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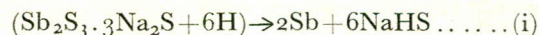
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Extraction of pure Sb_2S_3 and stibnite with aqueous sodium sulphide has been studied under different sets of conditions and the effect of Na_2S concentration and temperature have been examined. It was found that both the pure sulphide and the ore reacted with Na_2S in the same way. At the initial stage different reactions are involved but the main reaction responsible for extraction in the final stage can be represented as: $3Na_2S \text{ aq.} + Sb_2S_3 \rightleftharpoons Na_3SbS_3 \text{ aq.}$ In support of the proposed reaction, almost complete recovery of the dissolved antimony sulphide could be achieved in the form of pure crystals of $Na_3SbS_3 \cdot 9 H_2O(I)$. Results suggest that the method can be used for bulk leaching of stibnite ore and also for preparation of the pure sulpho-antimonite (I).

Leaching of stibnite with sodium hydroxide or sodium sulphide has been frequently employed in connection with electro-winning of antimony,¹⁻⁴ and also for beneficiation of low grade ores.^{3,5-8} With sodium hydroxide leaching, the solution contains a mixture of antimonites and sulpho-antimonites,¹ while with sodium sulphide, only sulpho-antimonites are believed to be formed. As the main purpose in most of these investigations had been to dissolve the antimony sulphide and use the solution for either electrolytic recovery of the metal or, separation of antimony sulphide, little attention seems to have been given to the study of the mechanism of dissolution (formation of different sulpho-antimonites) and less so to the isolation of the pure antimony compounds formed.

According to Mellor,⁹ Berzelius, Unger and Doelter first reported the isolation of impure sulpho-antimonites (composition not ascertained) from solutions obtained by treating antimony trisulphide with aqueous sodium sulphide. Pouget¹⁰ reported preparation of $Na_3SbS_3 \cdot 9 H_2O(I)$ by concentrating in an atmosphere of hydrogen, a solution of one mole of antimony trisulphide in three moles of sodium sulphide. It was also reported that the compound (I) is readily oxidised (to sulpho-antimonate) and that, after separation of sulpho-antimonate from a partially oxidised solution, a second crop of crystals having the composition $Na_6Sb_2S_9(II)$, were obtained. With one mole of antimony trisulphide dissolved in two moles of aqueous sodium sulphide, he claimed to have obtained a mixture of $NaSbS_2(III)$ and (I), the former separating out first. Unger however, dissolved the trisulphide in excess of sodium sulphide and reported the isolation of the compounds (I) and (III). Pouget further states that if a dilute solution of one mole of the trisulphide in two moles of sodium sulphide is evaporated *in vacuo*, besides crystals of (I), the compound $Na_2Sb_4S_7 \cdot 2H_2O(IV)$ can also be obtained.

Borchers³ recommends that during electrolysis of solutions of antimony sulphide in sodium sulphide, these should contain a 1:3 molar ratio of the two. Halske,² while proposing sodium sulphide as a solvent for electrolysis of antimony sulphide, represents the reaction at the cathode as:



(the compound $Sb_2S_3 \cdot 3Na_2S$, is believed to be formed in the solution). Perkins,¹¹ also suggests that during electrolysis, Na_3SbS_3 is reduced to the metal. These investigations indicate that in such solutions, the 1:3 compound may be predominantly present.

Recent work¹² on the solubility of antimony sulphide in alkali-alkali sulphide solutions in the presence or absence of H_2S has shown that the reactions are complicated due to the susceptibility of the products to oxidation. This appears to be the reason for the failure of attempts towards elucidation of the reaction mechanism and isolation of the reaction products. It is however, believed that, in such systems, several ions e.g. $SbSO^-$, Sb_2^- , SbS_2^- and SbS_3^{-3} etc., may be present.¹³ Study of the phase equilibrium in the system $Na_2S-Sb_2S_3-H_2O$ at $20^\circ C$. has shown that the solid compounds formed are $Na_2S \cdot 9H_2O$, $NaSbS_2$, $Na_2Sb_4S_7$ and Sb_2S_3 .

The above review indicates that the reaction between antimony trisulphide and aqueous sodium sulphide is not fully understood. Sulpho-antimonites are no doubt the principal products formed but one or more of these ($Na_3SbS_3 \text{ aq.}$, $NaSbS_2 \text{ aq.}$, $Na_2Sb_4S_7 \text{ aq.}$ etc.) may form depending on experimental conditions. Furthermore, susceptibility (as reported) of these to oxidation (or other changes) may give rise to side products such as sulpho-antimonate, antimonites, mixed oxysulphides or even antimonates. The system thus deserves further study. In order to understand the reactions that occur during dissolution of stibnite in sodium sulphide solutions, the author first studied the dissolution of pure Sb_2S_3 and found

* This work was carried out in the Department of Chemistry, University of Dacca.

that the final reaction can be satisfactorily represented by the equation:



Stibnite under comparable conditions also showed similar behaviour. The only difference between the two systems was decreased extraction in the case of the ore (as compared to the pure antimony sulphide). This is believably due to the difficulty of the leach liquor in reaching the sulphide particles incorporated in the silicious matrix of the ore, and not due to any other effect. In support of the proposed reaction, the author could recover, almost completely, all the antimony sulphide dissolved, in the form of pure crystals of the sulpho-antimonite, $\text{Na}_3\text{SbS}_3 \cdot 9\text{H}_2\text{O}$ (I), by a slight modification of Pouget's method (loc. cit). Results suggest a simple process for bulk extraction of the ore and for preparation of the pure sulpho-antimonite (I).

Materials

Antimony Trisulphide.—The sample was of E. Merck and was analysed for both antimony and sulphur by conventional methods.

Stibnite Ore.—This was obtained from Chitral (W. Pakistan) in the form of lumps. It was ground, sieved to 100 mesh size, dried at 105°C . for two hours and stored in a desiccator over fused calcium chloride. It was analysed for antimony, sulphide sulphur, and silica. Other elements were present only in insignificant amounts. The sample was free from elementary sulphur and sulphate.

Sodium Sulphide Solutions.—Approximately 3,6 and 9 percent w/v solutions (on the basis of anhydrous salt) were prepared from Howard's crystalline sample of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$. The solutions were finally standardised by iodimetric titration.

Other Solutions and Reagents.—These were prepared from A.R. products or Merck's certified samples by usual methods and each solution individually standardised.

Experimental

Analysis of Stibnite and also Pure Sb_2S_3 .—Weighed amounts of samples were dissolved in concentrated HCl and the H_2S completely boiled out in the presence of KCl.¹⁴ The antimony was next determined in the solution by iodimetric titration. Sulphur content of the samples were determined by evolution method employing standard hypochlorite as an absorbent for H_2S .¹⁵ Silica was determined by weighing after removal of the antimony

sulphide completely by acid treatment. The pure antimony sulphide contained 99.8 percent Sb_2S_3 ; the ore analysed as follows: Sb 37.42 percent S (sulphide) 14.73 percent and SiO_2 47.86 percent.

Extraction Experiments.—For experiments at room temperature, weighed portions (1.002 g. of pure sulphide or 1.0 g. of the ore) of the sample were treated with 2,5,10,15,20 and 25 ml. portions of the sulphide solutions of required concentration in covered glass beakers and magnetically stirred for half an hour in each case (this time was found sufficient for establishment of equilibrium). The mixture was next filtered through a sintered crucible by suction and the residue washed thoroughly with liberal amounts of freshly boiled, cold distilled water. The washings were collected with the filtrate and the mixture diluted to 500 ml. in a measuring flask. Fifty ml. portions were pipetted out and analysed. Excess of concentrated HCl was added till the sulphide first precipitated and finally dissolved. The H_2S was boiled out after addition of KCl. The solution was then cooled, treated with 2-5 g. of Rochelle salt and then neutralised with sodium carbonate. It was then finally made sufficiently alkaline with sodium bicarbonate and titrated with standard iodine in the presence of starch indicator.

For experiments at boiling temperature, 1.0 g. portions of the ore were treated with 5,10 and 15 ml. portions of 3.22 percent sodium sulphide and the mixture boiled under reflux, avoiding access of air, for five minutes. Afterwards the mixture was quickly filtered and the residue washed with boiling distilled water. The filtrate and washings collected together were cooled, made up to definite volume and analysed for antimony by the foregoing method.

For experiments with bulk amounts of the ore, 50.0 g. portions were boiled with 500 ml. of 3.22 percent sodium sulphide solution for 15 minutes under reflux. The mixture was processed in the same way as described and the antimony content of the final solution determined again by iodimetric titration.

Crystallisation of the pure thio-antimonite $\text{Na}_3\text{SbS}_3 \cdot 9\text{H}_2\text{O}$ (I) from the leach liquor was carried out by a simple modification of Pouget's method¹⁶ and is described at the end of this paper.

Results and Discussion

Extraction of Pure Antimony Sulphide.—For experiments at room temperature ($28-30^\circ\text{C}$.), a constant amount of the pure sulphide was treated with varying volumes of Na_2S solutions containing

different amounts of the extractant. Results are given in Table 1. It can be seen that the extraction initially increases with increasing amounts of leach liquor (increasing Na_2S input) for the

(curve 3) in Fig. 1 is again similar to the earlier two curves indicating overall similarity. Beneficial effect of boiling temperature (on extraction) can be seen from the data in Table 3.

TABLE 1.—DISSOLUTION OF PURE Sb_2S_3 IN SODIUM SULPHIDE SOLUTIONS.

Na ₂ S solution used		Sb ₂ S ₃ extracted				Molar ratio Na ₂ S/Sb ₂ S ₃ in leach liquor
Strength % w/v	Volume taken ml.	g. mole × 10 ⁻³	g.	%	g. mole × 10 ⁻³	
3.35	2.0	0.859	0.309	30.9	0.908	0.94
	5.0	2.147	0.642	64.2	1.888	1.13
	10.0	4.294	0.903	90.3	2.658	1.61
	15.0	6.442	0.951	95.1	2.798	2.30
	20.0	8.589	0.975	97.5	2.868	2.99
	25.0	10.737	0.975	97.5	2.868	3.74
6.42	2.0	1.646	0.550	55.0	1.618	1.01
	5.0	4.115	0.894	89.4	2.632	1.56
	10.0	8.230	0.932	93.2	2.742	3.00
	15.0	12.345	0.932	93.2	2.742	4.50
8.05	2.0	2.064	0.666	66.6	1.959	1.05
	5.0	5.160	0.874	87.4	2.572	2.00
	10.0	10.320	0.915	91.5	2.694	3.83
	15.0	15.480	0.915	91.5	2.694	5.74

Duration of treatment 30 minutes.

three sets of experiments employing 3.35, 6.42 and 8.05 percent solutions, but finally becomes constant indicating saturation. Dilute solutions of Na_2S appear to be somewhat more useful for extraction. The extraction behaviour has been graphically represented by curve 1 in Fig. 1.

Extraction of Stibnite.—Extraction of the ore carried out under comparable conditions indicated general similarity between the two systems studied. Results are given in Table 2, and graphically represented by curve 2 in Fig. 1. The only difference observed was the decreased extraction in the case of the ore even when only half the amount of Sb_2S_3 (compared to pure sulphide) was taken.

Results for experiments carried out at boiling temperature employing 3.22 percent Na_2S solutions are given in Table 3. The extraction curve

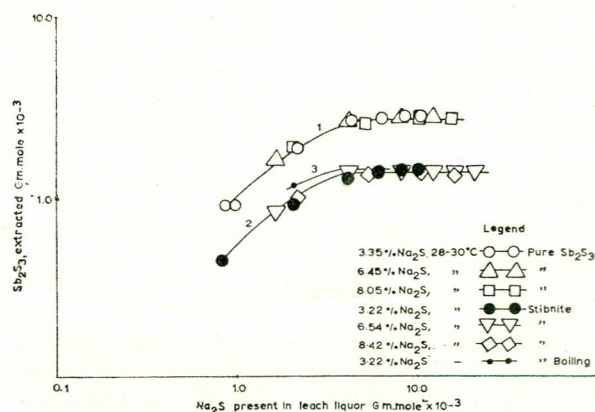


Fig. 1.

TABLE 2.—DISSOLUTION OF STIBNITE IN SODIUM SULPHIDE SOLUTIONS.

Na ₂ S solution used			Sb ₂ S ₃ extracted			Molar ratio Na ₂ S/Sb ₂ S ₃ in leach liquor
Strength % w/v	Volume taken ml.	g. mole × 10 ⁻³	g.	%	g. mole × 10 ⁻³	
3.22	2.0	0.825	0.150	28.7	0.441	1.87
	5.0	2.063	0.307	58.8	0.902	2.28
	10.0	4.125	0.435	83.4	1.280	3.22
	15.0	6.189	0.473	90.7	1.392	4.45
	20.0	8.251	0.482	92.5	1.420	5.81
	25.0	10.320	0.482	92.5	1.420	7.26
6.54	2.0	1.675	0.274	52.6	0.807	2.08
	5.0	4.189	0.468	89.7	1.377	3.04
	10.0	8.378	0.468	89.7	1.377	6.08
	15.0	12.567	0.468	89.7	1.377	9.13
	20.0	16.756	0.468	89.7	1.377	12.17
	25.0	20.945	0.468	89.7	1.377	15.21
8.42	2.0	2.157	0.337	64.5	0.990	2.18
	5.0	5.393	0.449	86.5	1.328	4.06
	10.0	10.786	0.449	86.5	1.328	8.12
	15.0	16.179	0.449	86.5	1.328	12.18

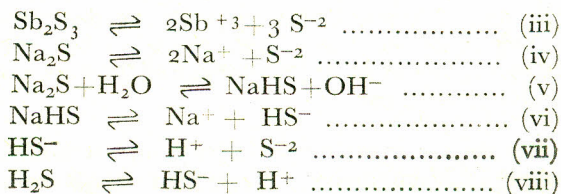
Duration of treatment 30 minutes.

TABLE 3.—DISSOLUTION OF STIBNITE IN SODIUM SULPHIDE SOLUTIONS EFFECT OF BOILING TEMPERATURE ON EXTRACTION.

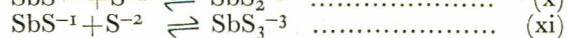
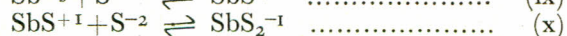
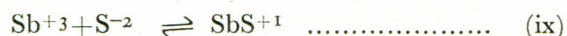
Na ₂ S/solution used			Sb ₂ S ₃ extracted			Molar ratio Na ₂ S/Sb ₂ S ₃ in leach liquor
Strength % w/v	Volume taken ml.	g. mole × 10 ⁻³	g.	%	g. mole × 10 ⁻³	
3.22	5.0	2.062	0.403	77.3	1.185	1.74
	10.0	4.125	0.478	91.7	1.407	2.93
	15.0	6.187	0.478	91.7	1.407	4.38

Stibnite used 1.00 g. 0.5215 g. Sb₂S₃ 1.535 × 10⁻³ moles; Duration of boiling 5 minutes.**Discussion**

In a system containing solid Sb₂S₃ and dissolved Sb⁺³, S⁻² and Na⁺ as major components and H⁺, OH⁻, HS and traces of H₂S as minor components, the overall picture must be built up on the basis of the following equilibria:

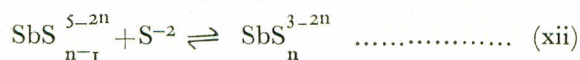


If the formation of thio-anions of Sb^{+3} is presumed to be a stepwise process, it can be written as follows:



... ..

... ..



If dissolution (or extraction) of the sulphide is directly dependant on formation of antimony (III)-thio-anions, then increased extraction on increasing the Na_2S input can be easily understood. The fact that dilute solutions of sodium sulphide are more effective in extraction can be explained on the basis of greater availability of S^{-2} ions in dilute solutions of the sulphide which would facilitate formation of antimony (III)-thio-anions. Increase in extraction in the case of pure antimony sulphide is believed to be due to the availability of greater surface of contact between the sulphide and the leach liquor. In the case of the ore, although it was taken in a fine state of subdivision, believably the sulphide particles were not completely dislodged from the silicious matrix, resulting in prevention of the leach liquor from approaching the entire mass of the sulphide present. Beneficial effect of boiling temperature on extraction can be explained on the basis of greater penetration of the leach liquor into the sulphide material and also due to greater solubility of the thio-complexes at those temperatures.

Since access of oxygen to the system was largely excluded, oxidation can not play a major role. Moreover, since no NaOH was added to the system, oxy-sulphides if at all formed, can only be derived from the OH ions produced by the hydrolysis of the Na_2S .

In Fig. 1., for all the systems studied, $\log (\text{Sb}_2\text{S}_3)_{\text{aq.}}$ has been plotted against $\log (\text{Na}_2\text{S})_{\text{aq.}}$ and the resulting curves designated as 'extraction curves'.

Since the author was mostly interested in the mechanism of extraction under practical conditions of leaching, no attempt was made to control either the ionic strength of the medium or the concentrations of the reactants and products at a level where activity corrections could be ignored. The pH of the solution was also not checked for similar reasons. Therefore, the results of the

author cannot be treated precisely, on the basis of the different equilibria proposed. However, the nature of the extraction curves leads to the assumption that initially several reactions of the type given in equations (ix) to (xii) may be involved, together with the equilibria represented in equations (iii) to (viii). But, with the onset of saturation, the overall effect leads to the formation of a 1:3 $\text{Sb}_2\text{S}_3 : \text{Na}_2\text{S}$ compound in the aqueous phase as the major product.

The author's success in isolating pure $\text{Na}_3\text{SbS}_3 \cdot 9\text{H}_2\text{O}$ from the leach liquor in almost theoretical yields lends strong support to the views given above.

Extraction of Bulk Amounts.—After establishing optimum conditions of extraction, 50.0 g. portions of the ore were treated with 500 ml. portions of 3.22 percent sodium sulphide. The reaction was found to attain equilibrium at boiling temperature, within 15 minutes and the leach liquor contained 91.79 percent of the sulphide content of the ore. The process thus appears quite simple and suitable for rapid leaching of bulk quantities of stibnite ores.

Crystallisation of the Pure Thio-antimonite from the Leach Liquor.—Pouget¹¹ has given a method for preparation of $\text{Na}_3\text{SbS}_3 \cdot 9\text{H}_2\text{O}$ and also a method for both this compound and NaSbS_2 . The author could not reproduce his later work but the former proved successful. A little modification enabled the author to use 6.54 percent sodium sulphide and stibnite ore (in place of the pure sulphide) for obtaining the pure thio-antimonite.

Method

Stibnite (10g.) was taken (the sample contained 5.215 g. pure Sb_2S_3 in 10 g.) Sodium sulphide solution (50 ml. of 6.54%) was added. The mixture was stirred for half an hour excluding access of air. It was filtered rapidly and excess of alcohol was added to precipitate out the thio-salt. The precipitate was washed with alcohol till it was free from sulphide (excess Na_2S) and then dissolved in a minimum volume of freshly distilled cold water, and any insoluble matter present (traces) was filtered off. It was evaporated on a water bath in a current of hydrogen and cooled in a desiccator (avoiding access of oxygen or carbon dioxide). The greenish yellow well-formed crystals were collected and dried over concentrated sulphuric acid for three days. Yield was 7.895 g. i.e. over 93 percent of theoretical. Analysis of the crystals: Found Sb, 26.93, 26.98; S^{-2} , 20.96, 21.19; S (total), 20.20 percent.

Calculated for $\text{Na}_3\text{SbS}_3 \cdot 9\text{H}_2\text{O}, \text{Sb}$, 27.11; S (sulphide and total) 21.42 per cent.

Since almost complete recovery of the antimony sulphide dissolved could be achieved in the form of the pure thio-antimonite, the final dissolution reaction appears to be well represented by the equation (vi).

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