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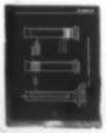

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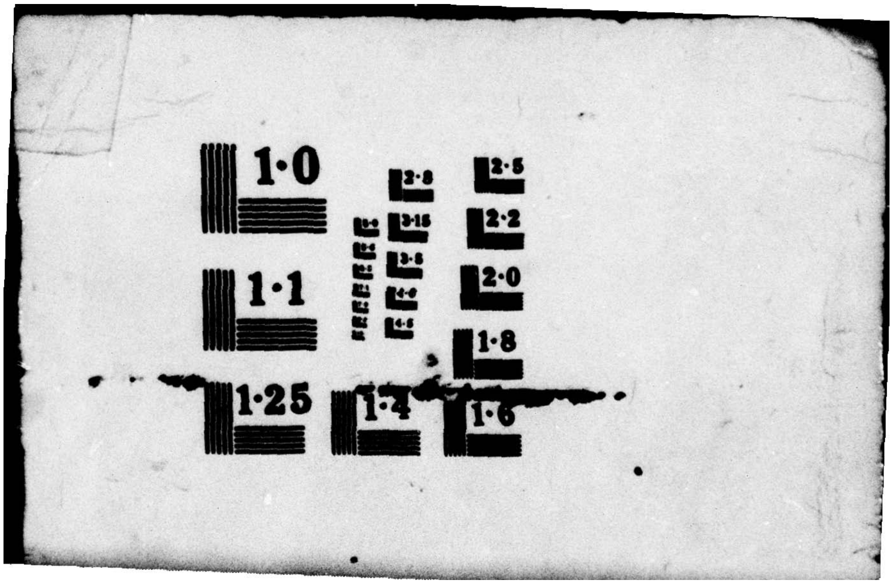
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LSI ER-314-40-6

EVALUATION OF A DEVELOPMENTAL HEAVY METALS WASTE TREATMENT SYSTEM (U)

TECHNICAL REPORT

by

J. B. Lantz

May, 1979

Project Officer: Richard D. Saam
Civil Engineering Laboratory
Naval Construction Battalion Center
Port Hueneme, CA 93043

Supported by

Civil Engineering Laboratory
Naval Construction Battalion Center
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Ft. Detrick, Frederick, MD 21701

Contract DAMD17-76-C-6063

Life Systems, Inc.
Cleveland, OH 44122

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The findings in this report are not to be construed as an official Department of the Navy or Department of the Army position unless so designated by other authorized documents.

Removal of metals from simulated mixed-metal wastes by hydroxide precipitation was shown to be superior to theoretical projections apparently due to co-precipitation of minor components. However, the studies showed that discharge criteria cannot be met by this process alone for all metals of interest in industrial wastes, particularly if seawater is present. Also, optimum pH's vary for the different metals, and co-precipitation will not be quantitatively reliable.

Hydroxide precipitation tests also showed that process demand for hydroxide reagent is roughly comparable to projections in the case of 0% seawater. However, treatment of 50% seawater can require as much as an order of magnitude higher reagent demand at high pH. The hydroxide process will therefore be uneconomical for treating or pretreating wastewaters containing high proportions of seawater, except at low pH's (e.g., 8 to 9).

Treatment of the same mixed metal wastes with soluble sulfide at pH 7.5, however, was shown to be capable of removing all metals tested, except hexavalent chromium, to within or below stringent effluent goals. The soluble metals residuals are virtually independent of total sulfide residual over nearly two decades of concentration (0.01 to 1.0 g/m^3 (8 x 10^{-5} to 8 x 10^{-3} lb/1000 gal).

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This contractor's report presents data from test and evaluation of a heavy metal sulfide precipitation process and compares to more conventional heavy metal treatment processes. Preliminary design criteria are presented.

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The Heavy Metals Waste Treatment System, consisting of a precipitation reactor, a precision control and monitor system and an experimental parallel plate clarifier, has been used to evaluate hydroxide and sulfide precipitation processes for removal of heavy metals from industrial wastes containing 0 and 50% seawater.

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EXECUTIVE SUMMARY

The Heavy Metals Waste Treatment System, consisting of a precipitation reactor, a precision control and monitor system and an experimental parallel plate clarifier (or separator), has been used to evaluate hydroxide and sulfide precipitation processes for removal of heavy metals from industrial wastes containing 0 and 50% seawater.

Preliminary tests were utilized to learn about the system and processes and to arrive at an improved test program. Off-line evaluations of precipitate separation characteristics were instituted following determination that the experimental clarifier did not perform as planned, for example.

Removal of metals from simulated mixed-metal wastes by hydroxide precipitation was shown to be superior to theoretical projections apparently due to co-precipitation of minor components. However, the studies showed that discharge criteria cannot be met by this process alone for all metals of interest in industrial wastes, particularly if seawater (or other complexing agents) are present. Also, optimum pH's vary for the different metals and co-precipitation will not be quantitatively reliable.

Hydroxide precipitation tests also showed that process demand for hydroxide reagent is roughly comparable to projections in the case of 0% seawater. However, treatment of 50% seawater can require as much as an order of magnitude higher reagent demand at high pH for reasons only partially understood. The hydroxide process will therefore be uneconomical for treating or pretreating wastewaters containing high proportions of seawater, except at low pH's (e.g., 8 to 9).

Nonlinear pH gain control, a special feature supplied with the Oxidation and Reduction Monitor and Control system, was shown to be necessary for hydroxide precipitation control.

Treatment of the same mixed metal wastes with soluble sulfide at pH 7.5, however, was shown to be capable of removing all metals tested, except hexavalent chromium, to within or below stringent effluent goals. The soluble metals residuals listed below are typical of those obtained and are virtually independent of total sulfide residual over nearly two decades of concentration (>0.01 to 1.0 g/m^3 (>8 x 10^{-5} to 8 x 10^{-3} lb/1000 gal).

Metal	Residual Goals, g/m^3 (lb/1000 gal x 10^2)	Residuals Obtained, g/m^3 (lb/100 gal x 10^2)
Copper	0.2 (0.17)	<0.01 (0.008)
Zinc	0.05 (0.042)	≤0.01 (0.008)
Cadmium	0.02 (0.017)	≤0.02 (0.017)
Nickel	0.1 (0.083)	<0.01 (0.008)
Lead	0.05 (0.042)	<0.05 (0.04)
Mercury	0.001 (0.008)	<0.0002 (0.0002)
Iron	0.5 (0.42)	<0.05 (0.04)
Chromium (+6) (pH 8.5, Iron Present)	0.005 (0.004)	0.02 (0.02)

Comparable results were also obtained at pH 8.5. One step removal of hexavalent chromium was achieved, provided iron (+2) was present as a catalyst.

The sulfide residuals found to be suitable for heavy metals removal are low enough to permit discharge of final process effluents directly into sewers. If desired, however, these residuals can be further reduced at low cost by addition of hydrogen peroxide prior to discharge.

Freshwater influents were shown to produce hydroxide precipitates with settling and sludge properties similar to those obtained typically in commerce. Commercial parallel plate clarifiers can be used to separate these precipitates from process effluents.

Precipitates obtained in the raw effluents from the soluble sulfide process are typically very fine. However, coagulant/flocculant dosage/type tests and settling tests showed that the clarifications of soluble sulfide effluents will be at least as good as those that can be obtained for hydroxide precipitates. Also, the soluble sulfide sludges are higher in density after settling and nongelatinous and therefore have improved handling, dewatering and disposal characteristics.

Chemical cost analyses were performed on the sulfide and hydroxide processes. These showed that chemical operating costs for the soluble sulfide process will be higher than for hydroxide treatment, as expected, but lower than for treatment with "insoluble" sulfide (ferrous sulfide as a sulfide source). Total operation costs for hydroxide and soluble sulfide processes may be comparable, however, if sludge dewatering and disposal costs are considered. Total operating costs for the "insoluble" sulfide process will be much higher.

A capital cost estimate was derived for a complete soluble sulfide heavy metals treatment plant versus capacity over the range 0.08 to 0.40 m^3/min (20 to 105 gal/min). The total system cost would be comparable to costs for an equivalent "insoluble" sulfide treatment unit. Costs for the soluble sulfide system are also expected to be comparable to those for a complete hydroxide process unit if the more expensive sludge processing hardware required is considered and lower if two-stage pH adjustment is implemented.

Upon weighing the considerations of process effectiveness and economics discussed in this report, it is concluded that the soluble sulfide process is the method of choice for a removal of mixtures of heavy metals from industrial wastes.

The capital cost model was based on a proprietary digital, 100% feed forward control and monitor system/reactor concept. Development of hardware based on this concept is recommended. Such a system is expected to be inherently resistant to process upsets due to variations in influent characteristics and to minimize the possibility of pH/sulfide interactions. Such interactions were observed during feedback control of some of the experiments discussed in this report. Other improvements to a next generation control system would include measurement of total sulfide as a control parameter, use of fouling resistant process sensor assemblies and optimization of hydraulic configurations.

If feedback control were to be ultimately selected for future process application (not recommended), nonlinear sulfide, as well as pH, control should also be implemented.

FOREWORD

The work described herein was conducted by Life Systems, Inc. covering the contractual period June, 1978 through May, 1979, under Contract DAMD17-76-C-6063. The Program Manager for this portion of the contract was Joel B. Lantz. The principal personnel contributing to this effort are listed below.

Personnel	Area(s) of Responsibility
R. W. Ellacott	System Modification and Test Hardware Fabrication
J. B. Lantz, Ph.D.	Program Management, Test System Design, Test Formulation, Execution and Interpretation, Economic Model
M. Prokopcak	Artwork and Drafting
L. Ramins	Test Hardware Fabrication, Program Testing
L. E. Wolfe	Program Testing
R. A. Wynveen, Ph.D.	Contract Administration

The Technical Monitor for this portion of the contract was R. D. Saam, Civil Engineering Laboratory, Naval Construction Battalion Center, Port Hueneme, CA 93043.

The author wishes to acknowledge the valuable information provided by the Technical Monitor.

TABLE OF CONTENTS

Table of Contents - continued

Table of Contents - continued

PAGE

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS

HMWTS	Heavy Metals Waste Treatment System
OARMAC	Oxidation and Reduction Monitor and Control
TSA	Test Support Accessories

INTRODUCTION

The U.S. Navy maintains 49 graving drydocks where hull cleaning and painting operations discharge mixtures of heavy metals into facility wastewaters. Electroplating facilities likewise generate such metallic wastes. When concentrations of the metals exceed levels permitted by the Environmental Protection Agency (EPA) or local governing bodies, reduction of these impurities is required prior to discharge of the water.

Precipitation of the heavy metals as insoluble sulfides has been proposed as a particularly suitable method for treating these effluents which contain variable proportions of seawater or complexing agents. This process requires the addition of sulfide at a controlled pH and removal of the precipitated heavy-metal sulfides. Alternately, conventional hydroxide precipitation of the heavy metals is under consideration. The general concept for these processes, as applied to drydock industrial wastes, is depicted in Figure 1.

Experimental investigation of the controlled pH and sulfide levels needed for treating influents of variable composition required prior development of an experimental precipitation reactor, an automatic control and monitor system, and ideally, some sort of precipitate separation apparatus. The U.S. Navy Civil Engineering Laboratory (CEL), Port Hueneme, CA, developed both a precipitation reactor and an experimental parallel plate effluent clarifier or precipitate separator.(1) Life Systems, Inc. (LSI), under the sponsorship of that agency and the co-sponsorship of the U.S. Army Medical Research and Development Command (Contract DAMD17-76-C-6063), developed the Oxidation and Reduction Monitor and Control (OARMAC) System for the process.(2,3) The two units combined form the developmental Heavy Metals Waste Treatment System (HMWTS).

The principal goal of the present study was to evaluate comparative capabilities of the sulfide and hydroxide metals removal processes using the HMWTS and to observe certain performance aspects of the process hardware. The results of this study are discussed in this report.

OBJECTIVES

The primary objectives of this study were as follows:

- Investigate the capabilities of the sulfide precipitation process for removal of a variety of heavy metals from both fresh water- and seawater-containing influents and compare results with projections.
- Investigate the capabilities of the hydroxide precipitation process comparatively for removal of metals from these influents.
- Investigate both the sulfide and hydroxide processes with respect to clarification characteristics of the effluent and precipitate removal.
- Develop an economic model to project chemical operating costs and capital costs for the process.

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(1) References cited at the end of this report.

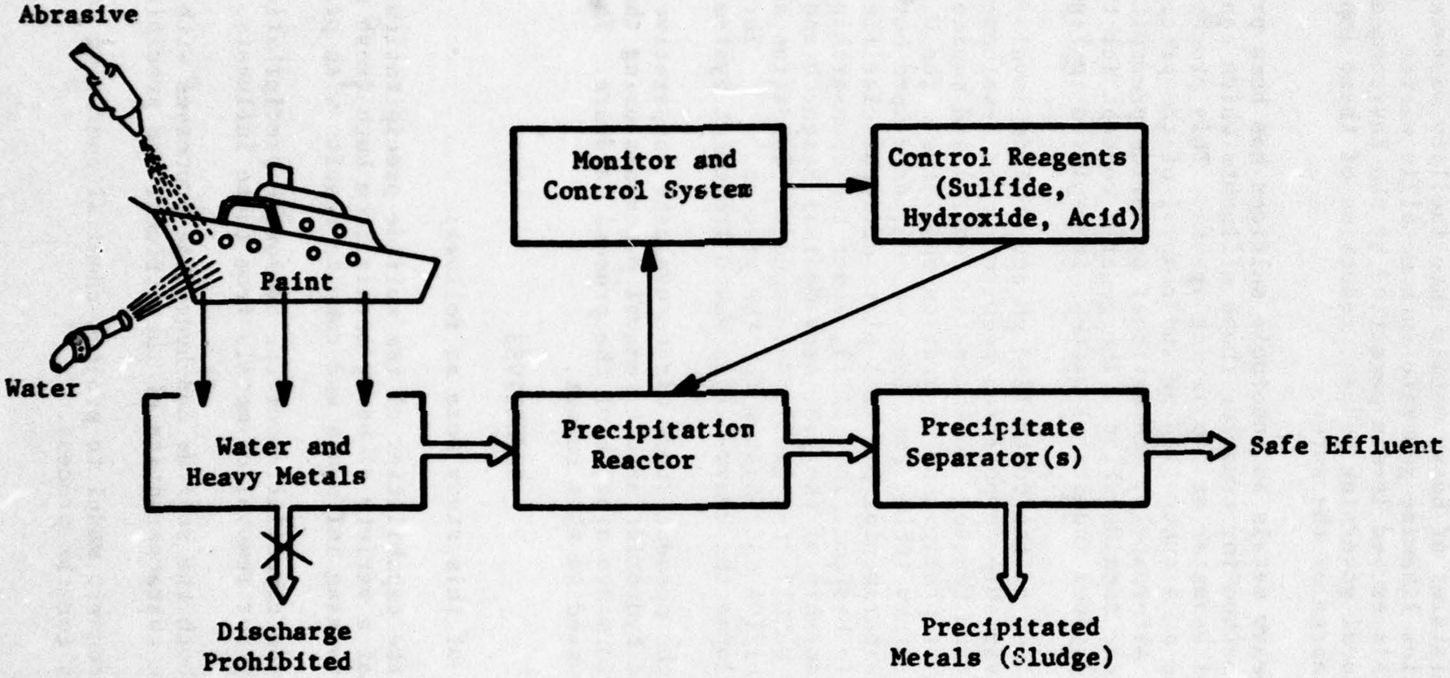


FIGURE 1 HEAVY METALS REMOVAL PROCESS (SIMPLIFIED)

- Observe HMWTS performance to aid in recommending the next step of process hardware development.

ACCOMPLISHMENTS

The above objectives were met. The following are highlights of key program accomplishments.

- Showed that the hydroxide process can remove some heavy metals from seawater-containing influents to below theoretical levels, apparently due to co-precipitation, but that the process will be inadequate for achieving stringent effluent goals.
- Showed that the soluble sulfide process typically removes all eight metals tested, except hexavalent chromium, to within stringent effluent goals at sulfide residuals low enough to permit direct effluent discharge into sewers.
- Demonstrated that hexavalent chromium can be removed by the soluble sulfide process to low levels in one step when iron (+2) is present as a catalyst.
- Elucidated measures that will successfully separate near-colloidal sulfide precipitates from effluents and comparatively quantified the settling properties of flocculated sulfide and hydroxide precipitates.
- Showed that the soluble sulfide process is superior to the hydroxide process in nearly all technical aspects.
- Showed that the "insoluble" sulfide process will compare unfavorably with the soluble sulfide process, both from technical and operating cost bases.
- Elucidated some key requirements for the next generation control and monitor system for the soluble sulfide process.
- Generated a capital cost model based on a precision 100% feed forward control and monitor concept and effective commercial precipitate separation hardware.

SYSTEM HARDWARE

The precipitation reactor and the OARMAC System has been described previously.(2,3) (However, the system reference electrodes have been replaced by other units to achieve some degree of sulfide fouling resistance.) The experimental parallel-plate effluent clarifier was provided as one means of determining the feasibility of such a unit for clarifying metals precipitate effluents.

Additional Test Support Accessories (TSA) were added to facilitate measurements, sampling, etc.

Functional Description

The basic system hardware, including the TSA, is described functionally in Figure 2. (Additional TSA items were added as required to achieve specific test objectives (see Analyses and Measurements subsection).)

Influent enters the precipitation reactor through a three-way selector valve V14, which facilitates switching between different influents. Peristaltic pump P2 pumps the influent through flow meter FM1 into the reactor. FM1 permits flow rates to be monitored and regulated periodically.

An auxiliary pump, P1, permits metering of a very low flow rate of special agents (e.g., flocculant during the checkout testing or iron solution during some special sulfide precipitation tests).

The effluent stream normally passes directly from the reactor through V2 and V1 into the outlet where it is sampled for metals analysis, collected for precipitate separation tests or discharged into the drain through FUN1. During checkout testing of the clarifier, effluent passes through V4, V5 and V1 prior to proceeding to the outlet. "After" clarifier samples were removed through V9 or monitored with the turbidity meter TM1. "Before" samples were withdrawn through V3 in a similar manner, after closing valve V4. The clarifier was not used, however, following the checkout tests.(4)

Graduated cylinders VS5, VS7 and VS9, in combination with valves V6, V7 and V8, permit measurement of hydroxide and sulfide usage rates via volumetric displacement. Pumps P4 through P6 meter sulfide, hydroxide and acid reagents from VS6, VS8, VS10 and VS11 into the reactor under the feedback control of the OARMAC instrumentation package and sensors.

Pictorial Description

The water processing system, the OARMAC control and monitor instrumentation package and the overall HMWTS and associated TSA are depicted in Figures 3, 4 and 5, respectively.

CONDITIONS AND PROCEDURES

The conditions employed during the testing, the effluent goals sought and the specific operating procedures utilized are discussed below. Any variations are indicated in specific discussions of test results.

Operating Conditions

Influent Composition

The make-up formulas of influents used in this study are defined in Table 1. Interactions between components of the C_0 influent and precipitation required

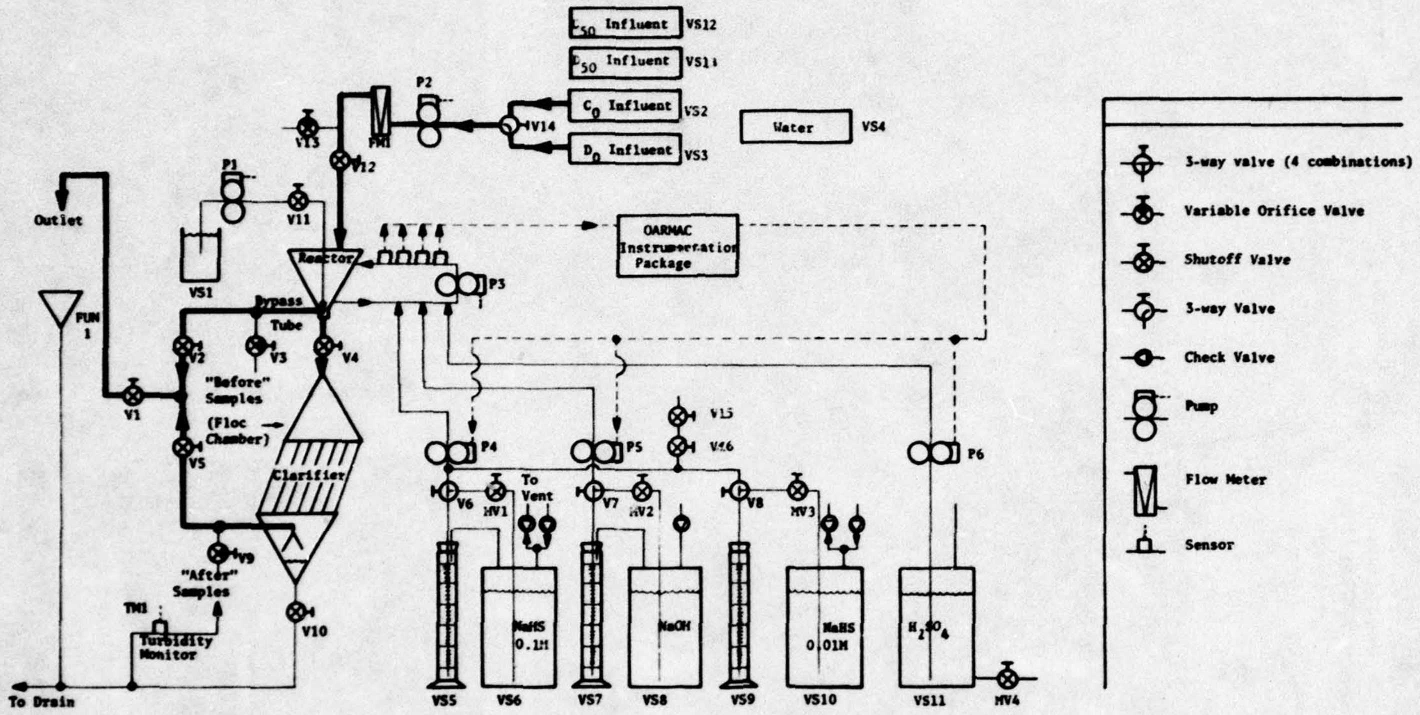


FIGURE 2 SCHEMATIC OF HMWTS AND TSA

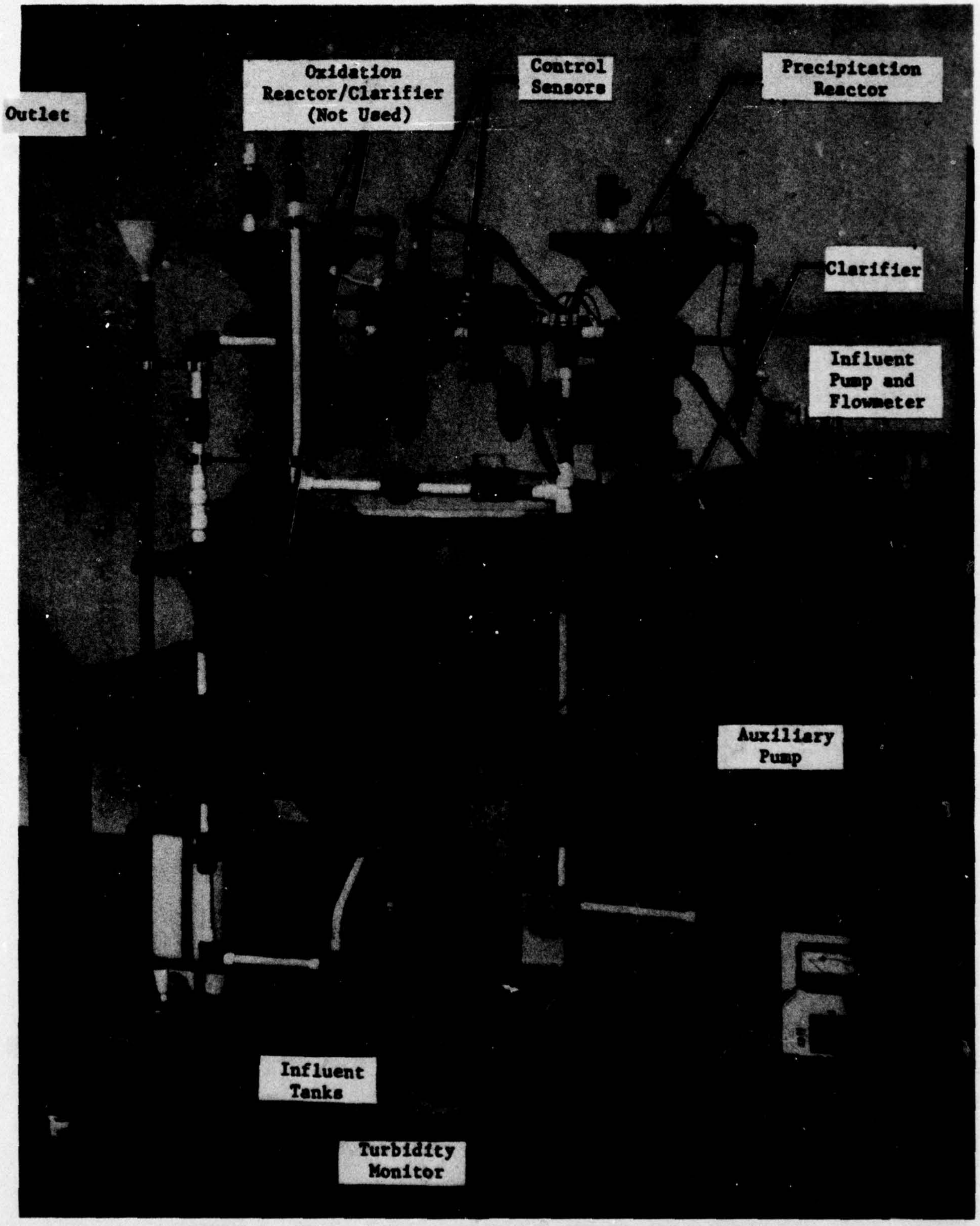


FIGURE 3 HMWTS WATER PROCESSING SYSTEM (PLUS TSA)

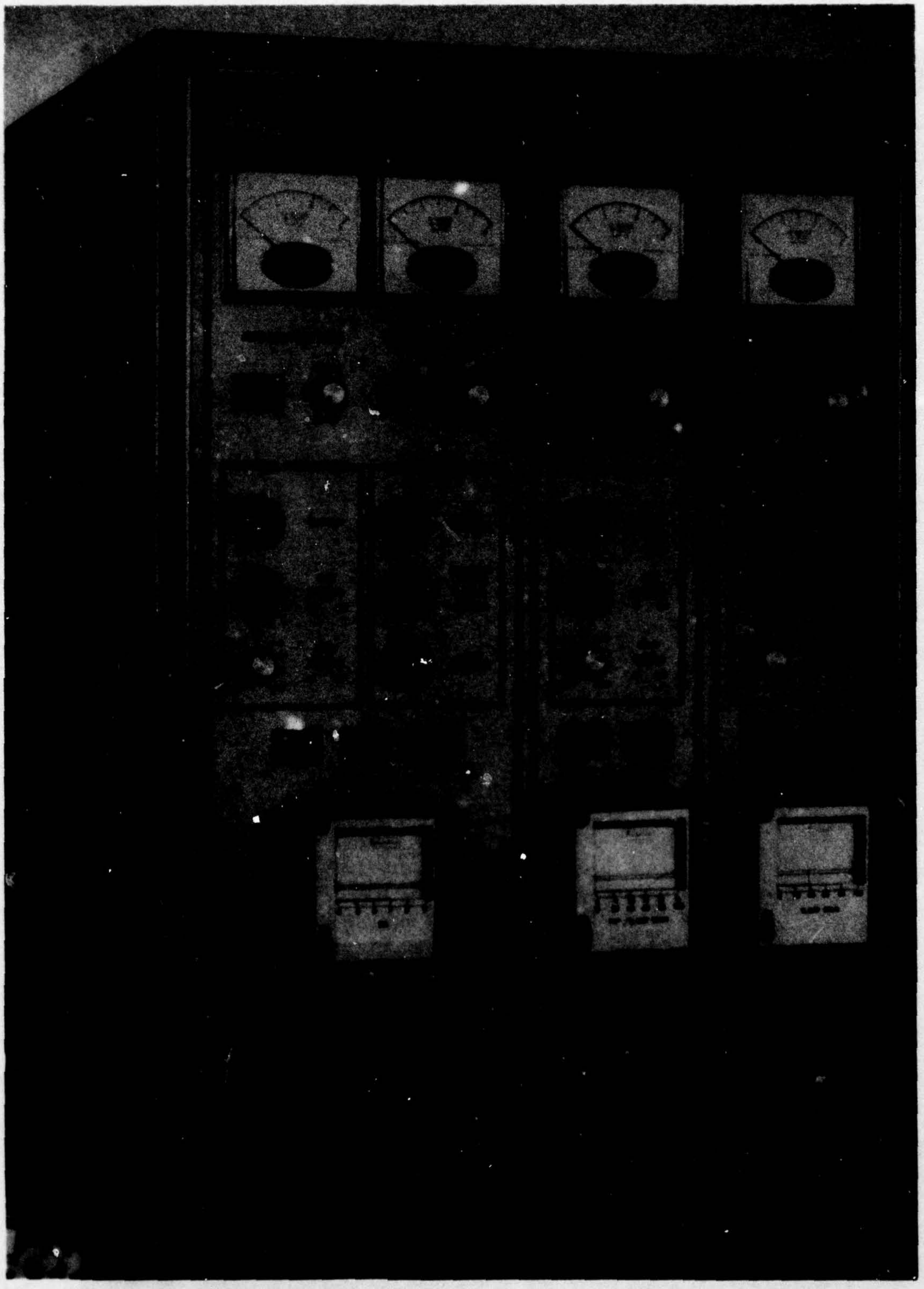


FIGURE 4 OARMAC CONTROL AND MONITOR INSTRUMENTATION PACKAGE

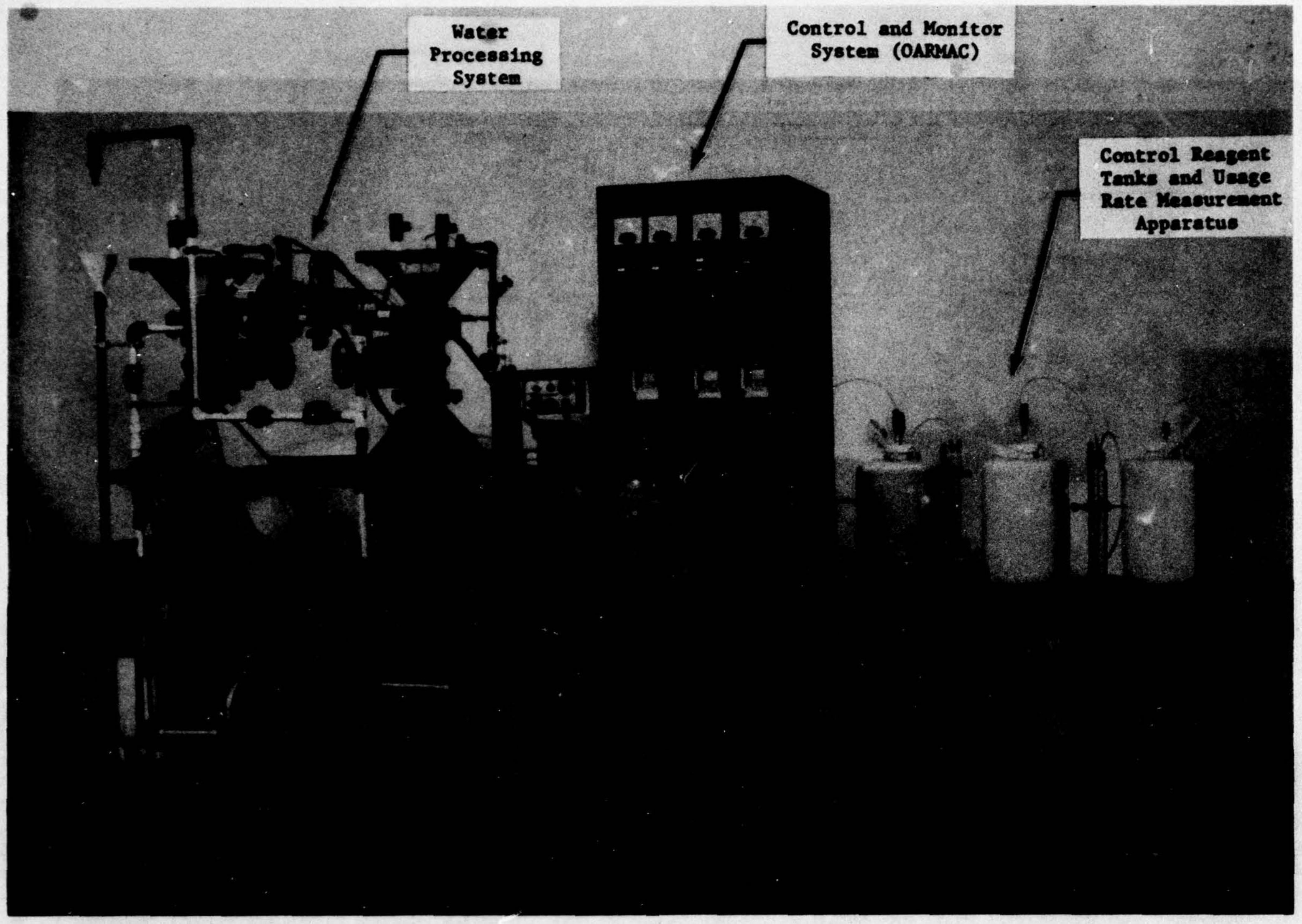


FIGURE 5 HMWTS SYSTEM (PLUS TSA)

TABLE 1 METALS CONCENTRATIONS: INFLUENTS AND EFFLUENT GOALS

	Influents, g/m^3 (lb/1000 gal x 10^2)		
Ion	Diluted Formula, "D"[a,b]	Concentrated Formula, "C"[a,c]	Effluent Goals, g/m^3 (lb/1000 gas x 10^2)
Cr (as K_2CrO_4)	0.01 (0.008)	0.3 (0.25)	0.005 (0.004)
Cu (as $CuSO_4$)	2 (1.7)	80 (67)	0.2 (0.17)
Pb (as $PbCl_2$)	0 (0)	2 (1.7)	0.05 (0.042)
Hg (as $HgCl_2$)	0 (0)	0.03 (0.025)	0.001 (0.0008)
Ni (as $NiSO_4$)	0 (0)	2 (1.7)	0.1 (0.083)
Sn (as $SnCl_4$)	0 (0)	5 (4.2)	2.5 (2.1)
Zn (as $ZnSO_4$)	1.8 (1.5)	70 (58)	0.05 (0.042)
Cd (as $CdSO_4$)	0.1 (0.08)	3 (2.5)	0.02 (0.017)

(a) "D_0" and "C_0" influents made up with 0% seawater (tapwater). "D_{50}" and "C_{50}" influents made up with 50% seawater simulant. (See Appendix 2). All metal influents adjusted to pH 4.9 ±0.1.

(b) Proportional to the make-up concentrations in "C" influents (except zero where concentration would approximate or be below discharge limit).

(c) Concentrations based on worst-case metals concentrations in the experimental leachates from used drydock abrasives, except for mercury, which corresponds to the worst-case levels detected in actual drydock effluents.(8) Due to precipitation interactions between components in the C_0 influent, however, only the supernatant was used. (An analysis of this influent was performed to determine typical metal concentration -- See Appendix 1). C_0 supernatant was used to prepare C_{50} influent.

iron to be eliminated from the original formulation, tin IV to be substituted for tin II, and only the supernatant to be utilized for the C_0 and C_{50} influents. An analysis of the C_0 supernatant is tabulated in Appendix 1. Influent matrix information is listed in Appendix 2.

Effluent Goals

The goals for metals levels in the treated effluents, as established by the U.S. Navy, are also listed in Table 1. These correspond to stringent national and local (southern California) discharge limits for wastewater.

Control Reagents

Solutions containing 0.1 M sodium sulfhydrate (NaHS) and 0.1 M sodium hydroxide (caustic, NaOH) were used as the principal control reagents. 0.01 M NaHS was also used as a control reagent for self-calibration experiments. 0.1 N sulfuric acid (H_2SO_4) was also in the dual acid/base control loop but was normally required only for acid flushes of the process section and for pH control during system startup.

Baseline Operation

Unless otherwise specified, the influent flow rate was approximately 380 cm^3/min (0.1 gal/ min), influent and effluent temperatures were ambient, sampling was through the system outlet and pH's were maintained to within ±0.1 unit of the specified level.

Analyses and Measurements

Metals Concentrations

Metals Samples. Hydroxide process metals samples were manually flocculated with an anionic polyelectrolyte and vacuum filtered directly into prepared sample bottles through 0.7 μ glass fiber filters.

Sulfide metals samples were coagulated with a cationic polyelectrolyte flash-mixed into the effluent upstream of the sampling point and vacuum filtered through 2.7 μ and 0.7 μ glass fiber filters in series with 0.2 μ membrane filters (usually required as a safety precaution only). Throughout the filtration interval, effluent was continuously generated by the HMWTS, flowed into the filter funnel at the filter surface and was pumped out the filter funnel at the top. Using these techniques filterable sulfide particle sizes were generated, handling and possible contamination of the effluent was practically eliminated and deterioration of the sulfide levels over the typically long filtration intervals was avoided by continuously refreshing the effluent at the filter surface.

Analyses. Metal concentrations in effluent samples were determined by atomic absorption analysis to within a precision less than or equal to the discharge goals. Tin analyses were not performed on effluent samples due to the low levels (below effluent goals) found in the C_0 supernatant. Chromium was not determined for hydroxide effluents since chromium (+6) is known not to form hydroxide precipitates.

Suspended Solids

Suspended solids were determined by a standard method,(5) modified to include a minimum 8 hr solids drying time and dessicator cooling under vacuum to aid in water removal. A very fine filter (Whatman GF/F, 0.7 μ) was used to insure particule retention.

Total Sulfide

All effluents generated during the sulfide precipitation studies were analyzed colorimetrically for total sulfide concentration via the spectrophotometric version of a standard method(6) (detection unit <0.1 g/m^3 (0.0008 lb/1000 gal)). Calibration curves were prepared in this case, however, via injection of small variable volumes of a concentrated sulfide stock solution directly into color development reaction vessels containing the specified sample volume of boiled distilled water, using microliter glass syringes. The stock solution was standardized via potentiometric titration with lead perchlorate.

Effluent samples were prefiltered through 0.7 μ and 0.2 μ filters mounted in a 12 mm (0.5 in) diameter syringe-type filter holder. Samples were injected directly into calibrated color development vessels using a disposable plastic tuberculin syringe. Coagulant was continuously added to the effluent stream during removal of the sulfide samples.

This filtration method (1) minimized loss of sulfide due to air oxidation, volatilization and adsorption and (2) permitted relatively rapid filtration despite filter clogging, due to the high pressures easily generated with the small-bore syringe.

During some preliminary tests total sulfide residual maintained in HMWTS effluents were determined via an indirect self-calibration method. The system control point was set approximately, the system was operated with plain (acidified) water and the sulfide reagent flow rate required to automatically maintain this control point was measured. After measuring the effluent flow rate and determining sulfide reagent concentration (via potentiometric titration), the sulfide residual control point can be calculated by:

$$\text{Sulfide Control Point} = \frac{\text{Sulfide Reagent Flow}}{\text{Total Process Flow}} \left(\begin{array}{c}\text{Sulfide Reagent} \\ \text{Concentration}\end{array}\right)$$

The HMWTS was then run with a regular influent at this control point. This method was not used, however, during metals removal studies due to some pH/sulfide control interactions observed prior to those tests.

Control Reagent Demand

Control reagent demand rates were determined by volumetric displacement of the reagent versus time in graduated cylinders. This method provided integration of cyclical fluctuations.

pH

pH's were measured with a Markson Model 4404 digital pH meter. A sulfide-resistant double-junction electrode was used as reference. All pH measurements during the sulfide metals removal experiments were made with a special stopped-flow effluent sampling technique to avoid pH errors due to hydrogen sulfide loss and electrical ground loops.

Effluent Turbidity

The turbidity of settled effluent samples was measured with a Hach Model 2100A Nephelometer. All samples were shaken prior to measurement to provide uniform dispersions of particulates.

Test Procedures

The principal experimental procedures utilized are discussed below.

Metals Removal/Effluent Generation

The general operating procedure for studying metals removal via hydroxide and sulfide precipitation, as well as for generation of effluents for precipitate separation studies, is outlined in Figure 6.

Precipitate Separation Studies

The procedure for coagulant/flocculant dosage/type studies is outlined in Figure 7.

The procedure for performing precipitate settling tests is outlined in Figure 8. These tests are based on procedures developed by a manufacturer of parallel plate clarifiers to simulate the settling action of these devices.(7) They are, however, similar to conventional jar tests.

Appendix 3 provides additional illustrations of these test procedures.

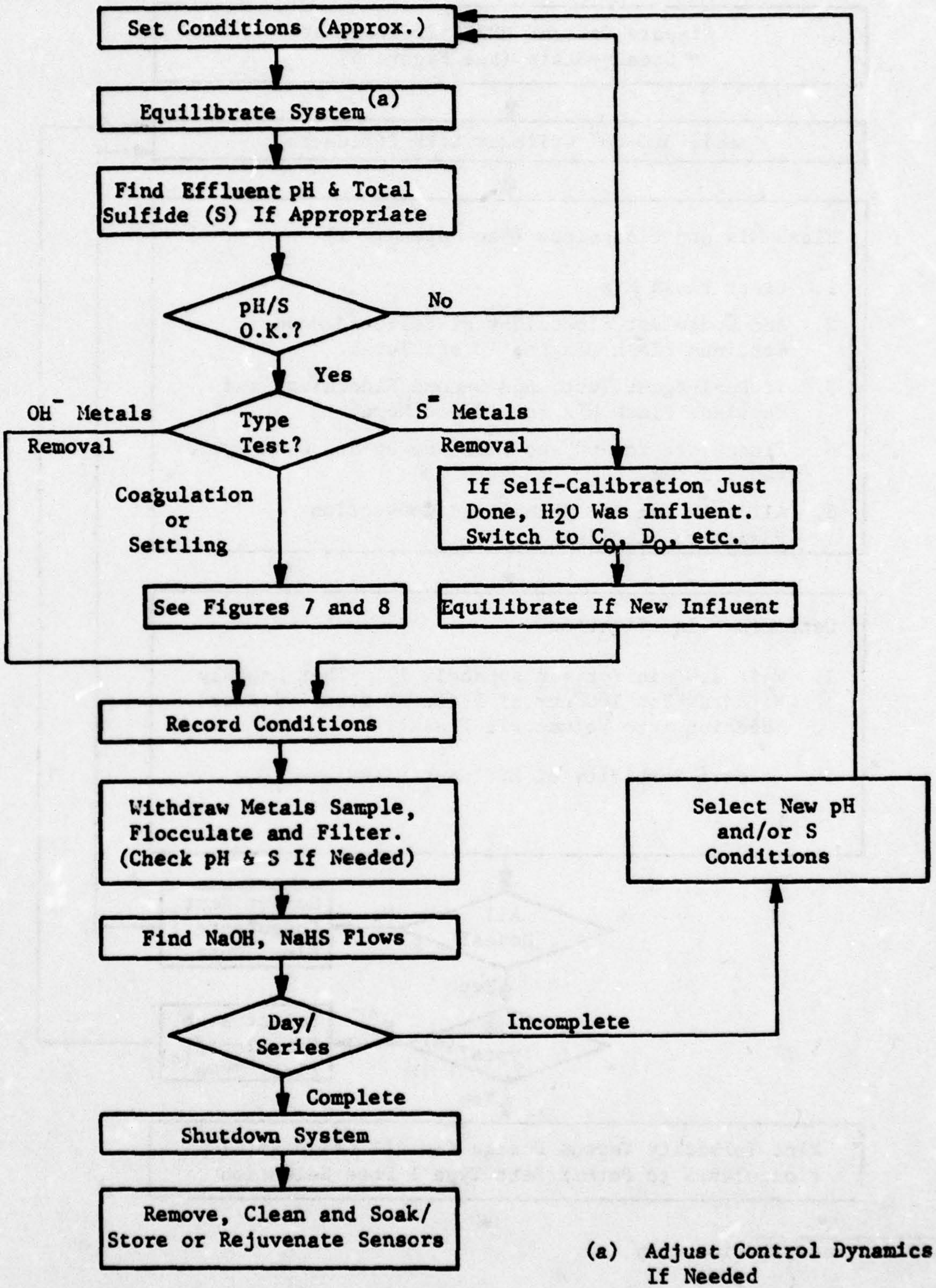
Miscellaneous

As a result of electrode fouling discovered during checkout tests of the experimental system, the process electrodes were typically cleaned daily and stored overnight in appropriate environments -- potassium chloride solution for the reference electrode, water for the glass electrode and air for the sulfide electrode. More stringent rejuvenation procedures were used if required.

Checkout tests were performed utilizing a variety of techniques. These will not be discussed here, since this work has been discussed previously.(4)

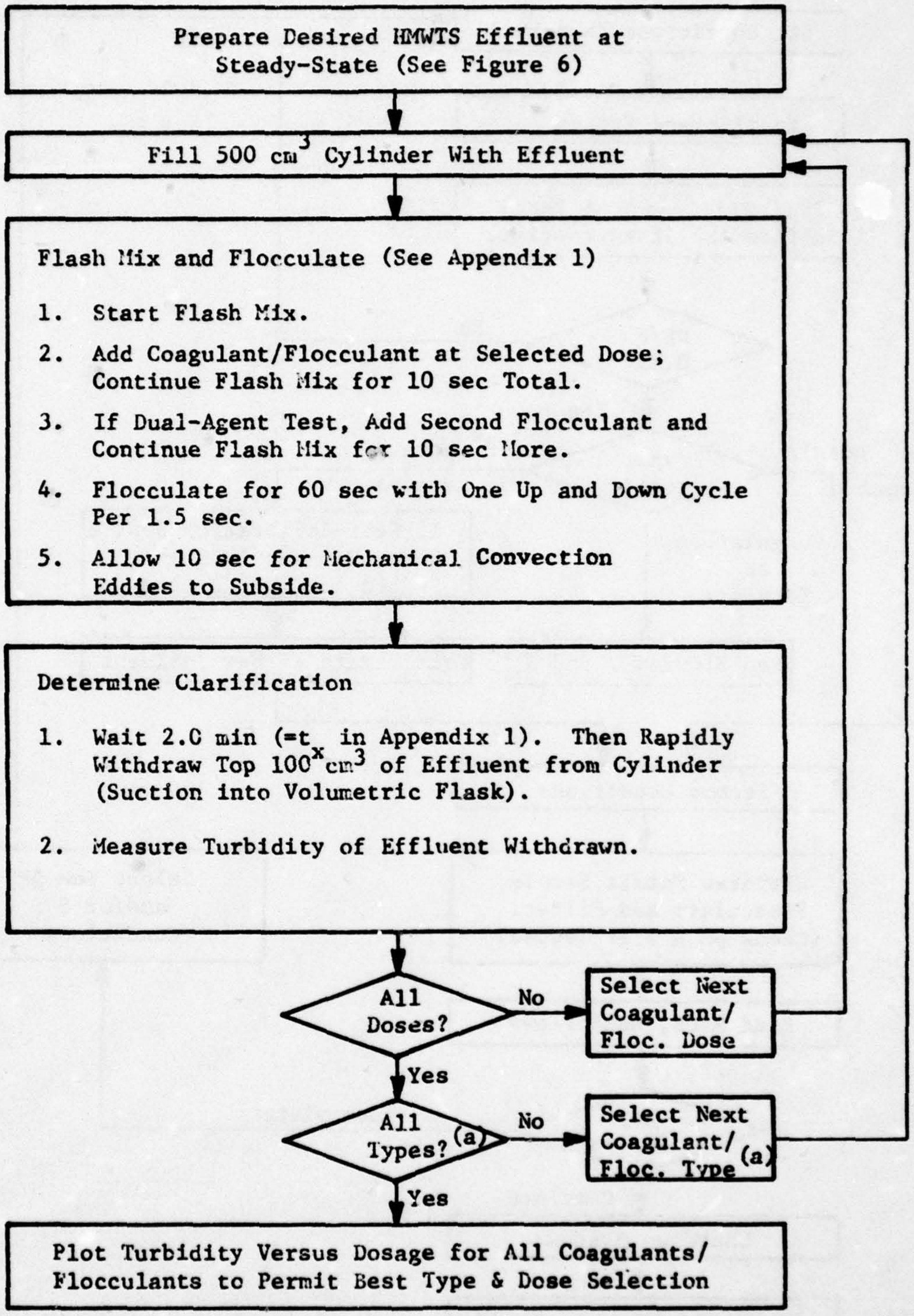
PRELIMINARY TESTS

These tests provided information on system performance and enabled upgrading of the basic test program.



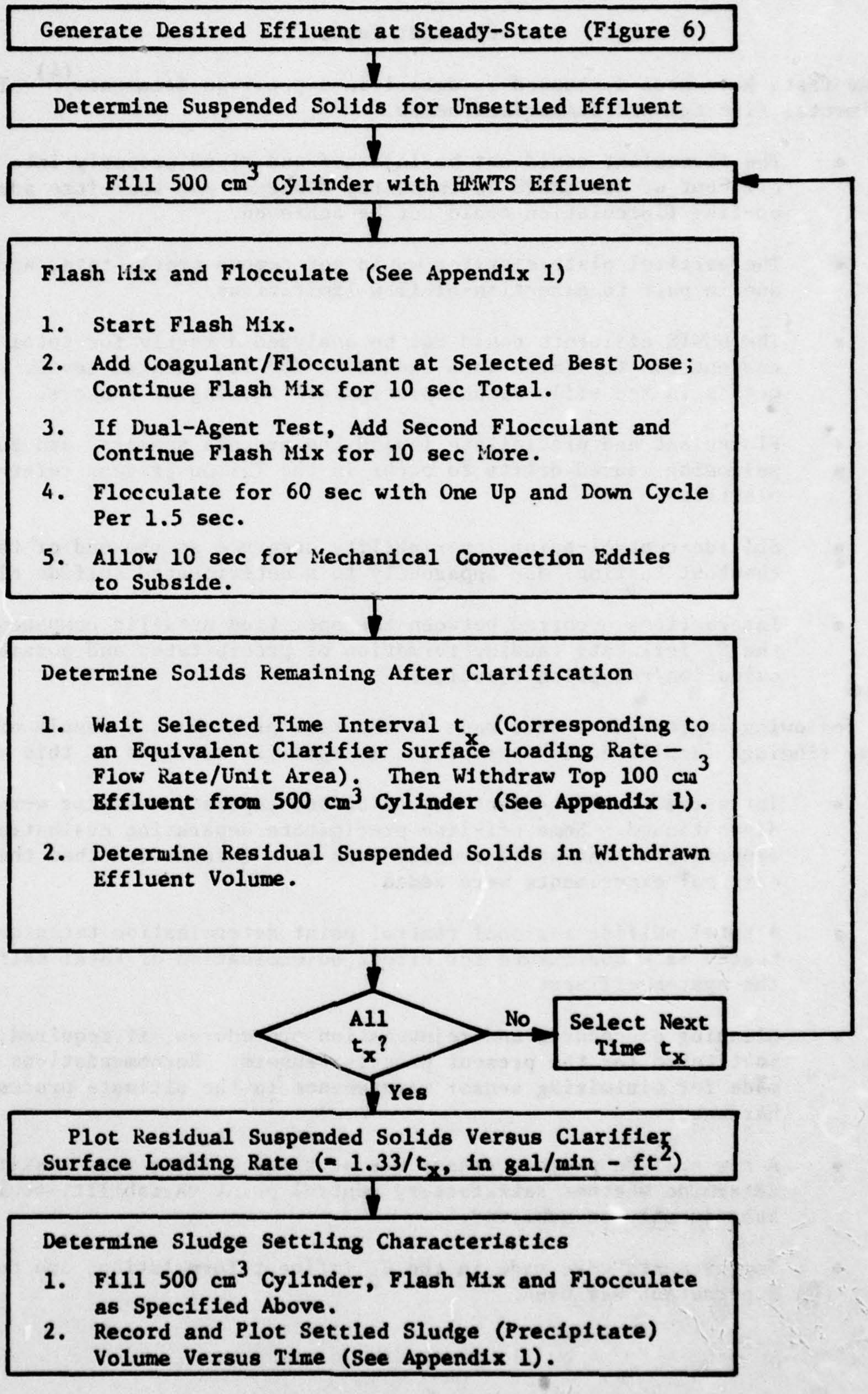
(a) Adjust Control Dynamics If Needed

FIGURE 6 PROCEDURE FOR METALS REMOVAL TEST/PRECIPITATE EFFLUENT GENERATION



(a) Sulfide Precipitation Only.

FIGURE 7 COAGULANT/FLOCCULANT DOSAGE/TYPE TEST PROCEDURE



Generate Desired Effluent at Steady-State (Figure 6)

Determine Suspended Solids for Unsettled Effluent

Fill 500 cm^3 Cylinder with HMWTS Effluent

Flash Mix and Flocculate (See Appendix 1)

1. Start Flash Mix.
2. Add Coagulant/Flocculant at Selected Best Dose; Continue Flash Mix for 10 sec Total.
3. If Dual-Agent Test, Add Second Flocculant and Continue Flash Mix for 10 sec More.
4. Flocculate for 60 sec with One Up and Down Cycle Per 1.5 sec.
5. Allow 10 sec for Mechanical Convection Eddies to Subside.

Determine Solids Remaining After Clarification

1. Wait Selected Time Interval t_x (Corresponding to an Equivalent Clarifier Surface Loading Rate — Flow Rate/Unit Area). Then Withdraw Top 100 cm^3 Effluent from 500 cm^3 Cylinder (See Appendix 1).
2. Determine Residual Suspended Solids in Withdrawn Effluent Volume.

Plot Residual Suspended Solids Versus Clarifier Surface Loading Rate (= $1.33/t_x$, in gal/min - ft^2)

Determine Sludge Settling Characteristics

1. Fill 500 cm^3 Cylinder, Flash Mix and Flocculate as Specified Above.
2. Record and Plot Settled Sludge (Precipitate) Volume Versus Time (See Appendix 1).

FIGURE 8 SETTLING TEST PROCEDURE

Checkout Tests

These tests have been discussed in detail in a previous document.(4) The experimental findings are summarized below.

- The flocculant could not be injected and mixed properly into the effluent of the HMWTS as currently designed and therefore adequate on-line flocculation could not be achieved.
- The parallel plate clarifer would not remove precipitate, apparently due in part to direction-of-flow limitations.
- The HMWTS effluents could not be analyzed directly for total sulfide content due to limitations caused by the low sulfide level, residual metals in the effluent and precipitate fouling of sensors.
- Flocculant and precipitate fouled the process sensors, and sulfide poisoning caused drifts to occur in the Teflon process reference electrode.
- Sulfide-control-point invariability occurred at the end of the checkout testing, due apparently to a deteriorated sulfide electrode.
- Interactions occurred between the specified metallic components of the C_0 influent, causing formation of precipitates and possibly oxidation/reduction reactions.

The following improvements were made to the test program as a result of the above findings (amplified as appropriate in specific sections of this report).

- Intra-reactor flocculant injection and separator testing were discontinued. Some off-line precipitate separation evaluation experiments that would provide even more information than the original experiments were added.
- A total sulfide residual control point determination technique was tested as a substitute for direct determination of total sulfide in the system effluent.
- Cleaning procedures and rejuvenation procedures, if required, were instituted for the present process sensors. Recommendations were made for minimizing sensor maintenance in the ultimate process hardware.
- A new sulfide process sensor was acquired. Tests were instituted to determine whether satisfactory control point variability could subsequently be achieved.
- Improvements were made in the C_0 influent formulation, and only the supernatant was used.

Sulfide Self-Calibration Method Test

The capability of the sulfide self-calibration method (see Analyses and Measurements subsection) was verified by generating tap water effluents containing approximately 10 g/m^3 (0.08 lb/1000 gal) in total sulfide, determining the sulfide residual control point via the self-calibration technique and performing a comparison analysis of the total sulfide concentration in the effluent via a rough potentiometric titration (possible at these concentrations, but with some significant limitations).

Point group C in Figure 9 shows that reproducibility ranging from complete agreement between the two methods to a factor of two difference was obtained, satisfactory for the purposes at hand (in fact, the titrations are more likely to be in error than the self-calibrations, since reliably sharp end points are difficult to obtain for the former).

To verify that the self-calibration conditions established would remain stable during an actual run with heavy metals in the influent, the self-calibration points were checked before and after a 1.3 hr run with C_0 influent with no change in control settings. Satisfactory reproducibility was obtained at 10 g/m^3 (0.08 lb/1000 gal) total sulfide (see squares in point group C of Figure 9).

The effective pH control point decreased somewhat (0.4 units) when the influent was switched from water to C_0. This was assumed to be due to pH/sulfide control interactions and to be correctable via a simple pH adjustment during application of the self-calibration method. Process stability variations during the water-C_0-water influent transitions were short and nearly inconsequential.

Control Point Variability Experiments

Control point variability experiments were carried out to determine the ability of the system to produce variable total sulfide control points as required for testing following the installation of the new sulfide process sensor. Sulfide control setpoints (corresponding to pH-dependent free sulfide concentration) were varied while operating the system with water influent. The total sulfide control points obtained during steady state system operation were measured via the self-calibration technique. Curves A and B of Figure 9 show that adequate variabilities were obtained.

METALS REMOVAL STUDIES

The comparative effectiveness of sulfide and hydroxide precipitation processes for the removal of heavy metals from both concentrated and dilute fresh water- and seawater-containing wastewater simulants to within established discharge concentration goals was evaluated. The experimental reagent usage rates under the various precipitation conditions were also determined to aid in understanding the process and to permit projection of chemical operating costs.

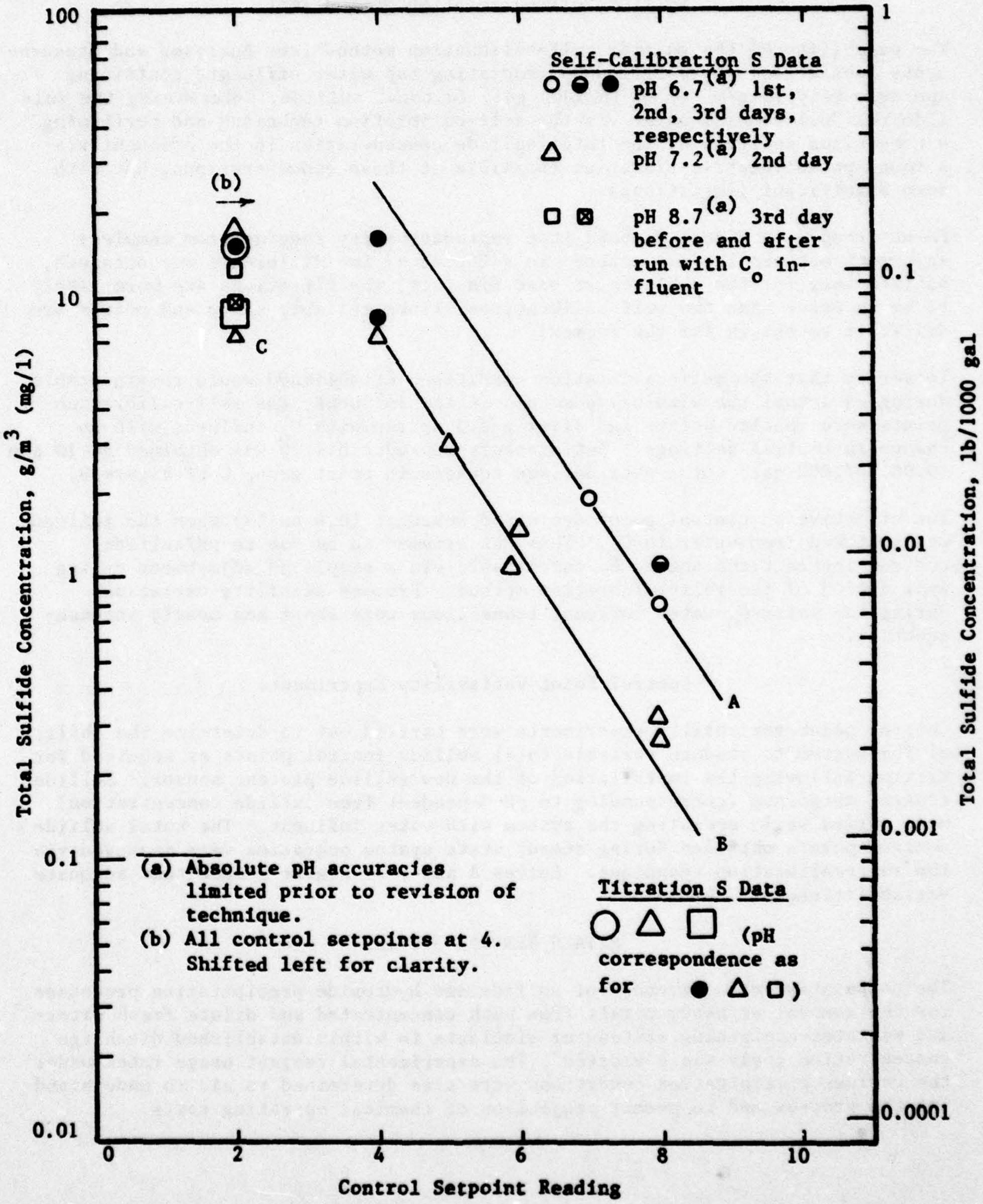


FIGURE 9 RESULTS OF SELF-CALIBRATION AND CONTROL POINT VARIATION EXPERIMENTS

Hydroxide Precipitation

Metals were removed continuously from each of the influents via formation of insoluble hydroxide precipitates by controlling the process pH over the range 8 to 11.

Metals Residuals

The evaluated effectiveness of the hydroxide precipitation method is discussed below in terms of the residual levels of soluble metals remaining in the effluent. Zinc, copper, cadmium and nickel residuals are plotted versus pH for each influent in Figures 10, 11, 12 and 13, respectively (arrows attached to points indicate "less-than" values, as governed by analytical detection limits).

Projected data (calculated from equilibrium expressions) have been taken from a related process suitability study by the U.S. Navy(8) for drydock wastes.

Zinc. Zinc residuals are nearly identical to projections for 0% seawater, although they are significantly lower than projected for 50% seawater. The latter result may indicate that chloride complex formation is inhibited by factors not covered by the original calculation. Based on the present data U. S. Navy drydock effluent goals for zinc can be met using the hydroxide precipitation process. However, the pH range for the dilute 50% seawater influents appears to be higher and more critical than for the others.

Copper. Copper residuals are somewhat higher than projected for 0% seawater, though they are well within effluent goals at pH levels suitable for zinc removal as well. For 50% seawater, the residuals are as much as three orders of magnitude lower than projected. As for zinc, the D_{50} residuals are higher than for the other influents, however, and are above effluent goals.

The lower-than-projected residuals for both copper and zinc in general may be due to co-precipitation of metal ions within the gelatinous hydroxide sludge. This action may be less effective in the case of a dilute suspension.

Cadmium. The levels attained are significantly lower than projected in all cases (although projections vary with the source, possibly due to different species considered in the calculations).(9,10) This is also likely due to co-precipitation of cadmium within the copper and zinc sludges. As in the previous cases, the metal ion is higher for C_{50} than for the other influents, possibly due to less effective co-precipitation in the dilute suspension.

Discharge goals cannot be met by hydroxide precipitation for influents containing variable seawater concentrations over the range 0-50%.

Nickel. The below-detection-limit nickel residuals observed for C_0 effluent probably correspond to levels similar to projections. Based on this data, effluent goals can be met by precipitation at pH 10, both for freshwater and seawater-containing influents.

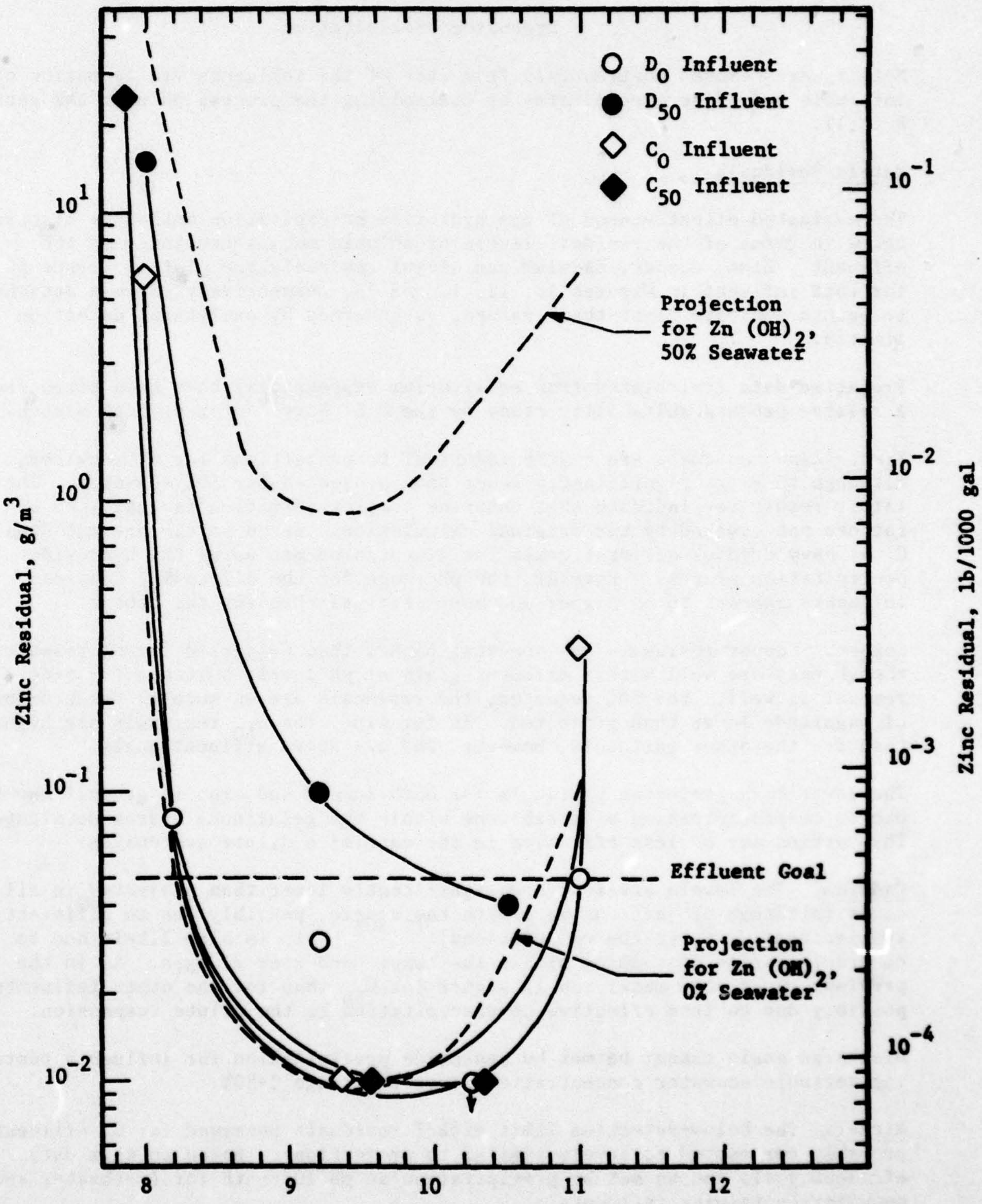


FIGURE 10 ZINC RESIDUAL VERSUS EFFLUENT pH

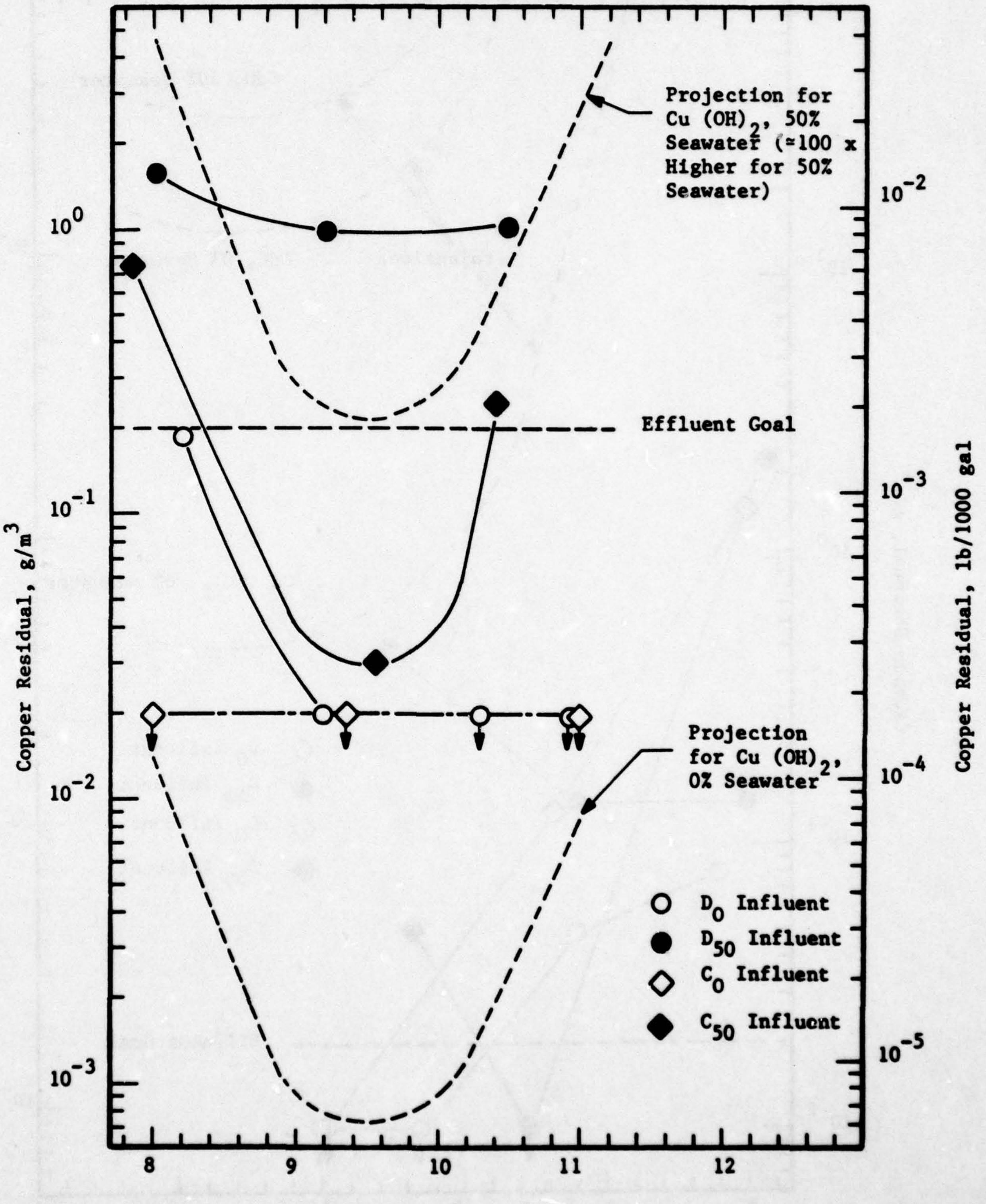


FIGURE 11 COPPER RESIDUAL VERSUS EFFLUENT pH

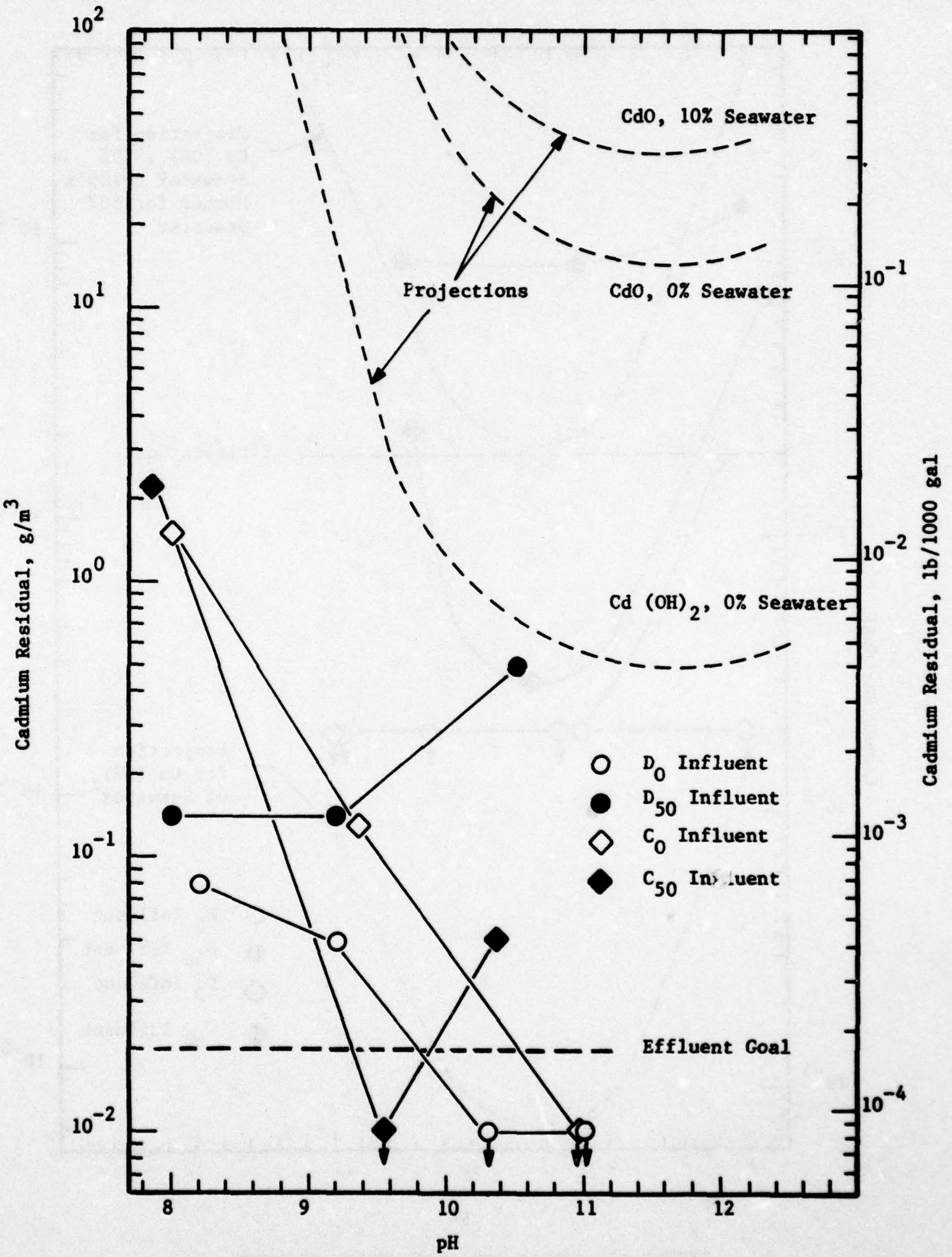


FIGURE 12 CADMIUM RESIDUAL VERSUS EFFLUENT pH

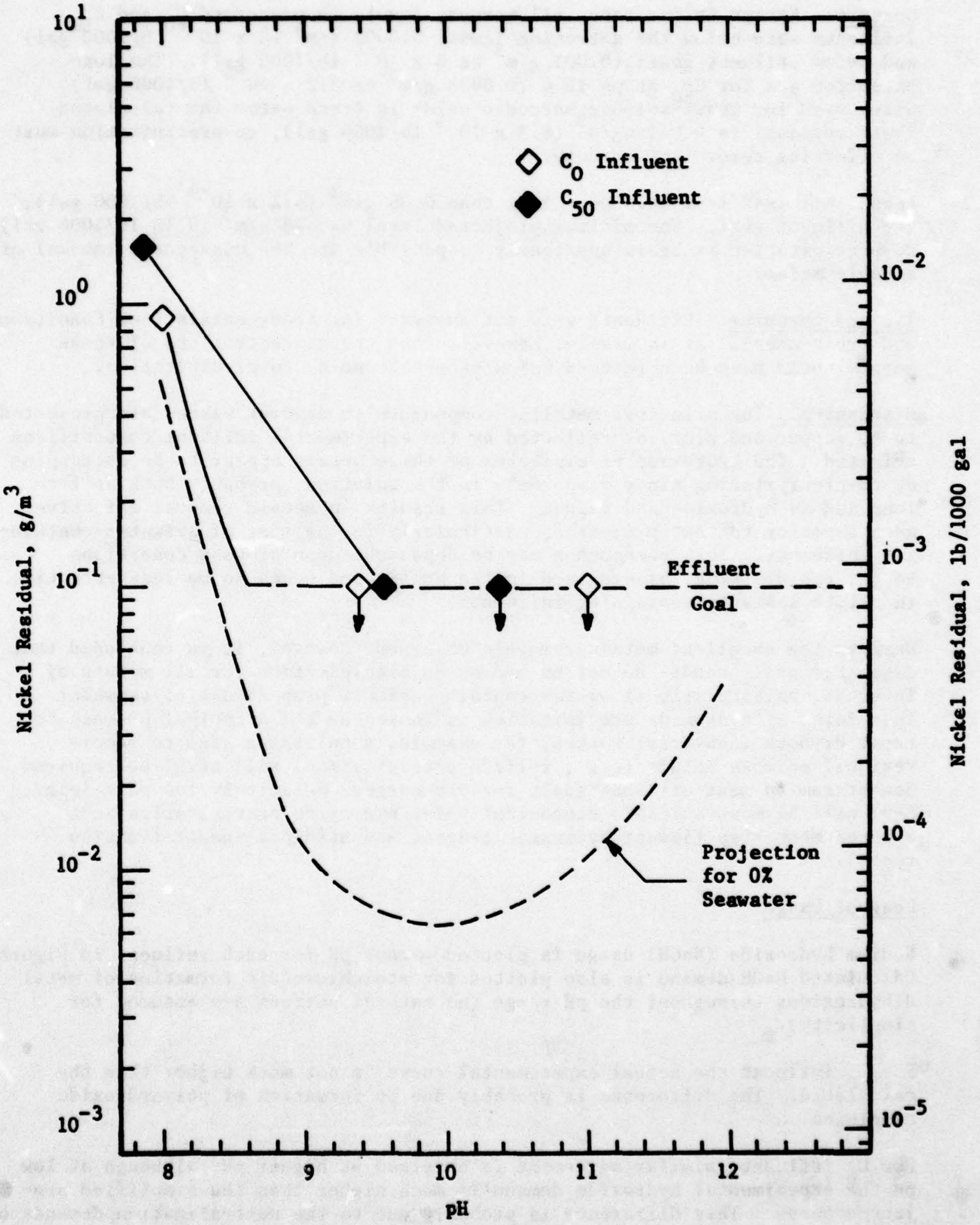


FIGURE 13 NICKEL RESIDUAL VERSUS EFFLUENT pH

Mercury. Except in one case, all mercury levels in processed C_0 and C_{50} influents were below the detection limit, 0.0002 g/m^3 (2 x 10^{-6} lb/1000 gal) and below effluent goals (0.001 g/m^3 or 8 x 10^{-6} lb/1000 gal). The lone exception was for C_{50} at pH 10.4 (0.0038 g/m^3 or 3.2 x 10^{-5} lb/1000 gal). Since even for least-soluble mercuric oxide in fresh water the calculated lower residual is 0.010 mg/m^3 (8.3 x 10^{-5} lb/1000 gal), co-precipitation must be effecting removal of mercury.

Lead. All lead residuals were less than 0.05 g/m^3 (4.2 x 10^{-4} lb/1000 gal), the effluent goal. The minimum projected level was 18 g/m^3 (0.15 lb/1000 gal). Co-precipitation is again apparently responsible for the unexpected removal of soluble metal.

Tin and Chromium. Effluents were not analyzed for these metals (see Conditions and Procedures). It is likely, however, that the concentrations of these metals would have been reduced below expectations by co-precipitation.

Discussion. The principal metallic components in drydock wastes are projected to be copper and zinc, as reflected by the experimental influent compositions selected. The hydroxide precipitates of these metals appear to be entrapping or co-precipitating minor components in the solution, probably both as free ions and as hydroxide and oxides. This results in metals removal effectiveness superior to that projected, particularly in the case of seawater-containing influents. This phenomenon may be dependent upon process conditions (e.g., rapid mixing, as employed in the HMWTS) and seems to be less effective in dilute seawater-containing influents.

Despite the excellent metals removals observed, however, it is concluded that discharge goals cannot be met by hydroxide precipitation for all metals of interest, particularly if wastes contain variable proportions of seawater. Therefore, if hydroxide precipitation is chosen as the principal process to treat drydock industrial wastes, for example, a polishing step to remove residual soluble metals (e.g., sulfide precipitation) will still be required downstream to meet effluent goals for discharge. Relatively low pH's (e.g., 8-9) will be most suitable economically for hydroxide precipitation as a pretreatment step (lowest hydroxide reagent and acid post-neutralization costs).

Reagent Usage

Sodium hydroxide (NaOH) usage is plotted versus pH for each influent in Figure 14. Calculated NaOH demand is also plotted for stoichiometric formation of metal dihydroxides throughout the pH range (no natural buffers are assumed for simplicity).

For C_0 influent the actual experimental curve is not much higher than the calculated. The difference is probably due to formation of polyhydroxide complexes.

For D_0 influent, similar agreement is obtained at higher pH, although at low pH the experimental hydroxide demand is much higher than the simplified projected curve. This difference is probably due to the neutralization demands of

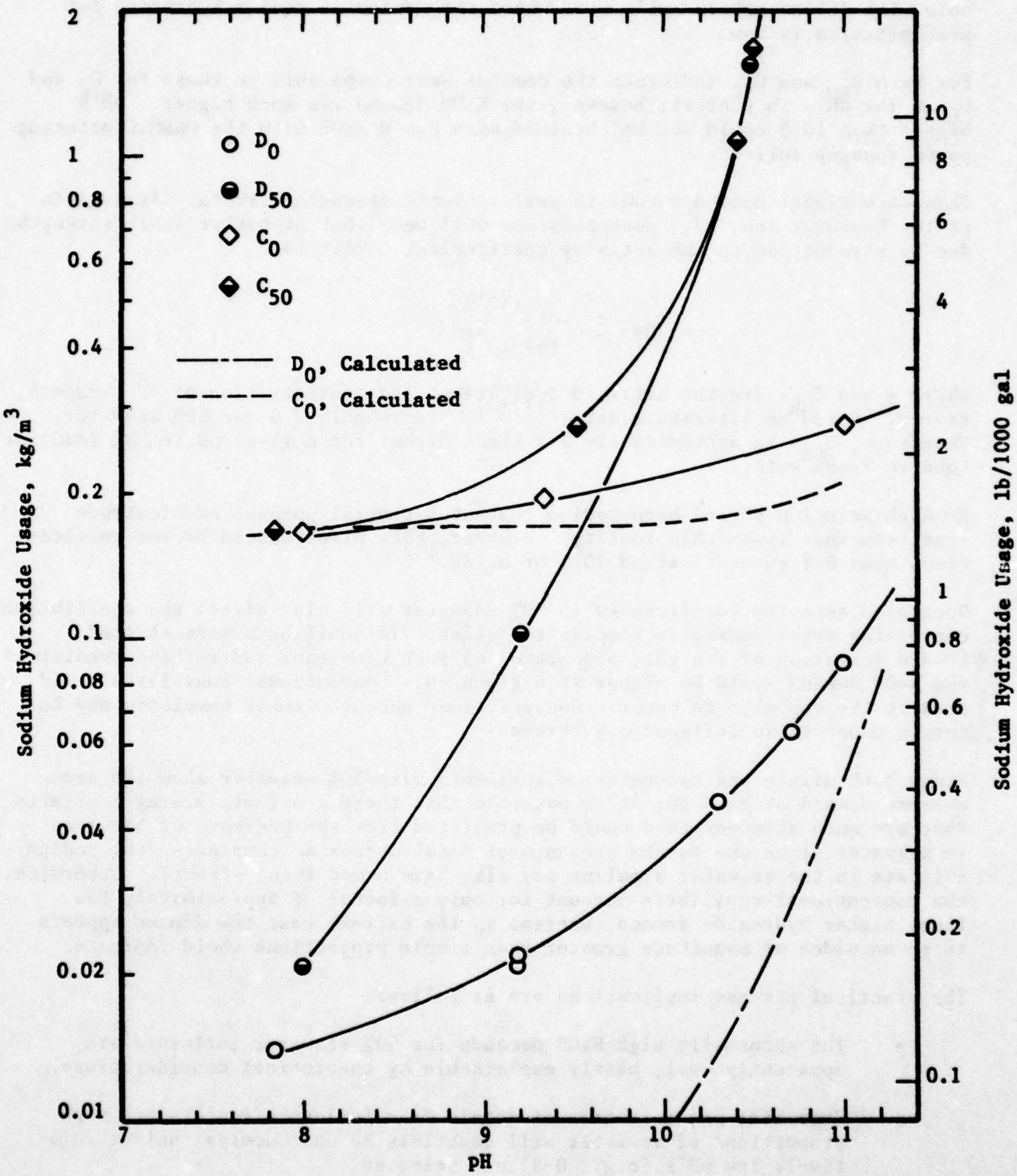


FIGURE 14 SODIUM HYDROXIDE USAGE FOR HYDROXIDE PRECIPITATION OF HEAVY METALS

natural buffers (e.g., carbonates) in the influents, which will be more noticeable with dilute metals influents, where the demand of sodium hydroxide for precipitation is low.

For both D_{50} and C_{50} influents the demands were comparable to those for D_0 and C_0 at low pH. In general, however, the NaOH demand was much higher. pH's higher than 10.5 could not be obtained with 0.5 M NaOH with the OARMAC metering pumps running full-on.

This much higher demand is due in part to ionic strength effects. At a given pH the hydroxyl ion (OH^-) concentration will be higher at higher ionic strengths due to a reduction in the activity coeffiecient. That is,

$$C_{OH^-} = \frac{10^{-14}}{(\gamma)\ 10^{-pH}}$$

where γ and C_{OH^-} are the activity coefficient and concentration of OH^- respectively. Based on literature data,(11,12) γ is roughly 0.6 for 50% seawater. Therefore, C_{OH^-} is approximately 1.7 times higher for a given pH in 50% seawater than in fresh water.

At high solution pH and high sodium content a general purpose pH electrode reads somewhat lower than reality. However, this error should be insignificant (less than 0.1 pH unit) at pH 10.5 or below.(13)

Decreased activity coefficients in 50% seawater will also affect the equilibrium concerning metal hydroxide complex formation. If equilibria were shifted toward formation of a higher proportion of such complexes under these conditions the NaOH demand would be higher at a given pH. Conventional equilibria would predict the opposite to occur. However, some unconventional complexes may be formed under these influent conditions.

Since both dilute and concentrated influents with 50% seawater show the same extreme demand at high pH, it is possible that there are ionic strength effects that are much stronger than would be predicted from the presence of the ions in seawater alone due to the presence of metal hydroxide complexes (the sodium silicate in the seawater simulant may also have a modifying effect). Otherwise, the conventional equilibria account for only a factor of approximately two times higher hydroxide demand, whereas in the extreme case the demand appears to be an order of magnitude greater than simple projections would indicate.

The practical process implications are as follows:

- The abnormally high NaOH demands for 50% seawater influents are apparently real, partly explainable by theoretical considerations.
- Hydroxide precipitation of metals from influents containing high proportions of seawater will doubtless be uneconomical unless relatively low pH's (e.g., 8-9) are selected.

Control Demands

The requirement for nonlinear pH gain compensation, a special feature incorporated into the OARMAC system, was observed during the hydroxide precipitation experiments with C_0 influent, as illustrated in Figure 15. Stable control points in the pH range 9 to 10 were difficult to obtain, and the control set points required to maintain a given pH were displaced somewhat from the ideal (graph 1). There appeared to be a correlation between the theoretical precipitation minima for hydroxides of copper and zinc,(8) the primary influent components, as illustrated in graph 2 of Figure 15. The reactions governing process equilibria and kinetics are changing from mostly precipitation to mostly complex formation at pH's bracketing the minima possibly influencing process gain and other dynamic factors. Therefore, nonlinear pH controller gain compensation was employed in this pH region, as illustrated in graph 3. Stable control and setpoint correspondence could then be obtained, as indicated by the blackened circles in graph 4.

Controlled pH's were up to 0.4 units higher for a given control setting when operating the system with influents containing 50%, versus 0%, seawater. Also, control stability requirements varied between the two influents (in two cases, manual adjustment of hydroxide reagent was used to control time consuming readjustments of control dynamics conditions). These effects are apparently related to unusual hydroxide reagent demands observed for saline influents in Figure 14.

Sulfide Precipitation

The metals residuals obtained, the usages of control reagents measured and observations made concerning process control are discussed below for continuous removal of metals by simultaneous control of pH and sulfide levels.

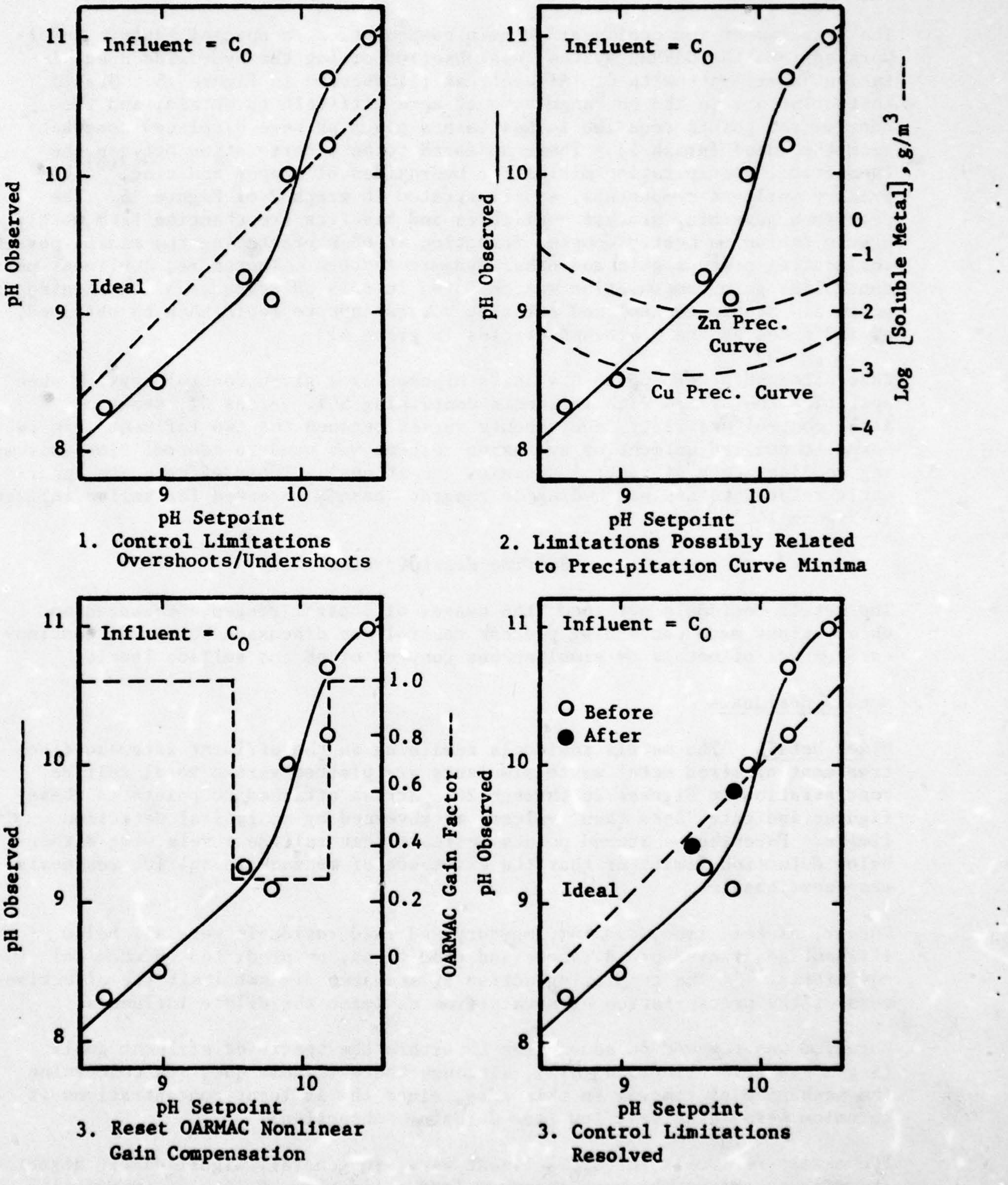
Metals Residuals

Mixed Metals. The metals residuals remaining in the effluent after sulfide treatment of mixed metal waste simulants are plotted versus total sulfide concentration in Figures 16 through 20. Arrows attached to points in these figures indicate "less than" values, as governed by analytical detection limits. Parentheses around points indicate that sulfide levels were either below detection limits or that the existence of measurable sulfide residuals was questionable.

Copper, nickel, zinc, cadmium, mercury and lead residuals were all below effluent goals over broad ranges and conditions, as predicted by chemical equilibria.(8) The complexing action of seawater did not limit the effectiveness of the precipitation of metals from at least the dilute influents.

Chromium was removed in some cases to within the specified effluent goals (5 g/m^3 (4 x 10^{-5} lb/1000 gal)), although there is some question concerning the mechanism of removal in this case, since the influent concentrations of chromium were relatively low (see Chromium subsection).

The metals residuals for C_{50} influent were, in general, significantly higher than for others. (The corresponding lead residuals, ≤ 0.16 g/m^3 (0.0013 lb/1000 gal), are not plotted in Figure 19.) Since typically much lower residuals



1. Control Limitations Overshoots/Undershoots

2. Limitations Possibly Related to Precipitation Curve Minima

3. Reset OARMAC Nonlinear Gain Compensation

3. Control Limitations Resolved

FIGURE 15 ILLUSTRATION OF HYDROXIDE PRECIPITATION CONTROL DEMANDS AND NEED FOR NONLINEAR GAIN COMPENSATION

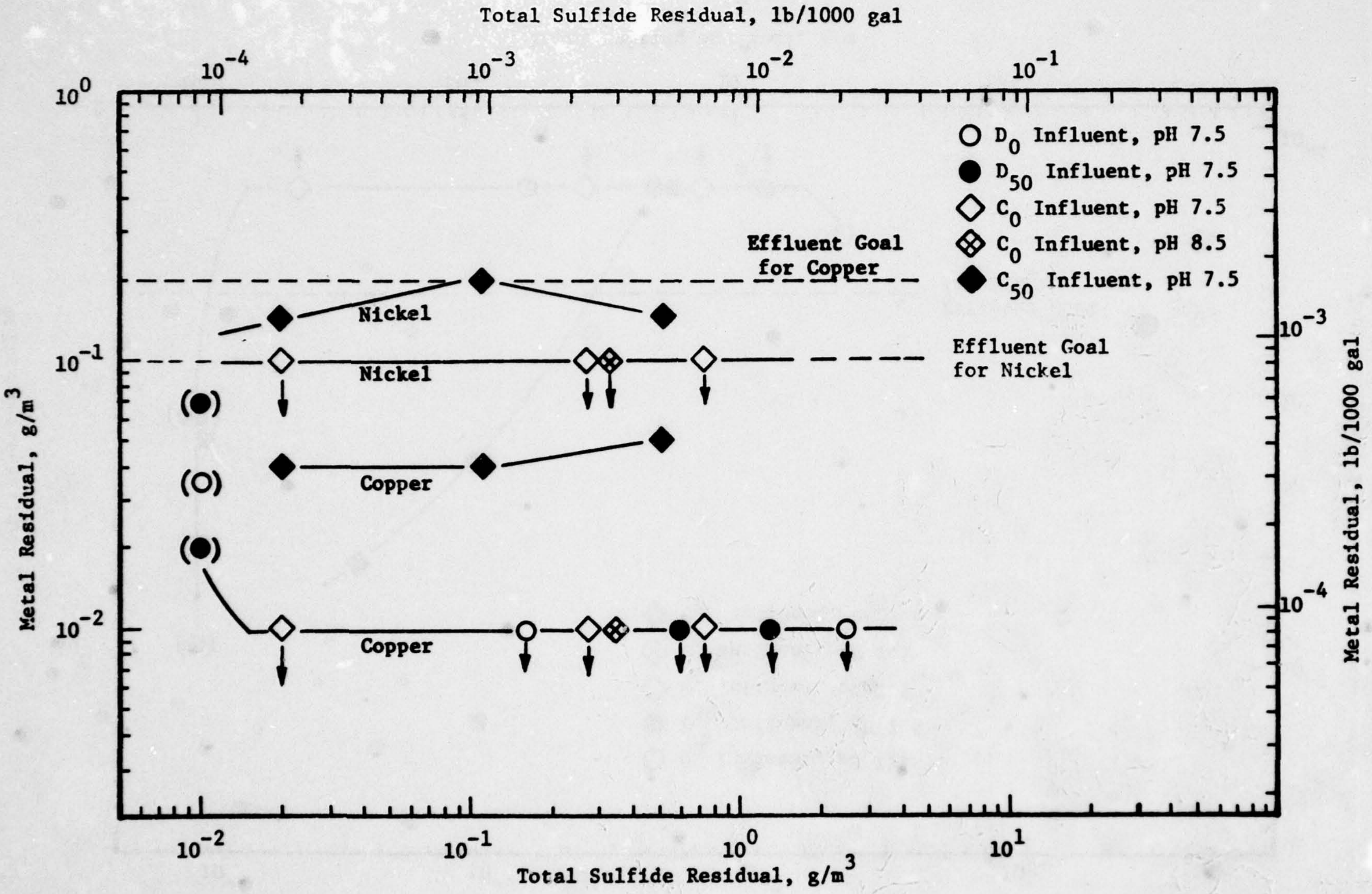


FIGURE 16 COPPER AND NICKEL RESIDUALS VERSUS SULFIDE RESIDUAL

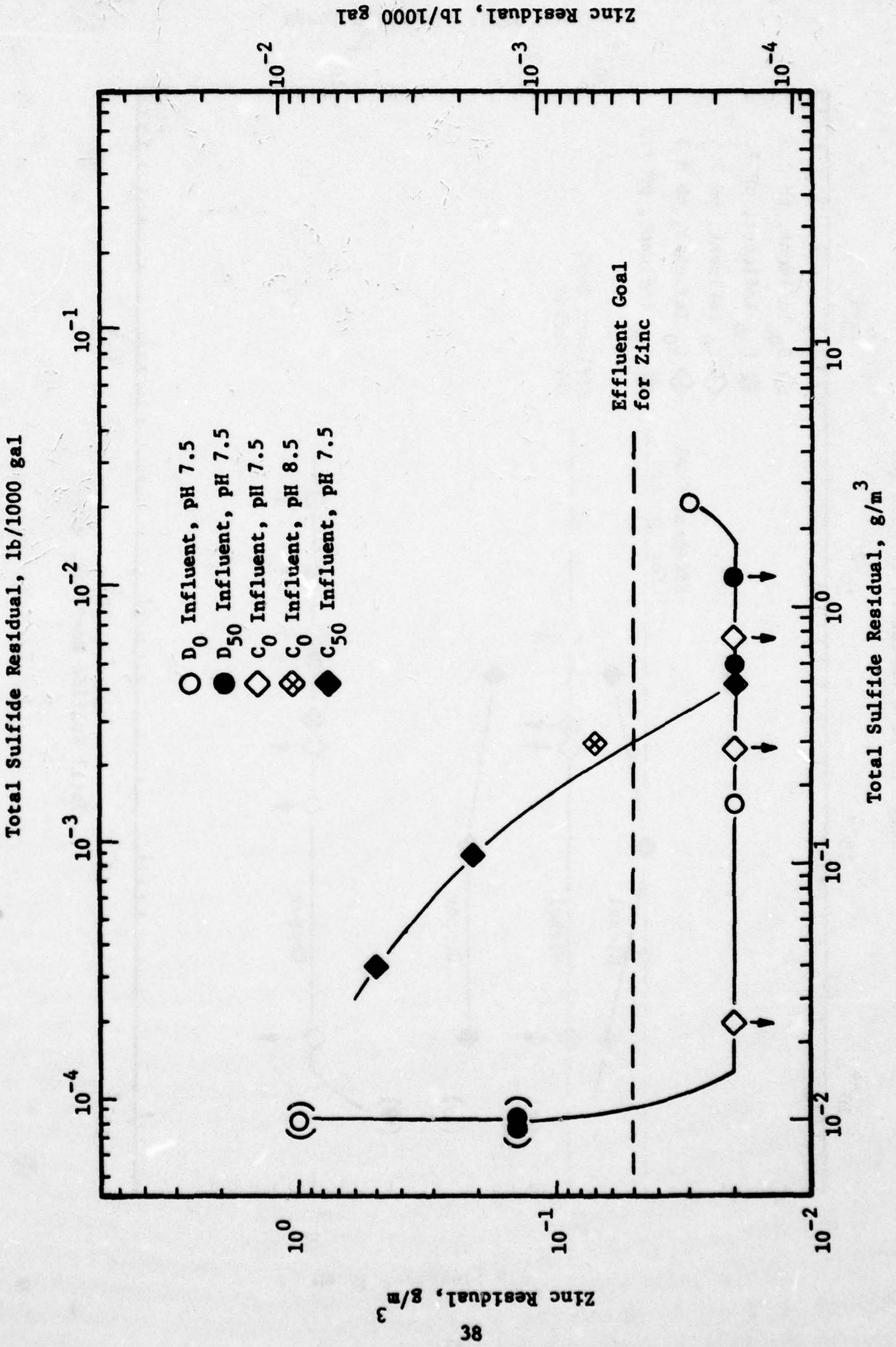


FIGURE 17 ZINC RESIDUAL VERSUS SULFIDE RESIDUAL

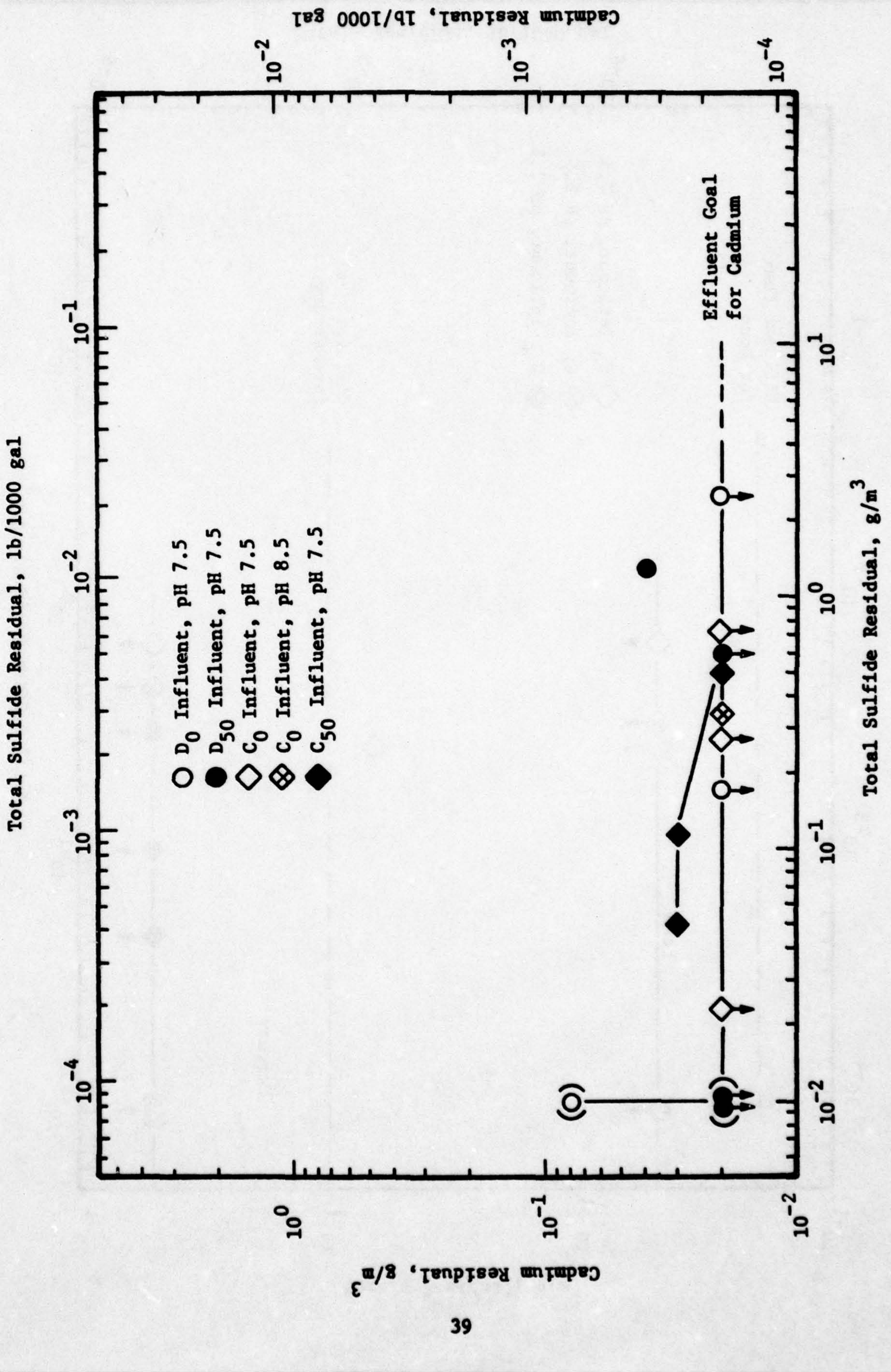


FIGURE 18 CADMIUM RESIDUAL VERSUS SULFIDE RESIDUAL

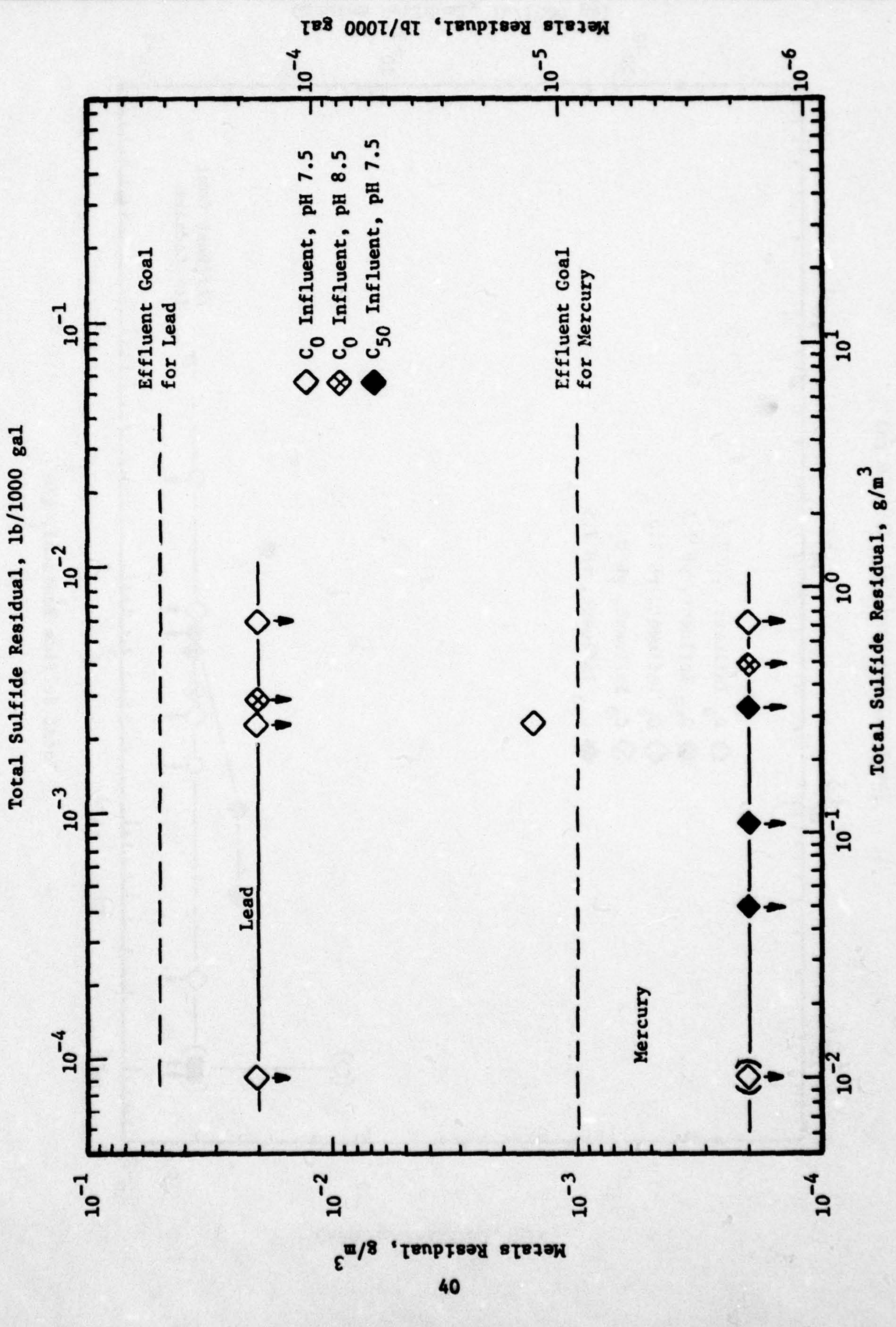


FIGURE 19 MERCURY AND LEAD RESIDUALS VERSUS SULFIDE RESIDUAL

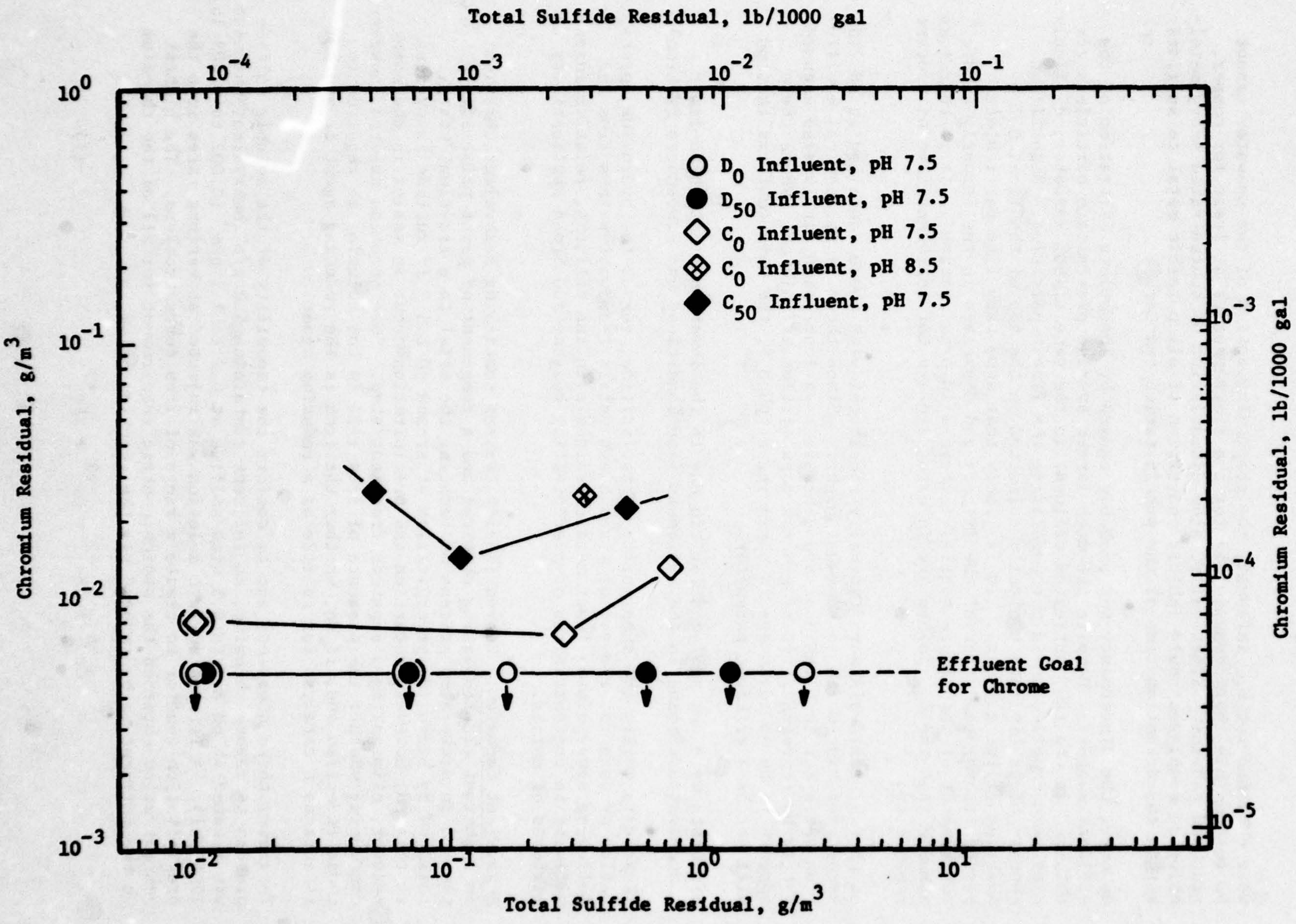


FIGURE 20 CHROMIUM RESIDUAL VERSUS SULFIDE RESIDUAL

were obtained for D_{50} influent, the complexing action of the seawater cannot be responsible thermodynamically for the discrepancies at least for copper, zinc and cadmium. Kinetically, slow dissociation of concentrated heavy metal-chloride complexes could inhibit conversion of all possible metal to sulfides within the detention time of the precipitation reactor.

However, the discrepancy was probably caused by incomplete filtration of the effluent samples. Despite the much larger average precipitate particle sizes obtained in the raw, untreated effluent in the case of 50% seawater, difficulties were experienced in precoagulating the finest particles. Significant amounts of precipitate typically collected on the top of the final 0.2 μ membrane filter elements. It is likely that some very fine particulates passed through the pores of the filters and dissolved in the strongly acidic environment of the sample bottles (nitric acid preservative). It is therefore assumed that the C_{50} points are in error and are not representative of process capability.

At pH 8.5, residuals were typically consistent with those contained at pH 7.5, except for zinc which is somewhat higher. Since there is no chemical equilibrium basis for this residual and since it is a lone point, it is also assumed not to be representative of process capabilities at this pH. While there appears to be no advantage in operating at pH 8.5, the data confirms that pH will not be a critical parameter.

Effluents were not analyzed for tin due to the lower-than-detection-limit concentrations found in the influents (see Conditions and Procedures Section).

These data verify the superiority of the sulfide, versus the hydroxide, precipitation process for removal of mixed heavy metals from wastewaters from the following standpoints: lower metals residuals in the effluent, relative insensitivity to concentrations of precipitating reagent and broad applicability to mixtures of metals.

Hexavalent Chromium. Conventionally, wastes containing hexavalent chromium, an important electroplating chemical and a component of paint primers, are treated in a two-step process by reducing the metal to a trivalent state, followed by hydroxide precipitation at around pH 8.5. If sulfide is present at this pH, however, reduction and precipitation occur in series in the same reactor, eliminating a separate treatment step. Some question existed, however, concerning whether the presence of iron (+2) in the solution is required to cause reduction and, if so, whether the iron is the reducing agent or whether it acts as a catalyst for sulfide as a reducing agent.

To answer these questions and to confirm the capability of the soluble sulfide process to remove chromium, an influent containing 5.0 g/m^3 hexavalent chromium was treated at pH 8.1 to 8.5 with sulfide at 0.2 to 1.1 g/m^3 (0.002 to 0.009 lb/1000 gal). A ferrous sulfate solution was injected at various rates into the precipitation reactor to create a range of iron concentrations. The highest concentration exceeded the stoichiometric requirement for all of the chromium in the influent to be reduced via the reaction below.

$$Cr^{+6} + 3Fe^{+2} = Cr^{+3} + 3Fe^{+3} \qquad (1)$$

The results of these tests are plotted in Figure 21 along with the projected curve that would be obtained if the stoichiometry of Equation 1 governed the reduction. It is apparent from the data that:

- Some removal (about 20%) took place without the presence of iron. A maximum of 4 g/m^3 (0.03 lb/1000 gal) of chromium was observed in the effluent.
- Much smaller than stoichiometric dosages of iron effected reduction of most of the chromium. However, nearly stoichiometric dosages resulted in the best reduction.
- Chromium residual falls exponentially, versus linearly, with iron concentration up to the point at which other factors apparently take over (although the residual is well above that predicted by chemical equilibrium, it is within the range of some of the better levels typically obtained in conventional practice.(14)

Based on these factors, it is concluded that:

- The presence of iron (or potentially some other suitable secondary metal) may be necessary for effective removal of hexavalent chromium via the soluble sulfide process. This could be effected simply by injection of appropriate levels of ferrous ion into the reactor when chromium is known to be present. (However, the data in Figure 20 suggests that other metals present in mixed wastes may aid the reduction.)
- The iron acts principally as a catalyst for chromium reduction, although near-stoichiometric dosages will be required to obtain the best metal removals.

Iron. Three of the effluents obtained in the chromium experiments just discussed were analyzed for iron residual, including the effluent containing iron at levels above the stoichiometric dosage for chromium reduction. All the iron residuals were below 0.05 g/m^3 (4×10^{-4} lb/1000 gal), versus an effluent goal of 0.5 g/m^3 (4×10^{-3} lb/1000 gal). This data confirms the effectiveness of the soluble sulfide process for removal of iron.

Sulfide Residuals

The metals removal data indicate that maintenance of sulfide residuals in the range <0.1 to 1 g/m^3 ($<8 \times 10^{-4}$ to 8×10^{-3} lb/1000 gal) provides low metals residuals in process effluents. Such levels are below or at the lower end of sulfide concentrations commonly found in sewage. Process effluents can therefore be discharged directly into sewers. If desired, however, the sulfide residuals can be reduced to negligible proportions economically by adding hydrogen peroxide to final process effluents and letting it oxidize the sulfide to elemental sulfur (plus some sulfate)(15,16) in the sewers.

Reagent Usage

The usage for sulfide and hydroxide control reagents are plotted versus total sulfide residual maintained in Figure 22.

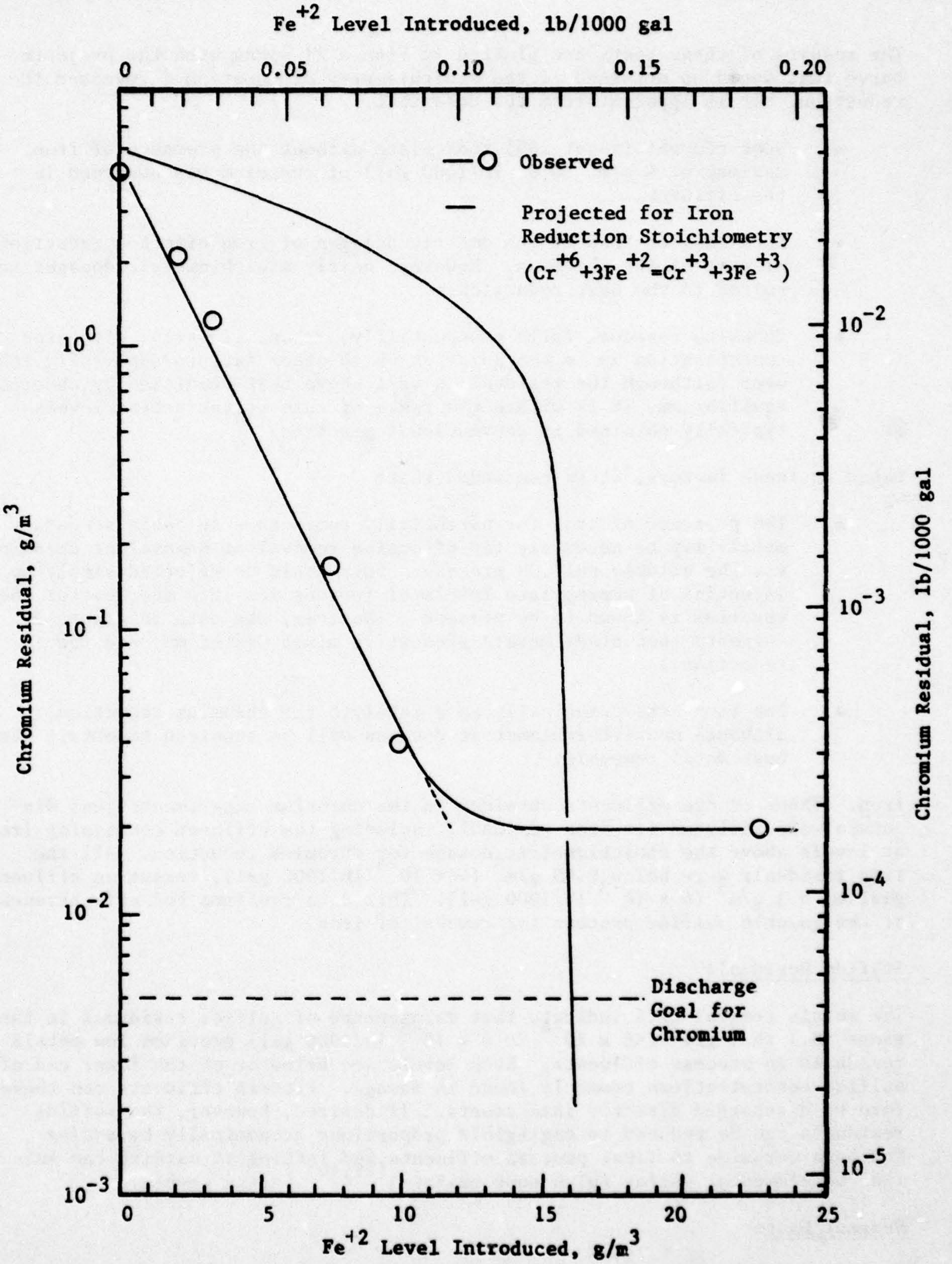


FIGURE 21 EFFECT OF IRON (+2) CONCENTRATION ON ONE-STEP CHROMIUM REMOVAL

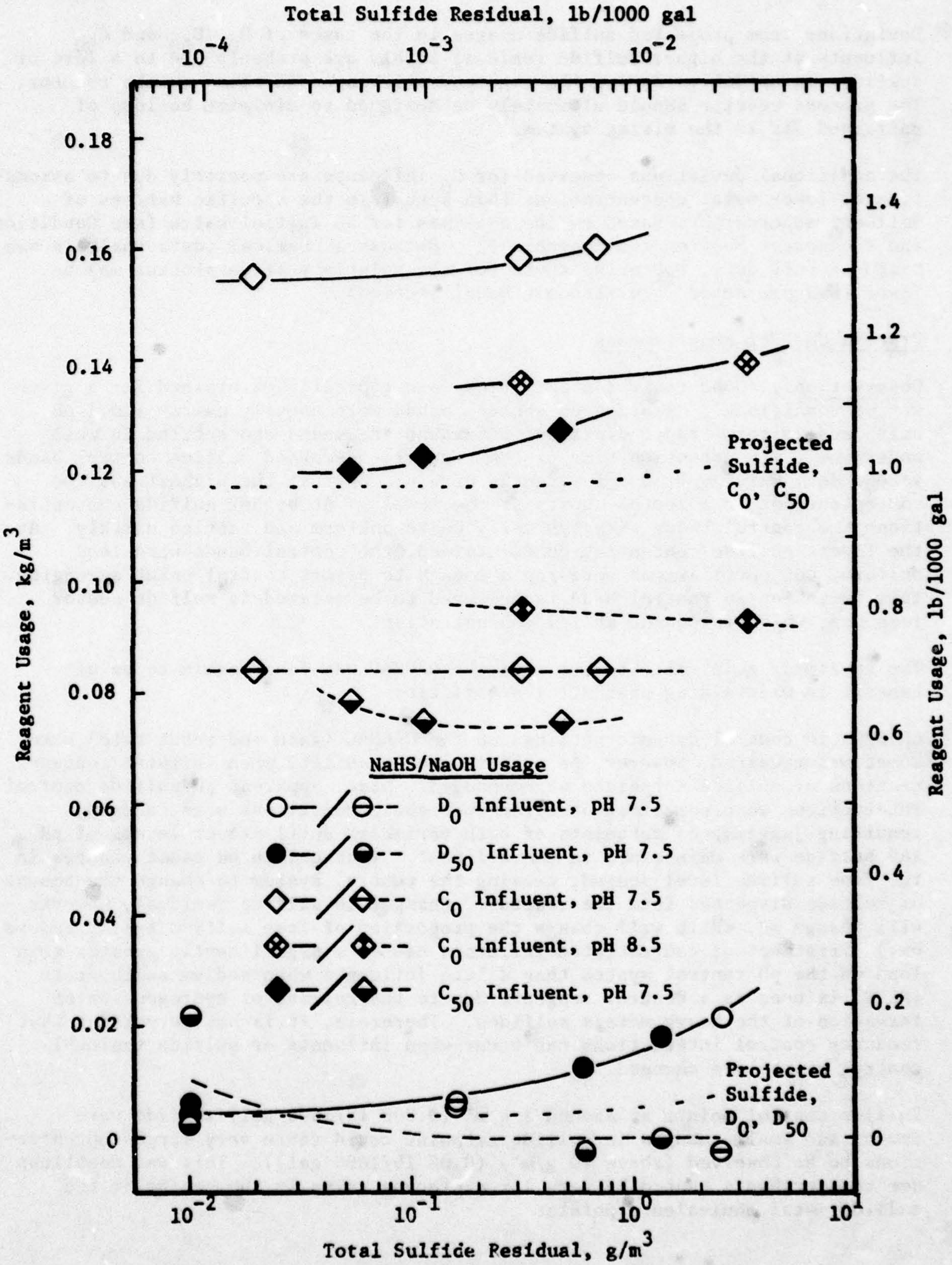


FIGURE 22 REAGENT USAGE FOR SULFIDE PRECIPITATION

Deviations from projected sulfide usages in the cases of D_O, D_{50} and C_{50} influents at the higher sulfide residual levels are probably due to a loss of sulfide via oxidation during the vigorous stirring conditions in the reactor. The process reactor should ultimately be designed to minimize buildup of entrained air in the mixing system.

The additional deviations observed for C_O influents are possibly due to assumption of lower metal concentrations than actual in the specific batches of influent supernatant, based on the analyses for an initial batch (see Conditions and Procedures Section and Appendix 1). Because a chemical costs analysis was based on this data, operating costs for the soluble sulfide process may be lower than projected (see Economic Model section).

Process Control Requirements

Observations. Good control stabilities were typically maintained for a given set of conditions. Recorded pH control bands were usually narrow (±0.1 pH unit) and uniform (rapid distribution around the mean) and settled in well under the 5 min detention time of the reactor. Recorded sulfide control bands were wider, varying from a few tenths of a $pS^=$ unit at the highest sulfide concentrations to a few $pS^=$ units at the lowest. At higher sulfide concentrations the control bands were typically quite uniform and settled quickly. At the lowest sulfide concentration maintained, the control bands were less uniform, but oscillations were rapid enough to permit control point averaging. This variation in control band is believed to be related to sulfide sensor response, which is poorer at low concentrations.

The nonlinear gain characteristic of the OARMAC was found again to be of benefit in maintaining pH control stabilities.

Changes in control dynamic settings on the OARMAC (gain and reset rate) were sometimes required, however, to achieve good stability when influent concentrations or sulfide setpoints were changed. Also, apparent pH/sulfide control interactions were sometimes observed when these conditions were changed, requiring juggling of setpoints of both variables until proper levels of pH and sulfide were maintained in the effluent. (Changes in pH cause changes in the free sulfide level sensed, causing the control system to change the amount of sulfide dispensed into the reactor. Changes in sulfide residual, however, will change pH, which will change the proportion of free sulfide again, and so on.) Treatment of concentrated influents causes a significantly greater acid load on the pH control system than dilute influents when sodium sulfhydrate (NaHS) is used as a control reagent, due to the release of hydrogen ion on formation of the heavy metals sulfides. Therefore, it is not surprising that feedback control interactions can occur when influents or sulfide residual control points are changed.

Sulfide control points at around 1 g/m^3 (0.008 lb/1000 gal) sulfide were touchy and small changes in sulfide setpoint could cause very large concentrations to be observed (above 10 g/m^3) (0.08 lb/1000 gal)). This was doubtless due to overshoots caused by very large process gains in the region of the sulfide/metal equivalence points.

Table 2 shows how condition changes affected the setpoints required to maintain given pH and sulfide levels. Seawater-containing influents affected controls the least, possibly due to the benefits of higher electrical conductivity in the water on sensor response, and therefore on system response. Some changes may be due to variations in sensor characteristics with time and cleaning cycles.

Special efforts were made to maintain precise pH control levels for the purposes of this study. It appears that such precise pH control will not be required however in the applied process and most of the pH control point variations listed in Table 2 may be tolerable.

Recommendations. The following recommendations are anticipated to reduce pH/sulfide control interactions if feedback control is selected for the next generation process hardware.

- Measure total, versus free, sulfide as a control parameter (by a relatively simple computation in the control system, utilizing a chemical equilibrium equation and sulfide and pH electrode potentials, for example).
- Incorporate a nonlinear gain feature in the sulfide control channel to compensate for nonlinearities in process gain in the region of the metal/sulfide equivalence point.
- Minimize sensor fouling which interferes with their response characteristics and can cause changes in control points with time, by using electrode cleaning devices and substituting a double-junction reference electrode for the sensor currently in use.
- Optimize hydraulic configurations.
- Possibly use sodium sulfide instead of sodium sulfhydrate as a control reagent (although substitution of this reagent in some preliminary tests did not improve pH/sulfide interactions).

However, a very well stirred reactor was used in this study. Comparable homogeneities may be impractical to attain at full-scale plant capacities. Therefore, it is obvious from prior discussions that attainment of good control of the soluble sulfide process is essential.

Comparison of these requirements to those for automatic breakpoint chlorination of sewage is helpful. In this process ammonia is oxidized by chlorine at controlled pH. The pH and chlorine levels tend to be interactive. A combination feed forward/feedback control system has been used, for example, to achieve low chlorine residuals of 4 ±2 g/m^3 (0.33 ±0.0017 lb/1000 gal) in combination with the large total chlorine dosages required, about 150 g/m^3 (1.3 lb/1000 gal).(17) The pH was controlled to between 6.6 and 7.8.

The process demands for precipitating metals from industrial wastes with large, quite variable metals concentrations (and therefore large and quite variable sulfide demands) while maintaining sulfide residuals at about 1.0 g/m^3

TABLE 2 CONTROL POINT OBSERVATIONS(a)

Day	Influent	pH Setpoint to Maintain pH 7.5 ±0.1	Total Sulfide, g/m^3 (lb/1000 gal)x10^2	Setpoint Required (Ideally, -100 Unit Change = +1 Decade Free Sulfide Change)
1	C_0	8.5	0.28 (0.23)	630
2	C_0	8.6	0.02 (0.02)	600
2	C_0	8.5	0.11 (0.09)	560
2	C_0	8.5	0.73 (0.61)	500
6	D_{50}	7.5	1.3 (1.1)	702
6	D_{50}	7.4	0.6 (0.5)	800
6	D_{50}	7.5	0.01 (0.01)(b)	1000
6	D_0	7.5	2.5 (2.1)	700
8	D_0	8.2	0.17 (0.14)	900
8	D_0	9.0	0.01 (0.01)(b)	1000
8	D_{50}	8.1	0.01 (0.01)(b)	900
9	C_0	8.6	0.01 (0.01)(b)	600
26	C_{50}	8.2	0.05 (0.04)	660
26	C_{50}	8.2	0.11 (0.09)	600
26	C_{50}	8.2	0.51 (0.43)	560

(a) Chronological; no interim control sensor calibrations.
(b) Below detection limit or in question.

(0.008 lb/1000 gal) are at least comparable. It is therefore anticipated that feed forward pretreatment of effluent upstream will be required to reduce the metals loading and process demands on a downstream feedback control unit, particularly if the system needs to process influent at variable flow rates.

Ideally, complete feed forward control would be most desirable. Feedback control is essentially a trial-and-error affair. Use of a proportional integral feature smooths out the fluctuations of this process at the expense of some dynamic response. However, feedback control is inherently susceptible to process upsets due to condition changes, its response characteristics are variable, and proper control settings are difficult to arrive at.(18)

Feed forward control, on the other hand, senses what action is needed in advance and implements the correct action. Chemicals are dosed in proportion to total mass requirements (reagent concentration demand x flow). Reliance on control dynamics is minimal, response can be very rapid and controlinteractions between reagents is eliminated. However, the accuracy with which this can be accomplished by conventional means is limited by up-front sensor accuracy, conversion of sensor signals into process reagent flow demands (often nonlinear), range and accuracy of control actuators and variations in control reagent concentrations versus the assumed levels. Feed forward control is therefore normally restricted to applications requiring limited control accuracy or range or for pretreatment.

However, a concept exists that is projected to minimize these limitations and provide precision, 100% feed forward control of the soluble sulfide process (e.g., to 1 g/m^3 (0.008 lb/1000 gal) sulfide residual) despite variations in influent characteristics. Hardware development of this concept is recommended as a part of process scaleup (see Recommendations section).

PRECIPITATE SEPARATION

The objective of this portion of the study was to investigate properties of the hydroxide and sulfide metal precipitate effluents to enable projection of the pretreatment agents required (coagulants and flocculants), the preliminary sizing for clarification devices (e.g., parallel-plate clarifiers) and the need for other precipitate-handling/effluent polishing devices.

Coagulant/flocculant dosage/type tests characterized clarification conditions.

- The dosage of a given coagulant and/or flocculant resulting in the best clarification of effluents was determined. This optimum dosage was employed in subsequent settling tests.
- If a series of coagulants and/or flocculants was investigated, the one producing the best clarification at its optimum dosage was determined. This was used in subsequent settling tests.

Settling tests characterized clarification rates and sludge properties.

- Projected effluent qualities that can be obtained from a clarifier versus selected surface loading rate (flow rate per unit clarifier settling area) were observed.
- Density of the settled precipitate (sludge) as a function of settling time was measured. These data permit projections to be made concerning sludge handling operations (e.g., dewatering).

Procedures for these tests have been described previously.

Both hydroxide and sulfide precipitates were generated from C_0 influent at the pH range and sulfide concentrations likely to produce the greatest precipitation of metals. C_0 was chosen as the basic influent for the following reasons:

- Concentrated precipitate suspensions are more likely candidates for gravity separation techniques than dilute suspensions, there being a limit on the practical clarifications obtainable in a dynamic system (e.g., 10 to 20 g/m^3 (0.08 to 0.17 lb/1000 gal) solids for hydroxide precipitates). Dilute suspensions (and clarified concentrated suspensions) will typically require filtration or other solids-removal polishing steps.
- 0% seawater effluents were expected to have more settling limitations than 50% seawater effluents, since the existance of fine hard-to-settle particles is less likely in a high ionic strength, charge-neutralizing environment.(19)

Hydroxide Precipitates

Hydroxide precipitates were generated at a steady state pH of 9.8. Samples were withdrawn from the effluent as required.

Coagulant/Flocculant Dosage Tests

A single flocculant could be selected a priori as a good agent based on the experience of a precipitate-handling equipment manufacturer and information supplied by the flocculant manufacturer concerning treatment of hydroxide precipitate-containing effluents. This high molecular weight, anionic polyelectrolyte, designated Flocculant A, is a very active, broad pH range liquid anionic agent. It is similar to a somewhat less active, earlier-generation agent commonly used for metal hydroxide precipitates.

Turbidity of the clarified effluent is plotted versus flocculant concentration in Figure 23. Based on these results, 1.3 g/m^3 (0.011 lb/1,000 gal) was selected as the flocculant dosage to be used in the subsequent settling experiments.

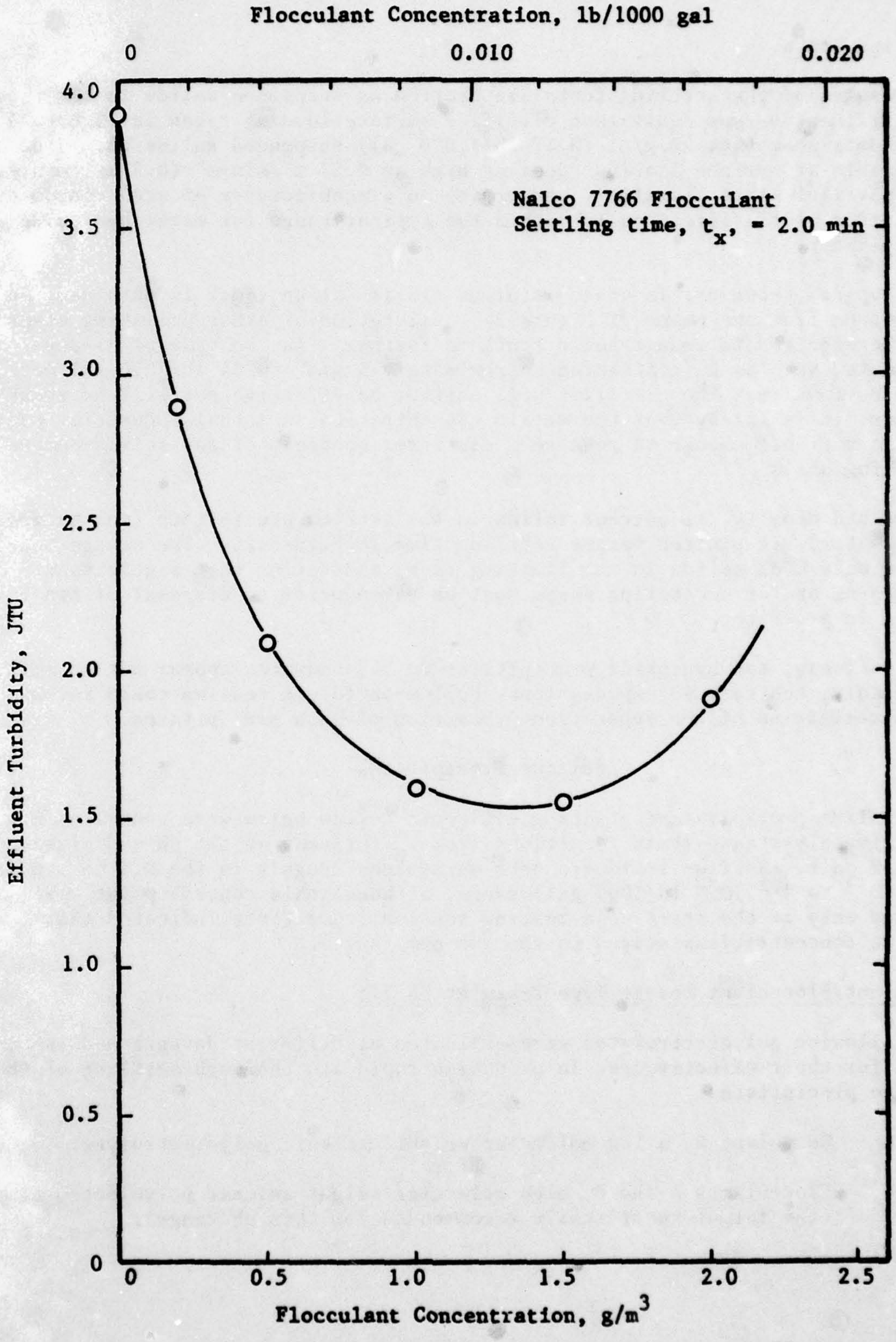


FIGURE 23 RESULTS OF METAL HYDROXIDE FLOCCULANT DOSAGE TEST

Settling Tests

The results of the settling tests are plotted as suspended solids in the clarified effluent versus equivalent clarifier surface loading rates in Figure 24. These data show that 20 g/m^3 (0.17 lb/1,000 gal) suspended solids should be obtainable at surface loading rates as high as 0.27 $m^3/min\text{-}m^2$ (0.7 $gal/min\text{-}ft^2$) in a parallel plate clarifier. According to a manufacturer of such equipment, this order of clarification is within the typical range for metal hydroxide precipitates.

Also typical, however, is that a minimum clarification limit is obtained, as is obvious from the shape of Figure 24. Filtration or other polishing steps will be required to reduce solid contents further. In the case of dilute influents, such as D_0 containing approximately 5 g/m^3 (0.04 lb/1000 gal metals), it is obvious that the clarifier will neither be effective nor will be required. However, it is likely that the metals concentration in actual industrial wastes will be variable enough to require a clarifier upstream of any solids-removal polishing units.

Sludge bed density, as percent solids in the settled precipitate (the balance being water), is plotted versus settling time in Figure 25. The sludge contained only 0.3% solids in the limiting case, indicating that significant thickening and/or dewatering steps must be taken prior to disposal of the sludge in practice.

Qualitatively, the hydroxide precipitates in 50% seawater appear not to settle as rapidly, contrary to expectations. Follow-on future testing could include characterization of the separation properties of such precipitates.

Sulfide Precipitates

The sulfide precipitate-containing effluents tested below were generated at approximately steady-state conditions from C_0 influent at the pH's designated, ±0.1 pH unit. Sulfide residuals were maintained roughly in the 0.1 to 1.0 g/m^3 (8×10^{-5} to 8×10^{-3} lb/1000 gal) range, although this control point was checked only at the start of a testing session (odor tests indicated that sulfide concentrations stayed in the sub-ppm range).

Coagulant/Flocculant Dosage/Type Tests at pH 7.5

The following polyelectrolytes were evaluated at different dosages and combinations for their effectiveness in producing rapid and thorough settling of the sulfide precipitates.

- Coagulant A, a low molecular weight cationic polyelectrolyte.
- Flocculants A and B, high molecular weight anionic polyelectrolytes, (the former specifically recommended for this pH range).

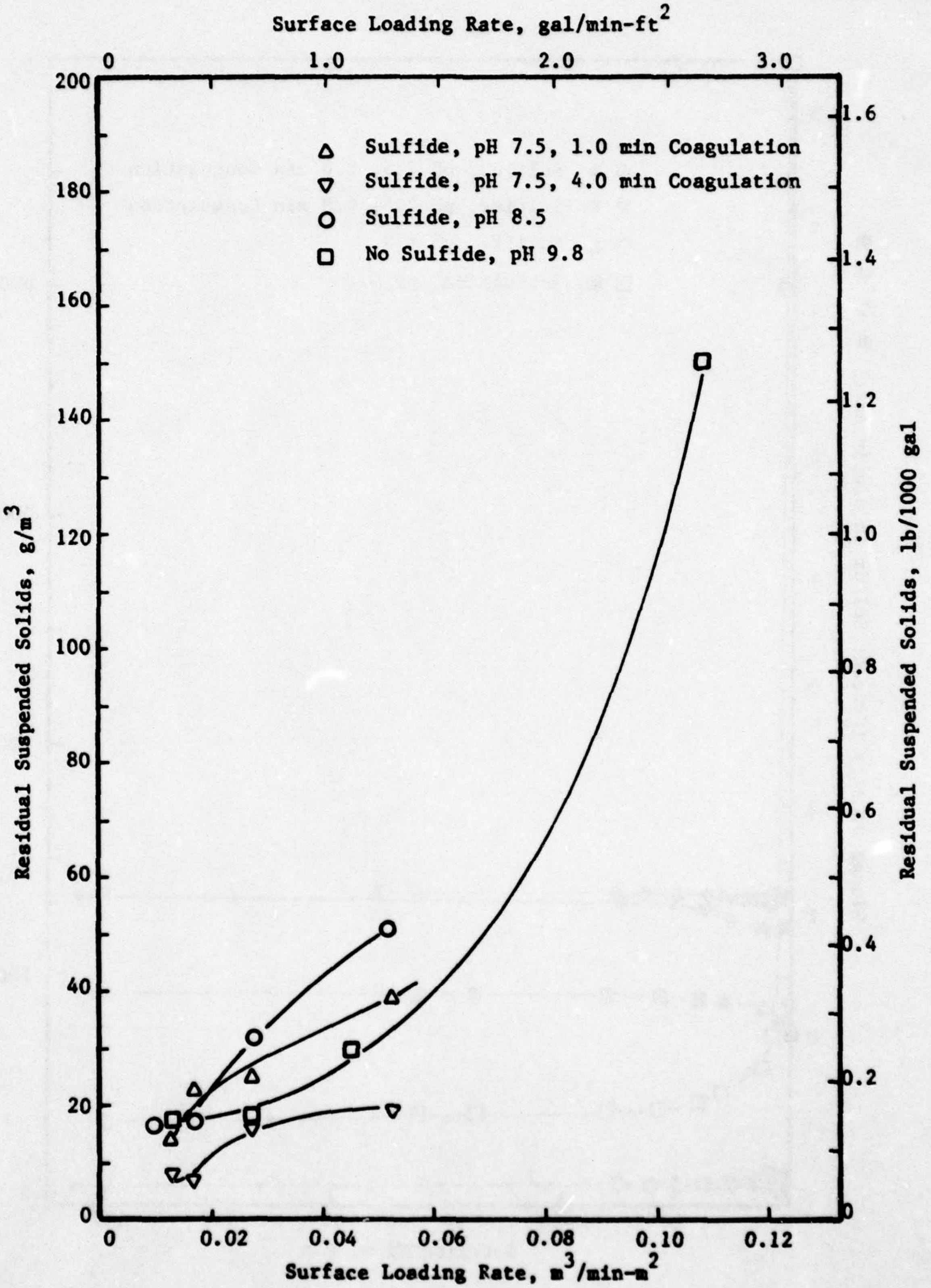


FIGURE 24 RESIDUAL SUSPENDED SOLIDS VERSUS CLARIFIER SURFACE LOADING RATE

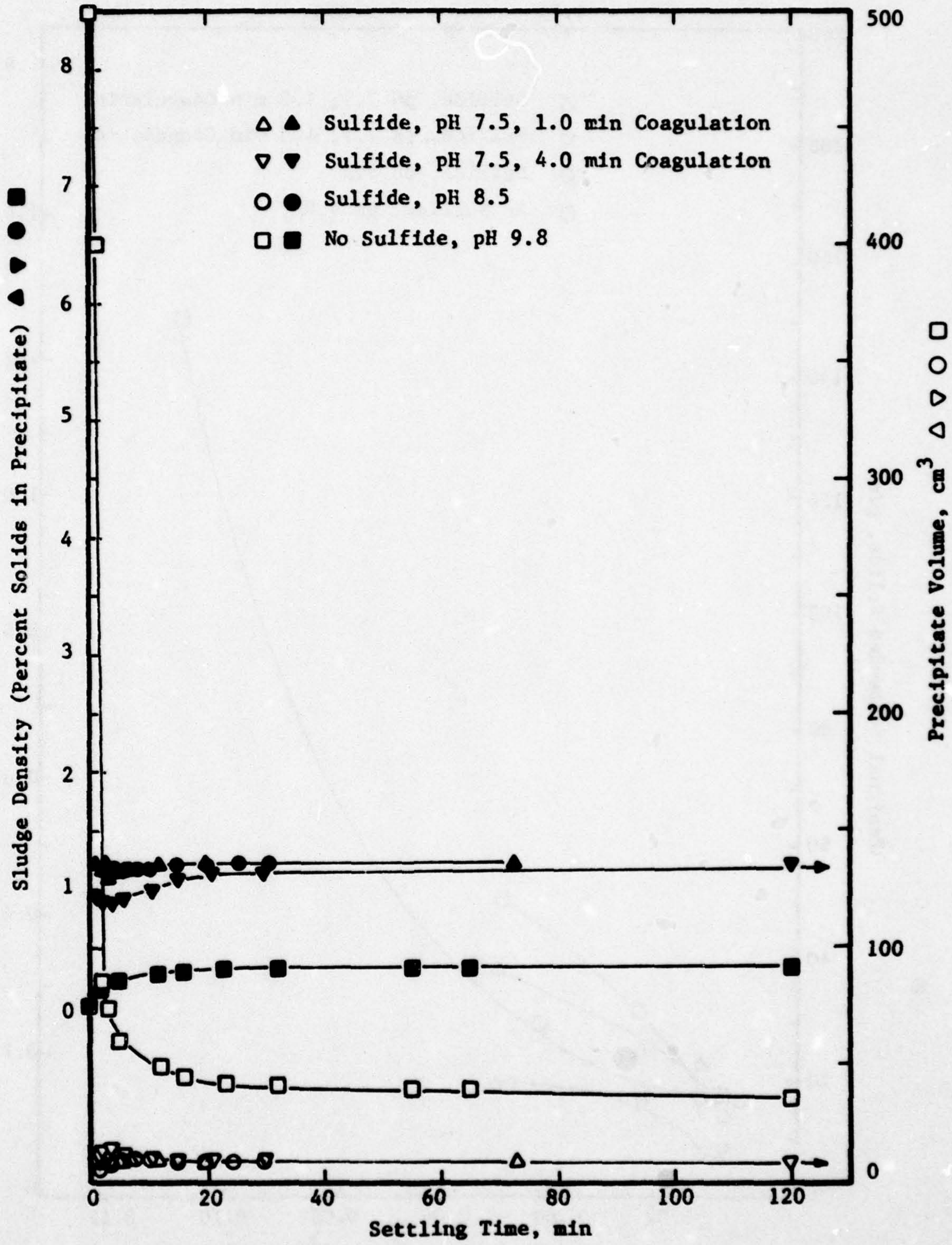


FIGURE 25 SLUDGE SETTLING CHARACTERISTICS

- Flocculant C, a medium molecular weight cationic polyelectrolyte.

Unless otherwise specified, the agents were flash mixed for ten seconds into the effluent which was then flocculated for 1.0 min (designated as "Mix/Floc" in the data).

Coagulant Alone. The precipitates in the raw effluent were finely divided. Significant portions passed through 0.2 μ membrane filters. Flash mixing of Coagulant A into the effluent to a 20 to 40 g/m^3 (0.17 to 0.3 lb/1000 gal) level produced precipitates that were almost entirely retained by a 2.7 μ glass fiber filter (Whatman (GF/D)). This coagulant was therefore evaluated by itself off-line to determine the best dosage.

The suspended solids and turbidity data from these evaluation are plotted in Graph A of Figure 26. This plot, corresponding to 2.0 min of settling, confirmed that the best dosage level was in the range 30 to 40 g/m^3 (0.25 to 0.33 lb/1000 gal). The lower of these two levels was selected for further tests. The clarifications obtained using Coagulant A alone, however, were not deemed to be adequate.

Contrary to normal observations, turbidity readings increased with increasing clarification, as confirmed both by suspended solids measurements and individual observations. This phenomenon is assumed to be due to more effective passage of light through the partially clarified effluents than through the very dark raw effluent (i.e., a partial densitometric versus true nephelometric effect). This trend was also observed in other tests where only partial clarification was obtained (e.g., Graph C of Figure 26).

Flocculant Alone. Because the precipitate in the raw effluent was near-colloidal, anionic flocculants alone were not expected to aid settling significantly. The required preadsorption of cationic counter ions is very limited for such small particles.(19) Since some flocculation was achieved in the past using anionic agents on the sulfide effluents(4), and the economic advantages of using only one settling agent are obvious, however, the effect of these substances alone on settling was evaluated (2.0 min settling time).

Graph B of Figure 26 shows that neither of the two anionic flocculants produced significant settling in 2.0 min, although the turbidities did change somewhat. Therefore, use of these agents alone is not adequate.

The cationic Flocculant C was also tried alone at a dosage of 1.0 g/m^3 (0.008 lb/1000 gal). This agent was also relatively ineffective.

Coagulant Plus Flocculant (Series Flash Mixed). A combination of cationic coagulant and anionic flocculant was required, the first to electrically destabilize and increase the particle size of the fine precipitates and the second to tie the resulting particles together to form large, fast-settling flocs.

It will obviously be economically desirable to minimize the number of operations to be performed on the metal wastes in the ultimate applications. Therefore,

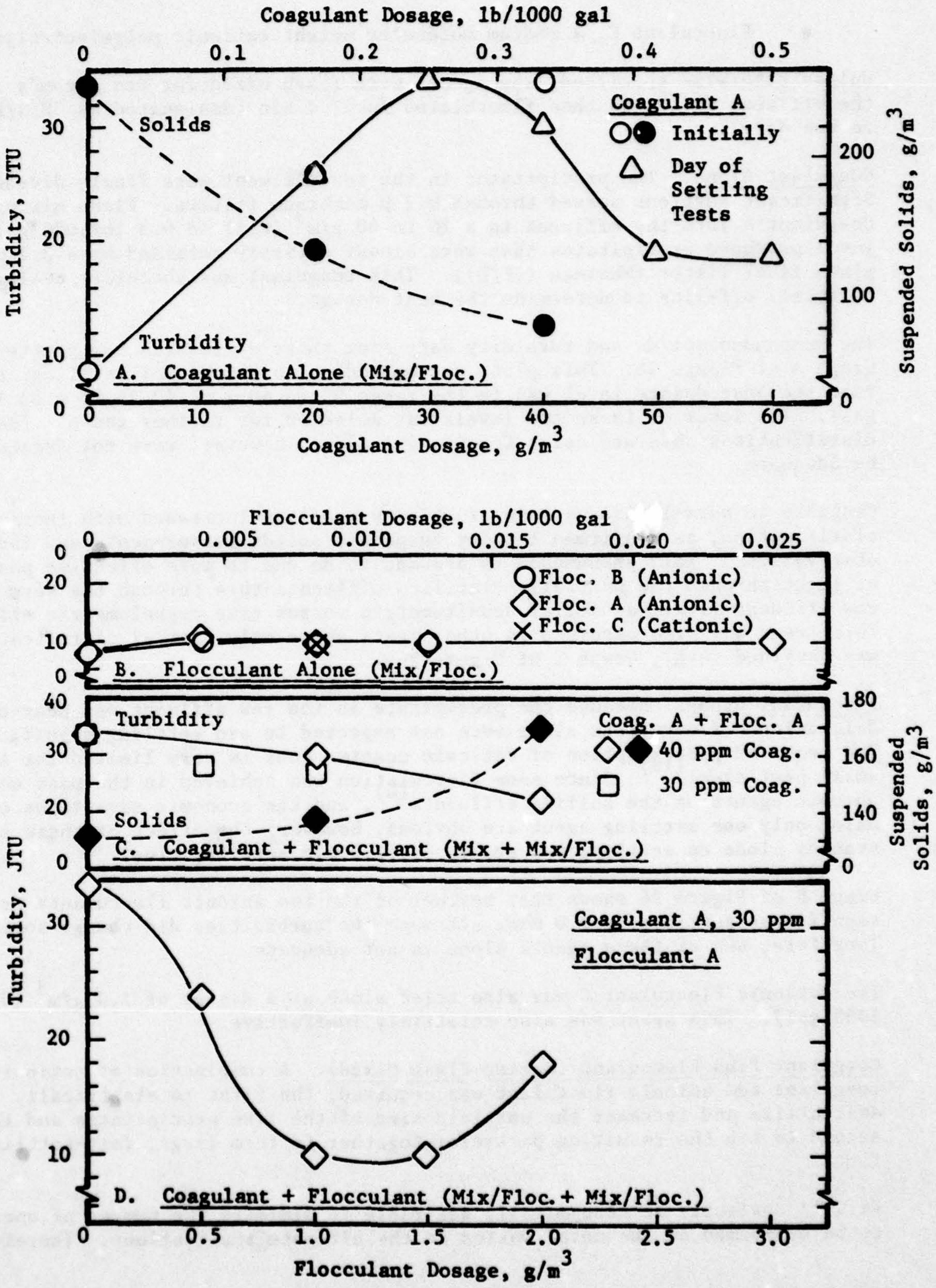


FIGURE 26 RESULTS OF COAGULANT/FLOCCULANT DOSAGE/TYPE TESTS FOR SULFIDE EFFLUENTS AT pH 7.5

the following sequential treatment of the effluent was tried initially: flash mixing in of Coagulant A, then immediate flash mixing in of Flocculant A (no intermediate coagulation period), then flocculation. However, as shown in Graph C of Figure 26, increasing concentrations of flocculant actually decreased the settling power of the Coagulant A (3.0 min settling time). Despite rapid precipitate charge neutralization by the coagulant, an intermediate flocculation step (coagulation period) was apparently required to stabilize the particles prior to addition of anionic flocculant (which in the present case probably neutralized the benefits of the coagulant).

Coagulant Plus Flocculant (Each Mixed and Flocculated). Use of complete flash-mix/flocculation steps, each after coagulant and flocculant addition, produced very rapid clarification, as illustrated in Graph D of Figure 26 (3.0 min settling time). Clarification was good and a normal turbidity/dosage curve was obtained. A dosage of 1.2 g/m^3 (0.01 lb/1000 gal) of Flocculant A was selected for treatment of the C_0 effluent.

Conclusion. Despite the occurrence of near-colloidal metal sulfide particulates, good settling characteristics were obtained with two complete flash mix/flocculation steps, using Coagulant A and Flocculant A, respectively. Although the required dosages of these agents will vary with influent characteristics, it is expected that in general good settling of heavy metal sulfide precipitates generated from industrial wastes will be achieved using this combination.

Settling Tests at pH 7.5

The clarifications obtained in the settling tests at pH 7.5 are plotted in Figure 24. This data shows that better clarifications, less than 10 g/m^3 (0.08 lb/1000 gal) suspended solids, were obtained for the sulfide effluents than for the hydroxide effluents once proper coagulation/flocculation conditions were established. A 4.0 min coagulation (flocculation) internal between the coagulant and flocculant flash mixing operations were shown to be necessary to obtain superior settling, as shown in Figure 27.

This order of settling is expected to be obtained using a parallel plate clarifier, since these settling tests are designed to closely correlate with the performance of such devices.

As for hydroxide precipitates, however, filtration may be required to further polish the effluent of suspended solids content. Otherwise, the low metals residuals obtainable by sulfide precipitation may not be realized due to some eventual redissolution of the particulates.

Sludge bed (settled precipitate) densities and test volumes are plotted versus settling time in Figure 25 for the pH 7.5 precipitates. The sulfide sludges are significantly more compact and settle far more rapidly than the hydroxide sludges. Further, the sulfide sludges are not gummy and gelatinous as are hydroxide sludges, which present special handling, dewatering and disposal problems. The relatively low densities, in terms of percent dry solids, observed for the sulfide precipitates are apparently due to the formation of rather loose interparticle bonds due to flocculation, not to the stubbornly

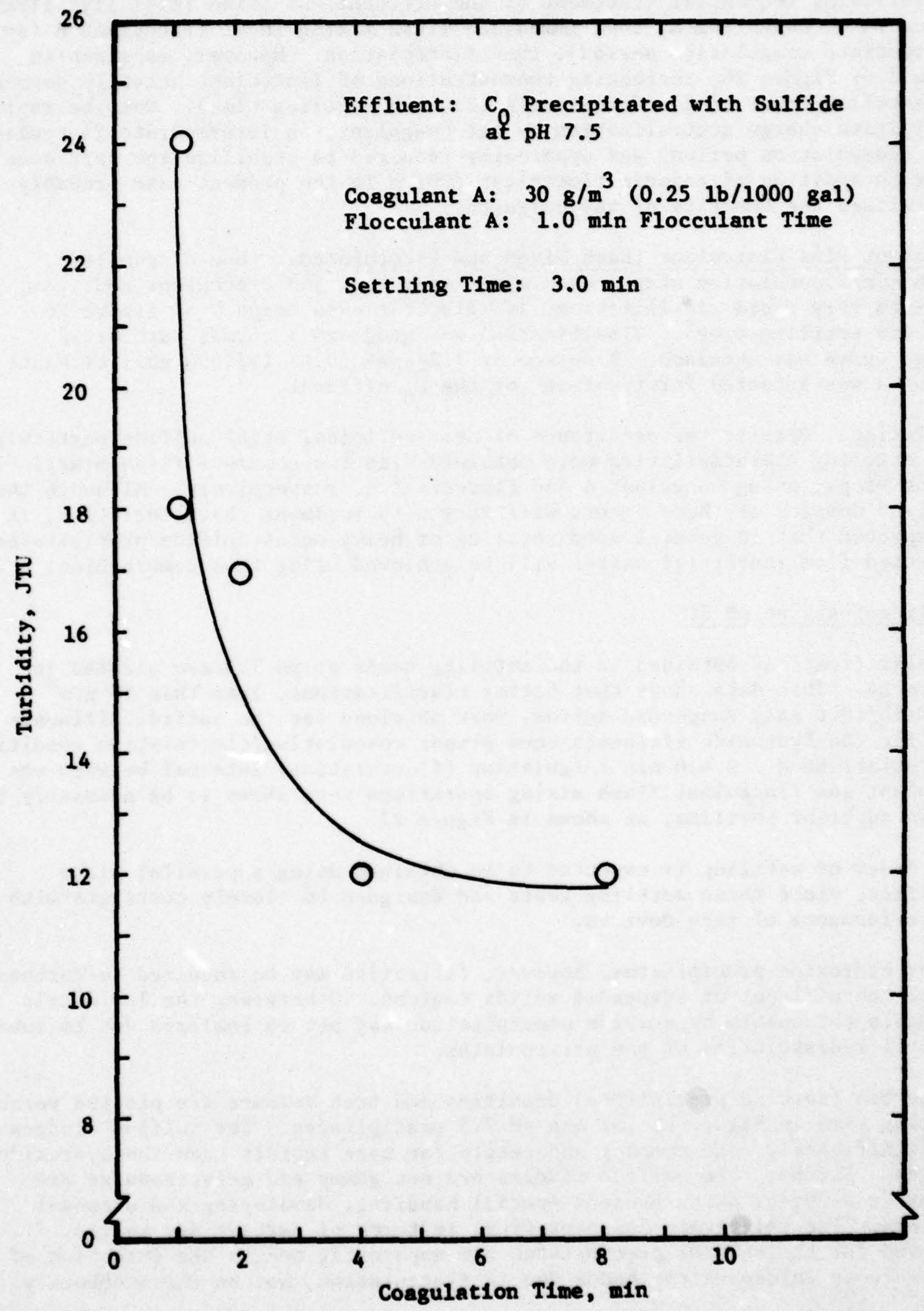


FIGURE 27 CLARIFICATION VERSUS COAGULATION TIME

bonded water-holding structures common to hydroxide precipitates. Sulfide sludge beds composed of more fully flocculated particles, such as obtained with coagulants only, were informally observed to be twice as compact as those obtained in the formal settling tests.

Coagulant/Flocculant Dosage/Type Tests at pH 8.5

The finely divided precipitates previously generated at pH 7.5 were observed to form at pH 8.5 as well. Based on the very successful settling of the former using Coagulant A and Flocculant A, these agents were tested again for their effectiveness at pH 8.5.

The results of these tests are plotted in Figure 28. Coagulation and flocculation times of 4.0 and 1.0 min each, respectively, were employed. Turbidity samples were collected after 3.0 min of settling.

As for pH 7.5 precipitates, settling via Coagulant A alone was inadequate and resulted in an inverse turbidity/dosage curve. Good settling was obtained with a series combination of coagulant and flocculant, at optimum dosages of 30 and 1.0 g/m^3 (0.25 and 0.008 lb/1000 gal), respectively. Clarifications were not quite as good, however, as obtained at pH 7.5.

Settling Tests at pH 8.5

Suspended solids versus time determinations were made on effluents pretreated with Coagulant A at a 30 g/m^3 (0.25 lb/1000 gal) dosage and 4.0 min coagulation time followed by Flocculant A at a 1.0 g/m^3 (0.008 lb/1000 gal) dosage and 1.0 min flocculation time, based on results of prior dosage/type tests. The results are plotted in Figure 24.

Suspended solids residuals in the clarified effluent corresponding to a 0.016 to 0.020 $m^3/min\text{-}m^2$ (0.4 to 0.5 $gal/min\text{-}ft^2$) surface loading rate were roughly 20 g/m^3 (0.17 lb/1000 gal), similar to clarifications observed for the hydroxide settling and worst-case pH 7.5 sulfide settling. The pH 8.5 clarifications were considerably poorer, however, than those obtained at 7.5 under nearly identical coagulation and flocculation conditions.

Figure 25 shows that good settling characteristics were observed for the sludges generated at pH 8.5, almost identical to those generated at pH 7.5. Therefore, although pH 7.5 appears to be more favorable with respect to overall clarification of sulfide precipitate effluents, pH variations over the range 7.5 to 8.5 will apparently not vary the properties of the resulting sludges.

Discussion

The suspended solids levels obtained in the clarified effluents for the various precipitates indicate suitability of a parallel plate clarifier(7) for settling of the bulk of suspended solids in the raw reactor effluents. The pH 7.5 sulfide effluents are apparently superior in this regard and sulfide treatment at this pH is recommended, at least for wastes similar to those studied. Suspended solids residuals of 20 g/m^3 (0.17 lb/1000 gal) were shown to be

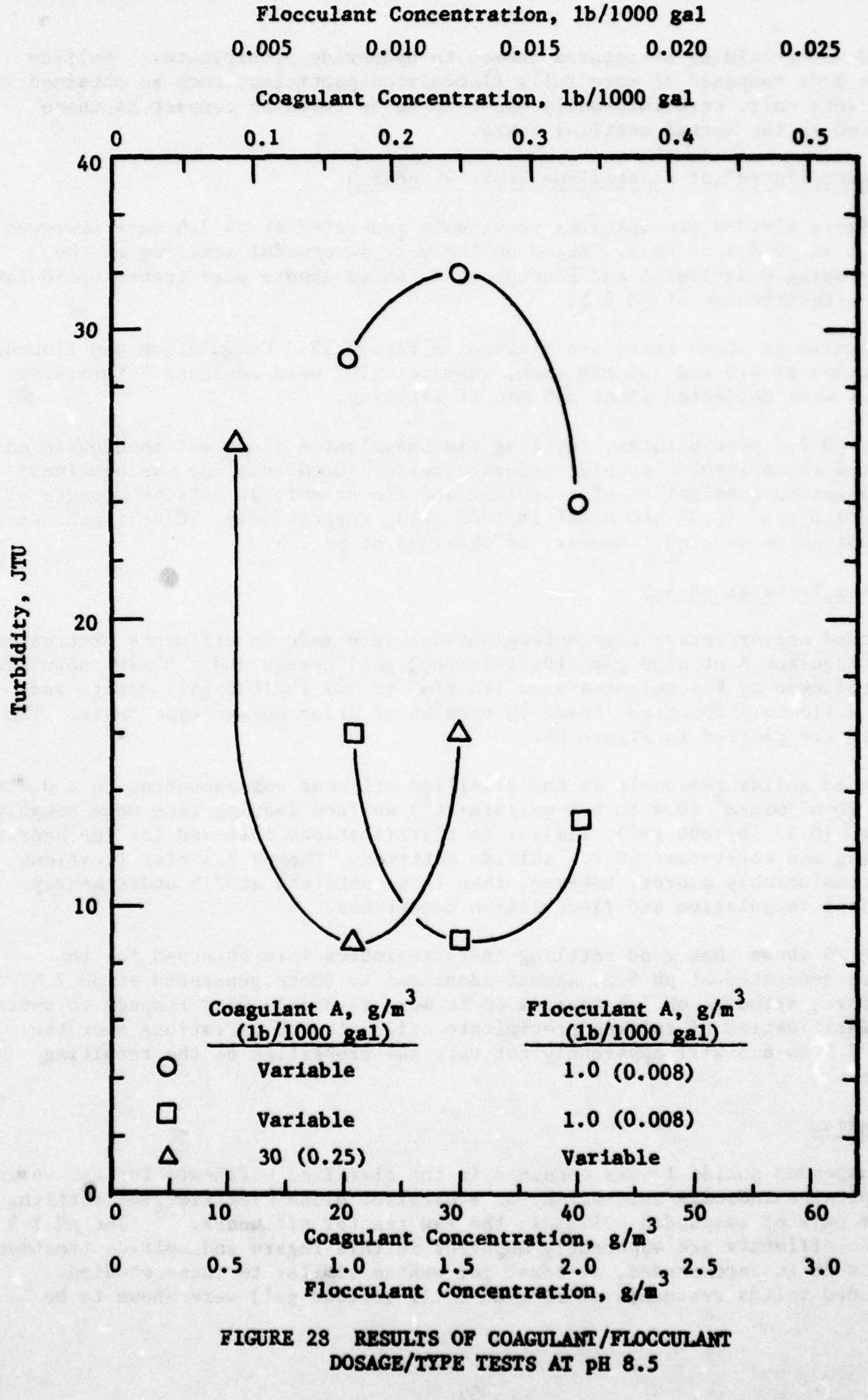


FIGURE 28 RESULTS OF COAGULANT/FLOCCULANT DOSAGE/TYPE TESTS AT pH 8.5

obtainable at surface loading rates over twice as high as for pH 8.5 effluents. Heavy metal effluent residuals obtained at pH 7.5 are typically below effluent goals.

ECONOMIC MODEL

An economic analysis was performed to determine chemical operating costs for hydroxide and sulfide processes (two types), to compare these processes quantitatively on the basis of chemical costs and qualitatively on the basis of other cost factors, and to select one of these processes and arrive at a rough preliminary capital cost estimate versus capacity for an appropriate waste treatment system.

Chemical Operating Costs

A chemical operating cost analysis was performed on all reagents and polyelectrolytes that will be required to complete the removal of heavy metals (except final sludge conditioning polyelectrolytes, the dosages of which have not yet been determined for the soluble sulfide process).

Both the soluble sulfide method being developed and an "insoluble" method currently in limited commercial use has been considered for comparison purposes. The "insoluble" sulfide process is based on transfer of the sulfide ion from an "insoluble" ferrous sulfide precipitate to heavy metals in the wastes that form much more insoluble sulfides. The remaining free iron forms either a hydroxide which precipitates or complexes with the ligand lost by the precipitated heavy metal.(20)

The results of the chemical cost analysis are plotted in Figure 29. Process data corresponding to each of these curves are identified in Table 3. Straight line relationships were typically assumed based on the data obtained experimentally for two influents with different total metals concentration.

Costs for hydroxide and sulfide precipitation were based on experimental reagent usage rates and current prices of commercial grades of chemicals. Prices for lime, sodium hydroxide, sodium sulfhydrate and ferrous sulfate were obtained from a current marketplace source.(21) Polyelectrolyte and sulfuric acid prices for the soluble sulfide and hydroxide processes were obtained from manufacturers (January, 1979). The price for the polyelectrolyte used in the "insoluble" sulfide method was increased by 17% from a 1975 price reported in the literature for that process.(20)

Hydroxide

Requirements for sodium hydroxide for the soluble sulfide and hydroxide processes were based directly on reagent usage rates plotted in Figures 14 and 22 of this report. Costs for hydrated lime ($Ca(OH)_2$) were calcuated from the sodium hydroxide usages, assuming all the lime was soluble and its hydroxide content corresponded to the formula above.

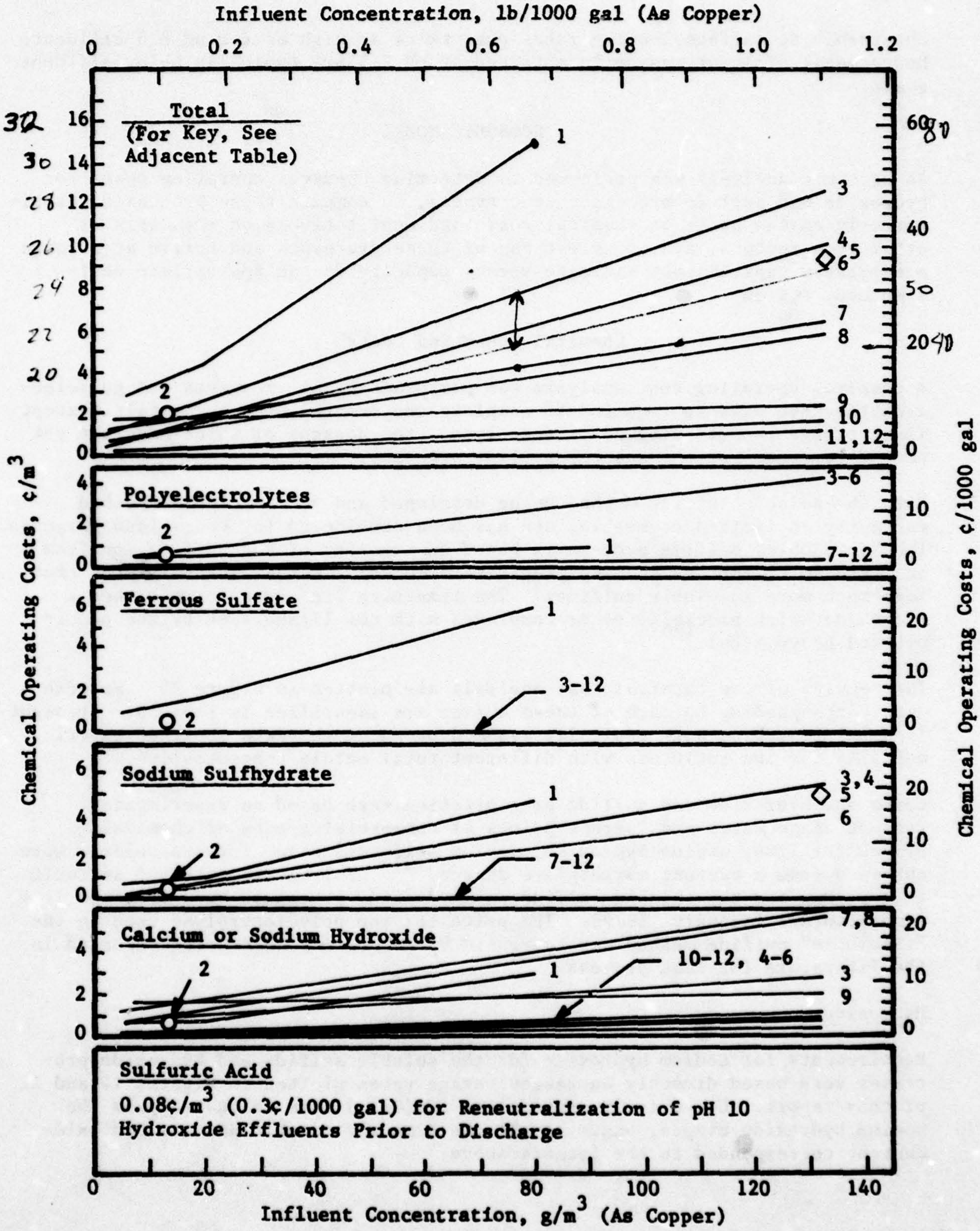


FIGURE 29 CHEMICAL OPERATING COSTS FOR SULFIDE AND HYDROXIDE PRECIPITATION

TABLE 3 CONDITIONS FOR CHEMICAL COST ANALYSIS, FIGURE 29

Curve No.	Process	Effluent pH	Effluent Total Sulfide Level, g/m^3 (lb/1000 gal)	Complexing Agents In Influent
1	Insoluble Sulfide	8.5	Solubility Level of Ferrous Sulfide	Tartrate + EDTA
2	Insoluble Sulfide	8.5	Solubility Level of Ferrous Sulfide	Nil
3	Soluble Sulfide, NaOH	7.5	0.1 (0.0008)	Nil
4	Soluble Sulfide, $Ca(OH)_2$	7.5	0.1 (0.0008)	Nil
5	Soluble Suflide, $Ca(OH)_2$	8.5	0.1 (0.0008)	Nil
6	Soluble Sulfide, $Ca(OH)_2$	7.5	0.1 (0.0008)	50% Seawater
7	Hydroxide, NaOH	8.5	Nil	50% Seawater
8	Hydroxide, NaOH	8.5	Nil	Nil
9	Hydroxide, $Ca(OH)_2$	10.0	Nil	50% Seawater
10	Hydroxide, $Ca(OH)_2$	10.0	Nil	Nil
11	Hydroxide, $Ca(OH)_2$	8.5	Nil	50% Seawater
12	Hydroxide, $Ca(OH)_2$	8.5	Nil	Nil

Hydrated lime requirements for the insoluble sulfide process were obtained from literature.(20)

The following chemical prices were used in the calculations: Hydrated lime (bags), 4.7¢/kg (2.2¢/lb); sodium hydroxide (50% solution in seller's tanks), 34.8¢/kg (15.8¢/lb), adjusted for 100% concentration.

Sulfide

Requirements for sodium sulfhydrate for the insoluble sulfide process were based on the reagent usages plotted in Figure 22 that corresponded to 0.1 g/m^3 (0.8×10^{-4} lb/1000 gal) sulfide residual. Requirements for this chemical in the insoluble sulfide process were obtained from literature.(20)

The price for sodium sulfhydrate (70 to 72% flakes in drums) was 35.2¢/kg (16.0¢/lb), equalized to 100% concentration.

Ferrous Sulfate

In the "insoluble" sulfide process, ferrous sulfide is prepared off-line from ferrous sulfate and sodium sulfhydrate. Requirements for ferrous sulfate were based on literature values.(20) The price for this chemical as the heptahydrate (granulated, bags) was 5.7¢/kg (2.6¢/lb).

Polyelectrolytes

Requirements for polyelectrolytes for the hydroxide and sulfide processes were based on the concentrations of the agents used during the settling tests discussed in this report (Coagulant A and Flocculant A). Coagulant concentrations were assumed to be linearly proportional to metals concentrations in the influent.

The prices for Coagulant A and Flocculant A (liquid, in drums) were $1.32/kg ($0.60/lb) and $2.93/kg ($1.33/lb), respectively. It is expected that a significantly lower cost coagulant will be used in the ultimate application, however, pending the results of some additional testing.

Sulfuric Acid

Sulfuric acid costs for reneutralization of pH 10 hydroxide effluents were based on equilibrium calculations and a price of 15.4¢/kg (7.0¢/lb) for 93% acid in drums.

Process Comparisons

The three processes included in Figure 29 are discussed comparatively on the basis of chemical costs and on other factors influencing operating effectiveness and economy.

Hydroxide Precipitation

Superficially, the hydroxide process has the lowest operating costs if only chemicals are considered, lime is used as the hydroxide source and the process is carried out at pH 10. Lime is very inexpensive. However, costs for hydroxide and sulfuric acid will increase dramatically if precipitation is carried out at pH 11 or pH 12. Metals residuals obtained in this process are often higher than discharge goals and are increased even more by the presence of complexing agents. Lime is difficult to dispense accurately, and metering systems are costly. Also, the sludges are very difficult to handle and dewater, and the dewatered sludges still have a relatively high water content. Use of lime (versus soluble hydroxides) generate particularly large volumes of sludge.(22) Disposal costs are therefore high.

If sodium hydroxide is used instead of lime, significant process advantages such as simplified reagent dispensing, improved process controllability and reduced sludge volumes are gained. However, chemical costs increase by nearly an order of magnitude and sludge volumes are still high.

Two complete hydroxide precipitation/separation processes in series are sometimes required to ensure precipitation of all metals in mixed-metal influents. The large capital cost investment, the greater system operating complexity and the remaining limitations on metals residuals that can be obtained must be weighed in comparing this approach with one of the sulfide processes.

Hexavalent chromium is not removed by the hydroxide process without a prior reduction of this metal to the trivalent form in a separate process step.

If metals are not removed to within specified discharge limits, the cost of discharge permits must be included in the total operating costs.

Soluble Sulfide Precipitation

The chemical operating costs of this process are notably higher than for the pH 10 hydroxide process with lime used as the precipitant. However, much of the difference disappears if sodium hydroxide is used or the hydroxide precipitation is done at higher pH's. The following advantages of the soluble sulfide process must also be weighed in comparing real total operating costs for the soluble sulfide and hydroxide processes, however.

- Very low metals residuals (no discharge permits).
- Adequacy of one set of precipitation conditions for treating a wide range of metals (single-stage reaction for mixed-metal wastes).
- Simultaneous removal of hexavalent chromium with no prereduction step (no additional reaction stages).
- Superior sludge characteristics (lower dewatering and disposal costs).

- Much smaller or negligible effect of complexing agents both on effluent metals residuals and on operating costs due to the chemically competitive sulfide residuals that can be obtained with a minimum excess of process reagent over the stoichiometric requirement. Particularly advantageous for mixed metal wastes (e.g., drydock and job-shop plating wastes)

Although the sulfide process requires more stringent control than the hydroxide process, a completely automated control and monitor system will minimize labor cost differences due to this factor.

Landfill disposal of hydroxide sludges requires special techniques to minimize contamination of ground waters by redissolution.(23) The solubility of sulfide sludges is much lower and much less pH dependent. Many natural metal ores are sulfides. However, the long-term stability of such sludges under landfill conditions needs to be established and analogous precautions may therefore need to be taken.

The data discussed in this report indicates that adequate process sulfide residuals for metals removal are below or at the lower end of sulfide concentrations commonly found in sewage.(24) Process effluents can therefore be discharged directly into sewers.

However, reduction of these low sulfide residuals to negligible levels can be accomplished, if desired, at a nominal chemicals cost (about a penny per *thousand gallons*) and capital cost by adding hydrogen peroxide to the effluent and letting it oxidize the sulfide to harmless substances in the sewers. A small drum (15 gal) of 50% peroxide, added at a two parts peroxide to one part sulfide dosage ratio(15,16) would supply a 0.15 m^3/min (40 gal/min) metals treatment unit about a year if post-clarification sulfide residuals were maintained at 1.0 g/m^3 (8 x 10^{-3} lb/1000 gal).

The chemical operating costs will probably be lower than those listed in practice. These costs reflect dual addition of coagulant and flocculant. In practice, a lower cost coagulant would almost certainly be used (preliminary tests, for example, have indicated that a particular chemically-treated natural product may coagulate the sulfide effluents at half the cost indicated in the economic analysis).

The soluble sulfide chemical process costs will be significantly lower than those for the "insoluble" sulfide process, particularly if complexing agents are present in the influents. Other factors concerning the latter process are discussed below.

"Insoluble" Sulfide Process

Chemical costs for this process are the highest included in the analysis. In fact, point 2 in Figure 29 is based on an approximately stoichiometric dosage of process chemicals, which is lower than actually used in practice.

This process has the advantage of maintaining low sulfide residuals with less stringent control and monitor requirements than the soluble sulfide process (the sulfide residual is governed by the solubility of ferrous sulfide).

Polymer costs are apparently lower as well. In theory, sulfide residuals in the effluent will be fundamentally low enough to avoid odor (although concentrated soluble sulfide is used in the iron sulfide make-up system).

However, the following factors must also be considered in the economics of the process.

- Difficult-to-handle product sludges (high percentage of gelatinous iron hydroxide).
- Very high sludge disposal costs (dosages for iron sulfide, e.g., at least 1.5 to 3 times the stoichiometric requirement leads to, for example, at least 2.5 to 4 times the sludge generated with a soluble reagent process).
- Periodic blowdown of the reactive ferrous sulfide precipitate blanket. This must be entirely removed and replaced at intervals of less than three weeks, requiring significant labor costs and loss of all chemicals required to make up the precipitate blanket (not included in the chemical cost analysis).
- Fundamentally greater susceptibility to competitive limitations of complexing agents in the influent, due to the lower sulfide residual being maintained, as governed by the solubility of ferrous sulfide (2×10^{-5} g/m^3 (2×10^{-7} lb/1000 gal)). Excessive soluble iron can also occur in the effluent due to the transfer of complexing agents to the iron from the wastes being treated.

Conclusion

Based on the factors discussed above, it is concluded that the soluble sulfide process is the best of the three considered for treatment of both complexed and uncomplexed heavy metal influents.

Capital Cost Model

A preliminary capital cost analysis was performed based on the estimated hardware and labor costs, plus a nominal profit margin, envisioned to fabricate a complete system to remove mixtures of heavy metals from wastewater streams via soluble sulfide precipitation.

Basis of Model

The following factors/assumptions were included in the cost analysis.

- First production unit assumed. All development work, including fabrication and testing of a prototype has been completed previously.
- Precision, feed forward control and monitor system concept is employed. (See Recommendations section concerning development of such a system.)

- Influent contains 5 to 200 g/m^3 (0.03 to 1.7 lb/1000 gal) concentration of mixed heavy metals.
- Selection of system components for this model system was based, when possible, on program test data and observations, including precipitate coagulation, flocculation, settling, filtration and sludge properties.
- Component prices were based on estimates, on catalog or product literature listings, or on late 1978/early 1979 quotes from selected manufacturers (specific manufacturers were assumed for major components).

A block diagram of the system model is depicted in Figure 30. The various components of this system, as well as some selected options which could be included, are further defined in Table 4.

Cost Analysis

Total estimated capital costs for systems in capacities of 0.08, 0.15 and 0.40 m^3/min (20, 40 and 105 gal/min) are plotted in Figure 31. Costs for individual sections of the system, as defined in Table 4, are plotted as well. The shaded areas represent the likely range in these values.

The overall costs vary little between the two lower system capacities because the capacities of the precipitate separation hardware selected vary in discrete steps. One of these steps covers this flow range.

The control and monitor system costs are not anticipated to vary significantly with system capacity.

Discussion

The estimated capital costs plotted in Figure 31 for the soluble sulfide process are believed to be comparable to those for hydroxide and "insoluble" sulfide processes. For example, the estimated installed cost for a 0.33 m^3/min (40 gal/min) capacity "insoluble" sulfide system listed in a report published on that process over two years ago(20) will fall within the total cost range in Figure 31 if compensated for inflation. Although control system costs can be lower for a conventional single pH hydroxide process, sludge processing hardware costs can be much higher. In many cases a plate-and-frame filter press is required to get good dewatering of hydroxide sludges. Further, a two-stage pH adjustment/separation process is required to precipitate some mixtures of metals via hydroxides, at an equipment cost obviously higher than for single-stage sulfide precipitation.

It is concluded that the advantages of the soluble sulfide process will be available at reasonable capital costs.

CONCLUSIONS

The following conclusions have been reached as a result of this study.

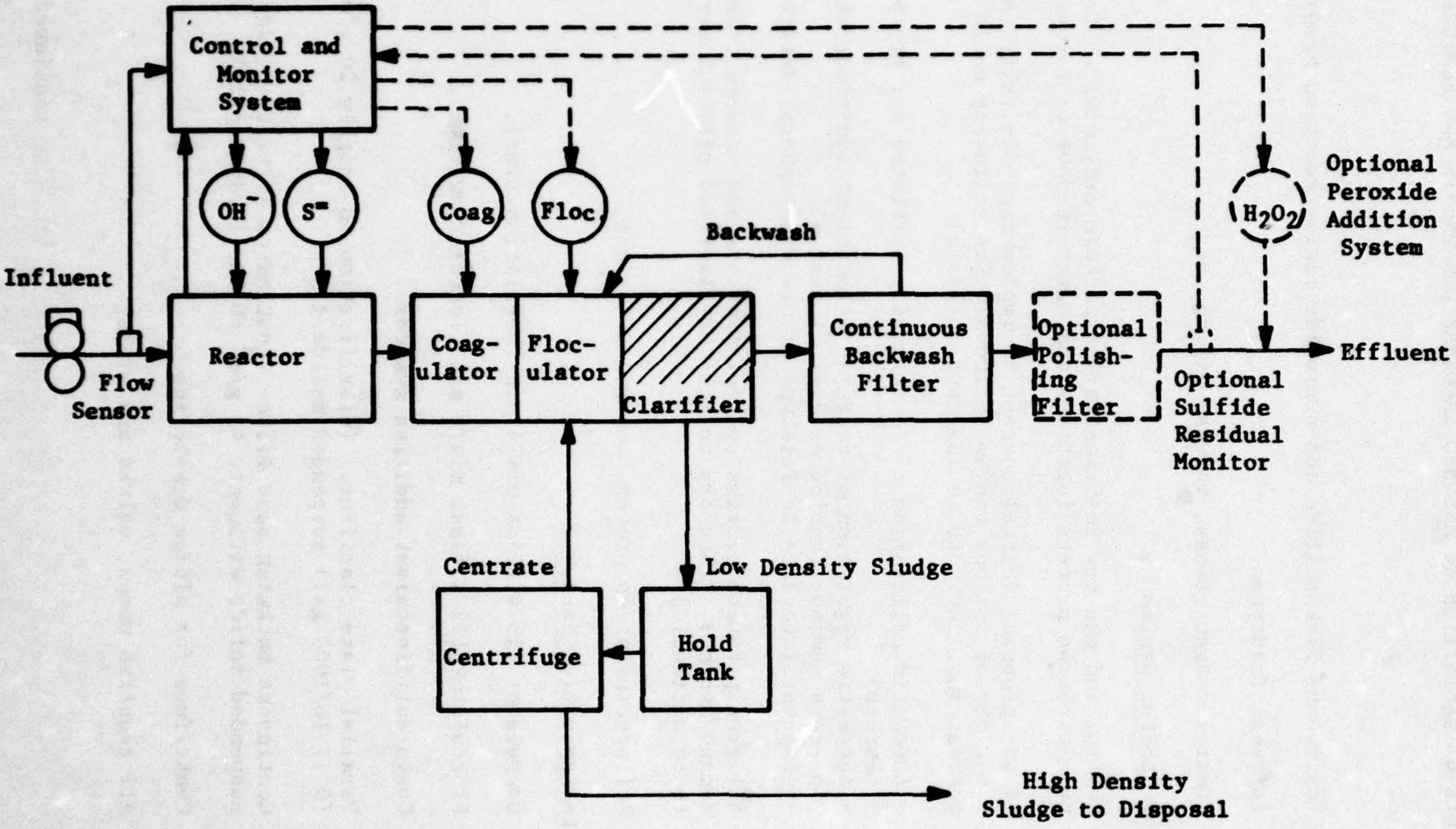


FIGURE 30 DIAGRAM OF SOLUBLE SULFIDE HEAVY METAL TREATMENT SYSTEM (SIMPLIFIED)

TABLE 4 DEFINITION OF ASSUMED HARDWARE COMPONENTS AND FEATURES

Reactor

- Continuous flow sulfide and hydroxide mixing/reaction hardware.
- Influent feed pump.
- Control reagent tanks, valves, piping, etc.

Control and Monitor System

- Control and monitor instrumentation package providing control of all precipitation process functions and meter readout of key parameters.

  If the proposed control concept is implemented digitally (not required) a variety of options can be included. The following would be desirable options (not included in the cost analysis).

  - Automatic calibration cycle (manually initiated for key process sensors).
  - Automatic regulation of coagulant/flocculant addition rates versus process demands (analog or digital system).
  - Computer interface to Teletype or other peripheral device
- All precipitation process control monitors and sensors (flow, sulfide demand and pH). (Sensors to monitor clarified effluent were assumed to be optional.)
- All precipitation process control actuators.

Precipitate Separation Hardware

- Coagulator (15 s flash mix/4 min coagulation time).
- Flocculator (15 s flash mix/1 min flocculation time).
- Coagulant/flocculant addition systems.
- Parallel plate clarifier. (Clarification to roughly 20 g/m^3 (0.17 lb/1000 gal) suspended solids.)
- Continuous backwash sand filter (continuous filtration, superior suspended solids effluent, <1 g/m^3 (0.008 lb/1000 gal)).
- Centrifuge for sludge dewatering.
- All required pumps, valves and piping.

continued-

Table 4 - continued

- A polishing filter is considered optimal at present. Such a unit will be required to remove small amounts of residual suspended solids (less than 1 g/m^3 (0.008 lb/1000 gal)) only if achievement of the lowest total metals residuals of which the sulfide process is capable is needed. The need for and sizing of such a unit must be determined experimentally.

Peroxide Addition System

- As an option, a simple peroxide addition system could be added to reduce final sulfide residual to negligible levels if desired. A constant feed rate addition system is projected to add only about a percent to the total system cost. Peroxide flow could also be regulated automatically by the control and monitor system in proportion to total system flow and sulfide residual.

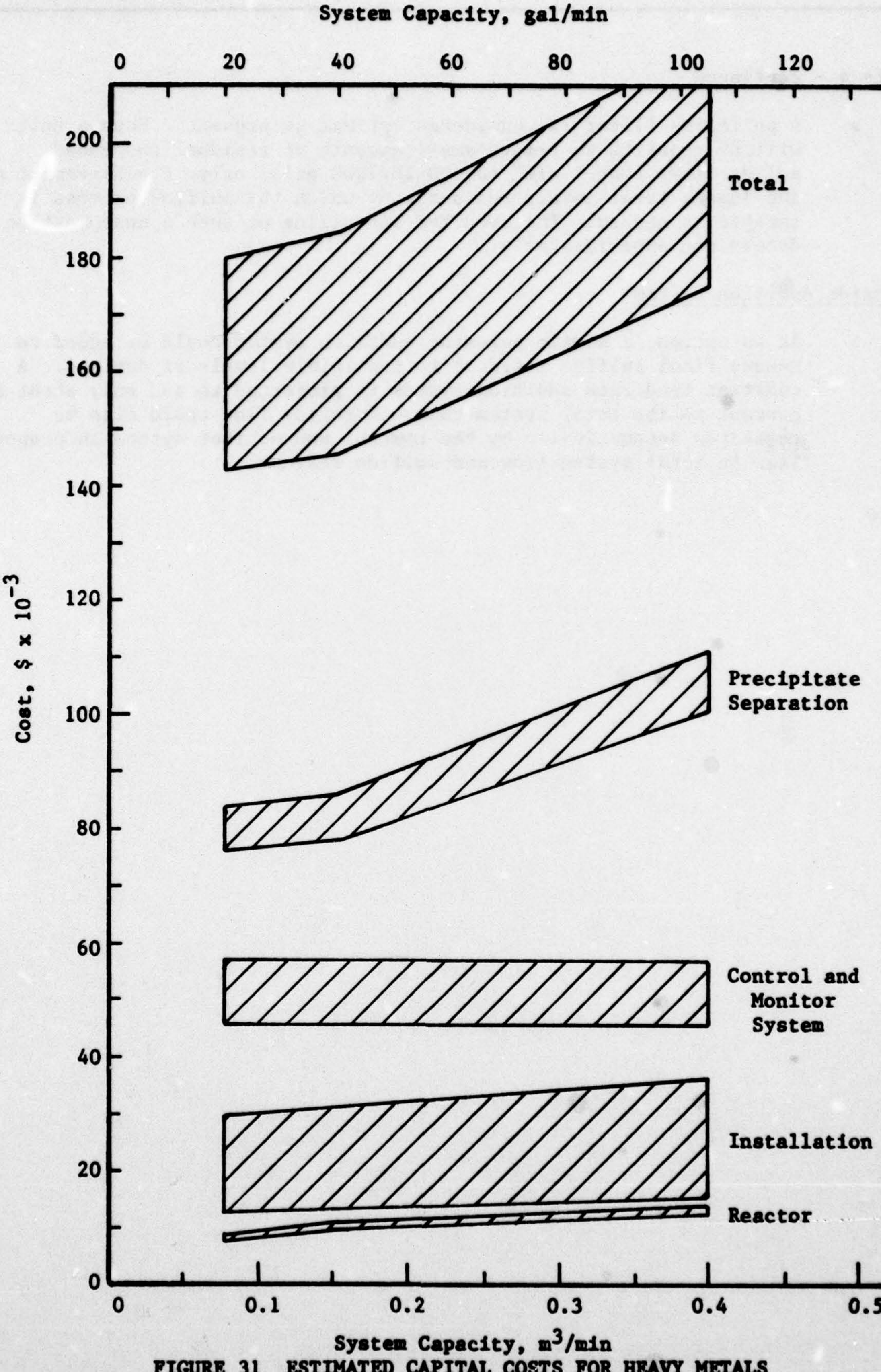


FIGURE 31 ESTIMATED CAPITAL COSTS FOR HEAVY METALS WASTE TREATMENT SYSTEM (PRODUCTION VERSION)

1. Satisfactory pH and sulfide control point variability have been obtained for the hydroxide and sulfide processes.

2. Hydroxide precipitation of metals from wastes containing high proportions of copper and zinc can be superior to theoretical projections, apparently due to co-precipitation of minor components. However, discharge criteria cannot be met by this process for all metals of interest in industrial wastes, particularly due to the presence of variable proportions of seawater (or other complexing agents).

3. Wastewaters containing high concentrations of seawater will be more difficult to treat via hydroxide precipitation at high pH from a chemical cost standpoint than freshwater wastes. Hydroxide usage rates at above pH 9.5 were much higher than theoretical projections.

4. The soluble sulfide process is capable of removing copper, zinc, cadmium, nickel, lead, mercury and iron in mixed metals wastes at a single set of conditions. The sulfide residuals required are low enough to permit discharge of effluents directly into sewers.

5. The soluble sulfide process effectively removes hexavalent chromium in one step at pH 8.5 when iron, or possibly some other secondary metal, is present as a catalyst.

6. The pH range and soluble sulfide level for sulfide precipitation is not critical.

7. The presence of high concentrations of complexing chloride ion does not hinder sulfide precipitation of low concentrations of heavy metals. Apparent effects observed at higher concentrations of metals were due to sample filtration limitations.

8. Clarification of process effluents containing heavy metal hydroxides in fresh water via settling will be comparable to that typically obtained in commercial practice with a parallel plate clarifier. However, effluent polishing will be required downstream of clarification equipment.

9. If sulfide effluents are pretreated with proper combinations of cationic coagulant and anionic flocculant, clarifications will be at least as good as for hydroxide effluents.

10. Secondary polishing filtration of heavy metals treatment system effluents (in addition to depth filtration) may be required to fully exploit the very low soluble metals residuals obtainable via the soluble sulfide method. However, this procedure is projected not to be necessary to obtain metals residuals meeting discharge limits.

11. The hydroxide sludge densities are quite low, similar to those obtained in commercial practice. Special provisions for sludge thickening and dewatering will be required in the ultimate application if hydroxide precipitation is selected for treatment of wastes.

12. Soluble sulfide sludges are higher in density after settling than hydroxide sludges and nongelatinous. Handling, dewatering and disposal costs are therefore projected to be lower than for hydroxides and much lower than for the voluminous sludges generated by the "insoluble" sulfide process.

13. Sulfide/pH control interactions observed with the experimental feedback-controlled process will be reduced in future generation control hardware by incorporating nonlinear sulfide gain control, measurement of total sulfide as a control parameter, minimization of sensor fouling and optimization of hydraulic configurations. However, use of a precision feed forward control system is projected to provide much greater immunity to such interactions due to the independent nature of the control measurements and action implemented.

14. Chemical operating costs will be lowest for the hydroxide process (generally), intermediate for the soluble sulfide process and highest for the "insoluble" sulfide process. Total operating costs will be comparable to those for hydroxide and much lower than for the "insoluble" sulfide process.

    Capital costs for the two sulfide processes are projected to be comparable. Qualitatively, capital costs for hydroxide process are projected to be comparable to (or even higher than) the other two processes for treatment of mixed metals wastes.

15. The soluble sulfide method is the best choice of the three processes considered for treatment of mixed heavy metal wastes.

RECOMMENDATIONS

The following recommendations for future work are made as a result of this study.

1. Perform feasibility of a new precision experiment to demonstrate a precision feed forward concept for control of the soluble sulfide process.

2. Develop and test a precision feed forward control and monitor system, combined with a pilot plant scale reactor, to treat mixed heavy metal wastes. As a goal, this system shall be capable of automatically maintaining sulfide residuals of approximately 1 g/m^3 (0.008 lb/1000 gal) with no process upsets or detrimental changes in effluent parameters despite the following influent variations:

    - Changes in total metals concentration
    - Changes in flow rate
    - Changes in composition

3. Optionally, include capability in the control and monitor system for automatic regulation of flocculant and coagulant feed rates, for hardcopy readout of parameter levels and for an automatic calibration sequence for key process control sensors (digital implementation).

4. Test the precision feed forward control and monitor system reactor on-stream with actual mixed-metal wastes generated at a drydock or job-shop electroplating facility to demonstrate capability in the field.

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APPENDIX 1 RESULTS OF ANALYSIS OF C_O SUPERNATANT(a)

Metal	g/m^3 (lb/1000 gal x 10^2)					
	Make-up		Analysis		Effluent Goals	
Cu	80	(67)	78	(65)	0.2	(0.17)
Zn	70	(58)	53	(44)	0.05	(0.04)
Hg	0.03	(0.25)	0.18	(0.15)	0.001	(0.0008)
Pb	2.0	(1.7)	1.3	(1.1)	0.05	(0.04)
Sn	5.0	(4.2)	<1	(<0.8)	2.5	(2.1)
Cr	0.3	(0.25)	0.06	(0.05)	0.005	(0.004)
Cd	3.0	(2.5)	2.3	(1.9)	0.02	(0.017)
Ni	2.0	(1.7)	2.0	(1.7)	0.1	(0.08)

(a) *Reductions in metals from original make-up levels due to precipitation or co-precipitation reactions. Levels of all metals except tin at least an order of magnitude above discharge goals and therefore suitable for precipitation treatment studies.*

APPENDIX 2 INFLUENT MATRIX COMPOSITIONS

0% Sea Water Infludent Matrix (C_0, D_0)

Tap water. (Drinking water, negligible heavy metals. Assumed similar to water sprayed during drydock and blasting.)

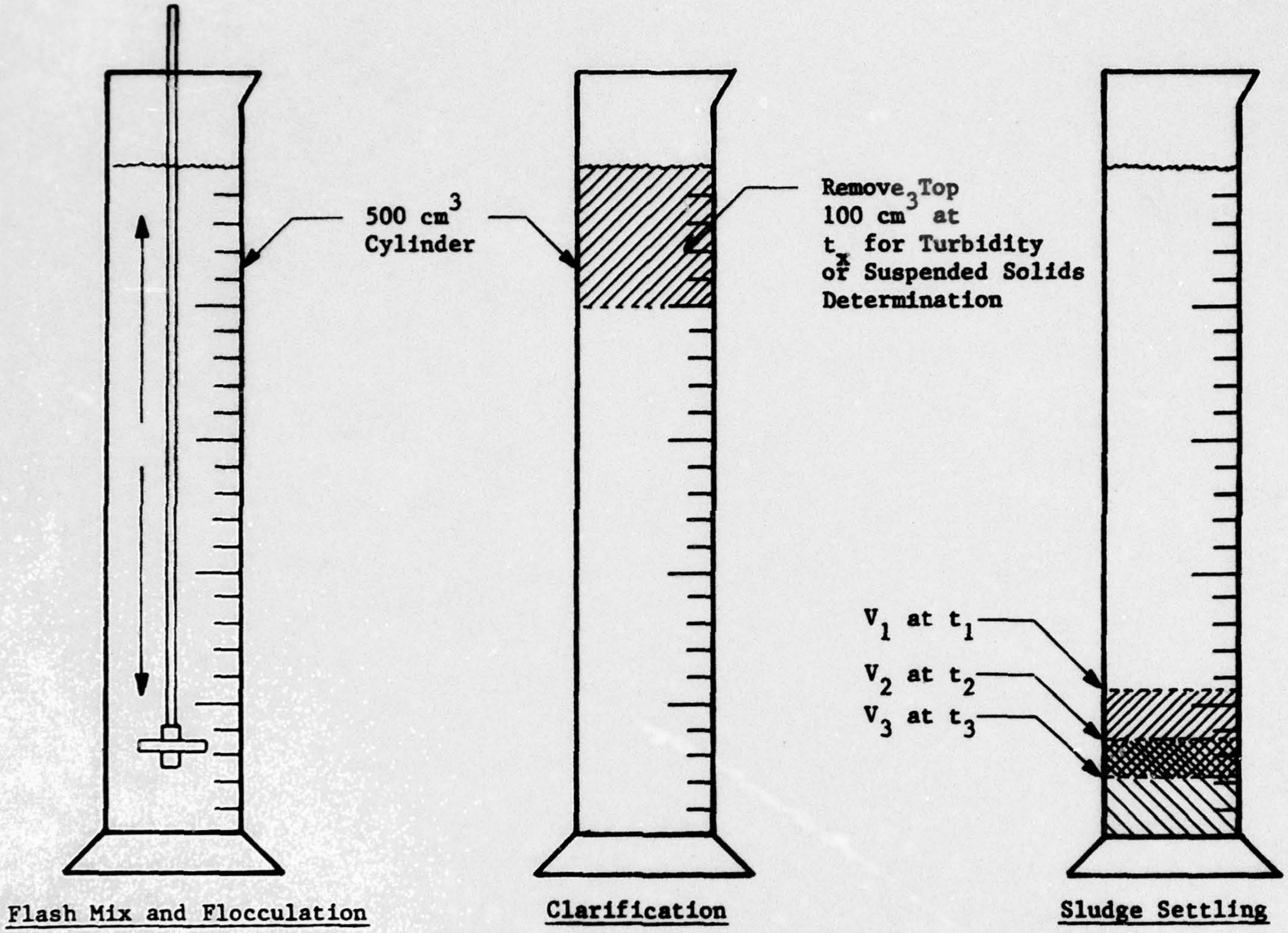
50% Sea Water Influent Matrix (C_{50}, D_{50})

Tap water, plus the following components.(a)

Principal Components	g/m^3 ($lb/1000$ gal x 10^2)
NaCl	13,200 (11,008)
$MgSO_4$	3,025 (2,523)
$MgCl_2.6H_2O$	2,540 (2,118)
Ca (as $CaCl_2$)	530 (442)
KCl	320 (267)
Ca (as $CaSO_4$)	150 (125)
KNO_3	50 (42)
$Na_2SiO_3.9H_2O$	50 (42)
KBr	11 (9)
KI	10 (8)
K_2HOP_4	5 (4)
Sr (as $SrCl_2$)	1.9 (1.6)
Rb (as RbCl)	0.003 (0.0025)
Li (as LiCl)	0.003 (0.0025)
Tris	0.02 (0.017)

Trace Metals	g/m^3 ($lb/1000$ gal x 10^2)
Mn	0.35 (0.29)
Zr	0.10 (0.08)
Fe	0.05 (0.04)
Co	0.04 (0.03)
Al	0.02 (0.017)
Mo	0.01 (0.008)
Pb	0.005 (0.004)
Cu	0.005 (0.004)

(a) From Rila marine mix: salts, buffers and trace elements to produce synthetic seawater. (Carolina Biological Supply Co.)



Flash Mix and Flocculation

1. Flash Mix (Rapid Motion Without Whipping in Air)
2. Flocculate (Slow Motion)

Clarification

Sludge Settling

APPENDIX 3 ILLUSTRATION OF COAGULANT AND SETTLING TESTS