ADSORPTION ON INORGANIC MATERIALS

VI. REACTION OF INSOLUBLE SULFIDES WITH METAL IONS IN AQUEOUS MEDIA*

HAROLD O. PHILLIPS AND KURT A. KRAUS
Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. (U.S.A.)
(Received July 8th, 1964)

The favorable properties of precipitated CdS (when used without diluents) for the recovery of several metal ions which form less soluble sulfides were discussed in an earlier communication[1]. At room temperature (25°) the exchange rates were found to be fast, and quantitative removal of a number of heavy metal ions was achieved from dilute and concentrated solutions essentially through metathetical reactions.

The present paper describes the reaction of precipitated sulfides of Ag(I), Fe(II), Cu(II), Zn(II), Pb(II), Cd(II), and As(III) with solutions containing macro amounts of heavy metal ions, such as Ag(I), Cu(II), and Hg(II), which form highly insoluble sulfides**. The ease and extent of substitution of metal ions by many of the sulfides seems noteworthy.

Although displacement reactions of this type have been studied for sulfide minerals, such as sphalerite[3-8] and galena[9] it was generally believed that these were surface reactions and, hence, that they occur only to a small extent. To improve the extent of reaction while maintaining the speed of surface reactions for chromatographic purposes, some workers have employed devices such as impregnation of papers with CdS[10, 11], cellulose (cotton) with CdS[12-15] or ZnS[16] and Filter Cel with ZnS[17]. High-fired ZnS as a "filter-medium" was studied by KUTZELNIGG[18]. He examined reactions with a number of metal ions in solution. While he did not report flow rates used or uptakes, we conclude from data presented in his tables that he was dealing with low degrees of conversion (usually less than 0.1 moles/l of bed). RYABCHIKOV and co-workers[19] reported as part of a routine study on selective "sorption" by a number of inorganic materials that CdS selectively adsorbs Cu(II) ions. This was thought to be a unique reaction.

In the present paper we would like to show that these reactions are not unique and that they frequently occur with high degrees of conversion even when the materials are not specially treated, or dispersed as thin layers on supports or diluents.

EXPERIMENTAL

Most sulfides were prepared by addition, with stirring, of excess ammonium sulfide to 0.2 to 0.4 M solutions of the metal ions; As(III) sulfide was prepared by the addition, with stirring, of excess H_2S gas to a 0.2 M As(III)–0.7 M HCl solution. The resultant precipitates were filtered, washed with water, dried at 25°, ground and sieved (80–170 mesh). Small columns (*ca.* 0.2 cm^2 × 1 to 2 cm) made from these materials (without use of diluents) have reasonably good flow characteristics. Some required a few lb/in.^{2} over-pressure for satisfactory flow. Bed densities (g/cc) were: AgS:1.5; FeS:1.0; CuS:1.5; ZnS:1.4; CdS:0.9; PbS:1.6; As_2S_3:0.5.

The effluents were usually analyzed for displaced metal ions by EDTA titrations; Ag(I) was determined by Volhard titration (SCN$^-$), Fe(II) by titration with $KMnO_4$, and As(III) by iodimetric titration in neutral solutions. Radiometric analyses were used to determine the breakthrough of added metal ions. Radiotracers (^{64}Cu, [110]Ag, [203]Hg) were obtained from the Isotopes Division of Oak Ridge National Laboratory and used without further purification though checked for purity. The stoichiometry of the reactions was obtained from the effluent analyses and the weight of sulfides used.

Composition of the solid was taken as the stoichiometric sulfide after drying at 105° for 24 h. The weight loss on drying was 6.7 % for ZnS and about 1 % for the other sulfides.

RESULTS AND DISCUSSION

We shall first discuss the stoichiometry of the reactions of various solid sulfides with solutions of adsorbable ions. We shall then present results concerning the uptakes of ions by the solids on a weight and volume basis; some comments on the rates of reactions are also included. Finally, we show that the adsorption properties of sulfides are not very well correlated with their structure and crystallite size.

(1) Stoichiometry of displacement reactions

Small columns of the sulfides were found to remove quantitatively, from a variety of solutions, metal ions [*e.g.*, Ag(I), Cu(II), Hg(II), Au(III)] which form more insoluble sulfides. The stoichiometry of the reactions can frequently be approximated by the metathetical reaction:

$$M_{2/m}S + 2/n \, N^{+n} \longrightarrow 2/m \, M^{+m} + N_{2/n}S \tag{1}$$

where M^{+m} is the metal ion in the original sulfide and N^{+n} is the displacing ion.

The exchange equivalence of the reactions was studied for a number of systems by determining the conversion ratio R of the number of moles of metal ions displaced from the solids to the number of moles of metal ions retained or "adsorbed".

(a) Ag_2S. Silver sulfide was found to react sufficiently rapidly with added Hg(II) to cause essentially quantitative removal of this element from solution. A typical adsorption–displacement experiment is illustrated in Fig. 1 which gives the conversion ratio R of moles Ag(I) eluted per mole Hg(II) adsorbed from a 0.053 M Hg(NO$_3$)$_2$–0.0002 M HNO$_3$ solution. Flow rate was 1 cm/min; temperature 25°.

According to eqn. (1), elution of 2 moles of Ag(I) per mole of Hg(II) would have been expected. Since $R < 2$, there is either some adsorption of excess Hg(II) on the HgS formed or some adsorption of Ag(I) on HgS; both reactions seem possible.

(b) CuS. Adsorption experiments were carried out with solutions of Ag(I) and Hg(II). A typical experiment with 0.098 M AgNO$_3$–0.1 M HNO$_3$ is illustrated in Fig. 1. Flow rate was 0.3 cm/min, temperature 25°. Copper(II) was found immediately in the effluent and R was 0.5 as expected from eqn. (1).
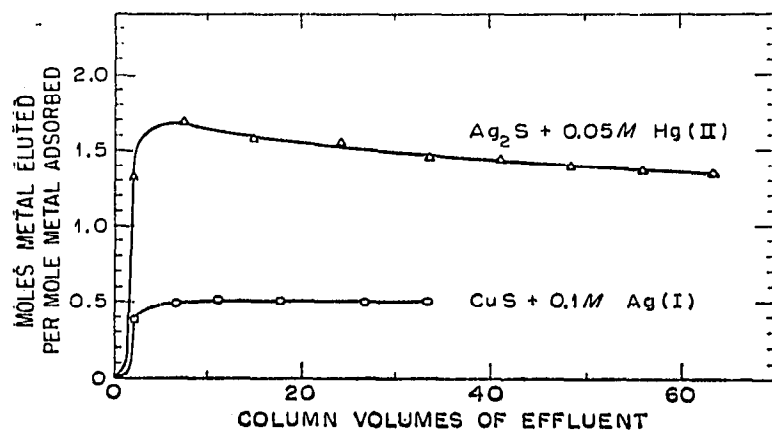

Fig. 1. Reaction of Hg(II) with Ag$_2$S and Ag(I) with CuS. Column 0.2 cm^2 × 1.2 cm; flow rate 0.3–1 cm/min; 25°.

Adsorption of Hg(II) by CuS was relatively slow at room temperature. At 97° essentially quantitative adsorption occurred for many column volumes with 0.05 M Hg(II)–0.0002 M HNO$_3$ solution at a flow rate of 0.9 cm/min. The conversion ratio ($R \approx 0.5$) was substantially less than expected from eqn. (1) and dependent on flow rate. Apparently the HgS forming during the reaction adsorbed excess Hg(II). This at least in part is due to formation of double salts of the type 2Hg$_2$S·HgX$_2$ (where X is an anion such as nitrate) since these double salts are white[20] and the columns slowly changed in color from black to grey.

(c) ZnS. Silver ions are quantitatively retained (or adsorbed) by a ZnS column; a black band is formed which, at reasonable flow rates, has a sharp frontal edge. Although some Zn(II) appeared immediately in the effluent, the conversion ratio R only gradually approached the theoretical value of 0.5 predicted from eqn. (1). A typical experiment with a 0.048 M AgNO$_3$–1 M NaNO$_3$–0.001 M HNO$_3$ solution is illustrated in Fig. 2. Temperature was 25° and flow rate 5 cm/min. There is apparently some retention of displaced Zn(II), perhaps through reaction with some excess sulfide incorporated in the precipitate.

Uptake of such "excess" Zn(II) by the material was demonstrated by passing a 0.044 M Zn(NO$_3$)$_2$ solution through a similar ZnS column. Fifty percent breakthrough of Zn(II) occurred after passage of 13 column volumes (c.v.) which corresponds to an adsorptive capacity of the solid of 0.4 moles Zn(II) per kilogram. While this value seems large, it must be recognized that it represents only 4 % of the theoretical conversion capacity of the solid. If this adsorption of excess Zn(II) is indeed due to excess sulfide in the solid, this adsorption technique would constitute an exceedingly sensitive method of analysis of such solids.

On addition of silver nitrate solution [0.048 M Ag(I)–1 M NaNO$_3$–0.001 M HNO$_3$] to such a Zn(II) pretreated ZnS, the conversion ratio R reached 90 % of the theoretical value [eqn. (1)] within 1 c.v. — *i.e.*, much more rapidly than with the untreated material. However, a small discrepancy between observed and predicted conversion ratios remained, implying a residual reaction of Zn(II) with the silver sulfide formed or some other parasitic reaction.

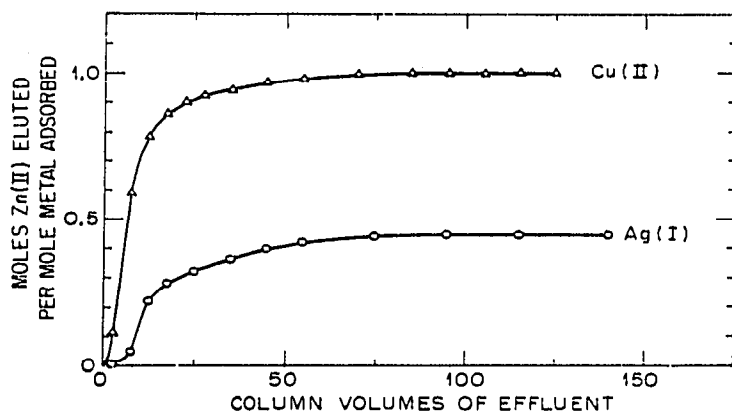Removal of Cu(II) from solution by adsorption on ZnS was tested with nitrate

Fig. 2. Reaction of Ag(I) and Cu(II) with ZnS. Column 0.2 cm^2 × 1.0 cm; 0.05 M metal solutions; flow rate *ca.* 5 cm/min; 25°.

solutions. A typical experiment involving addition of 0.052 M Cu(NO$_3$)$_2$–0.004 M HNO$_3$ is also illustrated in Fig. 2. Flow rate was *ca.* 5 cm/min, temperature 25°. On addition of the Cu(II) solution rapid conversion occurred with the formation of a black band with a sharp frontal edge. Although some Zn(II) appeared immediately in the effluent, the conversion ratio, as in the case of Ag(I), only slowly approached the theoretical value ($R = 1$).

Adsorption of Hg(II) by ZnS seems more complicated. Tests were made with *ca.* 0.053 M Hg(NO$_3$)$_2$–0.002 M HNO$_3$ solutions at 25°. Under these conditions, Hg(II) breakthrough occurred after 10 c.v. at a flow rate of 0.3 cm/min. While Hg(II) was absorbing, the column underwent a series of color changes (orange to black to grey) implying that a variety of compounds is formed. At elevated temperatures (97°) these color changes were faster but Hg(II) still showed significant breakthrough after approximately 10 c.v. Effluent analyses at both temperatures yielded very low values of R (*ca.* 0.1), presumably because of a combination of Zn(II) adsorption on ZnS and Hg(II) adsorption on the HgS produced.

(*d*) *CdS*. The stoichiometry for the displacement of Cd(II) from its sulfide by Ag(I), Cd(II) and Hg(II) was described earlier[1].

In more recent experiments, Au(III) (0.022 M AuCl$_3$–0.6 M HCl) was also found to react quantitatively with CdS to give a black band with sharp frontal edge. Displaced Cd(II) appeared immediately in the effluent (Fig. 3). The value for the conversion ratio, R, increased to about 1.1 after 19 c.v. Addition of more Au(III) was accompanied by a gradual decrease in R until after *ca.* 60 c.v. it approached an asymptotic value of 0.80. Presumably some of the Au(III) was retained by side reactions.
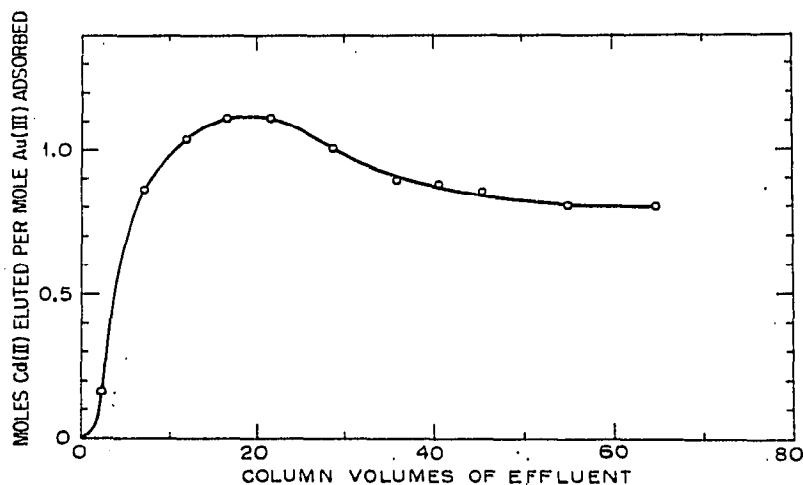
. Reaction of Au(III) with CdS. Column 0.2 cm² × 1.0 cm; 0.02 M Au(III); flow rate 3 cm/min; 25°.

(*e*) *PbS*. Reaction of PbS with Ag(I), Cu(II) and Hg(II) was found to be rapid and quantitative with small columns. The conversion ratios for Ag(I) and Cu(II) rapidly approached the theoretical values of 0.5 and 1.0 respectively as illustrated in Fig. 4 for 0.048 M AgNO₃-1 M NaNO₃-0.001 M HNO₃ and 0.052 M Cu(NO₃)₂-0.004 M HNO₃ solutions. The conversion ratio R in the case of Hg(II) [0.053 M Hg(NO₃)₂-0.0002 M HNO₃] was close to unity for the first 30 c.v. and then decreased to *ca*. 0.65. The color of the column slowly turned grey, presumably because of formation of the double salt Hg(NO₃)₂·2 HgS.

(*f*) *FeS*. Iron sulfide reacted sufficiently rapidly with Ag(I) (0.050 M AgNO₃), Cu(II) [0.052 M Cu(NO₃)₂-0.004 M HNO₃], and Hg(II) [0.053 M Hg(NO₃)₂-0.002 M HNO₃] to remove them quantitatively from their solutions at flow rates from 1 to 3 cm/min. Fe(II) appeared in the effluent in the expected ratio except in adsorption experiments with Hg(II) where R was about 90% of theoretical.

(*g*) *As₂S₃*. As shown in Fig. 5, addition of Ag(I) [0.048 M Ag(NO₃)₂-1 M NaNO₃-0.001 M HNO₃] to As₂S₃ gave quantitative adsorption at a flow rate of 7 cm/min; a black band with sharp frontal edge formed. After a few c.v. the conversion ratio reached the asymptotic value 0.33 as expected from eqn. (1). While
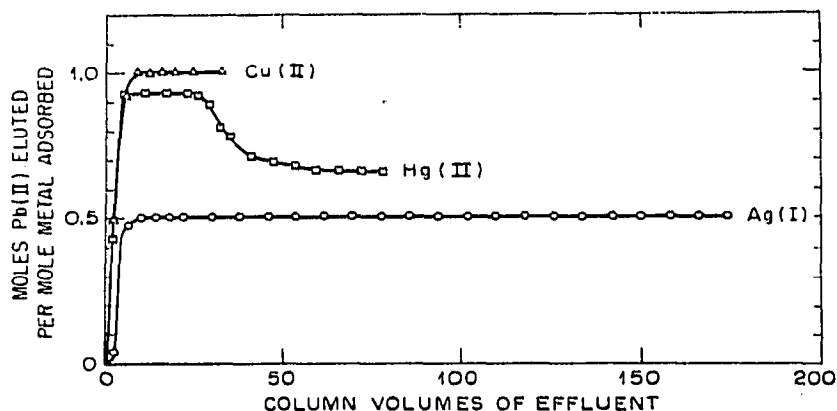

Fig. 4. Reaction of Ag(I), Cu(II) and Hg(II) with PbS. Column 0.2 cm² × *ca*. 1.4 cm; 0.05 M metal solutions; flow rate *ca*. 5 cm/min; 25°.

addition of Cu(II) [0.052 M Cu(NO$_3$)$_2$–0.004 M HNO$_3$] yielded a well defined dark band with sharp frontal edge at a flow rate of 3 cm/min, the extent of reaction was small and copper breakthrough occurred after *ca.* 7 c.v. As(III) appeared immediately in the effluent and reached an apparently asymptotic value $R = 0.75$ after 3 c.v. It is not clear why this value is larger than the theoretical value 0.67 expected from eqn. (1).
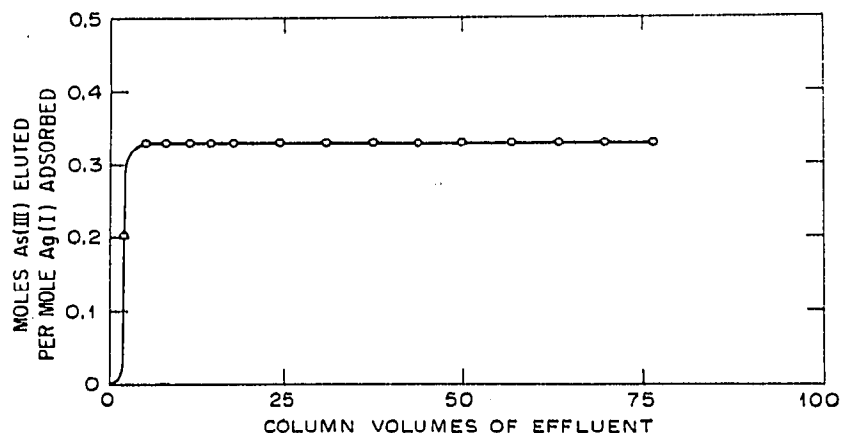

Fig. 5. Reaction of Ag(I) with As$_2$S$_3$. Column 0.2 cm^2 × 1.5 cm; 0.05 M Ag(I); flow rate 7 cm/min; 25°.

With Hg(II) [0.053 M Hg(NO$_3$)$_2$–0.0002 M HNO$_3$] removal was quantitative only for *ca.* 13 c.v. at a flow rate of 4 cm/min. There was no significant color change at first. Only after *ca.* 4 months did the column turn black. The conversion ratio R was *ca.* 0.3— *i.e.*, less than half the value predicted from eqn. (1).

(2) Uptakes and rates

The moles of metal per kg solid "adsorbed" by small (1–2 cm) columns of Ag(I), Cu(II), Zn(II), Pb(II), Cd(II) and As(III) sulfides varied from 0.5 to 14.5 at 50 % breakthrough (Table I) for the solutions given in Section 1 and at the flow rates given.

Values for the uptake by iron sulfide were variable and hence are not given in Table I. This variability may have been caused by partial oxidation of the original sulfide (FeS?) to ferric oxide and sulfur during the air-drying step. Some average values for metal ion uptakes (at 50 % breakthrough) by "iron sulfide" are Ag(I):5.8 moles/kg; Cu(II):2.0 moles/kg; Hg(II):2.5 moles/kg.

Most uptakes by the sulfides are enormous compared with standard ion exchange resin capacities. Particularly striking is uptake achieved with Ag(I); for the sulfides tested, it ranged between 5 and 20 moles per l of bed at 50 % breakthrough.

Indeed, for the reaction of Ag(I) with columns of many of the sulfides, flow rates as high as 50 cm/min were possible without smearing the frontal edge of the adsorption bands. Very high flow rates were also feasible for Hg(II) with PbS and Cu(II) with CdS and PbS. Except for CuS and As$_2$S$_3$ the uptakes of Ag(I) correspond to substantially more than 50 % of the value expected for the displacement reaction eqn. (1). For As$_2$S$_3$, the lower value obtained might imply that the final compound formed was Ag$_3$AsS$_3$ rather than Ag$_2$S which seems to be the case with the sulfides of Zn, Cd and Pb.

TABLE I

UPTAKE OF A NUMBER OF METALS BY VARIOUS SULFIDES (25°)

Sulfide	Metal ion	Flow rate (cm/min)	Uptake at 50 % breakthrough			
			Moles/kg	Moles per l/bed	Moles per mole M_xS_y	% of theoretical [eqn. (1)]
Zn	Ag(I)	7	14.5	20.3	1.4	71
	Cu(II)	4	6.6	9.3	0.6	65
	Hg(II)	0.3	0.5	0.8	0.05	5
Cd	Ag(I)	3	13.5	12.1	1.95	98
	Cu(II)	5	4.8	4.3	0.7	69
	Hg(II)	2	4.4	4.0	0.6	64
	Au(III)	3	3.6	3.2	0.5	78
Pb	Ag(I)	5	7.1	11.4	1.7	85
	Cu(II)	5	1.8	2.9	0.4	43
	Hg(II)	5	4.2	6.7	1.0	98
As	Ag(I)	7	11.1	5.5	2.7	46
	Cu(II)	3	0.9	0.5	0.2	7
	Hg(II)	4	2.1	1.1	0.5	17
Cu	Ag(I)	0.3	3.2	4.9	0.3	15
	Hg(II)*	0.9	3.3	5.0	0.3	32
Ag	Hg(II)	1	5.1	7.8	1.3	128

* Adsorbed at 97°.

Copper uptake by the various sulfides was consistently less than silver uptake. In the case of its reaction with ZnS, CdS and PbS very high uptakes were, however, achieved. With As_2S_3 the extent of reaction was so small as to imply that the reaction of Cu(II) occurs here only on the surface of the particles and that reaction within the particles is effectively arrested.

Uptake of Hg(II) by various sulfides was complicated because of the possible reaction of the HgS formed with additional Hg(II) to form double salts which could lead to "capacities" in excess of unity if computed with eqn. (1). In spite of this possibility, ZnS, As_2S_3 and CuS showed surprisingly low uptake of Hg(II)* at room temperature. This is particularly striking in the Hg(II)–ZnS system, since for it the free energy of the metathetical reaction is by far the largest but extent of reaction particularly small. Apparently reaction of Hg(II) with these sulfides occurs principally on the surface of the particles.

Uptake of Au(III) was tested only with CdS. At 50 % breakthrough uptake corresponded to 78 % of theoretical. In some preliminary experiments good adsorption was also found for platinum and bismuth with CdS.

(3) Crystal size and structure

Crystallite sizes were determined** for solids as precipitated and dried at 25° and for some solids after conversion (Table II). The observed rates of adsorption do not correlate in any direct and obvious way with the crystallite sizes or structure of

* In the reaction of Hg(II) with As_2S_3 the solid remained yellow at first which implies that the surface compound formed initially could be $Hg(AsS_2)_2$. This compound is yellow and has been described as a product of the reaction of Hg(II) with arsenic sulfide. See ref. 21.

** Crystallographic information was provided by R. L. SHERMAN of the ORNL Analytical Chemistry Division using X-ray low-angle scattering technique.

the sulfides. Although the ZnS crystallite size was smaller than that of CdS, the rates of conversion with Ag(I), Cu(II) and Hg(II) were all more rapid with CdS. Similarly, since ZnS and CdS may belong to the same zinc-blende type of structure, Hg(II) might be expected to react with them in about the same manner. However, as shown in Table I, Hg(II) converted ZnS about 5 % at 50 % breakthrough, while it converted CdS about 64 % at the same percent breakthrough and at a flow rate nearly 20 times faster.

TABLE II

STRUCTURE AND CRYSTALLITE SIZE FOR SULFIDES BEFORE AND AFTER CONVERSION

Sulfide	Structure (initial)	Size ($\mathring{A}$) (initial)	Converting ion	Structure (final)	Crystallite size ($\mathring{A}$) (final)
Zn(II)	Zinc-blende	$\sim$ 30	Ag(I)	Monoclinic	$\sim$ 430
Cd(II)	Zinc-blende	$\sim$ 70	Ag(I)	Monoclinic	550
			Cu(II)	Hexagonal	230
Pb(II)	Sodium chloride	215	Ag(I)	Monoclinic	$\sim$ 470
As(III)	Amorphous	20	Ag(I)	Monoclinic	$\sim$ 360
Cu(II)	—	$\sim$ 600	Ag(I)	Monoclinic	$\sim$ 700
			Hg(II)	—	$\sim$ 250
Ag(I)	Monoclinic	$\sim$ 290	Hg(II)	—	$\sim$ 250

The data in Table II show that the crystallite sizes of many converted sulfides were much larger than those of the original sulfides and, hence, that there was substantial crystal growth during the metathetical reaction. This would imply that the initial materials though largely amorphous, perhaps with crystalline "centers", have amorphous regions which are relatively continuous over many hundreds of $\mathring{A}$ and that during the reaction a large portion of this larger amorphous particle is transformed to a crystalline particle.

The rate and extent of conversion of these solids presumably are determined by rates of diffusion of the pertinent ions in the solids. Little is known about these diffusion rates for the type of micro-crystalline or amorphous materials with which we are dealing. However, the extreme rapidity of the reactions of Ag(I) with most sulfides and their large extent are probably in part connected with the large self-diffusion coefficient of Ag(I) in Ag_2S. PESCHANSKI[22] has reported it to be ca. $2 \cdot 10^{-9}$ cm^2sec^{-1} at 25°. This value is large enough to allow half times of reaction of the order of seconds with particles in the micron range provided that this diffusion step is rate determining. How far this is true cannot be established at present.

SUMMARY

Sulfides of Ag(I), Fe(II), Cu(II), Zn(II), Pb(II), Cd(II) and As(III) "adsorb" a number of transition metal ions from solution. The process proceeds primarily through metathetical reactions in which the metal of the sulfide is displaced by appropriate ions in solution. The reactions are usually fast and can be carried out in

small columns at flow rates of several cm/min. With Ag(I) and 1- to 2-cm columns of various sulfides, flow rates as high as 50 cm/min were feasible without breakthrough. The percent conversion of the sulfides at 50 % breakthrough varied from 5 % for the reaction of Hg(II) with CuS at 25° to about 128 % for the reaction of Hg(II) with Ag_2S. With ZnS uptakes as high as 20 moles of Ag(I) per liter of bed were obtained at 50 % breakthrough and a flow rate of 7 cm/min. While possibility of conversion must depend on relative stability of the sulfides, neither the rate of reaction nor the completeness of conversion seems related to the relative solubilities. The nature of the solid and the ease with which diffusion takes place are presumably important factors.

REFERENCES

1 H. O. PHILLIPS AND K.A. KRAUS, *J. Am. Chem. Soc.*, 85 (1963) 486.
2 W. M. LATIMER, *Oxidation Potentials*, 2nd Ed., Prentice Hall, New York, 1952.
3 O. C. RALSTON, C. R. KING AND F. X. TARTARON, *Trans. AIME*, 87 (1929) 389.
4 A. M. GAUDIN, *Trans. AIME*, 87 (1929) 417.
5 S. R. B. COOKE, *Advances in Colloidal Science*, Vol. 3, Interscience, New York, 1950, p. 357.
6 A. M. GAUDIN, H. R. SPEDDEN AND M. P. CORRIVEAU, *Trans. AIME*, 190 (1951) 780.
7 A. M. GAUDIN, D. W. FUERSTENAU AND M. M. TURKANIS, *Trans. AIME*, 208 (1957) 65.
8 A. M. GAUDIN, D. W. FUERSTENAU AND G. W. MAO, *Trans. AIME*, 214 (1959) 431.
9 R. PIONTELLI, *Bull. Soc. Chim. France*, (1949), D 197.
10 B. L. CLARKE AND H. W. HERMANCE, *Ind. Eng. Chem.*, 9 (1937) 292.
11 B. L. CLARKE AND H. W. HERMANCE, *Ind. Eng. Chem.*, 10 (1938) 591.
12 M. ZIEGLER, *Z. Anal. Chem.*, 180 (1961) 4.
13 M. ZIEGLER AND M. GIESELER, *Z. Anal. Chem.*, 191 (1962) 122.
14 M. ZIEGLER AND H. D. MATSCHKE, *Z. Anal. Chem.*, 191 (1962) 188.
15 M. ZIEGLER AND M. M. THA, *Z. Anal. Chem.*, 196 (1963) 81.
16 V. R. THOMAS, *Chemiker-Ztg.*, 88 (1964) 75.
17 R. O. BACH, *Anales Asoc. Quim. Arg.*, 37 (1949) 55.
18 A. KUTZELNIGG, *Z. Erzbergbau Metallhuettenw.*, 3 (1950) 77.
19 D. I. RYABCHIKOV, I. K. TSITOVICH AND M. K. TORPUDZHIYAN, *Dokl. Akad. Nauk SSSR*, 145 (1962) 825.
20 J. W. MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 4, Longmans, Green and Co., New York, New Impression, 1952, p. 961.
21 J. W. MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 9, Longmans, Green and Co., New York, New Impression, 1947, p. 296.
22 D. PESCHANSKI, *J. Chim. Phys.*, 47 (1950) 933.