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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Gannon, Keith and Wilson, David J.(1986) 'Removal of Antimony from Aqueous Systems', Separation Science and Technology, 21: 5, 475 — 493
To link to this Article: DOI: 10.1080/01496398608056130
URL: http://dx.doi.org/10.1080/01496398608056130

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SEPARATION SCIENCE AND TECHNOLOGY, 21(5), pp. 475-493, 1986

Removal of Antimony from Aqueous Systems

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Abstract

Antimony(III) is readily removed from aqueous systems by coprecipitation with ferric hydroxide and by adsorbing colloid flotation with ferric hydroxide and sodium dodecyl sulfate. Aluminum hydroxide is not effective in removing antimony. Precipitation with lime requires quite large quantities of lime in order to reduce residual Sb levels to desired levels. Precipitation of the sulfide in the presence of Fe(II) or Fe(III) may produce low residual concentrations, but runs the risk of exposure to highly toxic hydrogen sulfide.

INTRODUCTION

Antimony as the free metal and as the sulfide stibnite has been known from antiquity. Stibnite, Sb_2S_3, is the principal ore; it is smelted either by direct reduction with scrap iron or by roasting to form Sb_4O_6 and then reducing the oxide to the metal with carbon. Antimony is used in the production of Babbitt metal, Britannia metal, bearing metals, pewter, white metal, storage battery plates, printing type, ammunition, and cable sheathings. Its compounds are used in abrasives, as catalysts, and in ceramics, pigments, flameproofing chemicals, pharmaceuticals, dyeing, pyrotechnics, and metal finishing (*1*, *2*). Sax gives antimony compounds a toxic hazard rating of High for chronic systemic exposure by ingestion or inhalation (*3*); Sittig lists the symptoms of chronic oral antimony poisoning as dry throat, sleeplessness, dizziness, nausea, loss of appetite, and liver and kidney degeneration (*2*).

Two of the major sources of environmental antimony are the mining and smelting industries. We give a representative sampling of the

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literature on this. Bauer (*4*) noted the accumulation of antimony (as well as other toxic metals) in the sediments of the lakes of the Coeur d'Alene River, Idaho, in 1976. Also in 1976 the Environmental Protection Agency (EPA) published a review of antimony and its compounds as environmental contaminants (*5*). Another EPA report published that year discussed waste generation, treatment, and disposal in the metals mining and concentrating industries; this dealt with potentially hazardous wastes, including antimony (*6*). In 1979 Matos (*7*) noted high concentrations of toxic metals (including antimony) in three Bolivian rivers as a result of effluent discharges from metallurgical plants. Also that year Ugolini and Ottaviani (*8*) discussed environmental contamination resulting from the antimony extractive and derivative-producing industries, taking particular note of the orogenic changes in the extraction zones. Li (*9*) noted in 1981 that Greenland snows deposited since 1960 show large pollution inputs of a number of heavy metals, including antimony. Andreae and co-workers (*10*) reported substantial inputs of arsenic and antimony into an estuary in Portugal from a pyrite roasting plant. Ndiokwere and Guinn (*11*) noted the presence of elevated concentrations of toxic metals, including antimony, in Nigerian rivers and harbors in 1983 as a result of industrial pollution. A somewhat different source of environmental antimony was reported by Mumma and co-workers (*12*); they found elevated Sb levels in sewage sludge in a city in which there was a large glass manufacturing plant. The EPA has published guidelines for discharges of antimony in the primary aluminum smelting and secondary lead production industries (*13*).

Another significant source of environmental antimony is coal. Hildebrand, Cushman, and Carter (*14*) determined 55 elements in the aqueous effluents from a coal conversion pilot plant and discussed their potential toxicity and bioaccumulation in aquatic systems. Cherry and Guthrie (*15*) showed that the major mechanism for the removal of trace elements from ash basin effluent was sedimentation, but that bioaccumulation was also important. Griffin and co-workers have published extensively on the solubility and toxicity of potential pollutants from Lurgi gasification, H-coal liquefaction, and SRC-I liquefaction wastes; and from fly ash, slag, chars, and coal cleaning residues (*16–20*). Elseewi, Page, and Doyle (*21*) extracted a number of toxic trace elements, including Sb, from the fly ashes of western United States coals, finding that trace element release was highly dependent on the method of extraction. Popov, Rafel, and Zakusilova (*22, 23*) showed that coal combustion for electricity generation was responsible for the antimony found in snow samples taken in Frunze, Kirghiz SSR; they found that most of the antimony was water soluble. Rokukawa and Murayama (*24*) found that the strongly alkaline leachate from the fly ash of a coal-fired power plant contained up to 2 mg/L of antimony.

The toxicology of antimony has been reviewed by Stemmer (*25*) and by Elinder and Friberg (*26*). On the basis of toxicological findings, the United States EPA has set as a drinking water criterion a maximum Sb concentration of 146 μg/L; their water quality criterion document reviews antimony, its uses, and its toxicology (*27*). Sunagawa (*28*) has shown that the toxicity of antimony metal and Sb_2O_3 in rats is much less than that of arsenic.

The United States EPA has published effluent limitations guidelines for both the ore mining and dressing point source category (*29*) and the electric power generation point source category (*30*).

Chinese workers (*31*) have noted that mill effluents containing a number of heavy metals (including Sb), cyanide, and xanthate can be purified by destroying the cyanide complexes with H_2SO_4, precipitating the heavy metals with sodium sulfide, and removing the resulting sulfides by flotation. One expects that this process might be of some hazard to the operators. Parker and co-workers (32) have reviewed antimony removal technology for mining industry wastewaters. They noted that Sb concentrations in effluents from tailings ponds after settling were typically in the range 0.1–0.2 mg/L, which presents no problem. For wastewaters containing soluble antimony compounds, however, sulfide precipitation produces effluents containing 2–3 mg/L or more of Sb, and lime precipitation yields effluents containing at least 1.0 mg/L of Sb. The target level being sought was 0.5 mg/L, so these techniques cannot be regarded as satisfactory. These workers reviewed a number of other possible techniques for Sb removal, and concluded that ion exchange and the use of insoluble starch xanthate could be regarded as promising. Carbon adsorption, sodium borohydride reduction, and peat moss adsorption were regarded as less promising by these authors.

We have investigated the use of floc foam flotation for the removal of a number of metals (*33–35*). In the first stage of this operation, the toxic material to be removed is coprecipitated/adsorbed with a carrier floc, usually ferric or aluminum hydroxide. The resulting mixed floc is then removed by flotation. However, if the cost of land were low, there is no reason why this floc could not be removed by settling. We note that Csanady and Kelemen (*36*) and Pierce and Moore (*37*) have obtained good results removing low levels of arsenic from aqueous sytems by coprecipitation and adsorption with ferric hydroxide.

The inadequacy of the presently available techniques for antimony removal noted by Parker et al. (*32*) and the success we and others have had in removing trace heavy metals by various methods motivated the present work. We here describe procedures and results of several different antimony removal techniques. The techniques employed were:

(a) Floc foam flotation with ferric hydroxide and sodium dodecyl sulfate (SDS)
(b) Coprecipitation with ferric hydroxide
(c) Coprecipitation with aluminum hydroxide
(d) Coprecipitation with lime (CaO)
(e) Precipitation as Sb_2S_3

II. EXPERIMENTAL PROCEDURES

A. Chemicals

All reagents used were Fisher certified grade except the following. Antimony trioxide was Baker Analyzed reagent grade from J. T. Baker. The Rhodamine B was obtained from the G. Frederick Smith Chemical Company; the hydroxylamine hydrochloride and ceric ammonium sulfate came from Matheson, Coleman, and Bell; and the ferrous sulfate was granular technical grade from Sargent Welch. All aqueous solutions were made up with deionized water.

B. Foam Flotation Procedure

Antimony(III) samples for foam flotation runs were prepared by adding 10.0 mL of a 1000-mg/L Sb(III) stock solution to approximately 600 mL of water. The Sb stock solution was prepared by dissolving 1.197 g of Sb_2O_3 in 100 mL of concentrated HCl and then diluting the solution to 1.00 L with 1 *M* HCl. The ionic strength of the sample solution was then adjusted by addition of an appropriate volume of a 1.00 *M* $NaNO_3$ solution. 50.0 mL of a 1000-mg/L Fe stock solution [made from $Fe(NO_3)_3 \cdot 9H_2O$]) was then added to the stirring solution in two aliquots. The first step in the $Fe(NO_3)_3$ addition consisted of adding approximately 40 mL of the Fe(III) stock solution, then adjusting the pH of the solution to 7.0 with small additions of 1 *M* NaOH. To aid in the formation of $Fe(OH)_3$ flocculant, the solution was then allowed to sit unstirred for 3 min. After 3 min, a second $Fe(NO_3)_3$ aliquot (approximately 10.0 mL) was added, the pH readjusted to 7.0, and the solution again allowed to sit for 3 min. The final step in preparing the solution for addition to the foam flotation column was the addition of 40.0 mL of a 1000-mg/L SDS (sodium dodecyl sulfate) solution. After the 40-mL aliquot of stock SDS had been added to the solution, the solution pH was adjusted to roughly the desired value by addition of 1 *M* NaOH and 1 *M* HNO_3. The solution volume was then adjusted to 1.00 L and the pH accurately adjusted with small additions of 0.1 *M* NaOH and 0.1 *M* HNO_3.

The 1.00-L flocculant/Sb sample was then introduced into a batch flotation system (see Fig. 1). The Pyrex glass column was 6.5 cm in diameter and 60 cm in length. The top of the column was closed with a large rubber stopper; the bottom was equipped with a mounted stopcock for sample collection and a 40–60 mesh fine pore fritted glass sparger for introducing the air which generated the foam. Foam was discharged from a sidearm 6 cm from the top of the column. The flow of house air through the fritted glass sparger was controlled by a microvalve with a vernier control; flow rates were measured with a soap film flowmeter and stopwatch. The air was passed through Ascarite to remove acidic gases, through a water saturator, and through a 2 × 50 cm column packed with glass wool to remove dusts or mists (*38*).

Air flow rate was adjusted to 180 mL/min, and 25 mL solution samples were removed at 3, 5, and 10 min after the addition of the 1-L sample to the flotation column. The sampling stopcock was purged before each sample was taken to avoid sample contamination. The 25-mL samples

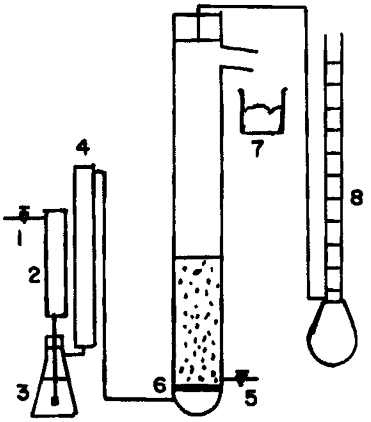

FIG. 1. The foam flotation column. (1) Air needle valve, (2) ascarite tube for CO removal, (3) humidifier, (4) glass wool column, (5) drain, (6) fritted glass disk, (7) discharged foam, (8) soap film flowmeter.

were then analyzed colorimetrically by a procedure described by Charlot (*39*). A detailed description of the technique is provided later in this paper.

C. Procedure for the Coprecipitation of Sb(III) with Ferric and Aluminum Hydroxides

Antimony(III) samples were prepared by adding an appropriate amount of 1000 mg/L Sb(III) stock solution to approximately 600 mL of water. The ionic strength of the solution was then adjusted to the desired level by the addition of one of three stock solutions (4.0 *M* $NaNO_3$, 4.0 *M* NaCl, or 2.0 *M* Na_2SO_4). To the stirring Sb(III) sample an appropriate volume of a 1000-mg/L flocculating agent stock solution was then added in one aliquot. The flocculating agents employed were ferric nitrate, aluminum nitrate, and ferric chloride. The solution pH was then adjusted to the desired level with small additions of 1 *M* NaOH. The solution was then diluted to 1.0 L and the pH exactly adjusted with small additions of 0.1 *M* NaOH and 0.1 *M* HNO_3. The flocculant was then allowed to precipitate for 10.0 min. After the precipitation period a 10.0-mL sample of the decantate was removed and analyzed colorimetrically by Charlot's procedure as described later.

D. Procedure for Sb/Lime Coprecipitation

Sb(III) samples for use in the Sb/lime coprecipitation study were prepared in the manner described in Section II-B. The desired amount of Sb(III) was added as stock solution, and the final solution volume was then adjusted to 1.0 L. To the stirring Sb(III) sample the desired amount of pulverized lime (CaO) was then quickly added. The solution was stirred for a few seconds and the lime was then allowed to precipitate. At 5, 15, and 30 min after precipitation was begun, 10.0 mL samples of the decantate were removed and analyzed colorimetrically for residual Sb.

E. Procedure for Antimony Trisulfide Precipitation

Sb(III) samples for use in the Sb_2S_3 precipitation study were prepared in the manner described in Section II-B. After the Sb(III) concentration of the solution had been adjusted to the desired level, the desired volume of a 10,000-ppm Fe(II) or Fe(III) solution was added in a single aliquot.

The pH of the stirring solution was then adjusted to the desired value by the slow addition of a 0.5-*M* Na_2S solution. The Sb solution volume was then adjusted to 1.0 L with water. Solution stirring was then stopped and precipitate was allowed to settle. 10.0 mL samples of the decantate were then removed at regular intervals after precipitation was begun. The samples were then analyzed colorimetrically for residual Sb(III).

F. Procedure for Colorimetric Analysis of Sb(III)

10.0 mL of concentrated HCl was added to 10.0 mL of each sample which was analyzed colorimetrically. 2.0 mL of a 1.0% Na_2SO_3 solution was then added to the acidic Sb sample. The Na_2SO_3 served to reduce Sb(IV) to Sb(III). Sb(III) present in the solution was then oxidized to Sb(V) by addition of a ceric ammonium sulfate solution prepared by saturating a 3.0-*M* H_2SO_4 solution with ceric ammonium sulfate. The ceric ammonium sulfate solution was added dropwise to the Sb solution until the Sb solution retained the deep yellow color of the ceric salt, at which point oxidation of Sb(III) was considered complete. Excess ceric ion and any Fe(III) which were present in the sample solution were then reduced by the dropwise addition of a 1% hydroxylamine hydrochloride solution. Reduction was complete when the sample solution returned to a clear, colorless state.

Sb(V) was then extracted with isopropyl ether which was saturated with 1 *M* HCl. The Sb sample was added to a separatory funnel which contained 10 mL of HCl saturated isopropyl ether and 60 mL of water. The solution was shaken for 30 s and allowed to separate for exactly 2 min. The aqueous layer was then drained and discarded. The remaining organic phase was then washed with 2 mL of 1% hydroxylamine hydrochloride and allowed to separate for 1 min. The retained organic phase was then washed with 1 mL of 1 *M* HCl, allowed to separate for 1 min, and the aqueous phase drained and discarded. Sb(V) was then complexed by addition of 2 mL of a 0.20% Rhodamine B solution in 1 *M* HCl. Sb(V) forms a red-violet complex with Rhodamine B and chloride ion which is readily extracted into isopropyl ether. After addition of Rhodamine B the solution was shaken for 30 s and allowed to separate for 1 min. Due to the relative instability of the Rhodamine B-Sb(V) complex, the amount of time between formation of the complex and any absorbance measurements must be consistent in all Sb(V) extractions. Once the solution had separated, the aqueous phase was drained off and discarded, and the organic phase was removed and diluted to 25.0 mL with HCl saturated isopropyl ether. Absorbance measurements were then made at 550 nm on a Beckman Model B spectrophotometer which had a cell with a 5-cm pathlength. HCl saturated isopropyl ether was used as a standard. Calibration curves for the instrument were obtained by analyzing dilutions of the 1000 mg/L stock solution of Sb. A diagram of the calibration curve used in the analysis is shown in Fig. 2.

III. RESULTS

The results of these studies are presented in tabular form as follows:

(a) The results of the foam flotation study are presented in Tables 1, 2, and 3.

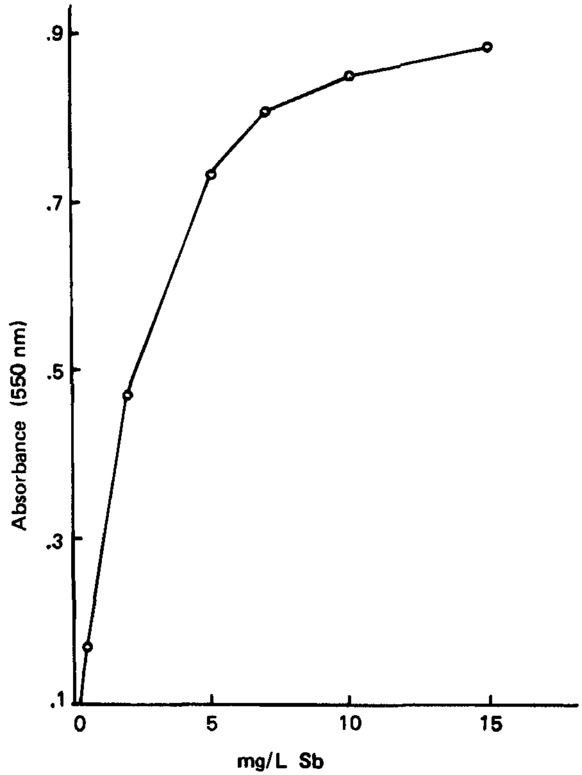

FIG. 2. A representative calibration curve for the colorimetric antimony analysis. Complex Sb(V)-Rhodamine B; cell path length 5 cm; wavelength 550 nm.

TABLE 1
Floc Foam Flotation of Antimony with $Fe(OH)_3$ and NLS. Residual Antimony (ppm) (3 min)[a]

	Added $NaNO_3$ (*M*)						
pH	0	0.001	0.0025	0.0050	0.100	0.250	0.500
2.0	3.2	1.8	—	—	—	—	—
2.5	1.8	0.7	0.6	2.8	1.5	3.8	—
3.0	0.8	0.8	0.6	0.6	1.0	4.6	—
3.5	1.5	1.5	1.2	2.3	3.5	—	—
4.0	1.7	2.6	4.1	—	—	—	—
4.5	2.7	2.9	4.2	—	—	—	—
5.0	0.8	2.5	—	—	—	—	—
5.5	1.9	—	—	—	—	—	—
6.0	1.6	—	—	—	—	—	—
6.5	4.8	—	—	—	—	—	—

[a] All runs were made with 10 ppm Sb(V), 50 ppm Fe(III), and 50 ppm SDS. Initial sample volume = 1 L, air flow rate = 180 mL/min, duration of runs = 10 min.

TABLE 2
Floc Foam Flotation of Antimony with $Fe(OH)_3$ and NLS. Residual Antimony (ppm) (5 min)[a]

	Added $NaNO_3$ (*M*)						
pH	0	0.01	0.025	0.050	0.100	0.250	0.500
2.0	4.6	1.4	10.0	—	—	—	—
2.5	2.2	0.7	0.5	1.6	0.8	2.8	—
3.0	1.2	0.7	0.4	0.4	0.5	1.2	4.9
3.5	1.2	0.8	0.4	0.6	0.7	2.3	—
4.0	1.2	1.2	1.9	1.5	3.8	—	—
4.5	1.2	1.2	2.7	5.4	—	—	—
5.0	0.4	2.0	4.8	5.7	—	—	—
5.5	1.0	—	—	—	—	—	—
6.0	1.0	—	—	—	—	—	—
6.5	4.8	—	—	—	—	—	—

[a] All runs were made with 10 ppm Sb(V), 50 ppm Fe(III), and 50 ppm SDS. Initial sample volume = 1 L, air flow rate = 180 mL/min, duration of runs = 10 min.

(b) The results of the precipitation study of Sb with ferric and aluminum hydroxides are presented in Table 4.

(c) The results of ionic strength effects on the ability of $Fe(OH)_3$ to coprecipitate Sb are presented in Table 5.

(d) The results of runs made to verify the Sb precipitating ability of lime are presented in Table 6.

(e) The results of the feasibility study of precipitating Sb as a sulfide are presented in Table 7.

IV. DISCUSSION

A. Foam Flotation

Antimony(V) was found to be most readily removed from aqueous solution by foam flotation when solution pH was adjusted to the 3.0 to 3.5 range. Residual Sb concentrations were reduced in this pH range to less than 1 ppm within 3 min after the solution was added to the flotation column. Ionic strength seemed to have less of an effect on Sb removal

TABLE 3

Floc Foam Flotation of Antimony with $Fe(OH)_3$ and NLS. Residual Antimony (ppm) (10 min)[a]

	Added $NaNO_3$ (*M*)						
pH	0	0.01	0.025	0.050	0.100	0.250	0.500
2.0	10.0	1.8	10.0	—	—	—	—
2.5	5.2	0.9	0.5	1.5	0.6	1.3	—
3.0	2.9	1.2	0.4	0.4	0.5	0.8	4.0
3.5	3.3	1.8	0.4	0.4	0.5	1.2	—
4.0	0.6	0.7	1.0	1.2	1.5	4.0	—
4.5	0.2	0.7	1.4	3.5	5.4	>6	—
5.0	0.2	1.4	4.1	4.0	>6	—	—
5.5	0.6	>6	—	—	—	—	—
6.0	0.6	—	—	—	—	—	—
6.5	4.8	—	—	—	—	—	—

[a] All runs were made with 10 ppm Sb(V), 50 ppm Fe(III), and 50 ppm SDS. Initial sample volume = 1 L, air flow rate = 180 mL/min, duration of runs = 10 min.

TABLE 4
Results of Precipitation Study

pH	Flocculating agent	Initial concentration of flocculant[a]	Initial concentration of antimony	Residual antimony
7.0	$Fe(NO_3)_3$	100	50	4.4
8.0	″	″	″	4.1
9.0	″	″	″	10.0
10.0	″	″	″	10.0
7.0	″	″	25	1.1
8.0	″	″	″	2.3
9.0	″	″	″	2.8
10.0	″	″	″	4.5
7.0	″	150	25	1.7
8.0	″	″	″	2.0
9.0	″	″	″	1.8
10.0	″	″	″	2.0
7.0	″	200	25	0.6
8.0	″	″	″	1.1
9.0	″	″	″	1.6
10.0	″	″	″	1.8
7.0	″	250	25	0.5
8.0	″	″	″	0.8
9.0	″	″	″	0.9
10.0	″	″	″	1.2
4.0	″	300	25	20.0
5.0	″	″	″	1.5
6.0	″	″	″	1.1
7.0	″	″	″	0.7
8.0	″	″	″	0.6
9.0	″	″	″	0.9
10.0	″	″	″	1.1
5.0	$Al(NO_3)_3$	300	25	25
7.0	″	″	″	25
8.0	″	″	″	25
9.0	″	″	″	25
10.0	″	″	″	25
7.0	$FeCl_3$	300	25	0.8
10.0	″	″	″	1.3

[a] All concentrations are in ppm.

TABLE 5
Effects of Ionic Strength of Coprecipitation of Sb (pH 7)

Ionic solution	Ionic strength (*M*)	Flocculant[a]	Initial antimony[b]	Residual antimony[b]
$NaNO_3$	0.010	$Fe(OH)_3$	25.0	0.40
"	0.025	"	"	0.70
"	0.050	"	"	0.80
"	0.100	"	"	0.45
"	0.250	"	"	0.60
"	0.500	"	"	0.30
"	1.0	"	"	0.35
"	2.0	"	"	0.20
NaCl	0.50	"	"	0.50
"	1.0	"	"	0.40
Na_2SO_4	0.50	"	"	0.30
"	1.0	"	"	0.65

[a] Each sample initially contained 300 ppm Fe(III).
[b] All antimony concentrations are in ppm.

rate in this pH range than at either higher or lower pH values. Residual Sb concentrations in this pH range were also found to be less than 1 ppm in solutions which contained $NaNO_3$ concentrations of as much as 1 *M*. At higher pH values, Sb removal rates were found to decline quite rapidly as the amount of $NaNO_3$ in the solution increased. At pH values less than

TABLE 6
Results of Lime Precipitation Study

Settling time (min)	Lime concentration (g/L)	Initial Sb[a] concentration	Residual Sb[a] concentration
5	50	25	4.0
15	"	"	4.0
30	"	"	3.1
5	100	"	0.9
15	"	"	0.6
30	"	"	1.0
5	"	75	1.1
15	"	"	0.9
30	"	"	0.9

[a] All Sb concentrations are in ppm.

TABLE 7
Results of Sulfide Precipitation Study[a]

pH	Initial Sb concentration	Initial Fe concentration		Settling time	Residual Sb	
		Fe(II)	Fe(III)		Filtrate	Decant
1.5	25.0	100	0.0	3 d	<0.35	0.35
″	50.0	1000	″	1 d	0.35	0.65
″	″	″	″	2 h	0.40	3.7
″	″	″	″	10 min	10.0	25
2.0	25.0	″	″	″	4.3	>10
″	″	2000	″	″	3.5	″
″	″	3000	″	″	2.8	″
2.5	″	200	″	20 min.	>10	25
″	″	″	″	1 h	″	″
5.0	″	1000	″	10 min		[b]
8.5	50.0	″	″	″		[b]
1.5	″	0.0	1000	″	10	25
2.0	25.0	″	″	″	4.0	>10
8.5	50.0	″	″	″		[b]

[a] All concentrations are in ppm.

[b] Unfilterable, colloidal solid present in solution.

2.5, Sb removal was again found to be significantly affected by $NaNO_3$ in the solution; $NaNO_3$ concentrations of 0.0025 *M* at low pH values (2.5) did not permit residual Sb concentrations to reach levels significantly different from initial Sb concentrations. This was due to the failure of the $Fe(OH)_3$ flocculant to form in such acidic solutions.

Even though adequate Sb removal was found to occur within 3 min after the solution was added to the flotation column, in some cases the metal was found to reenter the solution after it had been removed. At low values of pH (4.0) and low ionic strength (0.025 *M*), residual Sb concentrations in the solutions being foamed were found, at 5 and 10 min, to increase from the minimum values which were obtained at 3 min. This can be observed in Tables 1, 2, and 3. This increase was found to be the result of an inadequate amount of the surfactant (SDS) being present in the solution. SDS concentrations that were less than 40 ppm were unable to maintain sufficient foam on the surface of the solution to keep already floated Sb from reentering solution. This problem was alleviated in several unreported runs by simply increasing the concentration of SDS to 100 ppm. With an increase in the concentration of SDS, residual Sb concentrations at 5 and 10 min after flotation was begun were found to decrease, as expected, in that once Sb was removed from the solution, it did not reenter.

B. Coprecipitation of Sb with $Fe(OH)_3$

As seen from Table 4, 7.0 was found to be the optimum pH for the coprecipitation of Sb with $Fe(OH)_3$. Initial Sb concentrations of 25 ppm were found to be reduced to less than 1 ppm within 10 min after the addition of the flocculating agent ($Fe(NO_3)_3$ or $FeCl_3$). Initial flocculant concentrations which were 12 to 15 times as great as the initial Sb concentrations provided the best results. A study of the effects of pH on coprecipitation removal of Sb revealed that this precipitation technique is quite independent of pH over a wide range. Residual Sb concentrations at every pH value from 5.0 to 10.0 were within 0.5 ppm of the optimum values observed at a pH of 7.0. However, when the pH was reduced to a moderately acidic value (<4.5), residual Sb values were about 80% of the initial Sb concentration. The observation of an optimum precipitation pH is easily verified theoretically through equilibrium calculations which predict a minimum residual Sb concentration at some pH for this amphoteric element. Several runs were performed to determine if higher initial Sb concentrations are reduced by this procedure; it was found that the only parameter that needs to be adjusted in higher initial concentration reduction is the maintenance of an adequate concentration of flocculating agent.

The effects of varied ionic strength on the ability of $Fe(OH)_3$ to coprecipitate Sb were also studied; ionic strength has virtually no effect on the coprecipitation of Sb. High concentrations of ionic salts ($NaNO_3$, NaCl, or Na_2SO_4) were found, in certain cases, to enhance coprecipitation. Runs were made with solutions of $NaNO_3$, NaCl, and Na_2SO_4 of concentrations up to 2.0 *M*, and the results are presented in Table 5.

Several runs were also made in which $FeCl_3$ was used as the flocculating agent in place of $Fe(NO_3)_3$. All other parameters were kept exactly the same as in the $Fe(NO_3)_3$ runs. $FeCl_3$ behaved almost exactly like $Fe(NO_3)_3$ in terms of flocculating properties.

C. Coprecipitation of Sb with $Al(OH)_3$

We expected that $Al(NO_3)_3$ would have quite good flocculating properties. However, a study similar to the one conducted using $Fe(NO_3)_3$ as a flocculant revealed that $Al(OH)_3$ is a very poor flocculant for the coprecipitation of Sb (Table 4). A full study of the effects of pH on the flocculating properties of $Al(OH)_3$ was performed. At every pH value used, an ample amount of visible $Al(OH_3)_3$ floc was formed; however, analysis of the decantate showed that the residual Sb concentration was essentially unchanged from the initial Sb concentration. Due to the failure of $Al(OH)_3$ as a flocculating agent for the removal of Sb, no runs were made in which the initial flocculant concentration was changed from the 300 ppm used in the initial study. Since there was no Sb removal at 300 ppm $Al(NO_3)_3$, it can be assumed that adjusting flocculating agent concentration to substantially higher values would have little effect on Sb removal.

D. Coprecipitation of Sb with Lime

Although the coprecipitation properties of lime have been thoroughly analyzed in previous studies (*40*), several runs were made using lime to coprecipitate Sb; the results presented in Table 6 are similar to those already obtained in other studies. It was found that aqueous solutions which contain Sb concentrations of 75 ppm require the addition of 100 g/L of pulverized lime (CaO) to reduce the Sb concentration to less than 1 ppm. After 10 min, Sb concentrations were found to reach minimum values, and longer settling periods did not reduce Sb concentrations further. The large quantities of lime required are a major drawback to this method.

E. Coprecipitation of Sb as Sb_2S_3

Antimony(III) was found to be most readily removed from solution as Sb_2S_3 when:

(a) The solution pH was kept below 2.5
(b) The decantate was vacuum filtered
(c) Settling times >30 min were employed
(d) Initial Fe(II) or Fe(III) concentrations were >500 ppm

For runs in which the solution pH was adjusted to a value less than 2.5, an orange-red solid (presumably Sb_2S_3 and colloidal sulfur) formed immediately upon addition of Na_2S to the solution. Filtration of the decantate was an absolute necessity in the removal of the Sb_2S_3 solid due to the tendency of the solid to collect on the solution surface. Optimum residual Sb concentrations (<1 ppm) were recorded (Table 7) from initial Sb concentrations of 50 ppm when the decantate (initial pH = 1.5, Fe(II) or Fe(II) concentration = 1000 ppm) was allowed to sit for 2 h and was then vacuum filtered. When the solution pH was adjusted to values greater than 2.5, the solution tended to become very black and opaque due to the formation of colloidal, nonfilterable FeS. When colloidal FeS was present in the solution, no Sb removal was observed regardless of other parameter adjustments.

The concentration of Fe(II) or Fe(III) in the solution seemed to play an important role in the amount of time required for the Sb_2S_3 solid to form, and there appeared to be no detectable difference in solution behavior between those solutions that contained Fe(II) and those that contained Fe(III). When Fe(II) or Fe(III) concentrations of <250 ppm were employed, several hours (10–20) were required before residual Sb concentrations were reduced to less than 1 ppm; however, when Fe(II) or Fe(III) concentrations of >800 ppm were employed, residual Sb concentrations were reduced to less than 1 ppm within 2 h. In all cases where initial Fe(II) or Fe(III) concentrations were <25 ppm, the amount of time required for residual Sb concentrations to be reduced to the desired level (<1 ppm) was found to be extremely lengthy (>24 h). We do not have an explanation for the role Fe plays in the precipitation of Sb_2S_3.

V. CONCLUSIONS

Several of the Sb removal techniques used in this study were found to produce quite low residual concentrations and therefore appear to be acceptable industrial removal techniques. A brief summary of each technique studied is presented below.

A. Foam Flotation

Foam flotation was found to provide a quick route to quite low residual Sb concentrations through four simple parameter adjustments (pH, SDS concentration, $Fe(NO_3)_3$ concentration, and air flow rate). Although the solutions which provided optimum residual concentrations were moderately acidic, the acidity presents no significant problem since the solutions can be easily neutralized once Sb has been removed. Therefore, foam flotation appears to be feasible as a practical Sb removal technique.

B. Coprecipitation of Sb with $Fe(OH)_3$

Of the Sb removal techniques studied, coprecipitation with $Fe(OH)_3$ provides what appears to be the most versatile route to low residual Sb concentrations. Although coprecipitation with $Fe(OH)_3$ is not quite as fast as foam flotation, the minimum residual Sb levels reached are almost as low while consistent removal is obtained over a much wider range of pH and ionic strength. Barring possible limitations due to lack of available space for settling tanks, this Sb removal technique would appear to be potentially quite useful industrially.

C. Coprecipitation of Sb with $Al(OH)_3$

Our work showed that $Al(OH)_3$ is ineffective in removing antimony from solution.

D. Coprecipitation of Sb with Lime (CaO)

Although widely employed industrially for the simultaneous removal of many residual metals, coprecipitation with lime does not appear to be a very practical method for antimony removal. Quite large quantities of lime are required to reduce even relatively low initial antimony concentrations. Coprecipitation with lime is far less desirable than foam flotation or coprecipitation with $Fe(OH)_3$ for antimony removal.

E. Precipitation as Sb_2S_3

Precipitating Sb as a sulfide does not provide a practical route to low residual Sb concentrations. Along with the hazard of toxic H_2S gas, there are also more parameters to be controlled than in other precipitation methods in order to reach desired residual Sb concentrations (<1 ppm). As an industrial Sb removal technique, precipitation as Sb_2S_3 appears to be not as desirable as foam flotation or coprecipitation with $Fe(OH)_3$.

Acknowledgment

This work was supported by a grant from the National Science Foundation.

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Received by editor November 25, 1985