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Separation of Toxic Heavy Metals by Sulfide Precipitation

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Abstract

Sulfide precipitation with Na_2S is found to be highly effective to obtain a high degree of separation of heavy metal cations (Cd, Zn, Cu, and Pb) and of the oxyanions of arsenic and selenium from complex wastewaters. The metal separation characteristics are evaluated with a dilute synthetic mixture and with an actual copper smelting plant wastewater. The overall separation of arsenic and other heavy metals and precipitate settling rates are optimum at sulfide dosages about 60% of the theoretical values and at a final pH greater than 8.0. The removals of Cd, Zn, and Cu from the actual wastewaters are greater than 99%, and As and Se removals are 98 and >92%, respectively. Cd, Cu, and Zn concentrations in the range of 0.05 to 0.1 mg/l can be achieved with sulfide precipitation. The metal separations and settling rates obtained with conventional hydroxide precipitation (lime) are considerably lower than those obtained with sulfide precipitation.

INTRODUCTION

Sulfide precipitation is an effective method to achieve a high degree of separation of various heavy metals from industrial wastewaters. The high reactivity of sulfides (S^{2-}, HS^-) with heavy metal ions and the very low solubility of heavy metal sulfides over a broad pH range are attractive features when compared to the corresponding hydroxide precipitation process. Industries engaged in metal finishing or metal production operations use large quantities of contact process water, and the spent process wastewater streams contain moderate to high concentrations of As, Cd, Cu, Zn, Pb, etc. Heavy metals are also found in chemical cleaning wastes (high concentrations of copper–ammonia complexes) and in ash-pond effluents from coal-fired power plants.

Hydroxide (lime) precipitation of heavy metals followed by settling of the precipitates is most often used to treat industrial wastewaters (*1–4*). However, hydroxide precipitation of all the heavy metals present cannot be relied upon because the minimum solubilities of the various metals do not occur at the same pH value and often the presence of complexing agents, such as ammonia and EDTA, prevents effective precipitation.

For sulfide precipitation the sulfur compound can be added as a soluble sulfide salt (Na_2S or NaHS) or as a sparingly-soluble metal sulfide (such as FeS), the solubility of which is higher than that of the sulfides of the metals which are to be precipitated. A schematic diagram of a continuous-flow sulfide precipitation process for the removal of heavy metals from acidic wastewaters is shown in Fig. 1. The optimum sulfide dosage and pH adjustments are of course dependent on the wastewater characteristics.

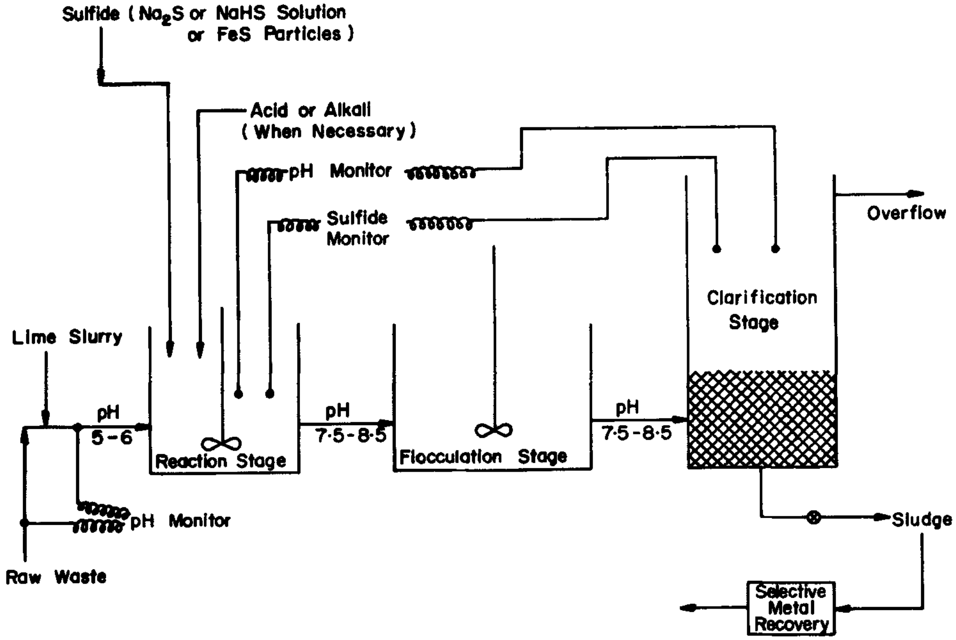

FIG. 1. Schematic diagram of a continuous sulfide precipitation unit.

Sulfide precipitation processes to remove heavy metals have gained considerable industrial importance (*5–7*). The treatment of mine drainage (*8*) and gold mine wastes (*9*) by Na_2S precipitation and of metal finishing wastewaters (with and without chelating agents) by FeS precipitation (*6*) has been reported in the literature. The overall objective of this investigation is to establish the effectiveness of the sulfide precipitation process (with Na_2S) for the batch treatment of wastewaters (synthetic and actual) containing mixtures of heavy metal cations and the oxyanions of arsenic and selenium. The separation behavior of metals is compared with the experimental results obtained by conventional hydroxide (lime) precipitation.

PRECIPITATION REACTIONS

Most heavy metal sulfides have very low solubilities, even at acidic pH. For example, the solubility product (K_{sp}) of HgS is 10^{-52}, CuS is 10^{-35}, CdS is 10^{-28}, and ZnS is 10^{-24}. The primary reactions (with M^{2+}-type ions) involved in sulfide precipitation are

$$H^+ + S^{2-} \rightleftarrows HS^-$$

$$H^+ + HS^- \rightleftarrows H_2S$$

$$M^{2+} + S^{2-} \rightleftarrows MS \text{ (solid)}$$

$$M^{2+} + OH^- \rightleftarrows M(OH)^+$$

For sulfide precipitation with less than the theoretical dosage, at alkaline pH metal hydroxide ($M(OH)_2$ (solid)) precipitation and/or coprecipitation also occur. The theoretical solubilities (mg/l M^{2+}) of heavy metal sulfides (single salts) are extremely low (see Table 1).

Even in the presence of complexing agents (chelating agents) such as EDTA and NH_3, sulfide precipitation is highly effective (*7, 10*). For a copper plating bath containing Cu–EDTA complexes, greater than 99.3% copper removal has been reported with Na_2S precipitation (*10*). Con-

TABLE 1

Metal	Solubility at pH 8.0 (mg/l)
Cu^{2+}	5×10^{-11}
Cd^{2+}	6×10^{-7}
Zn^{2+}	3×10^{-5}

ventional hydroxide precipitation is less effective in the presence of complex-forming chemicals. Hydroxide precipitates of many metals are also amphoteric in nature and tend to dissolve at high pH values because of the reaction

$$M(OH)_2 \text{ (solid)} + OH^- \rightleftarrows M(OH)_3^-$$

The minimum solubilities of most metal hydroxide precipitates do not occur at the same pH value; for example, $Cu(OH)_2$ has a minimum solubility at pH 9.5 whereas $Cd(OH)_2$ has a minimum solubility at pH 11.

EXPERIMENTAL

The laboratory-scale batch precipitation experiments were conducted in the following sequence. The wastewater (0.5 to 1.0 liter solution) pH was first elevated to pH 3.0 to 5.5 with lime slurry. Na_2S solution was then added to the wastewater under rapid mixing conditions and mixed for 60 sec; then the pH was adjusted (when desired) with hydroxide (lime) or acid (H_2SO_4) under rapid mixing conditions. Some pH elevation was automatically obtained because of the alkaline nature of the Na_2S salt. The rapid mixing step simulates the flash mixing operation of a coagulation-flocculation unit. The suspension was then mixed slowly for 10 to 30 min, and the samples were settled for 30 to 60 min. After settling, the supernatant solution was filtered through a 0.45-μm filter and analyzed for metals. The concentrations of various metals (As, Se, Cd, Zn, Cu, Fe, Pb, and Ca) were analyzed by atomic absorption. In all cases, no attempt was made to analyze As and Se below 1 mg/l.

Composition of Wastewaters

An initial series of precipitation experiments was conducted with a synthetic mixture (with a high SO_4^{2-} content) containing As, Se, Cd, Zn, and Pb in distilled water. The composition of the mixture and the chemicals (Reagent Grade) used are shown in Table 2. Extensive precipitation studies were also conducted with actual scrubber wastewaters (designated as Batch 1 waste) obtained from a large copper smelting plant. This wastewater (high in sulfate) is produced by the water scrubbing of sulfurous gas containing metallic dusts and volatile metallic vapors (*11*). The wastewater was analyzed for various metals, and the results are shown in Table 3. Except for Pb, all metals were present as soluble species. Soluble Pb was only 4 mg/l.

TABLE 2

Composition of Synthetic Mixture

Metal	Concentration (mg/l)
As (added as Na_2HAsO_4)	20
Se (added as H_2SeO_3)	10
Cd (added as $CdSO_4$)	10
Zn (added as $ZnSO_4$)	20
Pb (added as $Pb(NO_3)_2$)	5
SO_4 (added as Na_2SO_4)	1000

TABLE 3

Analysis of Actual Scrubber Wastewater from Copper Smelting Plant (Batch 1)

Parameter	Concentration
pH	1.65
Conductivity	9400 μmho/cm
Total suspended solids	370 mg/l
Total dissolved solids	2500 mg/l
As	100 mg/l
Se	3.0 mg/l
Cd	10.5 mg/l
Zn	85.5 mg/l
Cu	297 mg/l
Fe	149 mg/l
Pb	39 mg/l
Hg	~2 mg/l
Sulfate (SO_4^{2-})	800 mg/l

RESULTS AND DISCUSSION

All sulfide precipitation experiments were conducted with a soluble sulfide (Na_2S) salt. The separations achieved are reported in terms of either the removals of the metals (1-residual metal concentration/initial concentration of the same metal) or as residual metal concentrations after treatment; the residual metal concentrations correspond to the case of *complete* precipitate removal in the clarification stage (analyzing the filtrate from a 0.45-μm filter).

Precipitation of Metals from the Synthetic Mixture

The effect of sulfide dosage on metals precipitation at a postprecipitation pH of 6.7 and a final adjusted pH of 8.5 is shown in Fig. 2. Zero

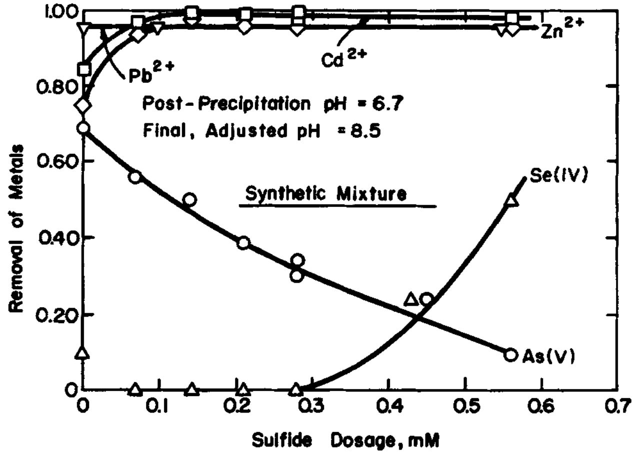

FIG. 2. Effect of sulfide dosage on the removal of metals from a synthetic mixture.

sulfide dosage corresponds to the removal due only to hydroxide precipitation at the final, adjusted pH of 8.5. The theoretical sulfide dosage is 0.43 m*M* (13.8 mg/l S) to form PbS, ZnS, and CdS: arsenic and selenium (present as oxyanions) removals are due to adsorption on the precipitates. Above a sulfide dosage of 0.2 m*M*, Cd removal was greater than 99% and Zn removal was 97%. The high removal of Pb (greater than 96%), even with no sulfide, was due to the formation of insoluble $PbSO_4$ (K_{sp} of $PbSO_4 = 1.3 \times 10^{-8}$).

In order to enhance the As and Se separation, experiments were also conducted at a postprecipitation pH less than 6.7 (final, adjusted pH maintained at 8.5). Best removals of all metals were obtained at a postprecipitation pH of 5.0 to 5.5 and at a sulfide dosage of 0.3 m*M* (less than the theoretical value of 0.43), where combined hydroxide and sulfide precipitates were present. Although Cd, Zn, and Pb removals were independent of the postprecipitation pH, As and Se removals increased considerably at pH 5.0 to 5.5 due to enhancement of oxyanion adsorption. The residual metal concentrations at the lower pH were As 10, Se 1.2, Cd 0.05, Zn 0.7, and Pb < 0.2 mg/l. For waters containing moderate to high concentrations of Fe, the arsenic removal was considerably higher, as shown below for experiments involving actual wastewaters.

In order to compare sulfide precipitation results with hydroxide precipitation results, several experiments were performed to study the removal of metals as hydroxide precipitates. The effect of pH (no sulfide) on the

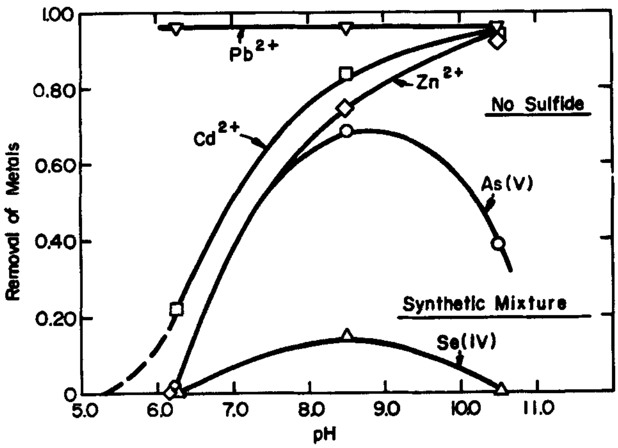

FIG. 3. Hydroxide precipitation of metals from a synthetic mixture.

removal of metals is shown in Fig. 3. Se, Cd, and Zn separations were considerably poorer (even at pH 10.5) than those obtained with the sulfide process. At pH 8.5 the residual metal concentrations of Se, Cd, and Zn were 9, 2, and 5 mg/l, respectively. At pH 10.5 the residual concentrations of Cd and Zn decreased to 0.6 and 1.1 mg/l, respectively.

Precipitation of Metals from Actual Wastes

Prior to the precipitation experiments, the selenium concentration in the actual wastes (Table 3) was increased to 15 mg/l. Most sulfide precipitation experiments were conducted after initial pH elevation (with lime slurry) of the waste to 5.5, for which 1.8 g/l of $Ca(OH)_2$ was required (*11*).

The theoretical (designated 1 ×) sulfide dosage (1 mole of sulfide for each mole of Cd, Zn, Fe, Cu, plus Pb) in the absence of any hydroxide precipitate formation is about 9 m*M* (288 mg/l S). The effects of sulfide dosage, postprecipitation pH, and final, adjusted pH (with H_2SO_4 or lime) were investigated. The effect of sulfide dosage (at the low postprecipitation pH of 5.7 to 6.0, also equal to the final, adjusted pH) on the separations of various metals is shown in Fig. 4. The use of a postprecipitation pH (also equal to the final, adjusted pH) less than 6.0 was investigated to demonstrate the insolubility of sulfide precipitates (in contrast to hydroxides) even at low pH values. The sequential precipita-

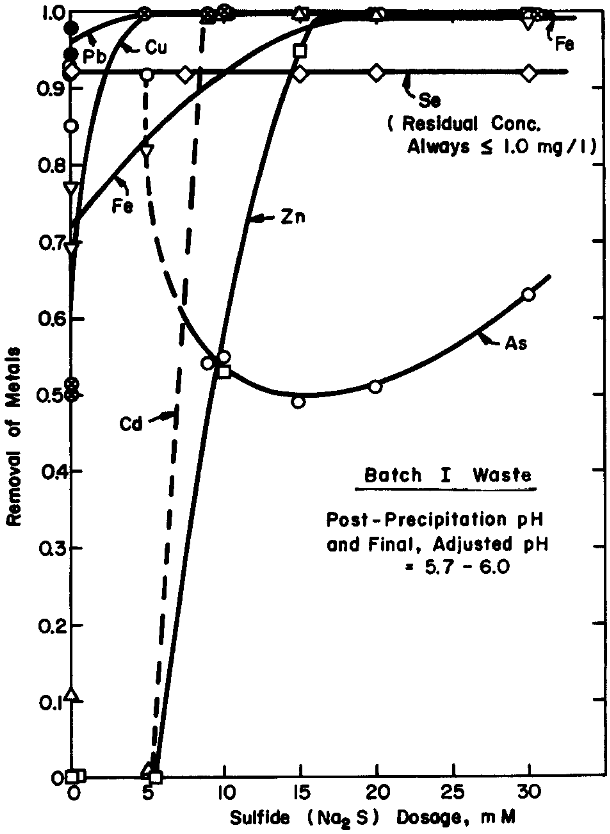

FIG. 4. Effect of sulfide dosage on the removal of metals from an actual smelting waste.

tion of Cu, Cd, and Zn agrees with the increasing K_{sp} sequence of the corresponding sulfide precipitates. For dosages above 8.0 mM the removals of Cd, Cu, and Pb were between 99% and 99.9%. The arsenic removal was maximum at 0 to 5.0 mM sulfide dosage due to strong adsorption on the hydroxide precipitates present at low sulfide dosages. At high Na_2S dosages the improved As removal was due to the formation of insoluble As_2S_3 in acidic solution.

Figure 5 presents the results for another series of experiments for which the final, adjusted pH was from 5.7 to 8.5, with the postprecipitation pH maintained at 5.7 to 6.0. The simultaneous achievement of a high separation of all metals can be obtained even at low sulfide dosages (5 to 8 mM)

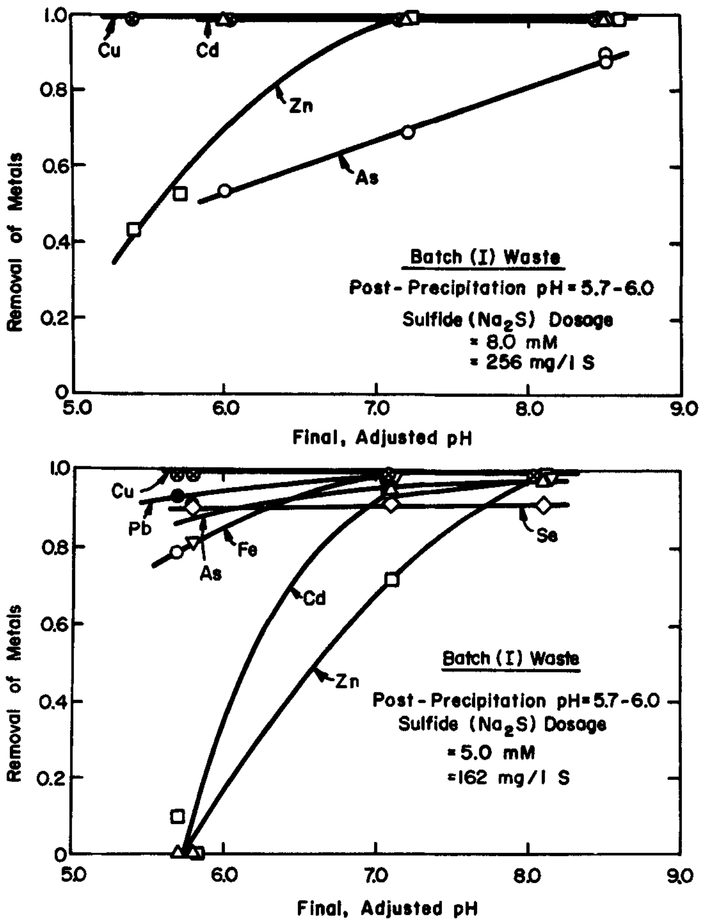

FIG. 5. Effect of final adjusted pH on the removal of metals from an actual smelting waste with less than 1 × Na$_2$S dosage.

by maintaining the final, adjusted pH greater than 7.5. Arsenic removal at all final, adjusted pH values was greater at the low dosage (5 m*M* corresponding to 0.6 × theoretical dosage), corresponding to the presence of both sulfide and hydroxide precipitates. At a 5.0 m*M* dosage and a final, adjusted pH of 8.1, the removals of As, Cd, and Zn were greater than 99%. Copper removal was always greater (even at pH 5.7) than 99.9%. Figure 5 also shows that selective metal separations can be achieved by adjusting the sulfide dosage and pH values.

Table 4 presents the residual metal concentrations obtained at three

TABLE 4

Effect of Na_2S Dosage on Residual Metal Concentrations (Batch 1 Waste)

Sulfide dosage (m*M*)	Residual concentration (mg/l)							
	pH[a]	As	Se	Cd	Zn	Cu	Fe	Pb
0	8.5	6.8	<1.0	0.6	3.1	0.5	<0.5	0.7
5.0	8.0–8.5	2.0	<1.0	<0.05	0.9	0.2	<0.5	0.4
8.0	8.0–8.5	11.0	1.2	<0.05	0.05	0.1	<0.5	0.4
12.0	8.0–8.5	21.0	1.0	<0.05	<0.05	<0.05	<0.5	0.3

[a] Final, adjusted pH.

different sulfide dosages. Hydroxide precipitation (zero sulfide dosage) results at pH 8.5 are also included for comparison. A sulfide dosage of 12.0 m*M* corresponds to 30% excess (1.3 ×); at this dosage the residual arsenic concentration is considerably higher than that obtained with the 5.0 m*M* (0.6 ×) dosage. With sulfide precipitation the residual concentrations of Cd, Zn, and Cu were considerably lower than those obtained with the conventional hydroxide precipitation process.

Several settling studies were also conducted at different sulfide dosages and pH conditions. Figure 6 shows that although the settling rate (subsidence velocity) is independent of pH (see Fig. 6, top), the settling behavior is a strong function of sulfide dosage. The maximum settling rate (see Fig. 6, bottom) occurred in the presence of combined sulfide and hydroxide precipitation. Poorer settling behavior was observed with hydroxide precipitation (zero sulfide) and with higher sulfide dosages. The settling rate with 0.6 × dosage was two times higher than that obtained with hydroxide precipitation.

CONCLUSIONS

The feasibility of sulfide precipitation with Na_2S is established to achieve a high degree of separation of heavy metal cations and the oxyanions of As and Se from complex wastewaters. Precipitation studies were conducted with a dilute synthetic mixture containing As, Se, Cd, Zn, and Pb in distilled water and with an actual scrubber waste (containing high concentrations of As, Zn, Cu, Fe, and other metals) from a copper smelting operation.

For both waste solutions the overall separation of arsenic and other heavy metals was best at sulfide dosages less than the theoretical values and at final, adjusted pH values greater than 8.0. The arsenic separation

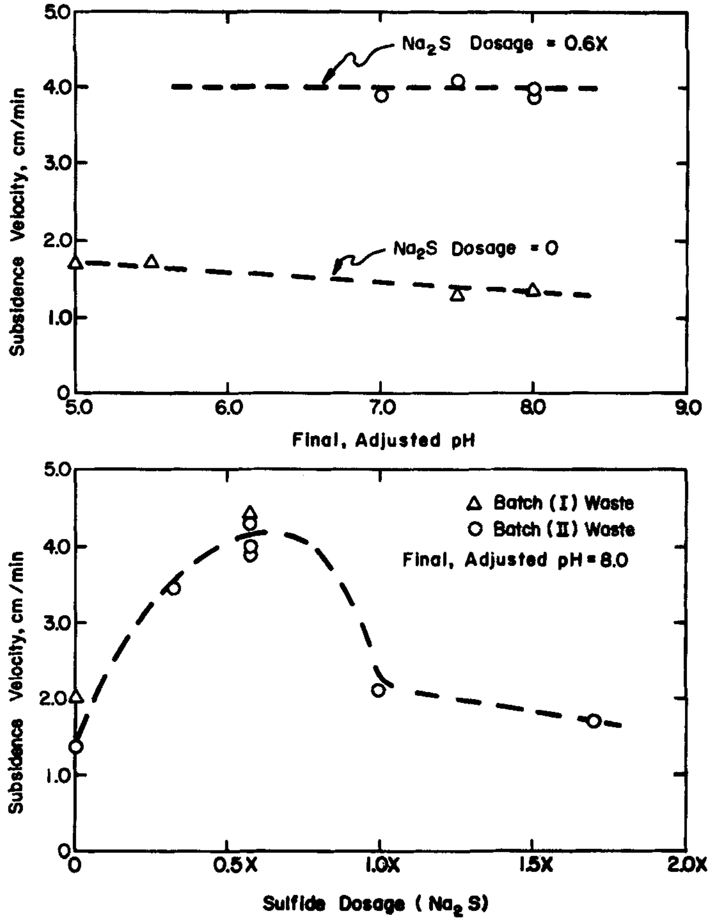

FIG. 6. Effects of pH and sulfide dosage on subsidence (settling) velocity.

decreased with an increase in the sulfide dosage. With the synthetic mixture, 50% removal of As and greater than 97% removals of Cd, Zn, and Pb were obtained. Extensive experiments conducted with the actual waste showed that a sulfide dosage of 5.0 m*M* (60% of the theoretical) and a final, adjusted (operating) pH of 8.0 to 8.5 were optimum. At these conditions the removals of Cd, Zn, and Cu were greater than 99%, and As and Se removals were 98 and >92%, respectively. The arsenic and selenium separations were primarily due to adsorption on precipitates.

The residual metal concentrations obtained with sulfide precipitation were considerably better than those obtained with hydroxide precipitation. Cu, Cd, and Zn concentrations in the range of 0.05 to 0.1 mg/l could be achieved with sulfide precipitation. The precipitate settling velocity was a maximum in the presence of combined sulfide and hydroxide precipitation (at pH 8.0 to 8.5 with 5 mM Na_2S), and the settling rate was two times higher than that obtained with conventional hydroxide (lime) precipitation.

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