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FORMATION AND REACTIVITY OF COPPER SULPHIDE, PART I, PRECIPITATION

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ABSTRACT

Copper sulphide samples have been prepared by precipitation from aqueous solution under different conditions of pH, temperature, time of ageing and copper ion activity, and with different precipitants. The phase composition and particle size and form of the precipitates have been studied by x-ray powder diffraction, electron microscopy and sedimentation techniques, and have been correlated with the conditions of precipitation.

The samples were prepared from copper(II) sulphate solutions, mainly of concentration 0.3 M, using hydrogen sulphide, thioacetamide and sodium sulphide as precipitants. The preparations were carried out at 22°C and 80°C, and were aged for different lengths of time. The copper ion was, in some cases, complexed by various ligands.

Hydrogen sulphide formed particles which are agglomerations of smaller particles. Thioacetamide formed uniform, discrete particles, and sodium sulphide formed a wide range of particle sizes.

Increasing the temperature and time of ageing encouraged precipitation of larger particles. Decreasing the pH and the copper ion activity (by using complexing agents) had the same general effect.

INTRODUCTION

Copper is most commonly found in the earth's crust in the form of sulphide ores, mainly as chalcocite (Cu_2S), covellite (CuS), and chalcopyrite ($CuFeS_2$). The copper can be extracted by pyrometallurgy; the operations include roasting the sulphide ores in air to oxide, and reduction of oxide to metal.

The various reactions in the processing of these ores are affected by the particulate properties of the material. Thus, for oxidation studies, copper sulphide samples have been prepared by preciptation from aqueous solution under different conditions of pH, temperature, time of ageing and copper ion activity. The particulate properties of the resulting samples have been correlated with the precipitation conditions, as has been attempted in earlier work on zinc, lead and antimony sulphides (refs. 1-3).

Early work on The precipitation of copper sulphide, as reported by Mellor (ref. 4), showed some variations with respect to crystallinity, empirical formula and other properties. Buerger (ref. 5) and Djurle (ref. 6) have shown the Cu-S system to be remarkably complex, having four phases of approximate compositions Cu_2S, $Cu_{1.96}S$, $Cu_{1.8}S$ and CuS. The differences in structures of

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these phases are described in detail by Wells (ref. 7). An additional phase of formula $CuS_{1.9}$ has also been produced (ref. 8) from the reaction of CuS with S at high pressure and high temperature. Further work on the precipitation of copper sulphides has been carried out by Roberts and Buchanan (ref. 9).

MATERIALS

BDH 'Analar' copper(II) sulphate was used as the copper salt. The preciptants used were BDH fused technical sodium sulphide, BDH 'GPR' thioethanamide (thioacetamide), and hydrogen sulphide gas, which was generated from a Kipps apparatus using iron(II) sulphide and dilute (2 M) hydrochloric acid.

Some of the copper solutions were acidified with dilute sulphuric acid (1 M and 5 M) and others were complexed with dilute hydrochloric acid (2 M and 5 M). Other materials used as complexing agents were aqueous ammonia (5 M), BDH 'Analar' EDTA disodium salt, BDH 'GPR' 1,2-ethanediamine (ethylenediamine), and Aldridge Chemicals technical grade N,N'-bis-(2-aminoethano-)-1,2-diaminoethane (triethylenetetramine).

EXPERIMENTAL

Samples of copper sulphide were precipitated in acidic media by passing hydrogen sulphide gas into stirred solutions (250 cm^3) of copper sulphate in water and in 1 M H_2SO_4, the concentration of copper ions in most cases being 0.3 M. The effect of different ligands on the precipitation was investigated by adding various complexing agents to the copper(II) solutions, in slight excess of stoichiometric quantities (4.1 moles of NH_3, 2.1 moles of ethylenediamine, 1.1 moles of EDTA, and 1.1 moles of triethylenetetramine per mole of copper(II)).

Copper sulphide samples were preciptated in alkaline media by the addition of sodium sulphide, in aqueous solution, into stirred, aqueous solutions (250 cm^3) of 0.3 M $CuSO_4$. The quantities of sodium sulphide used were stoichiometric, 20% in excess of stoichiometric and 20% less than stoichiometric amounts.

Further samples were prepared by homogeneous precipitation, using thioacetamide (CH_3CSNH_2) as the precipitant in slight stoichiometric excess. Solutions of thioacetamide were added to 0.3 M $CuSO_4$ solutions (250 cm^3), and the copper ion species were again varied by addition of the various complexing agents.

The precipitations were carried out at 22°C and at 80°C. After 15 minutes at 22°C, and after 4 hours at 80°C, the precipitates were centrifuged and washed three times with acetone to remove most of the water, in order to arrest any further ageing. The last traces of acetone and water were removed by vacuum desiccation.

The copper sulphide phases present were determined by x-ray powder diffraction using a Siemens Type F goniometer and Type T electronic measuring system (CuK_{α} radiation). The particle size and crystallinity of the samples were examined using a scanning electron microscope (JEOL JSM-35C model). Particle size was also investigated by measuring sedimentation velocities in water. The times taken for the whole sample and half the sample to settle were measured, to give an estimate of the particle (aggregate) size, assuming Stokes' Law (ref. 10).

RESULTS

The precipitation conditions for the preparation of the copper sulphide samples are given in Tables 1, 2 and 3. Table 1 lists samples prepared using hydrogen sulphide gas as the precipitant. The gas was passed until precipitation was complete. The second column shows the complexing agent added or the medium in which the precipitation was carried out. The table also lists the ageing time, temperature and code number identifying each sample. Table 2 lists samples prepared using thioacetamide as the precipitant, and Table 3 using sodium sulphide. The final column of Table 3 shows the number of moles of Na_2S used per mole of copper.

Tables 4, 5 and 6 present the resulting particulate properties of each precipitate.

TABLE 1

Precipitation conditions using hydrogen sulphide gas

Sample code	Concentration of $CuSO_4$ soln/M	Medium/Complexing agent	Ageing time	Temp /^{o}C
H1	0.3	1 M H_2SO_4	15 min	22
H2	0.3	1 M H_2SO_4	4 h	80
H3	0.3	en	15 min	22
H4	0.3	en	4 h	80
H5	0.3	tetren	15 min	22
H6	0.3	tetren	4 h	80
H7	0.3	NH_3	4 h	80
H8	0.3	EDTA	15 min	22
H9	0.3	EDTA	4 h	80
H10	0.3	-	15 min	22
H11	0.3	-	4 h	80

tetren = triethylenetetramine

TABLE 2

Precipitation conditions using thioacetamide

Sample code	Concentration of $CuSO_4$ soln/M	Medium/Complexing agent	Ageing time	Temp /°C
T1	0.3	1 M H_2SO_4	4 h	80
T2	0.3	1 M H_2SO_4	168 h	80
T3	0.3	5 M H_2SO_4	15 min	100
T4	0.01	0.5 M HCl	2.5 h	80
T5	0.3	2 M HCl	4 h	80
T6	0.01	5 M HCl	2.5 h	80
T7	0.01	5 M HCl	1.5 h	80
T8	0.3	5 M HCl	4 h	80
T9	0.3	-	4 h	80
T10	0.3	NH_3	15 min	22
T11	0.3	NH_3	4 h	80
T12	0.3	en	15 min	22
T13	0.3	en	4 h	80
T14	0.3	tetren	15 min	22
T15	0.3	tetren	4 h	80
T16	0.3	EDTA	15 min	22
T17	0.3	EDTA	4 h	80

tetren = triethylenetetramine

TABLE 3

Precipitation conditions using sodium sulphide

Sample code	Concentration of $CuSO_4$ soln/M	Equivalents of Na_2S	Ageing time	Temp /°C
S1	0.02	1.2	15 min	22
S2	0.3	0.8	15 min	22
S3	0.3	0.8	4 h	80
S4	0.3	1.2	4 h	80
S5	0.3	1 (+0.2 moles S)	15 min	22
S6	0.3	1 (+0.2 moles S)	4 h	80
S7	0.3 (+EDTA)	1	15 min	22

TABLE 4

CuS particle sizes using H_2S precipitant

Sample code	Electron Microscopy				Sedimentation	
	Fines /μm	Coarse /μm	U	D	Fines /μm	Coarse /μm
H1	0.3	5	x	x	8.0	56.4
H2	0.5	6	x	x	14.2	85.4
H3	0.3	4	x	x	8.4	47.0
H4	0.3	10	x	x	10.6	85.8
H5	0.3	1	x	x	9.2	33.6
H6	0.3	10	x	x	10.0	50.4
H7	0.2	5	x	√	8.6	56.4
H8	Impure product. EDTA complex stable.					
H9	Impure product. EDTA complex stable.					
H10	0.3	5	√	x	9.2	65.2
H11	0.2	4	x	x	10.2	64.0

U = uniform particles
D = discrete particles
√ = positive response
x = negative response

TABLE 5
CuS particle sizes using CH_3CSNH_2 precpitant

Sample code	Electron Microscopy				Sedimentation	
	Fines /μm	Coarse /μm	U	D	Fines /μm	Coarse /μm
T1	1.0	5	√	√	8.6	48.2
T2	1.5	2.5	√	√	9.8	59.2
T3	0.1	0.5	√	√	6.8	16.2
T4	1.0	2	√	√	7.2	38.2
T5	0.5	6	x	√	7.2	50.4
T6	0.5	5	x	√	8.0	36.8
T7	1.0	20	x	√	8.4	74.4
T8	3.0	6	√	√	18.2	85.4
T9	0.5	1.5	√	√	7.6	32.0
T10	0.2	0.5	√	√	18.0	86.0
T11	0.2	0.6	√	√	20.0	106.8
T12	0.2	0.5	√	√	18.2	92.4
T13	0.3	0.8	√	√	20.0	112.6
T14	0.2	0.8	√	√	10.0	65.4
T15	0.3	1.5	√	√	15.2	65.4
T16	No reaction					
T17	Impure product. EDTA complex stable.					

U = uniform particles
D = discrete particles
√ = positive response
x = negative response

TABLE 6

CuS particle sizes using Na_2S precpitant

Sample code	Electron Microscopy				Sedimentation	
	Fines /µm	Coarse /µm	U	D	Fines /µm	Coarse /µm
S1	1.0	100	x	x	10.4	186.0
S2	Impure product					
S3	0.5	3	x	x	9.0	36.0
S4	0.2	30	x	x	13.8	64.0
S5	0.5	10	x	x	12.2	75.2
S6	0.3	10	x	x	13.0	75.2
S7	Impure product					
BDH CuS	2.0	6	√	√	18.6	90.6
BDH CuS*	2.0	6	√	√	17.6	88.4

* = after extraction with CS_2
U = uniform particles
D = discrete particles
√ = positive response
x = negative response

In general, the x-ray powder diffraction traces did not give sharp peaks, which is an indication of poor crystallinity in the samples. The precipitates which were of small particle size, as indicated by electron microscopy and sedimentation, had broad x-ray diffraction peaks compared with those of larger particle size.

In the majority of the preparations, covellite, CuS, was found to be the sulphide of copper which was precipitated, together with varying amounts of sulphur. In two cases though, preparations S1 and S4, digenite, $Cu_{1.8}S$ was found to be the precipitated material.

DISCUSSION

In general, the three different precipitants gave products having different particulate properties. Hydrogen sulphide yielded a precipitate having a variable particle size, from 0.3 µm to approximately 10 µm in diameter, the latter appearing to be agglomerations of the smaller particles. Thioacetamide releases H_2S very slowly in the solution, and has thus produced homogeneous precipitation of copper sulphide, resulting in discrete, uniform-sized particles in all of the samples produced. Sodium sulphide yielded precipitates having highly variable particle sizes, especially in the two samples in which $Cu_{1.8}S$ has been identified as the precipitated material. Scanning electron micrographs (Figures 1-4) demonstrate the variety of particle sizes obtained when using the three different precipitants.

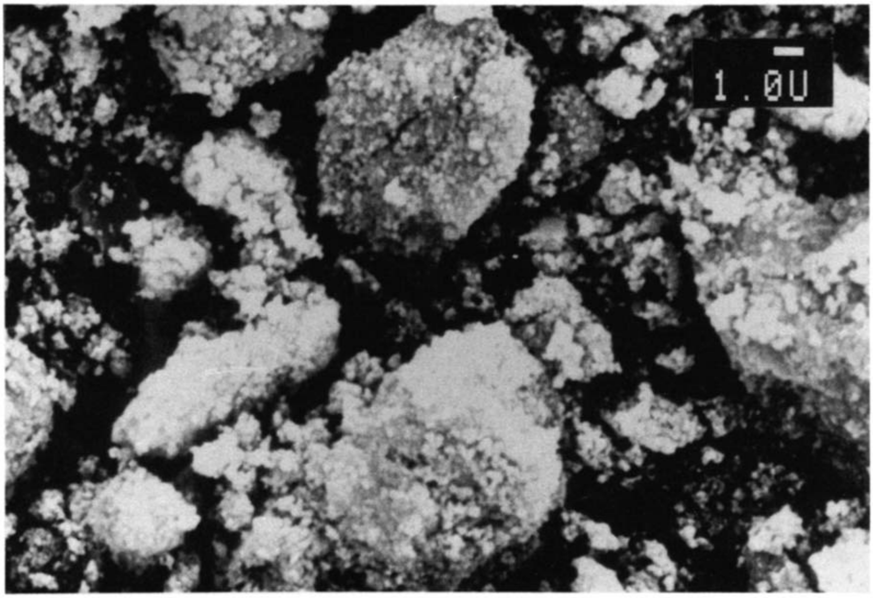
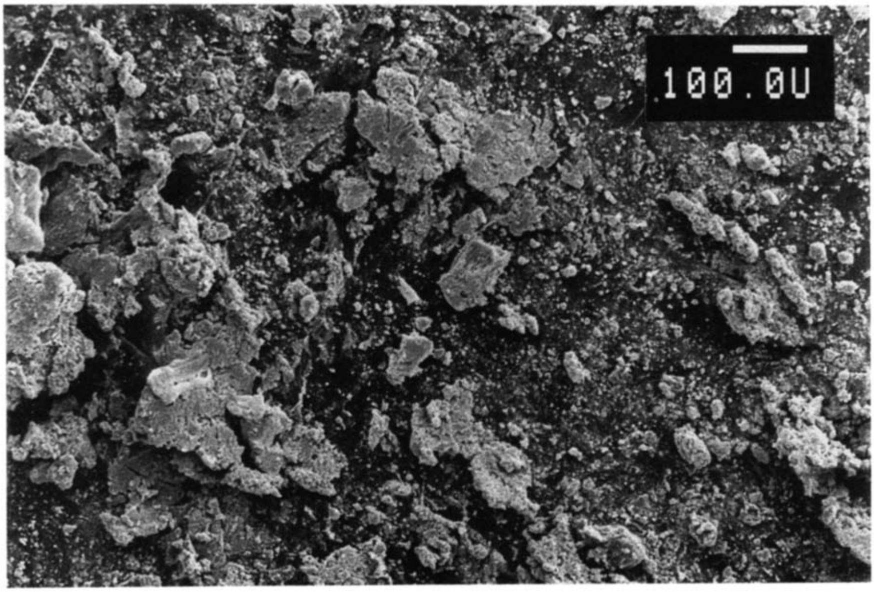


Figure 1 (above), Copper sulphide sample H3, Magnification x4000

Figure 2 (below), Copper sulphide sample S1, Magnification x 100



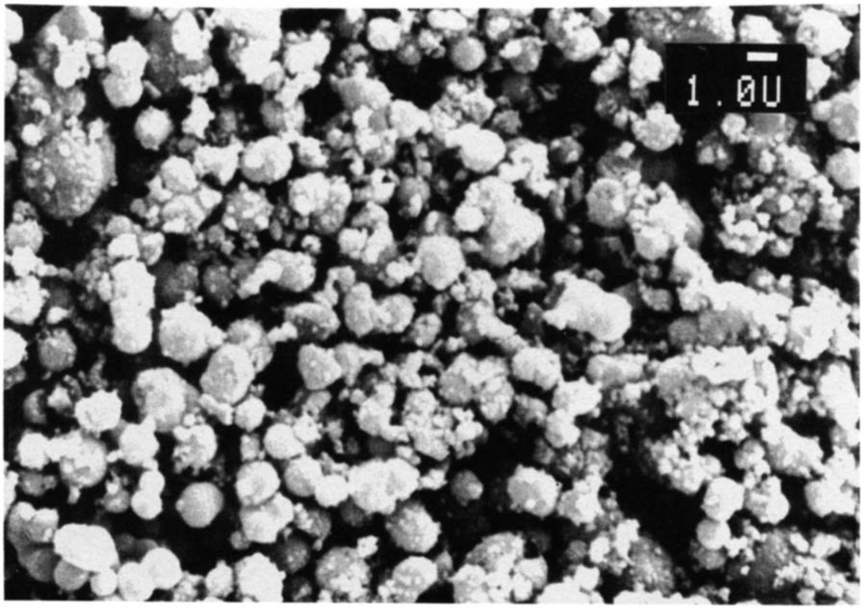
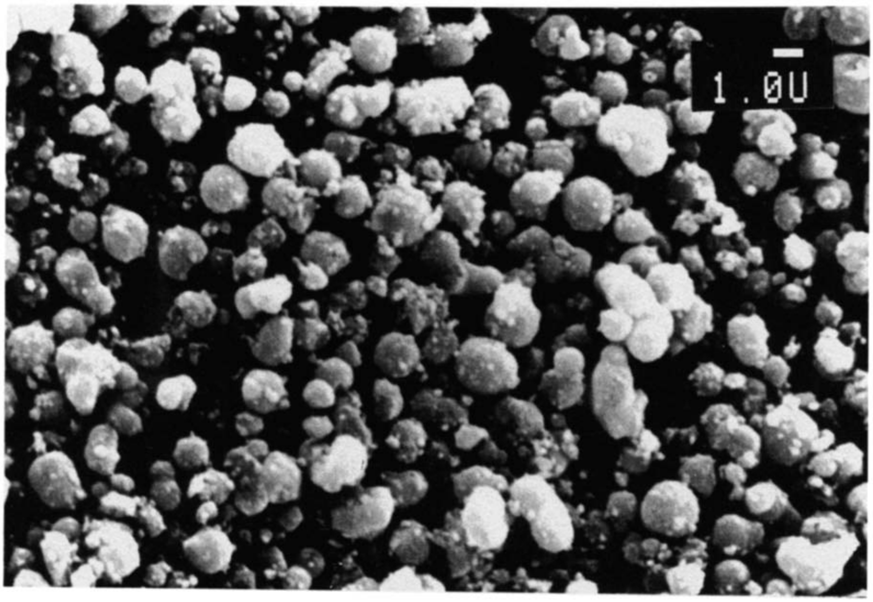


Figure 3 (above), Copper sulphide sample T1, Magnification x4000

Figure 4 (below), Copper sulphide sample T2, Magnification x4000



The effects of altering the pH of the solution, digestion, and complexing the copper ion on the resulting particulate properties can most easily be seen in the T set of preparations, in which thioacetamide has been used as precipitant, due to the homogeneous nature of the precipitates obtained. The same effects are still observed in the H and S sets of preparations, but not so clearly.

Decreasing the pH of the medium results in a larger particle size in the precipitate. This can be seen when comparing the particle sizes obtained from preparations T1 and T9, and also by comparing those obtained from preparation T9 with those from preparations T5 and T8, although here complexing of the copper by Cl^- also occurs. These observations are as expected, because the activity of the sulphide ion is reduced in more acid conditions, and this leads to a lower degree of supersaturation in the solution. The rate of nucleation is lowered so that growth of larger particles is encouraged. This behaviour is similar to that observed in earlier work on zinc and lead sulphides (refs. 1,2).

Generally, digesting the solution at an elevated temperature (80°C) both increases the particle size of the precipitate, and narrows the range of particle sizes in each precipitate. This is as expected, either because Ostwald ripening is promoted by elevated temperatures and longer ageing times, or because the rate of nucleation is slower from the less supersaturated solutions at higher temperatures, giving a larger crystal size. There is, however, evidence here that Ostwald ripening mainly occurs during the first few hours of digestion. This is seen when comparing the particle sizes obtained in preparations T1 and T2 (see Figures 3,4) which demonstrate different digestion periods of 4 hours and 168 hours respectively, at 80°C in 1 M H_2SO_4. There has been a slight particle growth after the initial 4 hours digestion, but this is very slight. When the particles obtained from preparation T3 are compared with those from T1 and T2, it is evident that particle growth occurs mostly during the first few hours. The precipitation conditions for preparation T3 were more acidic and at a higher temperature than those of T1 and T2, which would tend to increase the solubility, resulting in large particle sizes, contrary to the observations. Thus the increase in crystal size here must be due to Ostwald ripening.

Of the alkaline complexing agents used, EDTA formed the most stable complex with the copper ion. The stability was so high that none of the three precipitants used could form a pure sulphide of copper. EDTA was suspected to be a major impurity in each such precipitate, and in one instance (preparation T16) there was no precipitate whatsoever. The other alkaline complexing agents produced a trend of an increasing particle size with the more strongly complexing ligands used. Examples of this are given by samples from preparations H1 to H6 inclusive, and T10 to T15 inclusive. As before, this increase in particle size is as expected, as the activity of the copper ion decreases with increasing complexing power of the ligand. Again, a lower degree of supersaturation is attained, making nucleation more difficult and producing larger particles.

CONCLUSIONS

Particle growth of precipitated copper sulphide is promoted by increasing the temperature and time of ageing. Decreasing the pH also encourages precipitation of large particles, as does complexing the copper ion in the solution. All three precipitants (H_2S, CH_3CSNH_2, Na_2S) produce products having different particulate properties and/or phase compositions. Excess sulphur is formed in the majority of the preprations.

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