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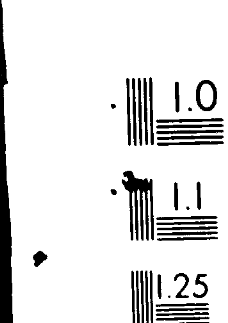

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TREATMENT OF PLATING WASTEWATERS BY FERROUS REDUCTION, SULFIDE PRECIPITATION, COAGULATION & UPFLOW FILTRATION

civil
engineering
research

Final Report To The
Mini-Grant Program
Air Force Office of Scientific Research
Bolling Air Force Base, DC

By

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Grant No. AFOSR-81-0044 NCW

May, 1981

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER AFOSR-TR-81-0559	2. GOVT ACCESSION NO. AD-A102 066
	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Treatment of Plating Wastewaters by Ferrous Reduction, Sulfide Precipitation, Coagulation and Upflow Filtration.	5. TYPE OF REPORT & PERIOD COVERED Final Report
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Thomas E. Higgins	8. CONTRACT OR GRANT NUMBER(s) AFOSR-81-0044
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Civil Engineering Arizona State University Tempe, AZ 85287	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 2303/D9 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research AFOSR/NC Bolling AFB, DC 20332	12. REPORT DATE May [illegible]981
	13. NUMBER OF PAGES 74
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) UNCLASSIFIED
	15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

HEAVY METALS, WASTEWATER TREATMENT, CHROMIUM REDUCTION, ALKALINE, FERROUS SULFATE, SULFIDE

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Current practice in treatment of mixed metal wastewaters containing hexavalent chromium consists of acidic (pH~3) chromium reduction followed by alkaline, metal-hydroxide precipitation; a two-stage process. A single-stage process could reduce capital and operation costs. Synthetic chromium, cadmium, and nickel wastewaters were successfully treated by ferrous sulfate and sodium sulfide in a single cell reactor at alkaline pH (7-10), thus clarifying conflicting reports in the literature. Batch tests were performed to study this process. Solids were removed by membrane filtration. Metal

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residuals were analyzed by atomic absorption spectrophotometry. Chromium was rapidly and stoichiometrically reduced by ferrous sulfate. Sodium sulfide by itself negligibly reduced chromium, and was no better than hydroxide in precipitating cadmium and nickel. However, in combination with ferrous sulfate, sulfide improved chromium reduction and metal removal. Alkalinity, EDTA and cyanide interfered with chromium reduction and metal removal; calcium hardness counteracted these interferences.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

Recent pre-treatment standards promulgated by the Environmental Protection Agency (EPA) are aimed at the reduction of significant discharges of heavy metals into domestic sewage systems. Small electroplating operations have limited facilities for treatment. Current Air Force practice in small electroplating shops is to discharge rinsewaters directly into sanitary sewers without pre-treatment. A treatment system is needed which has application at small installations to meet the new pre-treatment standards.

TABLE 1

Comparison of Pre-Treatment Effluent Guidelines, Water Quality Criteria, and NPDES Discharge Limits for Selected Metals (References 1, 2, and 3).

Pollutant	Cd	Cr(VI)	Cr(T)	Cu	Ni	Pb
EPA Pre-treatment Guidelines						
1 Day Max. (a)	1.2	-	-	-	-	0.6
4 Day Ave. (a)	0.7	-	-	-	-	0.4
1 Day Max. (b)	1.2	-	7.0	4.5	4.1	0.6
4 Day Ave. (b)	0.7	-	4.0	2.7	2.7	0.4
EPA Drinking Water Quality Criteria	0.01	0.05	0.05	1.0	-	0.05
Tinker AFB NPDES Permit (c)	0.019	0.05	0.11	0.01	0.22	0.06
Electroplating Waste (d)						
Max.	0.23	55	156	0.42	170	0.25
9 Day Ave.	0.14	28	43	0.09	37	0.06

NOTES:
a. Flows less than 10,000 gallons per day.
b. Flows greater than 10,000 gallons per day.
c. Based on 0.7 MGD flow from IWTP and 0.4 MGD stream flow.
d. Based on daily samples taken Nov. 10-18, 1977.
e. Concentrations in mg/l.

Minimum pre-treatment standards for selected metals are shown in Table 1. National Pollution Discharge Elimination System (NPDES) permit requirements can result in more stringent effluent standards (example shown). Principal contaminants in the wastewater (principally rinsewater) are chromium and nickel which, along with cadmium, are the principal metals used for electroplating by the Air Force.

This project is a continuation of a study initiated by the principal investigator as an AFOSR Summer Faculty Research Associate at the HQ AFESC, Tyndall AFB, FL. The initial objective of that study was to investigate the feasibility of sulfide precipitation, coagulation by iron salts and upflow filtration for removal of heavy metals from electroplating rinse waters at small Air Force facilities.

Literature indicated that chromium reduction by ferrous iron was essentially non-existent at a pH above three. Nevertheless, there were reports by Air Force Treatment personnel of successful reduction of hexavalent chromium by ferrous addition at alkaline pH.

The present study was undertaken to determine if reduction of hexavalent chromium by ferrous iron is reasonably rapid at alkaline pH. The coagulant properties of the resulting ferric iron were noted. The effectiveness of sodium sulfide as a reducing agent and as a precipitant for mixed metals was investigated by itself and in combination with ferrous sulfate. The effects of competing ions, normally present in plating wastewaters (hardness, alkalinity, EDTA, cyanide), on chromium reduction and precipitation were also investigated.

LITERATURE

Conventional treatment of mixed metal wastewaters containing hexavalent chromium is a multi-stage system (24,34a). Acidic (pH~3) chromium reduction, utilizing either a ferrous salt or a reduced sulfur compound (SO_2, H_2SO_3 etc.) is followed by hydroxide precipitation at alkaline pH (8-10). Solids removal is normally accomplished by sedimentation with improved removal efficiencies achieved by filtration.

The use of acidic and alkaline processes complicates the system and can result in excess chemical consumption. Alkaline reduction of chromium would result in combining the reduction and precipitation operations, and thus reduce capital and operational expenses.

Problems with hydroxide precipitation result from the relatively high solubility of metal hydroxides. The formation of soluble metal hydroxide complexes at high pH's prevents optimum removal of a mixed metal solution at a common pH. Figure 1 shows that minimum hydroxide solubilities of cadmium, chromium and nickel are not achieved at a common pH, and that safe drinking water standards for these metals cannot be achieved by hydroxide precipitation.

It has been reported (4,25) that, since metal sulfide solubilities are considerably less than corresponding hydroxides, improved removal efficiencies can be achieved by sulfide precipitation. Figure 2 shows the solubility of chromium (III), nickel (II) and cadmium (II) in the presence of 10^{-6} M total sulfide. A total sulfide concentration of 10^{-6} M was has been assumed that solubility of this metal is Minimum solubilities for these three metals of int pH between 8 and 9. Increasing the pH beyond solubility due to formation of soluble metal hyd strong reducing agent and could participate in chrom

The distribution of sulfide species with pH use Figure 2 is shown as Figure 3. Below pH 7 virtuall present as H_2S, a toxic gas. An alkaline pH f process helps to minimize the evolution of this toxi

Competing systems for sulfide treatment ar insoluble sulfide precipitation (SSP and ISP res consists of adding a soluble sulfide compound (Na_2S reactor at a controlled pH. Problems associated wi sulfide (H_2S) odor problems and removal of the fi metal sulfide precipitates. Solutions of the odor p of reactors, close control of sulfide dose with a and oxidation of residual sulfide with peroxide commonly used to flocculate the colloidal precipitat

ISP (Sulfex Process) consists of the addition FeS to the reactor (29,30,31). Since ferrous soluble, it is a source of sulfide for precipitation flow steam and yet controls sulfide solubility sulfide problems associated with SSP overdosing.

A third system of sulfide precipitation for the

Flocculation and solids removal are accomplished directly in a filter.

It is fairly well established that reduction of hexavalent chr reduced sulfur compounds is reasonably rapid at pH below 3 and t rate of this reaction slows logarithmically with increased pH. There is some disagreement, however, concerning the effects of pH rates of chromium reduction by ferrous iron. Using reactio determined by Espenson (15,16), Thomas (34a) estimated the reducti typical chromium concentration to be 99% completed in approxim seconds at pH 2, and 90 minutes at pH 3, with the rate decreasin orders of magnitude for each additional unit increase in pH. authors (9,20,24,36) have stated that a pH of less than 3 is requi reasonably rapid reduction of chromium by ferrous sulfide. Germaine (18) claimed that ferrous sulfate was effective regardless of pH. are reports of effective chromium reduction without pH control. (5)

Precipitated ferrous sulfide (ISP) is reported to effective rapidly reduce hexavalent chromium at alkaline pH (28). Addition of sulfide was ineffective for chromium reduction at pH above 7, (35) a when ferrous sulfate was added in combination with sodium s reduction was effected (34a). It was postulated (but not demons that ferrous iron is the effective reducing agent in the sulfex (35) and that ferrous iron acts as a catlyst for chromium reduct sulfide at alkaline pH (34a).

Following precipitation, removal of the solid metal hydroxi sulfides is normally accomplished by flocculation with polyme sedimentation. Further addition of polymer and filtration is n required to insure consistently high metal removal efficiencies.

The main disadvantage of conventional downflow sand filters is that the finest material is encountered first, and the greatest portion of the solids removal occurs in the top layer of the bed. As a result, high head losses develop in a short period of time, and the bottom portion of the bed is poorly utilized. The coarse to fine gradation in an upflow filter would indicate that good removals can be obtained without the head loss problems of conventional sand filters. Diaper and Ives (13) conducted a study on upflow filtration and concluded that: for a given headloss, upflow filtration allowed longer runs due to a more even distribution of solids; and upflow filtration has some disadvantages which include (a) a tendency for the bed to expand as pressure differences overcome the weight of the media, (b) difficulty in backwashing layers of material which tend to accumulate, (c) the possibility of deposits in the underdrain which may be difficult to remove, and (d) size graded media are best used with high flows and high concentration of solids.

Hamaam and McKinney (18a) reported similar advantages of upflow filtration. They also describe additional advantages: (a) a reduction in the size of the physical plant since flocculation and sedimentation facilities are not required; and (b) a reduction in the amount of chemical coagulant is required because a large, easy to settle floc is not needed. They found that effectiveness improved with bed depth.

Upflow filters have been found to perform as well or better than downflow filters for removal of turbidity (18a). Average reductions in bacteria have also been found to be approximately equivalent to those in a conventional plant (19).

If there is a more uniform distribution of solids with upflow filtration than with downflow, upflow should have less tendency to cake or mudball and be easier to clean (17). However, the studies by Diaper and Ives (14,19) and Hamaam and McKinney (18) have found difficulties with backwash. Bands of deposit tend to form within the bed (14,19). During backwash the bands of deposit are pushed into finer sand where the clogged media formed an impervious barrier. The barriers caused an arching effect which lifted the bed in layers (6,11). Compressed air was found necessary to break up the bands of deposit and adequately clean the entire bed (6,7,11).

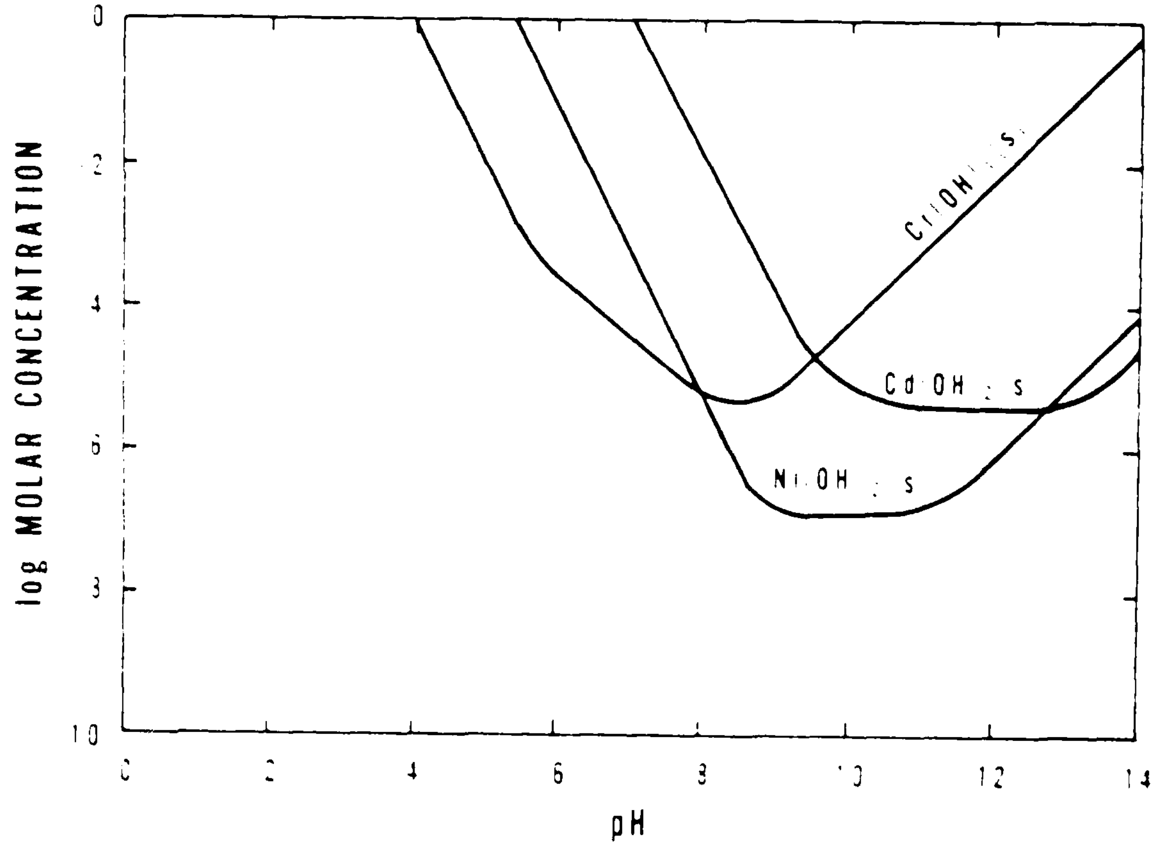


Figure 1. Solubilities of Cd, Cr and Ni as a function of pH.

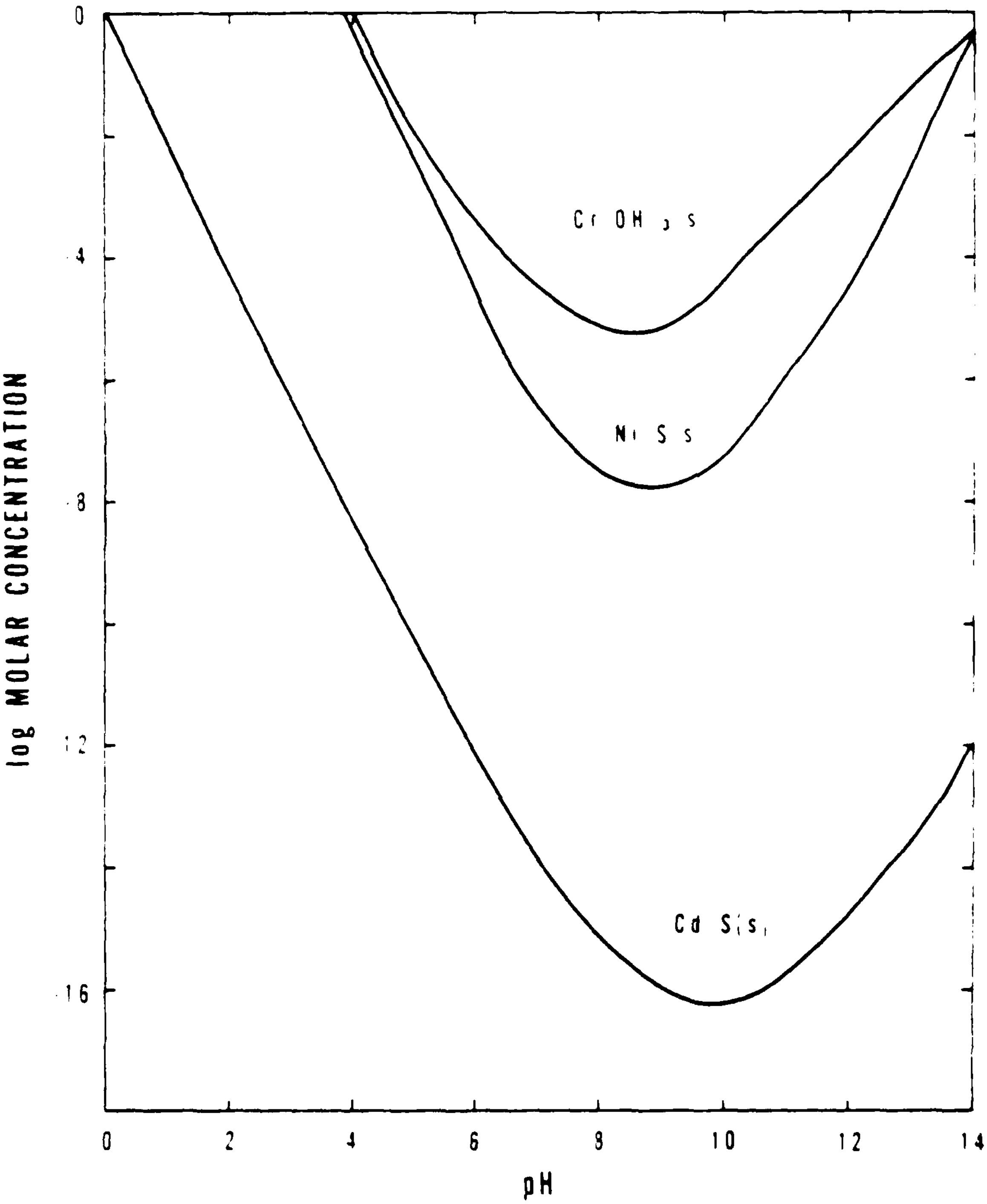


Figure 2. Solubilities of Cd, Cr and Ni with 10^{-6}M total sulfides.

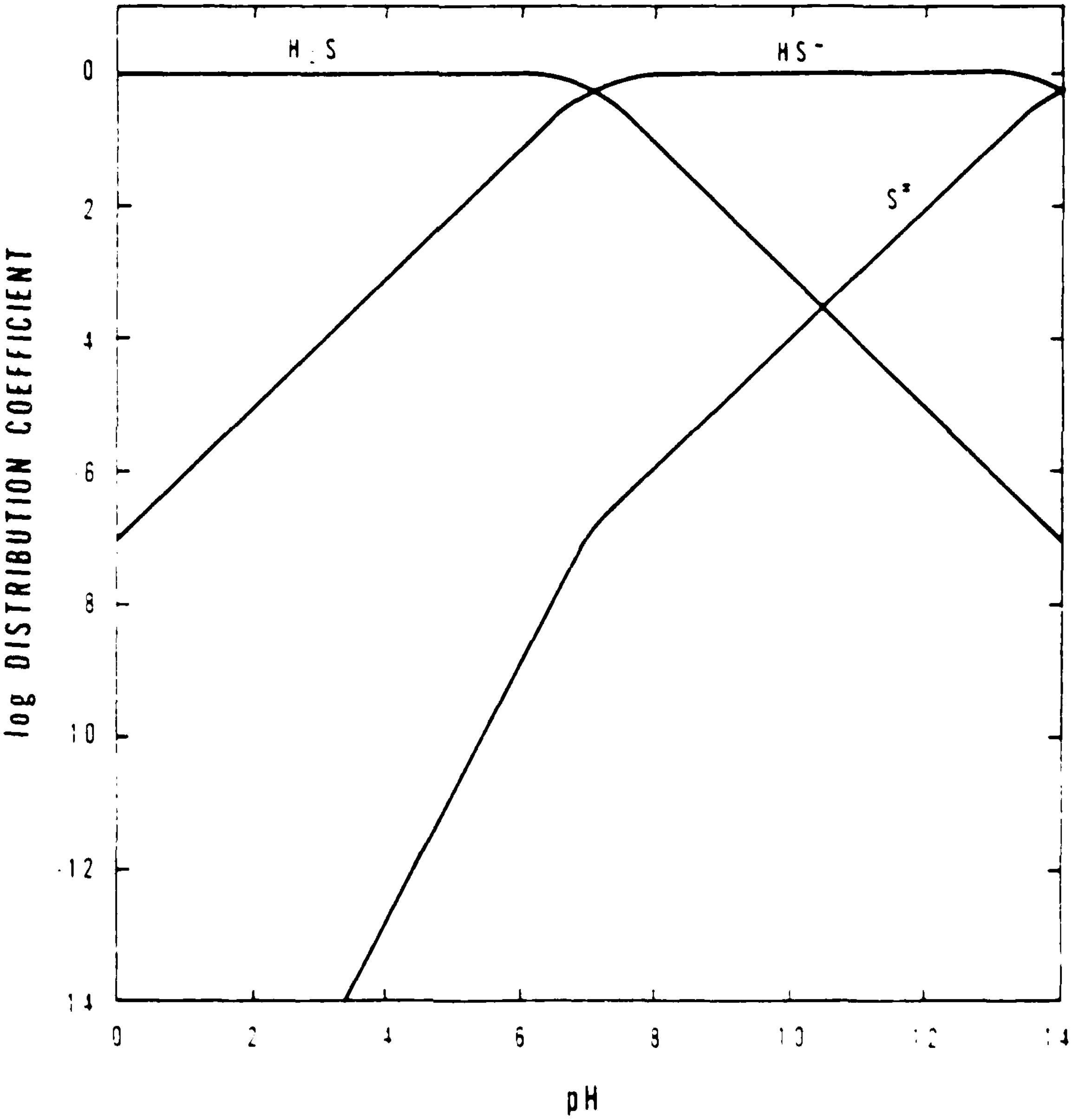


Figure 3. Distribution of sulfide species with pH.

RESEARCH OBJECTIVES & RATIONALE

Three metals, chromium, cadmium and nickel, were selected for experimentation due to their use in Air Force electroplating shops. Batch studies were performed to test process steps and optimize chemical dosages. Tests were designed to determine whether sulfide or ferrous iron or a combination of the two is responsible for the reported reduction of chromium (VI) at alkaline pH. A pH range of 7 to 10 was selected to minimize hydrogen sulfide evolution and heavy metals solubility.

It is reported that freshly prepared ferrous sulfide precipitate was more effective than aged precipitate in metal removal. Tests were performed to see if improvements in chemical usage efficiencies could be accomplished by separate addition of ferrous and sulfide to the precipitation reactors and to determine if combinations of iron to sulfide other than one to one were effective in metal removal. It is postulated that addition of soluble iron to the reactor would eliminate the need for additional coagulant chemicals.

The processes selected for testing in continuous flow experiments were chromium reduction, pH adjustment, metal precipitation and coagulation by the addition of ferrous sulfate, sodium sulfide and sodium hydroxide in one reactor followed by solids removal in an upflow filter. These processes were selected to provide maximum process control in a compact package. Separate addition of ferrous and sulfide in optimal combinations provides highly reactive chemicals for precipitation and coagulation.

Filtration is normally used in the sulfide precipitation process. Between sedimentation and filtration units there is usually a pumping unit employed to provide the required filtration head. Pumping creates turbulence and tends to break up flocculated solids. To keep solids flocculated, additional coagulants are used after pumping to facilitate good filtration. Direct filtration would preclude the need for double use of coagulants.

Separate control of sulfide and ferrous iron allows use of the ferrous iron for coagulation. Excess sulfide not precipitated by heavy metals can be removed by iron precipitation. Iron trapped in the filter would be available if needed during fluctuations in influent metal concentrations.

Upflow filtration was selected because of previous experience in metal sulfide precipitation which showed longer filter runs due to complete use of the filter (17).

METHODS AND MATERIALS

Waste Composition Chromium (VI), cadmium and nickel were selected for testing due to their common use in Air Force electroplating shops. Synthetic wastewaters were prepared using reagent grade salts and distilled or tap water. Metals were added as potassium dichromate ($K_2Cr_2O_7$), cadmium chloride ($CdCl_2$) and nickel chloride ($NiCl_2$). The effects of competing ions was determined by the addition of hardness as calcium chloride ($CaCl_2$), alkalinity as sodium bicarbonate ($NaHCO_3$), and complexing agents as disodium EDTA (Na_2H_2EDTA) or sodium cyanide (NaCN).

Batch Treatment All batch treatment experiments were conducted in borosilicate glass beakers stirred at a moderate speed by a teflon coated stirring bar on a magnetic stirrer. The pH was monitored with a glass electrode and double junction reference electrode with a pH meter. The pH was adjusted manually by the addition of dilute sodium hydroxide (NaOH) or nitric acid (HNO_3) as necessary. Stock solutions of ferrous sulfate ($FeSO_4$), acidified with 5 drops (0.25 ml) of nitric acid (HNO_3) per liter to prevent oxidation, and sodium sulfide (Na_2S) were prepared fresh daily.

Batch synthetic waste was prepared from stock solutions. An aliquot was transferred to a stirred beaker, and pH adjusted to the selected set point. Doses of ferrous sulfate and sodium sulfide were added by pipet, as the pH was manually maintained at the set point. Doses were based on stoichiometric requirements for reduction of chromium (VI) to chromium (III), assuming oxidation of ferrous (II) iron to ferric (III) and sulfide (-II) to elemental sulfur (0).

Chemical Analyses An atomic absorption spectrophotometer was used for metals analysis. Chromium analysis was performed by direct aspiration into a reducing nitrous oxide-acetylene flame; cadmium into an oxidizing air-acetylene flame; nickel into an oxidizing air-acetylene flame with background correction for non-atomic absorption. Other chemical analyses were performed in accordance with "Standard Methods" (8).

Continuous Flow Apparatus A schematic flow diagram of the treatment apparatus is shown in Figure 4. A 13-foot length of clear plastic tubing is used for the filter column. The column contains a 5-foot layer of sand supported by a 6-inch layer of gravel.

Manometer ports are located at the top and bottom of the filter bed and at one-foot intervals. Manometers are water-filled to allow a direct reading of the head loss. Due to height limitations mercury manometers are used for the bottom head readings.

Waste streams are prepared by diluting stock metal solutions prepared from metal salts with distilled water in a waste tank. Waste and treatment chemicals are fed to a mixer using variable flow pumps. Ferrous sulfate and sodium sulfide feed solutions are made fresh daily. Ferrous sulfate solutions are preserved with nitric acid (0.25 ml/1).

Tap water is used for backwashing through the same inlet used for the influent, compressed air injection is provided to aid in breaking up filter sand balls. The backwash effluent line is located five feet above the normal filter bed, allowing for sand expansion during backwash.

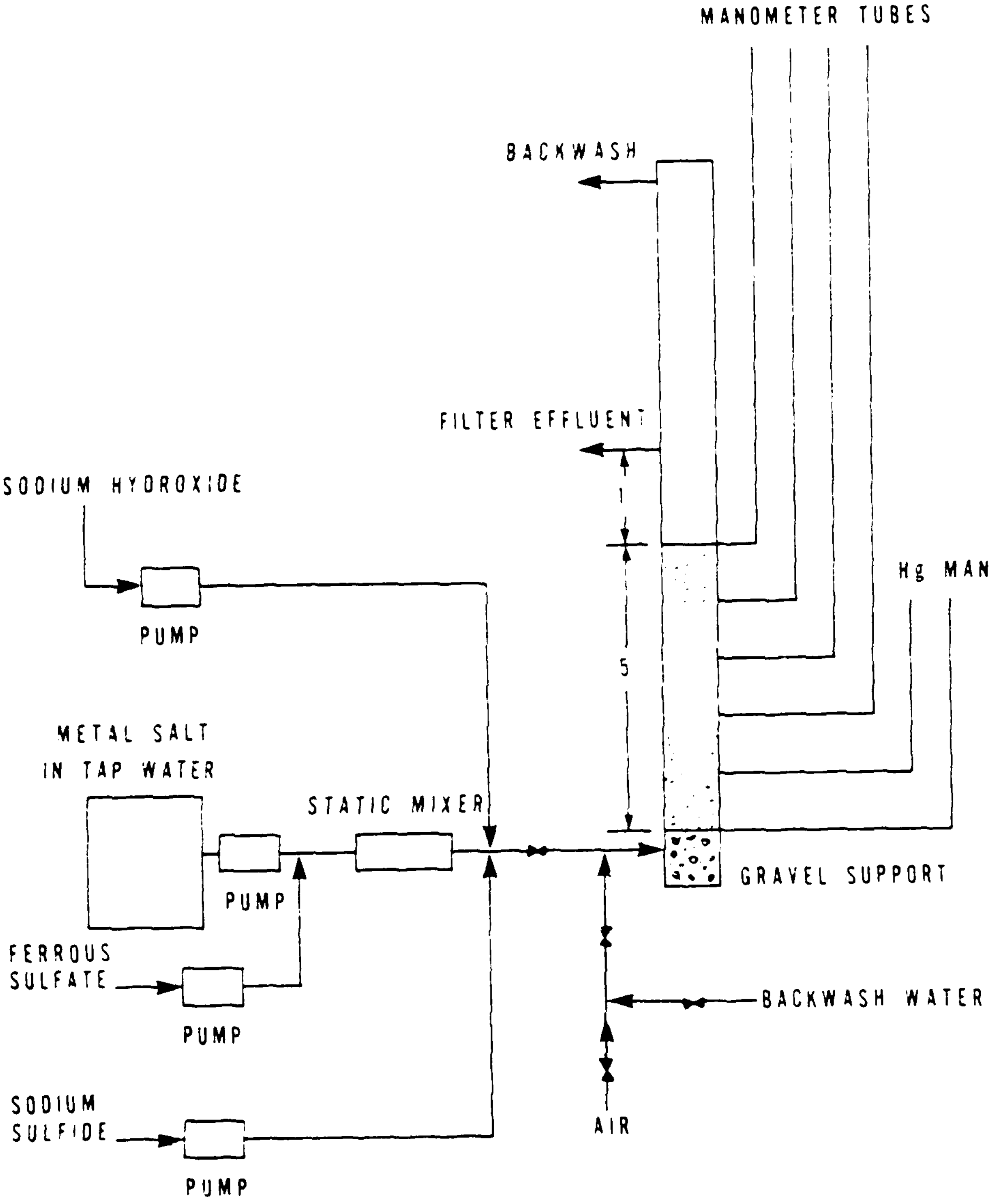


Figure 4. Upflow filtration apparatus.

RESULTS

Chromium Reduction and Removal Studies were designed to determine if chromium (VI) reduction was accomplished by sulfide, ferrous iron or a combination of the two at alkaline pH. Synthetic wastewater with a hexavalent chromium concentration of 10 mg/l (0.58 meq/l), was prepared in Tyndall Air Force Base tap water (Table 2).

TABLE 2 Typical Analysis of Tap Water, Tyndall Air Force Base, Florida.

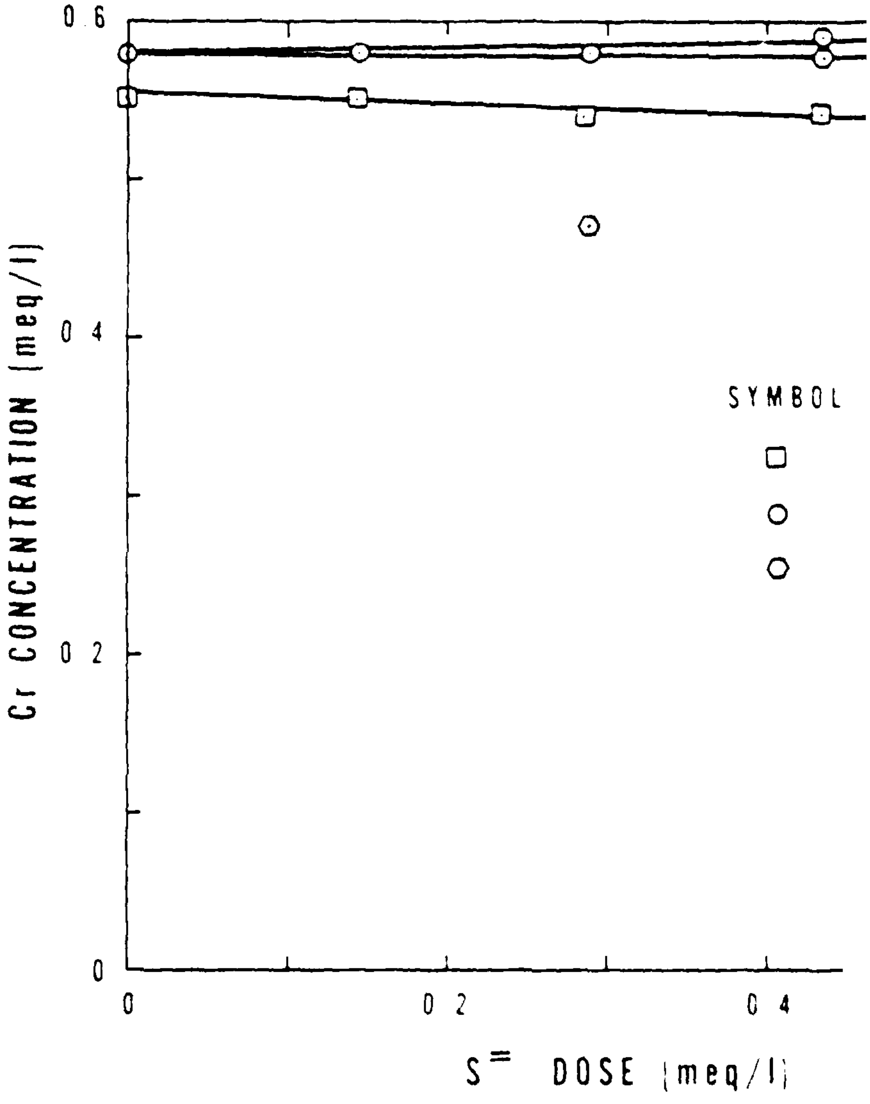
Constituent	Concentration
pH	8.1
Alkalinity (mg/l as $CaCO_3$)	34
Total Hardness (mg/l as $CaCO_3$)	78
Calcium Hardness (mg/l as $CaCO_3$)	70
Cl (mg/l)	16
TDS (mg/l)	134

Negligible chromium removal was effected by sulfide alone at pH 7 through 10 (Figure 5). This supported findings by Walden (35) that sulfide alone is ineffective for chromium reduction at alkaline pH. Reduction and removal of chromium was accomplished with a stoichiometric dose of ferrous iron, compared to a 3:1 dosage for the precipitated ferrous sulfide (sulfex) process (4). This removal by ferrous iron occured independently of pH between 7 and 10. Addition of sodium sulfide enhanced reduction and removal of chromium by ferrous iron at pH 7 (Figure 6). To a degree, sulfide replaced ferrous iron on a stoichiometric basis. A minimum concentration of ferrous iron was needed for sulfide to be effective. This seems to substantiate Walden's (35) conjecture that ferrous iron acts as a catalyst for sulfide reduction of chromium at alkaline pH. At pH 8.5

(Figure 7) the enhancement of reduction by sulfide diminished and disappeared at pH 10 (Figure 8).

Another way of showing the combined effects of ferrous and sulfide doses on equivalent chromium (VI) removal efficiencies is presented as Figures 9, 10, and 11. At pH 7 ferrous iron addition was sufficient to reduce and precipitate the chromium (VI), on a stoichiometric basis. To a degree, sulfide replaced iron on a stoichiometric basis. A minimum concentration of ferrous iron is needed for sulfide to be effective.

Increasing the pH of reaction to 8.5 (Figure 10) has negligible impact on the effectiveness of ferrous iron in removal of chromium (VI). Increased pH, however, reduced the effectiveness of sulfide addition, even in combination with ferrous iron (Figure 11).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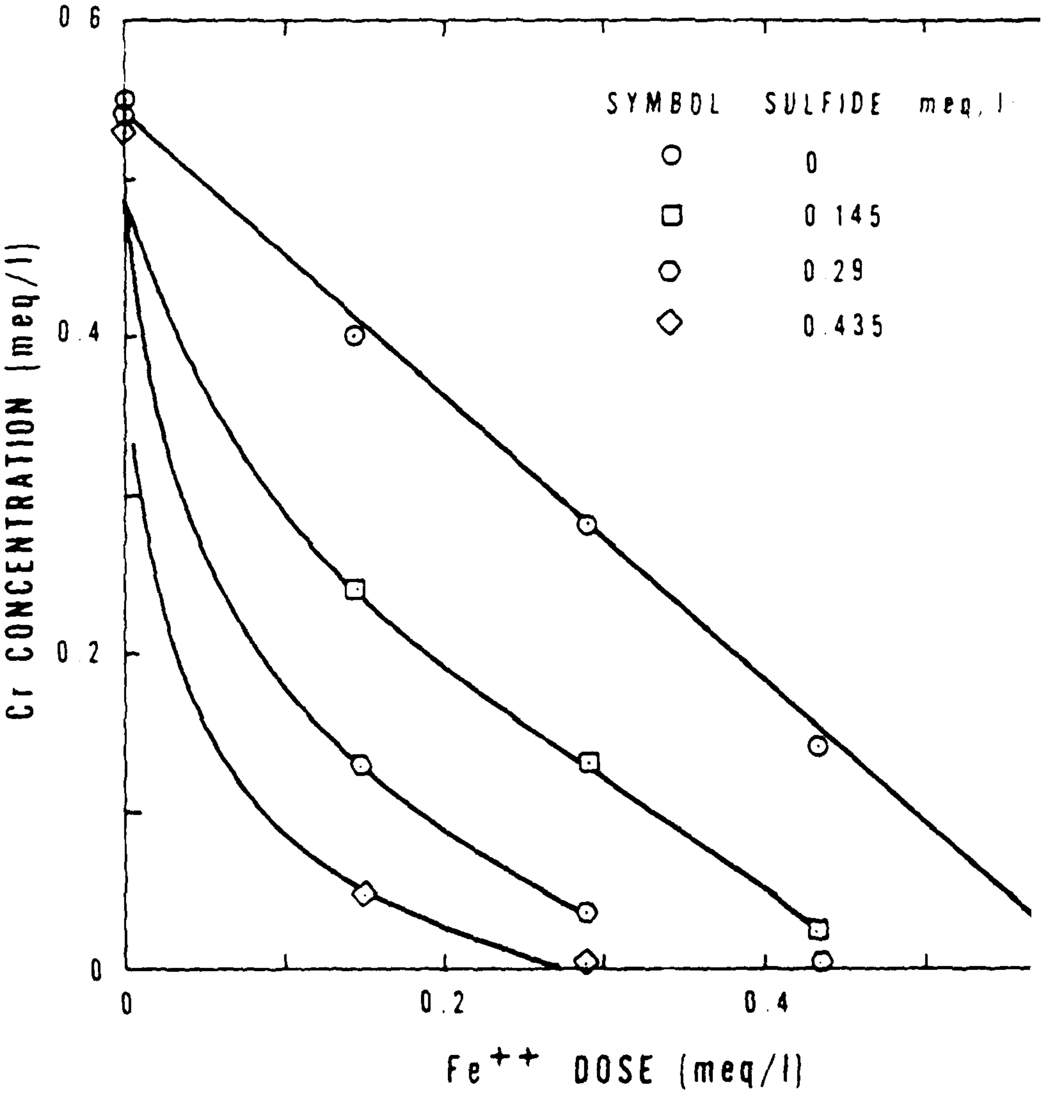

Figure 6. Chromium reduction by ferrous sulfate and sodium sulfide at pH 7.

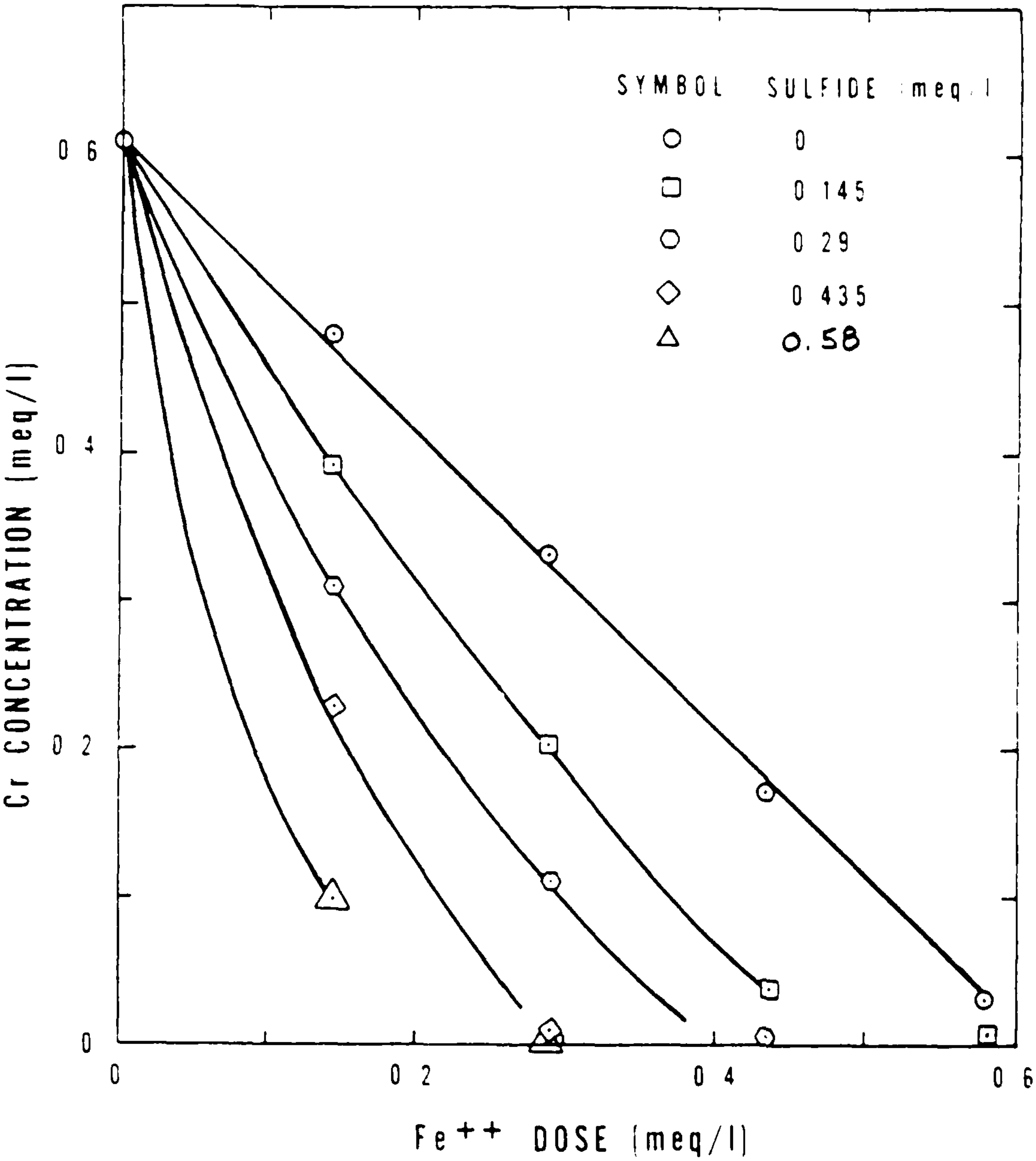

Figure 7. Chromium reduction by ferrous sulfate and sodium sulfide at pH 8.5.

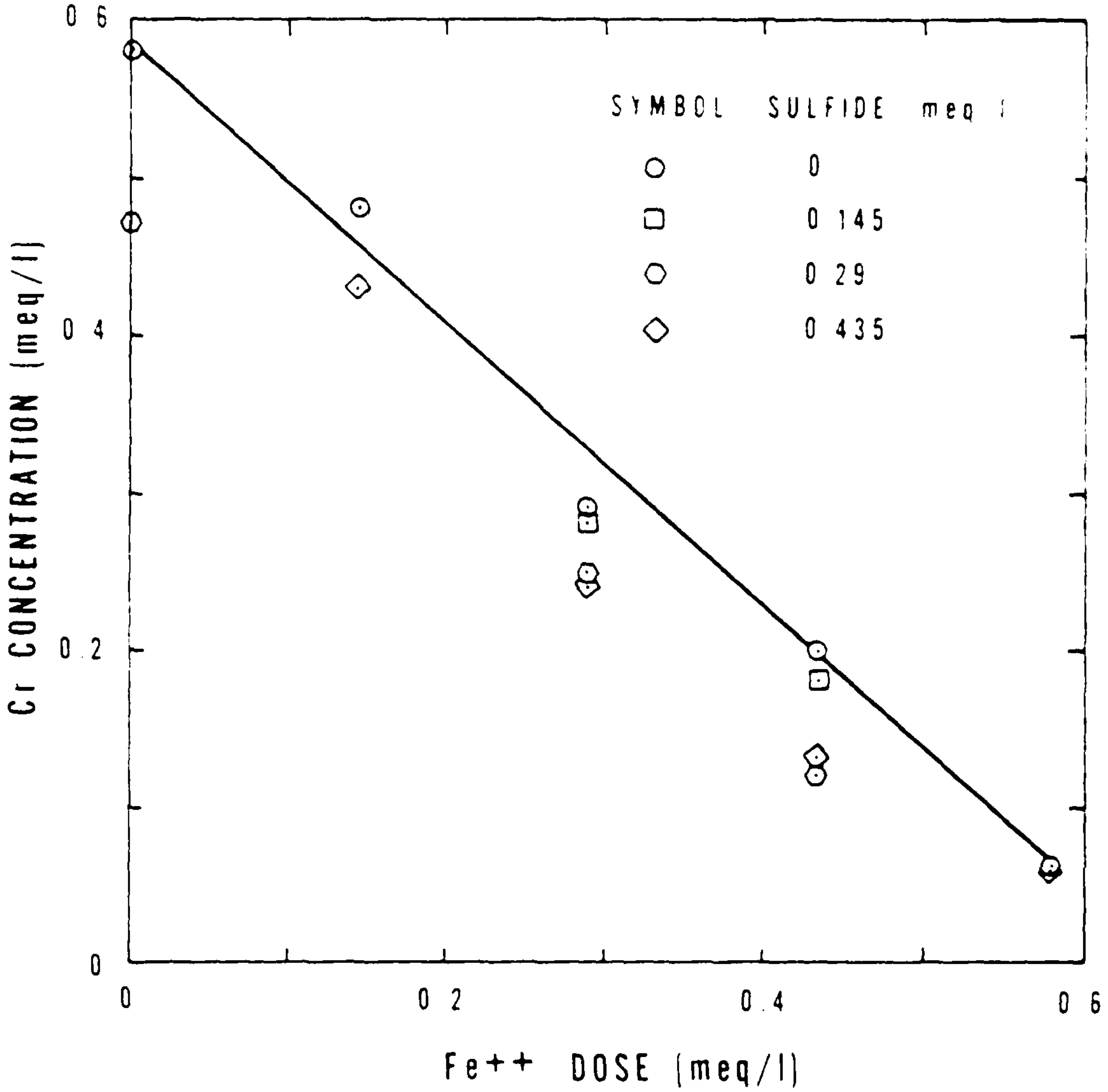

Figure 8. Chromium reduction by ferrous sulfate and sodium sulfide at pH 10.

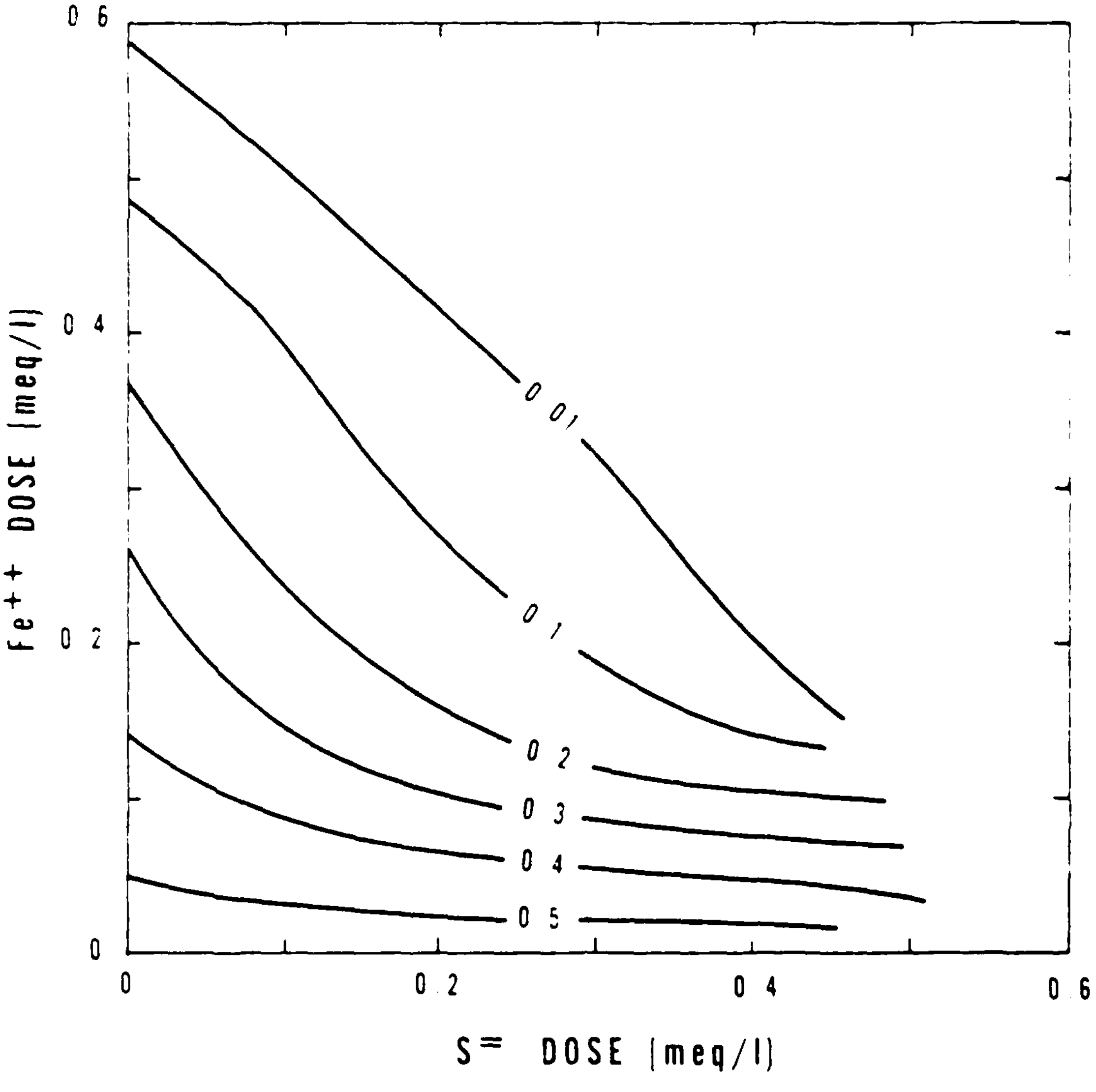

Figure 9. Isoequivalent chromium residuals (meq/l) for ferrous and sulfide doses at pH 7 (initial chromium = 0.58 meq/l).

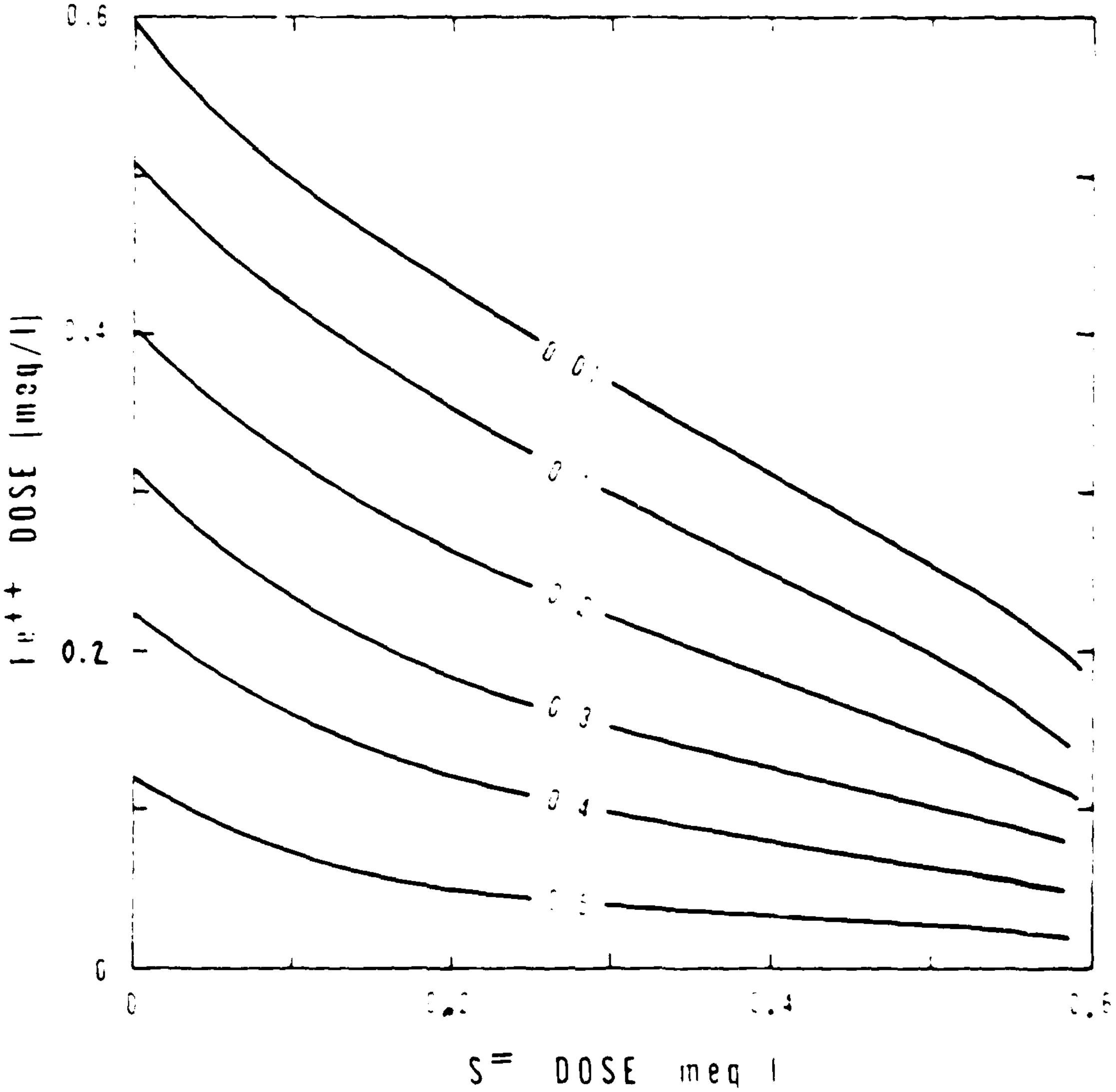

Figure 10. Isoequivalent chromium residuals (meq/l) for ferrous and sulfide doses at *pH* 8.5 (initial chromium = 0.58 meq/l).

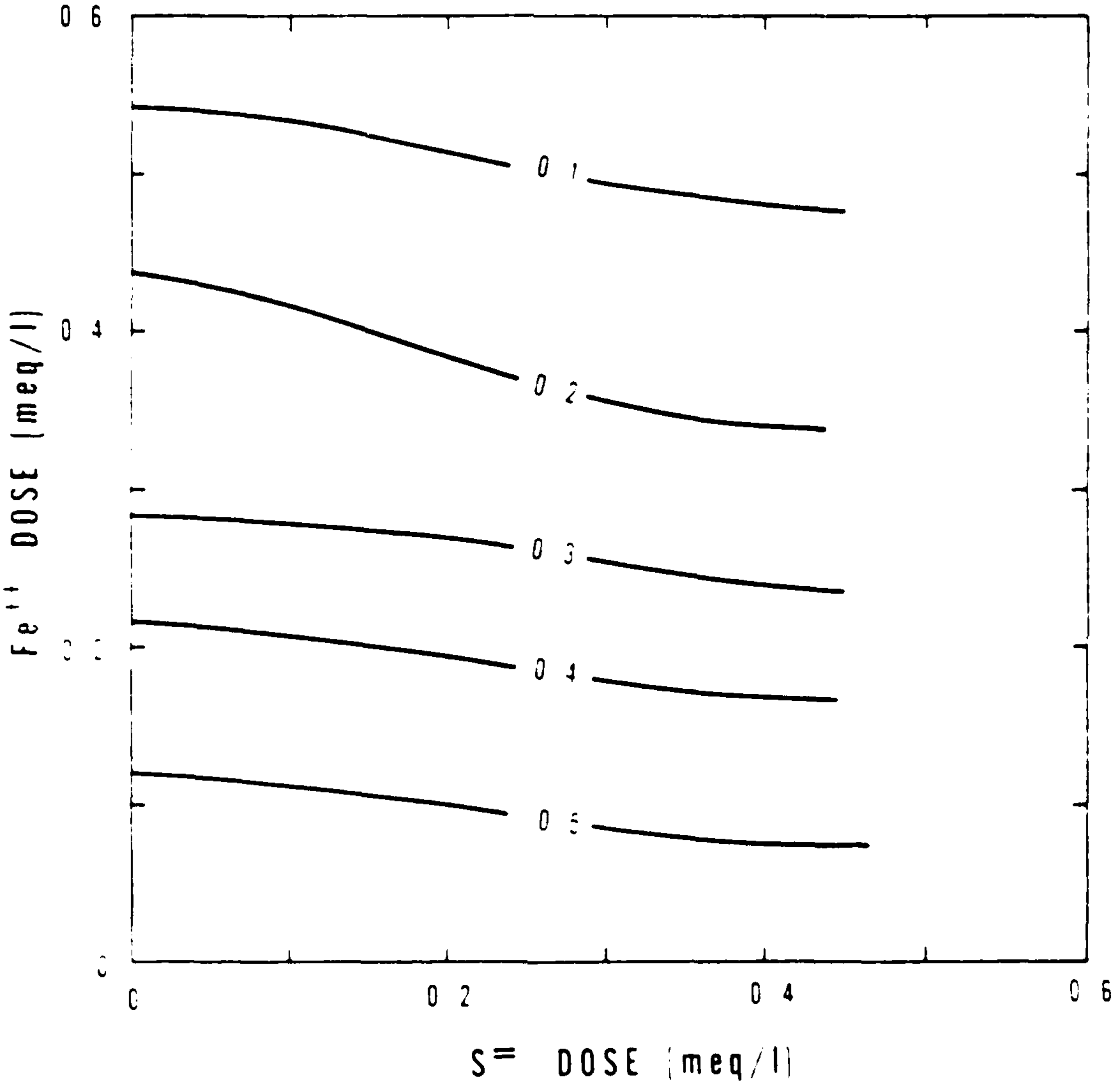

Figure 11. Isoequivalent chromium residuals (meq/l) for ferrous and sulfide doses at pH 10. (initial chromium = 0.58 meq/l).

Effects of Hardness Alkalinity and Complexing Agents Initial studies were performed on a synthetic wastewater prepared from a soft, low-alkaline tap water (Tyndall AFB). To investigate interferences of ions normally found in electroplating wastewaters, studies were performed on synthetic wastewaters prepared from reagent-grade salts of these ions and distilled water. These studies were performed at pH 8.5.

Studies of reduction and removal of chromium from synthetic wastewater prepared from distilled water were identical to those performed with Tyndall tap water (Figure 12). Ferrous iron rapidly and stoichiometrically reduced the chromium. Sulfide alone was ineffective. In combination with ferrous iron, sulfide aided in chromium reduction.

Alkalinity ($NaHCO_3$) was found to slightly interfere with chromium reduction and removal at low and intermediate ferrous sulfate doses (Figure 13). The interference by alkalinity is more pronounced when sulfide is used along with ferrous iron to reduce chromium (Figure 14). In both of these examples, floc size was greatly reduced with increasing alkalinity. This effect is not apparent in the figure due to the use of a membrane filter for solids removal. Reduced floc size would have a significant effect on removal efficiencies in an actual treatment system. In spite of this, interference by alkalinity would be classified as slight and its effect is eliminated by stoichiometric doses of ferrous sulfate.

Figure 15 shows that the addition of calcium hardness has little effect on chromium reduction and removal by ferrous sulfate alone. However, the addition of calcium hardness to the combination of ferrous sultate and sodium sulfide enhanced chromium reduction and removal (Figure 16). In slightly alkaline water hardness had no effect on treatment with ferrous sulfate alone (Figure 17), but slightly improved the effectiveness of sulfide (Figure 18), eliminating the alkaline interferences. In addition, the presence of hardness resulted in improved floc characteristics, partially eliminating the adverse effects of alkalinity.

To determine the combined effects of hardness and alkalinity in treatment of hexavalent chromium in a typical hard water, synthetic wastes were prepared in "Tempe Tap" Water (Table 3).

TABLE 3

Analysis of Tap Water, Tempe, Arizona.

Constituent	Concentration
pH	6.2
Alkalinity (mg/l as CaCO3)	100
Ca Hardness (mg/l as CaCO3)	150
Total Hardness (mg/l as $CaCO_3$)	165
$SO_4^=$ (mg/l)	60
Cl^- (mg/l)	44
Na^+ (mg/l)	24

Figure 19 shows the removal of chromium by ferrous sulfate and sodium sulfide for synthetic wastewater prepared from "Tempe Tap" water. There are no significant differences from similar runs with waste prepared from distilled water or "Tyndall Tap" water (softened low alkaline). Improved floc characteristics are noted with increased hardness. Apparently in the hard alkaline water (Tempe Tap) the opposing effects of alkalinity and hardness cancel each other out. It is also noted that no significant interferences to chromium reduction and removal are found in either of the tap waters tested.

Treatment of 100 mg/l of hexavalent chromium in "Tempe Tap" water by ferrous and sulfide (Figure 20) demonstrates the stoichiometric nature of the treatment process. It also shows that the rate of chromium reduction by ferrous iron at alkaline pH goes rapidly to completion even at such a high concentration of chromium.

Complexing agents (EDTA and cyanide) are used extensively in electroplating bath formulations. EDTA strongly interfered with chromium reduction and removal by ferrous sulfate and sodium sulfide (Figures 21,22) in wastewaters prepared using distilled water. Floc size was significantly reduced. When wastewater was prepared with Tempe tap water the effect of EDTA was greatly reduced and floc characteristics improved (Figures 23,24).

Cyanide is a strong complexing agent commonly used in plating bath formulations. Since cyanides form strong complexes with ferrous iron, it was anticipated that the presence of cyanide would interfere with ferrous reduction of hexavalent chromium. The molar ratio of CN to Fe in the ferrocyanide complex is 6 to 1. Therefore concentrations of cyanide up to 6 times maximum ferrous dose were selected to determine cyanide's effect on the process.

Cyanide interfered with chromium reduction by ferrous iron for synthetic wastes prepared in distilled water (Figure 25), with the adverse effect proportional to cyanide concentration. Even at the highest concentration of cyanide, some reduction was accomplished. The addition of 0.29 meq/l of sulfide (Figure 26) improved chromium reduction, but did not eliminate the cyanide interference. Cyanide was less of an interferent in reduction of synthetic chromium waste prepared with Tempe tap water. (Figures 27 and 28).

Cyanides interfere with chromium reduction by ferrous sulfate and sulfide; probably by forming ferrocyanide complexes. These complexes are hard to break and would interfere with cyanide treatment. It would be advisable to segregate cyanide containing wastes for cyanide removal prior to treatment with chromium containing wastes by this process.

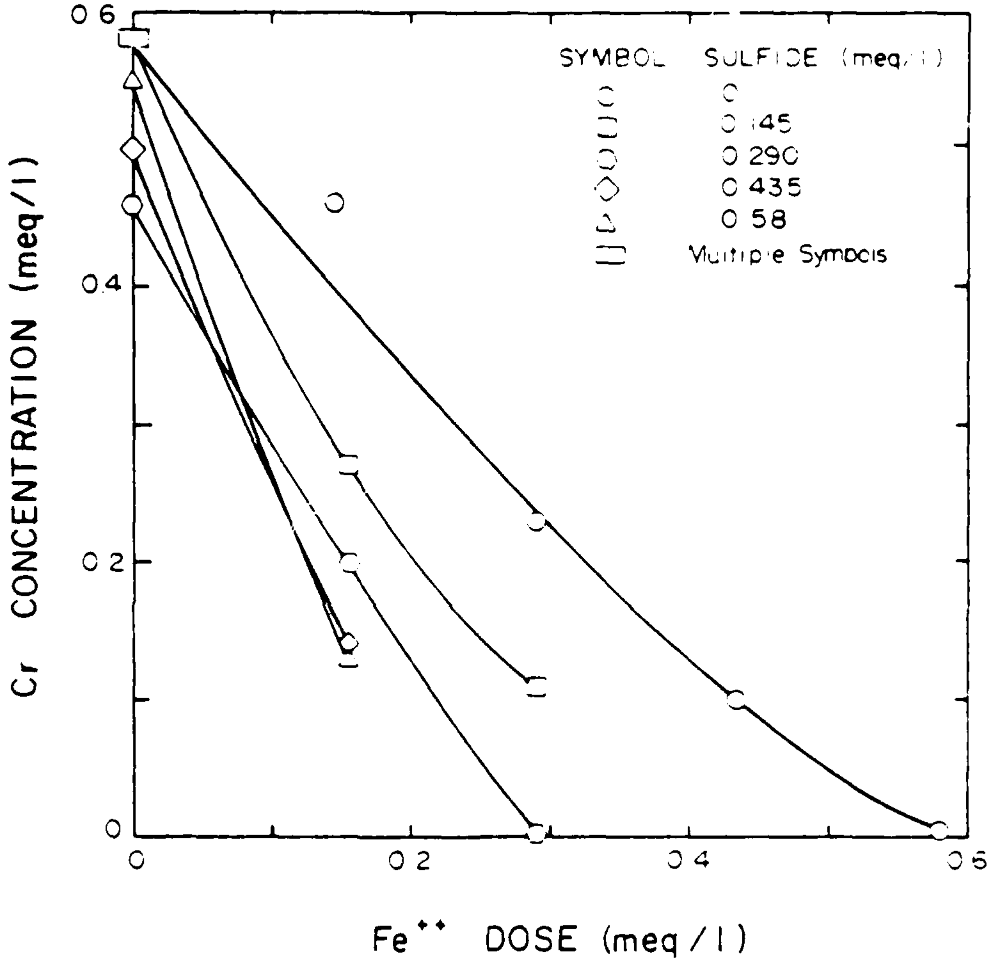

Figure 12. Chromium reduction by ferrous sulfate and sodium sulfide at pH 8.5 in distilled water.

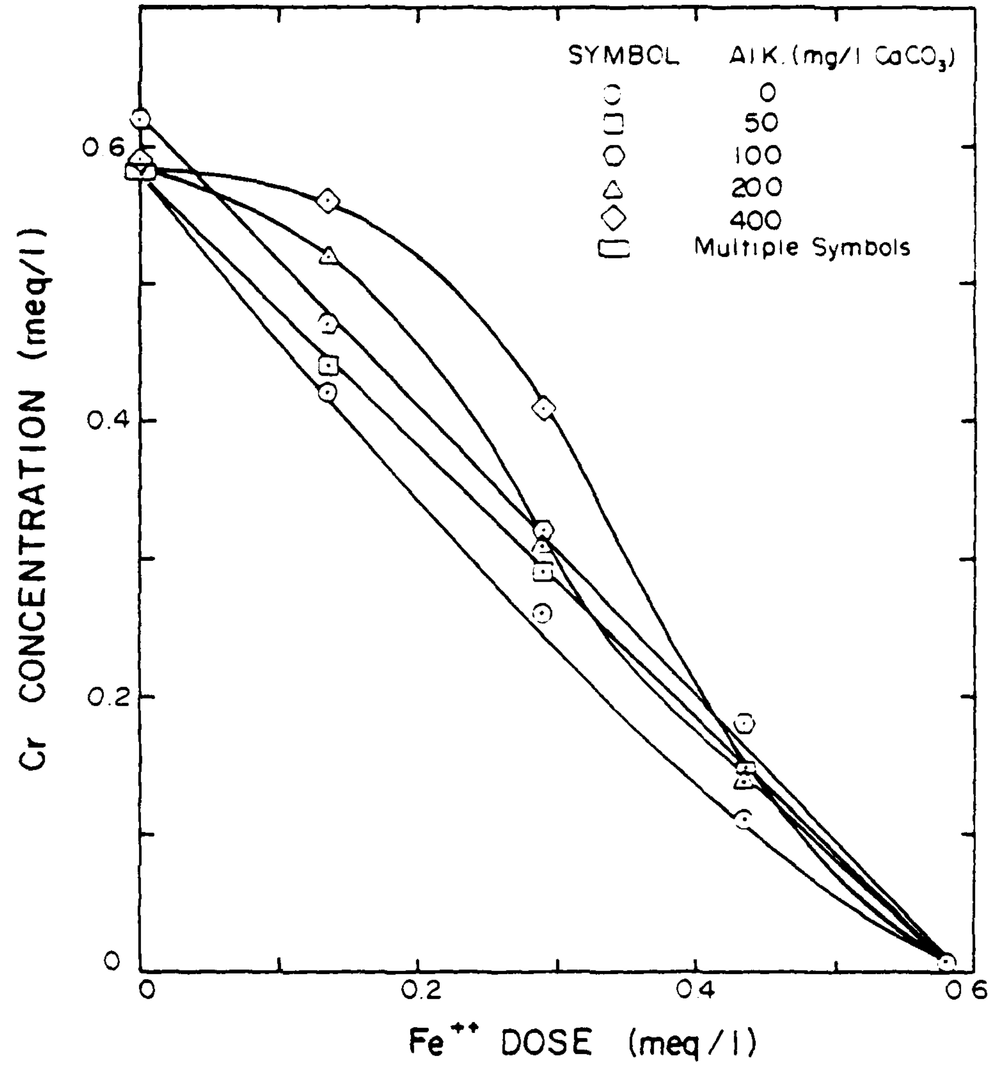

Figure 13. Effects of alkalinity on chromium reduction by ferrous sulfate pH 8.5.

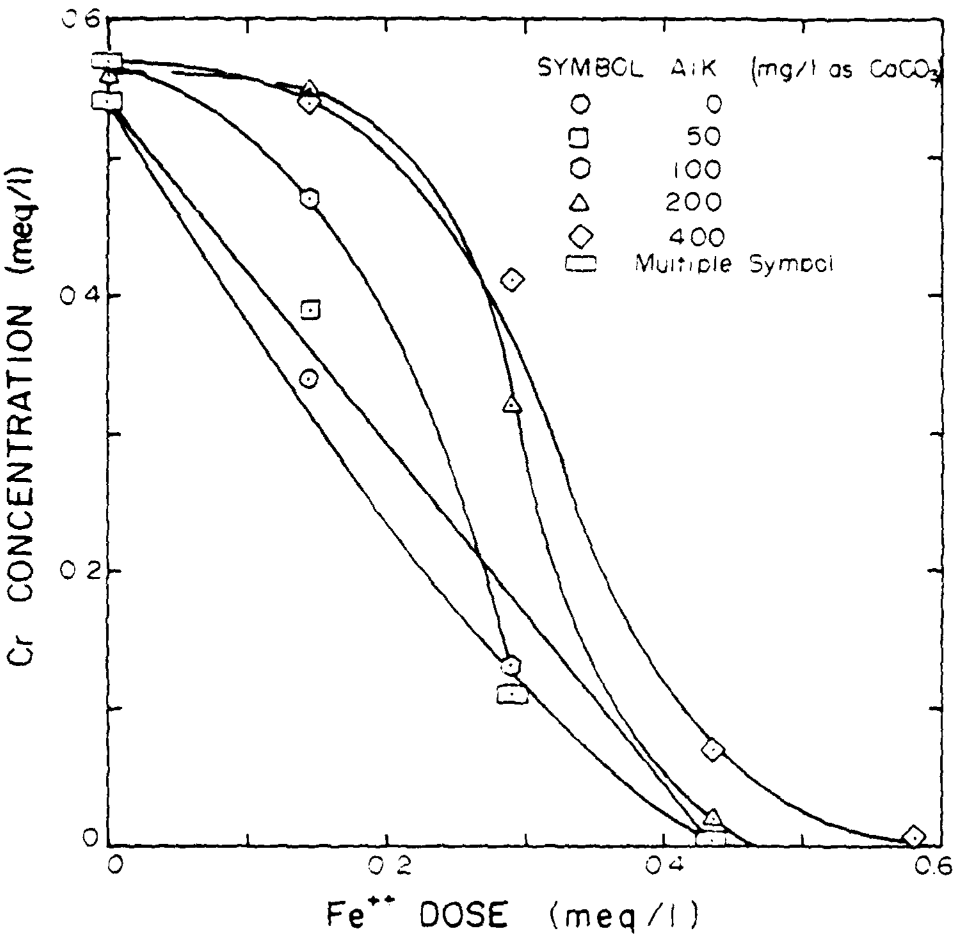

Figure 14. Effects of alkalinity on chromium reduction by ferrous sulfate and sodium sulfide (0.29 meq/l) at pH 3.5.

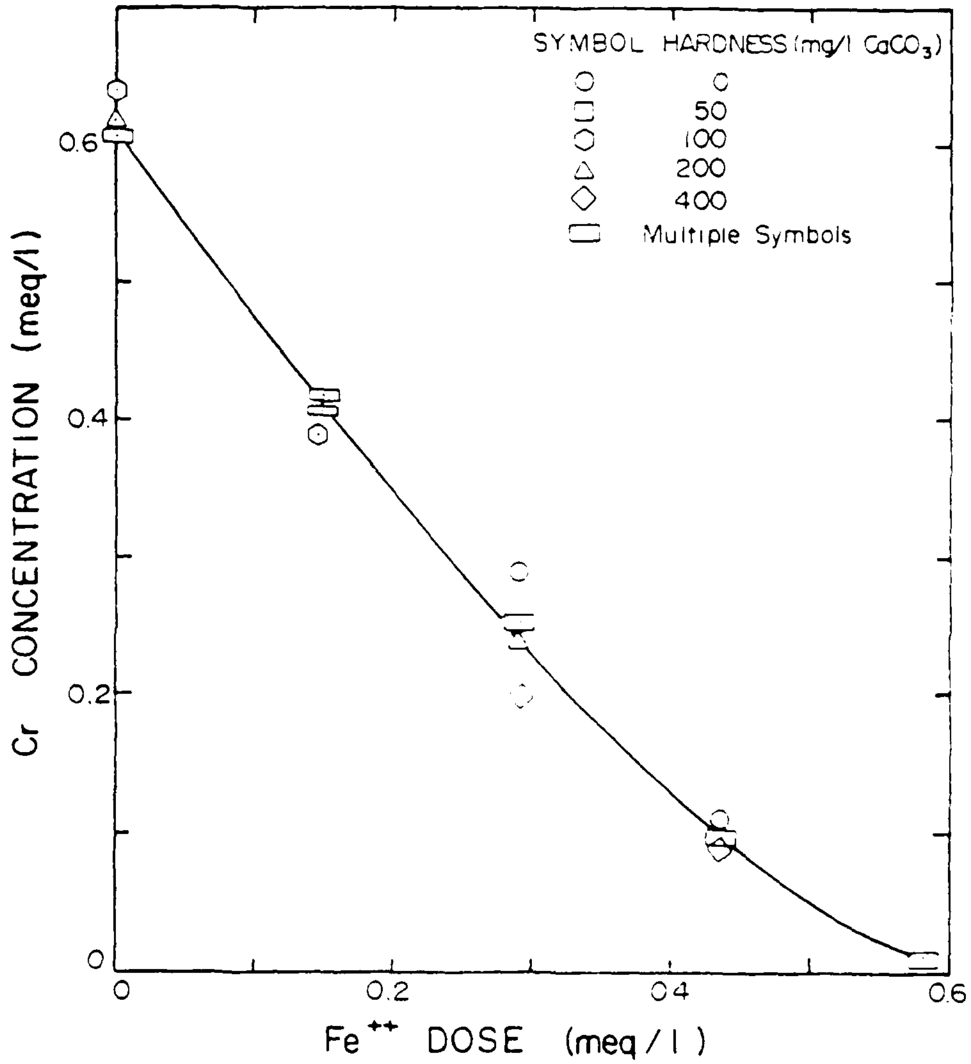

Figure 15. Effects of calcium hardness on chromium reduction by ferrous sulfate at pH 8.5.

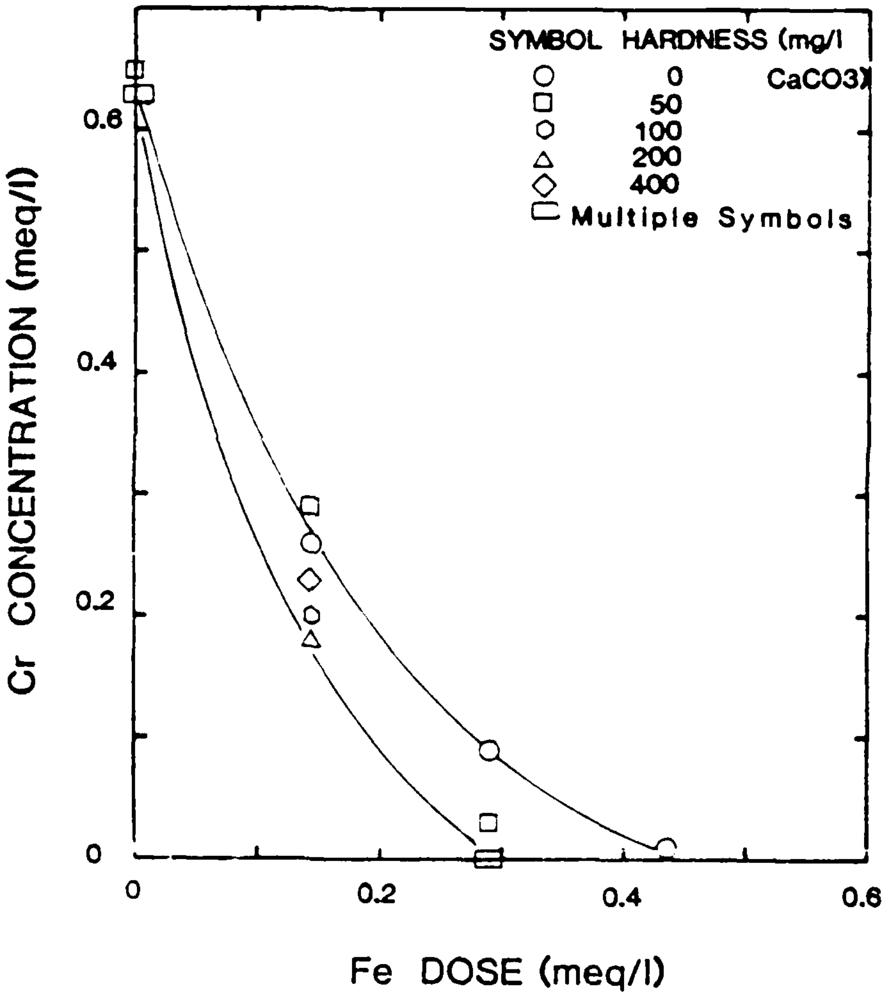

Figure 16. Effects of hardness on chromium reduction by ferrous sulfate and sodium sulfide (0.29 meq/l) at pH 8.5.

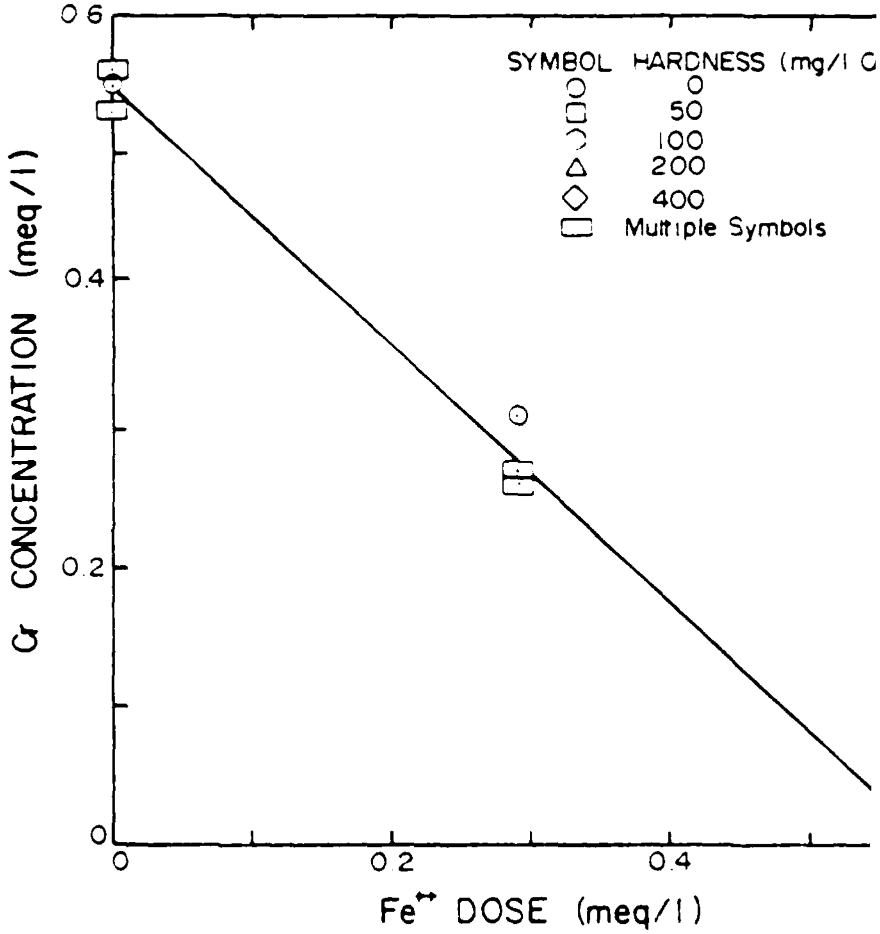

Figure 17. Effects of hardness and alkalinity (200 mg/l as $CaCO_3$) on chromium reduct by ferrous sulfate at pH 8.5.

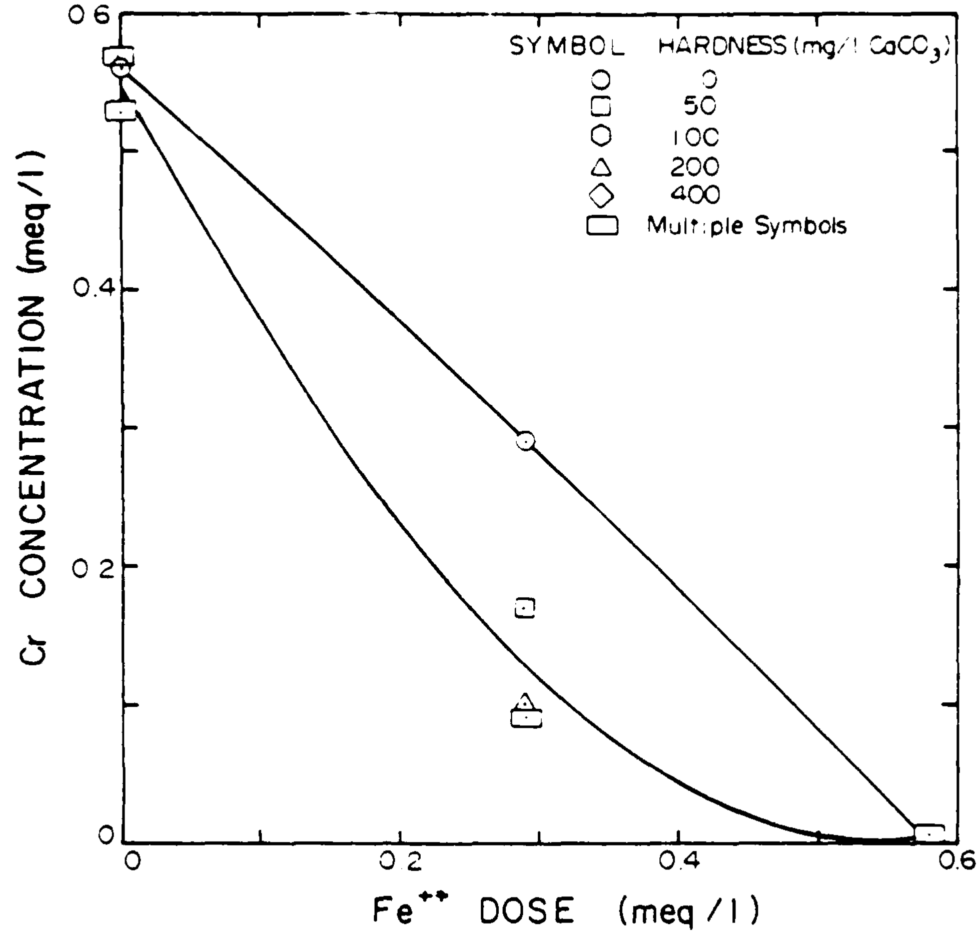

Figure 18. Effects of hardness and alkalinity (200 mg/l as $CaCO_3$) on chromium reduction by ferrous sulfate and sodium sulfide (0.29 meq/l) at pH 8.5.

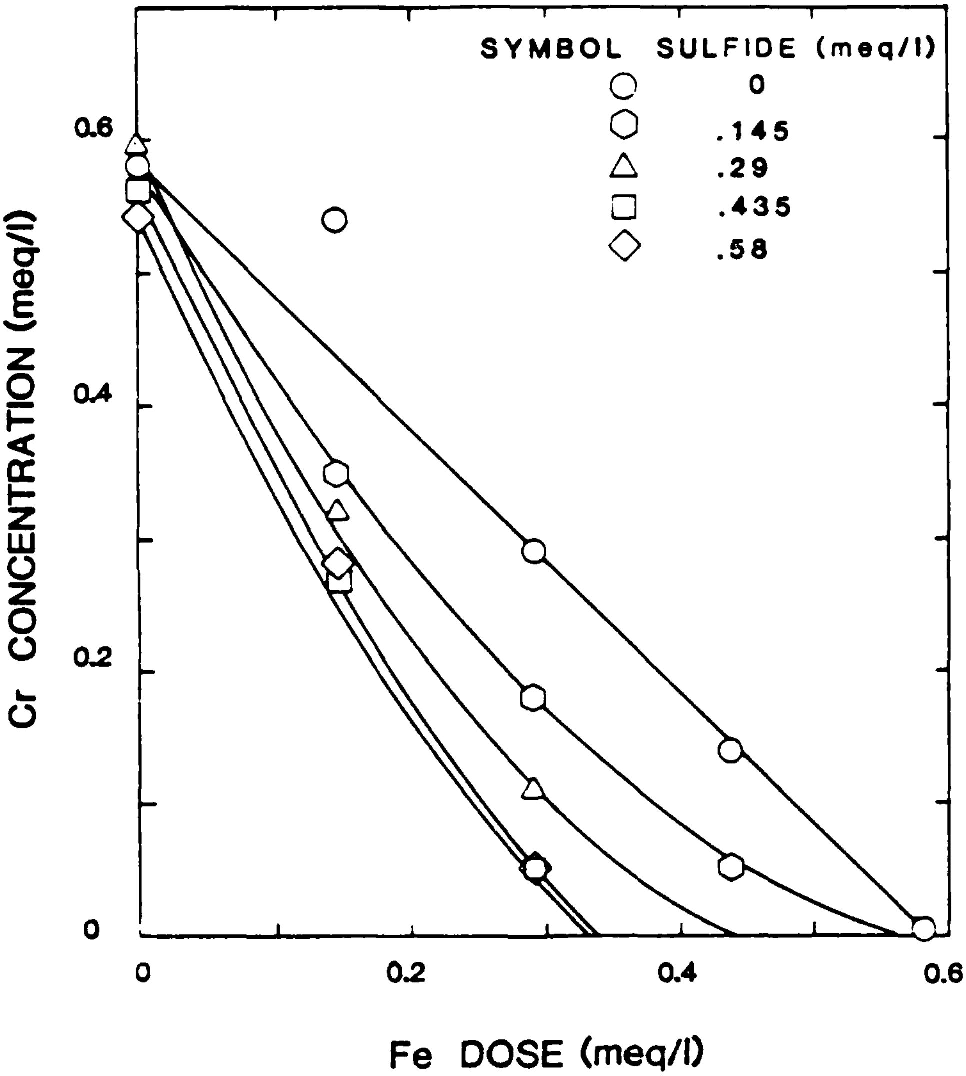

Figure 19. Chromium reduction by ferrous sulfate and sodium sulfide at pH 8.5 in a hard tap water.

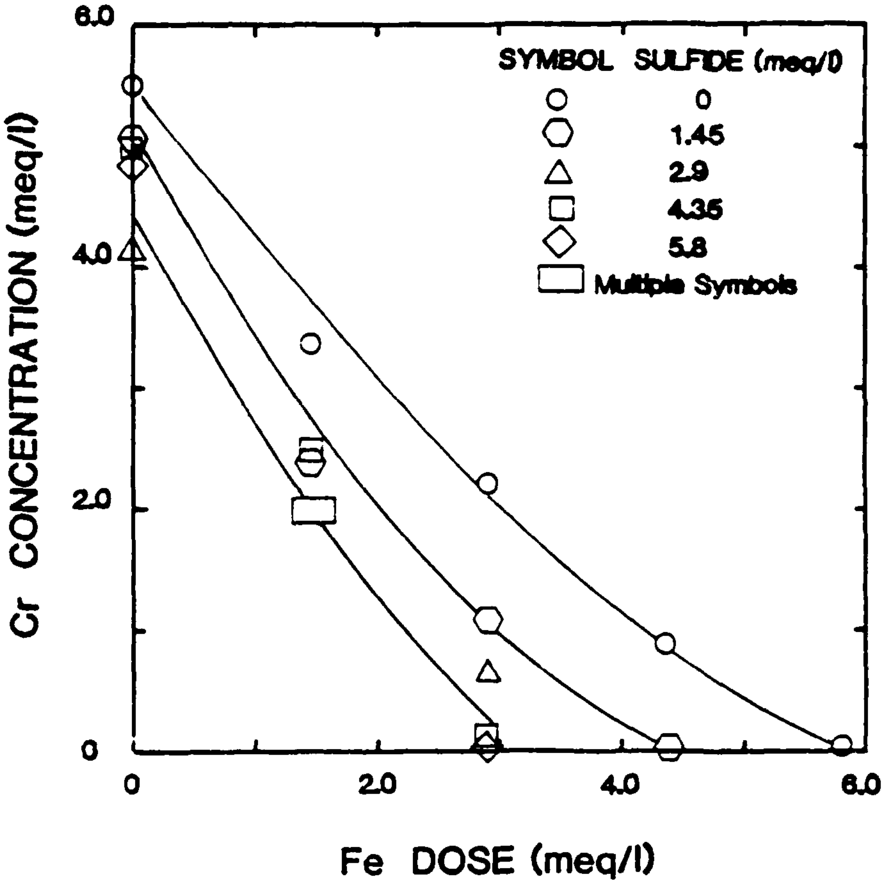

Figure 20. Chromium (100 mg/l) reduction by ferrous sulfate and sodium sulfide at pH 8.5 in a hard tap water.

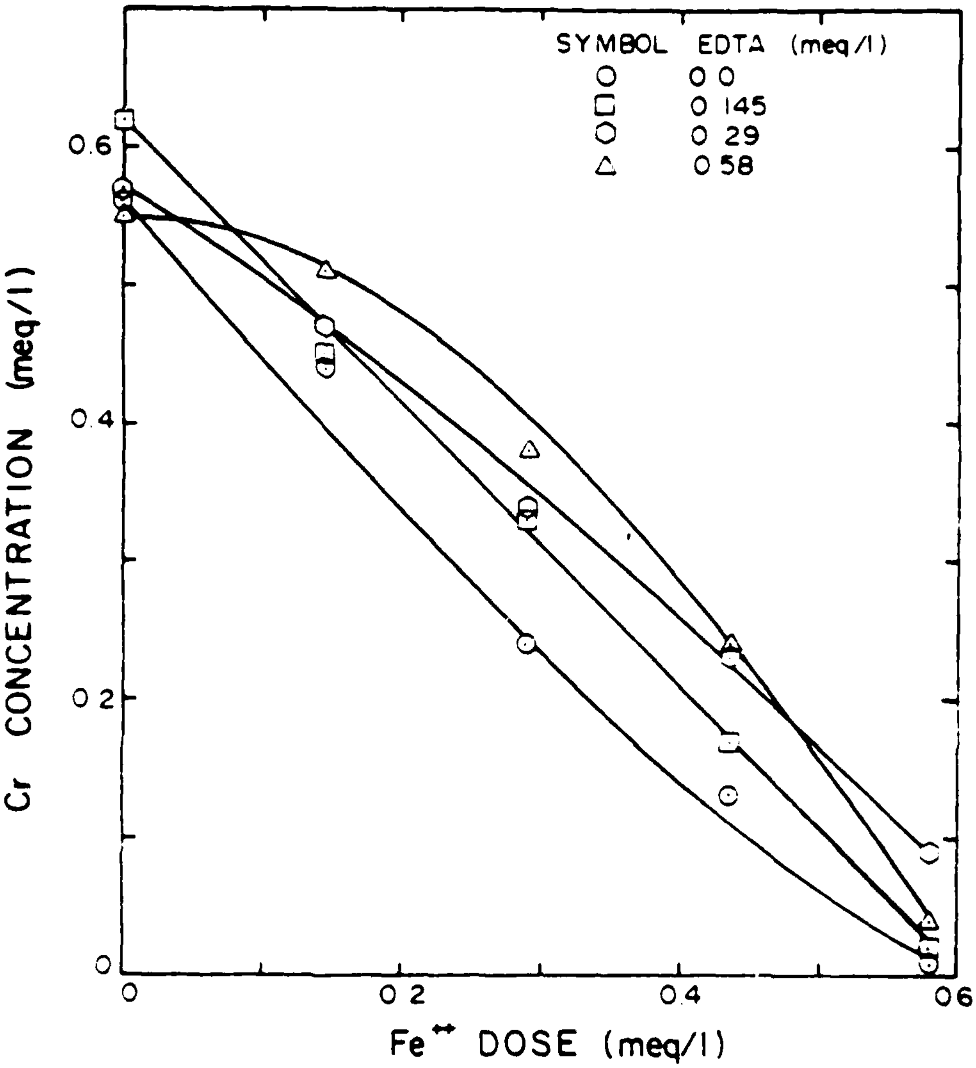

Figure 21. Effects of EDTA on chromium reduction by ferrous sulfate at pH = 8.5.

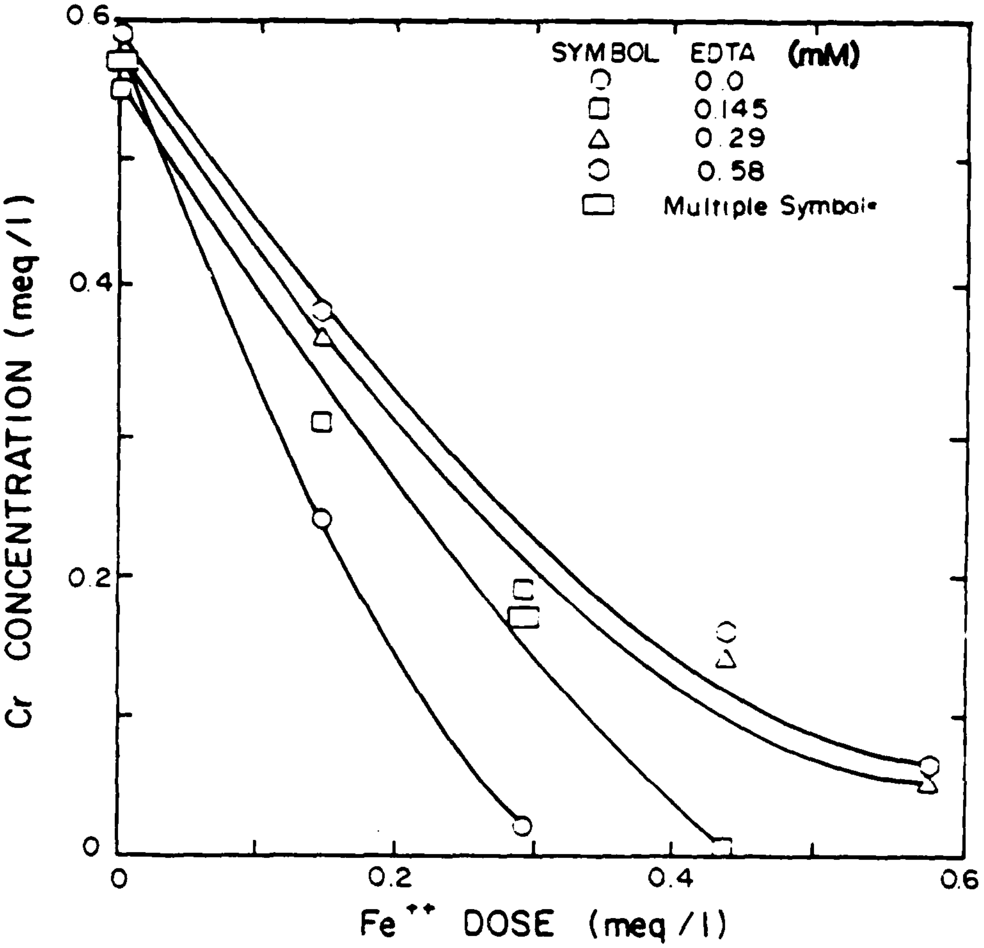

Figure 22. Effects of EDTA on chromium reduction by ferrous sulfate and sodium sulfide (0.29 meq/l) at pH 8.5.

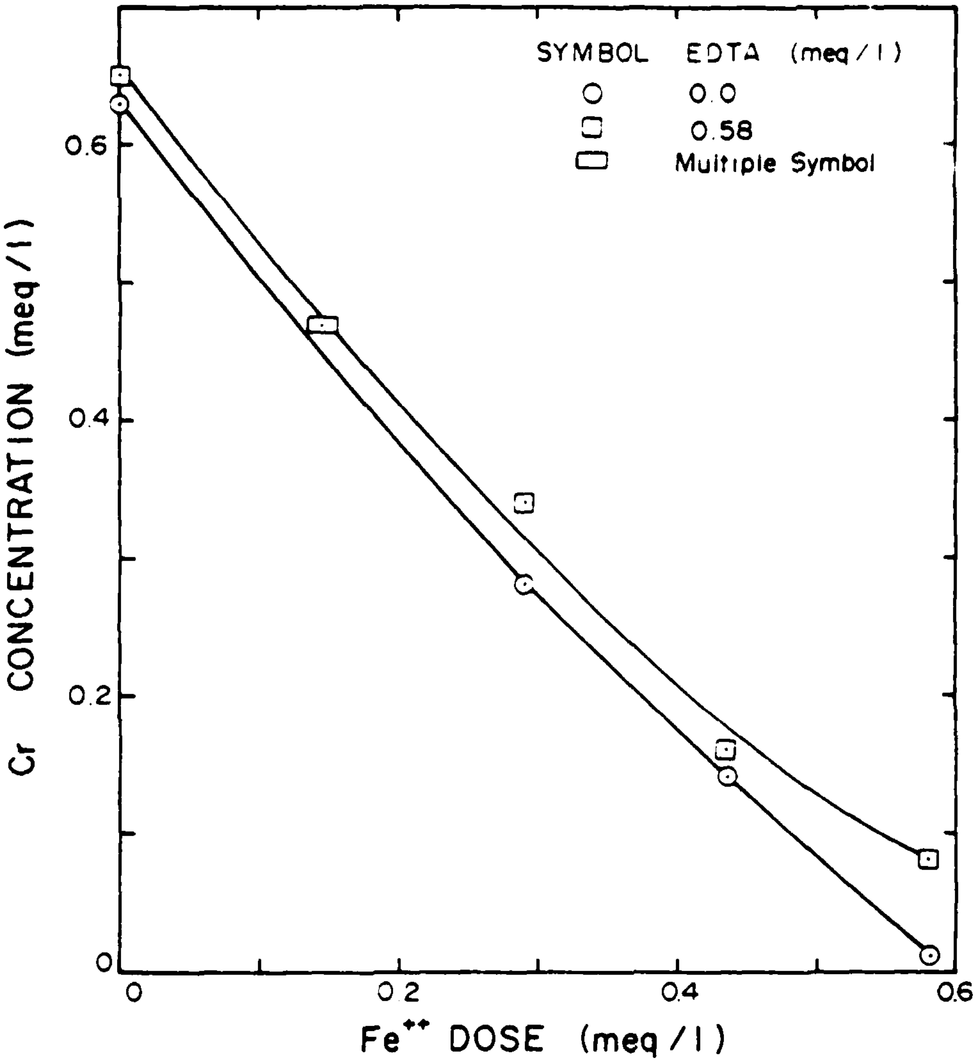

Figure 23. Effects of EDTA on chromium reduction by ferrous sulfate in hard tap water at pH 8.5.

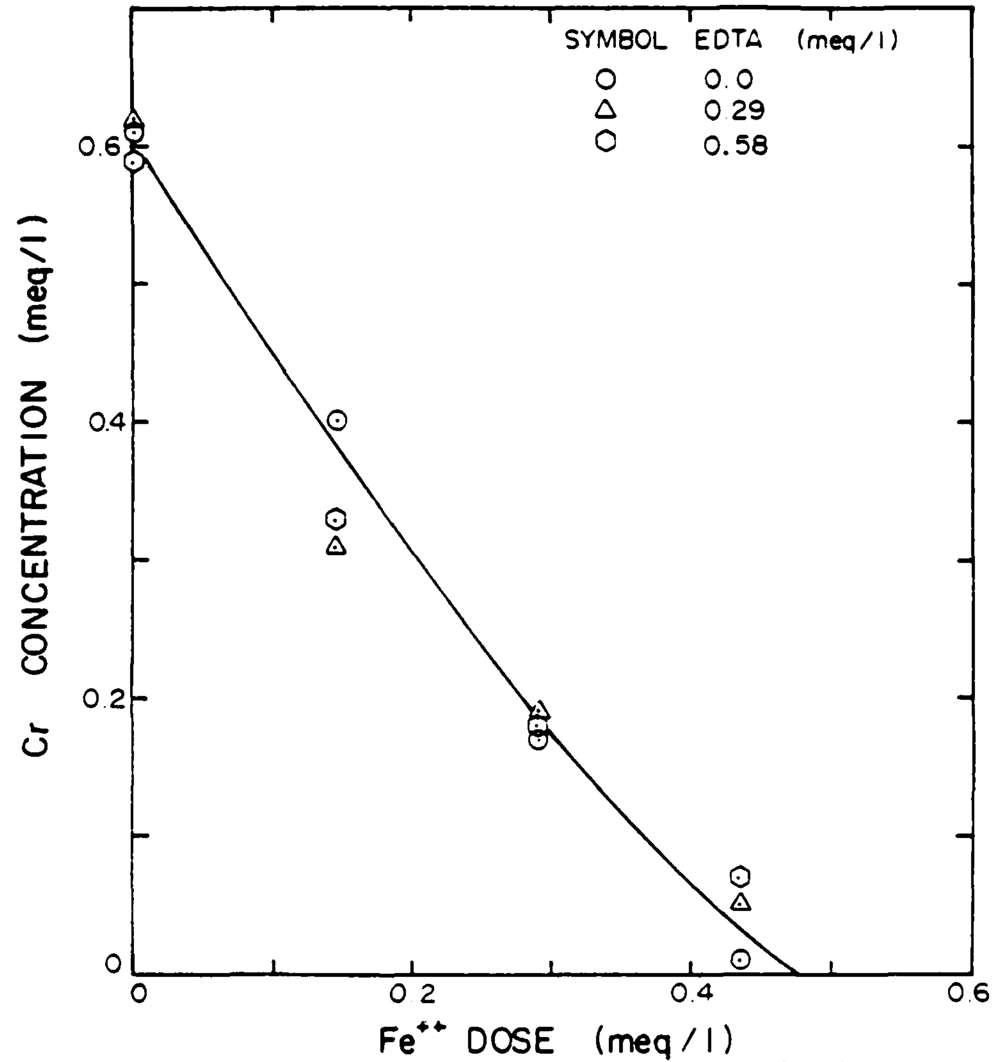

Figure 24. Effects of EDTA on chromium reduction by ferrous sulfate and sodium sulfide (0.29 meq/l) in hard tap water at pH 8.5.

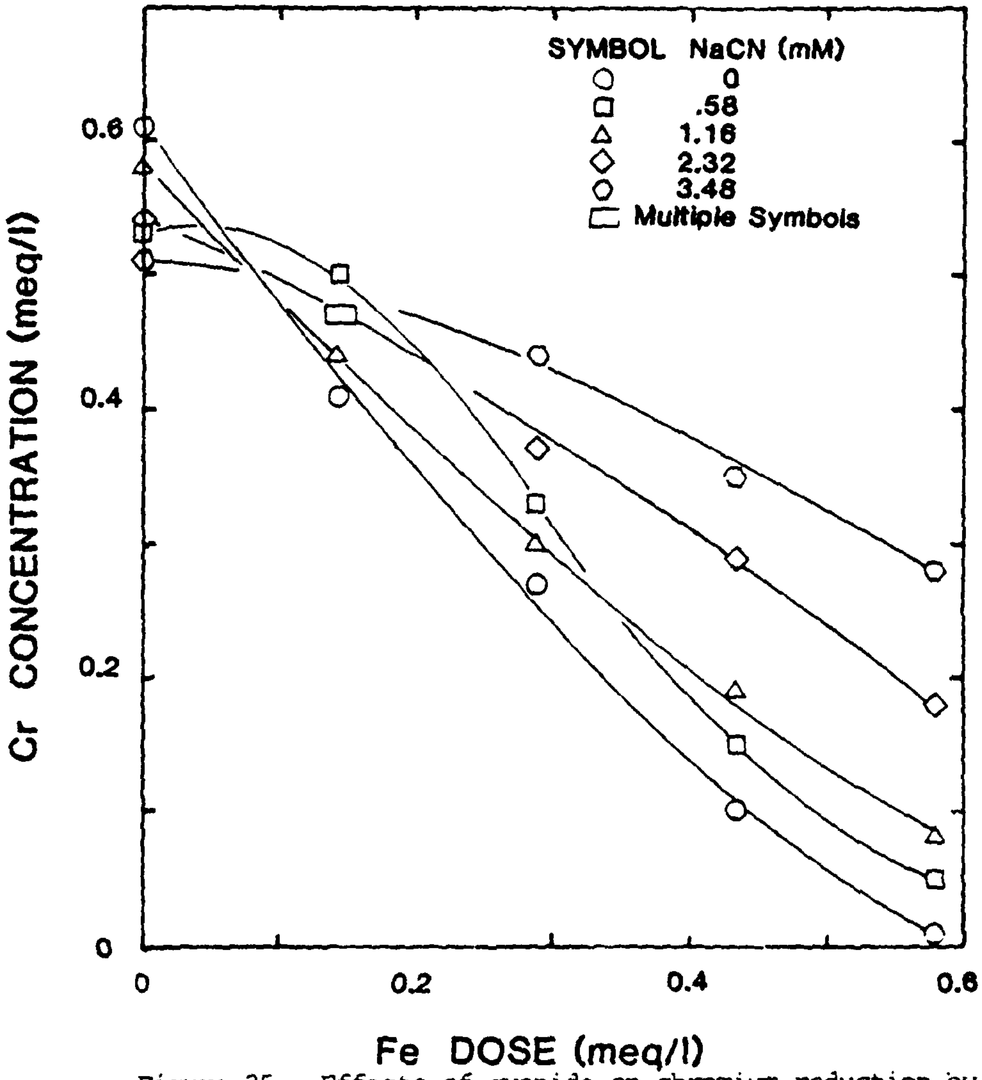

Figure 25. Effects of cyanide on chromium reduction by ferrous sulfate at pH 8.5.

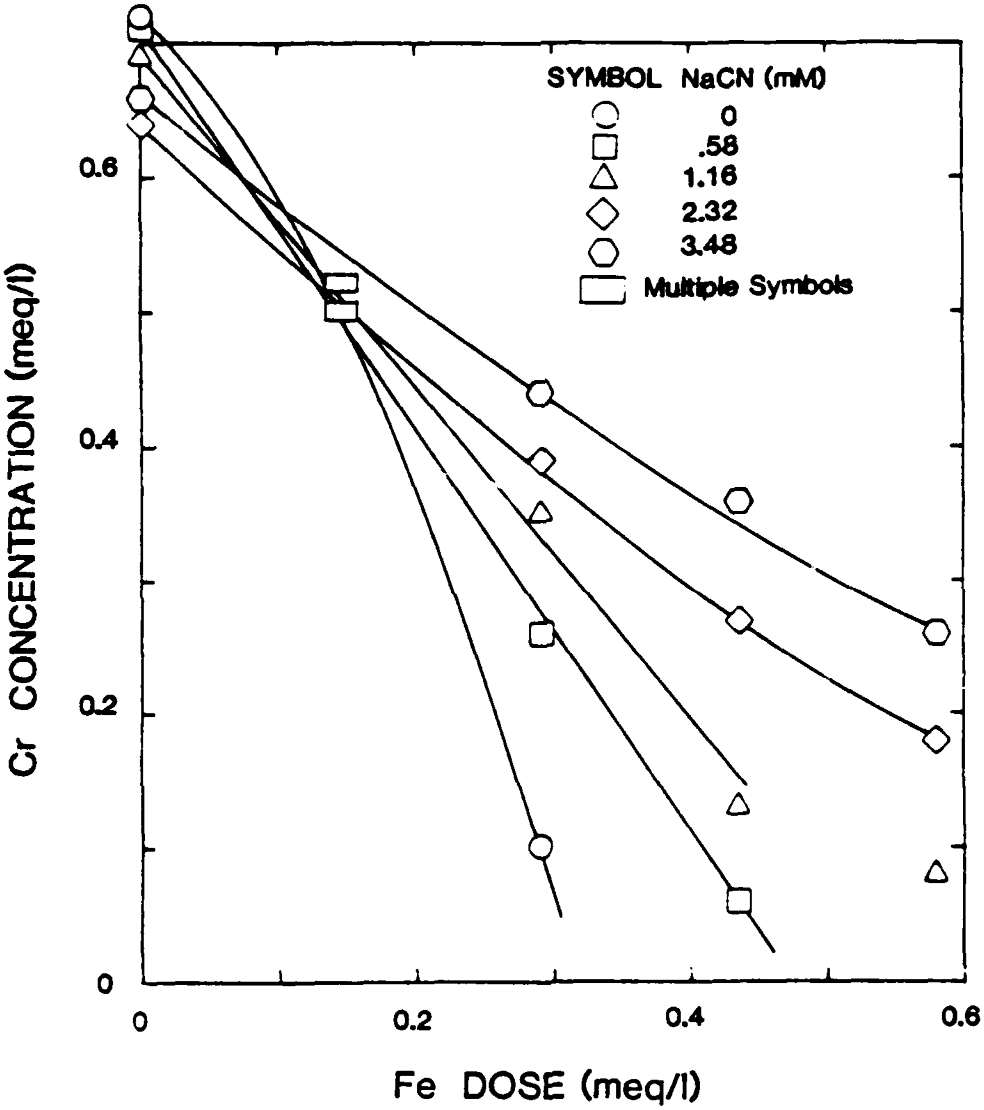

Figure 26. Effects of cyanide on chromium reduction by ferrous sulfate and sodium sulfide (0.29 meq/l) at pH. 8.5.

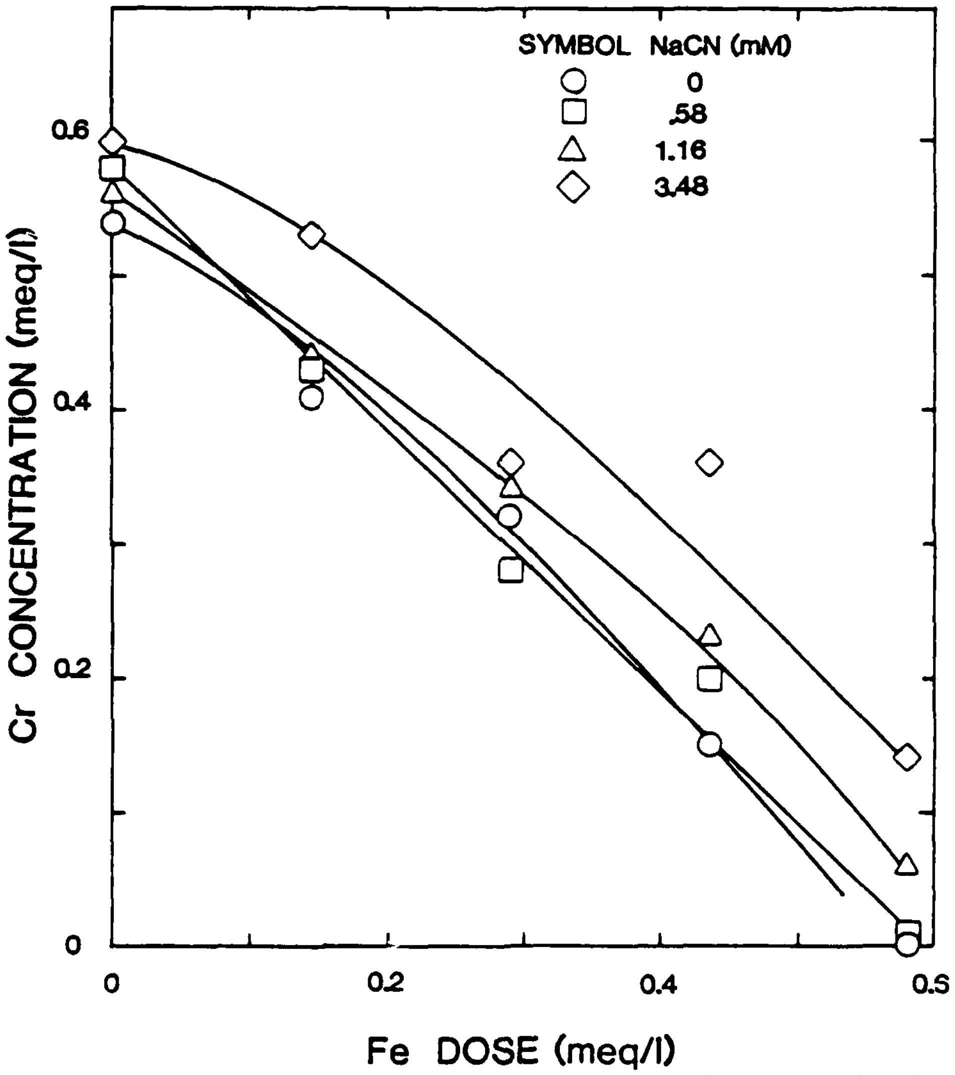

Figure 27. Effects of cyanide on chromium reduction by ferrous sulfate in hard tap water at pH 8.5.

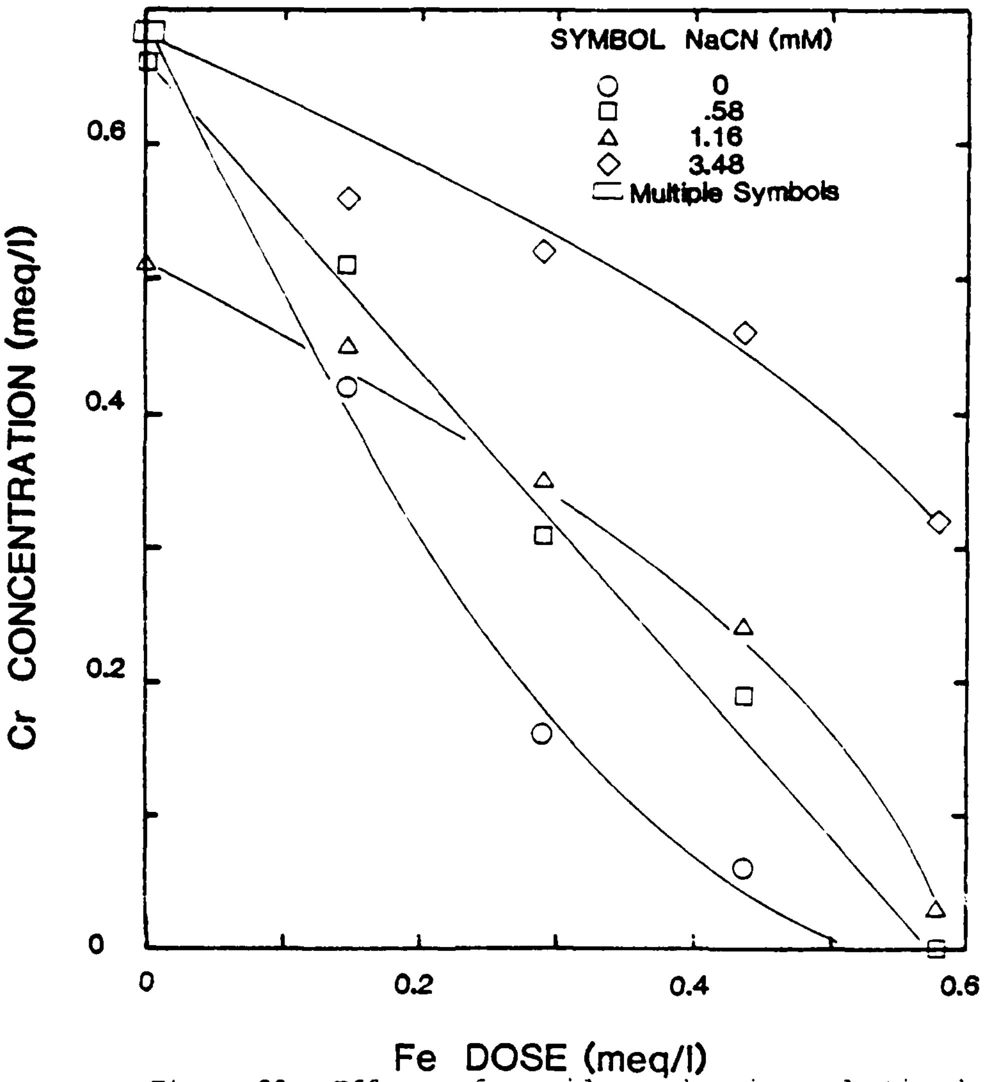

Figure 28. Effects of cyanide on chromium reduction by ferrous sulfate and sodium sulfide (0.29 meq/l) in hard tap water at pH 8.5.

Mixed Metal Treatment Treatment of a mixed metal waste was investigated. A synthetic mixed metal wastewater was prepared in Tyndall Air Force Base tap water using 5 mg/l (0.09 meq/l) of cadmium and 10 mg/l of chromium (0.58 meq/l).

Removal of chromium by sulfide alone was ineffective. At pH 7 (Figure 29), removal of over half of the cadmium was accomplished without sulfide addition, probably due to precipitation of cadmium hydroxide. Addition of sulfide further increased cadmium removal, although a sulfide dose of over 4 times stoichiometric was required to produce an effluent with a cadmium concentration below 0.01 mg/l. At pH 8.5 (Figure 30), additional cadmium removal is effected (by hydroxide precipitation) without sulfide addition. Sulfide is less effective at removal of additional cadmium except at doses greater than 4 times stoichiometric. Hydroxide precipitation of cadmium is further improved at pH 10 (Figure 31). At this pH, the addition of sulfide at doses above stoichiometric (.09 meq/l) resulted in resolubilization of cadmium. Results are for multiple runs of this experiment, both on cadmium only wastes and mixtures with chromium.

Cadmium had no noticeable effect on chromium removal by ferrous sulfate and sodium sulfide. Figure 32 shows lines of equal chromium residuals for combinations of ferrous sulfate and sodium sulfide doses at pH 8.5. This figure is identical to one prepared for treatment of a chromium only wastewater (Figure 10). Again this demonstrates that ferrous iron alone stoichiometrically removes chromium and that sulfide alone is ineffective, except in combination with ferrous iron.

Conversely, cadmium is significantly removed by sulfide addition at pH 7 (Figure 33). Treatment by ferrous iron alone is ineffective and removal of cadmium by sulfide is not significantly enhanced by its addition. At pH 8.5, (Figure 34) ferrous iron addition greatly enhances the removal of cadmium. In combination with ferrous iron, the dose of sulfide for complete removal is reduced to stoichiometric (.09 meq/l). At pH 10 (Figure 35), the cadmium resolubilizing effect of sulfide overdosing was eliminated by minimal addition of ferrous iron.

Synthetic mixtures of 10 mg/l each of chromium (0.58 meq/l) cadmium (0.18 meq/l) and nickel (0.34 meq/l) prepared in distilled water and Tempe tap water were treated with ferrous sulfate and sodium sulfide at pH 8.5. Treatment of this synthetic waste prepared with distilled water showed that chromium was removed stoichiometrically by ferrous sulfate (Figure 36). Addition of stoichiometric dose (0.58 meq/l) resulted in a chromium residual of less than 0.05 mg/l. Sulfide does not appreciably improve chromium removal in this mixture, probably due to its use in precipitation of the other metals.

Cadmium was essentially completely removed (0.02 mg/l residual) by pH adjustment to 8.5 (Figure 37). The addition of ferrous sulfate or sodium sulfide had either no effect or increased the cadmium solubility. Likewise nickel was removed to 0.15 mg/l by pH adjustment (Figure 38). Little benefit was effected by ferrous sulfate and sodium sulfide addition.

Similarly for synthetic mixed metal waste in Tempe tap water, chromium was removed stoichiometrically by ferrous sulfate (Figure 39). Sulfide was of little benefit. The residual chromium concentration for a stoichiometric dose of ferrous sulfate was 0.4 mg/l, considerably more than for treatment of the mixed metal waste prepared in distilled water. This increased in concentration could be due to carbonate complexation.

Likewise cadmium is considerably more soluble in tap water at pH 8.5 (Figure 40) than in distilled water, also probably due to carbonate complexation. Sulfide stoichiometrically reduces the cadmium concentration. Ferrous sulfate also improves cadmium removal. Minimum cadmium residual was 0.05 mg/l.

Nickel remains very soluble in this tap water at pH 8.5 (Figure 41). Ferrous sulfate and sodium sulfide improve removal, but the minimum residual nickel concentration is still over 1 mg/l. It is noted (Figures 1 & 2) that nickel sulfide and nickel hydroxide are considerably more soluble than cadmium sulfide, and hence nickel is more likely to be poorly removed by sulfide precipitation.

On the previous batch treatment tests the pH was adjusted by addition of sodium hydroxide or nitric acid. There are reports (34a) that improved metal removal can be accomplished by the use of lime ($Ca(OH)_2$) for pH adjustment, due to the improved coagulant properties of calcium over sodium. A mixed metal waste was prepared in Tempe tap water and pH adjusted to 8.5 with a dilute solution of lime. Removal of chromium was stoichiometric as usual (Figure 42). The chromium concentrations for stoichiometric dose of ferrous sulfate were reduced to less than 0.05 mg/l, as compared with 0.4 mg/l for the test when pH adjustment was with sodium hydroxide (Figure 43). Little effect is noted on cadmium removal. Minimum residual cadmium was 0.03 mg/l. No benefit is seen for nickel removal (Figure 44).

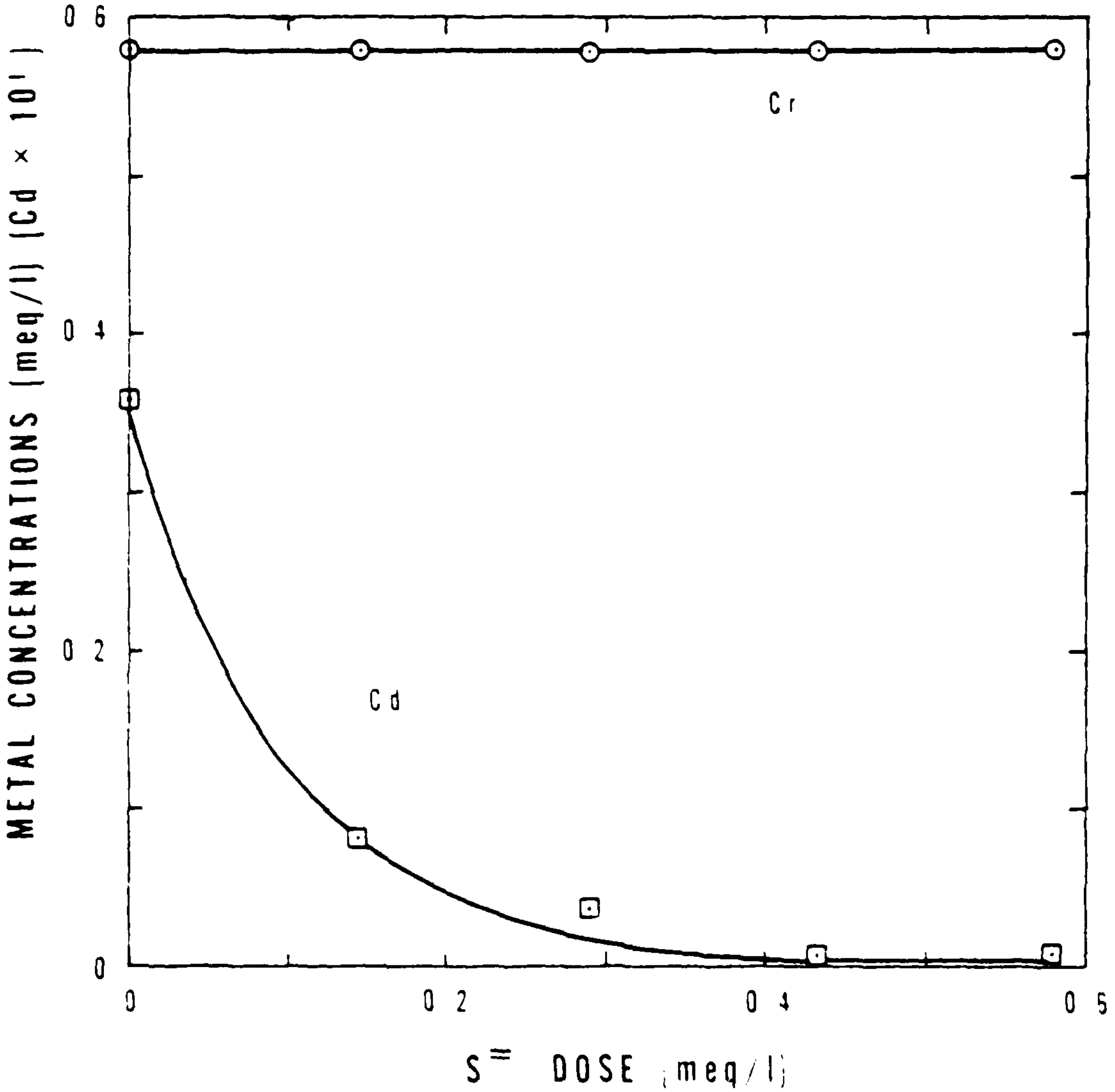

Figure 29. Cadmium and chromium removal by sodium sulfide in softened tap water at pH 7.

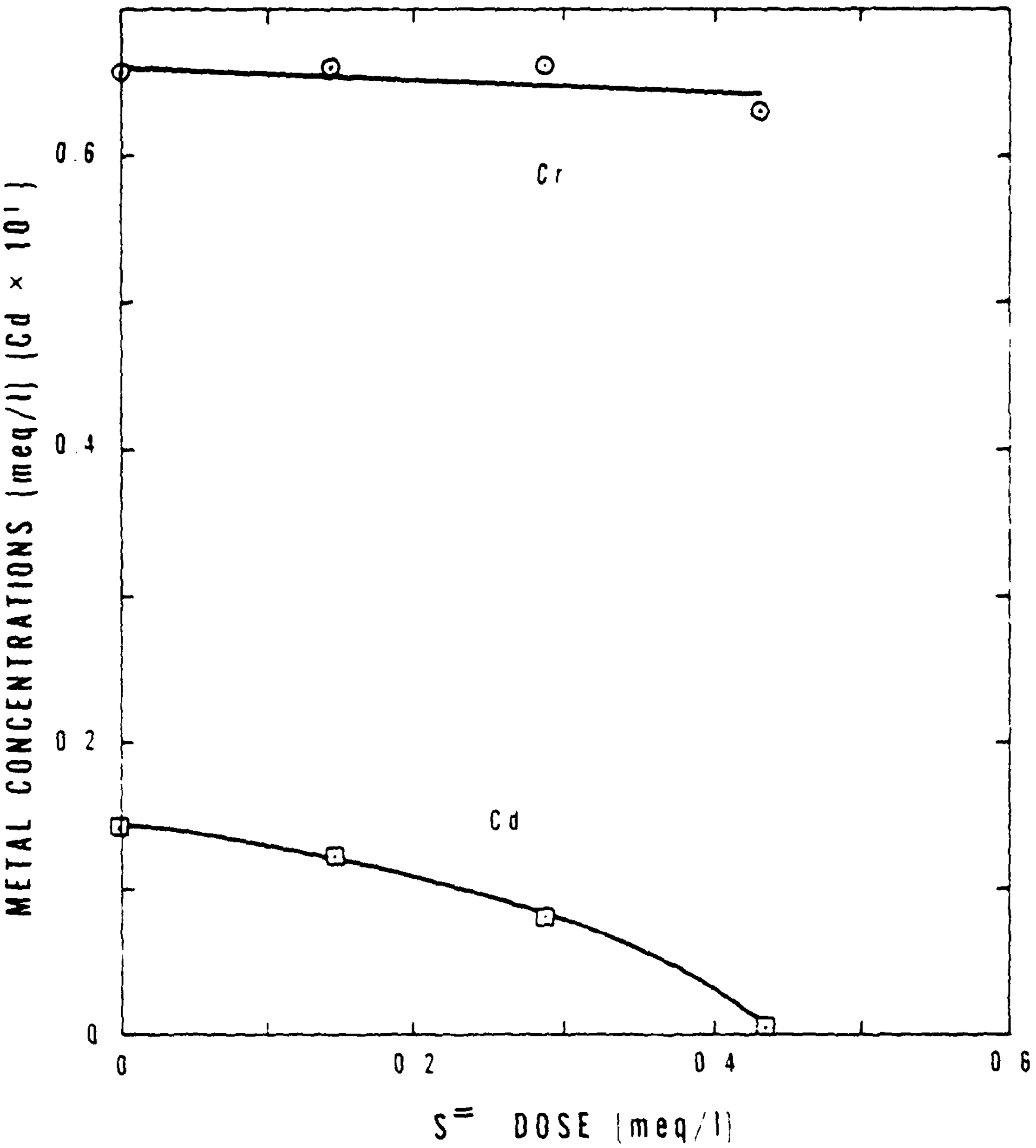

Figure 30. Cadmium and chromium removal by sodium sulfide in softened tap water at pH 8.5.

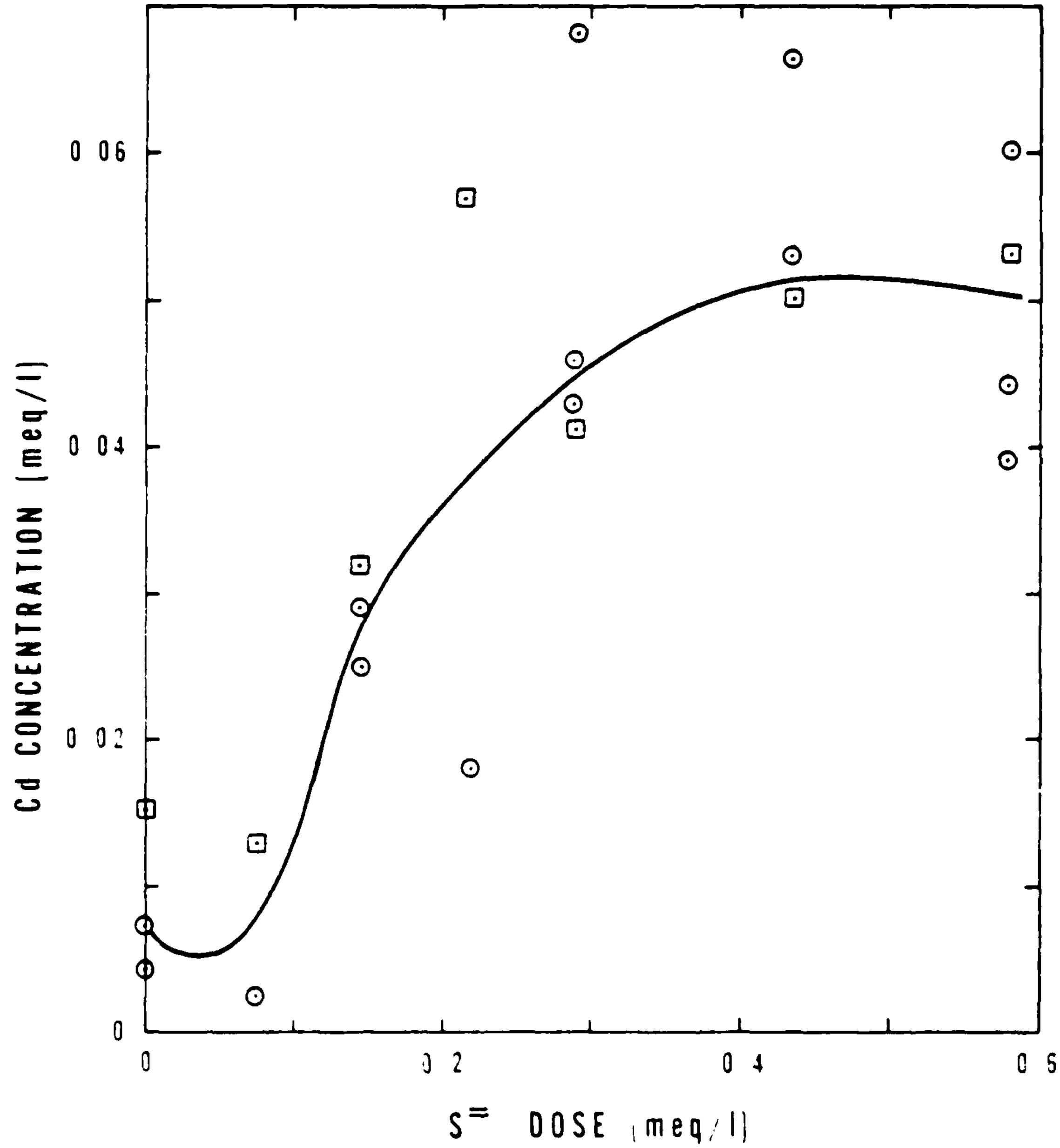

Figure 31. Cadmium removal by sodium sulfide in softened tap water at pH 10.

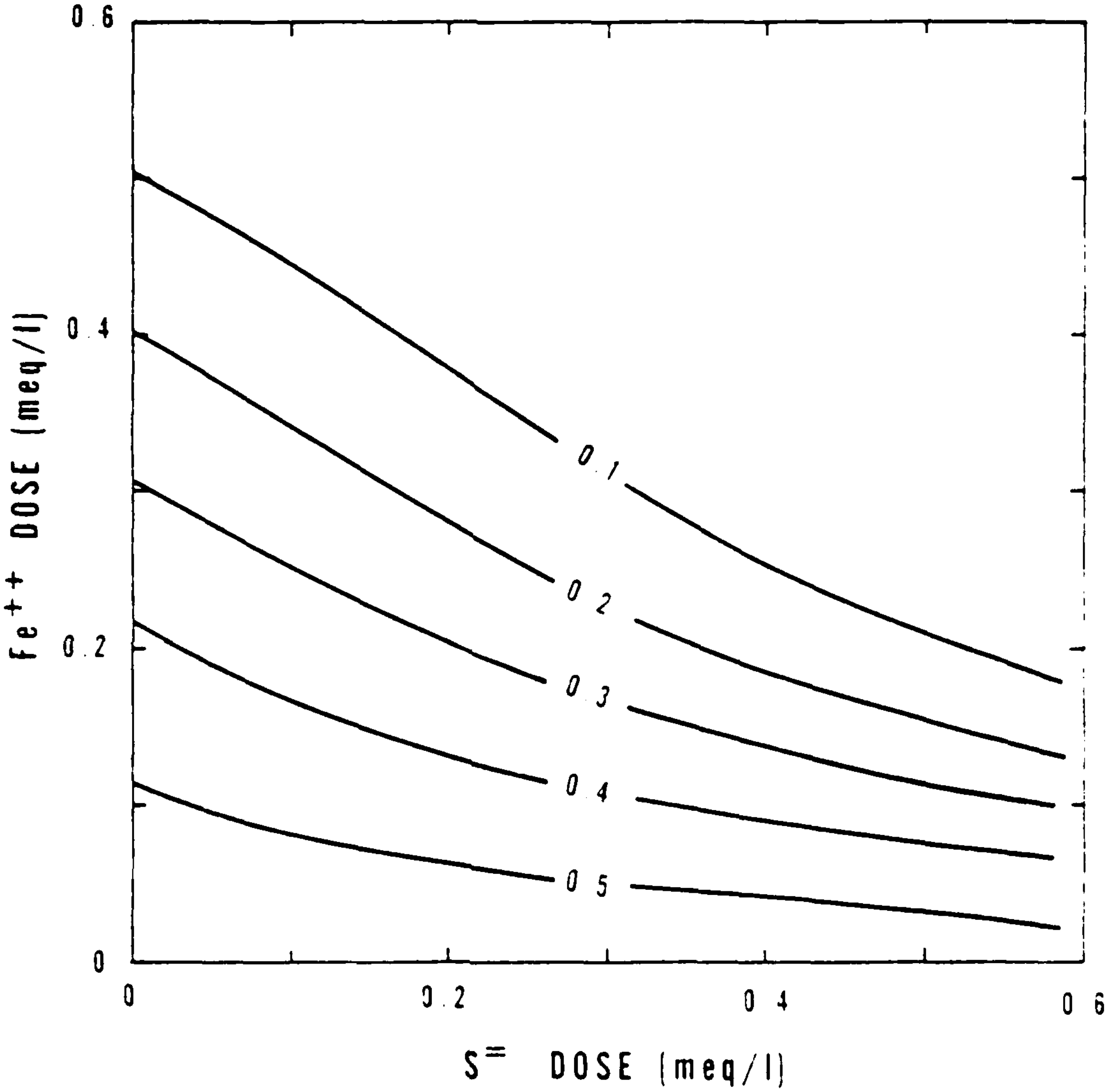

Figure 32. Isoequivalent chromium residuals (meq/l) for treatment of mixed metals in softened tap water at pH 8.5.

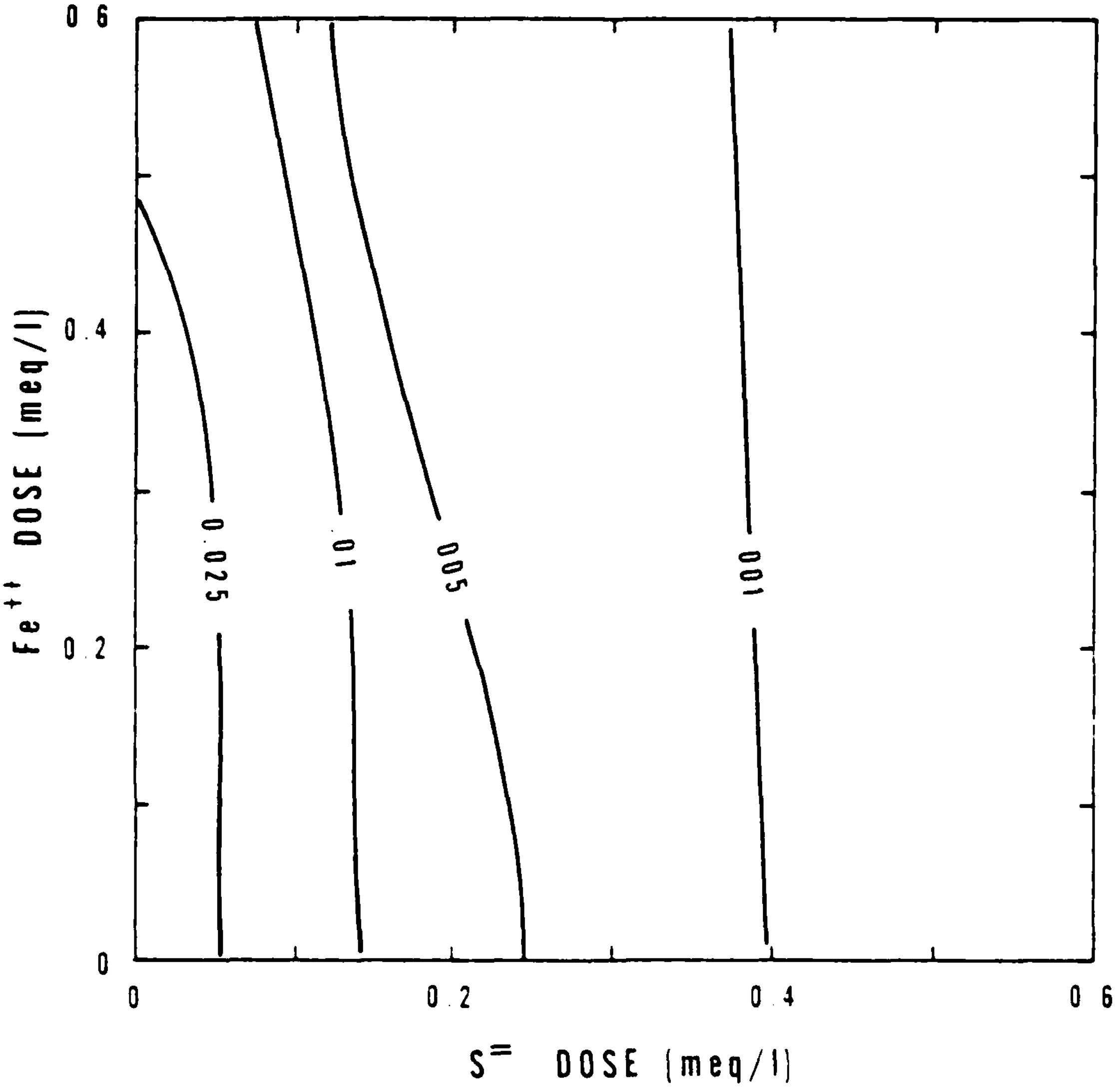

Figure 33. Isoequivalent cadmium residuals (meq/l) for treatment of mixed metals in softened tap water at pH 7.

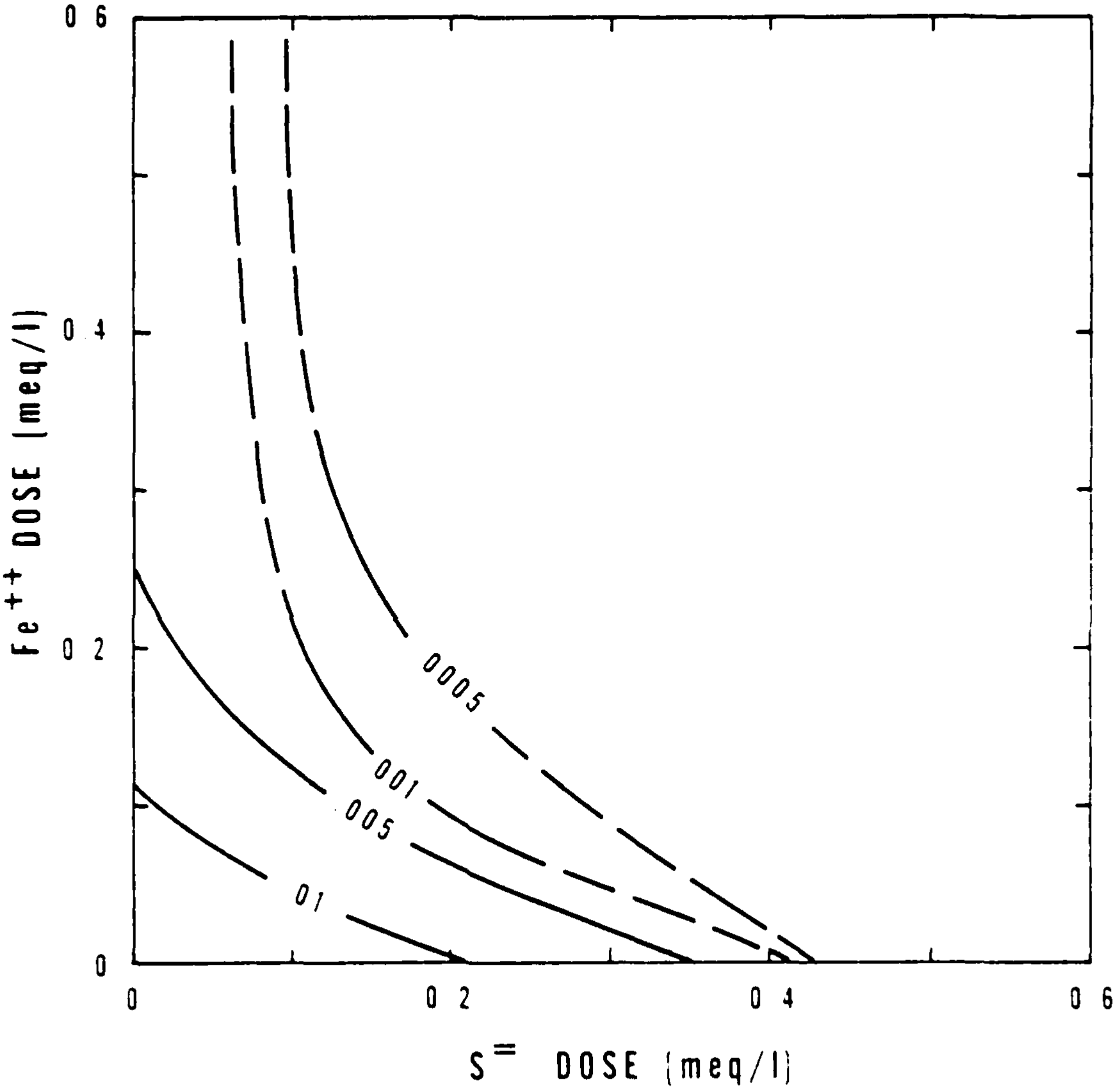

Figure 34. Isoequivalent cadmium residuals for treatment of mixed metals in softened tap water at pH 8.5.

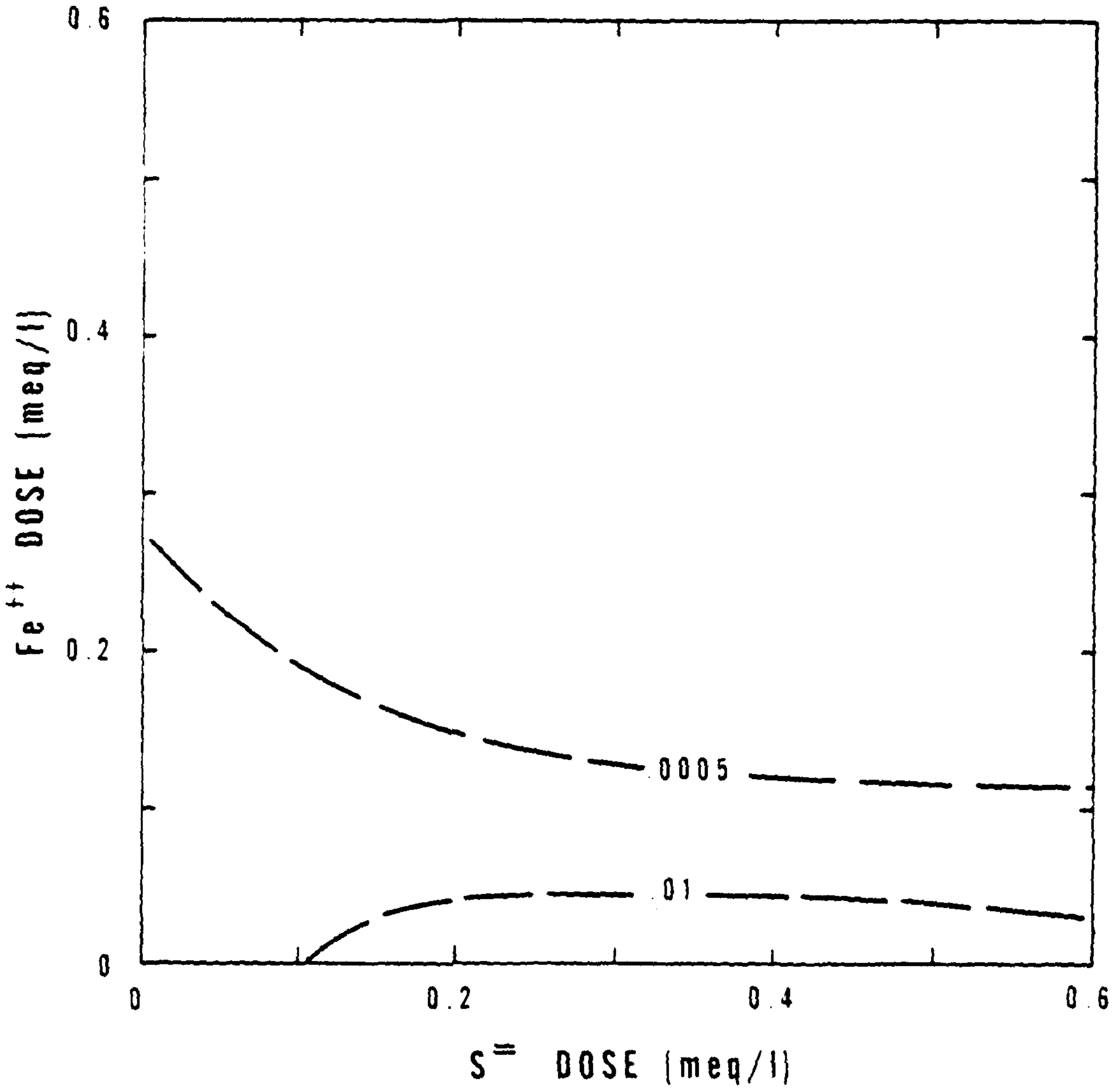

Figure 35. Isoequivalent cadmium residuals for treatment of mixed metals in softened tap water at pH 10.

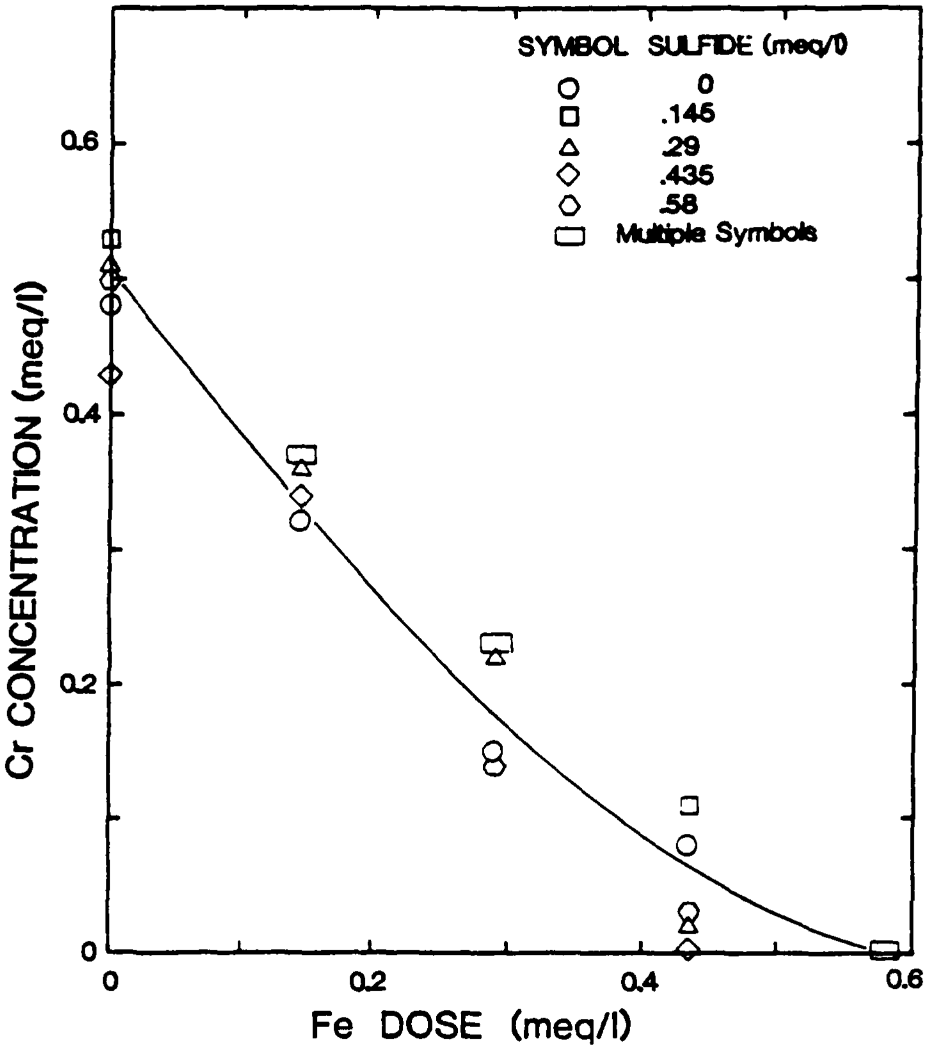

Figure 36. Chromium (0.58 meq/l) removal from a mixed metal waste at pH 8.5.

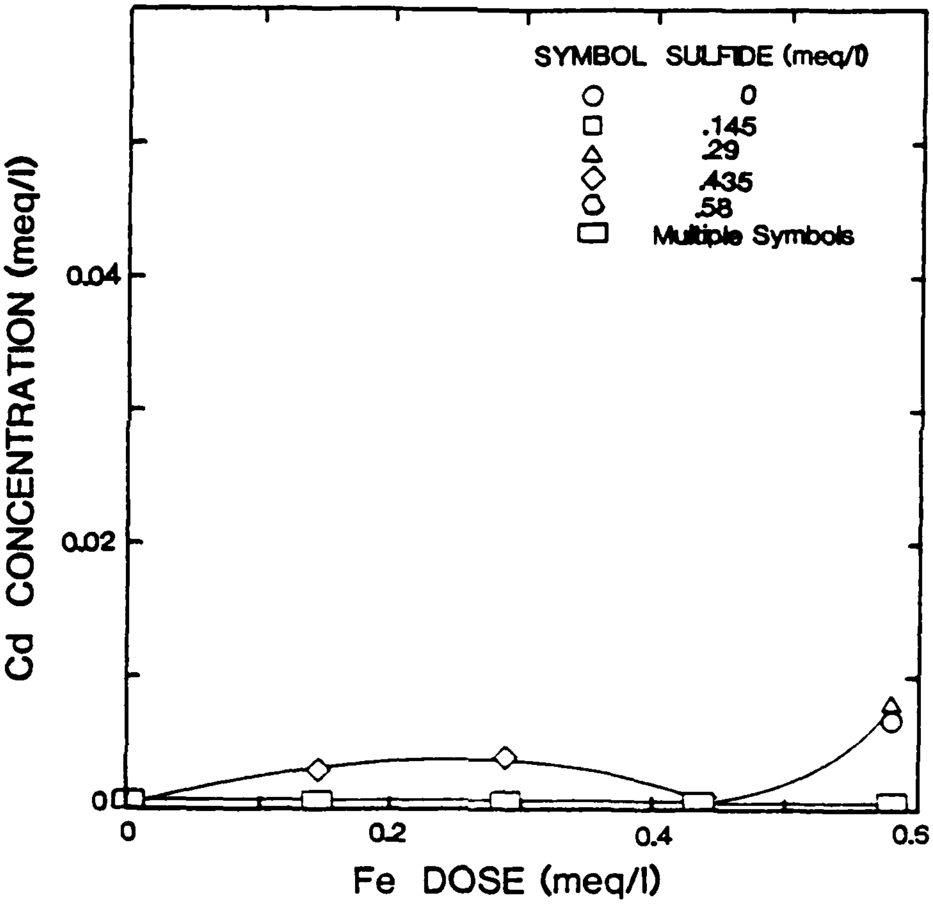

Figure 37. Cadmium (0.18 meq/l) removal from a mixed metal waste at pH 8.5.

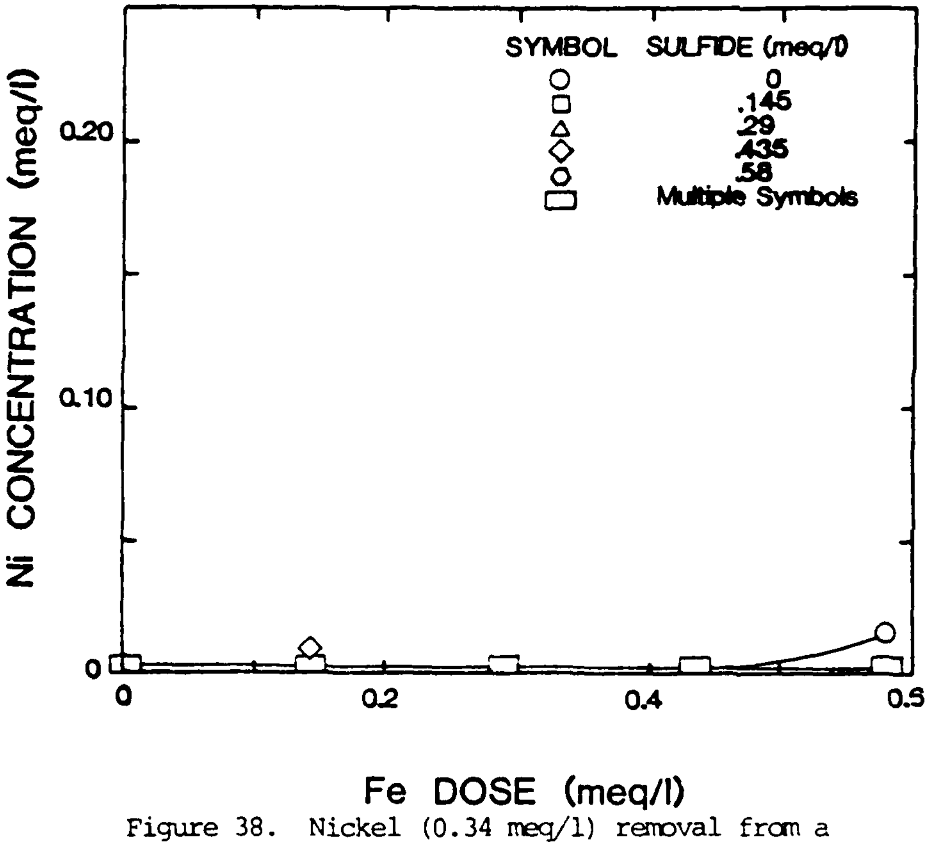

Figure 38. Nickel (0.34 meq/l) removal from a mixed metal waste at pH 8.5.

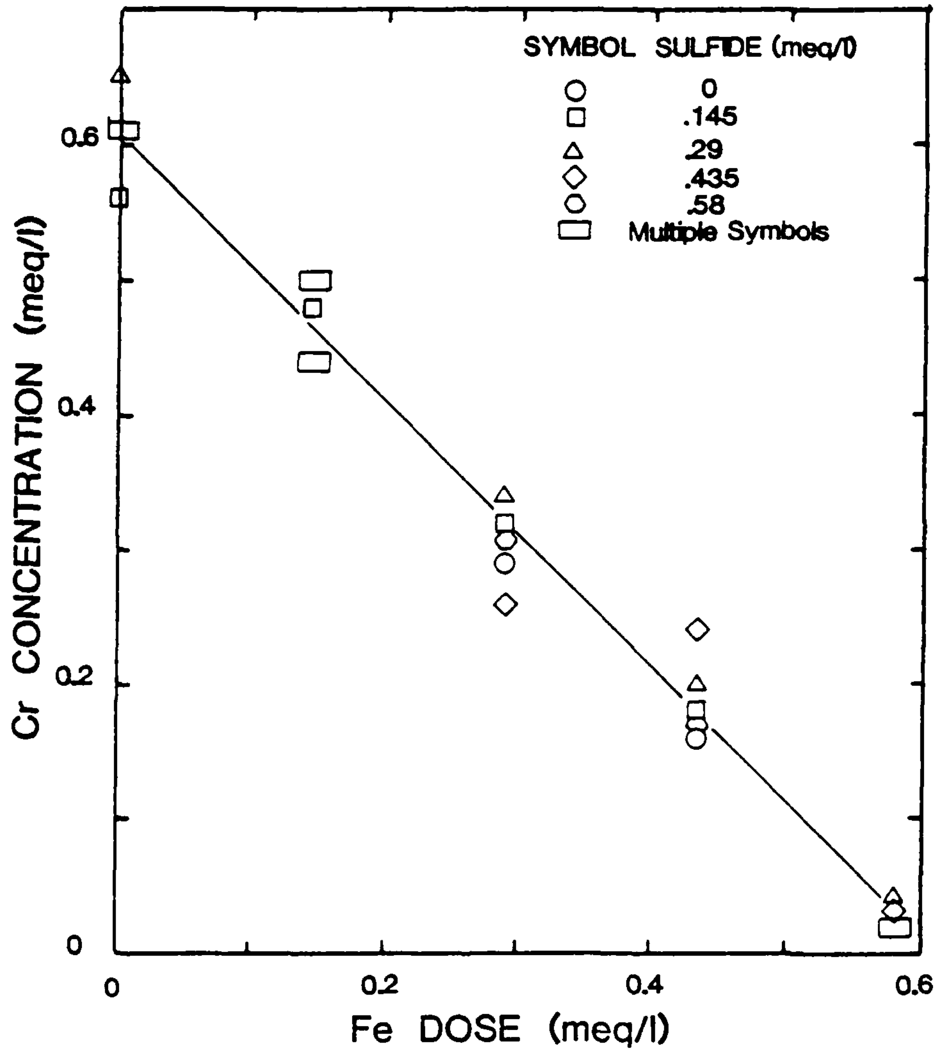

Figure 39. Chromium (0.58 meq/l) removal from a mixed metal waste in hard tap water at pH 8.5.

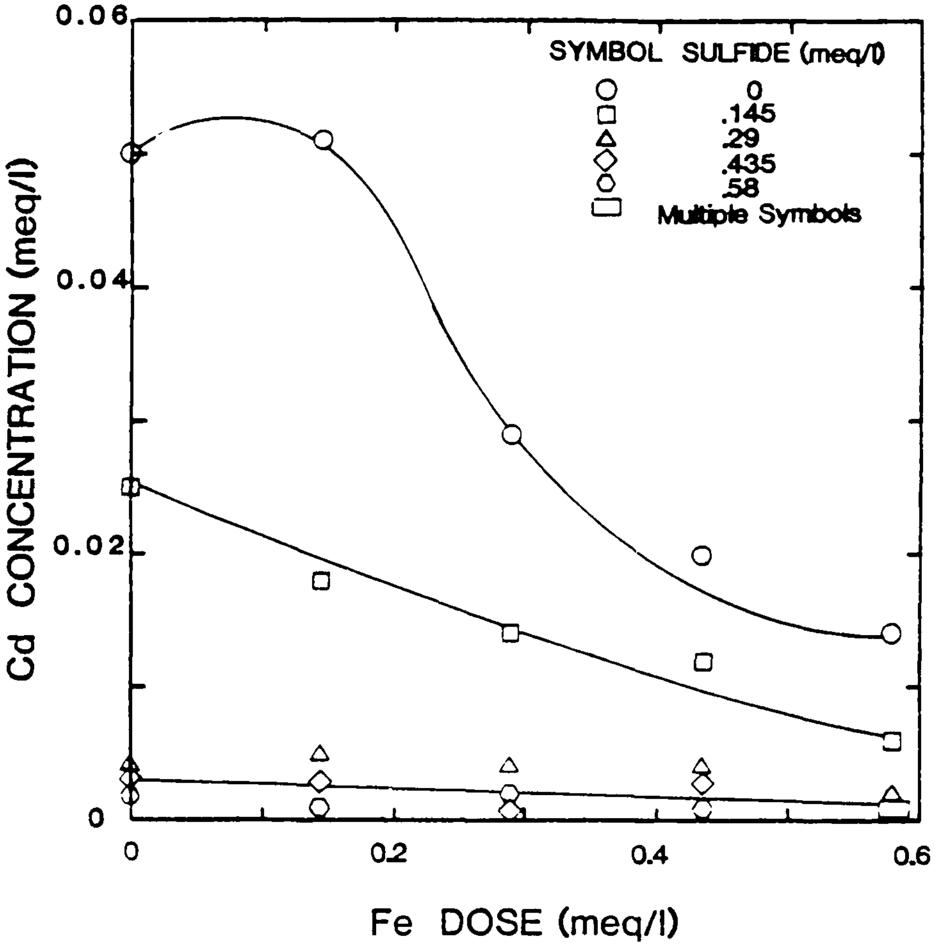

Figure 40. Cadmium (0.18 meq/l) removal from a mixed metal waste in hard tap water at pH 8.5.

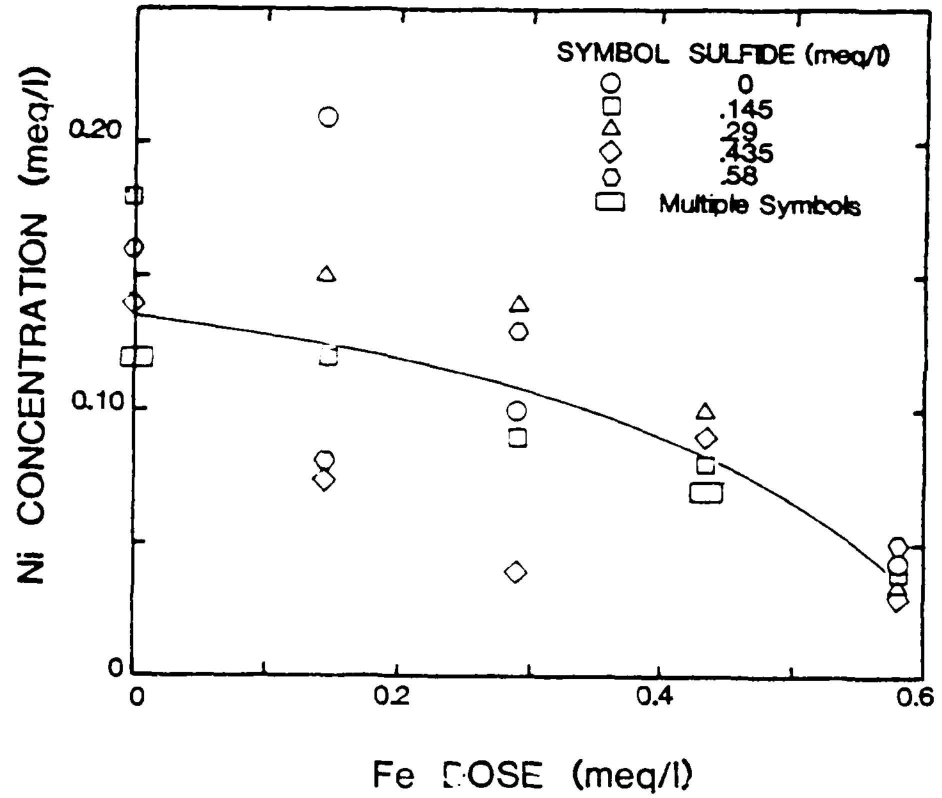

Figure 41. Nickel (0.39 meq/l) removal from a mixed metal waste in hard tap water at pH 8.5.

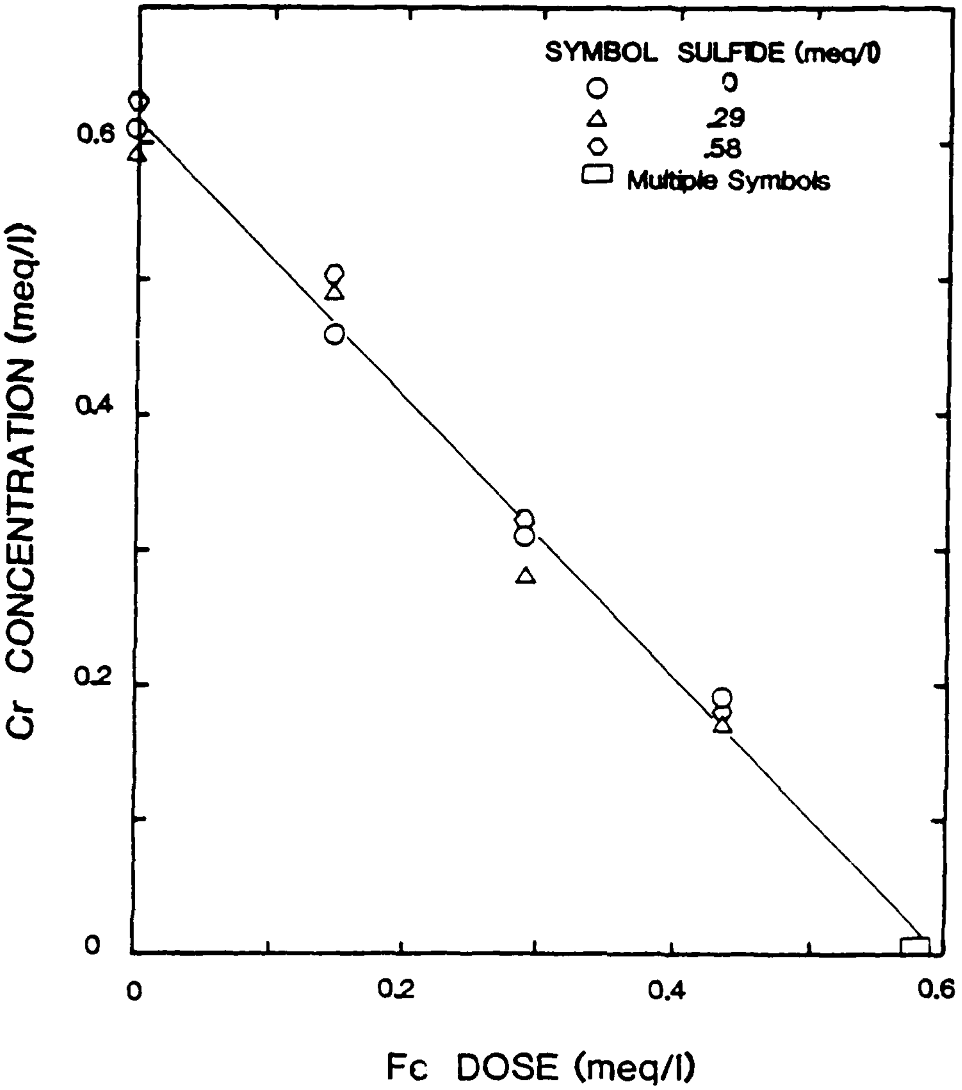

Figure 42. Chromium (0.58 meq/l) removal from a mixed metal waste in hard tap water ($Ca(OH)_2$) with pH adjusted to 8.5 with lime.

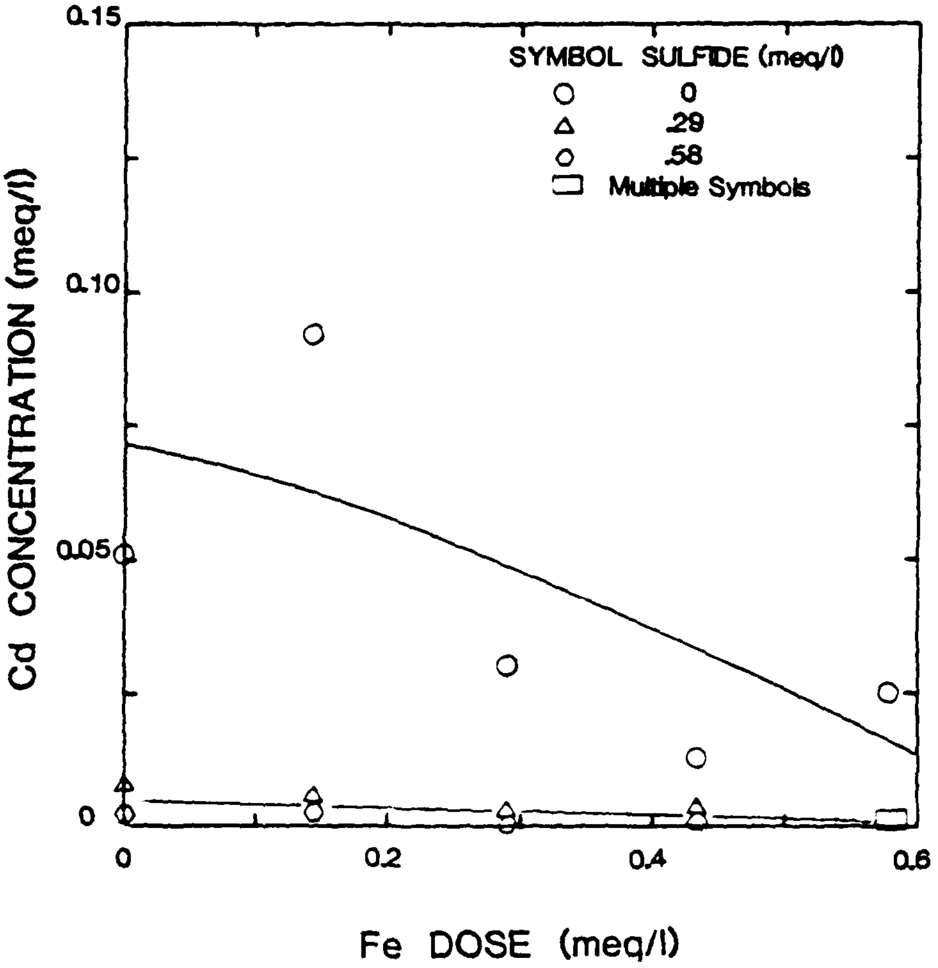

Figure 43. Cadmium (0.18 meq/l) removal from a mixed metal waste in hard tap water with pH adjusted to 8.5 with lime.

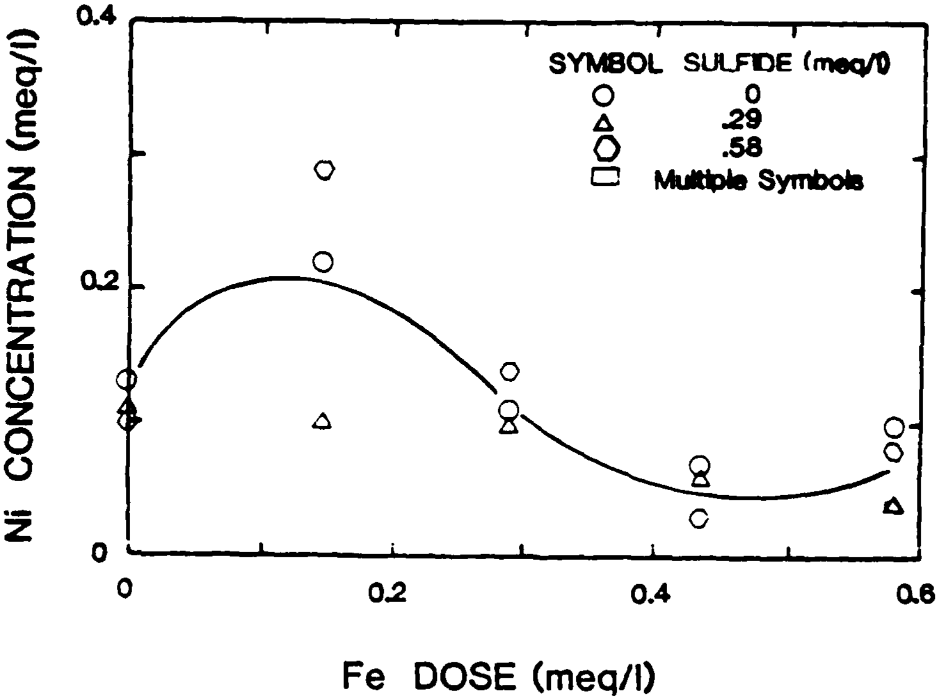

Figure 44. Nickel (0.39 meq/l) removal from a mixed metal waste in hard tap water with pH adjusted to 8.5 with lime.

Treatment of Plating Rinsewaters Plating bath rinsewaters were prepared by diluting plating solutions (from operating plating baths, Kelly Air Force Base, Texas), in distilled water and Tempe tap water (Figures 45,46). Ferrous iron effectively reduced and removed the hexavalent chromium. Sulfide addition benefitted treatment of the rinsewater prepared from distilled water, although it was more beneficial in tap water. There was no significant interference from anything in the plating solution to alkaline chromium reduction and removal by ferrous sulfate and sodium sulfide.

A mixture of plating baths, 10 mg/l each of chromium, cadmium and nickel, were prepared in distilled water to simulate plating rinsewaters that might be found in Air Force shops.

Chromium was removed stoichiometrically by ferrous sulfate (Figure 47). The chromium residual for stoichiometric dose of ferrous sulfate was less than 0.05 mg/l. The complexing agents normally found in these plating baths did not interfere with chromium reduction or removal.

Cadmium was considerably more soluble in the plating bath wastewater (Figure 48) than in synthetic wastes produced from metal salts (Figure 37). This is probably due to the presence of complexing agents in the plating bath formulations. Addition of ferrous sulfate alone resulted in some cadmium removal, probably due to competition by the iron for the complexing agents in the plating baths releasing cadmium to precipitate as a hydroxide. In combination, the sulfide probably broke the complex, precipitated the cadmium and the iron coagulated the resulting colloidal precipitates. Residual cadmium was reduced to less than 0.05 mg/l by treatment. Nickel was essentially unaffected by treatment (Figure 49). Nickel sulfide is considerably more soluble than cadmium sulfide. Unlike cadmium, sulfide is unable to break the nickel complex in the plating formulation.

Treatment of mixed plating solutions diluted in tap water resulted in the familiar chromium removal by ferrous sulfate with sulfide providing some improvement (Figure 50). Residual concentrations of chromium for stoichiometric doses of ferrous sulfate are less than 0.05 mg/l. Cadmium remains soluble at this pH, due probably to the complexing agents in the plating baths (Figure 51). Ferrous sulfate provides some removal, probably due to the competition mechanism mentioned previously. Sulfide reduces the concentration to less than 0.01 mg/l. The removal pathway is probably precipitation of cadmium sulfide followed by coagulation by the hardness present in the tap water.

Nickel removal was negligible (Figure 52).

Adjustment of pH by lime provided slight improvement in chromium removal from a mixed plating waste diluted in tap water (Figure 53). Cadmium and nickel removal were unaffected by use of lime rather than sodium hydroxide for pH adjustment (Figures 54 and 55).

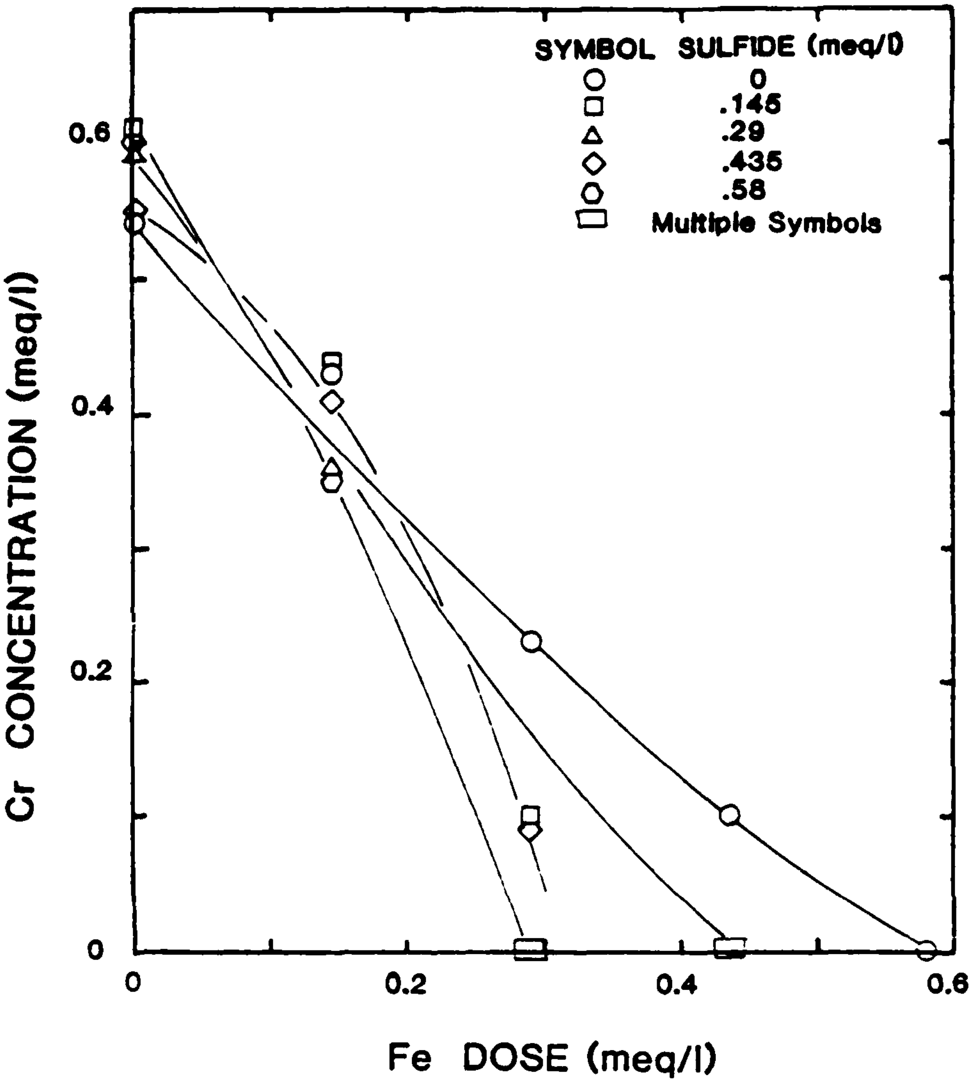

Figure 45. Chromium (0.58 meq/l) removal from a chromium plating waste in distilled water at pH 8.5.

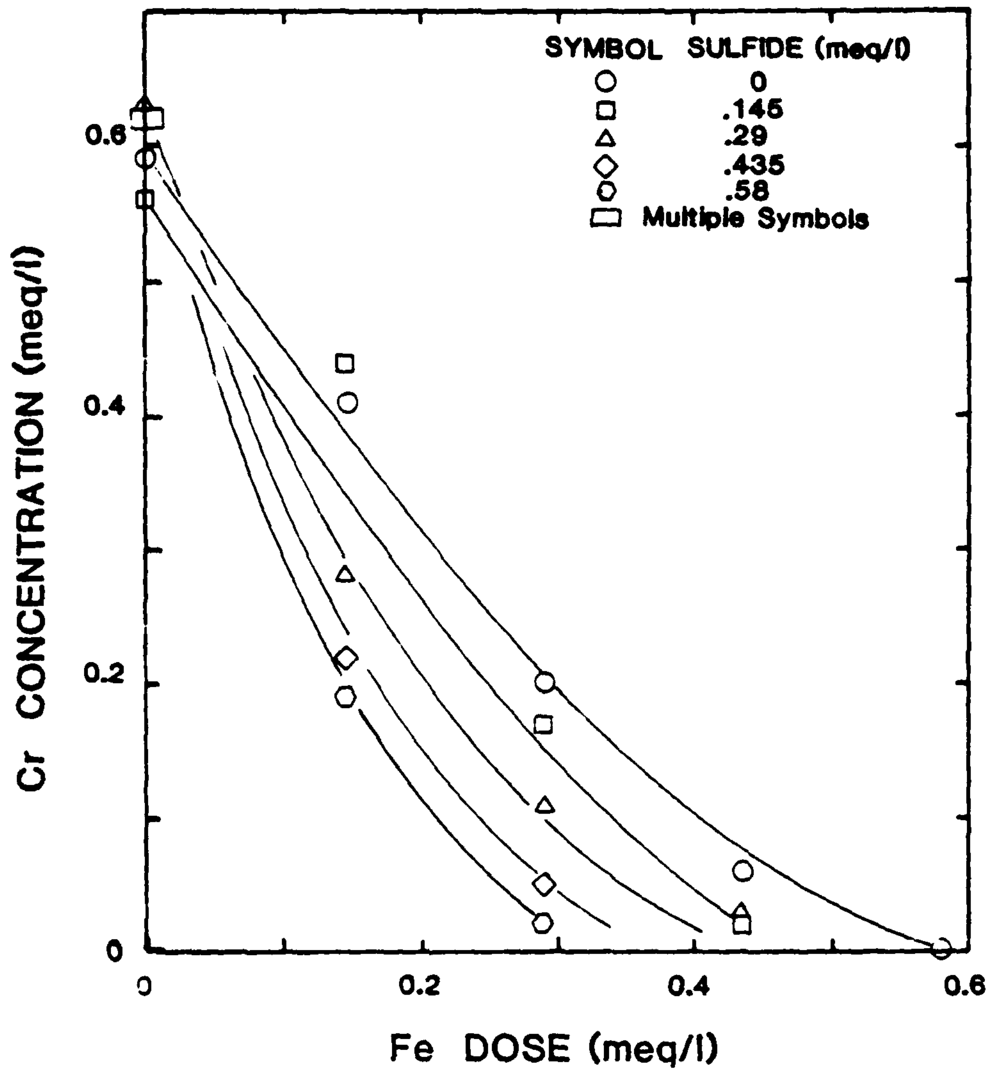

Figure 46. Chromium (0.58 meq/l) removal from a chromium plating waste in hard tap water at pH 8.5.

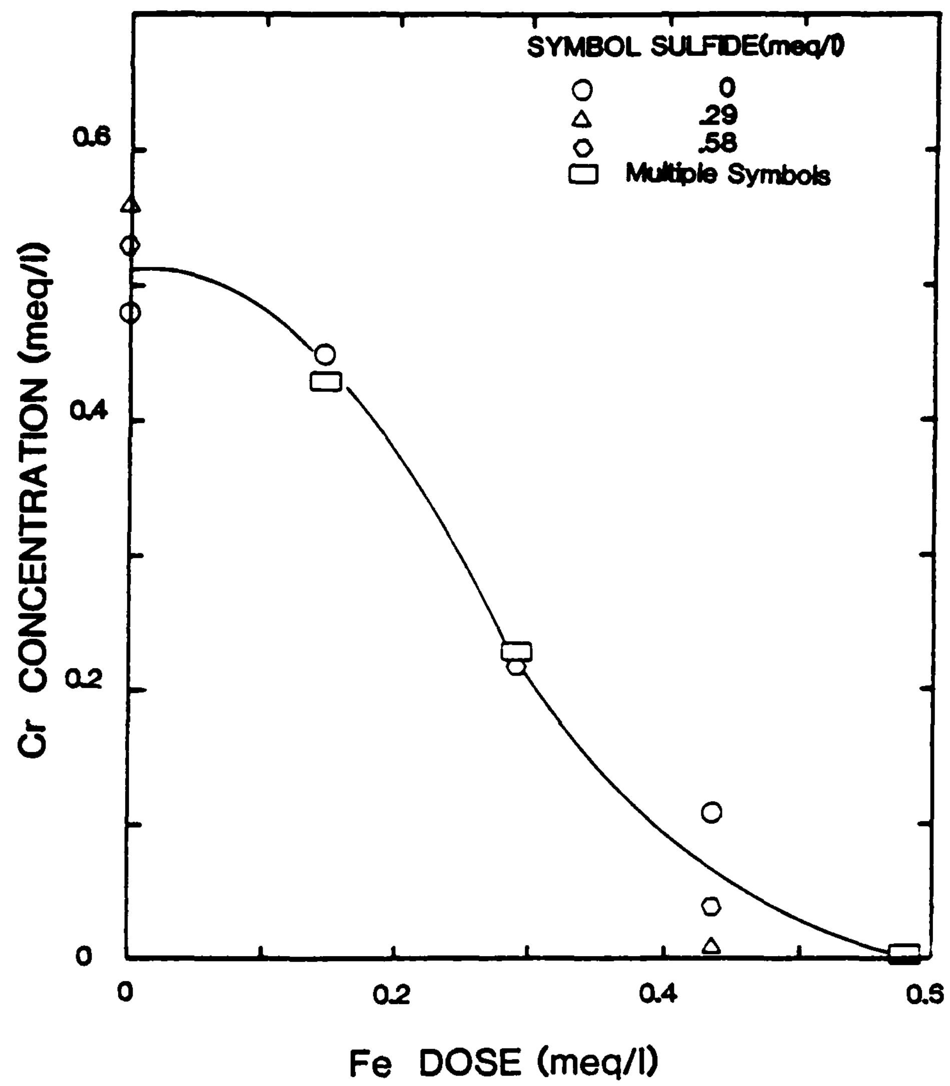

Figure 47. Chromium (0.58 meq/l) removal from a mixed metal plating waste in distilled water at pH 8.5.

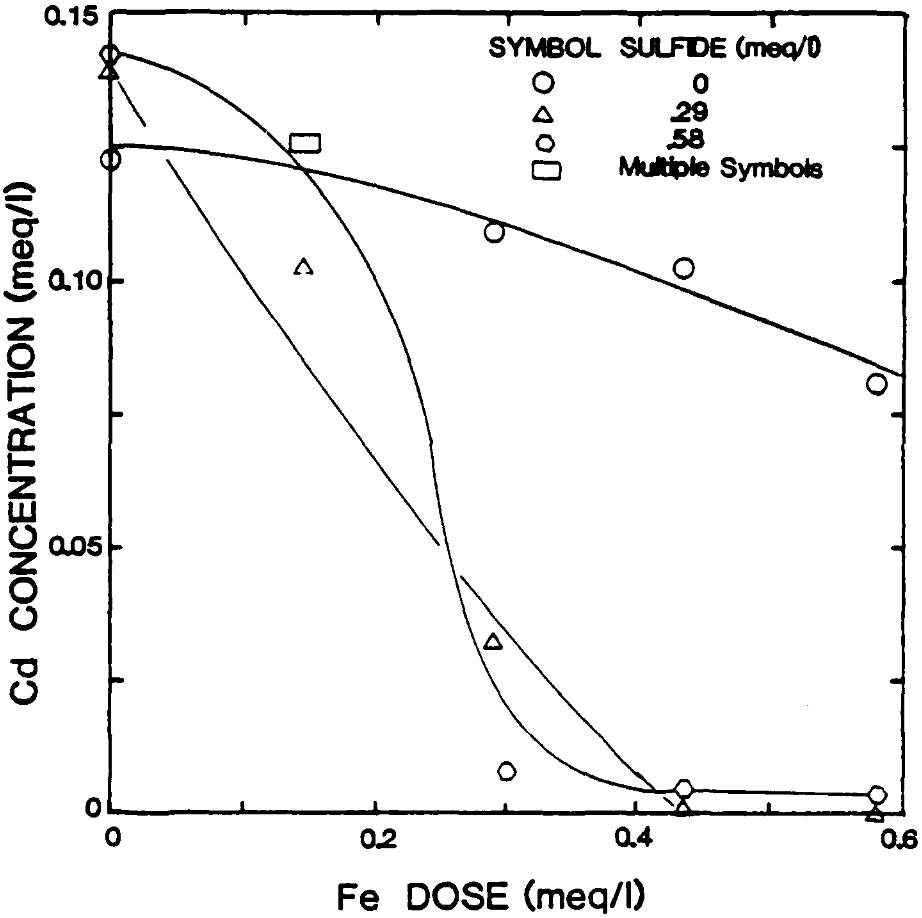

Figure 48. Cadmium (0.18 meq/l) removal from a mixed metal plating waste in distilled water at pH 8.5.

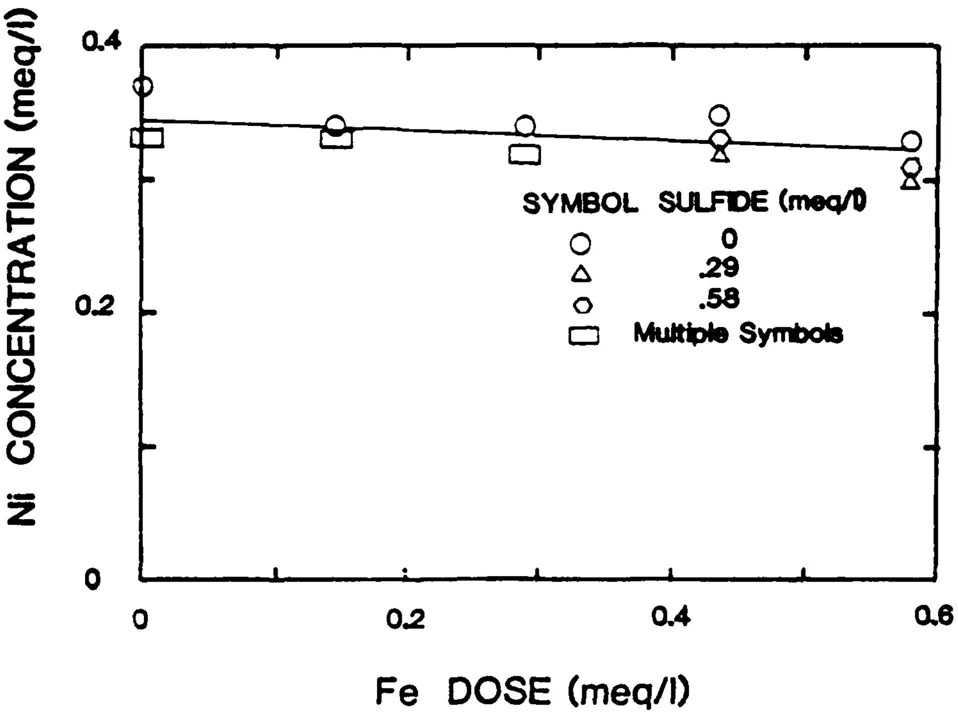

Figure 49. Nickel (0.39 meq/l) removal from a mixed metal plating waste in distilled water at pH 8.5.

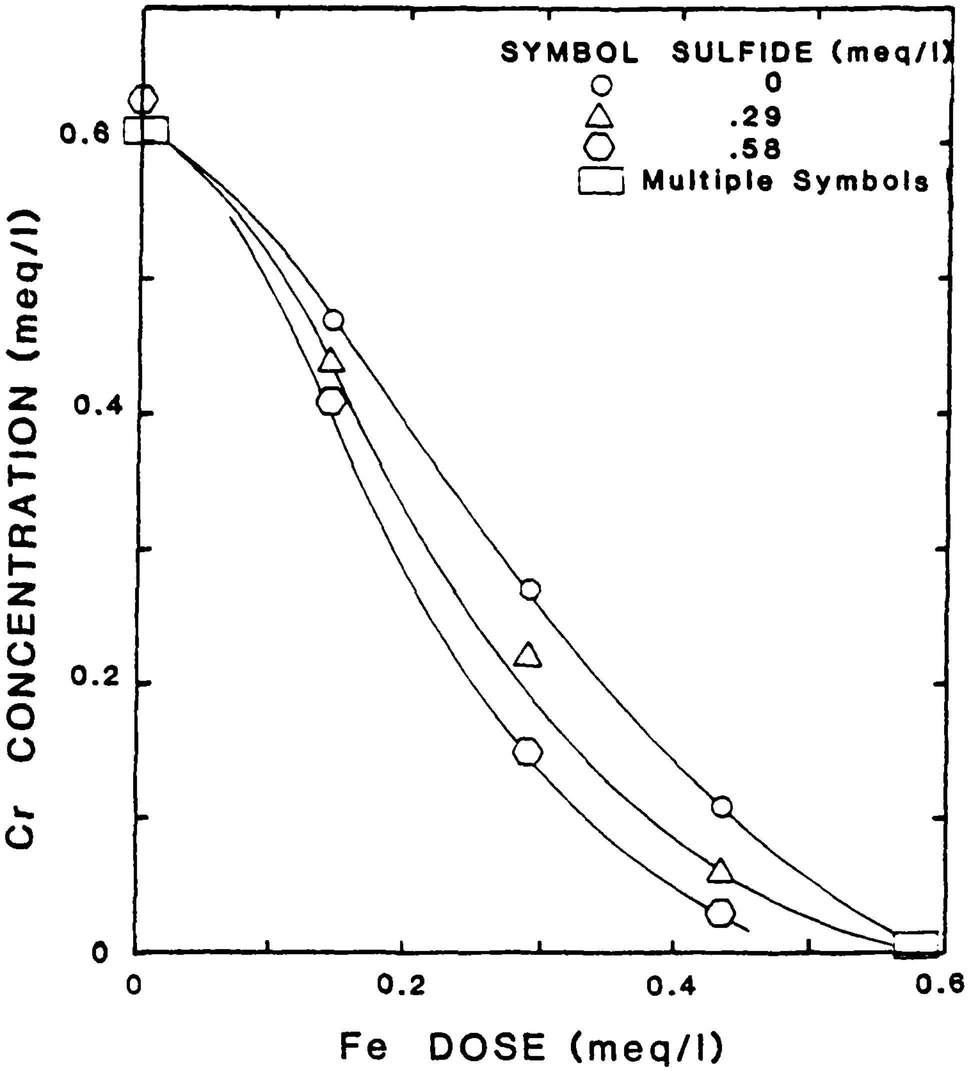

Figure 50. Chromium (0.58 meq/l) removal from a mixed metal plating waste in hard tap water at pH 8.5.

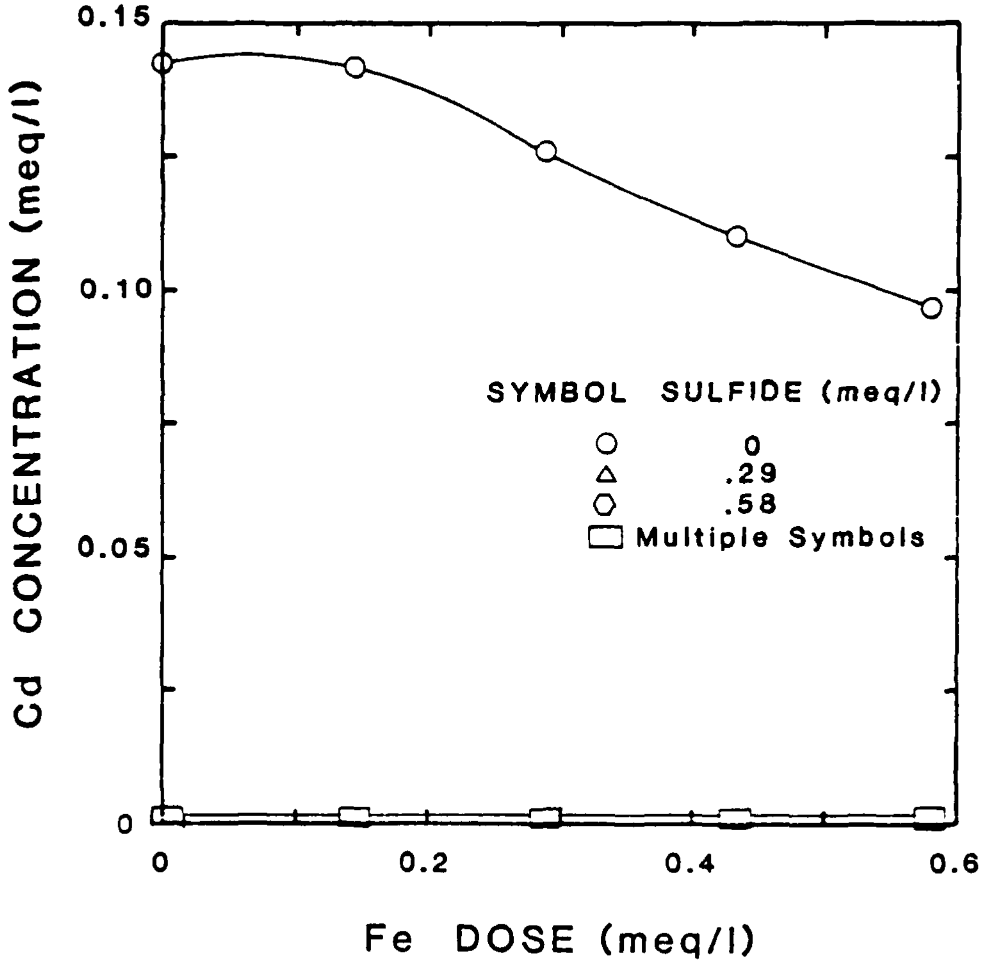

Figure 51. Cadmium (0.18 meq/l) removal from a mixed metal plating waste in hard tap water at pH 8.5.

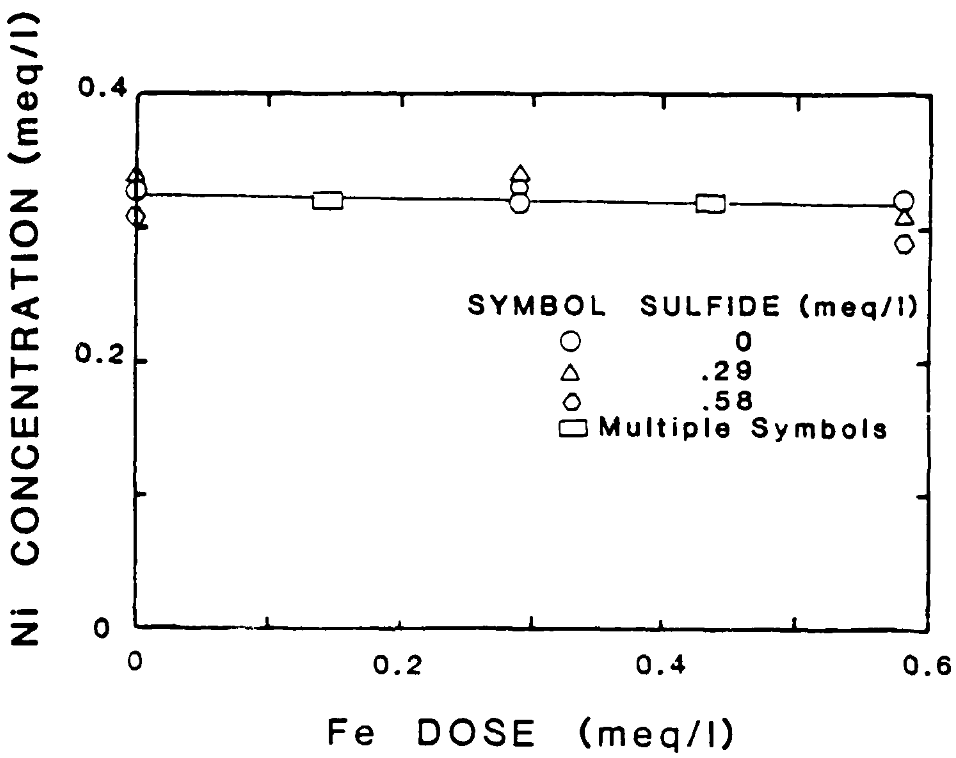

Figure 52. Nickel (0.39 meq/l) removal from a mixed metal plating waste in hard tap water at pH 8.5.

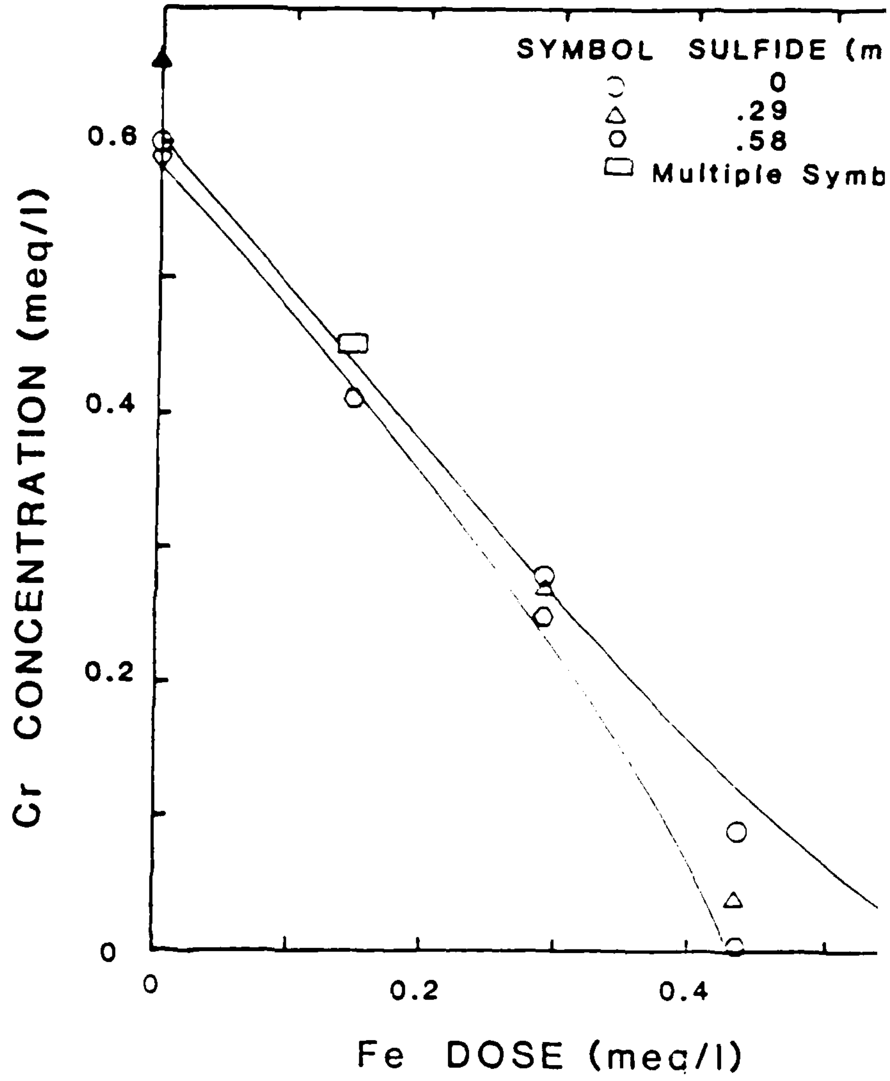

Figure 53. Chromium (0.58 meq/l) removal from
metal plating waste in hard tap wat
pH adjusted to 8.5 with lime.

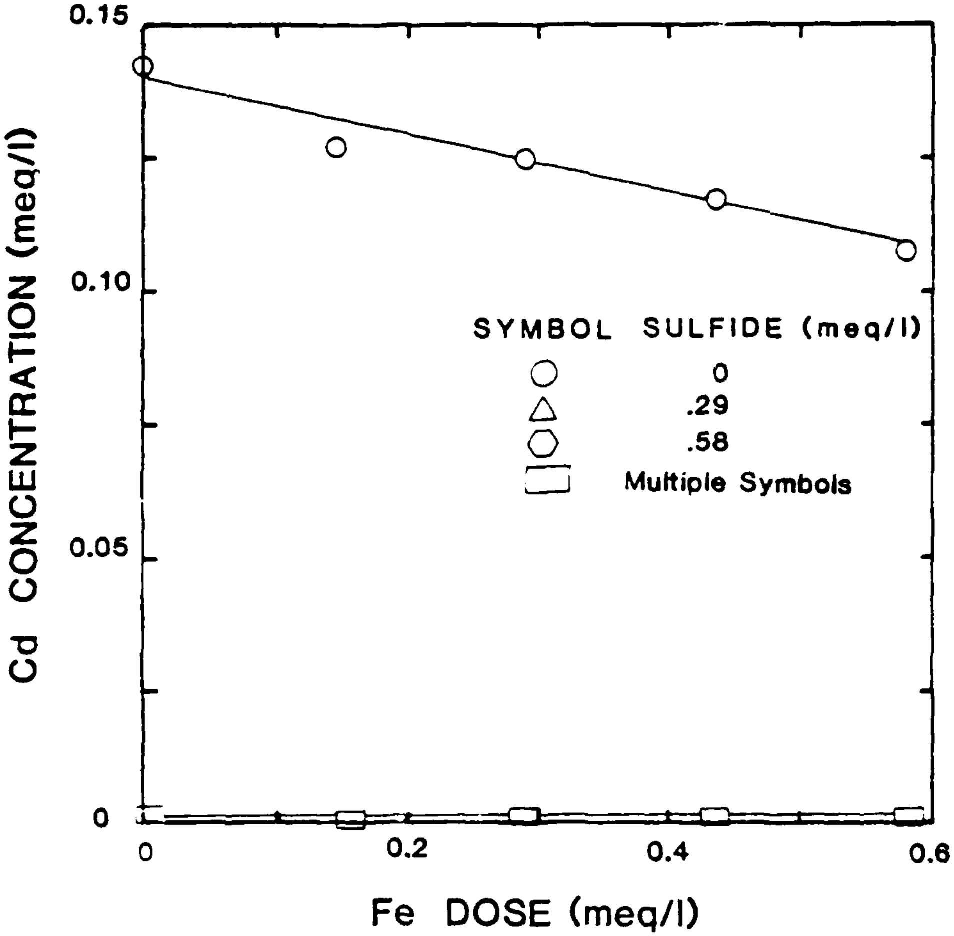

Figure 54. Cadmium (0.18 meq/l) removal from a mixed metal plating waste in hard tap water with pH adjusted to 8.5 with lime.

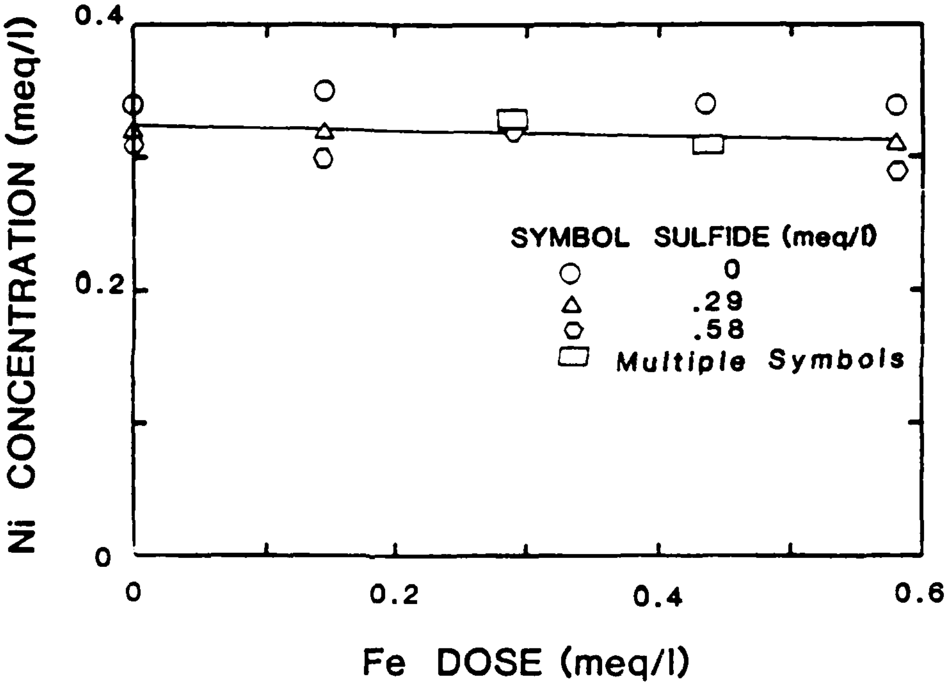

Figure 55. Nickel (0.39 meq/l) removal from a mixed metal plating waste in hard tap water with pH adjusted to 8.5 with lime.

Continuous Flow Studies Limited studies were performed on a continuous flow treatment system. Synthetic wastewaters were prepared in Tyndall Tap water.

The results of selected continuous flow runs are presented in Table 4. Sodium sulfide and ferric sulfate effectively removed cadmium at pH 9.4 (run 1). Head loss is low with a resulting long filter run. Chromium (VI) reduction and removal was not accomplished with ferric iron and sulfide addition at pH's at or above 7.

Runs 2 through 5 consisted of treatment of chromium (VI) and cadmium containing wastewater with ferrous sulfate and sodium sulfide. Figure 56 depicts variations in effluent concentrations and head loss during filter run 4. Manual pH adjustment of the low alkaline water resulted in large fluctuations in the beginning. Metal removal was constant despite pH fluctuations. Head loss climbed steadily to breakthrough. In other runs where high doses of ferrous iron was used relative to sulfide (runs 2,3), floc sizes were increased, removal took place near the entrance of the filter, better removal was effected, but head losses were higher and time to breakthrough was reduced. Breakthrough was by lifting of the filter sand from the bottom. Increasing the sulfide and lowering the ferrous dose (run 5) resulted in lower head losses, but increased floc penetration in the filter and chromium carry over to the effluent. Filter run times were not greatly increased because breakthrough resulted from lifting of the plugged fine sands at the surface of the bed.

Backwashing was accomplished by increasing the flow up through the bed, producing a concentrated sludge with minimal water usage.

TABLE 4

Operating Conditions and Results for Continuous Flow Treatment System

Run Number	1	2	3	4	5
Initial Cd (mg/l)	4.0	-	4.0	10.0	5.0
(meq/l)	0.07	-	0.07	0.18	0.09
Initial Cr (mg/l)	-	10.0	10.0	10.0	10.0
(meq/l)	-	0.58	0.58	0.58	0.58
Na_2 S Dose (mg/l)	5.5	5.5	10.5	13.6	19.5
(meq/l)	0.14	0.14	0.27	0.35	0.50
Fe SO_4 Dose (mgFe/l)	-	53	40	20	14
(meq/l)	-	0.95	0.72	0.35	0.25
$Fe_2(SO_4)_3$ Dose (mg/Fe/l)	5	-	-	-	-
(meq/l)	0.24	-	-	-	-
Filter Rate (gal/ft_2-min)	4	4	4	4	4
Effluent at 2 Hours					
Cd (mg/l)	0.04	-	<0.01	<0.02	<0.04
(meq/l)	0.0007	-	<0.0002	<0.0004	<0.0007
Cr (mg/l)	-	<0.05	<0.05	1.9	<0.05
(meq/l)	-	<0.003	<0.003	0.11	<0.003
pH	9.4	9.1	8.5	8.5	7.5
Head Loss (ft) at 2 hrs	1.5	6.5	5.4	2.5	2.4
at breakthrough	3.6	6.7	6.5	4.0	2.7
Time to Breakthrough (hours)	9	2.1	2.5	3.5	2.5

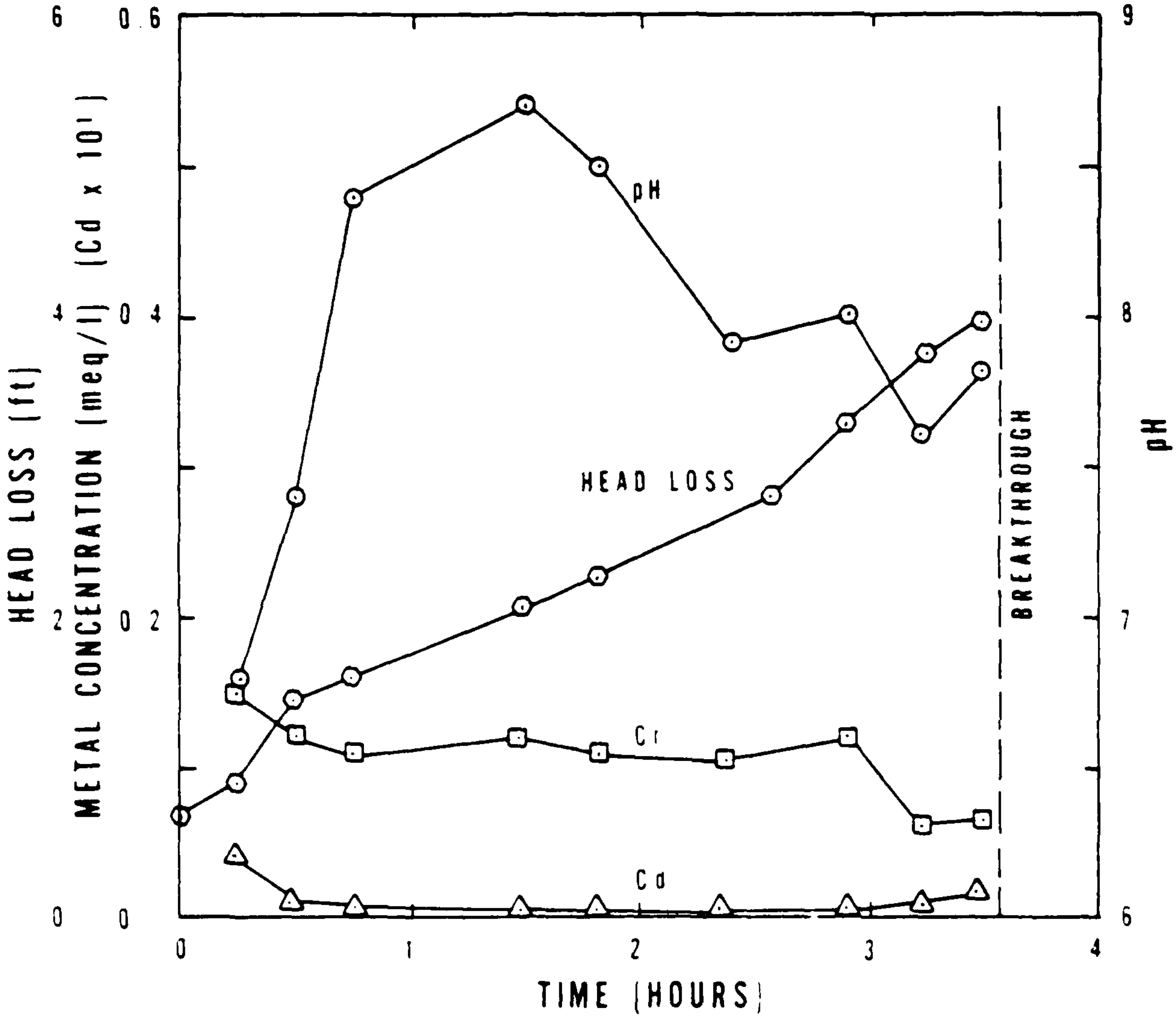

Figure 56. Treatment of mixed metal wastewater by ferrous and sulfide and upflow filtration.

CONCLUSIONS

1 Hexavalent chromium can be rapidly and stoichiometrically reduced by ferrous sulfate at alkaline pH (7-10).

2 Sodium sulfide alone was ineffective as a reducing agent for hexavalent chromium at alkaline pH.

3 In combination with ferrous sulfate, sodium sulfide aided in chromium reduction at alkaline pH, replacing ferrous sulfate. Ferrous iron seemed to act as a necessary catalyst for this reduction.

4 Alkalinity, EDTA, and cyanide interfered with chromium reduction, floc formation, and removal by ferrous sulfate and sodium sulfide.

5 Calcium hardness counteracted these interferences. Use of lime for pH adjustment would probably be preferable to soda ash.

6 Chromium reduction and removal by ferrous sulfate and sodium sulfide was virtually identical for wastes prepared in distilled water, in a softened, low-alkaline tap water and a hard, alkaline tap water; however treatment of hard water resulted in larger, better settling floc.

7 Cadmium was effectively precipitated by sulfide at pH 7-10, although doses greater than 4 times stoichiometric were required. Overdosing at pH 10 increased cadmium solubility. These problems were eliminated by the addition of ferrous sulfate.

8 Treatment in a mixture of cadmium and nickel had no noticeable effect on chromium removal. In distilled water, cadmium and nickel were effectively removed by hydroxide precipitation at pH 8.5. In a hard, alkaline tap water, cadmium and nickel were largely soluble at pH 8.5, probably due to inorganic complexation. Ferrous addition aided in cadmium removal, probably due to competition for the effective complexing agent. Sulfide effectively precipitated the cadmium, but not the nickel, probably due to the appreciably lower solubility of cadmium sulfide compared to nickel sulfide. Adjustment of pH with lime (rather than sodium hydroxide) improved floc size and settling, but had little effect on metal removal.

9 Treatment of plating rinsewaters prepared from plating bath solutions in both distilled and tap waters demonstrated a lack of significant interferences to alkaline chromium reduction by ferrous sulfate and sodium sulfide. Cadmium was not removed by hydroxide precipitation, even in distilled water, probably due to complexation with constituents in the plating baths. Ferrous sulfate improved cadmium removal, probably due to competition for the complexing agents. Sulfide precipitation was sufficient to break these complexes. Ferrous sulfate was required to coagulate the sulfide precipitate in distilled water. In hard tap water, hardness cations provided sufficient coagulation. Nickel was not removed by treatment of the mixed plating bath waste, apparently due to the high solubilities of nickel hydroxide and sulfide.

10 Upflow filtration in conjunction with direct addition of ferrous sulfate and sodium sulfide effectively removed a mixture of hexavalent chromium and cadmium from solution. The system provides a single step (unit process) treatment of mixed metal wastewater. However, additional work is needed to optimize chemical addition and filter media to increase length of filter runs.

ONGOING RESEARCH

Objectives The objective of future research is to develop and test a pilot plant incorporating alkaline ferrous reduction of hexavalent chromium, metal sulfide precipitation and solids separation processes. Individual work areas have been identified as:

A. Investigate effects of chemical dosages on solids removal characteristics (floc size) of metal precipitates.

B. Improve run times in upflow filtration of metal precipitates by:

   1. including pre-sedimentation without intermediate pumping prior to filtration (can cause floc breakup);

   2. improve depth and size characteristics of media used in upflow filters.

C. Develop control methods to pace chemical addition to variations in waste flow rate, metal concentrations pH, and alkalinity.

D. Plan, design and construct pilot plant.

E. Test pilot plant on synthetic wastewaters, making modifications as necessary.

Proposed Process Development These findings are substantially based on batch studies using membrane filtration for solids separation. While these results compared favorably with results using upflow filtration, it is proposed that a pilot plant be developed, incorporating alkaline ferrous reduction of hexavalent chromium, sulfide precipitation of metals and iron coagulation for possible use by small Air Force electroplating facilities. The treatment objective would be to produce an effluent of higher quality than conventional metal hydroxide precipitation and to do so with a compact treatment process (elimination of the separate acidic reduction step, and possible use of upflow filtration). Direct upflow filtration produced an effluent with low concentrations of metals, but resulted in short filter runs. Work needs to be done to extend filter runs by such modifications as increasing filter depth, varying filter sand effective size and uniformity, or by providing sedimentation prior to filtration.

Instrumentation and Control Because of the importance of pH and concentrations of the sulfide and ferrous ions on the proper operation of the process, these variables should be constantly monitored and controlled.

The initial phase of this portion of the research will be a study of the currently available instrumentation which would permit continuous monitoring of the variables mentioned above. (A suitable reference is the "Survey of the Instrumentation for Environmental Monitoring" put out annually by the Lawrence Berkeley Laboratory). Cost, sensitivity, suitability for use in a production environment, and response time would all be factors to be considered.

The next phase will be directed to a study of the process itself in terms of developing models based on expected operating parameters such as waste stream flow rates, levels of ions, etc. Such a model would lead to a decision as to whether the process scheme should be continuous or perhaps run as a batch system. For low volume effluents, the batch process would generally be preferred while a continuous process is usually optimal for processing large volumes from continuous plating operations.

Once the processing scheme is established for the laboratory scale prototype, the attention will be directed toward the design and implementation of a control system which will allow setting and maintaining desired process conditions such as the feed flow rate, pH, etc. Two different control strategies, feedforward and feedback, will be examined. In feedback control, the most commonly used, the end result is measured and compared to a desired value and then some action is taken to modify an input to the process to bring this output to the desired level. An example would be the monitoring of the sulfide ion concentration in the reactor and based on the difference between the actual value and the desired, the flow rate of sulfide solution added to the reactor would be adjusted. Feedforward control makes use of a measurement of an input to the process; for example, the concentration of the nickel ion in the feed stream to calculate what amount of sulfide ion solution to add to the reactor to maintain a desired sulfide level. This strategy requires a good model or description of the reactions in order to predict the amount of sulfide to add. If properly used this strategy will prevent upsets in the reactor output that could occur using feedback control. It may be that the final scheme would involve a combination of the two strategies.

Because of the number of control loops on the system (waste stream feed, pH, sulfide and ferrous ion) and the number of parameters to be monitored, it may be advantageous to use a microcomputer-based real-time data acquisition and control system rather than conventional analog controllers and recorders. The pros and cons of these alternatives will also be studied both with respect to the laboratory research system and use with a final plant-scale unit.

Pilot Plant Proposed pilot plant would be built and tested using synthetic plating rinsewater during the first year of the study. If the process developed proves promising, the pilot plant would be moved to an appropriate electroplating facility for field testing during a follow-on year of the project.

BIBLIOGRAPHY

1. "EPA to Propose Relaxed Effluent Guidelines", Plating and Surface Finishing, 28 (April, 1980).

2. Quality Criteria for Water, USEPA, Office of Water and Hazardous Material (July, 1977).

3. Evaluation of Industrial Wastewater Treatment at Tinker AFB, OK, USAF Occupational and Environmental Health Laboratory, AFSC, Brooks, AFB, Texas.

4. Control and Treatment Technology for the Metal Finishing Industry - Sulfide Precipitation, U.S. EPA Technology Transfer Summary Report, EPA 625/8-80-003 (1980).

5. Industrial Operating Treatment Logs, Kelly AFB, Texas.

6. "Chloralkali Industry Has Hg Headache," Canadian Chemical Processing, 54/10, 44, (Oct. 1970).

7. "Extraction cuts Mercury From Wastewater, Solids", Chemical News, Chemical Manufacture Assoc. (Mar, 1973).

8. Standard Methods for the Examination of Water and Wastewater, 14th Edition, American Public Health Association, New York, (1976).

9. Bennet, J.R. "The Treatment of Effluents from Metal Cleaning and Finishing Processes", Metal Finishing Journal, 18, 272 (1972).

10. Bhattacharyya, D., Jumawan, A.B., & Grieves, R.B., "Separation of Toxic Heavy Metals by Sulfide Precipitation", Separation Science & Technology, 14, 441 (1979).

11. Conley, W.R. Jr., Integration of the Clarification Process", Journal AWWA, 57, 1333 (1965).

12. Conley, W.R. Jr., and Pittman, R.W., "Test Program for Filter Evaluation at Hanford", Journal AWWA, 52, 205 (1960).

13. Diaper, E.W.J., and Ives, K.J., Filteration Through Size Graded Media", Jour. San. Engr. Div., Amer. Soc. Civil Engr., 91, SA 3, 89 (1965).

14. Diaper, E.W.J., and Ives K.J., "Discussion, Filteration Through Size Graded Media", Jour, San. Engr. Div., Proc. Amer. Soc. Civil Engr., 92, SA 4, 73 (1966).

15. Espenson, J.H. and King, E.L., "Kinetics and Mechanisms of Reactions of Chromium (VI) and Iron (II) In Acidic Solution", Journal of the American Chemical Society, 85, 3328 (1963).

16. Espenson, J.H., "Rate Studies on the Primary Step of the Reduction of Chromium (VI) by Iron (II)," *Journal of the American Chemical Society 92*, 1880 (1970).

17. Fox, G.T.J., "Discussion, Filtration Through Size Graded Media", *Jour. San. Engr. Div. Amer. Soc. Civil Engr.*, *92*, SA 1, 326 (1966).

18. Germain, J., Vath, C. & Griffin, C. "Solving Complex Waste Disposal Problems in the Metal Finishing Industry", Paper presented at Georgia Water Pollution Control Assn. Mtg. (1968).

18a. Hamaan, C.L., and McKinney, R.E., "Upflow Filtration Processes", *Journal AWWA*, *60*, 1023 (1968).

19. Ives, K.J., "Discussion, Russian Water Supply and Treatment Practices," *Jour. San. Engr. Div.*, *Amer. Civil Engr.*, *86*, SA 4, 101 (1960).

20. Kunz, R.G., Hess, T.C. & Yen, A.F. "Kinetic Model for Chromate Reduction in Cooling Tower Blowdown", *JWPCF*, *52*, 2327 (1980).

20a. Lantz, J.B., "Evaluation of a Developmental Heavy Metals Waste Treatment System", Tech. Report to Civil Engineering Laboratory, Naval Const. Bat. Center, Port Huenene, CA, May (1979).

21. Latimer, W.M., *The Oxidation States of the Elements and Their Potentials in Aqueous Solution*, Prentice Hall, 1952.

22. Ling, J.T., "Progress in Technology of Water Filtration", *Water and Sewage Works*, *109*, 315 (1962).

23. Mracek, W.A., "Control & Automation of Chromate Waste Reduction Plants", Engineers Society of Western Pennsylvania Proceedings (1969).

24. Patterson, J.W., *Wastewater Treatment Technology*, Ann Arbor Science (1975).

25. Robinson, A.K., "Sulfide vs. Hydroxide Precipitation of Heavy Metals from Industrial Wastewater", *First Conference Advanced Pollution Control for the Metal Finishing Industry*, p. 59, EPA-600/8-78-010 (May, 1978).

26. Saam, R.D., Hearst, P.J., Schwab, L.K., & Chan, D.B., "Drydock Waste Treatment Study", TN no. N-1490, Civil Eng. Lab., Naval Construction Batallion Center, Port Huenene, CA (1977).

27. Saltzman, R.S., & Bonam, W.L., "Continuous Monitoring of Low Chromium VI Concentrations with a Photometric Analyzer System", *ISA AID* 74418, 95 (1974).

28. Schlauch, R.M., and Epstein, A.C., "Treatment of Metal Finishing Wastes by Sulfide Precipitation", p. 267-284, EPA-600/2-77-049 (1977).

28a. Schroeder, D.C., & Lee, G.F., "Potential Transformations of Chromium in Natural Waters", *Water, Air, and Soil Pollution*, *4*, 355 (1975).

29. Scott, M.C., "An EPA Demonstration Plant for Heavy Metals Removal by Sulfide Precipitation", *Second Conference on Advanced Pollution Control for the Metal Finishing Industry*, p. 106-113, EPA-600/8-70-014 (1979).

30. Scott, M.C., "Sulfide Process Removes Metals, Produces Disposable Sludge", *Industrial Wastes*, July-August (1979).

31. Scott, M.C., "Sulfex - A New Process Technology for Removal of Heavy Metals From Waste Streams", *Proceedings, 32nd Industrial Waste Conference Purdue University*, 622 (1977).

32. Sillen, L.G., and Martell, A.E., *Stability Constants of Metal Ion Complexes*, The Chemical Society, London (1964).

33. Smith and Martel, *Critical Stability Constants, Vol 4 Inorganic Complexes*, Phenum (1976).

34. TerMaath, S.G., *Heavy Metals Removal by Sulfide Precipitation, Coagulation and Filtration*, M.S. Thesis, University of Texas at Austin, (1974).

34a. Thomas, M.J., *Colloid Properties of Chromic Hydroxide Applied to Metal Finishing Wastes*, Ph.D. Dissertation, University of Notre Dame, South Bend, IN (1975).

35. Walden, *Engineering Analysis and Feasibility Study for Treatment of Plating Shop Rinsewaters at Tobyhanna Army Depot* (1979).

36. Watson, M.R., *Pollution Control in Metal Finishing*, Noyes Data Corp., Park Ridge, NJ (1973).

37. West, C.M., Bonner, W.P., and Bustamante, R.B., "[illegible] From Wastewater Treatment Plant by Chemical [illegible] *Purdue Ind. Waste Conf.* 117 (1972).