

## OXIDATION OF SULPHIDES.

H. A. BUEHLER AND V. H. GOTTSCHALK.

An examination of that portion of any body of sulphide ores occurring within the zone of weathering usually gives ample evidence of extensive solution. The occurrence of oxidized ores in this zone indicates that oxidation has preceded solution and that the transfer of the metal is largely due to the solubility of the metallic salts formed during this process. In most cases, the slight solubility of the natural sulphides precludes an extensive transfer through simple solution. Field evidence is ample to show that under natural conditions the sulphides are oxidized. The relative speed of oxidation, however, has not been definitely determined and the influence of the oxidation of one sulphide upon another is as yet only inferred from field relations. It was for the study of these problems that the experiments cited below were undertaken.

To assign a definite figure for the speed of oxidation of any one sulphide is quite impossible, since the rapidity of the action depends upon the nature and extent of the surfaces exposed, upon the details of the experimental arrangement, as well as upon the incidental variations during the course of the determination.

Under natural conditions it is very probable that certain salts dissolved at or near the surface exert an oxidizing or solvent effect upon the metallic ores and in this way hasten transportation. Without doubt certain impurities in every ore body also materially affect solution, either by direct chemical action or through simple removal, whereby the sulphide becomes porous exposing a larger surface to the action of oxidizing waters. Likewise the occurrence of other impurities may tend to decrease the solubility and thus hinder transportation.

Two recent papers<sup>1</sup> on the oxidation of pyrite, lead to the

<sup>1</sup> Winchell, *ECONOMIC GEOLOGY*, Vol. II., p. 290 (1907); Grout, *ECONOMIC GEOLOGY*, Vol. III., p. 632 (1908).

conclusion that this mineral is quite slowly oxidized. A somewhat different method of treatment has given us fairly consistent results since its first trial nearly four years ago. Our experiments show not only a measurable oxidation for most sulphides treated, but also indicate that pyrite or marcasite, when mixed with other sulphides, causes a much more rapid oxidation of the second sulphide. We find, for instance, that sphalerite, galena, covellite and enargite are oxidized from eight to twenty times faster in the presence of an equal amount of pyrite or marcasite than when treated alone under the same conditions. Whether or not marcasite and pyrite are the only sulphides acting as an accelerator has not as yet been determined. Experiments are now being carried on to determine this fact.

#### EXPERIMENTAL.

The apparatus (Fig. 1) consisted of a 6-cm. funnel, fitted with a 4-cm. Hirsch filtering plate on which was spread a double

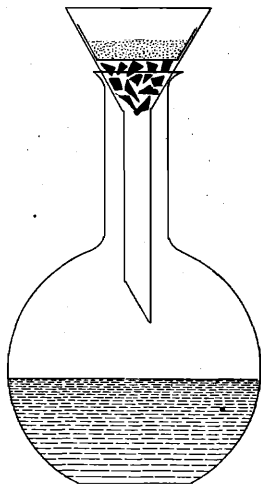


FIG. 1.

layer of 9-cm. S. & S. ash-free filter paper. The filter plate was supported by pieces of broken porcelain. The funnel rested upon the neck of a 700-c.c. Jena flat-bottom flask, as shown.

In the various experiments, the following sulphides were used: pyrite, marcasite, chalcopyrite, sphalerite, galena and covellite (containing some pyrite). The purest minerals available were selected and were especially sorted before being ground to pass a 100-mesh sieve.

The various sulphides were treated alone and when mixed with an equal portion, by weight, of pyrite or marcasite. In series "A," 10 grams of the sulphides were used, while in series "B" and in the case of the copper ores, 5 grams were used. In each experiment the ore was spread evenly upon the filter paper prepared as described above. The sulphides were then washed twice daily with 5 c.c. of distilled water, treatment being continued for about three months. The amount of solution in each flask at the end of the experiment was ordinarily from 400 to 600 c.c. The experimental results follow:

#### PYRITE.

The evidences of action were manifested soon after beginning the treatment; the filter paper shows yellow stains of oxide of iron; the solution collected in the flask soon assumes a yellowish tint and deposits yellowish brown basic oxide. The filter paper at the end of the experiment was found to be hard and brittle.

	Grams of Iron Washed Through.	Percentage of Iron Washed Through.
Pyrite, Series "A,"	.1185 <sup>1</sup>	2.5 per cent.
Pyrite, Series "B,"	.0857	3.7 per cent.

<sup>1</sup> A portion lost.

#### SPHALERITE.

Alone, the sulphide shows no visible trace of action either on the filter or in the solution. When mixed with pyrite there was a small amount of iron oxide on the filter.

	Grams of Zinc Washed Through.	Percentage of Zinc Washed Through.
Sphalerite, Series "A,"	.0125	.2 per cent.
Sphalerite and pyrite, Series "A,"	.2788	4.2 per cent.

#### GALENA.

Alone, the sulphide shows no visible trace of action either on the filter or in the solution. When mixed with the pyrite,

oxide of iron occurs on the filter paper; the solution is colorless, but in all such cases a white precipitate of lead sulphate forms in the flask. The precipitate consists of fine tabular crystals.

	Grams of Lead Washed Through in Solution.	in Precipitate.	Percentage of Lead Washed Through.
Galena, Series "A,"	.0005	none	.005
Galena and Pyrite, Series "A,"	.0125	.0504	.7
Galena, Series "B,"	.002	none	.05
Galena and pyrite, Series "B,"	.0111	.0149	.6

#### COPPER ORES.

In general the evidences of action vary with each ore treated Alone, chalcopyrite gives a slightly bluish colored solution; enargite shows no perceptible action, while the covellite, which contained some pyrite, and the mixed copper ore gave slightly colored solutions. When mixed with marcasite or pyrite all the solutions have a deep blue color, depositing a slightly brownish precipitate in the flask. The chalcopyrite was not treated with pyrite or marcasite. The mixed copper ore contained 48.34 per cent. copper, and 19.33 per cent. iron.

Copper Ores.	Grams of Copper Washed Through	Percentage of Copper Washed Through.
Covellite,	.0905	Greater than 2.7 per cent.
Covellite and marcasite,	.9187	Greater than 27.6 per cent.
Mixed ore,	.0170	0.35 per cent.
Mixed ore and pyrite,	.3288	6.8 per cent.
Enargite,	none <sup>1</sup>	none
Enargite and pyrite	.2169 <sup>1</sup>	About 10.0 per cent.
Chalcopyrite,	.0183	About 1.0 per cent.

<sup>1</sup> No arsenic in solution.

In the results cited, only the metallic ion has received consideration. To obtain exact figures covering the oxidation of the iron sulphide in each case will require accurate analyses of the residue remaining on the filter paper. The proportion of ferrous and ferric ions occurring in the solution is no doubt materially influenced by the presence of the organic matter of the filter paper. That some action takes place is indicated by the decomposition of the filter. This factor has been eliminated by the use of asbestos in experiments now in progress. In those

experiments where pyrite was used the solution invariably shows an excess of sulphate ions indicating the presence of free sulphuric acid.

Winchell and Grout have recently published figures on the rate of oxidation of pyrite. They give a maximum of .08 of one per cent. of the sulphide oxidized after a year's treatment, while we obtain an oxidation of approximately 3 per cent. after treating the sulphide only three months. In order to determine if this difference is due to the fineness of grinding or due to the method of treatment, we have recently started two experiments using pyrite of the same size as in the experiments by Grout and by Winchell, ten grams of the sulphide being used in each case. The sulphides were washed three time daily with 10 c.c. of distilled water. While Winchell was unable to make quantitative determinations of the constituents in solution at the end of three months and was unable to find any evidences of solution at the end of one month, we are able to make quantitative determinations at the end of the first week and have made weekly analyses in order to determine the rate of oxidation in each case. The following are our results showing the amount of material oxidized each week, the analyses being started at the end of three weeks' treatment, the solution of the third week only being used in the first case. These analyses usually show a slight excess of sulphur, indicating the presence of free sulphuric acid.

Weeks.	Through 20 on 40 Mesh.		Through 40 on 60 Mesh.	
	FeSO <sub>4</sub> Grams.	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> Grams.	FeSO <sub>4</sub> Grams.	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> Grams.
Third	.0016	.0005	.0028	.0024
Fourth	.0011	.0013	.0035	.0016
Fifth	.0009	.0016	.0026	.0041
Sixth	.0009	.0017	.0026	.0026
Seventh	.0015	.0001	.0033	.0074
Eighth	.0009	.0005	.0032	.0024
Ninth	.0010	.0007	.0022	.0011

According to the above results at the end of seven weeks there has been a total oxidation of .0072 gram of iron when using particles the same size as used by Winchell (through 20- on 40-mesh) and .019 gram of iron when using particles the same

size as used by Grout (through 40- on 60-mesh). These figures are 0.107 and 0.28 of 1 per cent. respectively of the original sulphides used. Assuming that the rapidity of oxidation remains uniform throughout the year, we would obtain under our conditions, a total oxidation of 0.8 of 1 per cent., and 1.08 per cent. in that time.

The above experiments indicate to some extent the influence of the fine grinding upon the speed of oxidation and while we realize that by grinding the sulphides to pass a 100-mesh sieve the speed of oxidation has been measurably increased, we do not believe that the general nature of the results is affected by such treatment.

Whatever values are given ultimately for the rate of oxidation of a single sulphide, the results of the above experiments show beyond a doubt that the admixture of pyrite or marcasite with sphalerite, galena or copper sulphides, increases the rate of oxidation of the latter very materially. Whether or not there is a reciprocal action upon the pyrite or marcasite, has not yet been definitely determined.

In the above experiments we have endeavored to place the sulphides under conditions similar to those obtaining in the zone of oxidation; namely, alternate wet and damp periods, sufficient water being used to intermittently wash away the soluble salts formed.

The possible influence of one sulphide upon the speed of oxidation of another, was first called to our attention in the case of lead and zinc ores through field observations in the Joplin district of southwest Missouri. The ore bodies in this district usually show extensive oxidation and solution and in those areas where marcasite or pyrite is present the mine waters usually carry a considerable quantity of zinc.

That fine grinding is not a requisite to perceptible oxidation is shown by samples of marcasite which have been stored in the loft of the Bureau of Geology and Mines for the past few years. At the present time many of these are partly covered by crystals

of ferrous sulphate, which salt also occurs along the cracks and cleavage planes throughout the specimens. The samples are badly disintegrated simply through the medium of moisture in the air. They have not at any time been subjected to usual weathering conditions.

The influence of pyrite and marcasite upon the oxidation of sphalerite is apparent from the analyses of mine waters collected in the Joplin district. The following are taken from a series of ten, and are representative in every way:

	Arkansas.	Victor.	O K	Winslow.
KCl .....	9.5	6.1	0.0	4.0
K <sub>2</sub> SO <sub>4</sub> .....	0.0	0.0	0.0	2.2
NaCl .....	0.0	1.3	4.5	0.0
Na <sub>2</sub> SO <sub>4</sub> .....	130.3	38.5	30.8	14.7
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ..	68.3	73.6	3.3	2.2
CaSO <sub>4</sub> .....	1528.0	924.6	371.5	59.7
Ca(HCO <sub>3</sub> ) <sub>2</sub> ..	0.0	0.0	0.0	250.6
MgSO <sub>4</sub> .....	Trace	192.6	60.4	0.0
FeSO <sub>4</sub> .....	611.9	387.7	2.6	6.4
ZnSO <sub>4</sub> .....	586.2	851.7	1.2	0.0
PbSO <sub>4</sub> .....	0.04	0.0	0.0	0.0
SiO <sub>2</sub> .....	23.2	23.2	7.4	11.3
H <sub>2</sub> SO <sub>4</sub> .....	170.9	251.7	0.0	0.0
CO <sub>2</sub> (free ..	12.0	87.0	19.7	8.8

(Figures indicate parts per million.)

The waters from the Victor and Arkansas mines contain large quantities of free sulphuric acid and ferrous sulphate, and are heavily charged with zinc sulphate. The waters from the O. K. and Winslow mines, on the other hand, which contain no free sulphuric acid and but small quantities of ferrous sulphate, carry only traces of zinc in solution. At other points throughout the Joplin district similar conditions are found and it is very evident that the presence of pyrite or marcasite increases the rate of oxidation.

#### SUMMARY.

The experiments described in the foregoing pages show: (1) That natural sulphides are perceptibly oxidized by atmospheric air in the presence of water. (2) That pyrite and marcasite

in contact with other natural sulphides greatly increases the rate of oxidation of the latter sulphides. (3) That fine grinding affects the rate of oxidation. (4) That analyses of mine waters from the southwest Missouri lead and zinc district indicate the similarity of natural oxidation processes to those obtained in the laboratory.