used up by the sulfide minerals of the ore. This is believed to be a definite piece of evidence, previously lacking, which shows that the copper sulfate added to an ore pulp ultimately is converted to a sulfide of copper.

CONSUMPTION OF COPPER HYDRATE IN A LIME CIRCUIT

A series of pulps was made up to which lime was added in amounts of 8 lb. CaO per ton of ore, causing the resulting pulp to have a pH of 11.8. To samples of this pulp increasing amounts of copper sulfate were added with instantaneous conversion of copper sulfate to copper hydrate and the samples were agitated for 30 min. in closed bottles without contact with air. Unreacted copper hydrate was leached out with ammonia and the tabulated data are given in Table 5. The copper hydrate converted into sulfide is expressed in the fifth column in pounds per ton ore for comparison with the original amount of copper hydrate added. When compared with the series run in acid pulp there is a smaller consumption of copper. For instance, when 100 lb. of bluestone was added (equivalent to 39.0 lb. of Cu(OH)₂) the copper equivalent to only 30 lb. CuSO₄·5H₂O was consumed by the ore in a lime circuit, whereas in an acid circuit 82 lb. was consumed by the ore.

In the last column of Table 5 are given the amounts of zinc dissolved in the ammonia solution, so that one must presume that the bulk of copper

TABLE 5.—*Consumption of Copper Hydrate in Lime Circuit*

Temperature, Deg. F.	pH	Bluestone Used	Cu(OH) ₂ Equivalent	Cu(OH) ₂ Consumed, Lb. per Ton Ore	Zn in NH ₃ Solution, Lb. per Ton Ore
84	11.8	blank		0.39 deduct- ed below	Trace
84	11.6	1	0.39	0.25	0.352
84	11.4	3	1.17	0.84	0.333
84	11.4	5	1.95	1.16	0.292
84	11.2	10	3.9	1.80	0.222
84	11.0	20	7.8	3.36	0.259
84	10.0	50	19.5	7.6	0.666
84	8.0	100	39.0	11.7	1.006

hydrate consumed by the ore reacted with other minerals than with the sphalerite. In the case of 100 lb. of bluestone added to the ore, of which the equivalent of 30 lb. was ultimately converted to sulfide, the actual copper involved in the 30 lb. of bluestone is 8.5 lb. and there was found in solution only 1 lb. of zinc. As they are almost of the same atomic weight, 1 lb. of copper should be replaced by about 1 lb. of zinc, and therefore out of the 8.5 lb. of copper converted to sulfide 7.5 lb. must have been used up on something else in the ore—probably pyrite. This conclusion is supported by the fact that pyrite is also activated by copper sulfate, although not in the same proportion as sphalerite.

ACTION OF COPPER SULFATE ON PURE MINERALS

This work indicated the desirability of studying the action of copper sulfate on individual pure minerals and therefore samples of sphalerite, chalcopyrite, pyrite and barren schist were obtained for this purpose. They were placed in dilute copper sulfate solutions and allowed to stand for 24 hr. with resulting copper consumption tabulated in Table 6. In this

TABLE 6.—*Action of Copper Sulfate on Pure Minerals*

Mineral	Condition of Circuit	Copper Consumed, Milligrams per Gram of Mineral	Zn or Fe Liberated, Lb. per Ton Ore
ZnS.....	Neutral	3.04	1.06
ZnS.....	Alkaline	2.68	1.24
ZnS.....	Acid	1.66	2.00
CuFeS ₂	Neutral	6.08	0.00
CuFeS ₂	Alkaline	5.93	0.00
CuFeS ₂	Acid	2.51	trace
FeS ₂	Neutral	8.80	
FeS ₂	Alkaline	9.30	
FeS ₂	Acid	7.90	
Schist.....	Neutral	3.70	

} Zn in soln.

} Fe in soln.

case the copper consumed is expressed in milligrams per gram of mineral used, and again the last column contains information on the amounts of zinc or iron liberated. Ferric hydrate was plainly visible in the pulp and was extracted by a quick leach with dilute hydrochloric acid. Apparently copper sulfate is consumed by all four constituents of the ore in the following order: pyrite, chalcopyrite, schist, sphalerite. Presumably, the copper sulfate absorbed by the schist is either precipitated by calcium carbonate or is adsorbed.

In the face of this evidence we must conclude that if sphalerite is activated by formation of a film of copper sulfide on its surface, the properties of this film must be considerably different from the properties of the films produced on pyrite and chalcopyrite. In the case of the sphalerite we can expect a cupric sulfide film and the zinc from the zinc sulfide should pass into solution as the soluble zinc sulfate or as the slightly soluble zinc hydrate. In the case of the pyrite and chalcopyrite the iron that is displaced by copper cannot pass into solution in an alkaline pulp because ferric hydroxide has an exceedingly low solubility and the probability is that the film of copper sulfide is contaminated by ferric hydroxide precipitate, so that the floatability of the filmed pyrite and chalcopyrite should be less than the floatability of filmed sphalerite.

METATHESIS BETWEEN SPHALERITE AND COPPER SULFATE

To make certain that there is a metathetical reaction, $\text{CuSO}_4 + \text{ZnS} = \text{CuS} + \text{ZnSO}_4$, samples of pure sphalerite were ground under water and treated with copper sulfate solution for 24-hr. periods, after which the pulps were filtered and the filtrate analyzed for copper and zinc. Nearly twice as much zinc was found in solution as there was copper displaced, indicating excess zinc passing into solution over what could be expected. However, in these tests air had access to the pulp and could have caused corrosion of the sphalerite with formation of more than the expected quantity of zinc in the solution, therefore the tests were repeated in pulp from which oxygen was excluded and in which also the sphalerite received a preliminary dilute acid wash to remove all indications of oxidation. The result was about equal amounts of zinc (0.9) found in solution as compared to the copper which had disappeared. These tests were carried on with about 2 lb. of copper sulfate per ton of ore and in no case was a film visible under the microscope or perceptible and yet the chemical evidence shows that a metathetical reaction has taken place between the zinc sulfide and copper sulfate solution.

GENERAL OBSERVATIONS

The ore with which we worked contains chalcopyrite, and most flotation reagents, under conditions of low alkalinity, form a brassy chalcopyrite froth. However, after activating with copper sulfate

the froth takes on a silvery appearance due to the finely ground marmatite which it carries and for clean flotation of the marmatite the alkalinity of the pulp must be increased.

It is a matter of observation on the Jerome ores that when the natural cupric sulfide, covellite (CuS); is present in the ore it is floated with difficulty. Nevertheless, our observations indicate that the film of copper sulfide on sphalerite is cupric sulfide. This anomaly is difficult to explain. The natural cuprous sulfide, chalcocite (Cu_2S), is known to be much more easily floatable and our tendency during the research had been to expect results to point toward the formation of a cuprous sulfide film on activated marmatite, whereas we found cupric sulfide.

Another interesting point in connection with the Jerome ores is the fact that zinc-bearing sulfide ores from near the mine-fire zones behave as though the marmatite had already been activated and require little or no addition of copper sulfate during flotation concentration. Presumably they have already received a bath in copper sulfate solution caused by the mine fires. Furthermore, ores from the upper levels of the mine, not associated with fire zones but showing enough chalcocite to indicate enrichment caused by weathering of the outcrops, are already activated when they reach the flotation machine. Presumably, the ground water passing through them has contained copper sulfate from weathering and has left imperceptible films of the sulfides of copper in every open crack and even in cleavage planes.

The copper sulfate for activation is best added to the flotation pulp after grinding but can be added to the pulp entering the grinding mill. In the laboratory, if copper sulfate was added to the pulp before grinding, about four times as great an amount of copper was needed to get the pulp to the same degree of floatability. This is easily understood because a film of copper sulfide once formed and ground off by attrition is probably inert. Only the unutilized suspension of copper hydroxide or basic carbonate remains in the pulp to activate fresh surfaces exposed by grinding. It is possible that agitation of the pulp with free access of air after the grinding operation will cause rapid oxidation and resolution of inert copper sulfide precipitate and allow it once more to react with zinc sulfide surfaces, activating them. Eventually, any compound of copper, if present in the pulp during long conditioning, will tend to activate the sphalerite toward flotation. Only the natural carbonate minerals of copper, malachite and azurite have been tested by us in this connection and they cause relatively rapid activation but are not as efficient as the copper sulfate.

Another bit of evidence favoring the copper sulfide film theory of activation is contained in the work of experimenters of this laboratory, which will be fully discussed in another proposed paper. We were able to deactivate⁶ an activated marmatite ore by treating it with a solution

⁶ Patent applications are being made on inventions involving this discovery.

of sodium cyanide, a known solvent for the precipitated sulfides of copper. After the cyanide treatment the chalcopyrite in the ore could be floated in the presence of the marmatite with the ordinary flotation reagents, whereas before the treatment the marmatite was floated with the chalcopyrite. He was able to activate, deactivate and reactivate the marmatite toward flotation. A cyanide solution is more efficient than other solvents of cupric sulfide in deactivating marmatite surface because the copper goes to form a very stable cuprocyanide ion from which it is precipitated as sulfide only with difficulty. This is very strong circumstantial evidence that the mechanism of deactivation is the dissolving away of a cupric sulfide film.

CONCLUSIONS

We feel justified in the following conclusions:

1. Copper sulfate, when used as an activator in flotation of sphalerite, forms an invisible but physically detectable film of cupric sulfide on the surface of the sphalerite particles, as evidenced by increased electric conductivity, by chemical metathesis, and by the ability to deactivate with solutions of alkali cyanides, which are known as solvents of copper sulfides.

2. Pyrite, chalcopyrite and some of the gangue minerals likewise consume copper sulfate.

3. In neutral or alkaline pulp the first reaction is precipitation of basic copper carbonate or copper hydroxide and it is these slightly soluble precipitates which are present in solution and suspension during the real activation.

4. The time necessary for efficient activation by copper sulfate, hydrate or basic carbonate is only about one minute, although to provide good mixing or stirring it is probably wise in any flotation machine to allow as much as five minutes.

5. Evidence has been presented to show that most of the copper consumed by sulfide ore is converted to cupric sulfide, through only a portion of the copper sulfide is filmed on the zinc sulfide.

6. While the flotation of pyrite is activated by copper sulfate, it is not so highly activated and a theory is presented to explain this fact.

7. Whether the increased flotation of the activated particles is due to superior floatability of the sulfides of copper or to the tendency of the flotation collector to form a compound with copper, thereby "greasing" the particle surface, is unknown but for the purposes of the present investigation it seems reasonable to claim that one important step in activation consists in filming zinc sulfide with copper sulfide.