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OXIDIZED COPPER MINERALS



BY

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By John D. Sullivan<sup>2</sup>

INTRODUCTION

The present article is one of a series which is being prepared by the Southwest Experiment Station of the United States Bureau of Mines in cooperation with the Department of Mining and Metallurgy, University of Arizona, Tucson, Ariz., of papers dealing with factors involved in the leaching of copper ores.

A knowledge of the time required to dissolve the various copper minerals present in ores, as well as of the consumption of leaching reagents is very desirable, because with the decrease of the Nation's total tonnage of sulphide ores increasing attention is being given to the recovery of copper by leaching methods from low-grade disseminated ore containing both oxidized and sulphide minerals. As leaching has already been applied with success and profit, this study was undertaken to determine certain fundamental characteristics that are applicable to all ores suitable for leaching.

Preceding articles have dealt with the ingress of leaching solutions into rocks<sup>3</sup> and the removal of soluble copper from leached ores.<sup>4</sup> In this paper the dissolution of certain oxidized copper minerals will be discussed.

ACKNOWLEDGMENTS

The author wishes to acknowledge the assistance and helpful suggestions of Mr. G. L. Oldright, supervising engineer, nonferrous metallurgical section United States Bureau of Mines.

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- 1 - The Bureau of Mines will welcome reprinting of this article but requests that the following footnote acknowledgment be used: "This paper represents work done under a cooperative agreement between the U. S. Bureau of Mines and the University of Arizona. Printed by permission of the Director, U.S. Bureau of Mines. (Not subject to copyright.)"
  - 2 - Associate metallurgical chemist, U.S. Bureau of Mines Southwest Experiment Station, Tucson, Ariz.
  - 3 - Sullivan, J. D., Keck, W. E., Oldright, G. L., Factors Governing the Entry of Solutions into Ores During Leaching: Tech. Paper 441, Bureau of Mines, 1929, 38 pp.
  - 4 - Sullivan, J. D., Sweet, A. J., Factors Governing the Removal of the Soluble Copper from Leached Ores: Tech. Paper 453, Bureau of Mines. In press.

## MINERALS INVESTIGATED

Tests on one sample of azurite, one of malachite, one of tenorite, and five of chrysocolla are here reported.

The azurite was from the Calumet and Arizona mine, Bisbee, Ariz.; the malachite was from the Mammoth mine, Mammoth, Utah; the tenorite from the Old Dominion mine, Globe, Ariz.; and the five samples of chrysocolla were from Miami, Ariz., Globe, Ariz., Ludwig mine, Yerington, Nev., Silverbell, Ariz., and from an unknown source.

### Chemical Composition of Minerals

The chemical composition of the minerals used is given in Table 1.

Table 1. Analysis of Minerals

Minerals	Total Cu, per cent	Acid Soluble Cu, per cent	Fe, per cent	S, per cent	Insol- uble, per cent	SiO <sub>2</sub> , per cent	CaO, per cent	Mn, per cent
Azurite.....	55.35	55.34	0.23	0.02	0.46	-	0.32	0.17
Malachite.....	55.43	55.34	0.49	0.045	0.42	-	0.56	0.24
Tenorite.....	29.86	29.56	4.35	tr.	26.88	-	-	5.0
Chrysocolla, Miami....	29.14	29.04	0.63	-	-	46.04	-	-
Do. Globe....	26.36	26.36	0.46	-	49.32	47.10	-	-
Do. Nevada...	34.64	34.44	3.82	0.38	29.52	29.14	-	-
Do. Silverbell	67.10	17.89	1.62	15.71	4.24	-	-	-
Do. Unknown..	47.76	41.92	1.66	-	15.72	-	-	-

Note: Dashes indicate that no analysis was made.

The pure minerals azurite ( $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ ), malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ), and tenorite ( $\text{CuO}$ ) contain 55.32, 57.45, and 79.89 per cent copper, respectively. True chrysocolla,  $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$  contains 36.14 per cent copper.

All minerals were crushed and sized to minus 100 plus 200 mesh with Tyler standard screens.

### EXPERIMENTAL WORK

#### Experimental Procedure

Samples of from 2 to 10 grams were weighed, put into 5-pint acid bottles, and 500 cubic centimeters of the leaching reagent was added. The bottles and contents were then put on revolving rolls. The temperature was 35°C. in all tests; the bottles and solutions were brought to the required temperature before the tests were started. Unless specifically stated to the contrary, all bottles were open (not stoppered) to the air.

In this report a 5 per cent solution of ferric sulphate indicates a solution containing 50 grams of iron per liter as ferric sulphate. A 5 per cent solution of sulphuric acid indicates a solution containing 50 grams of  $H_2SO_4$  per liter. The author is aware that defining a solution containing 50 grams per liter as 5 per cent, neglects the fact that the specific gravity of the solution is slightly higher than water, but for ease in reporting results it is so termed in this article. This system of nomenclature is common with copper hydrometallurgists.

Table 2 gives a summary of the treatment to which each of the mineral specimens was subjected.

Table 2.- Data on the leaching treatment to which the oxidized copper minerals were subjected.

Mineral	Weight of sample, grams	Leached with:
Azurite.....	4	1 per cent sulphuric acid.
	4	2 do.
	4	5 do.
	10	1 per cent neutral ferric sulphate. <sup>1</sup>
	10	5 do.
	10	Distilled water.
	8	2 per cent ferric sulphate plus 10 per cent sulphuric acid.
	8	5 per cent ferric sulphate plus 10 per cent sulphuric acid.
Malachite.....	4	1 per cent sulphuric acid.
	4	2 do.
	4	5 do.
	10	1 per cent neutral ferric sulphate.
	10	5 do.
	10	Distilled water.
	8	2 per cent ferric sulphate plus 10 per cent sulphuric acid.
	8	5 per cent ferric sulphate plus 10 per cent sulphuric acid.
Chrysocolla from Miami, Arizona..	7	1 per cent sulphuric acid.
	7	2 do.
	7	5 do.
	10	2 per cent ferric sulphate plus 10 per cent sulphuric acid.
	10	5 per cent ferric sulphate plus 10 per cent sulphuric acid.
	10	2 per cent neutral ferric sulphate.
	10	5 do.
	10	Distilled water.

<sup>1</sup> Neutral ferric sulphate as used in this report means chemically pure ferric sulphate without the addition of any acid from outside sources. The solution actually has an acid reaction and usually contains some free acid.

Table 2.- Data on the leaching treatment to which the oxidized copper minerals were subjected - Continued

Mineral	Weight of sample, grams	Leached with:
Chrysocolla from Globe, Arizona, in both open and closed bottles..	2	2 per cent sulphuric acid.
	2	5 do.
	2	2 per cent neutral ferric sulphate.
	2	5 do.
	2	2 per cent ferric sulphate plus 2 per cent sulphuric acid.
	2	5 per cent ferric sulphate plus 2 per cent sulphuric acid.
Chrysocolla from Nevada	2	2 per cent sulphuric acid.
	2	5 do.
	2	2 per cent neutral ferric sulphate.
	2	5 do.
	2	2 per cent ferric sulphate plus 2 per cent sulphuric acid.
	2	5 per cent ferric sulphate plus 2 per cent sulphuric acid.
Chrysocolla from Silverbell, Ariz.	2	5 per cent sulphuric acid.
	2	5 per cent ferric sulphate plus 2 per cent sulphuric acid.
Chrysocolla from an unknown source	2	5 per cent sulphuric acid.
	2	5 per cent ferric sulphate plus 2 per cent sulphuric acid.
Tenorite, in both open and closed bottles	2	2 per cent sulphuric acid.
	2	5 do.
	2	2 per cent neutral ferric sulphate.
	2	5 do.
	2	2 per cent ferric sulphate plus 2 per cent sulphuric acid.
	2	5 per cent ferric sulphate plus 2 per cent sulphuric acid.

The procedure in the closed bottle tests was as follows: The solution was poured into the bottles and oxygen-free nitrogen was bubbled through the solutions to remove the air in the solution and in the bottle above the solution. The samples of mineral were then added, and the bottle was corked tightly with a rubber stopper. In this manner the dissolution tests were carried out in the absence of oxygen, whereas in the open bottles there was free access to atmospheric oxygen.

The mineral from Silverbell, Ariz., was a mixture of chrysocolla and chalcocite. The purpose of the tests on this specimen was to study the solubility of the silicate rather than the sulphide portion, as it has often been said that the copper silicate from the Silverbell district is acid-insoluble. The chemical analysis given in Table 1 shows that the mineral was largely the sulphide.

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The sample from an unknown source contained both chrysocolla and cuprite. The tenorite sample contained some malachite as well as tenorite.

The results obtained in these tests are given in Table 3.

Table 3.- Dissolution of Oxidized Copper Minerals

Mineral	Extraction of copper, per cent										H <sub>2</sub> O
	1 per cent H <sub>2</sub> SO <sub>4</sub>	2 per cent H <sub>2</sub> SO <sub>4</sub>	5 per cent H <sub>2</sub> SO <sub>4</sub>	1 per cent Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2 per cent Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	5 per cent Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2 per cent Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> +10 per cent H <sub>2</sub> SO <sub>4</sub>	5 per cent Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> +10 per cent H <sub>2</sub> SO <sub>4</sub>	2 per cent Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> +2 per cent H <sub>2</sub> SO <sub>4</sub>	5 per cent Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> +2 per cent H <sub>2</sub> SO <sub>4</sub>	
<u>Azurite</u>											
1 hour.....	100	100	100	61	-	99	100	100	-	-	-
2 hours.....	-	-	-	72	-	-	-	-	-	-	-
3 hours.....	-	-	-	84	-	-	-	-	-	-	-
21 hours.....	-	-	-	100	-	-	-	-	-	-	-
32 days.....	-	-	-	-	-	-	-	-	-	-	0.11
<u>Malachite</u>											
1 hour.....	100	100	100	58	-	100	98	100	-	-	-
2 hours.....	-	-	-	70	-	-	-	-	-	-	-
3 hours.....	-	-	-	86	-	-	-	-	-	-	-
21 hours.....	-	-	-	100	-	-	-	-	-	-	-
32 days.....	-	-	-	-	-	-	-	-	-	-	0.22
<u>Chrysocolla</u>											
<u>Miami</u>											
1 hour.....	89	98	100	-	50	98	100	100	-	-	-
2 hours.....	95	100	-	-	58	-	-	-	-	-	-
3 hours.....	99	-	-	-	60	-	-	-	-	-	-
4 hours.....	-	-	-	-	61	-	-	-	-	-	-
5 hours.....	-	-	-	-	69	-	-	-	-	-	-
6 hours.....	-	-	-	-	77	-	-	-	-	-	-
32 days.....	-	-	-	-	-	-	-	-	-	-	1.00
<u>Globe</u>											
<u>Open bottles:</u>											
1 hour.....	-	100	100	-	55	100	-	-	100	100	-
3 hours.....	-	-	-	-	66	-	-	-	-	-	-
8 hours.....	-	-	-	-	85	-	-	-	-	-	-
30 hours.....	-	-	-	-	99	-	-	-	-	-	-

Table 3.- Dissolution of Oxidized Copper Minerals - Continued

	Extraction of copper, per cent										H <sub>2</sub> O
	1 per cent H <sub>2</sub> SO <sub>4</sub>	2 per cent H <sub>2</sub> SO <sub>4</sub>	5 per cent H <sub>2</sub> SO <sub>4</sub>	1 per cent Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2 per cent Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	5 per cent Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2 per cent Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> +10 per cent H <sub>2</sub> SO <sub>4</sub>	5 per cent Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> +10 per cent H <sub>2</sub> SO <sub>4</sub>	2 per cent Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> +2 per cent H <sub>2</sub> SO <sub>4</sub>	5 per cent Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> +2 per cent H <sub>2</sub> SO <sub>4</sub>	
Closed bottles											
1 hour.....	-	100	100	-	44	100	-	-	100	100	-
3 hours.....	-	-	-	-	68	-	-	-	-	-	-
8 hours.....	-	-	-	-	87	-	-	-	-	-	-
24 hours.....	-	-	-	-	97	-	-	-	-	-	-
48 hours.....	-	-	-	-	99	-	-	-	-	-	-
Nevada											
1 hour.....	-	100	100	-	72	80	-	-	100	100	-
3 hours.....	-	-	-	-	77	97	-	-	-	-	-
8 hours.....	-	-	-	-	93	99	-	-	-	-	-
30 hours.....	-	-	-	-	99	100	-	-	-	-	-
With Chalcocite											
1 hour.....	-	-	28	-	-	-	-	-	-	61	-
3 hours.....	-	-	29	-	-	-	-	-	-	66	-
24 hours.....	-	-	35	-	-	-	-	-	-	80	-
With Cuprite											
1 hour.....	-	-	94	-	-	-	-	-	-	100	-
3 hours.....	-	-	98	-	-	-	-	-	-	-	-
24 hours.....	-	-	100	-	-	-	-	-	-	-	-
Tenorite											
Open bottles:											
1 hour.....	-	98	98	-	51	96	-	-	97	99	-
2 hours.....	-	99	99	-	-	-	-	-	-	-	-
3 hours.....	-	99	-	-	87	98	-	-	99	99	-
8 hours.....	-	-	-	-	94	100	-	-	-	-	-
24 hours.....	-	100	-	-	-	-	-	-	-	-	-
30 hours.....	-	-	-	-	99	-	-	-	-	-	-
54 hours.....	-	-	99	-	-	-	-	-	-	-	-
Closed bottles:											
1 hour.....	-	99	99	-	81	100	-	-	100	100	-
3 hours.....	-	-	-	-	92	-	-	-	-	-	-
8 hours.....	-	-	100	-	98	-	-	-	-	-	-
24 hours.....	-	-	-	-	100	-	-	-	-	-	-

Reagent consumption

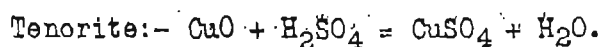
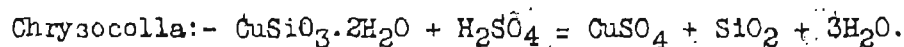
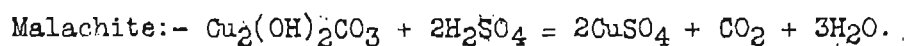
Table 4 contains data on the consumption of reagents in dissolving the minerals.

Table 4.- Consumption of reagents in dissolution tests on oxidized copper minerals

Mineral	Leaching solution	Ratio of acid consumed to copper extracted, by weight	Ratio of ferric iron consumed to copper produced, by weight
Azurite	1 per cent sulphuric acid	1.59	-
	2 do.	1.60	-
	5 do.	1.69	-
Malachite	1 per cent sulphuric acid	1.62	-
	2 do.	1.67	-
	5 do.	1.71	-
Chrysocolla from Miami, Ariz.	1 per cent sulphuric acid	1.77	-
	2 do.	1.90	-
	5 do.	2.06	-
Chrysocolla from Silverbell, Ariz.	5 per cent sulphuric acid	1.13 (1 hour)	-
	do.	1.38 (3 hours)	-
	do.	1.55 (24 hours)	-
	5 per cent ferric sulphate +2 per cent sulphuric acid	0.95 (1 hour)	0.46 (1 hour)
	5 per cent ferric sulphate +2 per cent sulphuric acid	0.81 (3 hours)	1.43 (3 hours)
	5 per cent ferric sulphate +2 per cent sulphuric acid	0.78 (24 hours)	1.40 (24 hours)
Chrysocolla from unknown source	5 per cent sulphuric acid	1.11 (1 hour)	-
	do.	1.41 (3 hours)	-
	do.	1.52 (24 hours)	-
	5 per cent ferric sulphate +2 per cent sulphuric acid	1.99 (1 hour)	0.70
Tenorite, open bottles	2 per cent sulphuric acid	1.13 (1 hour)	-
	do.	1.15 (2 hours)	-

## REACTIONS

The chemical reactions in the dissolution of the oxidized copper minerals by sulphuric acid are:

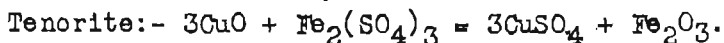
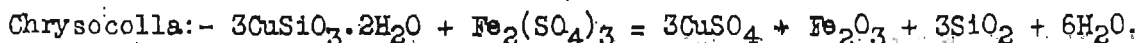
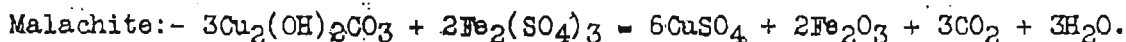
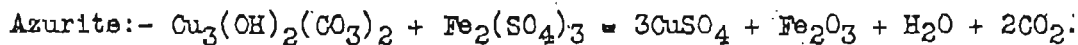




In each case 1 Cu  $\approx$  1 H<sub>2</sub>SO<sub>4</sub>, or 1.54 parts H<sub>2</sub>SO<sub>4</sub> by weight, are theoretically required to extract 1 part Cu by weight.

In the experiments the acid consumption was a little higher than the theoretical amount. It was also noted that the stronger the acid used the greater was the consumption.

Although the formation of basic sulphates of iron in the decomposition of oxidized copper minerals by ferric sulphate has made difficult the determination of the reactions involved, the following equations probably represent what occurs:



In each instance 3 Cu require 1 Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> to furnish sufficient SO<sub>4</sub> = to convert the copper into the soluble sulphate.

When the oxidized minerals in the quantities used in these experiments were leached with 1 or 2 per cent neutral ferric sulphate, the solutions became cloudy in about one hour. In two hours there was considerable evidence of ferric oxide (or hydroxide) suspended in the solution, and upon standing several hours this precipitated. In 21 hours the precipitate was very heavy and, after standing for a few minutes without agitation, the solution became perfectly clear while the solid settled to the bottom. There was no evidence of precipitation with 5 per cent ferric in any case. This may have been due to the fact that inasmuch as a large excess of solution was used, the acidity was not reduced sufficiently to cause precipitation. Also it is well known that basic sulphates of iron are easily formed and may remain in solution without precipitation.

When the oxidized minerals are dissolved in acidified ferric sulphate solutions, the ultimate reactions are probably the same as those represented when the minerals dissolve in sulphuric acid, because even though the minerals may be attacked by the ferric sulphate, the ferric oxide or hydroxide formed probably is reconverted into the sulphate by the acid present.

#### CONCLUSIONS

Experiments have shown that the oxidized minerals of copper-azurite, malachite, chrysocolla, and tenorite are soluble in sulphuric acid and ferric sulphate solutions. Approximately 100 per cent of the copper is soluble in one hour in sulphuric acid or acidified ferric sulphate solutions. In 1 or 2 per cent neutral ferric sulphate the dissolution is somewhat slower, but in nearly every instance the minerals are completely decomposed in 24 hours or less. The rate of dissolution in 5 per cent neutral ferric sulphate is about the same as in sulphuric acid or acidified ferric sulphate.

Chrysocolla is often said to be insoluble in sulphuric acid or in solutions containing ferric iron, but such insoluble silicates of copper are probably diopside and not chrysocolla. The silicate portion of the mineral from Silverbell, was found to be acid soluble.

The dissolution of chrysocolla and tenorite was practically the same in open bottles as in bottles from which the oxygen had been removed by oxygen-free nitrogen.

The consumption of acid in dissolving the minerals is a little higher than theoretical. This is due to impurities in the minerals, which consume the acid.

Since nearly all of these oxidized minerals are dissolved in one hour in the two reagents which would be used in practice - namely, sulphuric acid and acidified ferric sulphate - it seemed useless to treat particles of various sizes at different temperatures.

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