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TOTAL LEACHABLE COPPER DETERMINATION USING THE BOILING FERRIC SULFATE METHOD

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The purpose of this paper is to present an assay method which may be used to quickly determine total leachable copper in mixed oxide-sulfide ores. The method is particularly suited to routine grade control assay work where numerous samples must be processed in a relatively short time and conventional copper assay methods may not yield accurate indicators of recoverable grade.

Introduction

Mixed oxide – sulfide ores are becoming increasingly important in the U.S. for leaching using SX-EW technology. Low grade chalcocite dominant orebodies in particular, are now recognized as amenable to leaching under certain conditions. However, the standard, commonly used methods to determine leachable copper are often not adequate when applied alone to the mixed oxide sulfide mineralogic type. The standard commercial oxide copper analysis may be misleading as an indicator of ore grade for sulfuric acid leaching, if the mineralogic composition of the sample is not considered. Oxide copper minerals such as cuprite, dioptase and impure native copper will contribute to production under proper leaching conditions but do not report significantly to the standard types of oxide copper assay. Economically important leachable secondary sulfides such as chalcocite likewise contribute only a small percentage to the oxide copper assay, sometimes referred to as the non-sulfide copper assay. This problem has typically been overcome through the use of a second analysis by the cyanide soluble copper method. The cyanide soluble copper assay usually reports 90 to 100% of the chalcocite, bornite, covellite, native copper and 8 to 10 % of the chalcopyrite copper in the sample. A significant portion of the oxide copper is also selectively dissolved from some minerals with the CN solution so the test is best run sequentially on leached pulp from the oxide assay to obtain an additive recoverable copper assay from the pair (Parkinson & Bhappu, 1995). An alternative to this somewhat complicated dual assay procedure, particularly for ore grade control where numerous routine analyses are required, is the boiling ferric sulfate method.

Background

In order to successfully operate a sulfuric acid based heap leach on chalcocite dominant ore, the leach solution must contain an adequate amount of oxidant, usually ferric sulfate, with access through the gangue, to attack the chalcocite. A solution containing at least 1 gram/liter may be considered a minimum with many active dump leaches in the southwestern U.S. reporting considerably higher levels ranging from 2 to 9g/l ferric iron (private benchmark report and Sheffer & Evans 1968). Without the oxidant, the typical 1 to 2 % sulfuric acid in water solution used to start oxide copper leaching would have a slow and incomplete reaction with chalcocite or most other secondary sulfides.

Sullivan (1933) and Brown and Sullivan (1934) reported on the dissolution behavior of various copper minerals in both weak sulfuric acid solutions and sulfuric acid with ferric sulfate solutions. Cuprite was found to dissolve in two stages with the second stage producing native copper. An aerated weak sulfuric acid solution only reacted slowly on the copper over several days while the same solution with ferric sulfate added reacted rapidly to completely dissolve the copper. Chalcocite was also shown to dissolve in two stages. In acidified ferric sulfate solution the chalcocite rapidly released one half of its copper that converted the mineral to the formula CuS, a synthetic polymorph of covellite. Covellite in turn leaches slowly in either solution. A 1% sulfuric acid solution required 35 days to dissolve 16% of the copper in covellite while a 1% solution of ferric sulfate dissolved 62% in 24 days.

Sloan (1934) in conjunction with Brown and Sullivan's work compared the dissolution of various minerals in ten assay methods in use at the time for copper oxide determinations. Two of these digestion methods are used commonly today depending on the laboratory as the standard commercial oxide copper analysis. The procedures are shown on Table 1 Analytical Methods Used in Copper Analyses. Selected data, primarily from Sloan (1934), is listed in Table 2 Copper Assay Methods -Comparison of Mineral Dissolution. A ferric sulfate leach method was added to the Table, as was the CN soluble copper method. The boiling ferric sulfate method was not listed on this table due to lack of specific data on some minerals.

Based on the Bureau of Mines work, a method similar to the one here presented, was developed for grade control at the Johnson Camp Mine, Cochise Co, Arizona. In 1989, the author successfully instituted a boiling ferric sulfate assay method at the mine using an additional additive thought to limit chalcopyrite dissolution. To minimize assay costs, usually about half to one quarter of the blast holes in a pattern had samples tested with this method with the results compared to total copper results on all the holes. Actual copper production from the mixed oxide-sulfide ore was observed to be directly impacted within the month when the method was at times replaced with the standard methods.

Discussion of Test Work

The boiling ferric sulfate method was developed as a laboratory tool used to mimic the actual chemical leaching behavior in the heap leach process. Two significant factors must be accounted to scale down the process. Reaction rate times and particle size must of necessity be reduced for laboratory scale logistics. Representative sampling procedure for laboratory samples is well established and utilizes sample pulverized to 200 mesh. The finely divided sample has a maximized surface area available for reaction with the lixiviant, which accelerates the reaction rate over that of coarse ore in a heap. The reaction rates even using fine material are still too slow to achieve the level of extraction expected from either column tests or leaching operations conducted over 6 to 12 months duration. Sullivan(1933) demonstrated a 25 % increase from 48% to 73% in the dissolution of relatively pure chalcocite during day one of leaching when the temperature was increased from 35 degrees C to 50 degrees C in acidified ferric sulfate solution. Similarly, bornite was 98% reacted in 5 days at 50 C while only 68% reacted at 35C during the same time.

Methods

Test work conducted for the present study compared identical splits of samples digested with the same acidified ferric sulfate solution under three temperature conditions followed with total and cyanide soluble copper analyses. One sample that consisted predominantly of the mineral chalcocite in massive form and ten samples of low grade disseminated chalcocite ore were tested. Samples were subjected to (1) a one-hour room temperature digestion on a shaking table (2) a one hour 75 degrees C digestion with stirring and (3) a 5-minute boiling followed by a one-hour cooling digestion.

After completion of the initial scoping work to determine the general conditions of the analysis method, 34 additional samples were tested for total copper, acid soluble copper, and ferric sulfate soluble copper. Sample aliquot sizes of 0.5 grams and 1 gram were also compared. The 1 gram size was selected for further test work since it provided a marginal increase in accuracy.

See Figure 1.

With the exception of the chalcocite mineral isolate, samples for the test work were taken from drill core collected at the Hall Copper Project, Nye County Nevada, U.S.A. The copper deposit is a wall rock porphyry type primarily hosted in locally siliceous argillite. The deposit is oxidized to a shallow depth and has a low grade oxide cap overlying a chalcocite blanket of about 0.4% cu. The samples were visually categorized as to mineralogic zone: leached capping, upper transition, enriched, lower transition, and primary sulfide. There is of course, a certain amount of overlap between these subjectively assigned zones. Samples were also selected based on copper content, which was intended to range from ore grade through sub-ore cut off grade to waste rock. The secondary sulfides in the enriched zone occur predominantly as less than 30-micron disseminations and as replacement rims around pyrite and chalcopyrite. The secondary sulfides are primarily chalcocite and covellite. In the better leaching material the matrix is mostly quartz with moderate amounts of feldspar and some sericite. Hematite and other hydrous iron oxides often comprise 10% or more of the rock. Some native copper is found in the enriched and upper transition zones. Oxide minerals such as melaconite, tenorite, brochantite, and chrysocolla occur locally in the leached cap and upper transition. Sulfide mineralization in the primary sulfide zone consists of pyrite with chalcopyrite.
Table 4 lists sample data including the assigned geologic zone and grade.

Results

Between 1993 and 1998 eleven long-term column leach tests were conducted on chalcocite bearing, enriched and transition zone ore. Once optimal leach conditions were established, all tests indicated a 75% to 88% recovery of copper based on the total copper assay. Although the recoveries may be considered as ultimate without regard to solution head grade, the column test work may still be used as a benchmark for comparison.

Results of the initial scoping tests are shown on Table 3 and Figure 1. The boiling condition was found to accelerate the reaction rate and provide the maximum copper extraction with results closest to that reported from the metallurgical column tests of similar rock. Boiling ferric sulfate soluble copper analyses from the larger sample group, as shown on Figure 2 Comparison of Assay Methods, indicated the following average recoveries compared to total copper: Leached oxide capping 82%, Upper Transition 81%, Enriched 74%, Lower Transition 61%, Primary Sulfide 25%. Maximum recovery in the primary sulfide zone was 44% of total.

In contrast, the CN soluble recovery averaged 91% in the Enriched zone, 94% in the Lower Transition ore grade material and 32% in the Primary Sulfides. Maximum reported recovery in the primary zone was 68% of total. These CN recoveries are believed to be unlikely in leaching practice particularly in that mineralogic zone with mixed secondary and primary sulfides as the Lower Transition.

Standard deviations in the CN soluble data are substantial while standard deviations for the boiling ferric sulfate method are minimal. This generally indicates improved reproducibility and thus inferred reliability of the ferric sulfate method.

These test data although somewhat limited in number and variety, support the premise that the boiling ferric sulfate method for the determination of leachable copper is a valid tool to approximate copper recovery from mixed oxide-sulfide ore. The method should be especially useful in daily ore grade control activities where numerous samples are processed daily and a simple but accurate analysis is required.

References

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FIGURE 1 Comparison of Ferric Leach Temperature

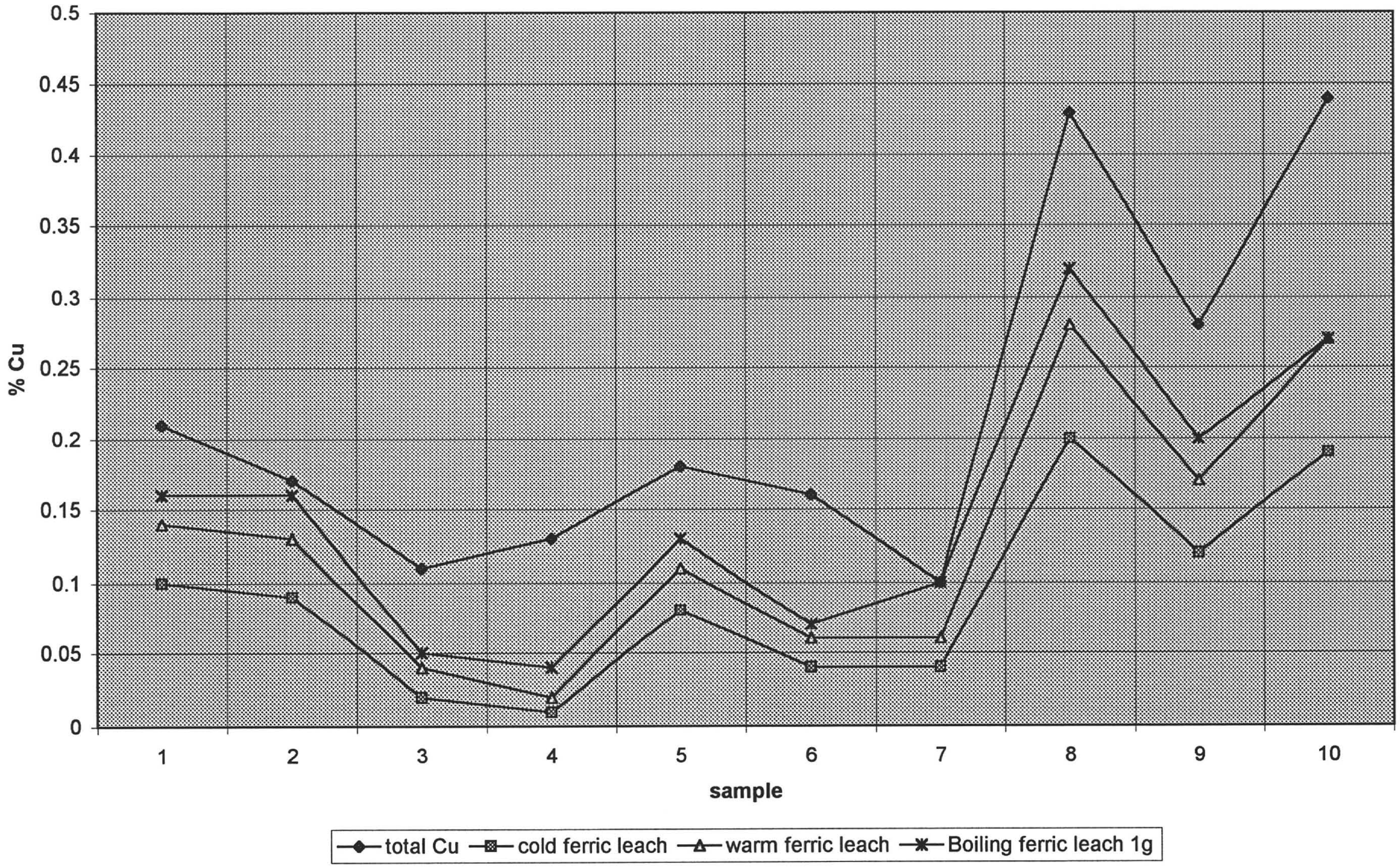

FIGURE 2 Comparison of Assay Methods

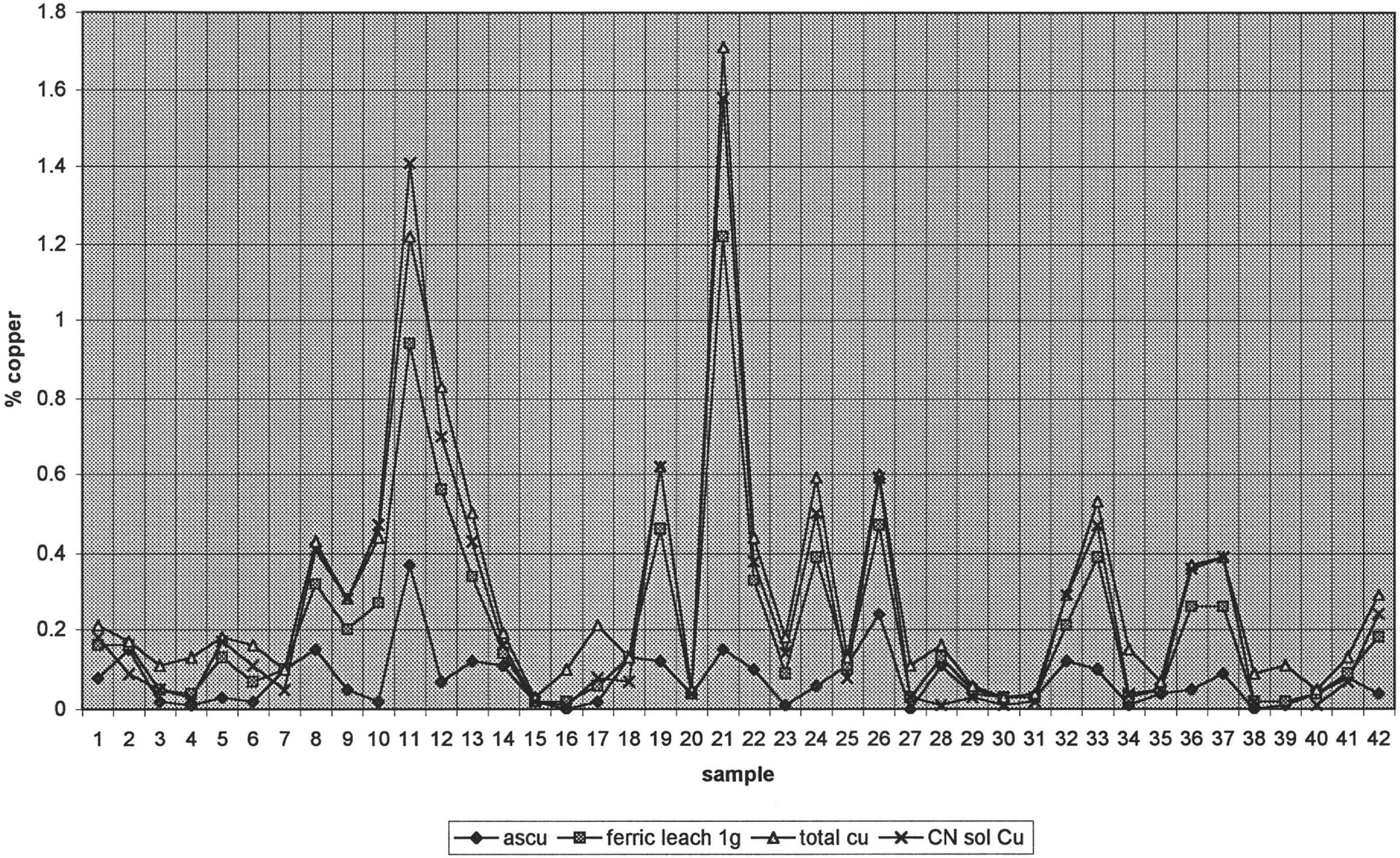

Table1

ANALYTICAL METHODS USED IN COPPER ANALYSES

Method	Description
Total Copper	0.500 gram of pulverized sample, digestion with boiling in 5 percent solution of hydrochloric (HCl), nitric (HNO_3) and perchloric ($HClO_4$) acids, read leach solution on AA
Oxide Method 1	1.000 gram of pulverized sample,digestion in long tube with 15 ml of 5 percent sulfuric (H_2SO_4) acid on shaking table at room temperature (25°C) for one hour.Then centrifuge sample and decant solution to 200 ml flask. Residue is washed three times with 30 ml water by shaking, centrifuging and decanting with wash solutions added to 200 ml flask. Read leach solution in 200 ml flask on AA.
Cyanide Soluble Copper	1.000 gram pulverized sample or residue from acid soluble step is digested with 25 ml of 10 percent sodium cyanide (NaCN) on shaking table at room temperature (25°C) for one -half hour (30 minutes). Centifuge and wash samples as per acid soluble step. Read leach solution on AA.
Residual Total Copper (used in sequential analysis)	Residue from cyanide soluble step s transferred into 200 ml flask and digested as per total copper step above. Read leach solution on AA.
Boiling Ferric Sulfate Soluble Copper	1.000 gram of pulverized sample,digestion in 250 ml beaker with 100 ml of 24.5 g/l Fe2(SO4)3 and 1 percent sulfuric (H2SO4) acid. Gently boil for ten minutes at about 300 degrees F. Allow to cool 1 hour. Filter and wash three times with DI. Dilute to volume of flask, mix read solution on AA. Calculate % Cu at AA reading ppm (x0.25)
Oxide Copper Method 2	0.500 gram sample, digestion with 100 ml of 5% H_2SO_4 (sometimes 10 ml 6% H_2SO_3 added) Bring to rapid boil for 5 minutes, wash , dilute, read on AA.

Table 2

Copper Assay Methods
Comparison of Mineral % Dissolution

MINERAL OXIDES	1) 1 HR COLD STIRRED 5%H_2SO_4	1) 3 min. BOIL 10%H_2SO_4	1) 1 HR COLD STIRRED 1-5% FERRIC SULFATE IN .5 TO 1% H_2SO_4	2) SHAKE 1/2 HOUR, 10% NaCN SOLUTION
Azurite $2CuCO_3\ Cu(OH)_2$	100.00	100.00	100	100
Malachite $CuCO_3.\ Cu(OH)_2$	100.00	100.00	100	100
Cuprite Cu_2O	59.56	67.90	100	100
Chrysocolla $CuSiO_3.\ 2H_2O$	100.00	99.66	100	45
Native Copper	3.82	4.90	75	100
SULFIDES				
Chacocite Cu_2S	1.16	1.68	49	100
Bornite $CuFeS_2$	0.46	0.92	27	100
Chalcoprite $CuFeS_2$	0.63	0.63	<1	7
Covellite CuS	3.16	3.77	<8	100

1. Source of Information USBM RI 3228 (1934)
2. Parkinson & B happu 1995

Data as % wt

TABLE 3

COMPARISON OF ASSAY METHODS ON MINERAL ISOLATE

Sample	Total Copper	CN sol Cu	Warm FerricSulfate Sol Cu	Cold Ferric Sulfate Sol Cu	Boiling Ferric Sulfate Sol Cu
	%	%	%	%	%
Chalcocite	74	73.8	29.5	20.8	41