

Preparation of high-purity antimony by electrodeposition

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Detailed studies were carried out on the electrowinning of antimony from $\text{SbCl}_3\text{-HCl-H}_2\text{SO}_4$ and $\text{SbCl}_3\text{-HCl}$ baths using a graphite anode and a tantalum cathode, the anode being enclosed in a cylindrical glass compartment provided with a sintered disc. Disintegration of the graphite anode increased with increase in anode current density and duration of electrolysis. Analysis of gas evolved at the anode indicated that the presence of sulphuric acid increased the production of CO_2 . The anodic disintegration was reduced to a negligibly low value by circulation of 6M HCl through the anode compartment. Optimum conditions were determined for electrowinning of antimony from a $\text{SbCl}_3\text{-HCl}$ bath. The tantalum content in the metal was 0.1-0.2 p.p.m.

1. Introduction

High-purity antimony (99.999%) finds use in the semiconductor industry as a dopant and for making compound semiconductors such as indium antimonide and antimony telluride. The commonly used methods for the purification of commercial antimony are: (i) distillation of SbCl_3 dissolved in 6M HCl [1, 2] (> 99.99%, arsenic is easily removed); (ii) fractional distillation of SbCl_3 [2-4] (~99.999%); (iii) vacuum distillation [5-8] (arsenic, lead, tin and bismuth are removed only partially and hence the purity depends on the concentrations of these impurities in the starting material; and (iv) electrorefining from aqueous medium [9-15] (~99.99%, copper, arsenic and bismuth cannot be eliminated). The methods available for converting the purified SbCl_3 to the metal are: (i) reduction with hydrogen [2-4]; (ii) conversion to oxide followed by reduction with hydrogen [8] and electrowinning from a suitable bath [2, 12, 14]. The purity of the metal obtained (99.99-99.999%) depends on the levels of impurities in the purified SbCl_3 and the extent of further purification and/or contamination during conversion to the metal, as the case may be. This metal is further purified by zone refining [6, 16, 17] (arsenic, if present, cannot be removed by this process) to obtain > 99.999% purity.

Recently, Kiswa *et al.* [18] have reported a method for preparing 99.9995% pure antimony by electrorefining technical grade metal from a bath of antimony trihalides in acetonitrile medium.

The commercial antimony obtained indigenously contained 0.1-0.2% arsenic. All the arsenic, copper and bismuth were easily removed by the distillation of SbCl_3 in 6M HCl. In order to improve the purification and to convert the chloride to the metal, detailed studies had been carried out earlier [12] from chloride, tartrate and fluoride baths using graphite electrodes. For regular production of the metal, the tartrate bath and graphite electrodes were employed. The metal, as deposited on graphite, is very adherent and can be removed only by melting in an inert atmosphere. This leads to the graphite cathodes developing cracks after repeated use, thus increasing considerably the cost of the metal produced. Hence we replaced the graphite cathode by tantalum, the deposit on which could easily be removed. However, the metal ingot obtained by the melting of the deposit on tantalum from a tartrate bath contained carbon as an impurity arising from the decomposition of tartaric acid. Therefore, it was necessary to replace the tartrate bath. Beau [11] employed a $\text{SbCl}_3\text{-HCl-H}_2\text{SO}_4$ bath to prevent the precipitation of oxychlorides of Sb(V) in the anode

compartment which causes swelling and bursting of the graphite anode. However, it has been reported that the presence of sulphate increases anode disintegration in the electrolysis of both brine [19, 20] and hydrochloric acid [21]. Gallone and Messner [21] found that the graphite consumption in the electrolysis of hydrochloric acid was less than 100 g per ton of chlorine. Hence detailed studies were carried out using $\text{SbCl}_3\text{-HCl-H}_2\text{SO}_4$ and $\text{SbCl}_3\text{-HCl}$ baths to arrive at a suitable method for the preparation of high purity antimony involving very low anode consumption. The results are presented in this paper.

2. Experimental details

High-purity antimony trichloride prepared by the method reported earlier [8] was used for the experiments. All other reagents used were of Analar grade. Pure tantalum (99.9%) sheet (0.2 mm thick) obtained from the Nuclear Fuel Complex, Hyderabad was used as cathode. Graphite rods (12 mm in diameter) of high purity and high density (UF 4S grade) procured from Ultracarbon Corporation, USA, were employed as anodes. Electrolytic experiments were carried out in glass beakers. The anode was enclosed in a cylindrical glass compartment provided with a sintered disc. The catholyte was agitated by means of a magnetic stirrer. Circulation of anolyte was achieved by gravity flow whenever required. For collection of the gas liberated at the anode, the anode

compartment was connected to a spiral of glass tubing provided with stopcocks at both ends. A hole plugged with elastomer was provided in the central part of the spiral to remove gas samples for analysis.

A 3-l beaker with two built-in cylindrical anode compartments (30 mm o.d.), provided with an inlet and an outlet for circulation of electrolyte (Fig. 1), was used for preparation of the metal under the optimized conditions. A sintered glass disc (30 mm in diameter) of No. 2 porosity was fused to the cylindrical part of the anode compartment, approximately 2 cm above the bottom. The discs in the two compartments were parallel to each other. PVC screens were provided between the cathode and the anode compartments. The cathode was of T shape so as to be self supporting in the cell and to provide electrical connection without any possibility of contamination.

The effect of various parameters on the nature of the deposited metal and the disintegration of the anode was investigated. The catholyte and anolyte were analysed for total acidity, antimony(III), antimony(V), chloride and sulphate by standard methods. The CO_2 , O_2 and N_2 contents of the chlorine evolved at the anode were determined by using a home-made gas chromatograph equipped with a thermal conductivity detector (columns used: molecular sieve 5A for separation of O_2 and N_2 , and Prorapak Q for separation of CO_2). The impurity contents in the metal were estimated by spark source mass spectrometry.

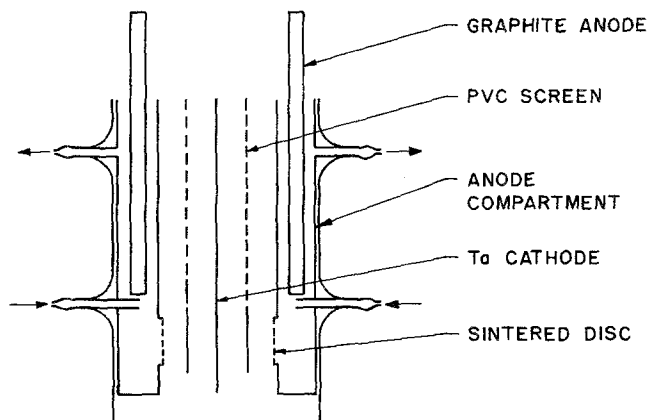


Fig. 1. Electrolytic cell.

3. Results and discussion

3.1. Deposition of antimony on the cathode

The nature of the deposit on tantalum from $\text{SbCl}_3\text{-HCl-H}_2\text{SO}_4$ and $\text{SbCl}_3\text{-HCl}$ baths was almost the same. The deposit was grey and granular, but not very adherent. The deposited metal was readily detachable from the cathode. The nature of the deposit did not vary much with cathode current density. At low concentrations of SbCl_3 ($< 20 \text{ g dm}^{-3}$) the deposit was loose and black. When an anode compartment with a sintered disc at the bottom was used, the thickness of the deposit was not uniform and dendritic growth was considerable. To overcome this problem the location of the sintered disc was shifted from the bottom to the side of the anode compartment and a PVC screen was provided between the disc and the cathode.

The metal deposited on tantalum contained 5–10 p.p.m. tantalum. By ultrasonic cleaning of the surface of the cathode prior to use, the tantalum contamination decreased to $\sim 0.1\text{--}0.2$ p.p.m. By zone refining of this metal, the tantalum content further decreased to < 0.1 p.p.m. The contents of the other impurities observed (in p.p.m.) in the zone refined metal were: Br, 0.1; As, 0.06; Cu, 0.6; Ni, 0.2; Fe, 0.5; and Cr, 0.5.

3.2. Disintegration of graphite anode

With the $\text{SbCl}_3\text{-HCl-H}_2\text{SO}_4$ bath, although there was no precipitation in the anode compartment, the anodic disintegration increased with increasing anode current density and duration. Data on the analysis of the bath and anode consumption at low anode current density are summarized in Table 1. In these cases, a sintered

disc of porosity No. 4 was provided in the anode compartment. The hydrochloric acid concentration in the anolyte decreased with increasing duration of electrolysis, the value being negligible after 24 h. The sulphuric acid concentration was nearly the same after 6 h, but increased considerably after 24 h. Anode disintegration was appreciable when the chloride concentration was very low. These results indicate that depletion of chloride ion concentration promotes anode disintegration. When the anode current density was increased to 4 A dm^{-2} , the anode consumption at the end of 6 and 24 h was 35 and 100 g per kg of metal deposited, respectively.

The chlorine evolved at the anode oxidizes Sb(III) to Sb(V) which causes precipitation of oxychlorides of Sb(V) at lower acidities. Hence it was considered better not to have SbCl_3 in the anolyte initially. Although Beau [11] employed low anode current densities to minimize anode disintegration, to reduce anode inventory and to achieve higher rates of deposition of antimony, a higher anode current density is desirable. In order to determine the side reactions at the anode under these conditions, anolytes of different compositions were investigated. In all the experiments the concentration of SbCl_3 in the catholyte was maintained constant at 70 g dm^{-3} and the concentrations of HCl and/or H_2SO_4 were the same as those in the anolyte. The CO_2 and O_2 contents in the anodic gas are given in Table 2. In all cases CO_2 was invariably present in the anodic gas. The presence of H_2SO_4 along with HCl resulted in the formation of more CO_2 . With HCl alone, the O_2 content was much higher than that of CO_2 . When 6 M HCl was used as anolyte, both the CO_2 and O_2 contents increased with increasing anode current density. With

Table 1. Change in bath composition and anode consumption during electrowinning of antimony. Anode current density, 1.5 A dm^{-2} ; cathode current density, 0.4 A dm^{-2}

Duration (h)	Anolyte composition			Catholyte composition			Anode consumption (g kg^{-1} of metal deposited)
	Sb(V) (g dm^{-3})	HCl (M)	H_2SO_4 (M)	Sb(III) (g dm^{-3})	HCl (M)	H_2SO_4 (M)	
0	0	1.6	1.45	36.2	1.7	1.45	—
6	0.6	0.5	1.35	33.1	1.8	1.5	0
24	0.9	0	1.8	21.6	2.1	1.4	12

Table 2. Variation of CO_2 and O_2 contents in the gas evolved at the anode after electrolysis for 2 h

Initial anolyte composition	Anode current density (A dm^{-2})	CO_2 (% by vol)	O_2 (% by vol)
1.5 M HCl	15	2.1	0
1.5 M H_2SO_4			
6 M HCl	15	1.7	0.1
1.5 M H_2SO_4			
1.5 M H_2SO_4^a	15	76.0	5.5
6 M HCl	15	0.8	3.5
6 M HCl	20	1.5	7.4
6 M HCl	25	3.3	9.7

^a 1.5 M H_2SO_4 used as catholyte.

1.5 M H_2SO_4 , the anodic gas contained 76% CO_2 . From these results it may be concluded that the presence of sulphate increases the formation of CO_2 , thereby increasing the anode disintegration.

3.3. Effect of circulation of HCl through the anode compartment

The high-purity graphite rods used for the electrowinning of antimony are more porous than the oil impregnated graphite traditionally used in chlor-alkali cells. Since acidity and chloride ion concentration inside the pores are considerably lower than those at the surface of the electrode, these regions corrode at a higher rate. To maintain the acidity and chloride ion concentration sufficiently high during electrowinning, 6 M HCl was circulated through the anode compartment. With a flow rate of 31 h^{-1} , the anodic

Table 3. Optimum conditions for electrowinning

Parameter	Value
Catholyte	100–120 g SbCl_3 , dm^{-3} , 4 M HCl
Anolyte	6 M HCl
Cathode	Tantalum
Anode	Graphite
Cathode current density	5–6 A dm^{-2}
Anode current density	20–25 A dm^{-2}
Rate of circulation of anolyte	2–2.5 $\text{dm}^3\text{ h}^{-1}$
Current efficiency (overall)	0.85–0.90

corrosion was negligible even at high anode current densities (25–30 A dm^{-2}).

3.4. Optimized process for electrowinning of antimony

Based on the results given above, conditions were standardized for regular production of antimony metal from SbCl_3 . These conditions are given in Table 3. The catholyte was prepared by dissolving molten SbCl_3 (melting point, 494 K) in 4 M HCl, and a 2.5 dm^3 sample of catholyte was placed in the 3-l cell. The anolyte was circulated independently through the two anode compartments. During electrolysis the temperature of the bath rose to 323–333 K. When the SbCl_3 concentration in the bath decreased to $\sim 50\text{ g dm}^{-3}$, molten SbCl_3 was added to raise the concentration to the original value. When 250–300 g of metal had been deposited, the cathode was replaced. The deposit was washed with water, HCl, water, ammonia and again with water and then removed from the cathode by twisting the plate. The deposit was converted to ingot form by melting in a current of nitrogen or hydrogen at 973–1023 K.

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