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Foam Separation of Lead(II) and Cadmium(II) from Waste Water

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Abstract

Foam separation techniques are evaluated to determine if they would be feasible for removing lead(II) and cadmium(II) from highly contaminated waste water. Variables such as pH, ionic strength, collector concentration, and interfering ions were studied to determine their effects on ion flotation. Increased ionic strength, calcium(II), and phosphate interference made ion flotation impractical. Precipitate flotation of lead sulfide and cadmium sulfide left approximately 0.20 ppm lead(II) and 0.08 ppm cadmium(II) in the bulk solution under optimum conditions—somewhat above the levels considered safe to release into the environment. Adsorbing colloid flotation gave excellent results; lead sulfide and cadmium sulfide were adsorbed to ferrous sulfide which was then removed by foaming with hexadecyltrimethylammonium bromide. Lead(II) levels were reduced from 0.80 to 0.025 ppm in 34 min foaming with 15 ppm iron(III) added. Cadmium(II) levels were reduced from 1.0 to 0.008 ppm in 45 min foaming with 25 ppm iron(III) added.

As the requirements for clean water have become more stringent, industry has been in constant search for techniques to produce the cleanest possible effluent with the minimum cost. Foam separations have been

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used for years to remove certain organic molecules, clays, and some bacteria and algae from sewage. Recent reviews by Lemlich (*1*), Perry (*2*), and Somasundaran (*3*) indicate the importance and varied applications of foam separations. The reader is referred to those books and that article for background information and original references.

Karger et al. (*4*) have proposed nomenclature for the entire field of adsorptive bubble separation techniques but only three divisions will be of importance at this time. The foam separations of interest here are ion flotation, precipitate flotation, and adsorbing flotation. Foam separation is due to a surfactant (a surface-active agent) causing a nonsurface-active material to become surface active by forming a product which is surface active; the product is then removed by bubbling a gas through the bulk solution to form a foam.

Rubin and his co-workers have studied ion flotation and precipitate flotation of several metal ions and compared the two techniques where possible. They studied the separation of lead(II) (*5*), of zinc(II) (*6*), and of copper(II) and iron(III) (*7–9*). Grieves and his co-workers have devoted much effort to applying flotation techniques to waste treatment problems. They have studied the flotation of dichromate (*10*) and chromic hydroxide (*11*).

Kim and Zeitlin have made use of adsorbing colloid flotation to remove trace metal ions from seawater (*12–14*). Schonfeld and Kibbey (*15*) developed a foam separation apparatus to concentrate radioactive strontium by factors of greater than 10^3. A much more complete listing of foam separation applications is found in the article by Somasundaran (*3*).

Thus far no application of adsorption bubble separation techniques has been made to the removal of heavy metal ions from highly contaminated industrial waste water. We here present such a method for removal of lead(II) and cadmium(II) from these waters.

If the surfactant, also known as a collector, forms an insoluble product with the nonsurface-active material, the process is known as ion flotation. If the nonsurface-active material forms a precipitate with something other than the collector, which is in turn made surface active by the collector, the process is called precipitate flotation. Adsorbing colloid flotation is defined as the removal of dissolved material by adsorption on colloidal particles followed by the removal of the colloidal particle, dissolved material, and the collector by flotation.

Ion flotation requires stoichiometric or greater amounts of the collector since the ion and the collector actually form a compound. Precipitate and adsorbing colloid flotation, on the other hand, do not require stoichiometric amounts of the collector since only electrical attraction exists between the collector and the precipitate. Still, enough surfactant must be used to form a stable foam.

An attempt was first made to evaluate the work reported by Rubin and Lapp (*5*) to determine if ion flotation could be used to remove lead(II) from contaminated waste water. The effectiveness of precipitate flotation of PbS and CdS was then compared to removal by adsorbing PbS and CdS to FeS followed by foaming.

EXPERIMENTAL

The flotation system shown in Fig. 1 was used for the bulk of the work. Pre-purified nitrogen was the gas principally used although compressed air and purified compressed air were used for comparison purposes. A Nupro needle valve was used to regulate the gas flow. Pressure upstream of the valve was maintained at 5 psig and the gas flow was adjusted with the valve and a soap bubble flow meter. The saturated gas flow is reported in millliliters per minute at atmospheric pressure and room temperature.

The column was a piece of Pyrex glass tubing 3.5 cm × 90 cm with a side arm 7 cm from the bottom for insertion of a glass pH electrode. The bottom of the column was closed with a rubber stopper with holes for the gas sparger (a "fine" gas dispersion tube from Lab Glass, Inc., Catalog No. LG-8680–130), a stopcock to remove the samples, and a septum through which collector, acid, base, etc., could be injected.

Laboratory grade sodium lauryl sulfate (NLS), purchased from Fisher Scientific Co., was the anionic collector used; hexadecyltrimethylam-

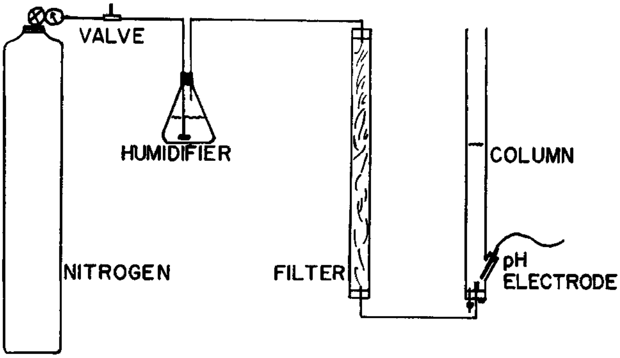

FIG. 1. The principle apparatus used. At times the humidifier and filter were left out when compressed air was used.

monium bromide (HTA), purchased from Eastman Kodak Co., was the cationic collector. The NLS was dissolved in water to give a 2.5×10^4 ppm stock solution. The HTA was prepared by dissolving the HTA in 1 ml of ethanol and then diluting to 100 ml to give a 2.5×10^3 ppm stock solution. A frother was not used in any of the runs.

Stock solutions (1000 ppm) of lead(II) and cadmium(II) were prepared from A.C.S. grade $Pb(NO_3)_2$ and $Cd(NO_3)_2 \cdot 4H_2O$, respectively. Five milliliters of concentrated reagent grade nitric acid per liter of solution was added to insure that adsorption of the metal ion on the container walls did not take place. All other chemicals used were reagent grade and were used without further purification.

A Heath Digital pH Meter with a microelectrode was attached to a Heath Variable-Speed Recorder to allow continuous pH monitering of each run.

Lead(II) and cadmium(II) concentrations were determined with an Aztec Model Mark II Atomic Absorption Spectrophotometer using the 2170 Å lead line and the 2288 Å cadmium line. Checks on the concentrations were made with a Perkin-Elmer Model 305B Atomic Absorption Spectrophotometer, and excellent agreement was found. Lead(II) concentrations below 0.2 ppm and cadmium(II) concentrations below 0.04 ppm were determined by extraction with ammonium pyrolidine dithiocarbamate (APDC) into methyl isobutyl ketone (MIBK) using standard techniques (*16*). The MIBK solution of the metal chelate was then aspirated into the burner of the spectrophotometer.

Most experiments were batch type using 250 ml of solution. The solutions were mixed and adjusted approximately to the desired pH in a volumetric flask, then transferred to the flotation column. The gas was flowing when the solution was poured into the column; a final check was made on the gas flow rate to insure it was ±0.5 ml/min of the desired value, and a final pH adjustment was made if necessary. The collector was then injected to start the foaming (this was time = 0). Samples were taken initially, during the run, and then a large sample was taken at the end of the run for analysis as described above.

RESULTS AND DISCUSSION

The study is divided into three parts. The first part is a comparison of our results with the work of Rubin and Lapp (*5*) on lead(II), and that was done to see if ion flotation is a feasible way to remove lead(II) from waste water. The second part deals with the precipitate flotation of lead sulfide and cadmium sulfide. The third part evaluates adsorbing colloid flotation with ferrous sulfide as a method of lead(II) and cadmium(II) removal.

Ion Flotation

The basic differences in the procedures and techniques employed by Rubin and Lapp (*5*) and ours were (a) column shape and capacity, (b) gas flow rate, (c) use of frother (they employed a frother and we did not), and (d) collector concentration (we used greater concentrations than they did). As a result, we would expect to observe the trends they found, but not to duplicate their figures.

A comparison of the removal of lead(II) with NLS at different gas flow rates showed that the rate of removal was faster with high flow rates but that the maximum amount removed was the same. Figure 2 substantiates this. The 40 ml/min flow rate was chosen for most of the work to allow shorter run times and to allow the use of a lower collector concentration and still obtain sufficiently stable foams.

A decrease in removal of lead(II) was noted with increasing ionic strength as shown by Figs. 3 and 4. The ionic strength was adjusted with sodium nitrate since this did not add any new ions to the system and since the tendency of nitrate to complex with lead(II) is negligible (*17*).

The scatter of points in Fig. 3 at low ionic strengths is due to the instability of the foam. Under these conditions only a scum was formed, and thus removal from the bulk solution did not take place as it did when

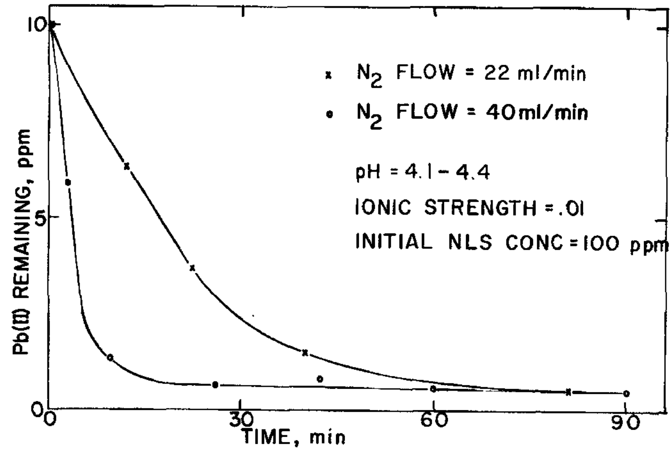

FIG. 2. The effect of gas flow rate on ion flotation of Pb(II).

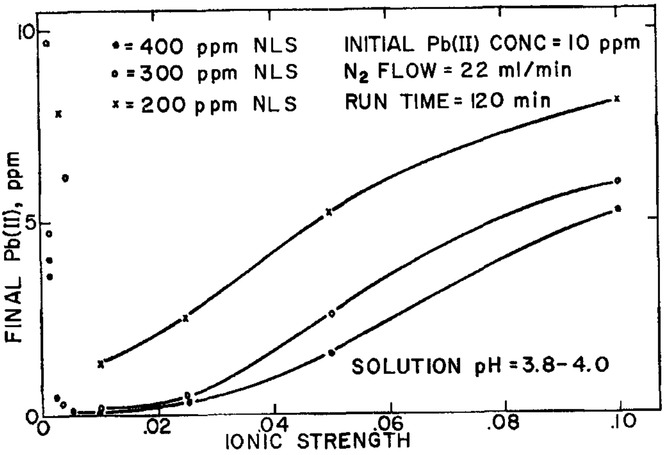

Fig. 3. The effect of increasing ionic strength on Pb(II) removal.

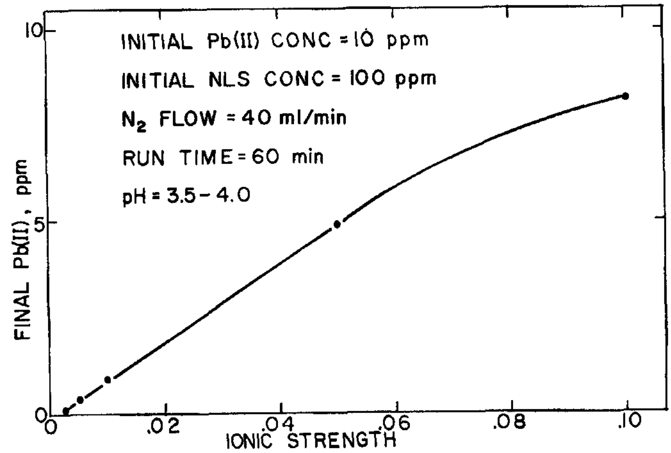

Fig. 4. The effect of increasing ionic strength on Pb(II) removal.

a stable foam was present. Increasing the ionic strength increases the stability of the foam.

Rubin and Lapp (5) report almost 100% removal of lead(II) with NLS at pH 8.2. Removals are less for other pH values. They explain that this is expected due to the hydrolysis of Pb^{2+}. At pH 8.2, $PbOH^+$ predominates and the lauryl sulfate would form the most stable complex with $PbOH^+$. This may very well be the case, but the data obtained may be in error since lead(II) adsorbs extensively to glass at these pH's.

Figure 5 illustrates the adsorption of lead(II) on glassware. These data were taken using 250 ml of solution placed in the Pyrex column used for experimental runs. Nitrogen was bubbled through the column at the rate of 40 ml/min, but no collector was added during the time the solution was in the column. The pH was raised each time with a small amount of sodium hydroxide. Figure 6 shows the variation of pH with time upon addition of NaOH to the solution. It also shows how the lead(II) concentration in the bulk solution returned to approximately the original value upon acidification. The slightly higher concentration was expected since samples were removed throughout the run thus decreasing the volume of the solution.

Similar adsorption in the pH range 5 to 10 was found for stainless steel, polyethylene, paraffin, glass coated with Desicote, and glass coated with dimethyldichlorosilane. The extent of adsorption varied with the surface

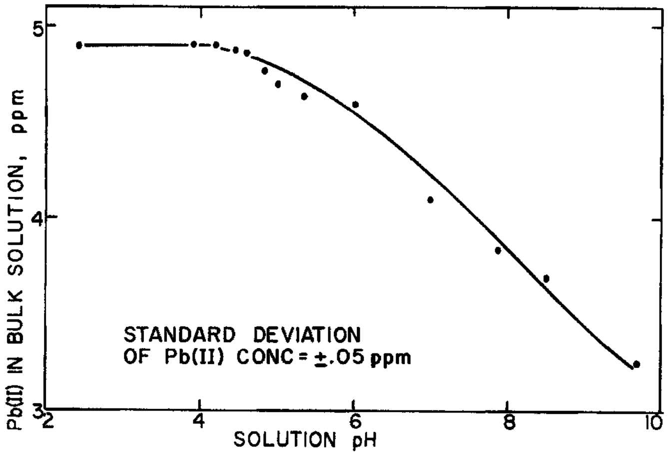

FIG. 5. The adsorption of Pb(II) to glassware.

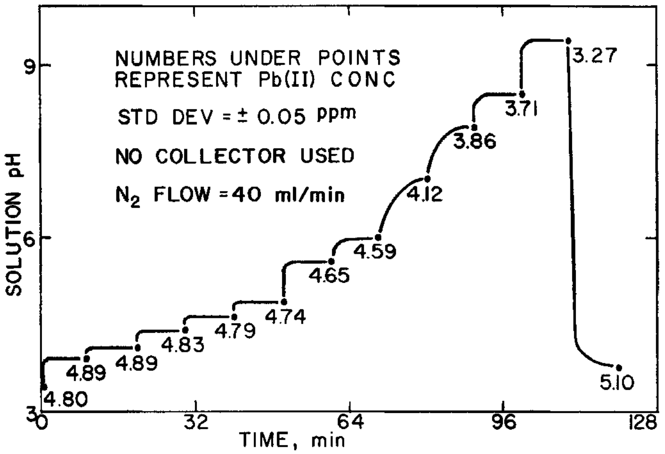

FIG. 6. Increasing Pb(II) adsorption as a function of time and pH.

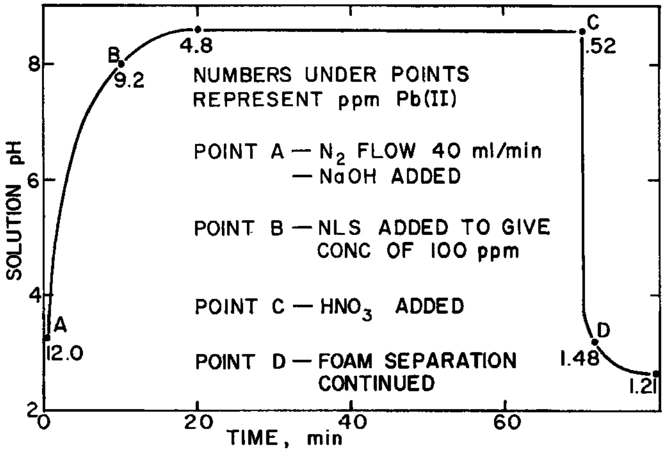

FIG. 7. Adsorption of Pb(II) during ion flotation.

area exposed to the lead(II) solution and the type surface, but in each case the adsorption was noticeable.

Figure 7 indicates that adsorption takes place during a foam separation as well as when no collector is present. As a result of the study on lead(II) adsorption, it was concluded that accurate values for lead(II) removal by ion flotation could not be obtained for pH values greater than 5 unless some way could be found to prevent adsorption. Rubin (*18*) states that the lead(II) removals reported by Rubin and Lapp (*5*) are not affected by adsorption on glass since they worked at an order of magnitude higher concentration of lead than we did and they equilibrated all glassware with lead solution prior to testing.

Figure 2 indicates the removal of lead(II) at approximately pH 4. Runs at other pH values in the range 2 to 5 showed lead(II) removal to be unaffected by pH in that narrow range. No way could be found to obtain accurate data on the extent of lead(II) removal at higher pH.

The effect of other ions in solution upon the foam separation would be a major factor in determining whether a foam flotation process for treatment of industrial waste water would be feasible. The more common ions found in waste water, such as chloride, sulfate, phosphate, iron, and calcium, were checked in concentrations of 250, 500, and 1000 ppm. If interference was noted, smaller concentrations were used to find the value at which interference began.

The addition of chloride and sulfate had almost the same effect as increasing the ionic strength with nitrate. Table 1 summarizes the effect.

Figure 8 shows the effect of adding phosphate to the test solution. Insoluble lead phosphate was formed and showed little tendency to be removed by the NLS foam.

TABLE 1

A Comparison of the Effects of Adding Sodium Chloride, Sodium Sulfate, or Sodium Nitrate. Initially 10 ppm Pb(II) and 100 ppm NLS Were Present. N_2 Flow was 40 ml/min; Run Time Was 60 min. Table Entries are ppm Pb(II) Left in Solution at the End of the Runs

Ion added	Ionic strength	$NaNO_3$	NaCl	Na_2SO_4
250 ppm Cl^-	0.007	0.1	0.4	—
500 ppm Cl^-	0.014	1.3	1.4	—
1000 ppm Cl^-	0.028	2.8	3.8	—
250 ppm SO_4^{2-}	0.008	0.1	—	1.1
500 ppm SO_4^{2-}	0.016	1.5	—	1.8
1000 ppm SO_4^{2-}	0.032	3.2	—	2.8

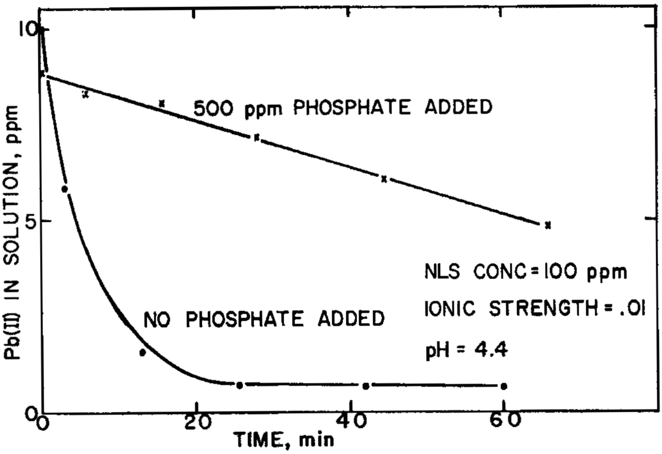

FIG. 8. The effect of phosphate on ion flotation of Pb(II).

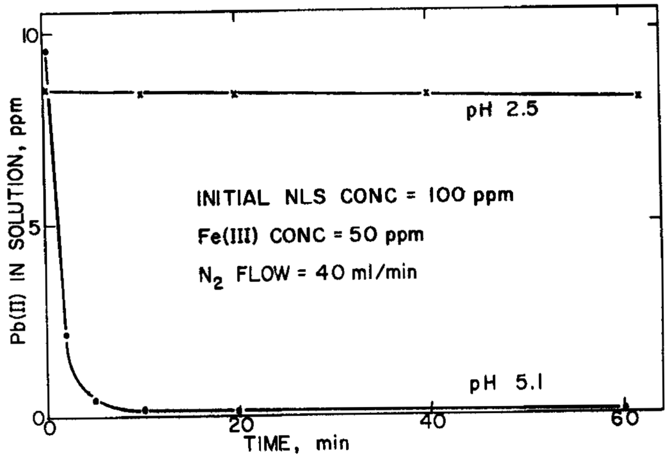

FIG. 9. The effect of Fe(III) on Pb(II) removal.

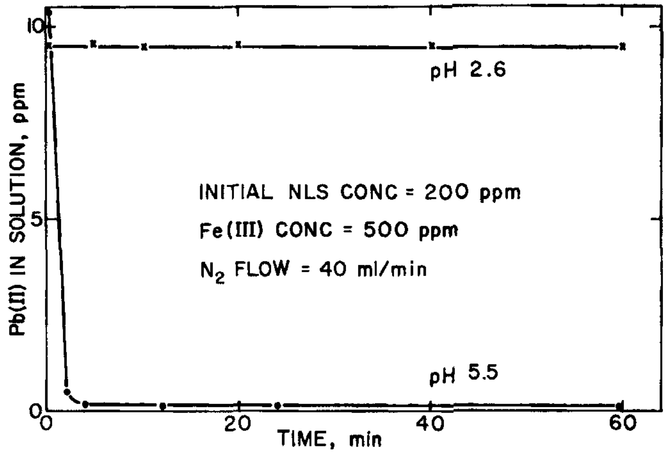

FIG. 10. The effect of Fe(III) on Pb(II) removal.

Iron(III) affected the solution in two different ways depending on the pH of the solution, as shown by Figs. 9 and 10. If the pH was above 3, the iron(III) existed as ferric hydroxide and the lead(II) was removed very effectively by adsorbing colloid flotation with the NLS. If the pH was below 3, the iron(III) prevented the removal of the lead(II). In decreasing the iron(III) concentration below 50 ppm, the removal by adsorbing colloid flotation became less effective. At higher iron(III) concentrations, more collector was required for the removal by adsorbing colloid flotation.

No foam at all could be obtained with 500 ppm NLS in the presence of 250 ppm calcium(II). Even very small concentrations of calcium(II) markedly reduced the lead(II) removal as shown by Fig. 11. With calcium (II) concentrations less than 15 ppm, the foam was unstable—very similar to the foam in the runs with low ionic strength. The foam was most stable in the region where lead(II) removal was best, but the stability of the foam decreased rapidly with increasing calcium(II) concentrations.

The effect of calcium(II) upon adsorbing colloid flotation with $Fe(OH)_3$ was found by adding 100 ppm calcium(II) to a test solution containing 10 ppm lead(II), 100 ppm iron(III), and 500 ppm NLS. The pH was 4 and the gas flow of 40 ml/min. Since no foam at all was obtained, the NLS concentration was increased to 1000 ppm; still the solution did not foam.

Based on poor removals at higher ionic strengths and the interferences from calcium(II) and phosphate, it can be concluded that ion flotation with NLS would not be an effective way to remove lead(II) from in-

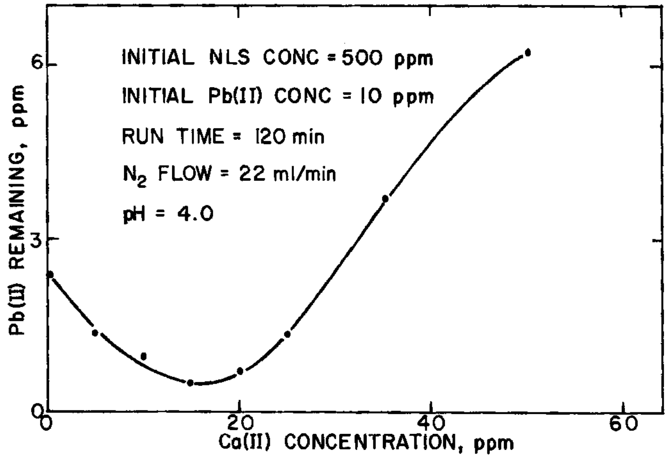

FIG. 11. The effect of Ca(II) on Pb(II) removal.

dustrial waste water. Since the same types of interferences would be experienced no matter what metal ion was to be removed, ion flotation would not be expected to efficiently remove cadmium(II). Therefore no further work was done with ion flotation.

Precipitate Flotation of the Sulfides

On examination of Rubin's work (*9*) comparing the rate of removal of iron(III) with that of ferric hydroxide, it appeared that the best approach to lead(II) and cadmium(II) removal might be precipitate flotation rather than ion flotation. Given the solubility of lead hydroxide (*17*), some precipitate other than the hydroxide must be chosen since the solubility of lead hydroxide would be some 76 ppm Pb^{2+}.

$$Pb(OH)_2(s) \rightleftarrows Pb(OH)_2(aq), \quad pK_d = 3.44$$

Since metal sulfides are among the most insoluble precipitates known, we planned to try to remove lead(II) and cadmium(II) as sulfides by precipitate flotation. Lead sulfide was chosen to develop the techniques for best removal; these were then applied to cadmium(II).

Kapustinsky in 1940 found the solubility product constant for PbS to be 6.8×10^{-29} at 25° (*19*). Given this value and on taking into account sulfide hydrolysis at pH 7, PbS should be soluble to the extent of 7.5×10^{-7} ppm. Figure 12 indicates that this is not the case. PbS is much more soluble than calculations would indicate. The scatter of the points is due

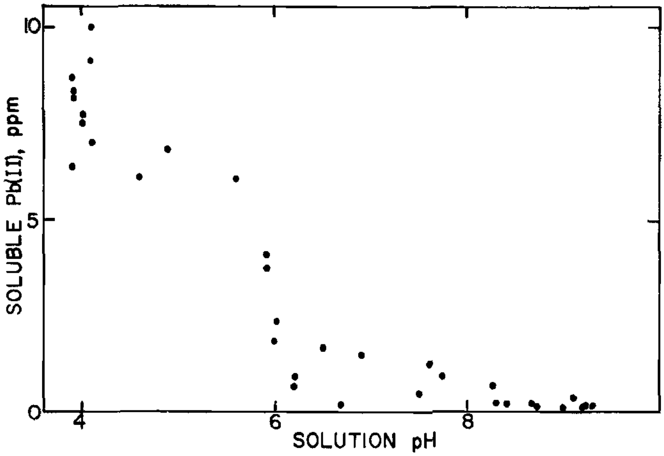

FIG. 12. Solubility of PbS at different pH values. A small amount of solid PbS was added to the sample bottle with warm boiled distilled water. The pH was then adjusted to the desired value and allowed to stand 24 hr to reach equibrium.

to the release of H_2S at lower pH's and to the formation of other complexes of sulfide as suggested by Hemley (*20*). This helps to explain why removals of the sulfides by foam separation were not always as good as might have been expected.

NLS would remove no lead sulfide at all, but the cationic surfactant hexadecyltrimethylammonium bromide (HTA) removes the precipitate very effectively. Figure 13 indicates the increased rate of removal of lead sulfide even though the amount removed when the run was terminated was no greater than that removed by ion flotation.

No problem was encountered with adsorption of lead(II) to the container walls when sulfide was present. Figure 14 indicates a very small amount of adsorption of PbS even at higher pH's. At the termination of runs at pH values above 7, acidification of the solution in the column resulted in no increase in the lead(II) concentration of the bulk solution.

Slightly better removals were obtained with basic solutions, presumably because lead sulfide is more insoluble in that pH region. All runs left between 0.2 and 0.6 ppm lead remaining in solution after foaming 30 min with 40 ml/min nitrogen. The initial collector concentration was 20 ppm HTA and all runs were at room temperature. The initial lead(II) concentration was 10 ppm and the initial sulfide was varied between 3.2

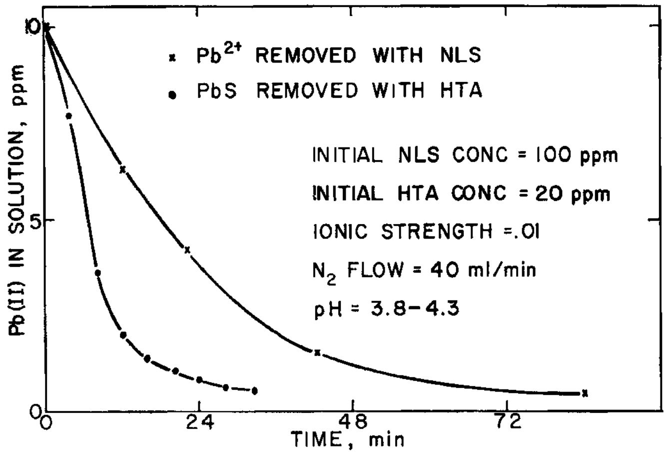

FIG. 13. Comparison of the rate of removal of Pb(II) and PbS.

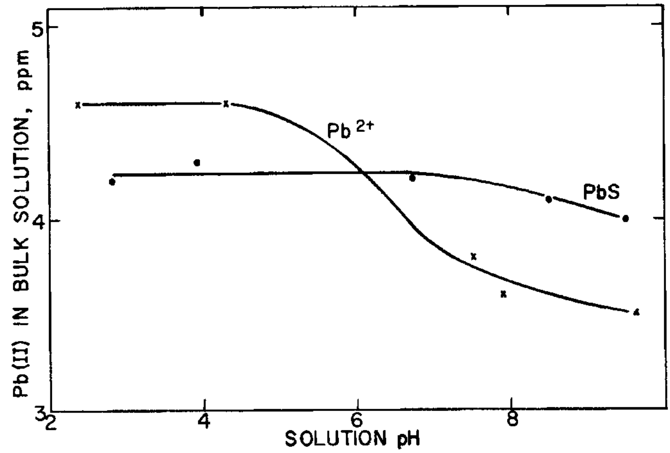

FIG. 14. Adsorption of Pb(II) compared to adsorption of PbS. The Pb(II) was put in the column initially and 10^{-3} M S^{2-} was added to form PbS. The pH was adjusted with NaOH. The concentration in the bulk solution returned to the initial value upon acidification.

and 32 ppm. No difference in the maximum amount of lead(II) removed was found upon varying the sulfide concentration in that range.

A better removal rate was found when addition of the collector was distributed over the course of the run (that is, add 5 ppm HTA initially and 2 ppm every 4 min to maintain the foam). Figure 15 shows the removal is poor initially, probably due to micelle formation by the HTA. Further foaming with continued additions of collector reduced the lead content of the bulk solution to 0.2 ppm but the concentration stabilized at that point.

Increasing the ionic strength of the solution with sodium nitrate slightly reduced the amount of lead(II) removed during a 30-min run. For instance, a solution of ionic strength 0.1 was reduced from 10 to 2.2 ppm lead(II) using 20 ppm HTA and a N_2 flow of 40 ml/min, but upon addition of another 10 ppm HTA and foaming an additional 15 min the lead concentration was reduced to 0.8 ppm. A slightly longer foaming time is required but the ionic strength does not affect the removal by precipitate flotation as much as it affects the removal by ion flotation.

Chloride, sulfate, and calcium(II) present in concentrations up to 1000 ppm did not affect the removal of lead sulfide by precipitate flotation.

Optimum conditions for removal of lead sulfide by precipitate flotation were found to be minimum ionic strength, a pH range of 8 to 9, and a collector concentration of 2 to 5 ppm in the solution. With these conditions the best removals still left 0.15 to 0.20 ppm lead in the bulk solution.

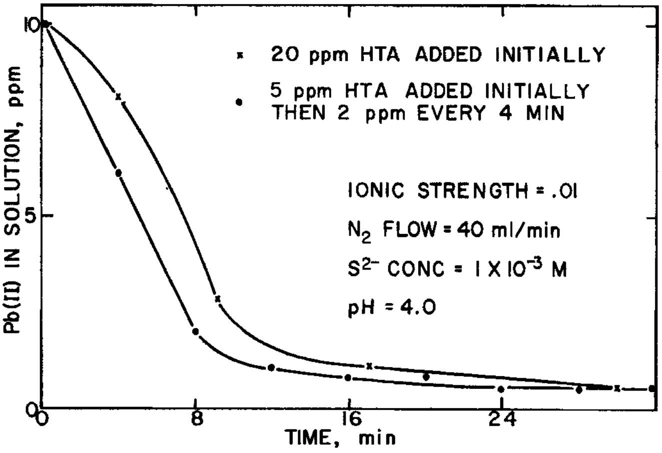

FIG. 15. A comparison of pulsed addition of surfactant with initial addition.

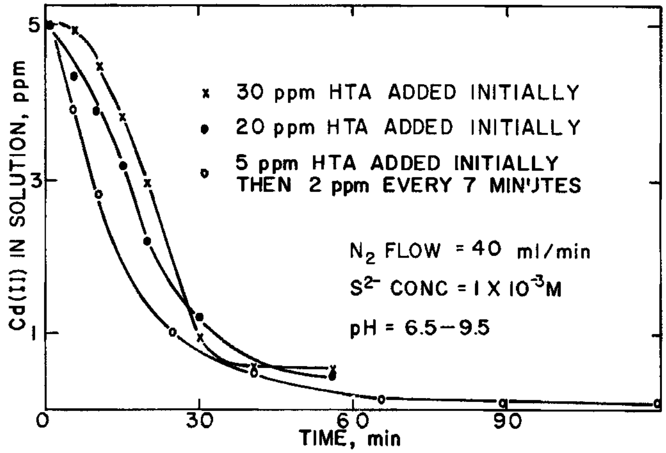

FIG. 16. Removal of CdS by precipitate flotation.

Longer foaming times, the addition of more collector, or the addition of excess sulfide did not give better removal.

These methods were then applied to cadmium sulfide removal. Cadmium sulfide should be most insoluble in basic solution, and the majority of the runs were made in near neutral or basic solution.

Figure 16 shows typical results obtained when removing cadmium sulfide with HTA. Addition of the collector at various time intervals gave better and more consistent results than a single addition at the beginning of the run. The effect of micelle formation is very clear when one observes the rate of removal during the first few minutes of a run made when 30 ppm HTA was added initially. When the HTA was added in a single portion, the foam was very stable and wet initially but after about 40 min the solution would not form any stable foam at all. An initial HTA level of 5 ppm gave a less stable foam but it was much drier and gave better removal. Pulsed addition maintains the foam at the initial height in the column. As a result of the data shown in Fig. 16, all runs with cadmium(II) were done with pulsed addition of the collector.

Cadmium sulfide was found not to adsorb to the container walls at any of the pH values studied. After runs were made, the solution was acidified to pH 3 or below, and no increase in the cadmium concentration in the bulk solution was found.

The pH of the solution did not seem to affect the ultimate removal of CdS or the removal rate. The pH was varied from 2 to 10, and after a

TABLE 2

Effect of Increasing Ionic Strength on CdS Removal. The Initial Conditions were N_2 flow = 40 ml/min, 5 ppm HTA Initially with 2 ppm Added Every 7 min, and pH Range = 5 to 6. The Run Time Was 60 min. Lower Entries Are Cd(II) Concentrations at the Ends of the Runs

Ionic strength	0.003	0.01	0.025	0.053	0.104	0.5	1.0
Cd(II), ppm	0.17	0.32	0.37	0.34	0.50	0.52	0.53

run time of 40 min approximately 0.5 ppm Cd(II) remained in the bulk solution. The majority of runs were made in the pH range of 5 to 9 to keep from forming H_2S in an acidic solution.

The ionic strength of the solution was increased to 1.0 with a very minor decrease in observed removal. Table 2 gives the results found for increasing the ionic strength of the solution with $NaNO_3$.

An initial sulfide concentrate of 32 ppm is sufficient excess to keep adequate sulfide in the solution throughout the run. No addition of sulfide is necessary unless the pH is below 2.

Since no interference from other ions was found for lead sulfide removals with HTA, none would be expected with cadmium sulfide. Again the lower limit of removal was only limited by the solubility of CdS.

Precipitate flotation offers a great improvement over ion flotation, but still the process would not reduce the lead(II) or cadmium(II) in solution to levels that are considered safe for discharge into streams and waterways (*21*).

Adsorbing Colloid Flotations

The most effective way of removing lead(II) and cadmium(II) was found to be adsorbing colloid flotation by adsorbing the PbS or CdS to ferrous sulfide, then foam removal with HTA as collector.

Upon addition of Fe(III) to a basic solution of sulfide, the following reaction occurs:

$$2Fe^{3+} + 3S^{2-} \rightarrow 2FeS + S^0$$

In acid solution the FeS is not formed, but in basic solution the FeS remains stable for several hours until air oxidation takes place. Upon addition of HTA to the solution of the colloidal FeS and CdS or PbS, the precipitate coagulates and the CdS or PbS adsorbs. The solution may then be filtered to remove the bulk of the precipitate, and then foamed to remove the remaining traces. The solution may also be foamed initially

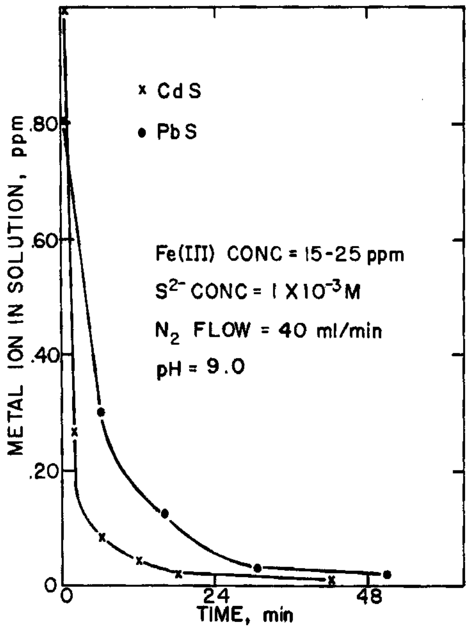

FIG. 17. The removal of PbS and CdS by adsorbing colloid flotation.

with HTA as a collector without filtering, resulting in the removal of the FeS and CdS or PbS in the foam. Studies were made with both procedures.

Figure 17 shows typical results for adsorbing colloid flotation for PbS and CdS with FeS. Extremely fast removal was found for both cases. Five to 100 ppm Fe(III) was added, but the removal rate and the maximum removal of the PbS or CdS were very nearly the same. The foam was not so stable in runs made with more Fe(III), and much more collector was needed to remove the precipitate. When 5 ppm Fe(III) was added, the removal rate was not quite as fast but the same removal limits indicated in Fig. 17 were obtained after 60 min foaming. The runs using 5 ppm Fe(III) were actually more efficient since less collector was required for the removal.

Compressed air was found to be as effective as nitrogen for the gas; air oxidation during the course of the run presented no problem. After the runs were completed, a small sample was acidified with 2 drops of concentrated HNO_3 to decompose the FeS and then a small amount of sodium thiocyanate was added to check for the presence of the ferric ion. No color was detected, indicating that the iron level remaining in solution was quite low. (No iron analyses of the solution were done to determine the exact amount of iron remaining in solution.)

If a more concentrated basic solution (greater than 10 ppm) of PbS or CdS was filtered after the addition of the iron(III) to remove most of the precipitate, the lead(II) or cadmium(II) concentration in solution was found to be 0.3 to 0.4 ppm. After foaming for 30 min using the same conditions as in Fig. 17, the cadmium(II) concentration was 0.003 ± 0.001 ppm and the lead(II) concentration was 0.016 ± 0.003 ppm.

A 0.8-ppm PbS solution was treated with Na_2S to give a sulfide concentration of at least 32 ppm, then Fe(III) was added to give an Fe(III) concentration of 5 ppm. The pH [which was kept basic throughout the addition of the S^{2-} and Fe(III)] was adjusted to between 8 and 9. This solution was then dripped through the inlet tube of the continuous flow apparatus shown in Fig. 18. The volume of the solution in the column was approximately 500 ml. The solution inlet rate was 10 ml/min, the collector was added at the rate of 0.4 ppm/min, and the air flow was 40 ml/min. After the continuous flow system began operation, the foam

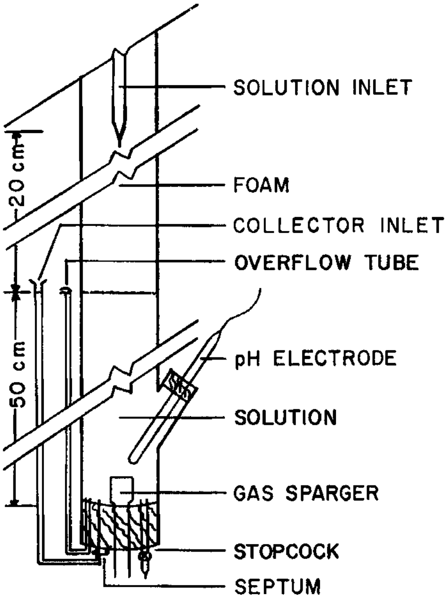

FIG. 18. Flotation column for continuous flow.

around the inlet tube became extremely black, indicating FeS removal at that point. The foam, PbS, and FeS were removed from the top of the column. After 70 min of operation the maximum efficiency of the system was attained, and the lead(II) concentration of the solution coming out of the overflow pipe was 0.08 ppm. This concentration was then maintained for the remainder of the run. The lead(II) concentration of the above solution was chosen since precipitation of lead(II) with sulfide followed by neutralization will reduce the lead concentration well below this value.

Waste water from old lead-acid storage batteries furnished by a local lead smelter initially contained over 300 ppm lead (mainly in the form of the sulfate) and was approximately 2 *N* in sulfuric acid. After the addition of Na_2S and neutralization with lime, the lead concentration had been reduced to 0.20 to 0.40 ppm lead depending on the final pH of the solution. After adding sulfide, 5 ppm iron(III), and then foaming with HTA as a collector, the lead concentration was in each case reduced to less than 0.01 ppm.

The study with adsorbing colloid flotation shows that this is an excellent method to reduce lead(II) and cadmium(II) concentrations in waste water to acceptable levels. Continuous flow studies were not done with cadmium, but the batch studies with cadmium(II) and the continuous flow studies with lead(II) indicate the feasibility of the process.

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