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THESIS

Subject THE RATE OF REDUCTION OF ACIDITY OF
DESCENDING WATERS BY CERTAIN ORE AND GANGUE
MINERALS AND ITS BEARING UPON SECONDARY
SULPHIDE ENRICHMENT.

Name George S. Nishihara.

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THE RATE OF REDUCTION OF ACIDITY OF
DESCENDING WATERS BY CERTAIN ORE AND GANGUE MINERALS
AND ITS BEARING UPON
SECONDARY SULPHIDE ENRICHMENT.

A thesis submitted to the Faculty of the
Graduate School of the University of Minnesota by
George Shikataro Nishihara
in partial fulfillment of the requirements for the
degree of Master of Science, May 1914.

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R E P O R T
of
C O M M I T T E E O N T H E S I S

THE undersigned, acting as a committee of the Graduate School, have read the accompanying thesis submitted by George Nishibara, for the degree of Master of Arts. They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Arts.

W. H. Cummings,
Chairman

A. F. Girard,
Samuel A. Hoyt

The rate of reduction of acidity of descending waters by certain ore and gangue minerals and its bearing upon secondary sulphide enrichment.

Introduction.

Since the announcement of the theory of secondary sulphide enrichment by S.F. Emmons¹, W. H. Weed², and C.R. Van Hise³ in 1900 there has been an increasing interest shown in the chemistry and physics of the process involved. A summary of the process of enrichment of copper deposits by J. F. Kemp⁴ appeared in 1906 and the criteria of downward sulphide enrichment were reviewed by F. L. Ransome⁵ in 1910. An important study of sulphides was made in 1888 by Schuerman⁶, and was followed by the contributions of many others⁷.

In the earlier papers on this subject much emphasis was placed upon the permeability of the deposits as controlling the depth at which precipitation goes on. It is known, however, that certain minerals react on the solu-

- 1 Emmons, S. F., The secondary enrichment of ore deposits; Tran. Ame. Inst. Min. Eng., vol. 30, 1900, pp. 117-217.
- 2 Weed, W. H., The enrichment of gold and silver veins; Tran. Ame. Inst. Min. Eng., vol. 30, 1900, pp. 424-448.
- 3 Van Hise, C. R., Some principles controlling the deposition of ores; Tran. Ame. Inst. Min. Eng., vol. 30, 1900, pp. 27-177.
- 4 Kemp, J.F., Secondary enrichment in ore deposits of copper; Econ. Geol. vol. 1, 1906, pp. 11-12.

tion to precipitate the metals much more rapidly than others, and that the chemical and mineralogical composition as well as the permeability of the deposits is important.

Analyses of mine waters in the sulphide ore deposits⁸ show considerable differences as to acidity and state of oxidation, but they are essentially acid sulphate solutions of metals, alkalies, and alkaline earth and in depth the acidity gradually decreases until they become neutral or slightly alkaline. The following experiments were undertaken with a view to ascertaining the rate at which various minerals react with and reduce the acidity of solutions like those that are commonly supposed to be active in sulphide enrichment.

Series 1. Experiments with H₂SO₄

Carefully selected specimen of primary sulphides and gangue minerals common to sulphide ore deposits were crushed in three sizes, and taken in samples of one and five grams. The first size was that passed through No. 20 mesh and caught on No. 80 mesh screen; the second

5 Ransome, F.L., Criteria of downward sulphide enrichment; Econ. Geol. vol. 5, 1910, pp. 205.

6 Schuerman, E., Über die Verwandtschaft der Schwermetalle zum Schwefel; Liebigs Ann. der Chemie, vol. 249, 1888, p. 326.

7 Wiegel, O., Die Löslichkeit von Schwermetallesulfiden in reinem Wasser; Zeitsc. physik. Chemie, vol. 58, 1907, pp. 293-300.

(3)

size, passed through No. 80 mesh and caught on No. 200 mesh screen; the third size, passed through No. 200 mesh screen. Thirty cubic centimeters of 1/8 normal sulphuric acid was added and the bottles were corked but no other precautions were taken against oxidation. The acidity of the solutions was tested by taking out two cubic centimeters of the extract and titrating against tenth normal sodium carbonate at several intervals. The relative activity of minerals in reducing acidity is shown in the following table;

- 7 Wells, R.C., The fractional precipitation of sulphides; Econ. Geol. vol. 5, 1910, pp. 1-14.
Winchell, H. V., Synthesis of chalcocite and its genesis at Butte, Montana; Bull. geol. Soc. Ame., vol. 14, 1903, pp. 259-276.
Sullivan, E.C., Interaction of minerals and water solutions; Bull. U.S.G.S. No. 312.
Read, T.T., Secondary enrichment of copper and iron sulphides; Tran. Ame. Inst. Min. Eng. vol. 37, 1907, p. 300.

Table 1.

relative activity of minerals in reducing acidity of N/8 H₂SO₄.

Minerals in order of activity.	1 day	1 week	2 weeks	3 weeks	1 month	2 months	3 months
Calcite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Rhodochrosite	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Siderite	2.0	0.3	0.0	0.0	0.0	0.0	0.0
Nephelite	1.9	0.6	0.2	0.1 ^b	0.0	0.0	0.0
pyrrhotite	2.2 ^a	1.1 ^a	0.6 ^a	0.1 ^b	0.0	0.0	0.0
Leucite	1.2	1.0	0.8	0.6	0.4	0.3	0.3
Tetrahedrite	2.3	1.9	1.7	1.6	1.5	1.4	1.1
Labradorite	2.3	2.3	2.0	2.0	1.9	1.6	1.3
Hornblende	2.3	2.3	2.1	2.1	1.9	1.8	1.4
Galena	2.5 ^a	2.5 ^a	2.4 ^a	2.4 ^a	2.3 ^a	1.9 ^a	1.4 ^a
Augite	2.4	2.3	2.2	2.2	2.2	1.7	1.6 ^a
Sphalerite	2.5 ^a	2.5 ^a	2.5 ^a	2.5 ^a	2.4 ^a	2.3 ^a	2.1 ^a
Biotite	2.4	2.4	2.3	2.3	2.3	2.2	2.2
Fluorite	2.5	2.5	2.5	2.5	2.5	2.4 ^c	2.3
Orthoclase	2.5	2.5	2.4	2.4	2.4	2.4	2.3
Chalcopyrite	2.5	2.5	2.5	2.4	2.4	2.4	2.4
Arsenopyrite	2.5	2.5	2.5	2.5	2.5	2.5	2.4
Marcasite	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Muscovite	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Pyrite	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Quartz	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Minerals one gram, 80-200 mesh in 30 c.c. acid solution. 2 c.c. extract was titrated against N/10 Na₂CO₃ in each test.

a. H₂S odor. b. H₂S odor very slight. c. White needles of gypsum(?) formed.

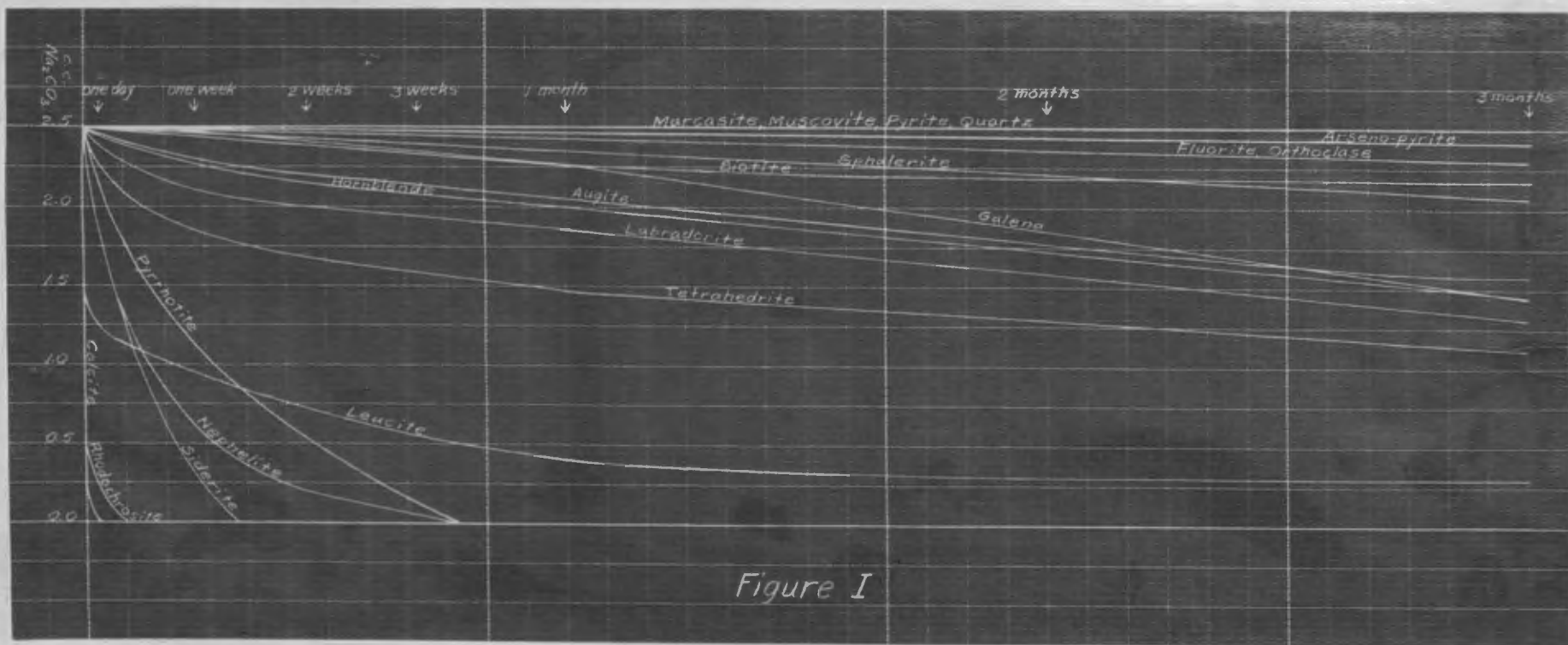


Figure I

Graph showing relative activity of minerals in reducing acidity of $N/8 \text{ H}_2\text{SO}_4$. Minerals one gram, 80-200 mesh, in 30 c.c. acid solution. 2 c.c. extract was titrated against $N/10 \text{ Na}_2\text{CO}_3$ in each test.

Considerable difficulty was experienced in securing perfectly pure specimens, as there were more or less impurities present. The chalcopyrite was so contaminated with calcite that it had to be separated in heavy solution and by the subsequent digestion with dilute acid.

As might be expected the difference in size of grains affected the reducing activities more markedly than different quantities taken or length of time as is shown in the following example;

	Labradorite 1 gr.			Labradorite 5 gr.		
	20-80	80-200	200+	20-80	80-200	200+
1 day	2.4	2.3	2.2	2.2	2.0	1.7
1 wk.	2.4	2.3	2.0	1.8	1.8	1.1
2 wk.	2.2	2.0	1.8	1.6	1.2	0.5
3 wk.	2.2	2.0	1.6	1.5	1.1	0.3
1 mo.	2.1	1.9	1.6	1.0	0.8	0.2
2 mo.	1.8	1.6	1.1	0.8	0.5	0.1
3 mo.	1.7	1.3	1.0	0.6	0.3	0.0

The reduction of acidity by carbonates was rapid. Among sulphides pyrrhotite was the most active and was as active as some of the carbonates. Among silicates leucite and nephelite were strikingly active.

As soon as the neutral point was reached there

7 Allen, E.T., Crenshaw, J.L., and Johnston, J., *Ame. Jour. Sci.* vol. 33, March 1912.

Stokes, H.N., *The action of solutions on pyrite and marcasite*; *Econ. Geol.* vol. 2, 1907, p.22.

Buehler and Gottchalk; *The oxidation of sulphides*; *Econ. Geol.* vol. 5, p. 28 and vol.7, p.15.

Winchell, A.N., *The oxidation of pyrite*; *Econ. Geol.* vol. 2, p. 290.

Erout, F.F., *The oxidation of pyrite*; *Econ. Geol.* vol.3, p.532.

(6)

was no indication of further change toward either alkalinity or acidity. According to Kengott⁹ and Cornu¹⁰, apatite, aragonite, calcite, dolomite, feldspars, magnetite, micas, nephelite, olivine, pyroxenes, serpentine, siderite, spodumine, talc and tourmaline give alkaline reactions to litmus or phenolphthalein, and it was possible that some alkalies have been contributed to the solution in the experiment herein described, but the amount was too small to have affected the solution greatly.

With some minerals activity varied with the length of time. Leucite, for example, was at the beginning more active, but later became less active than pyrrhotite. Initial and persistent activities are, therefore, important factors to be considered.

During the experiment it was noticed that, besides pyrrhotite and sphalerite, the marcasite and galena also evolved hydrogen sulphide gas copiously and reduced acidity with unexpected rapidity. A chemical analysis revealed the presence of manganese, probably as sulphide. As much as 0.04 per cent of manganese was found in a cube of apparently pure galena. Lead and zinc ores from

⁷ Bard, D.C., Econ. Geol. vol.5, p.59.

Cooke, H. C., Secondary enrichment of silver ores; Jour. Geol. vol.21, p.1.

Brokaw, A.D., The solution of gold in the surface alteration of ore bodies; Jour. Geol. vol.18, p.322.

Emmons, W.H., Bull. U.S.G.S., No. 529.

Grout, F.F., Econ. Geol. vol.8, p.407.

Graton, L.C., and Murdock, J., The sulphide ores of copper; Tran. Ame. Inst. Min. Eng. vol.4, p.754.

Wisconsin, and argentiferous galena from several mining districts in California, Nevada, Montana, Colorado, and Spain were analyzed and were found to contain more or less manganese almost certainly as sulphide. The argentiferous galena from Idaho Springs, Colorado, gave 0.12 per cent of manganese. Several marcasites of radiating structure contained nearly 0.1 per cent. Pyrrhotite and sphalerite were also analyzed, but there were no trace of manganese. A print made on a lead acetate paper from a polished surface of galena after an application of dilute acid showed large areas of equal darkness suggesting an exceedingly intimate mixture of galena and alabandite. Both galena and alabandite belong to the same crystallographic system, and might form an isomorphous mixture.

Series 2. Experiments with
ferric sulphate solution.

The decrease of ferric sulphate in mine waters with depth suggests that ferric sulphate has been reduced. In order to determine relative activities of minerals in reducing ferric sulphate a second series of ex-

- 7 Brokaw, A.D., *Jou. Geol.* vol. 21, pp.251-267.
- Spencer, A.C., *Econ. Geol.* vol. 8, p.621.
- 8 Emmons, W.H., *U.S.G.S. Bull.* No.529.
- Emmons, W.H. and Harrington, G.L., *Econ. Geol.* vol.8, p.653.
- 9 Kengott, *Neues Jahrbush*, 1867, p.302.
- 10 Cornu, F., *Tsch. Mitteilung*, vol.24, 417-32, a25, 489.

periment was made. The minerals were treated with ferric sulphate solution, tenth normal with respect to iron, and tested for acidity with tenth normal sodium carbonate and for amount of reduced iron with potassium permanganate solution, one c.c. of which was equivalent to 0.0016 gram of FeO. The order of activity in reducing iron agrees fairly well with that determined by Grout¹¹ with a few exceptions. Table II and III show the relative activities of minerals in reducing ferric sulphate solution.

¹¹ Grout, F.F., Econ. Geol. vol. 8, p.417.

Table II.

Relative activity of minerals in reducing acidity of ferric sulphate, tenth normal with respect to iron.

Minerals in order of activity.	1 day	2 days	3 days	5 days	7 days
Calcite	0.1	0.0	0.0	0.0	0.0
Olivine	2.4	2.0	1.5	1.1	0.0
Sodalite	1.8	1.4	0.8	0.2	0.1
Rhodochrosite	2.4	2.1	1.6	0.8	0.2
Siderite	2.6	2.4	2.1	1.4	0.7
Pyrrhotite	2.7	2.4	2.1	1.4	0.8
Leucite	2.5	2.3	2.2	1.9	1.6
Tetrahedrite	2.7	2.6	2.4	2.2	1.7
Galena	2.7	2.6	2.4	2.3	2.0
Arsenopyrite	2.9	2.9	2.8	2.7	2.5
Labradorite	3.0	3.0	2.8	2.7	2.6
Sphalerite	3.0	2.8	2.8	2.7	2.6
Pyrite	3.0	3.0	3.0	2.6	2.6
Hornblende	3.0	2.9	2.9	2.7	2.6
Enargite	3.0	3.0	3.0	2.9	2.6
Marcasite	3.0	3.0	2.9	2.6	2.6
Kaolinite	2.9	2.9	2.8	2.8	2.7
Augite	3.0	2.9	2.9	2.8	2.7
Chalcopyrite	3.0	3.0	3.0	2.8	2.8
Biotite	3.0	3.0	3.0	3.0	2.9
Orthoclase	3.0	3.0	3.0	3.0	3.0
Muscovite	3.0	3.0	3.0	3.0	3.0
Fluorite	3.0	3.0	3.0	3.0	3.0
Quartz	3.0	3.0	3.0	3.0	3.0

Minerals one gram, 80-200 mesh in 30 c.c. ferric sulphate, N/10 with respect to iron. 2c.c. extract was titrated against N/10 Na_2CO_3 in each test.

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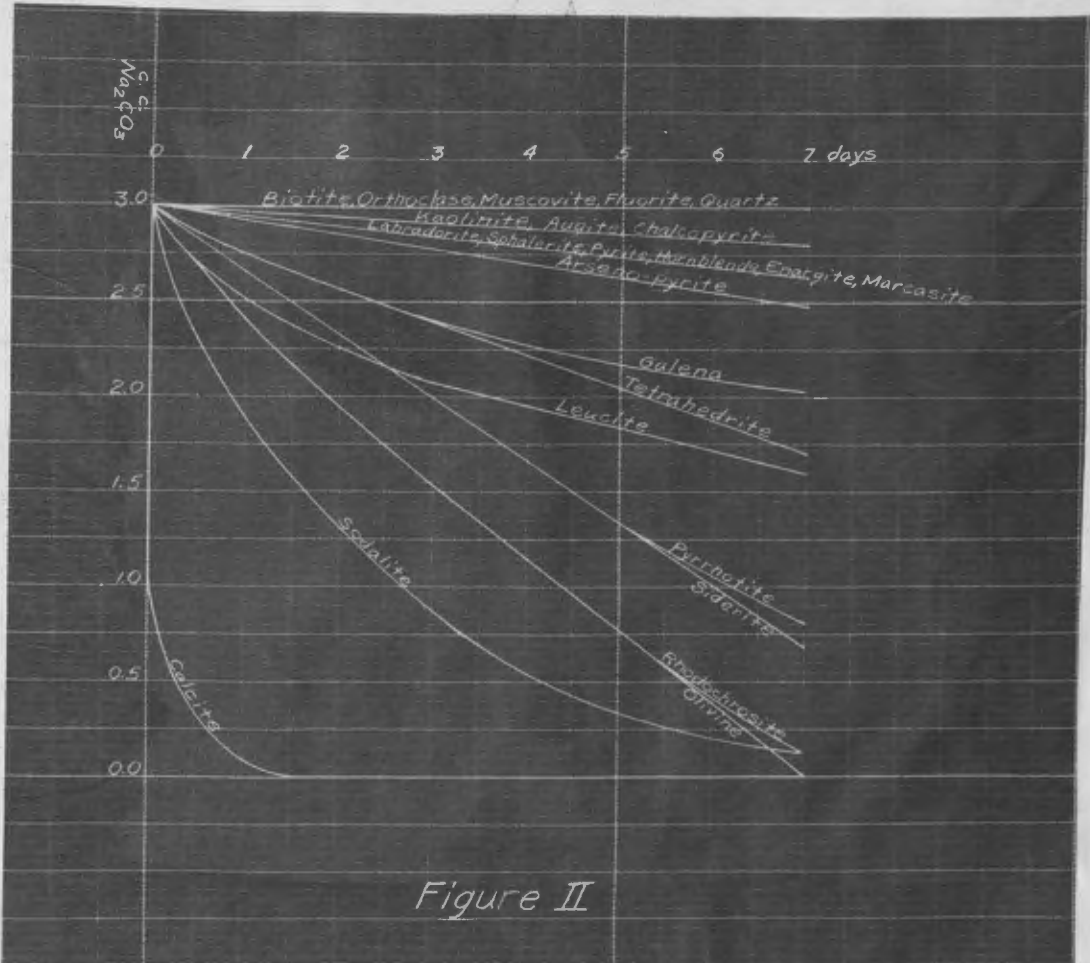


Figure II

Graph showing relative activity of minerals in reducing acidity of ferric sulphate solution, N/10 with respect to iron. Minerals one gram, 80-200 mesh, in 30 c.c. acid solution. 2 c.c. extract was titrated against N/10 Na_2CO_3 in each test.

Table III.

Relative activity of minerals in reducing iron in ferric sulphate solution, N/10 with respect to iron.

Minerals in order of activity.	1 day	2 days	3 days	5 days	7 days
Pyrrhotite	0.2	1.2	1.9	3.2	4.3
(Siderite)	0.2	1.0	1.6	2.7	3.8
Tetrahedrite	0.2	0.7	1.2	1.9	2.3
Arsenopyrite	0.3	0.5	0.6	1.2	1.7
Galena	0.6	0.7	1.0	1.2	1.5
Enargite	0.2	0.3	0.5	0.6	1.1
Marcasite	0.2	0.4	0.4	0.8	0.9
Pyrite	0.2	0.3	0.5	0.7	0.8
Sphalerite	0.1	0.3	0.4	---	0.5
(Olivine)	0.0	0.2	0.2	0.3	0.4
Chalcopyrite	0.1	0.2	0.2	0.2	0.3
(Hornblende)	0.0	0.0	0.0	0.1	0.2
Orthoclase	0.0	0.0	0.0	0.0	0.0
Calcite	0.0	0.0	0.0	0.0	0.0
Rhodochrosite	0.0	0.0	0.0	0.0	0.0
Fluorite	0.0	0.0	0.0	0.0	0.0
Labradorite	0.0	0.0	0.0	0.0	0.0
Leucite	0.0	0.0	0.0	0.0	0.0
Muscovite	0.0	0.0	0.0	0.0	0.0
Quartz	0.0	0.0	0.0	0.0	0.0
Sodalite	0.0	0.0	0.0	0.0	0.0
Augite	0.0	0.0	0.0	0.0	0.0
Biotite	0.0	0.0	0.0	0.0	0.0
Kaolinite	0.0	0.0	0.0	0.0	0.0

(10)

Minerals one gram, 80-200 mesh in 30 c.c. ferric sulphate, N/10 with respect to iron. 2 c.c. extract was titrated against KMnO_4 1 c.c. = 0.0016 gr. FeO in each test.

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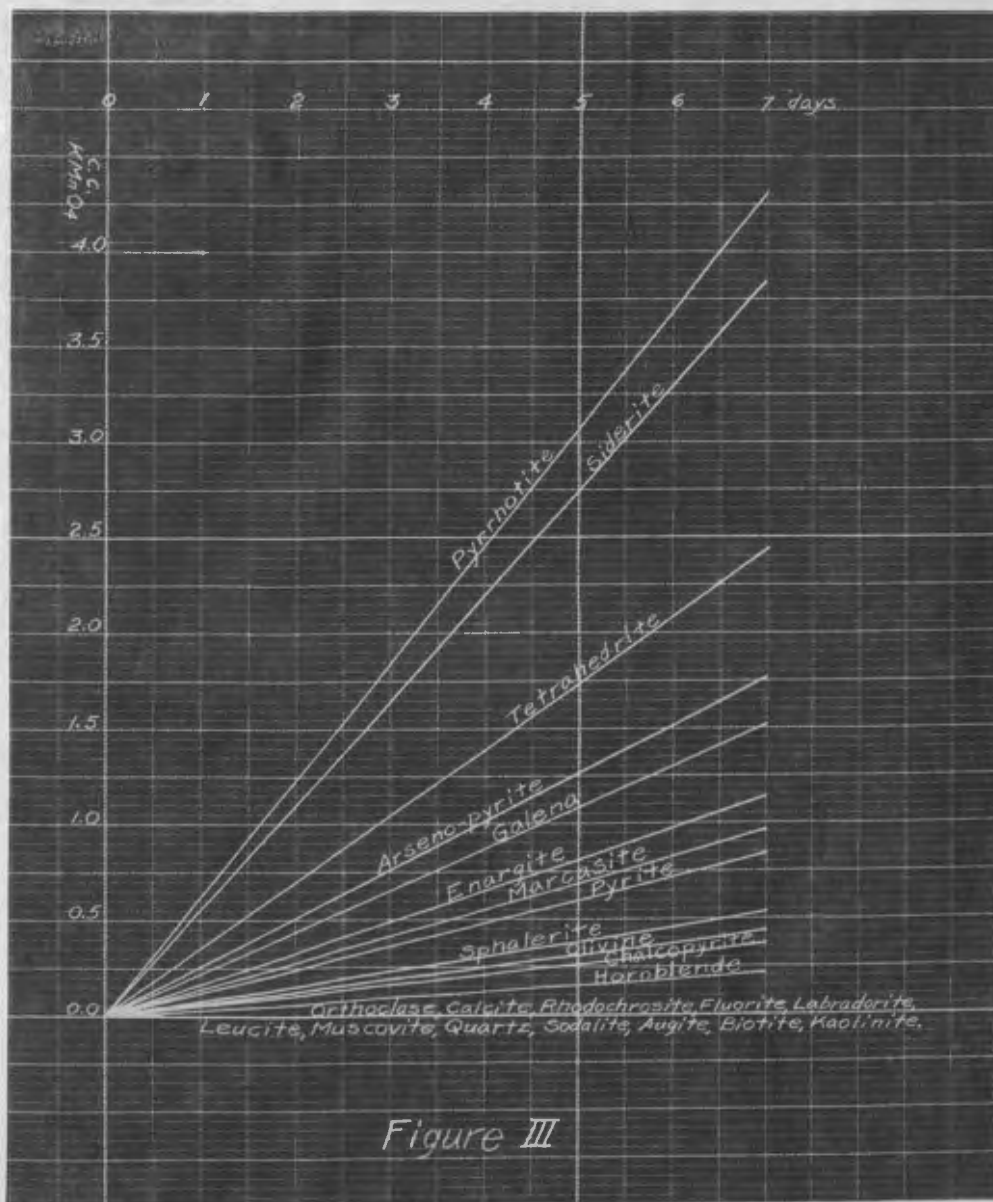


Figure III

Graph showing relative activity of minerals in reducing iron in ferric sulphate solution, N/10 with respect to iron. Minerals one gram, 80-200 mesh, in 30 c.c. acid solution. 2 c.c. extract was titrated against KMnO_4 , one c.c. of which was equivalent to 0.0016 gr. FeO, in each test.

As shown in the Tables II and III the reduction of acidity is in general nearly proportional to the amount of iron reduced. Pyrrhotite and siderite, however, not only reduced acidity, but they also supplied ferrous iron.

Comparing Table I and II it may be noted that arsenopyrite and pyrite are more active on ferric sulphate than on sulphuric acid.

The calcite which was the most active in both series of experiments did not reduce iron, but precipitated it as ferric hydroxide.

As in the series of experiments in sulphuric acid no further change in acidity or alkalinity could be detected after the neutral point had been reached. Moreover the amount of reduced iron remained the same for three months. A quantitative analysis confirmed the supposition that the total iron was combined with SO_4 in the form of FeSO_4 .

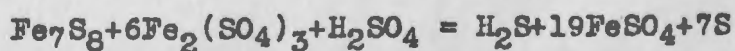
According to Stokes¹² the action of ferric sulphate on pyrite proceeds as follows;

Bull 186 U.S.G.S P15
 12 Stokes, H.N. Econ. Geol. vol. 2, p.22.

(12)



This indicates a considerable amount of sulphuric acid is generated. Titration against tenth normal sodium carbonate solution, however, showed a gradual decrease of acidity, and finally the solutions with active sulphides became neutral. With pyrrhotite the solution became neutral at the end of two weeks when evolution of hydrogen sulphide gas ceased and hydroxide of iron had begun to form. A probable reaction in this case may be indicated by the following equation, which was suggested by Grout;



It is known that gypsum and kaolinite are formed by acid solution attacking calcite of limestone and feldspars of igneous rocks. Gypsum and kaolinite are associated with chalcocite at many places and inference is plausible that acid is produced by the chalcocite forming process. These experiments described above, however, show that acid sulphate and ferric sulphate

reacting on pyrite and several other sulphides may be reduced without generation of acid.

Series 3. Experiments with ferrous and cupric sulphate solution.

All the carbonates are active in reducing acidity. Calcite readily precipitates iron and copper out of a mixed solution of ferrous and cupric sulphate. This led D. C. Bard¹³ to conclude that calcite gangue would tend to inhibit secondary enrichment of sulphides. There are, however, numerous examples of secondarily enriched sulphide ore bodies in limestones.

Recently A. C. Spencer¹⁴ obtained secondary bornite and other sulphides coating on chalcopyrite in a cupric and ferrous sulphate solution in the presence of calcite, and he suggests that calcite does not inhibit the downward migration of copper, as in his experiment the calcite did not precipitate copper. In a solution even slightly acid bornite is not precipitated on chalcopyrite, and this suggests that the presence of a reducing substance is necessary.

13 Bard, D.C., Econ. Geol. vol.5, p.5.

14 Spencer, A.C., Econ. Geol. vol.8, p.621.

In an experiment a solution of iron sulphate and copper sulphate was brought simultaneously in contact with calcite and chalcopyrite, and was found that the calcite precipitated iron as ferric hydroxide and copper as carbonate, and at the same time chalcopyrite was coated with the secondary bornite. When ferric sulphate was introduced the bornite coating was quickly destroyed, but later when the calcite had neutralized ferric sulphate the secondary deposition went on again without interruption. The calcite precipitated the iron as ferric hydroxide and copper as carbonate, and at the same time reduced the acidity of the solution, and the sulphide was deposited as before the introduction of ferric sulphate. In order to ascertain the chemical composition of the coating the following test was made;

A selected specimen of chalcopyrite was crushed and passed through a No. 20 mesh sieve and caught on a No. 40 mesh sieve and washed with dilute acid to remove any calcite present. After drying two equal portions of the chalcopyrite were weighed into beakers, and into one

of them cupric and ferrous sulphate and calcium carbonate were added. A boiling temperature was employed in order to accelerate the chemical action. When sufficiently tarnished the content was dumped on a No. 40 mesh sieve and washed thoroughly with hot water until the wash water no longer showed copper. The mineral then was treated with a fairly strong hydrochloric acid and the coating was dissolved out. At the same time the same amount of hydrochloric acid was added to the other beaker in which an equal portion of the chalcopyrite had been placed. Some ammonia water was added to both solutions and brought to boiling to precipitate iron. The equal volumes of the solutions were compared for copper contents. The tube containing the solution from the tarnished chalcopyrite had decidedly more copper than that from the chalcopyrite alone. Also the iron precipitate obtained from the minerals treated with cupric and ferrous sulphate solution was more than that from the one that was not treated with acid solution. This was to show that ~~that~~ the coating was not a mere

physical change but a change in chemical composition. Further in connection with this experiment the following results were obtained in hot solutions;

Chalcopyrite and pyrite in contact with	Color of original mineral
1. Cupric sulphate,	Unchanged.
2. Ferrous sulphate,	Unchanged.
3. Ferric sulphate,	Unchanged.
4. Cupric and ferric sulphate,	Unchanged.
5. Cupric, and ferric sulphate, and calcite,	Unchanged.
6. Cupric sulphate and calcite,	Unchanged.
7. Ferrous sulphate and calcite,	Unchanged.
8. Cupric and ferrous sulphate,	Tarnished chalcopyrite.
9. Cupric, ferrous, and ferric sulphate,	Tarnished chalcopyrite, but in a less degree.
10. Cupric, ferrous, ferric sulphate and calcite,	Tarnished chalcopyrite.

As indicated by the preceding experiments a solution of cupric and ferrous sulphate coming in contact with carbonate will precipitate carbonate of copper and hydroxide of iron, and at the same time deposit bornite on chalcopyrite. Where pyrite occurs abundantly there is more likely to be an excess of ferric sulphate over ferrous sulphate. In the absence of calcite gangue secondary bornite would not be deposited on primary chalcopyrite in the zone of oxidation where sulphuric acid and ferric sulphate are present. Unless active sulphide sulphides or gangue minerals are present ferric sulphate will not readily be reduced and cupric sulphate will migrate farther down without being impoverished. Enrichment of sulphide in this case would be expected at greater depth.

Under similar geologic condition, the vertical extent of enriched sulphide zone, therefore, depends on the mineral composition of the primary ore, as has already been pointed out by Emmons¹⁵. If deposits carry alabandite, or pyrrhotite, or sphalerite, or tetrahedrite or other active sulphides ferric sulphate is readily

15 Emmons, W.H., U.S.G.S. Bull. No. 529.

reduced and causes precipitation of secondary sulphide. Pyrrhotite bearing sulphide deposits at Ducktown, and Encampment district, Wyo. and several other mining districts the secondary sulphide zone is rich but less extensive in depth compared with other districts where pyrrhotite does not occur in the primary ores.

Other conditions being equal the rate of activities of minerals with acid waters as shown in Table I and II may be regarded to be approximately proportional to the relative extent of enriched sulphide zone. The character of mineral composition of the primary ore bears, therefore, an important relation to the vertical extent of enriched ores.

Series 4. Experiments with ferric and Cupric sulphate solution.

In the upper zone of sulphide ore deposits cupric and ferric sulphate are abundant. Secondarily deposited sooty chalcocite is supposed to have been precipitated by several reducing agent including hydrogen sulphide gas which can be generated by active sul-

phides when they are brought in contact with acids.

Preliminary to the experiment the acidity of important sulphates that occur in mine waters in sulphide ore deposits was tested, using methyl orange as an indicator.

Acid to indicator	Neutral or alkaline to indicator
$\text{Fe}_2(\text{SO}_4)_3$	FeSO_4
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	ZnSO_4
H_2SO_4	MnSO_4
	MgSO_4
	CaSO_4

Pyrrhotite, sphalerite, and alabandite were treated with those sulphates reacting acid to the indicator and the following results were obtained;

Action of acid solutions on pyrrhotite, sphalerite, and alabandite.

Acid solution	Pyrrhotite	Sphalerite	Alabandite
H_2SO_4 $\text{Fe}_2(\text{SO}_4)_3$ CuSO_4	H_2S evolved. H_2S evolved. No H_2S .	H_2S evolved. H_2S evolved. No H_2S .	H_2S evolved. H_2S evolved. No H_2S .

(20)

The behavior of mixed solution of ferric and cupric sulphate was determined in the following experiment. Minerals one gram each, 80- 200 mesh, were put in test tubes and 25 c.c. of tenth normal cupric sulphate and 25 c.c. of ferric sulphate, tenth normal with respect to iron, were added. The acidity and the amount of reduced iron were tested at several intervals. The results are shown in the following tables IV and V.

Table IV.

Relative activity of minerals in reducing acidity of N/10 CuSO_4 and $\text{Fe}_2(\text{SO}_4)_3$, N/10 with respect to iron.

Minerals in order of activity.	1 day	2 days	4 days	8 days	18 days
Calcite	1.5	0.0	0.0	0.0	0.0
Siderite	3.1	2.8	2.4	1.6	0.3
Tetrahedrite	3.3	3.2	3.0	2.6	1.9
Galena	3.3	3.2	3.1	2.7	2.2
Pyrrhotite	3.3	3.2	3.2	3.1	2.6
Arsenopyrite	3.2	2.9	2.8	2.7	2.7
(Chalcocite)	3.2	3.2	3.2	3.1	2.7
Sphalerite	3.2	3.2	3.2	3.1	2.7
Pyrite	3.2	3.2	3.2	3.1	2.9
Marcasite	3.2	3.2	3.2	3.1	3.1
Enargite	3.3	3.3	3.3	3.3	3.2
Chalcopyrite	3.3	3.3	3.3	3.3	3.3

Minerals one gram, 80-200 mesh in 25 c.c. each N/10 CuSO_4 and $\text{Fe}_2(\text{SO}_4)_3$, N/10 with respect to iron. 2 c.c. extract was titrated against N/10 Na_2CO_3 in each test.

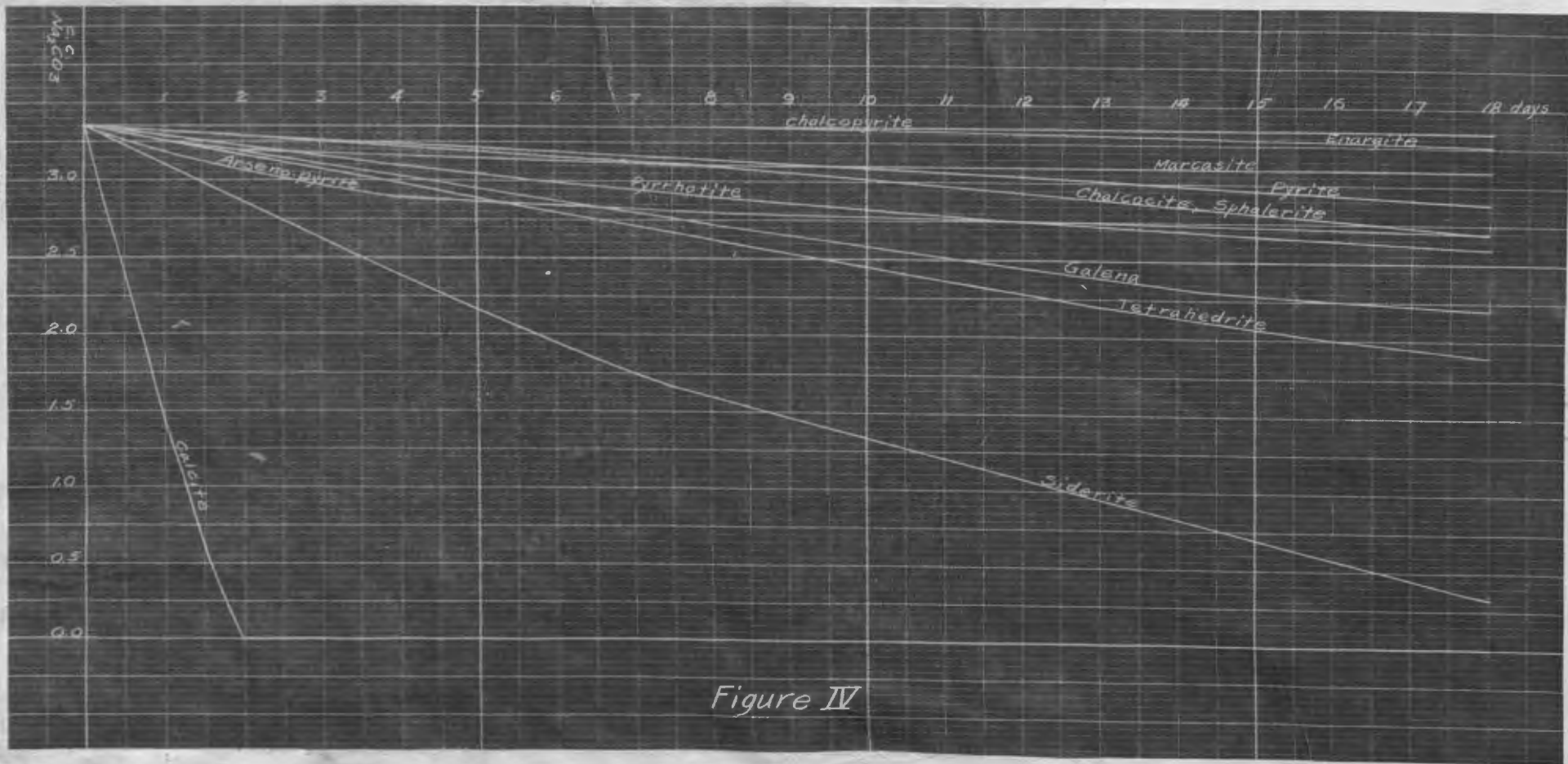


Figure IV

Graph showing relative activity of minerals in reducing acidity of mixed solution, 25 c.c. each N/10 CuSO₄ and Fe₂(SO₄)₃, N/10 with respect to iron. Minerals one gram, 80-200 mesh, in acid solution. 2 c.c. extract was titrated against N/10 Na₂CO₃ in each test.

Table V.

Relative activity of minerals in reducing iron in solution of N/10 CuSO_4 and $\text{Fe}_2(\text{SO}_4)_3$, N/10 with respect to iron.

Minerals in order of activity.	1 day	2 days	4 days	8 days	18 days
Siderite	0.2	0.3	0.6	1.5	4.2
Arsenopyrite	0.2	0.4	0.7	1.5	2.6
Pyrrhotite	0.0	0.1	0.4	1.0	2.5
Tetrahedrite	0.0	0.0	0.2	0.8	2.3
(Chalcocite)	0.1	0.1	0.2	0.6	1.7
Galena	0.1	0.1	0.2	0.6	1.6
Sphalerite	0.0	0.0	0.0	0.3	1.4
Pyrite	0.0	0.0	0.0	0.2	1.2
Marcasite	0.0	0.0	0.0	0.2	1.2
Chalcopyrite	0.0	0.0	0.0	0.0	0.5
Calcite	0.0	0.0	0.0	0.0	0.0

Minerals one gram, 80-200 mesh in 25 c.c. each N/10 CuSO_4 and $\text{Fe}_2(\text{SO}_4)_3$, N/10 with respect to iron. 2 c.c. extract was titrated against KMnO_4 , one c.c. was equivalent to 0.0016 gram FeO , in each test.

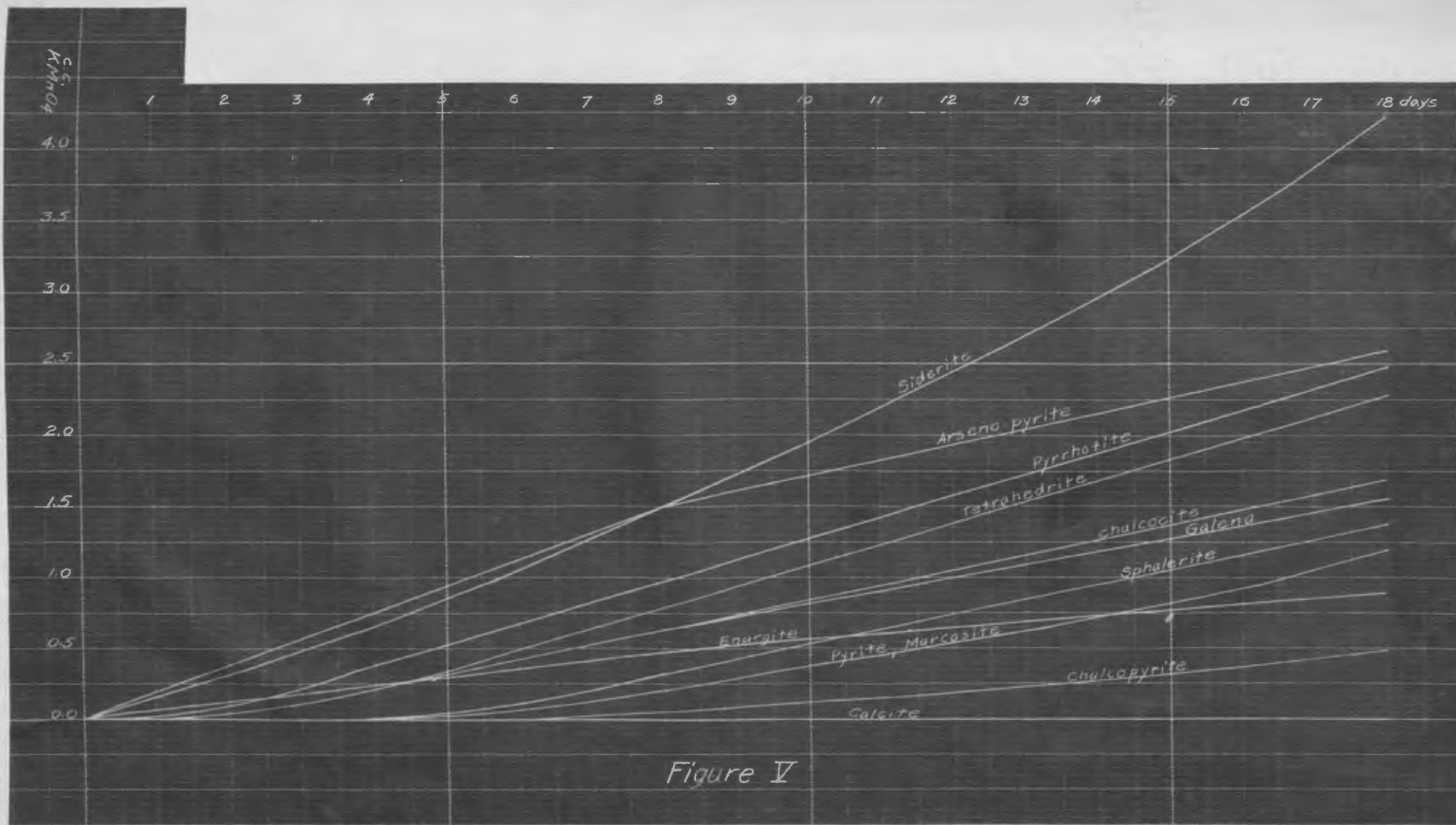


Figure V

Graph showing relative activity of minerals in reducing iron in mixed solution, 25 c.c. each N/10 CuSO_4 and $\text{Fe}_2(\text{SO}_4)_3$, N/10 with respect to iron. Minerals one gram, 80-200 mesh, in acid solution. 2 c.c. extract was titrated against KMnO_4 , one c.c. of which was equivalent to 0.0016 gram FeO , in each test.

It was found that pyrrhotite and sphalerite did not evolve hydrogen sulphide gas in the presence of N/10 CuSO_4 as has already been noted by Grout¹⁶. Even high temperature was employed no H_2S was generated. It was thought that a thin film of copper precipitate might have been formed around the mineral grains and prevented further action of acid, consequently inhibiting evolution of hydrogen sulphide gas. The following test was, therefore made;

One gram of pyrrhotite passed through a No. 20 and caught on a No. 40 mesh was treated with 25 c.c. of cupric and ferric sulphate solution and heated for five minutes. It was filtered and the mineral was washed thoroughly with hot water until the wash water showed no trace of copper. A few c.c. of fuming nitric acid was added to dissolve mineral coating which was supposed to be there. The same amount of nitric acid was added to the blank. Both solutions were filtered, and sufficient ammonia was added and warmed to precipitate iron. The two filtrates were colorimetrically compared. A

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slight indication of an addition of copper could be detected. The retarding action by CuSO_4 is possibly due to the formation of thin film of secondary sulphide upon primary mineral or it may be attributed to some property of CuSO_4 .

In connection with this experiment further study on the precipitation of sulphide was made with alabandite. A piece of pyrite and chalcopyrite and ground alabandite were put in a test tube, and cupric and ferric sulphate solution were introduced. At the end of two days it was noted that hydrogen sulphide gas was generated and copper sulphide was precipitated, and pyrite and chalcopyrite were coated with chalcocite and bornite respectively. A trace of chalcocite coating on bornite coating was noted on the chalcopyrite.

Summary and Conclusions.

The action of sulphuric acid or metallic sulphate solutions on metallic sulphides and other minerals results in a gradual decrease in acidity and general tendency toward neutralization.

Ferric sulphate attacking sulphides in the presence of some oxygen did not increase acidity at any stage of the experiment.

In the reduction of acidity as well ^{as} in the reduction of ferric iron, the rate of activity of sulphide minerals varies greatly.

Acidity of descending solutions should decrease with depth, and ultimately the solutions would become neutral or alkaline.

Other factors being equal, the vertical extent of secondary sulphide zone should show a relationship to the mineral composition of the primary ores.

Either sulphuric acid or ferric sulphate or both generate hydrogen sulphide gas when brought in contact with pyrrhotite or sphalerite or alabandite, but cupric

sulphate does not generate hydrogen sulphide.

It was found that manganese sulphide ,probably alabandite, is present in small amounts in many specimens of galena and marcasite from widely separated regions. Of specimens of galena in the laboratory collection at the University of Minnesota not one was found to be free from manganese sulphide. Since alabandite is nearly fifteen time as active as pyrrhotite, according to Grout, it appears certain that the hydrogen sulphide evolved from these sulphides was due almost wholly to the manganese sulphide.

In a mixed solution of cupric and ferrous sulphate in the presence of calcite the deposition of bornite on chaloopyrite began only when the solution had become nearly neutral.

In the presence of cupric sulphate,pyrrhotite, and sphalerite, very weak acids do not generate hydrogen sulphide gas.

The writer is much indebted to Dr. W. H. Emmons under whose personal direction this problem has been worked out and Professor F. F. Grout, who outlined the experiments and who has kindly given valuable suggestion and assistance throughout the investigation.