Chapter 6

Treatment of an Anionic Metal by Adsorption on Iron Oxides

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Adsorption of antimony onto amorphous iron hydroxide (ferrihydrite) as a treatment method for industrial wastewater was evaluated. The effects of pH, iron hydroxide to antimony ratio, temperature, time and interference due to sulfate were investigated. Adsorption was found to occur within a narrow pH range at a reasonable antimony to iron hydroxide ratio. Elevated temperature inhibited antimony adsorption. Sulfate also inhibits adsorption but can be overcome with additional iron hydroxide even at relatively high (1.2 molar) sulfate concentration. The reaction was rapid, reaching maximum adsorption within 15 minutes. This treatment has been successfully applied an industrial wastewater.

Antimony is used in the manufacture of lead-acid batteries. The hardness of lead is increased by the addition of 1 to 10 percent antimony. Lead-acid batteries are intensively recycled, and the antimony in these batteries is introduced into the secondary lead smelters.

The soluble antimony content in the sulfuric acid electrolyte of lead acid batteries is relatively modest. Larger quantities of antimony are leached into water due to the use of sodium carbonate to neutralize sulfuric acid and to reprecipitate lead hydroxide or lead carbonate from lead sulfate. Lead hydroxide is more readily smelted, but a wastewater containing from 2 to 65 mg/l antimony is generated. This wastewater requires treatment to remove antimony to less than 1 to 1.5 mg/l to comply with federal wastewater regulations.

Lime or sodium hydroxide addition in the existing wastewater treatment plants has proven ineffective in antimony removal from these solutions. Addition of sodium

hydroxide to a 1,000 mg/l antimony solution (from antimony (III) chloride or antimony (V) chloride) does not produce a precipitate.

Transition metals are strongly adsorbed on metal oxides. The effects of solution pH, the concentration of transition metal, the absorbing metal oxide and the presence of other ions on the adsorption have been studied [1,2]. Adsorption of metals which are present in aqueous solutions as anions has had less attention in the published literature. Antimony, selenium and arsenic are metals of environmental interest which are incorporated in anionic species in aqueous solutions. Several papers have been published on adsorption and precipitation of selenium and arsenic. Little has been published on the behavior of antimony.

At pH 4.0 selenium is strongly adsorbed on amorphous ferric iron hydroxide, which is known as ferrihydrite. Adsorption is dependent on oxidation state. Selenate is completely desorbed at pH 9, and selenite is completely desorbed at pH 12 [3,4]. Sulfate ion interferes with selenium (VI) adsorption [4]. Adsorption of transition metals enhances selenium adsorption [5].

Arsenic is known to react with iron oxides to generate an insoluble ferroarsenate [6]. Antimony may react in a similar fashion, since it is in the same group (VA) on the periodic chart.

Antimony (V) is known to be incorporated in an anionic species $[Sb_3O_9]^{3-}$ in water solution. Only in weak sulfuric acid solutions of <1.5 M does antimony (III) exist as a cation: SbO^+ and $Sb(OH)_2^+$. In 1 to 18 M sulfuric acid, antimony (III) is incorporated into an anionic species: $SbOSO_4^-$ and $Sb(SO_4)_2^-$ [7]. In hydrochloric acid, antimony (III) and antimony (V) have been found to exist as a number of chloride and mixed chloride and hydroxide species, all of which are anionic [8]. Due to the high concentration of sulfate in the samples being treated in this study, it is likely that most of the antimony is in anionic species.

An investigation of antimony and arsenic contamination of a river bed produced some data of interest. Antimony was found to be almost entirely Sb(V) in the river water at neutral pH. River bottom samples were extracted at different pH values, and the amount of total antimony extracted was found to vary with the concentration of iron and manganese in the sediment. The total antimony extracted from the sediment reached a minimum at pH 4.3 [9].

Adsorption of anions such as fluoride and phosphate on iron oxides has been investigated and found to occur at acid pH and is readily reversible at more alkaline pH [10].

At pH 8.5, the average surface charge on ferrihydrite is zero. This is known as the pH_{pzc} [11,13]. At lower pH, the surface charge becomes more positive, and at higher pH, the surface charge becomes more negative. Anionic species are more likely to be adsorbed to a surface with positively charged sites, which are more prevalent in the lower pH range. Selenium and antimony are expected to be adsorbed at low pH.

An experimental program was designed to evaluate the possibility of adsorbing antimony from secondary smelter wastewater, to develop an industrial wastewater treatment process utilizing this adsorption, and to install the process in existing facilities.

Experimental

A sample of a wastewater collected from a secondary lead smelter is described in Table I. Unless otherwise specified, all tests were performed on this sample. Antimony (III) chloride was used to prepare antimony solutions in demineralized water. Sodium sulfate and ferric sulfate, both ACS grade, were added as needed. The solution pH was adjusted with sulfuric acid, trace metals grade.

TABLE I. TEST SOLUTION COMPOSITION

Component	Concentration	
	mg/l	Molar ($\times 10^{-6}$)
Arsenic	15.7	210
Barium	<0.1	<0.7
Cadmium	0.16	1.4
Copper	0.28	4.4
Iron	0.45	8.1
Nickel	0.70	1.2
Lead	10.9	5.3
Antimony	95	780
Selenium	1.3	11
Tin	<0.3	<2
Zinc	1.0	15
Chloride	65	1830
Fluoride	0.4	20
Sulfate	89,900	936,000
Total Dissolved Solids	189,400	-
pH	2.5	-
Specific Gravity	1.147	-

Amorphous iron oxides were prepared by addition of ferric sulfate to the test solutions. The pH was adjusted with sodium hydroxide solution (10N) to precipitate ferrihydrite and initiate adsorption of metals. No attempt was made to control carbon dioxide or bicarbonate in the test solutions, other than to prepare fresh sodium hydroxide.

Sample aliquots were collected and immediately filtered with a 0.45 micron membrane filter. Samples were preserved for metals analysis with nitric acid, trace metal grade. Soluble antimony was determined using a Perkin-Elmer, Zeeman background corrected, graphite furnace atomic absorption spectrometer. This is a

routine analysis in the analytical services laboratory, and extensive quality control records are maintained on this analysis.

The reaction time interval of 30 to 60 minutes was selected to fall within typical reaction tank retention times in industrial practice.

Results and Discussion

The pH_{pzc} is usually slightly higher for freshly precipitated ferrihydrite and decreases with aging. The adsorption edge for copper and zinc is at a higher pH for fresh precipitate than for precipitate that is a few hours old. This indicates that aged precipitate is a stronger adsorbent than fresh precipitate (*12*). For copper and zinc, the use of iron could be reduced if the iron were precipitated and aged before use as an adsorbent. Since the system is simpler if the iron is added as a solution, this loss of efficiency was accepted.

Effect of pH. Iron at 300 mg/l (5.4×10^{-3} M) was added to the wastewater described in Table I. An aliquot of the solution was adjusted rapidly to the specified pH using sodium hydroxide and held at that pH with thorough mixing for 60 minutes. The test procedure was repeated on a fresh aliquot at each pH (Figure 1). The adsorption maximum is centered at pH 5.0 and decreases at higher pH. Adsorption at higher pH may be due to a short residence time within the pH 4 to 5 range. Adsorption of antimony occurs at about the same pH as the precipitation of iron in this matrix.

Arsenic precipitation from this solution occurs at a slightly higher pH. The adsorption increases rapidly to nearly 100 percent and is not further affected by increases in pH. The contrast between these adsorption curves may indicate that the mechanism of antimony removal is not the same as that of arsenic.

Another test with sequential pH adjustment and collection of sample at each pH was performed (Figure 2). This curve provides less indication of the narrow range of pH at which the most effective adsorption occurs. The results of duplicate sample titrations above pH 6.5 are caused by slightly different rates of sodium hydroxide addition. Dependence on the rate of addition is understandable, since the degree of antimony removal is determined by the time the mixture remains in a narrow pH window.

Rate of Reaction. The rate of the reaction is critical to the design of an industrial process. 300 mg/l of iron (5.4×10^{-3} M) was added to the test solution, and the pH adjusted to 4.5 with sodium hydroxide. The reaction was nearly complete within 15 minutes, when the first aliquot was collected (Figure 3). The percent adsorbed decreased slightly after a few hours. The affinity of ferrihydrite for cadmium increased with aging (2), but decreased with aging for antimony. This effect may by due to the slow shift in pH_{pzc} of the ferrihydrite which occurs in the first few hours after precipitation (*11*).

Effect of Temperature and Concentration. Two samples were treated by addition of 100 mg/l (1.8×10^{-3} M) Fe^{+3}, sodium hydroxide addition to pH 4.5, and mixing for 30 minutes at a constant temperature. One sample was at 22°C, and the other, at
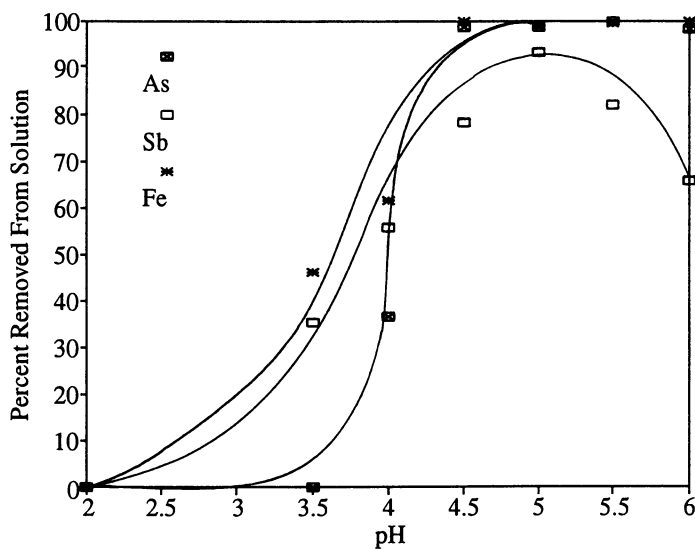
Figure 1. Effect of pH on removal of arsenic and antimony from aqueous solution by adsorption on ferrihydride.
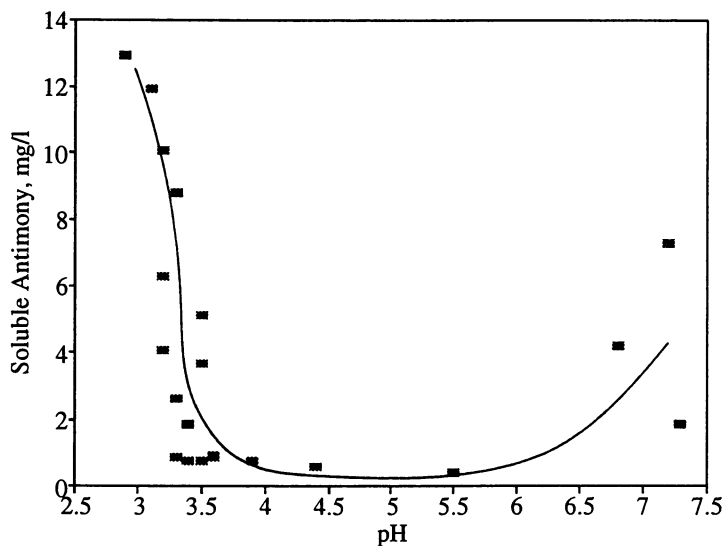

Figure 2. Solubility of antimony with pH changes due to slow addition of sodium hydroxide solution.

62°C. Soluble antimony in a sample collected from the warm sample was 5.8 mg/l (4.8×10^{-5} M), compared with 4.1 mg/l (3.8×10^{-5} M) in the room temperature sample. Antimony in the warm sample was found to decrease to 4.6 mg/l (3.8×10^{-5} M) after the mixture was allowed to cool overnight. An increase in temperature was found to increase adsorption of cadmium on ferrihydrite (2), but is observed to cause a decrease in antimony adsorption. This decrease is reversible upon cooling.

The influence of an increasing amount of adsorbate on the percent antimony adsorbed was investigated by adding increasing amounts of iron to aliquots of sample, adjusting the pH to 4.5 and holding that pH for 30 minutes before collecting a sample for soluble antimony analysis (Figure 4). Little improvement was found above a molar ratio of 10 moles of iron to one mole of antimony.

Interference by Sulfate. All of the testing done to this point was on an industrial wastewater sample containing about 0.95 M sulfate after ferric sulfate addition. Antimony removal from this solution was successful. To determine the effect of sulfate on antimony removal from solution, solutions of antimony, sodium sulfate, and sulfuric acid were prepared in deionized water. Aliquots of this solution were treated by sodium hydroxide addition to pH 4.5 and maintenance of this pH for 30 minutes.

At a given iron to antimony ratio, an increase in sulfate concentration resulted in a decrease in antimony removal from solution (Figure 5). Even at a molar ratio of 2.1 iron to antimony and a sodium sulfate concentration of 1.20 M, the antimony was 87 percent adsorbed. At a molar ratio of 22 iron to antimony, no change in the percent antimony adsorbed was observed with an increase in sulfate concentration to 1.2 molar. Sulfate is only a modest interference for antimony adsorption, which can be overcome by increasing the molar ratio of antimony to iron. The absence of a stronger interference by sulfate may indicate that antimony is not adsorbed on ferrihydrite on the same active surface sites as selenate. Sulfate competes for the same sites, and is adsorbed by the same mechanism, as selenate (3,5,13).

To further investigate the mechanism of antimony adsorption from solution, a sample was prepared containing 0.37 M sulfate at pH 2.0 and a molar ratio of 2.18 moles of iron per mole of antimony (100 mg/l each of iron and antimony). Sodium hydroxide was added to adjust the pH to 4.5, where it was held for 30 minutes. The pH was then increased to 9.0, mixed for 30 minutes, and an aliquot collected for analysis.

The pH of the sample was adjusted back to pH 2.0 with sulfuric acid, and antimony was added to double the initial concentration (an additional 100 mg/l). Deionized water was added as necessary to maintain a constant sulfate concentration. This cycle was repeated five times. At the end of the fifth cycle, the iron to antimony molar ratio was 0.43 or 2.3 moles of antimony per mole of iron. The antimony was over 90 percent adsorbed through the entire procedure.

Adsorption was initially postulated to be the mechanism of removal of antimony from solution. The term adsorption must be used cautiously to describe a system where 2.3 moles of antimony are removed from solution by 1 mole of iron. If adsorption is understood to be a surface effect in the absence of a precipitate, then the term has some validity.
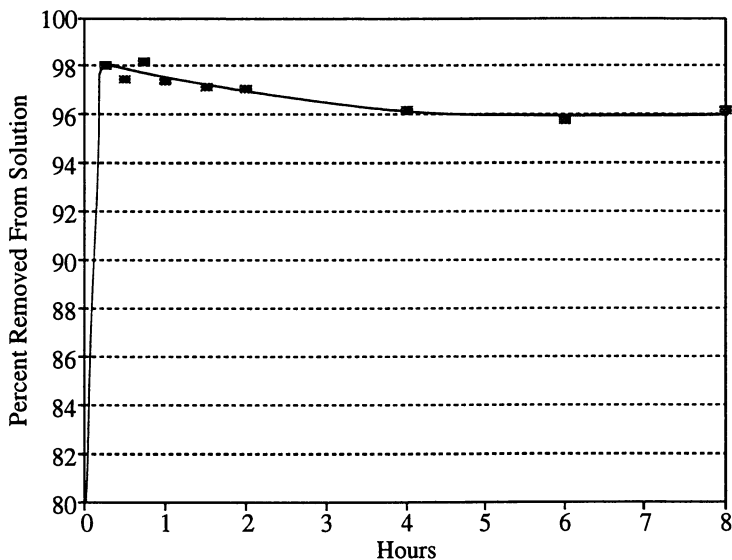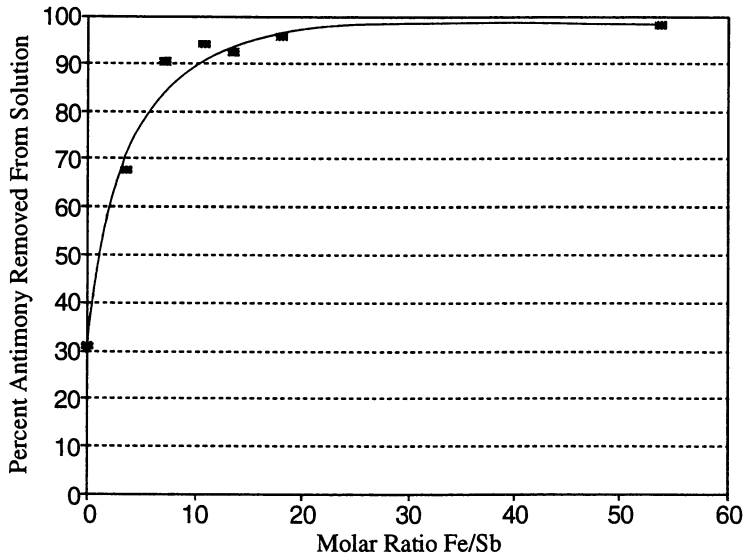
Figure 3. The rate of antimony adsorption.

Figure 4. Percent antimony removed from solution at various iron to antimony ratios.
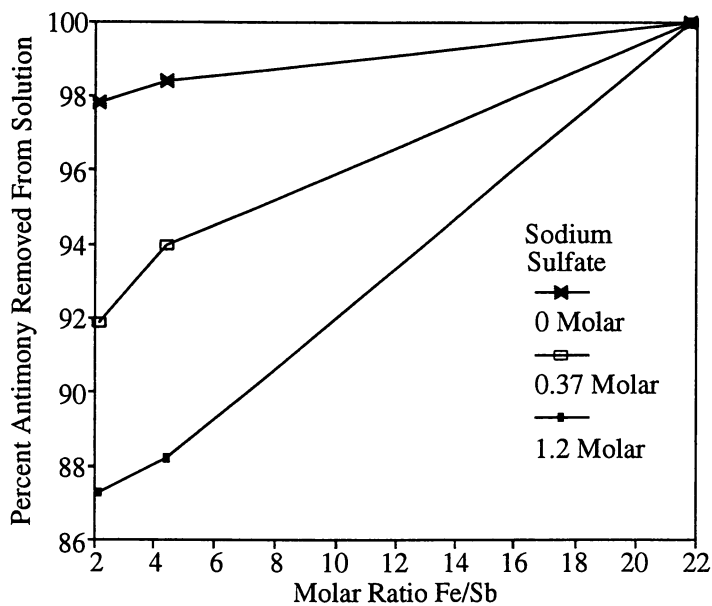
Figure 5. Sulfate interference on antimony adsorption at various sulfate concentrations and iron to antimony ratios.

The possibility of an insoluble iron compound being formed, analogous to that formed with arsenic, was considered. Neither the surface adsorption nor precipitation mechanisms seem adequate to explain the observations made above. Surface precipitation, initiated by the iron surface but not dependent on that surface once started, seems to be an adequate explanation of the observations.

To evaluate antimony desorption at alkaline pH, samples of a slurry of solids produced from treatment of wastewater by adsorption on ferrihydrite were collected. The slurry total metals and soluble metals after 24 hours of extraction of the slurry using sodium hydroxide, sodium carbonate and sulfuric acid to adjust the pH are in Table II. Antimony, once adsorbed on iron, appears to be stable and is not readily desorbed in alkaline solution. No difference was found in the desorption of antimony and arsenic.

TABLE II. SOLUBILITY OF METALS FROM FERRIHYDRITE SOLIDS IN PERCENT

	Antimony	Arsenic	Iron
Slurry (mg/l)	286	327	35900
NaOH - pH 12	0.07	<0.01	-
Na_2CO_3 - pH 11.5	0.3	0.06	-
H_2SO_4 - pH 1.2	25.4	<1	65.6

In sulfuric acid solution at pH 1.2, much more antimony was desorbed than arsenic. Antimony is only partially solubilized at low pH. No arsenic is measurable in the acidic extract. The coprecipitate between arsenic and iron is either much more difficult to dissolve or reprecipitation occurs upon dissolution.

Conclusions

A process has been evaluated which is capable of removing antimony from solution using a reasonable concentration of freshly precipitated ferric hydroxide (ferrihydrite) as an adsorbent. The pH is critical for this reaction, and sulfate interferes with the reaction to some degree. The necessary treatment reagent is available at a reasonable price, as either ferric chloride solution or ferric sulfate.

In practice, it has been necessary to extend the time required for this reaction to allow for less precision in the pH control and less agitation in the vessel used.

This process has been successfully installed at several industrial wastewater treatment plants located throughout the country. Scale up problems were mostly related to requirements for additional mixing and precise pH control to establish the pH window for antimony removal. More extensive operator training was required to enable the operators to detect and compensate for changes in the wastewater stream. Careful training and communication with the operators was found to be the most

critical step in maintaining daily facility operation within compliance with regulatory requirements.

Iron addition at approximately 300 mg/l was found to be effective and sufficient to handle the routine changes in the composition of the influent stream.

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