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INVESTIGATION OF NOVEL ADSORPTIVE SEPARATION METHODS FOR REMOVAL OF TRACE HEAVY METALS FROM POLLUTED AREAS

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ABSTRACT

The removal of trace amounts of cadmium and zinc from wastewater samples from the Bunker Hill mine as well as from synthetic wastewaters was evaluated. The heavy metals were chelated with the surfactants, sodium lauryl sulfate, sodium lauryl benzene sulfate, and cetyl pyridinium chloride. The chelated metals were then separated by the generation of a foam by sparged air or dissolved air. As much as 95% of the metal entering the foam generation unit was removed and carried out with the foam. The foam generated constituted about 25% of the feed. The removal efficiency was correlated with feed flow rate and foam drainage height by means of a simple equilibrium model. Qualitative predictions based upon the model fit the experimental results although quantitative agreement was not good. Recommendation for further experimental work are presented.

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INTRODUCTION

Ground water heavy metal contamination is becoming a serious problem in parts of the United States and the world. Man made generation of lead, antimony, zinc, and cadmium pollution is ten or more times that from natural sources (Brown, et al., 1987). Concentrations in the rivers and streams at the Bunker Hill superfund site in Kellogg have been measured as high as 12.5 microgram/liter for antimony, 33 microgram/l for cadmium (standard is 10), 79 microgram/l for lead (standard is 50 microgram/l) and 9.5 milligram/l for zinc (standard is 5 milligram/l) as late as 1984 (E.P.A. STORET system data) when much of the smelting operations were curtailed. Concentrations in streams around the Bunker Hill site during the period 1974 to 1984 when the smelter was actively operating rose to as high as 0.5 mg/l, 1.7 mg/l, 10 mg/l, and 165 mg/l for antimony, cadmium, lead, and zinc respectively (E.P.A. STORET system data).

These concentrations were measured in streams receiving water treated by lime precipitation. Slightly lower concentrations have been measured in groundwater from wells. Lime precipitation is an accepted method for removal of heavy metals (Manahan, 1979) and may result in concentrations as low as 0.2 mg/l for cadmium and zinc at pH values between 10 and 11. However, in doing so, large amounts of lime may be required and one has only turned a water pollution problem into a solid waste problem.

Lime or alkali precipitation of heavy metals relies upon

significant amounts of chemical additives to change the bulk liquid phase chemistry. A more efficient method would involve the addition of small amounts of additives that are selective for complexation and removal of the heavy metals. There is a range of metal chelating compounds that utilize carboxyl, nitryl, amino, and sulfoxy groups to bind to metal ions. The subsequent complex can contain enough hydrophilic groups to be water soluble, such as the ethylene diamine tetraacetic acid chelates of calcium and magnesium, or have hydrophobic groups which render it relatively insoluble, such as chelates of zinc or cadmium with sodium lauryl benzene sulfonate.

These chelating agents form strongly bound complexes with metals and essentially completely tie up the metal as an organic complex. Therefore, low concentrations of the chelate are required. The hydrophobic chelating agents, in addition, form strongly bound metal organics that tend to adsorb at interfaces. This phenomena can be utilized in the separation of the chelated metal by foaming (ion flotation) or activated carbon adsorption. In a foam separation unit, gas bubbles serve as the surface upon which the chelated metal is adsorbed. These bubbles may be generated by passing the gas through porous material such as fritted glass or by saturating the liquid with gas at an elevated pressure then releasing the pressure to produce extremely small bubbles. This latter process is called dissolved air flotation and is often used as a means of separating oil from municipal waste waters.

In order to correlate results from the operation of a foam separation column, one may apply material balances and assume equilibrium partitioning of the chelated metal between the bulk liquid

phase and the liquid-gas interface in the simple ideal foam model (Carleson, 1988). This model relates the enrichment ratio, C_o/C_b (concentration of metal in the overflow or foam phase divided by concentration in the underflow or raffinate phase) or the removal efficiency, $E = C_oO/(C_fF)$ (ratio of rate of metal leaving in the foam to rate of metal entering in the feed) to the coalesced foam flow rate, O; the feed rate, F; the bubble diameter, D; the gas flow rate, G; the surface concentration of chelated metal, A; and the feed concentration of metal, C_f.

$$R = C_o/C_b = 1 + G(6/D)A/(C_bO) \tag{1.}$$

$$E = C_oO/(C_fF) = O/F + (6/D)(A/C_f)(G/F)(1 - O/F) \tag{2.}$$

The surface concentration or adsorption of the chelated metal or surfactant at the gas-liquid interface can be determined by experiments with a foam column or from measurement of interfacial tension as a function of concentration and the use of Gibbs adsorption isotherm,

$$A = - (1/RT) (ds/dlnC) \tag{3.}$$

where R is the gas constant, T the absolute temperature, s the surface tension, and C the bulk phase concentration. This equation is valid for low concentrations of surfactant. At extremely low concentrations, below about 1 ppm, A is near zero. The surface concentration then rises to a constant value for surfactant concentrations between about 20 and 150 ppm and then falls to zero as the concentration of surfactant in the bulk phase approaches the critical micelle concentration. At this concentration, the surface is saturated with surfactant molecules and any additional amounts of surfactant added end up in the

formation of small "islands" of surfactant molecules called micelles in the bulk liquid phase.

To measure surface tension a Wilhelmy slide apparatus is often used. In this apparatus, a platinum black slide is pulled through the interface. As the slide is pulled through the interface, the force required to pull it from the surface is measured by a microbalance. From a force balance and knowledge of the slide dimensions, one can calculate the surface tension.

In the work summarized in this report, foam separation has been evaluated as a means of separating cadmium and zinc, at low concentrations, from water. Cationic and anionic surfactants have been evaluated as chelating agents for the metals. In addition, the operation of a sparged gas and a dissolved gas foam separation unit are compared.

EXPERIMENTAL APPARATUS

The sparged gas foam separation unit is depicted in Figure A. This unit consists of a 50 mm I.D. Buchner glass funnel with a fritted glass bottom section of porosity size C (ASTM 40-60). The upper section of the funnel converged to a ground glass joint of 14.4 mm I.D. A 20 mm I.D. by 250 mm long vertical glass tube was used to drain and convey the foam to the round bottom glass flask in which the foam coalesced. The liquid pool depth in the column ranged from 4 to 10 cm. The foam height was varied from 23 to 150 cm.

The dissolved air separation unit is depicted in Figure B. This unit consists of two one liter chambers with associated valving and a pressure source. The unit operates continuously with liquid recycling between the excess air separator tank and the

separator tank. A bleed line from the excess air separator tank is used to maintain stable levels in the tanks. Filtered, compressed air is introduced into the recycle loop through an eductor. Since the recycle pump and pressure relief valve cause the temperature in the recycled fluid to rise, a heat exchanger in the recycle line is used to cool the fluid. Liquid exiting the excess air separator tank passes through a pressure reducing valve and into the separator tank. Small bubbles of gas form in the line to this tank and generate foam which rises through a length of glass tubing. As the foam rises it drains. The drained foam is coalesced in a beaker. To conserve liquid, the foamate (overflow) and underflow are combined and recycled.

EXPERIMENTAL PROCEDURE

Two types of samples were run in the foam separation units – synthetic waste and wastewater samples (treated and untreated) from the Bunker Hill site. Fifteen experiments were conducted with the sparged gas column and the dissolved air column. Four runs were performed with the dissolved air flotation unit and eleven with the sparged gas column. Six runs were performed with synthetic waste prepared from dissolving cadmium nitrate in tap water to make a solution with concentrations ranging from 7.7 to 10 ppm in cadmium. Three runs were made with synthetic waste prepared from dissolving zinc sulfate in water to make concentrations between 0.4 and 2 ppm in zinc. Samples of untreated mine seepage water and treated (lime precipitation followed by neutralization) mine seepage

water obtained from the Bunker Hill site were used in five test runs with both units. The surfactants sodium lauryl sulfonate (NLS) and sodium lauryl benzene sulfonate (NDBS) (both cationic surfactants) were evaluated as well as cetyl pyridinium chloride (a cationic surfactant). Table 1 summarizes the sample runs. The untreated wastewater was diluted 1:1 with distilled water before chelation and foam separation. Samples were analyzed by atomic absorption.

For the sparged gas column, the air flow was maintained at 10 cm^3/min while the liquid feed rate was adjusted between 0.73 and 5 ml/min. In addition, the tubing height through which the foam rose and drained was varied between 23 and 152 cm. Samples of the foamate and underflow were taken after 30 minutes of operation and of the cumulated product at the end of the run after 6 - 12 hours.

In the dissolved air column runs, the excess air separator and separator were initially charged with liquid, the air line was pressurized and recycle pump started. After the pressure in the separator reached 50 psig and the flow stabilized, the feed and raffinate (underflow) valves were opened. Samples of all streams were taken after 30 minutes and after the completion of a run (after about 1 hour).

RESULTS

Samples from the Bunker Hill mine site consisted of effluent from the lime precipitation and neutralization treatment plant and untreated pumped liquid from the mines. The untreated sample contained about 72 ppm of zinc. The treated sample contained about

0.8 ppm of zinc and 0.018 ppm of cadmium. The pH of the untreated sample was 2 and the treated 5. The addition of 300 ppm NLS to the samples resulted in the formation of a white "fibrous" precipitate. Similar results were obtained with NBDS but not with CPC. The precipitate was soluble in nitric or hydrochloric acid and may be the result of the precipitation of other metals in the waste (i.e. antimony) with the surfactant. For evaluation of the waste in the foam separation units, the precipitate with NDBS was dissolved in nitric acid at pH 2.

Tables 1 and 2 summarize the conditions and some of the results of the runs. Runs 1 through 10 and runs 15, 16, and 16-1 were conducted with synthetic waste containing cadmium chloride or zinc sulfate and NLS surfactant. All of these runs (except 15 and 16-1) were performed in the sparged gas column. Runs 11 and 13 were performed with the sparged gas column and untreated wastewater. Run 14 was conducted with the sparged gas column and the treated wastewater. Run 12 (untreated waste), run 14-1 (treated waste) and run 15 and 16-1 (synthetic waste) were conducted with the dissolved air flotation unit.

Table 1 - The results of experiments made on synthetic and
Bunker Hill samples - Part I

July 8 - Sept. 3, 1987

Run #-unit (cm)	Surfact. (ppm-type)(ml)	Metal (ppm)*(ml)		Air ml/min	Feed ml/min	height foam	height pool	Raff. Vol.	Extr. Vol. (cm)
1 SG	300 NLS	7.7	Cd	10	3.6	66	9	910	175
2 SG	300 NLS	7.7	Cd	10	4	23	9	1025	485
3 SG	300 NLS	7.7	Cd	10	2.5	152	4	525	83
5 SG	300 NLS	7.7	Cd	10	5	148	8	1400	400
6 SG	300 NLS	7.7	Cd	10	1.3	147	9	830	275
7 SG	300 NLS	7.7	Cd	10	0.73	147	9	435	112
10 SG	300 NLS	0.4	Zn	10	1.2	147	9	1500	130
11 SG	300 CPC	36	Zn1	10	2.1	146	10	1400	140
12 DAF	300 CPC	36	Zn1	-	67a	150	-	1865	135
13 SG	300 CPC	36	Zn1	10	2.1	146	10	1070	83
14 SG	88.5 NDBS	25	Zn2	10	3.6a	150	10	830	36
14-1DAF	88.5 NDBS	25	Zn2	-	62.2a	150	-	1850	15
15 DAF	300 NDBS	10	Cd	-	65.7a	150	-	1500	470
16 SG	300 NLS	3.6a	Zn	10	2.7a	150	10	1300	345
16-1DAF	300 NLS	8a	Zn	-	55a	150	-	3100	200

Notes:
   SG = sparged gas unit, DAF = Dissolved air unit
* metal type Zn1 = untreated waste from Bunker Hill
          Zn2 = treated waste from Bunker Hill
a = flow rate or concentration calculated from product volumes, run times,
and product or feed concentrations.

Table 2 - The results of experiments made on synthetic and Bunker Hill samples - Part II

July 8 - Sept. 3, 1987

Run #	Run Time (hr.)	Feed Conc. ppm	Raffinate Conc. ppm	Extract Conc. ppm	Foam res. time min.	Removal Efficiency %	Enrichment Ratio
1	5	7.7	2	29.4	5.18	73.8	14.7
2	6	7.7	1.5	25.2	1.8	88.8	16.8
3	4	7.7	1.0	53.6	11.9	89.4	53.6
5	6	7.7	1.3	31.5	11.6	87.4	24.2
6	14	7.7	0.6	31.5	11.5	94.6	52.5
7	12	7.7	0.4	35.7	11.5	95.8	89.2
10	33	0.4	0.1	-	11.5	77.0	-
11	12	36	36	34	11.3	8.6	0.94
12	.5	36	36	31	-	5.8	0.86
13	10	36	24	42	11.3	8.3	1.75
14	4	25	23	42	11.5	7.3	1.82
14-1	.5	104*	37*	108*	-	1.4	2.91
15	.5	10	6.7	16.8	-	44	2.51
16	10	3.6a	9	8	11.5	19.1	0.89
16-1	.5	3.6	0.26	36.4	-	90	140

Notes:
  a = calculated from feed or product concentrations and flows.
  * = contaminated samples
  The efficiencies for runs 14 - 16 were calculated from material balances

DISCUSSION OF RESULTS

Between 1 and 32% of the feed exited the sparged foam column as foam.
The sparged gas runs 1 - 7 resulted in data depicted in Figures 1 -6.
Figure 1 depicts the foam liquid flow rate as a function of feed rate. The
data points at feed rates of 4 and 3.6 ml/min correspond to column heights
of 23 and 66 cm respectively. All of the other data correspond to column
heights between 147 and 152 cm. The shorter column height showed a higher
foam liquid flow rate (wetter foam). Evidently for heights at or above 66
cm, the foam drainage did not increase significantly. Figure 2 is a plot
of foam liquid flow rate/feed rate as a function of feed rate. For column
heights above 66 cm this ratio varies between 0.15 and 0.25 and does not
show any trend with feed rate.

Figure 3 illustrates the effect of feed rate upon removal
efficiency. A slight decrease is seen with removal efficiency. Note
that the shorter column height data for a feed rate of 3.6
ml/min (column height of 66 cm) lies below those for the taller column
heights. This may illustrate the effect of column height (and consequently
foam drainage) upon removal efficiency. The trend is the same as that
predicted by the simple model based upon lower overflow of liquid. Figure
4 shows the dramatic effect of feed rate upon the enrichment ratio. Note
that the enrichment ratios for the shorter column spacings (23 and 66 cm)
are somewhat lower than that for the higher (147-152 cm). This is a
consequence of the drier foam for the taller column. Figures 5 and 6
represent data for the higher column spacing runs (147-152 cm). The
enrichment ratio was plotted as a function of the gas flow rate divided by
the product of the underflow concentration and the foam liquid flow rate.
According to the simple model the slope of the plot should equal (6/D)A and

the intercept should be unity. A linear regression on the data indicates a slope of 0.000367 and an intercept of 32 with an r squared of 0.89. Figure 6 is a plot of the adjusted removal efficiency – the removal efficiency less O/F all divided by the product (1 – O/F) as a function of the gas flow rate divided by the feed rate. The model equations indicate that the slope should correspond to (6/D) (A/C_f). The intercept is 0.83 and the slope is 0.009495 with an r squared of 0.88. Although the r squared values are good, the two slopes are not consistent with a feed concentration of 7.7 ppm.

The data of Figures 1 through 6 represent data from runs 1 through 7 which were performed with NLS surfactant and a constant cadmium concentration. Run 10 with a cadmium concentration of 0.4 ppm indicates a removal efficiency of 77% was achieved. Run 6 with a comparable feed rate showed a removal efficiency of 94%. This indicates that the surface concentration is lower due to the lower metal ion bulk phase concentration and consequently the separation is poorer at this low concentration. Runs 11, 12, and 13 were all run with surfactant CPC and untreated wastewater. Run 12 was run with the dissolved air flotation unit and the others with the sparged unit. Uniformly low removal efficiencies were obtained (5.9 to 8.4%). These results indicate that ionic repulsion between the metal ion (positively charged) and the surfactant (CPC also positively charged) or ionic attraction (NLS or NDBS negatively charged) govern the formation of the chelate.

For runs 14 through 16, problems with sample analysis occurred. The data presented in Table 2 were determined for samples analyzed somewhat after the tests were run, consequently comparison with samples run earlier was poor. The analytical results that were consistent are presented.

These results show low efficiencies were obtained for both units for the NDBS surfactant and the treated waste as well as the synthetic waste with NLS. Further work is required to better compare the units. Runs 14, 14-1, and 15 show the effect of surfactant concentration on fraction of liquid carried over as foam. For the 300 ppm concentration of SLBS about 24% of the liquid was carried over as foam (comparable to that for SLS and higher than the same concentration of CPC) compared to 1 to 4% for 88.5 ppm SLBS. It also appeared that there was less foam produced per unit volume of feed for the dissolved air unit. Comparing run 14 and 14-1 indicate an O/F ratio of 0.0415 and 0.00804 for the sparged and dissolved air units respectively and runs 16 and 16-1 indicate ratios of 0.209 and 0.0606, respectively. It may be that the recirculation in the dissolved air unit resulted in depletion of the surfactant in the recirculated liquid and a consequent reduction in foam flow.

CONCLUSIONS

The following conclusions can be drawn from the experimental results for the system of cadmium — sodium dodecyl sulfate and the sparged foam column:

(1.) The flow rate of foam liquid increased with feed rate.

(2.) Removal efficiency slightly decreased with feed rate.

(3.) Enrichment ratio decreased sharply with feed rate.

(4.) The simple model agrees qualitatively with the experimental data. Quantitative agreement is not good, however.

(5.) For the system studied, foam drainage is important up to a point, feed rate effects are important over the entire range studied.

Other conclusions based upon the experimental results in Tables 1 and 2 are:

(6.) Anionic surfactants or chelating agents are required for the formation and removal of chelated metals by foam separation.

(7.) In order to generate reasonable amounts of foam, a sufficient amount of surfactant (around 100 ppm) must be used.

(8.) Although the dissolved air unit appeared to generate less foam than the sparged unit, they had comparable low separation efficiencies for both the synthetic waste as well as the treated waste. These results are inconclusive as the analytical results are questionable.

RECOMMENDATIONS FOR FURTHER WORK

Further research will be conducted to allow comparison of the sparged and dissolved air flotation unit for removal of cadmium and zinc from Bunker Hill wastewaters. Ranges of parameters identified in the completed work will be used as guidelines for this additional work. Rather than acidifying the surfactant treated samples to dissolve the precipitate, the samples will be neutralized with sodium hydroxide solution and separated in the foam units. In this manner the precipitated solids also may be floated off. Atomic absorption analysis will be performed on acidified samples and unacidified filtered samples to determine the amount and type of chelated metal in the solids. Similar analyses will be performed on the foamate and underflow. Photographs of the foam layers will be taken for determination of bubble size and foam density. The experiments will be planned to check and modify the ideal foam model to allow for the effects of foam drainage.

In addition, the equilibrium between the free metal ion and its chelate

will be evaluated in a series of experiments in which the initial concentration of metal ion is maintained constant while various amounts of surfactant are added. Surface tension of the solution will be measured as a function of added surfactant concentrations. The Wilhelmy slide method will be used. In addition, separate measurements of unchelated metal will be made by quantitative analysis of the free metal and unchelated surfactant. Based upon these results, an equilibrium coefficient and surface activity will be determined for the metal surfactant complex. These parameters will be used to check and modify the ideal foam model.

A similar set of experiments will be conducted in which the chelated metal and free surfactant are adsorbed on powdered activated carbon. The activated carbon may be used to remove the chelated metal and surfactant from the foamate. A series of adsorption isotherm experiments will be conducted in which batches of chelated metal with surfactant are contacted with different amounts of powdered activated carbon. After mixing to equilibrium and filtration, the liquor will be analyzed for surfactant and metal concentration. A material balance will yield the amount adsorbed per amount of activated carbon and the resultant data will be used to prepare and adsorption isotherm. Regeneration and recovery of the chelated metal by leaching with organics or acids will also be investigated.

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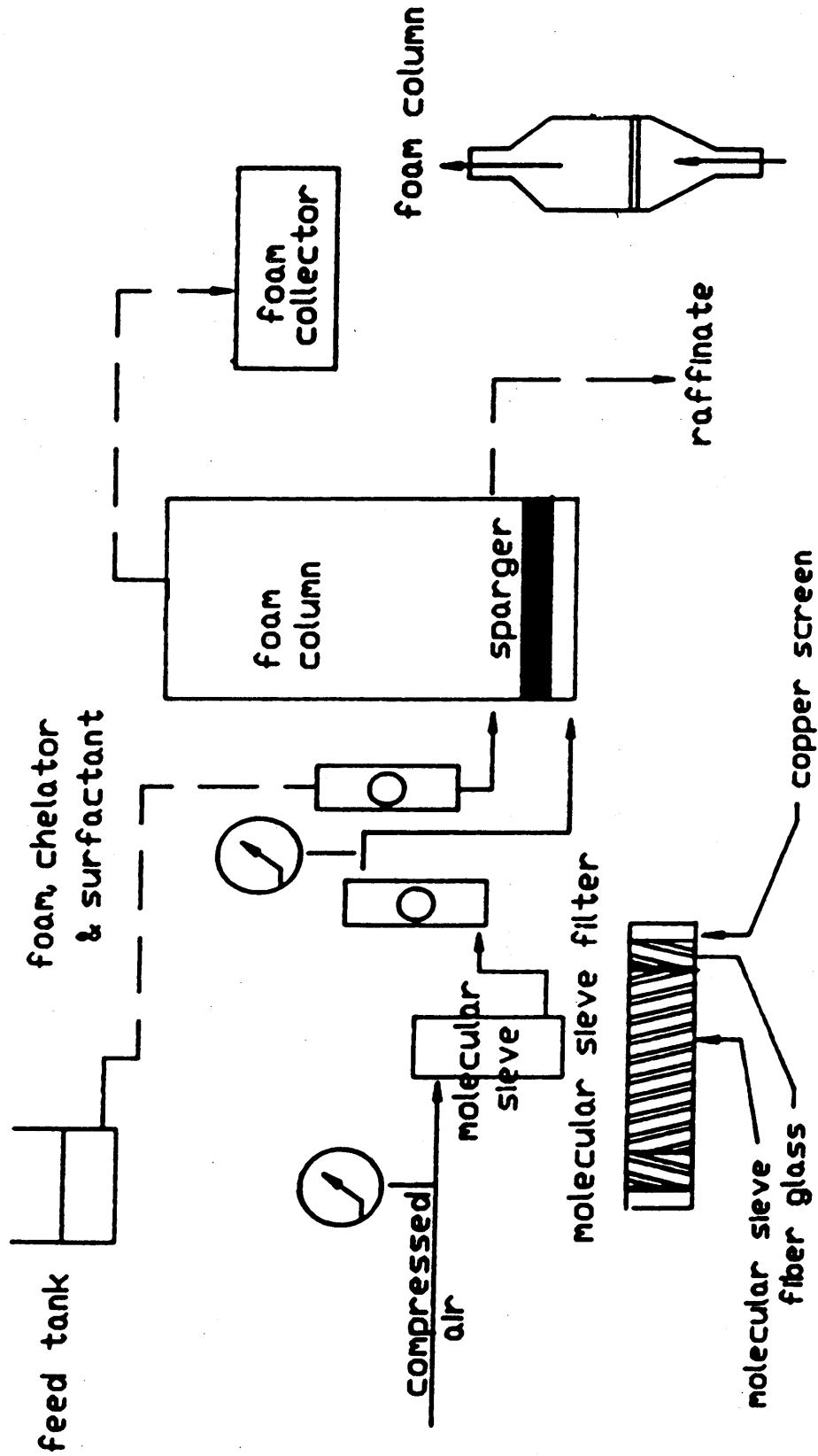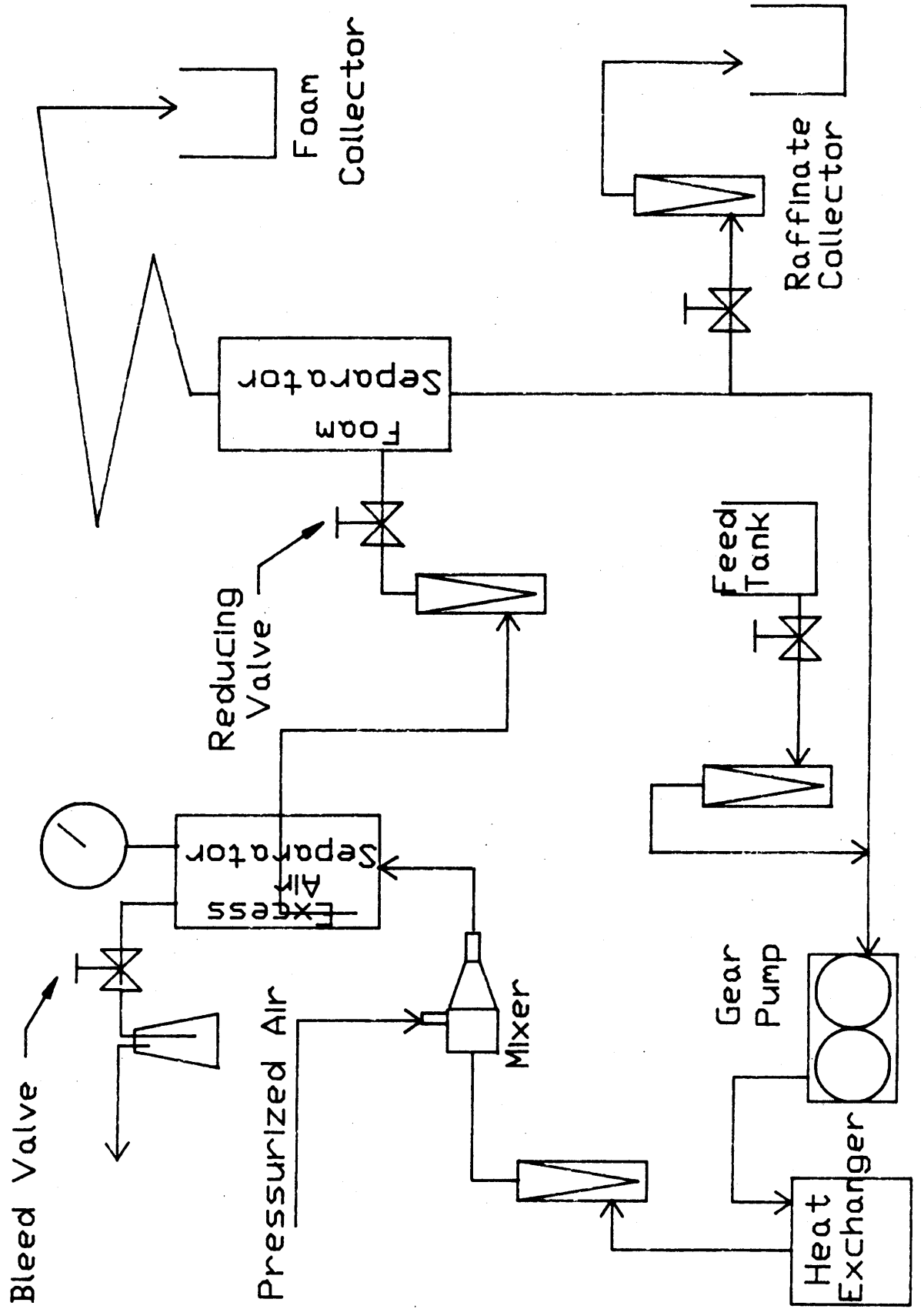
FIG. A   FLOW DIAGRAM

Figure B. Dissolved Air Flotation Unit

Foam Collector

Raffinate Collector

Foam Separator

Reducing Valve

Excess Air Separator

Bleed Valve

Pressurized Air

Mixer

Feed Tank

Gear Pump

Heat Exchanger

Figure 1 – Cadmium

Foam Flow Rate vs. Feed Rate

Foam Flow, ml/hr

Feed Rate, ml/min
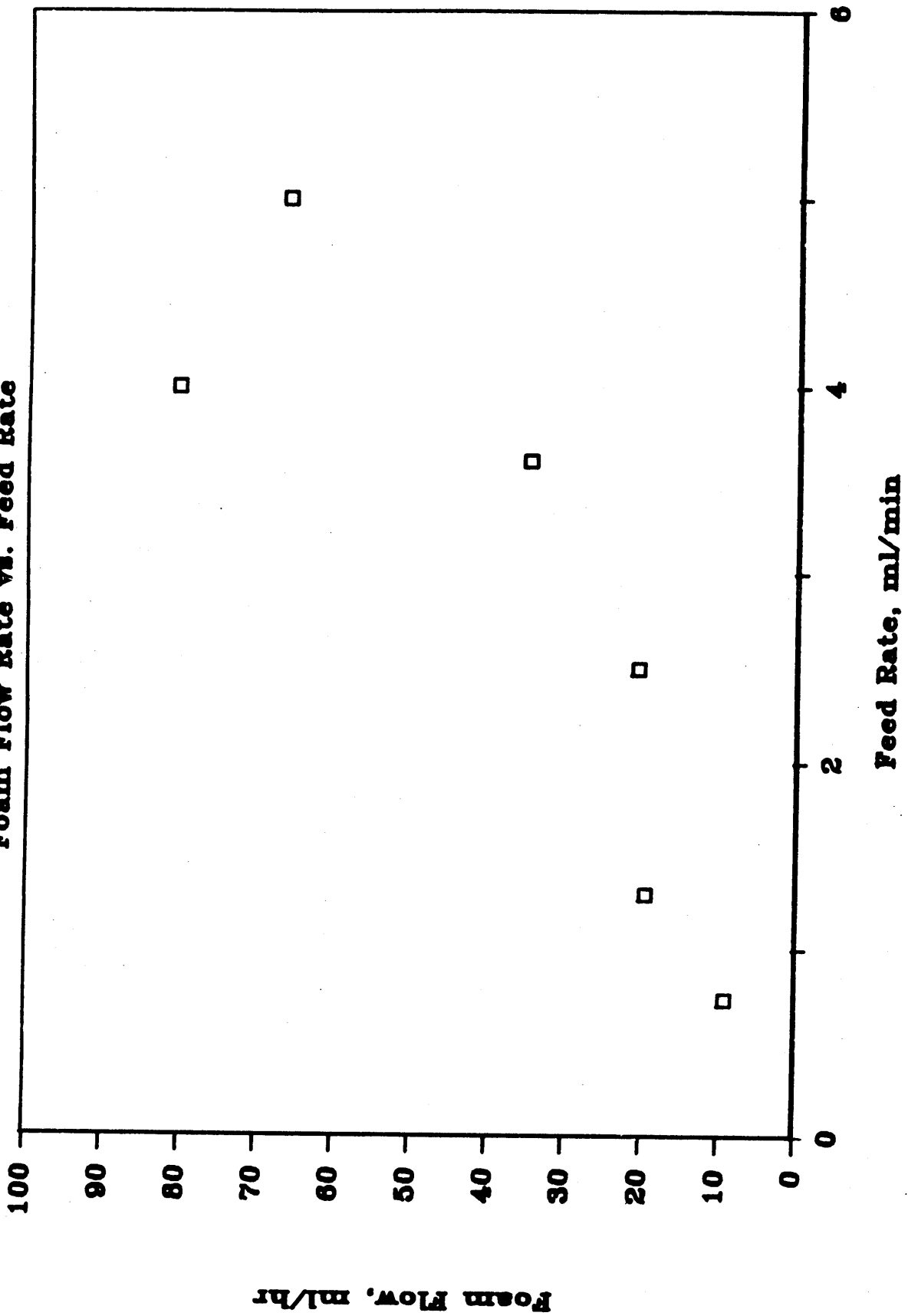
Figure 2 — Cadmium
Foam Liquid/Feed vs. Feed Rate
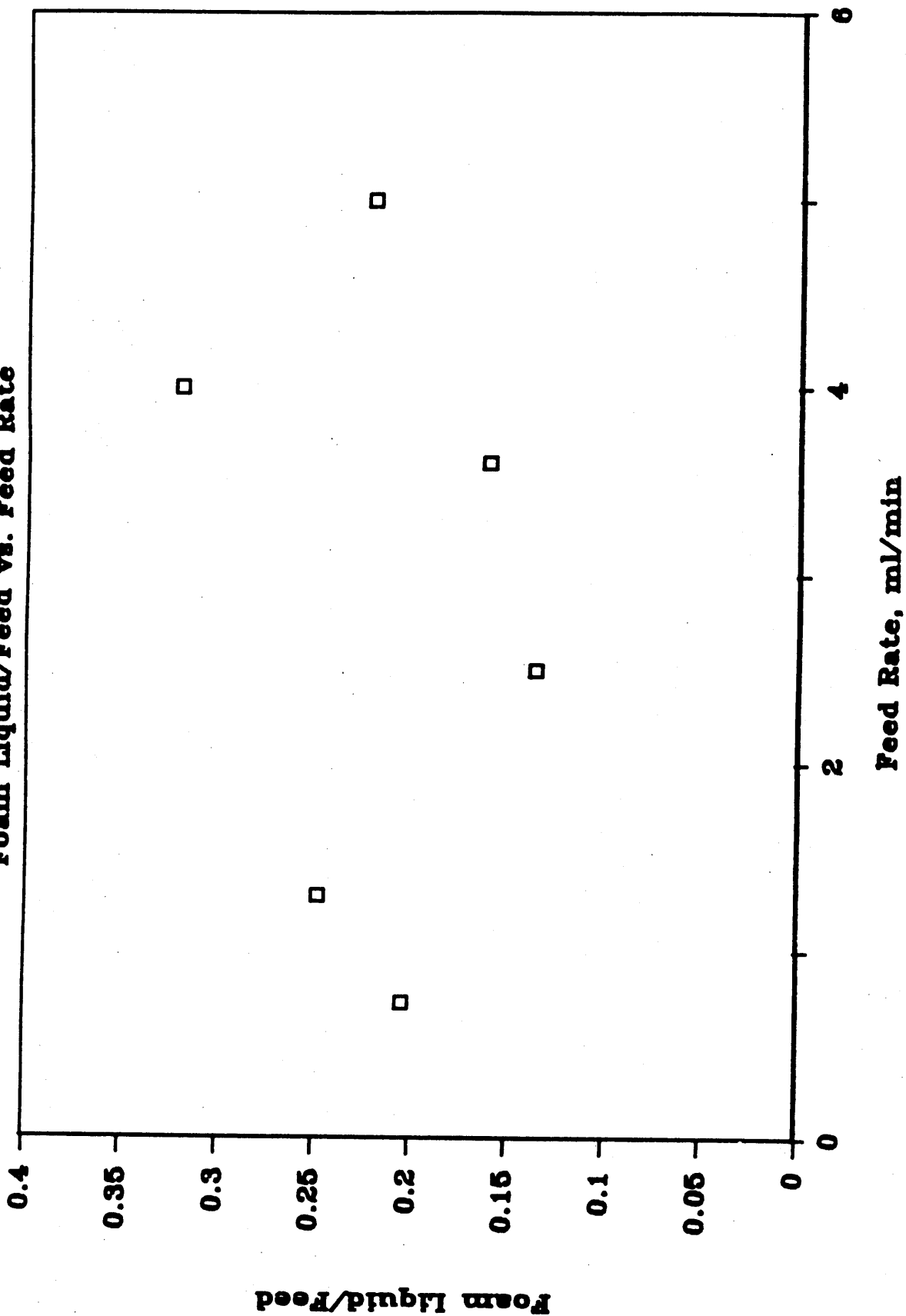
Figure 3 – Cadmium
Removal Efficiency vs Feed Rate

Feed Rate, ml/min

Removal Efficiency
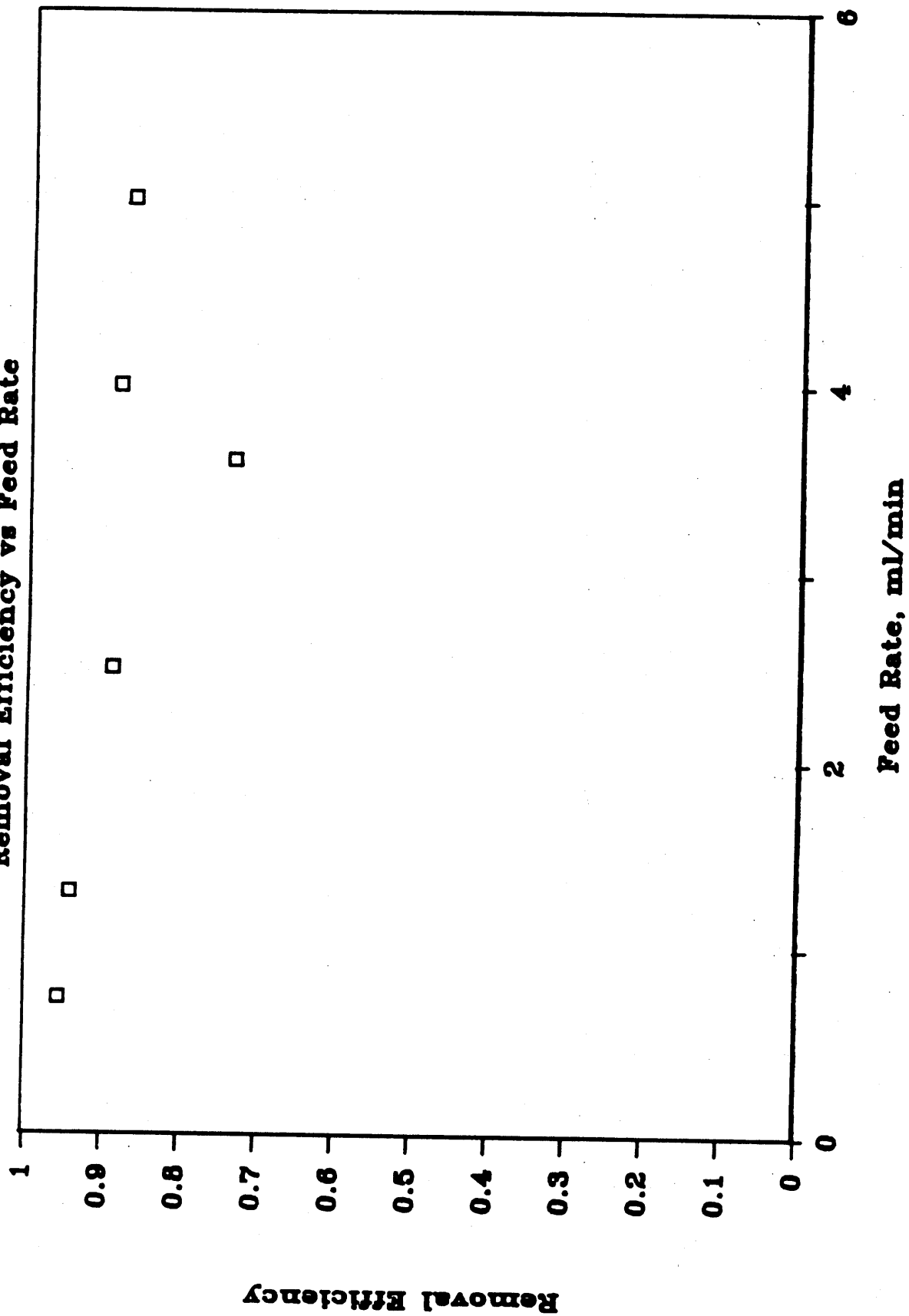
Figure 4 – Cadmium
Enrichment Ratio vs Feed Rate
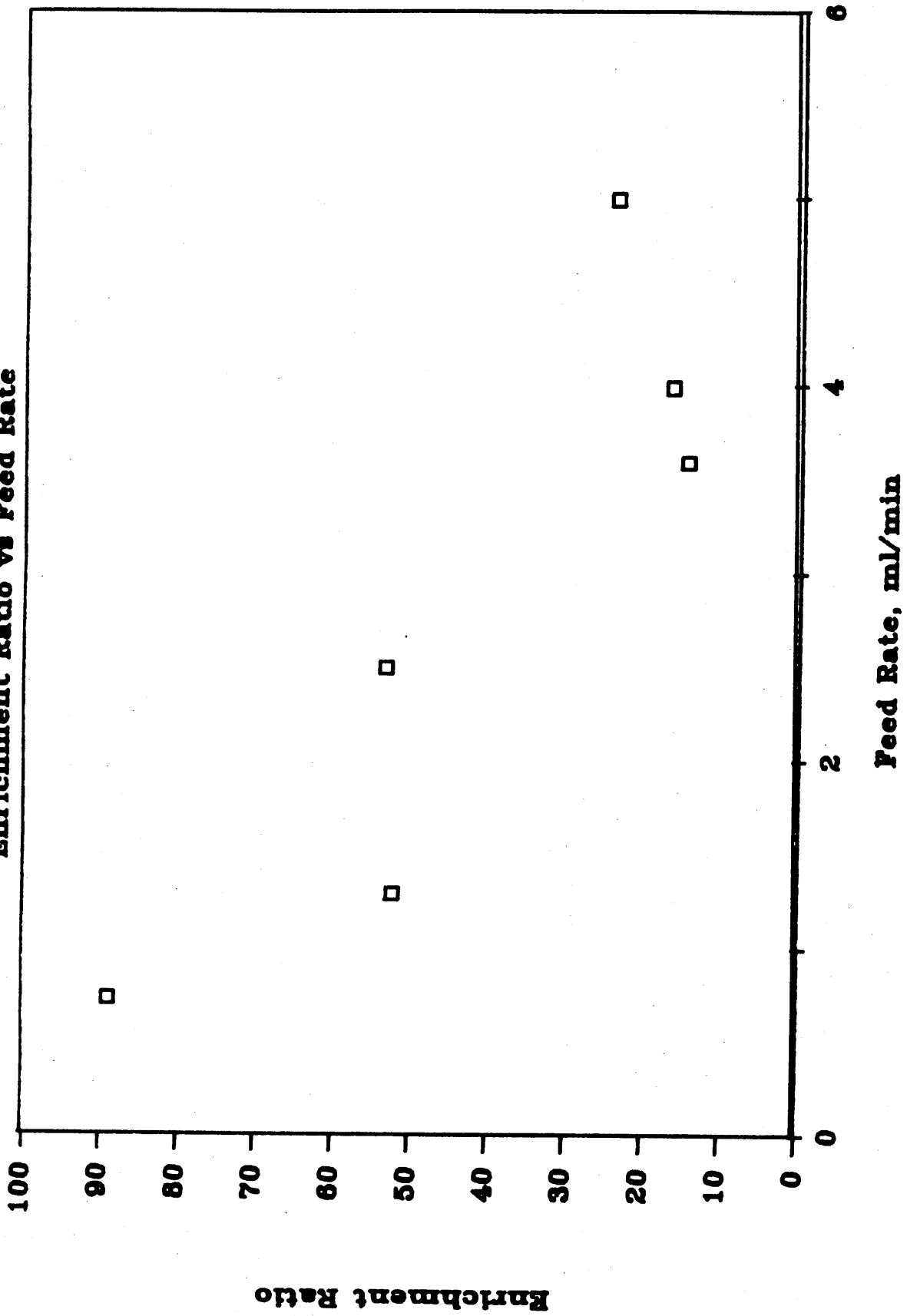
Figure 5 — Cadmium

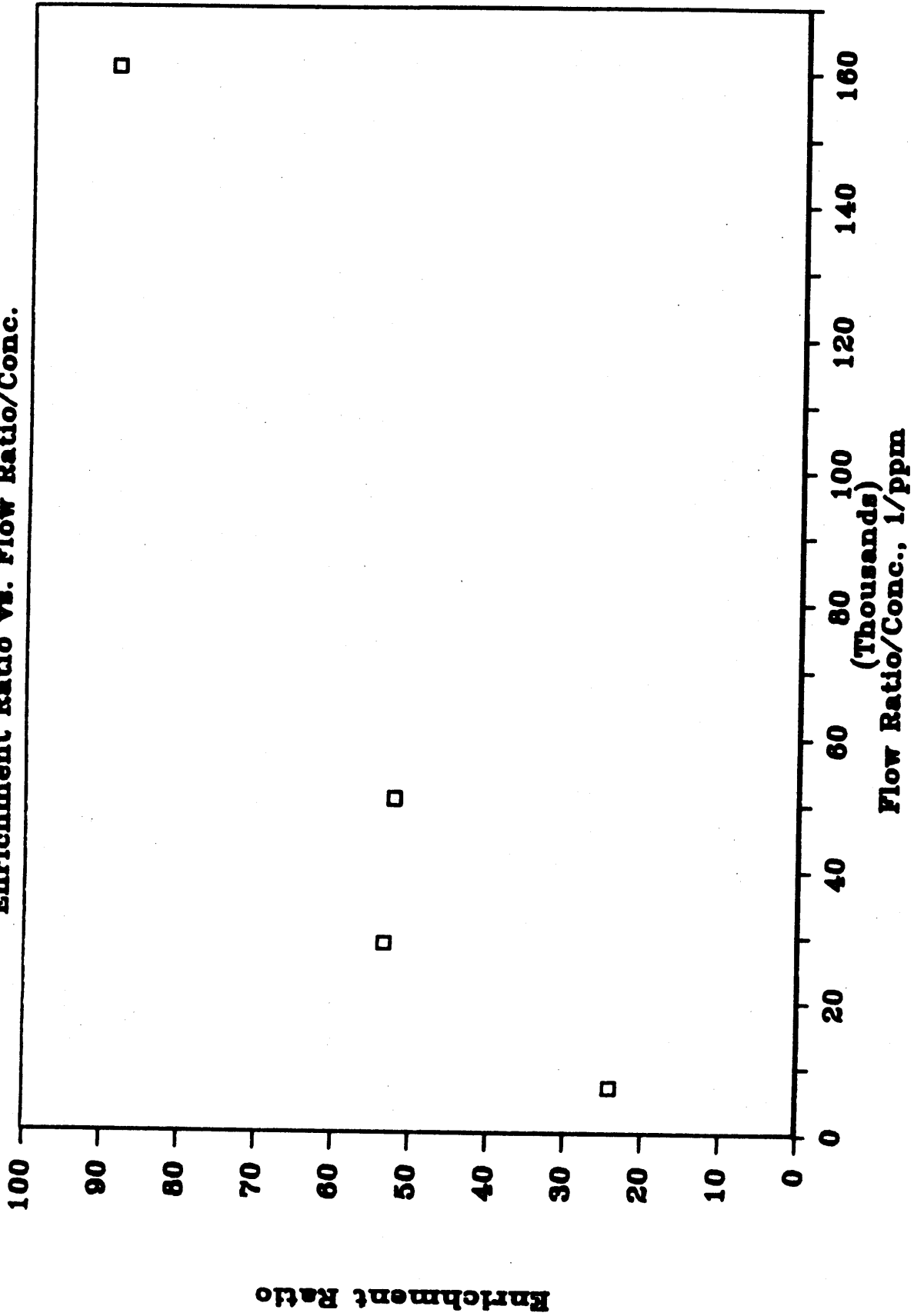Enrichment Ratio vs. Flow Ratio/Conc.

Flow Ratio/Conc., 1/ppm
(Thousands)

Enrichment Ratio

Figure 6 – Cadmium

Adj. Separation Eff. vs Flow Ratio