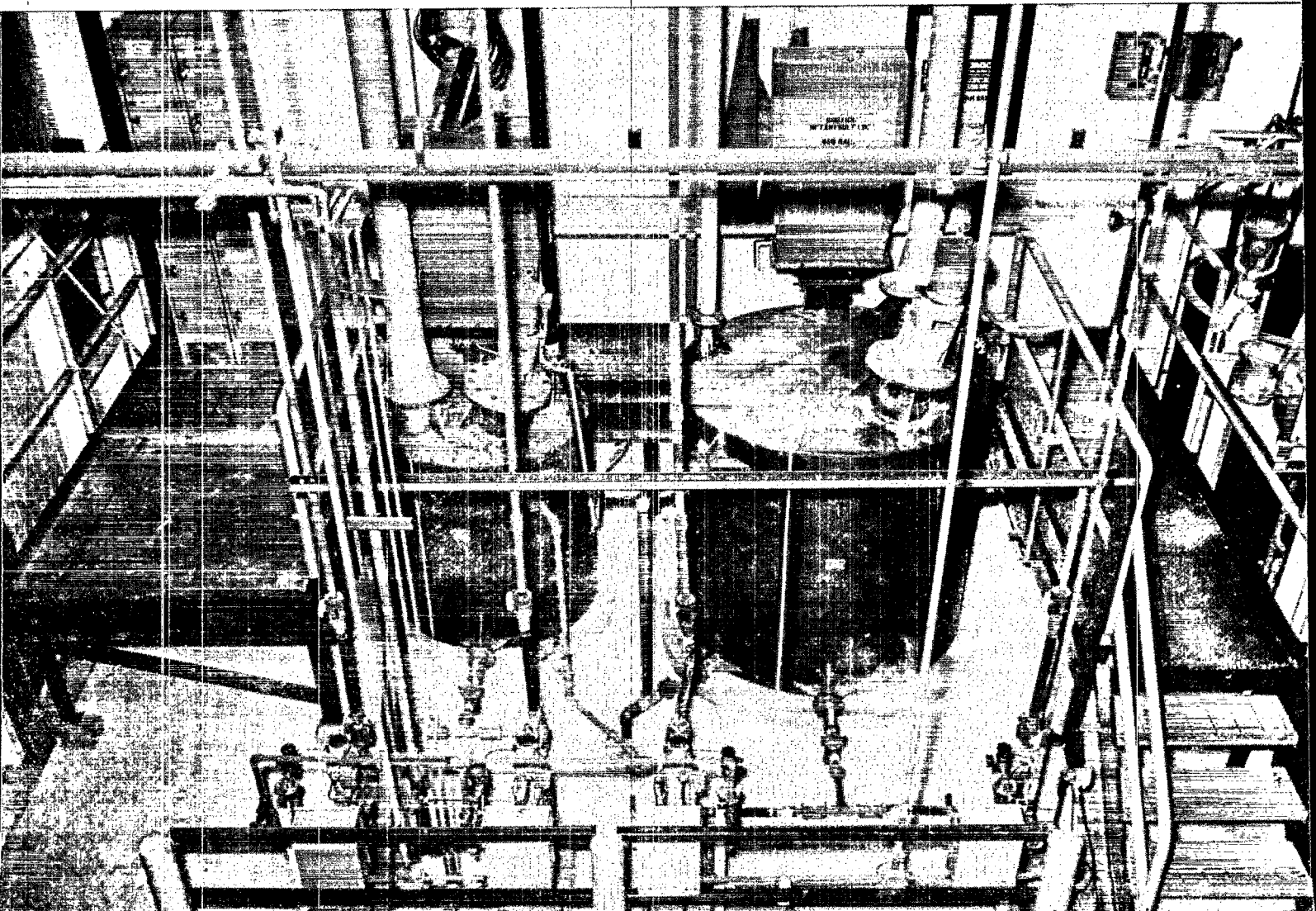


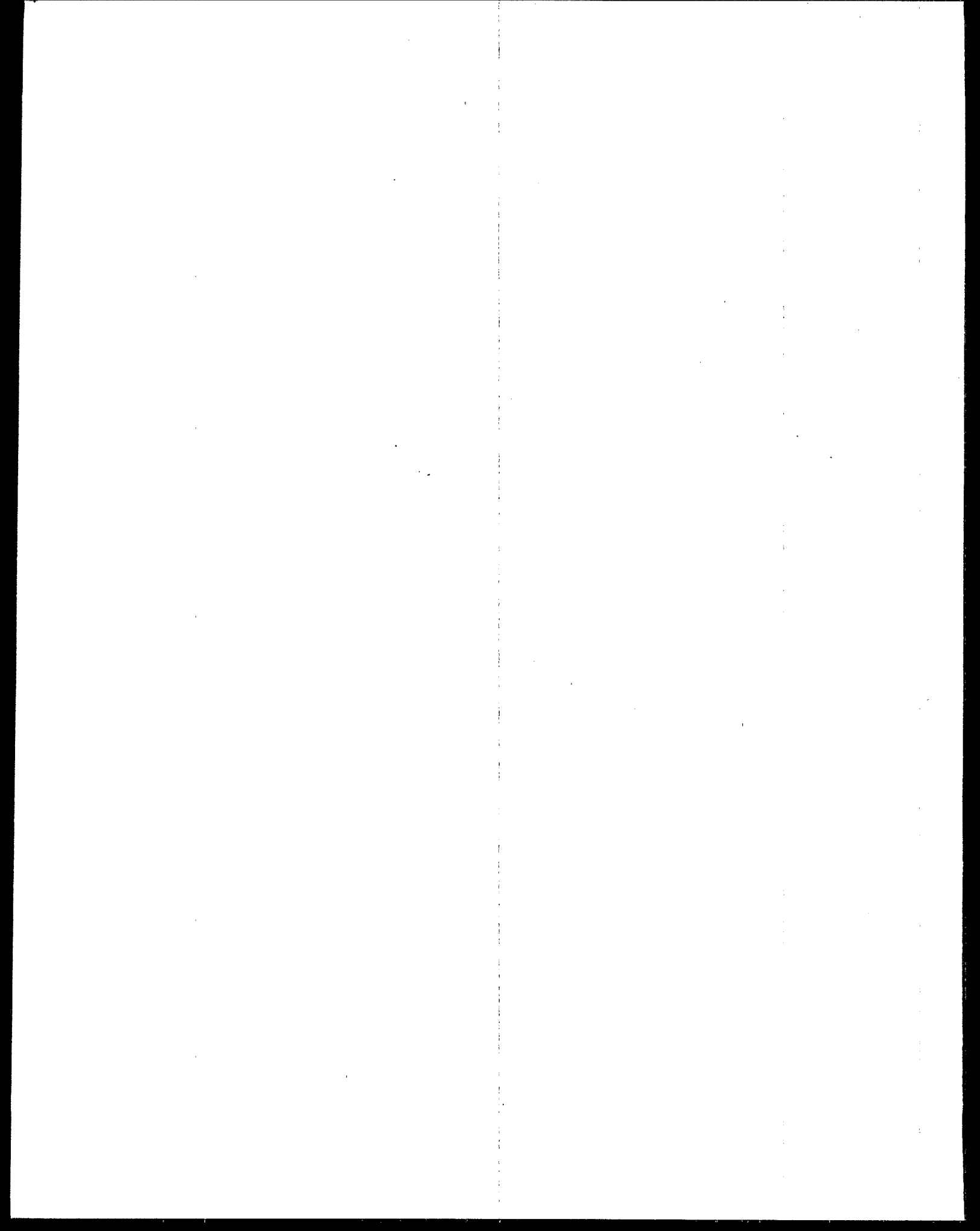


# Summary Report

## Control and Treatment Technology for the Metal Finishing Industry

### Sulfide Precipitation





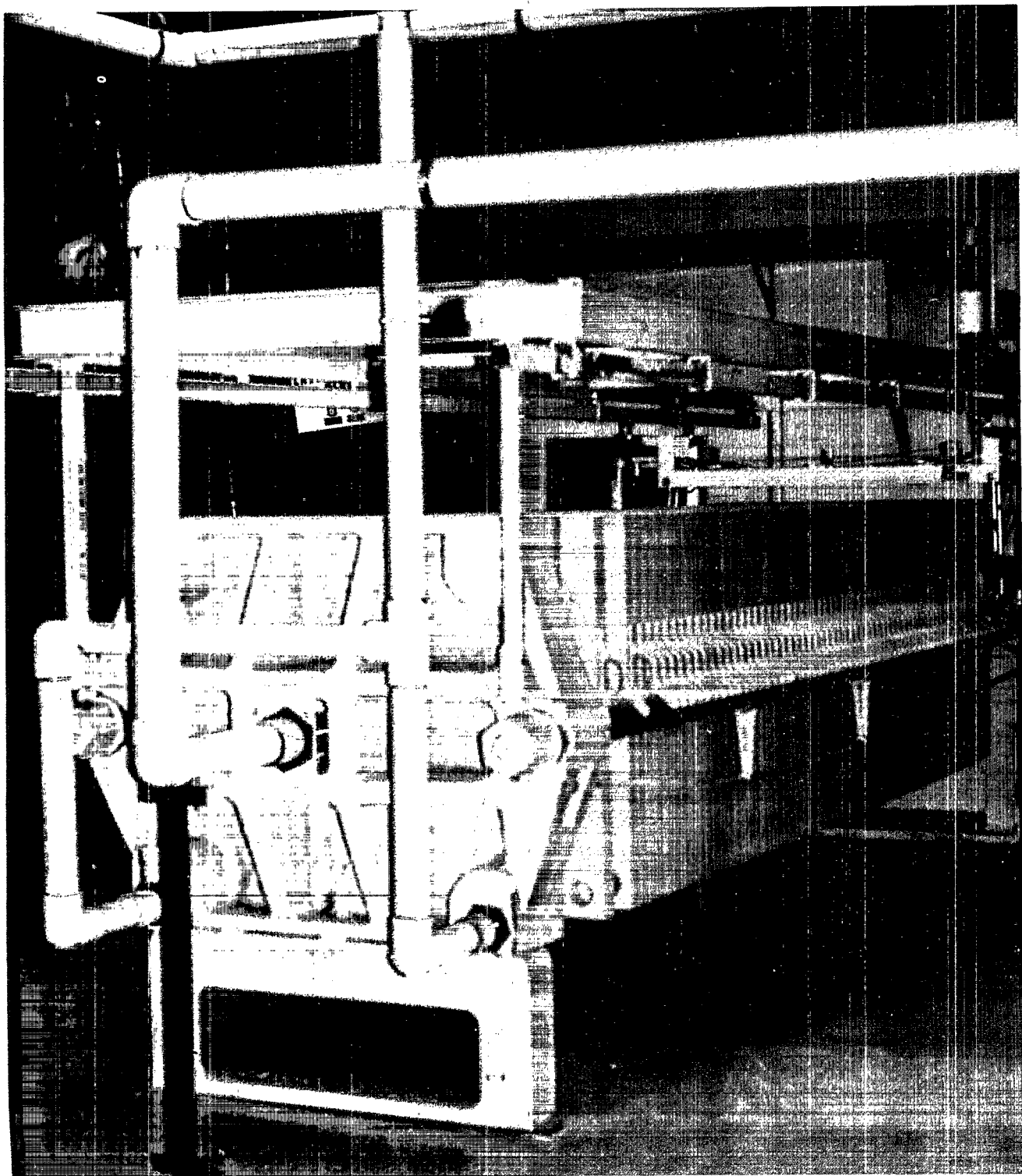
# **Summary Report**

## **Control and Treatment Technology for the Metal Finishing Industry**

### **Sulfide Precipitation**

**April 1980**

This report was developed by the  
Industrial Environmental Research Laboratory  
Cincinnati OH 45268



Sludge dewatering filter press

## Overview

Today more than 13,000 firms in the United States are engaged either wholly or partially in electroplating or other metal finishing operations. These firms discharge their spent process water to either waterways or publicly owned treatment works (POTW's), and they comprise more individual wastewater discharges than any other industrial category. The pollutants contained in this process water are potentially toxic; therefore, to comply with the Clean Water Act of 1977 (Public Law 95-217), the water must be treated before being discharged to a waterway or a POTW. The regulations require oxidation of cyanide, reduction of hexavalent chromium, removal of heavy metals, and control of pH.

Sulfide precipitation is one among many methods available for removing metals from metal finishing process wastewaters. This summary report series presents information on various technologies that have been demonstrated. Other publications in the series discuss different control alternatives. By providing process descriptions, advantages and disadvantages, and economic characteristics of each system, these reports can facilitate the evaluation of effective means of pollution control by those involved in metal finishing wastewater pollution control.

Metals are usually removed by adding an alkali, such as hydrated lime  $[\text{Ca}(\text{OH})_2]$  or caustic soda (NaOH), to adjust the pH of the wastewater to the point where the metals exhibit minimum solubilities. The metals precipitate as metal hydroxides and can be removed from the wastewater by flocculation and clarification. In many cases, the addition of a postfiltration step can reduce further the total metal concentration in the effluent by removing any metal hydroxide carryover.

Some common limitations of the hydroxide process follow:

- The theoretical minimum solubilities for different metals occur at different pH values (Figure 1). For mixtures of metal ions, it must be determined whether a single pH can produce sufficiently low, though not minimum, solubilities for the metal ions present in the wastewaters.
- Because hydroxide precipitates tend to resolubilize if the solution pH is increased or decreased from their minimum solubility points, maximum removal efficiency will not be achieved unless the pH is controlled within a narrow range.
- The presence of complexing ions—such as phosphates, tartrates, EDTA,<sup>1</sup> and ammonia—that are commonly found in cleaner and plating formulations may have an adverse effect on metal removal efficiencies when hydroxide precipitation is used. Figure 2 shows the solubility of nickel ions as a function of pH when precipitated with other metal ions in the presence of certain complexing ions used in a proprietary electroless nickel plating bath.

Despite these limitations, hydroxide precipitation (particularly when followed by flocculation and filtration) produces a high-quality effluent when applied to many waste streams. Often coprecipitation of a mixture of metal ions will result in residual metal solubilities lower than those that could be achieved by precipitating each metal at its optimum pH. In other cases, modification of the hydroxide process has improved its performance in treating waste streams containing complexed heavy metals. This improved performance is usually realized by dissolving another positively charged ion—such as  $\text{Fe}^{+2}$  or  $\text{Ca}^{+2}$ —into the wastewater and then precipitating the metals. High-pH lime treatment

<sup>1</sup> Ethylenediaminetetraacetic acid.

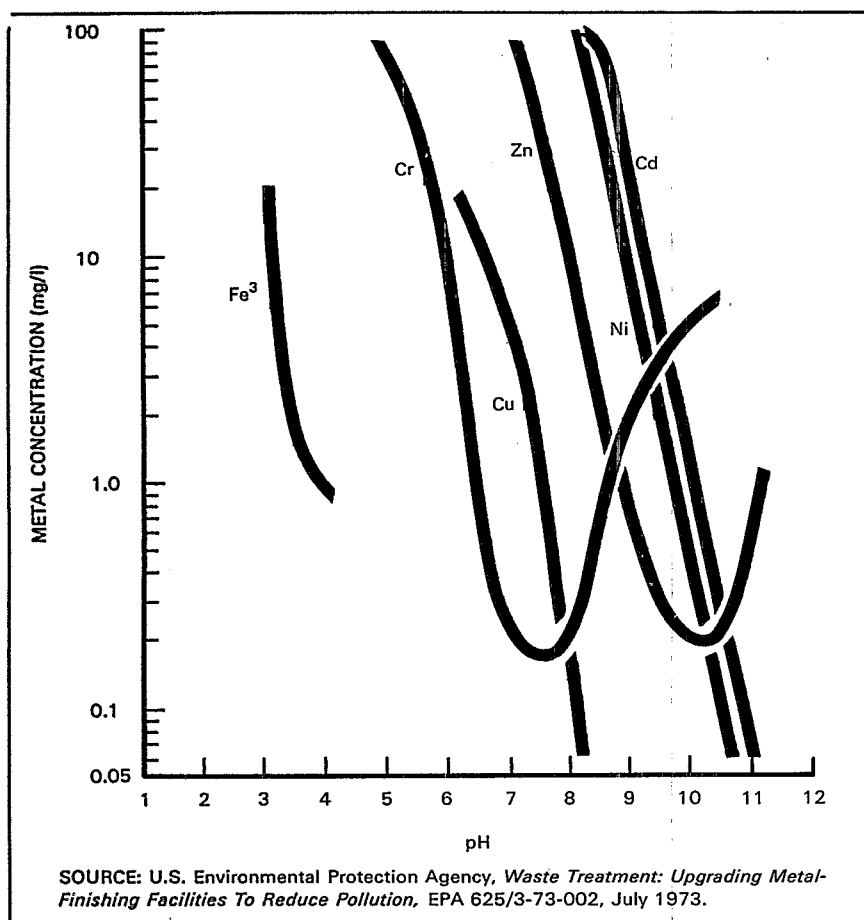


Figure 1.  
Metal Solubility as a Function of pH

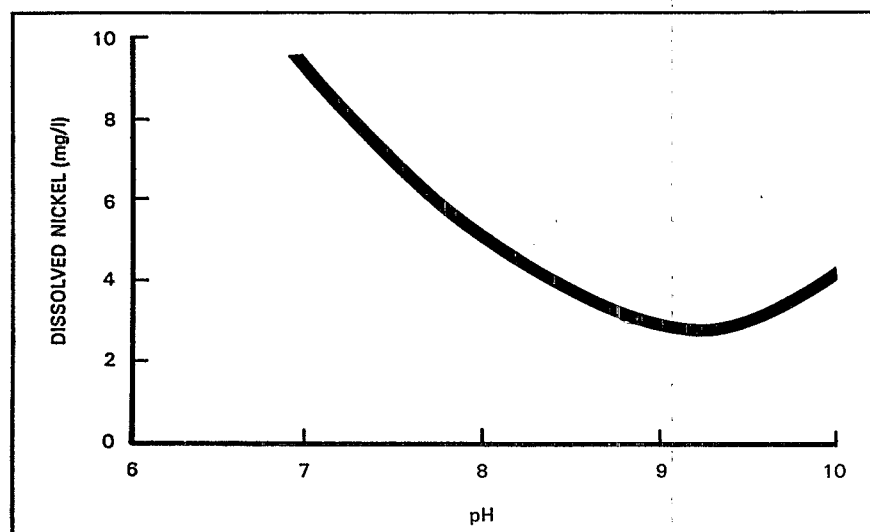


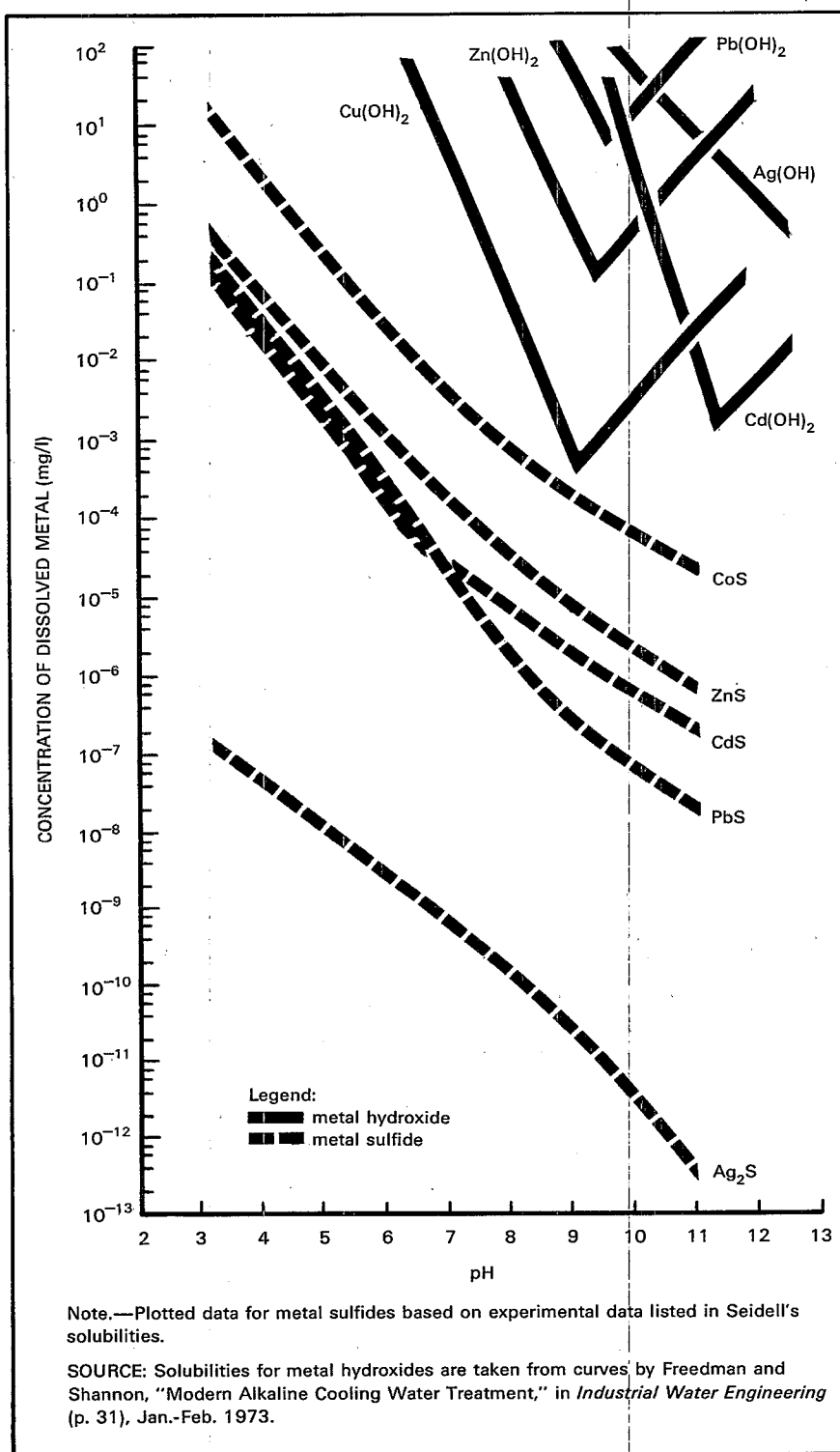
Figure 2.  
Solubility of Complexed Nickel When Precipitated With Caustic Soda

and ferrous sulfate ( $\text{FeSO}_4$ ) precipitation techniques use this principle.

Sulfide precipitation has been demonstrated to be an effective alternative to hydroxide precipitation for removing various heavy metals from industrial wastewaters. The high reactivity of sulfides ( $\text{S}^{2-}$ ,  $\text{HS}^-$ ) with heavy metal ions and the insolubility of heavy metal sulfides over a broad pH range are attractive features compared with the hydroxide precipitation process (Figure 3). Sulfide precipitation can also achieve low metal solubilities in the presence of certain complexing and chelating agents.

The main difference between the two processes that currently use sulfide precipitation is the means of introducing the sulfide ion into the wastewater. In the soluble sulfide precipitation (SSP) process, the sulfide is added in the form of a water-soluble sulfide reagent such as sodium sulfide ( $\text{Na}_2\text{S}$ ) or sodium hydrosulfide ( $\text{NaHS}$ ). A more recently developed process adds a slightly soluble ferrous sulfide ( $\text{FeS}$ ) slurry to the wastewater to supply the sulfide ions needed to precipitate the heavy metals.

In the past, operational difficulties prevented more than minimal application of the SSP process. Recent investigations, however, have eliminated or reduced these problems. Technological advances in the area of selective-ion electrodes have provided a probe that



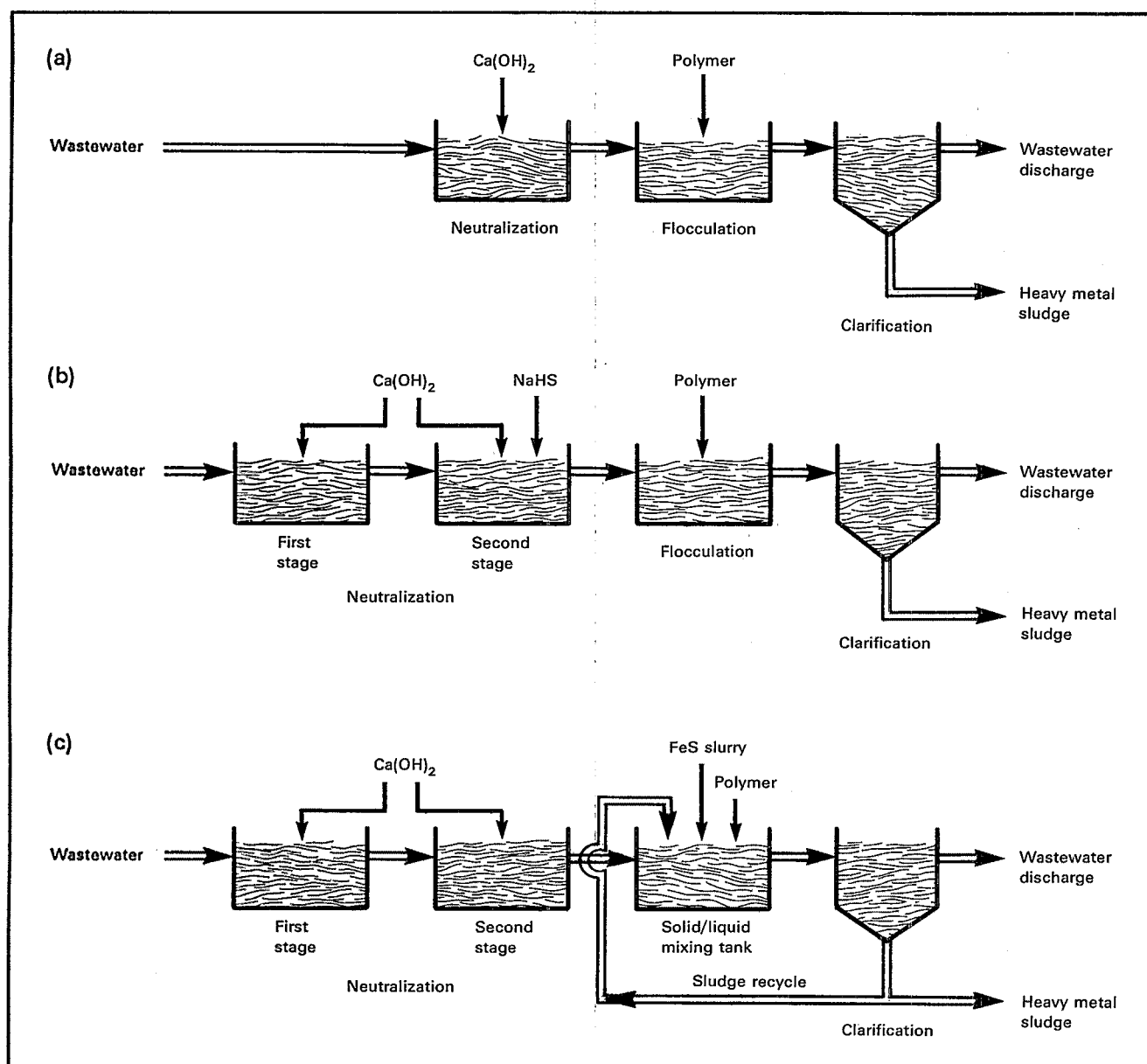
**Figure 3.**

Solubilities of Metal Hydroxides and Sulfides as a Function of pH

has proven successful in pilot-scale evaluations for controlling the addition of soluble sulfide reagent to match reagent demand. Eliminating sulfide reagent overdose can prevent the odor problem commonly associated with these systems. In currently operated soluble sulfide systems that do not automatically adjust reagent dosage to match demand, the process tanks must be enclosed and vacuum evacuated to minimize sulfide odor problems in the work area. The formulation of poly-electrolyte conditioners that effectively flocculate the fine metal sulfide particles has eliminated the difficulty in separating the precipitants from the discharge and has resulted in sludges that are easily dewatered.

Recently, a patented sulfide precipitation process called Sulfex™ has proven effective in separating heavy metals from plating waste streams. The process uses a freshly prepared ferrous sulfide slurry (prepared by reacting  $\text{FeSO}_4$  and  $\text{NaHS}$ ) as the source of the sulfide ions needed to precipitate the metals from the wastewater. The process operates on the principle that  $\text{FeS}$  will dissociate into ferrous ions and sulfide ions to the degree predicted by its solubility product. As sulfide ions are consumed, additional  $\text{FeS}$  will dissociate to maintain the equilibrium concentration of sulfide ions. In alkaline solutions, the ferrous ions will precipitate as ferrous hydroxides. Because most heavy metals have sulfides less soluble than ferrous sulfide, they will precipitate as metal sulfides.

An advantage of the insoluble sulfide precipitation (ISP) process is the absence of any detectable hydrogen sulfide ( $\text{H}_2\text{S}$ ) odor—a problem historically associated with SSP treatment systems. Another



**Figure 4.**

Wastewater Treatment Processes for Removing Heavy Metals: (a) Hydroxide Precipitation, (b) SSP, and (c) ISP

advantage is that the ISP process will reduce hexavalent chromium to the trivalent state under the same process conditions required for metal precipitation, thus eliminating the need to segregate and pretreat chromium waste streams. Disadvantages of the ISP process include considerably higher than stoichiometric reagent

consumption and significantly higher sludge generation factors than either the hydroxide or soluble sulfide treatment processes.

Figure 4 compares typical process flow diagrams of a hydroxide

treatment system and both types of sulfide systems. Most of the elements of the sulfide systems are common to the hydroxide precipitation treatment sequence. The sulfide treatment processes also can be used as a polishing system after a conventional hydroxide precipitation/clarification process to



significantly reduce the consumption of sulfide reagent.

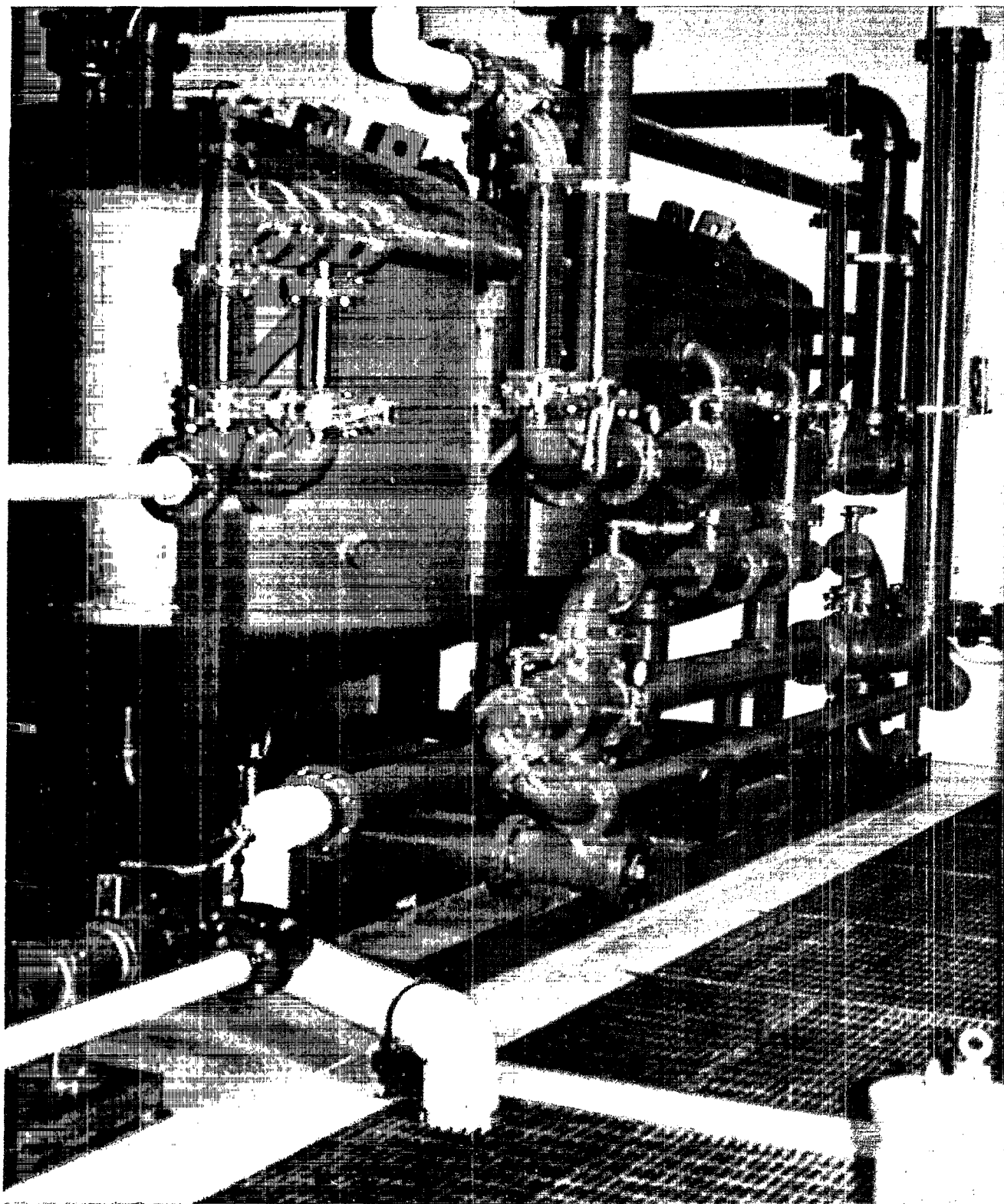
The final selection of a hydroxide or sulfide process should also consider any different constraints for disposal of the resulting sludge. Preliminary studies have indicated that metal ion leachability is lower for metal sulfide sludges than for hydroxide sludges. However, the long-term impacts of weathering and of bacterial and air oxidation of sulfide sludges have not been evaluated.

At this time, the necessary precautions for environmentally safe disposal of sulfide sludge have not been established. This lack of information prevents an evaluation of the impact of generating a sulfide sludge instead of a hydroxide sludge.

This report will evaluate the sulfide precipitation process, assuming that disposal of the residue incurs the same constraints as the hydroxide process.

The importance of design safeguards to avoid the potential hazards associated with sulfide precipitation processes cannot be overemphasized. For example, a sulfide reagent coming into contact with an acidic waste stream can result in the evolution of toxic  $H_2S$  fumes in the work area. The potential danger can be minimized by fairly conventional design safeguards, but the safeguards must be well maintained to be effective. Another potential problem for plants discharging to enclosed sewers is the danger associated with residual levels of sulfide in the wastewater. This problem occurs primarily with the SSP processes because the low solubility of  $FeS$  in the ISP process controls the residual sulfide concentration at a very low level. Elimination of the  $H_2S$  hazard to sewer workers would require either oxidation of the wastewater before discharge or process controls to ensure a low sulfide residual in the discharge.

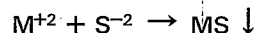
This summary report is intended to promote an understanding of the use of sulfide precipitation for the removal of heavy metals from industrial waste streams. The report includes a general discussion of sulfide precipitation process theory and an evaluation of both soluble and insoluble sulfide treatment systems in terms of state of development, performance, cost, and operating reliability.



Dual-bed effluent polishing filters

## Process Theory

The precipitation of a dissolved metal ion as a metal sulfide (MS) occurs when the metal ion ( $M^{+2}$ ) contacts a sulfide ion ( $S^{-2}$ ):



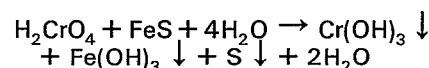
Most heavy metals encountered in electroplating wastewater will form stable metal sulfides; common exceptions include the trivalent chromic and ferric ions.

The two processes currently employed to precipitate metals as sulfides differ mainly in the method used to introduce the sulfide ions into the wastewater. The SSP process uses a water-soluble sulfide compound; consequently, the concentration of dissolved sulfide depends on the quantity of reagent added. The ISP process mixes the wastewater with a slurry of slightly soluble FeS, which will dissociate to satisfy its solubility product, yielding a dissolved sulfide concentration of approximately 0.02 ppb in the wastewater. Use of FeS as the source of sulfide ions controls the level of dissolved sulfide at a concentration low enough to eliminate any detectable emission of  $H_2S$  but still provide an inventory of undissolved sulfide

that automatically replaces the sulfide consumed in precipitation reactions.

In the ISP process, the dissolved sulfide ions will precipitate as a metal sulfide any metal with a sulfide solubility less than that of FeS. As shown in Table 1, the only heavy metal with a sulfide more soluble than FeS is manganese. In an alkaline solution, the ferrous ions generated in the dissociation of the FeS will precipitate as hydroxides. Maintaining low levels of ferrous ions in the effluent requires that the pH be controlled between 8.5 and 9.5.

One advantage of the ISP process is the ability of the sulfide and ferrous ions to reduce hexavalent chromium to its trivalent state, which eliminates the need to segregate and treat chromium wastes separately. Under alkaline conditions, the chromium will then precipitate as chromium hydroxide  $[Cr(OH)_3]$ . The overall reduction reaction is:

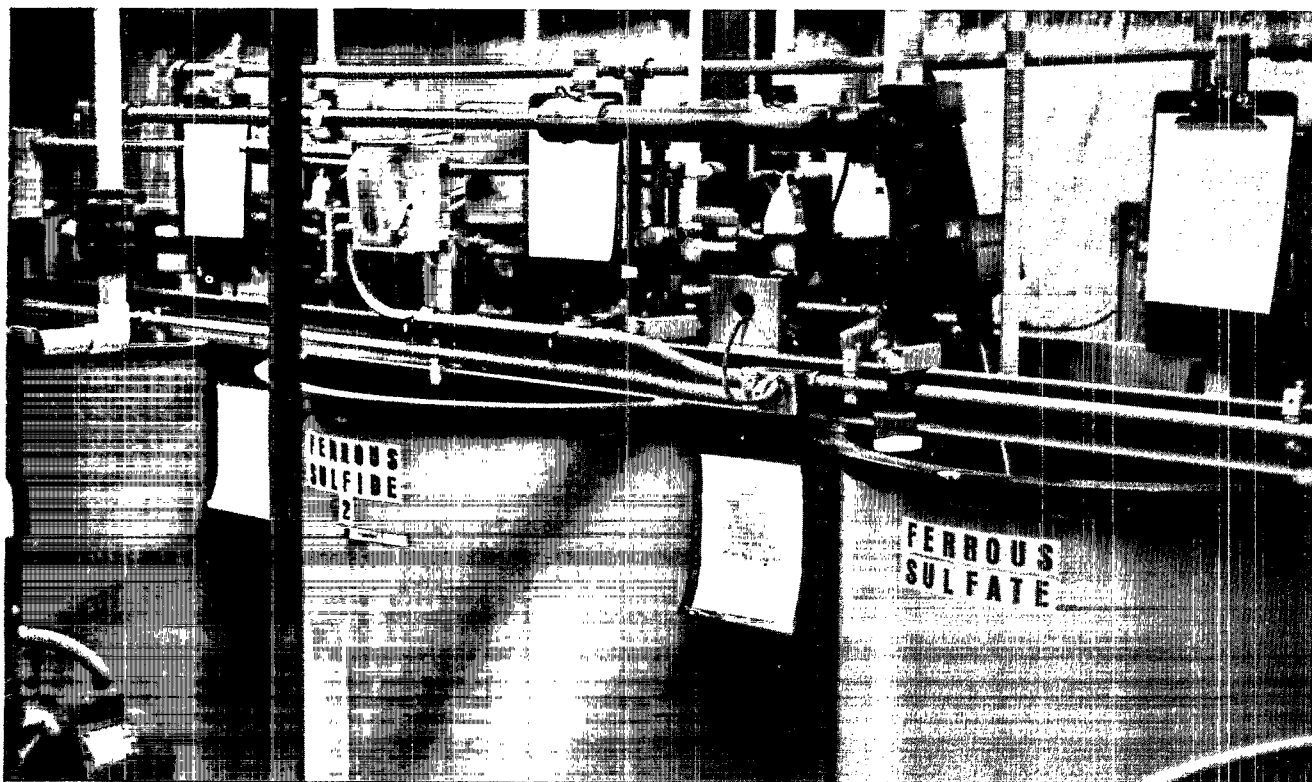


**Table 1.**  
Solubilities of Sulfides

Metal sulfide	$K_{sp}$ (64° to 77° F) <sup>a</sup>	Sulfide concentration (mol/l)
Manganous sulfide.....	$1.4 \times 10^{-15}$	$3.7 \times 10^{-8}$
Ferrous sulfide.....	$3.7 \times 10^{-19}$	$6.1 \times 10^{-10}$
Zinc sulfide.....	$1.2 \times 10^{-23}$	$3.5 \times 10^{-12}$
Nickel sulfide.....	$1.4 \times 10^{-24}$	$1.2 \times 10^{-12}$
Stannous sulfide.....	$1.0 \times 10^{-25}$	$3.2 \times 10^{-13}$
Cobalt sulfide.....	$3.0 \times 10^{-26}$	$1.7 \times 10^{-13}$
Lead sulfide.....	$3.4 \times 10^{-28}$	$1.8 \times 10^{-14}$
Cadmium sulfide.....	$3.6 \times 10^{-29}$	$6.0 \times 10^{-15}$
Silver sulfide.....	$1.6 \times 10^{-49}$	$3.4 \times 10^{-17}$
Bismuth sulfide.....	$1.0 \times 10^{-97}$	$4.8 \times 10^{-20}$
Copper sulfide.....	$8.5 \times 10^{-45}$	$9.2 \times 10^{-23}$
Mercuric sulfide.....	$2.0 \times 10^{-49}$	$4.5 \times 10^{-25}$

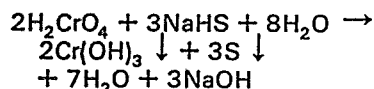
<sup>a</sup>Solubility product of a metal sulfide,  $K_{sp}$ , equals the product of the molar concentrations of the metal and sulfide.

SOURCES: Robert C. Weast (ed.), *Handbook of Chemistry and Physics*, 50th ed., West Palm Beach FL, The Chemical Rubber Company (p. B252), 1969. Louis Meites (ed.), *Handbook of Analytical Chemistry*, New York NY, McGraw-Hill (pp. 1-15, 1-19), 1963.



Ferrous sulfide makeup and feed system

In the SSP process, the sulfide ion is capable of reducing hexavalent chromium as follows:



The question of whether a soluble sulfide reagent can reduce and precipitate hexavalent chromium in one step was addressed in a pilot study conducted for the U.S. Navy. The study concluded that the reduction could be accomplished in the presence of ferrous ions (or conceivably some other suitable secondary metal). The ferrous ion acts principally as a catalyst for chromium reduction. Less than stoichiometric dosages<sup>2</sup> of iron are required to effect

reduction of most of the chromium. Nearly stoichiometric dosages, however, are required to achieve levels typical of other reduction processes. No operating systems currently employ this one-step process.

#### SSP Process Chemistry

The addition of a sulfide reagent that has a high solubility in wastewater will yield a relatively high concentration of dissolved sulfide, compared with the ISP process. This high concentration of dissolved sulfide causes a rapid precipitation of the metals dissolved in the water as metal sulfides, which often results in the generation of small particle fines and hydrated colloidal particles. The rapid precipitation reaction tends more

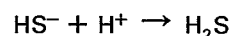
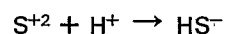
toward discrete particle precipitation than toward nucleation precipitation (the precipitation of a particle from solution onto an already existing particle). The resulting poor-settling or -filtering floc is difficult to separate from the wastewater discharges. This problem has been solved by the effective use, separately or combined, of coagulants and flocculants to aid in the formation of large, fast-settling particle flocs.

Another disadvantage of an SSP system is the  $\text{H}_2\text{S}$  odor often associated with it. The odor detection level of hydrogen sulfide—0.1 to 1.0 ppm—is very low compared with the workplace  $\text{H}_2\text{S}$  concentration limit of 10 ppm specified by the Occupational Safety and Health Administration (OSHA) for worker safety.

The rate of  $\text{H}_2\text{S}$  formation in a water solution is a function of pH

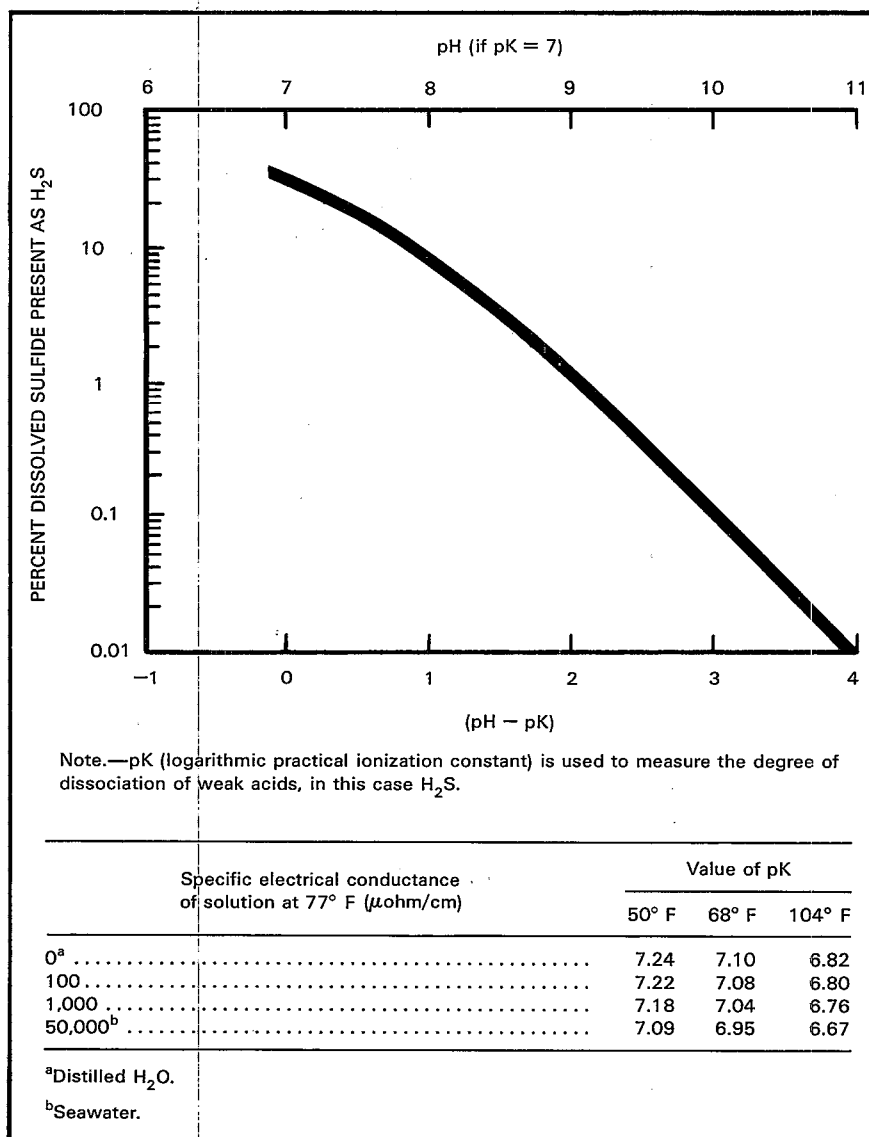
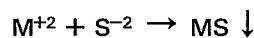
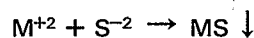
<sup>2</sup>Stoichiometric dosage = dosage of reagent required per unit of contaminant based on the chemical formula and relative atomic weights as predicted by the treatment reaction.

(concentration of hydrogen ions) and sulfide ion concentration. The formation of  $H_2S$  from dissolved sulfide ions proceeds as follows:



Actually, the strong base  $S^{2-}$  is not present in any significant amount except at high pH. For example, at a pH of 11, less than 0.05 percent of the dissolved sulfide is in the  $S^{2-}$  form; the remainder is in either the  $HS^-$  or  $H_2S$  form. Figure 5 is a graph for determining the percentage of the dissolved sulfide in the form of  $H_2S$  as a function of the pH of the solution. The relationship shows that at a pH of 9,  $H_2S$  accounts for only 1 percent of the free sulfide in solution. The rate of evolution of  $H_2S$  from a sulfide solution per unit of water/air interface will depend on the temperature of the solution (which determines the  $H_2S$  solubility), the dissolved sulfide concentration, and the pH. In practice, considering typical response lags of instruments and incremental reagent addition, control of the level of dissolved sulfide and pH would require fine tuning and rigorous maintenance to prevent an  $H_2S$  odor problem in the work area. In currently operating treatment systems, the  $H_2S$  odor problem is eliminated by enclosing and vacuum evacuating the process vessels.

Adding sulfide reagent to wastewater containing precipitated metal hydroxides will result in resolubilization of the metal hydroxides. The dissolving of the metal hydroxides occurs because the dissolved metal ion concentration is now lower than the equilibrium level predicted by the hydroxide solubility. These newly liberated metal ions will be precipitated by any excess sulfide present. The following reactions occur:



**Figure 5.**  
Percent of Dissolved Sulfide in the  $H_2S$  Form

Normally, the precipitated solids are in contact with the wastewater long enough to result in an almost complete conversion of metal hydroxides to metal sulfides. Therefore, the sulfide reagent demand depends on the total metal concentration contained in a wastewater. Consequently, a significant reduction in sulfide reagent consumption could be

achieved by separating the precipitated metal hydroxides from the wastewater before adding the sulfide reagent.

### ISP Process Chemistry

The Sulfex™ process precipitates dissolved metals as sulfides by mixing the wastewater with an  $FeS$  slurry in a solid/liquid contact chamber. The  $FeS$  dissolves to

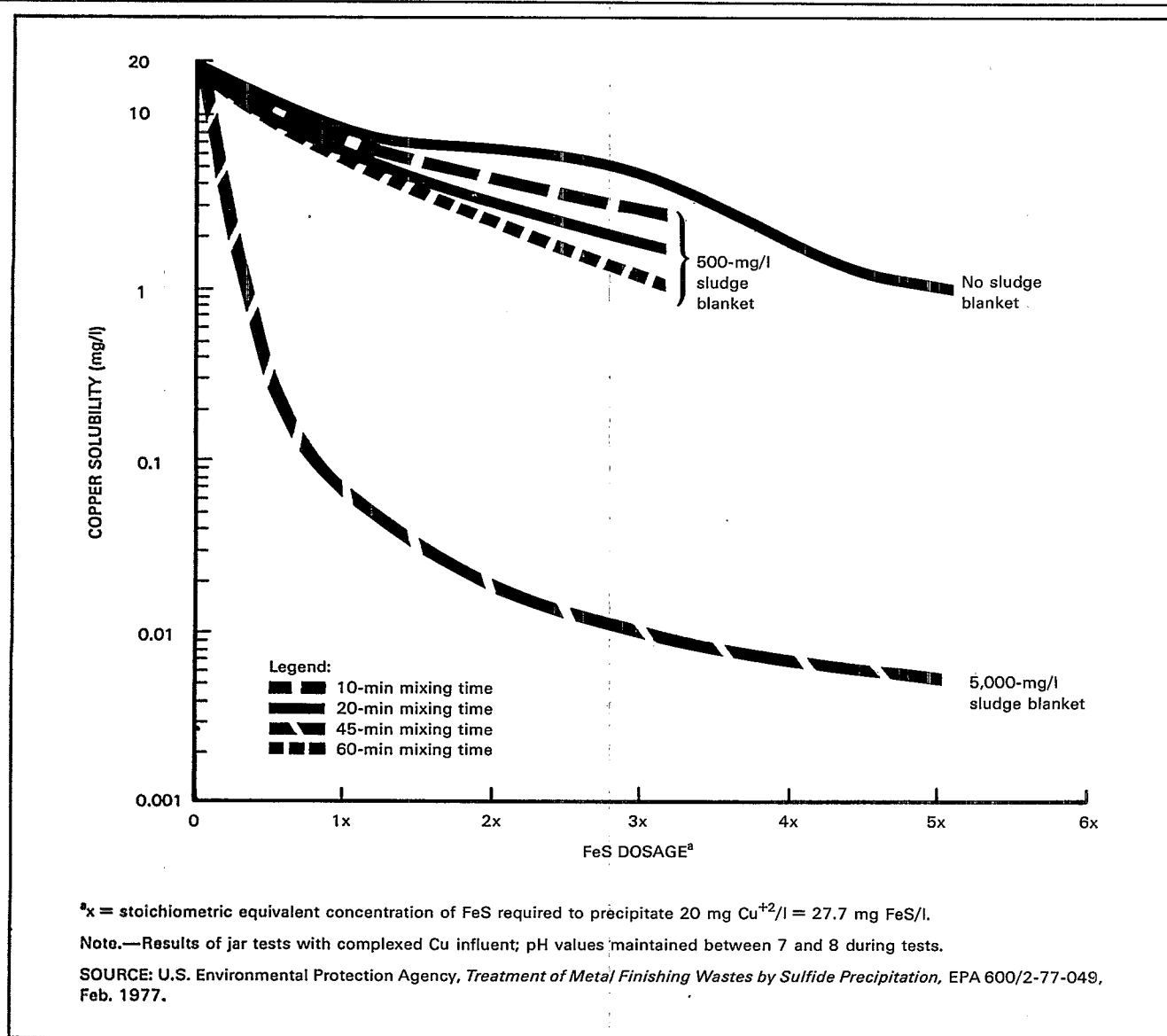
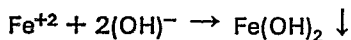
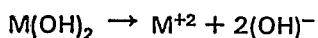
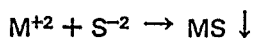


Figure 6.

Influence of FeS Dosage, Sludge Blanket Concentration, and Mixing Time on Copper Solubility

maintain the sulfide ion concentration at a level of 0.02 ppb.

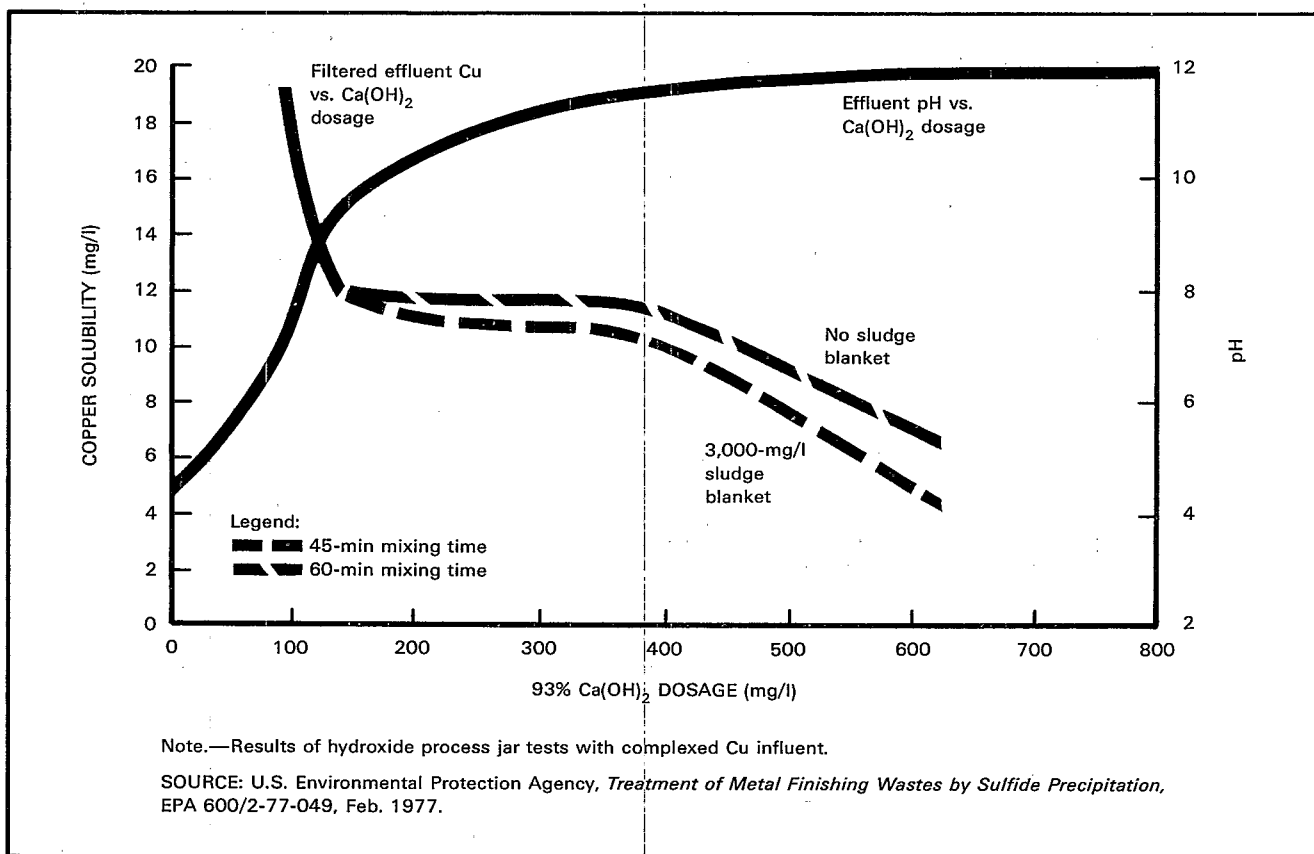
The following reactions occur when FeS is introduced into a solution containing dissolved metals and metal hydroxide:



The addition of ferrous ions to the wastewater and their precipitation as ferrous hydroxide  $[\text{Fe}(\text{OH})_2]$  results in a considerably larger quantity of solid waste from this process than from a conventional hydroxide precipitation process.

As with SSP, the ISP process achieves an almost complete conversion of previously precipitated metal hydroxides to metal sulfides. The reaction goes to completion because of the long residence time of the solids in the treatment system before discharge.

Figure 6 shows three different factors that affect the ability of FeS



**Figure 7.**

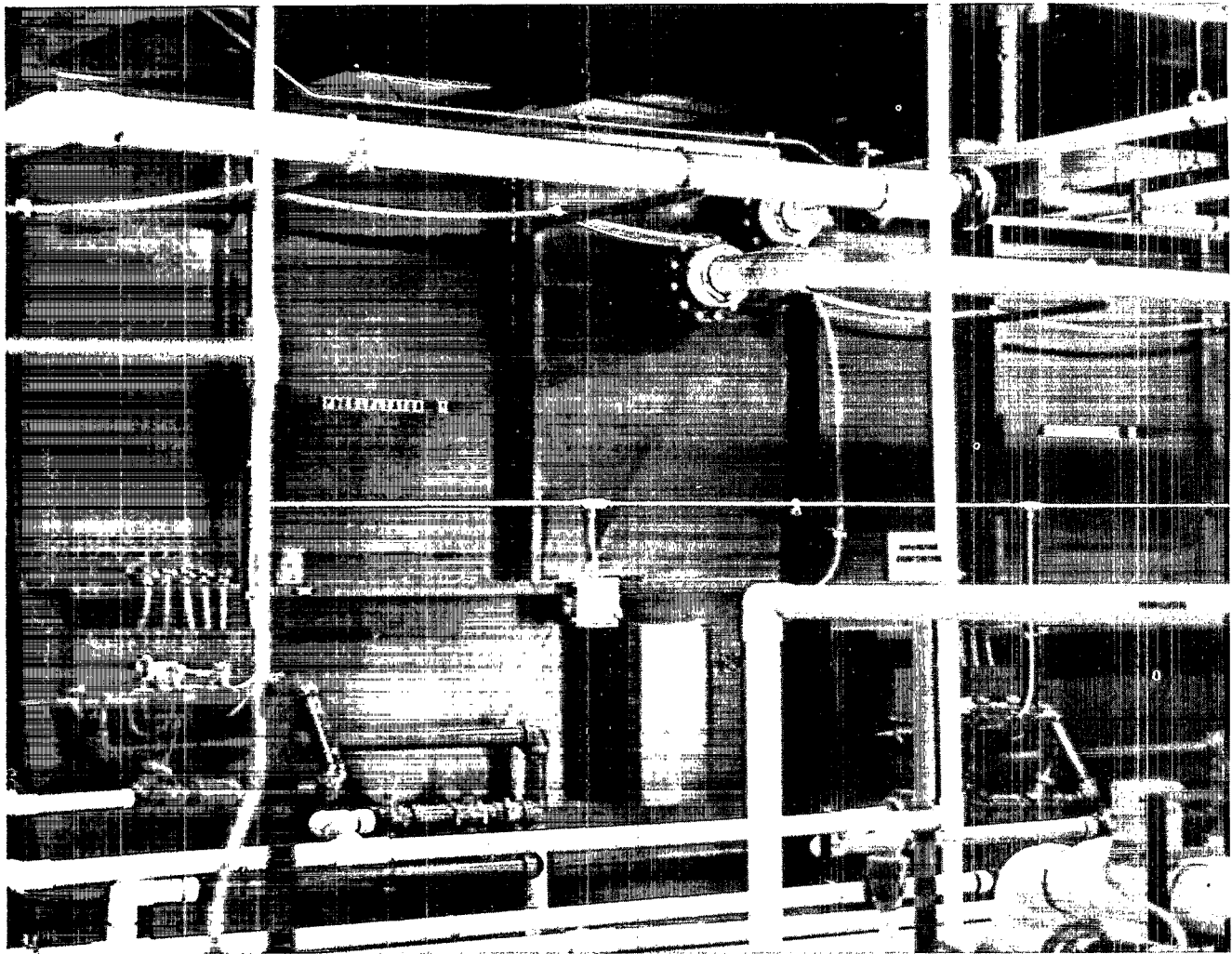
Influence of  $\text{Ca}(\text{OH})_2$  Dosage, Sludge Blanket Concentration, and pH on Copper Solubility

to precipitate copper from a solution containing metal complexing compounds. The design criteria that must be addressed are:

- A dense sludge blanket must be maintained in the solid/liquid contact zone.
- Adequate mixing time is required for the precipitation reaction to reach equilibrium.

- From 2 to 4 times the required stoichiometric amount of reagent is needed to realize the low levels of dissolved copper achievable by sulfide precipitation.

To illustrate the relative effectiveness of sulfide precipitation, Figure 7 represents the solubility of copper in the same complexing compound solution as a function of pH. Even at a pH of 12, the level of dissolved copper cannot be reduced below 2 mg/l.



Hydroxide and sulfide mixer/clarifiers



## Soluble Sulfide Precipitation

Use of a water-soluble sulfide compound to reduce the solubility of heavy metals in a wastewater discharge is an effective method of improving the performance of a hydroxide precipitation treatment system. This section describes the results of a recent investigation of the use of SSP and presents information on systems currently using the technology.

### Pilot Plant Evaluation

**Test Description.** Currently, there are only a few applications of SSP to treat metal finishing wastewater. To provide a source of the data needed by firms interested in using the treatment process, the U.S. Environmental Protection Agency's (EPA's) Industrial Environmental Research Laboratory funded a pilot study by the Boeing Commercial Aircraft Company to compare and evaluate five treatment systems using variations of SSP and hydroxide precipitation processes to treat metal finishing wastewater. The pilot tests were designed to simulate the three basic process systems shown in Figure 8. The five process variations tested were:

- Lime only, clarified (LO-C)—the conventional process using lime as a neutralizing agent to precipitate the dissolved metals and clarification to separate the suspended solids from the discharge (System A)
- Lime only, clarified, filtered (LO-CF)—the LO-C process with a filtration step downstream of clarification to improve the suspended solids removal (System A)
- Lime with sulfide, clarified (LWS-C)—the LO-C process with controlled addition of a soluble sulfide reagent in the neutralizing chamber (System B)
- Lime with sulfide, clarified, filtered (LWS-CF)—the LWS-C process with a filtration step downstream of clarification to improve the suspended solids removal (System B)

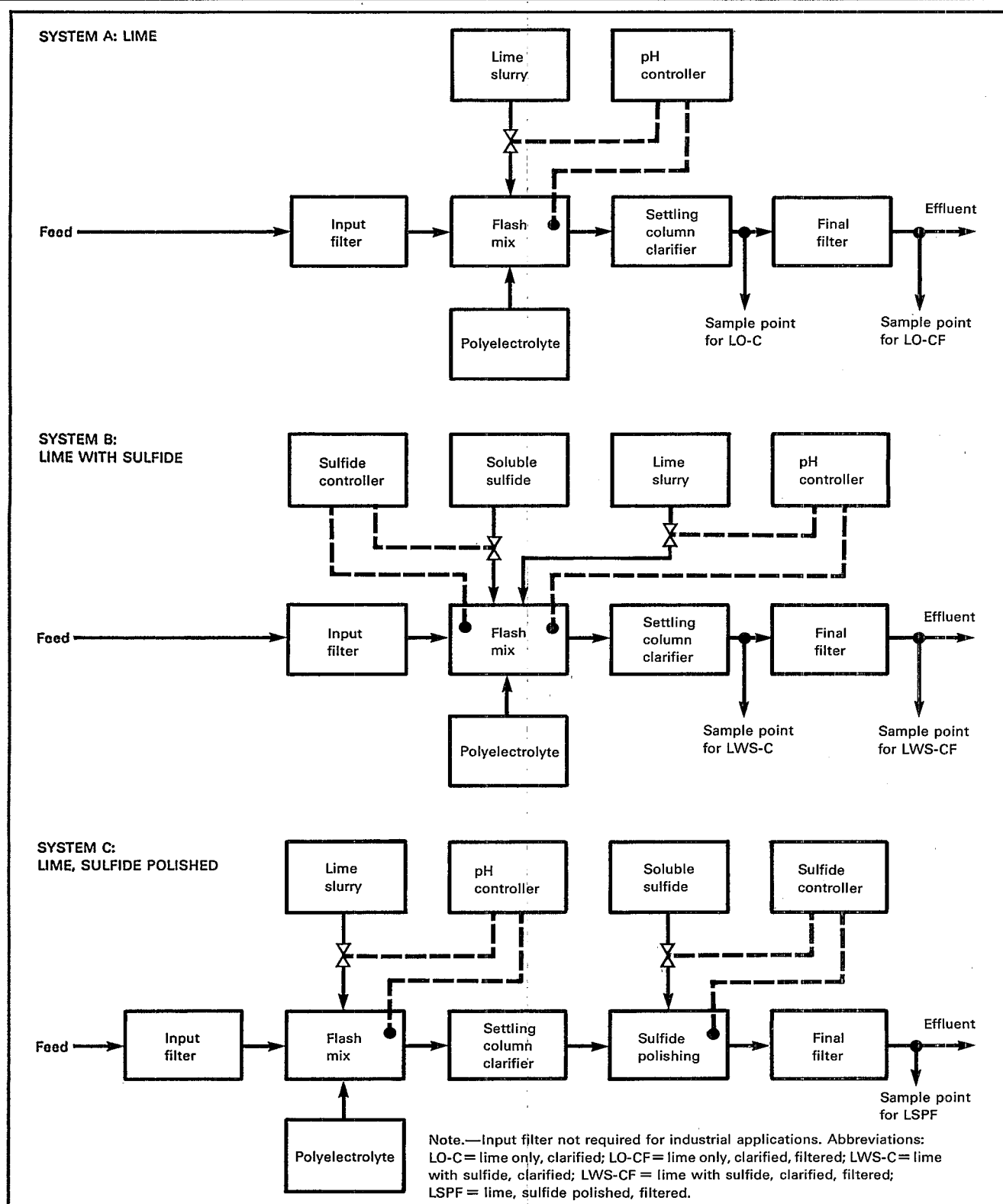
- Lime, sulfide polished, filtered (LSPF)—a polishing sulfide precipitation process featuring lime neutralization and clarification to remove the metal hydroxides followed by addition of a soluble sulfide reagent to reduce the metal solubility and a filtration step to remove the precipitated solids (System C)

These process variations were evaluated with 14 actual raw wastewater feed samples obtained from various industrial firms engaged in electroplating and metal finishing. The pilot plant could operate in any of the five modes and could process 0.034 gal/min (130 ml/min) of wastewater in a continuous treatment sequence. Samples were pretreated as required for chromium reduction and cyanide oxidation. Attempts were not made to reduce hexavalent chromium with sulfide reagent.

In the sulfide process variations, the soluble sulfide reagent addition was controlled automatically by a specific-ion sulfide reference electrode pair to maintain a preselected potential of -550 mV with respect to the reference electrode. The value of -550 mV corresponds to about 0.5 mg/l of free sulfide, which was selected as the control point because at that concentration:

- The curve of electrical potential versus sulfide concentration has its maximum gradient.
- The wastewater solution has no detectable sulfide odor.

The study reported that the dependability of the sulfide specific-ion electrode was excellent during the 6-month test period.



**Figure 8.**  
Metal Precipitation Processes Evaluated in Pilot Study

Table 2.

## Wastewater Treatment Process Details of Pilot Tests

Characteristic	Pilot test <sup>a</sup>				
	1	2 <sup>b</sup>	3	4	5
Raw feed before treatment:					
pH.....	1.7	1.2	6.4	2.4	7.1
Conductivity ( $\mu\text{mho/cm}$ ).....	10,600 at 72° F	149,000 at 68° F	12,100 at 77° F	5,600 at 66° F	1,500 at 70° F
Color.....	Yellow	Colorless	Colorless	Colorless	Pale green
Precipitation pH for LO and LWS processes .....	8.5	6.2/9.0	9.0	10.0	8.5
Sludge volume (%): <sup>c</sup>					
LO process.....	18	78/23	( <sup>d</sup> )	43	5
LWS process.....	16	78/13	( <sup>d</sup> )	37	6
Process consumables (mg/l):					
Sulfuric acid for $\text{Cr}^{+6}$ reduction.....	0	0	0	0	339
Sodium sulfite for $\text{Cr}^{+6}$ reduction .....	226	31	0	41	25
Calcium oxide for neutralization .....	1,530	14,380	911	2,680	145
Sulfide for LWS process.....	8	381	( <sup>d</sup> )	400	91
Sulfide for LSPF process .....	1	5	( <sup>d</sup> )	141	67

<sup>a</sup>Wastewater by pilot test: 1—high-chromium rinse from aluminum cleaning, anodizing, and electroplating; 2—chromium, copper, and zinc rinse from electroplating; 3—high-zinc rinse from electroplating; 4 and 5—mixed heavy metal rinse from electroplating.

<sup>b</sup>Because of the exceptionally large volume of sludge generated by this wastewater, precipitation was accomplished in two stages. First- and second-stage values are separated by a diagonal line; single values apply to the total process.

<sup>c</sup>Sludge volume per solution volume, percent after 1 hour settling.

<sup>d</sup>Data not available.

Note.—LO = lime only; LWS = lime with sulfide; LSPF = lime, sulfide polished, filtered.

SOURCE: *Sulfide Precipitation of Heavy Metals*, EPA Grant 5805413, in preparation.

**Test Results.** Results of five of the pilot tests are presented in Tables 2 and 3. Table 2 lists the characteristics of the wastewater before treatment, the volume of sludge generated, and the amount of reagents consumed in the treatment. Table 3 compares the amount of metal per liter of raw feed before treatment and wastewater after treatment using the five process variations.

Pilot Test 1 simulated treatment of a wastewater containing a high concentration of chromium and moderate levels of copper and zinc. As can be seen from the effluent quality of the LO-CF process, the hydroxide solubilities of the metals in this wastewater were quite low and use of a sulfide reagent to achieve lower metal solubilities was not required. The significant reduction in the chromium concentration across the filter can be seen by comparing the effluent quality of the LO-C and

LO-CF processes. This situation points out how poor solids removal can have significant adverse effects on an otherwise effective metal precipitation treatment system.

Pilot Tests 2 and 3 were performed with wastewaters that were not effectively treated by hydroxide precipitation. In these tests, significantly improved effluent quality was achieved by sulfide precipitation treatment. In Pilot Test 2, the effluent produced by the LO-CF process contained relatively high levels of zinc and copper, 2.3 and 0.8 mg/l, respectively. Treatment with a soluble sulfide compound considerably reduced the effluent concentration of

these metals. In Pilot Test 3, soluble sulfide treatment of wastewater with a high zinc concentration was significantly more effective than hydroxide precipitation.

Tests also were conducted on wastewaters containing an assortment of heavy metals at relatively high concentrations. The results of Pilot Tests 4 and 5 (shown in Table 3) indicate that low levels of all metal pollutants could not be achieved by treatment of these particular wastewaters with either hydroxide or sulfide precipitation. In Pilot Test 4, sulfide precipitation removed the cadmium, copper, and zinc to considerably lower levels than the hydroxide precipitation process, but both processes had a high residual nickel concentration in the effluent. A similar situation occurred with nickel in Pilot Test 5.

Table 3.

## Chemical Analysis of Raw and Treated Wastewater Used in Pilot Tests

Contaminant (µg/l)	Raw feed before treatment	Wastewater after treatment <sup>a</sup>				
		LO-C	LO-CF	LWS-C	LWS-CF	LSPF
Pilot Test 1						
Cadmium.....	45	15	8	11	7	20
Total chromium.....	163,000	3,660	250	1,660	68	159
Copper.....	4,700	135	33	82	18	3
Nickel.....	185	30	38	33	31	18
Zinc.....	2,800	44	10	26	2	11
Lead.....	119	119	88	104	59	120
Pilot Test 2						
Cadmium.....	58	7	12	<5	<5	<5
Total chromium.....	6,300	4	2	5	7	3
Hexavalent chromium.....	<5	<1	<1	<1	<1	<1
Copper.....	1,100	860	848	13	13	132
Nickel.....	160	30	34	33	23	34
Zinc.....	650,000	2,800	2,300	104	19	242
Mercury.....	<1	NA	NA	NA	NA	NA
Silver.....	16	NA	NA	NA	NA	NA
Pilot Test 3						
Cadmium.....	34	21	21	1	1	1
Total chromium.....	3	NA	NA	NA	NA	NA
Copper.....	20	7	8	2	1	4
Nickel.....	64	29	29	72	34	31
Zinc.....	440,000	37,000	29,000	730	600	2,000
Mercury.....	<10	NA	NA	NA	NA	NA
Lead.....	45	13	14	9	11	13
Silver.....	61	4	4	1	3	4
Tin.....	200	<10	<10	<10	<10	<10
Ammonium.....	( <sup>b</sup> )	NA	NA	NA	NA	NA
Pilot Test 4						
Cadmium.....	58,000	1,130	923	26	<10	<10
Total chromium.....	5,000	138	103	49	50	37
Copper.....	2,000	909	943	60	160	929
Nickel.....	3,000	2,200	2,300	1,800	1,900	2,600
Zinc.....	290,000	1,200	510	216	38	12
Iron.....	740,000	2,000	334	563	229	305
Mercury.....	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Silver.....	14	14	10	7	7	8
Tin.....	5,000	129	81	71	71	71
Pilot Test 5						
Cadmium.....	<40	<1	<1	<1	<1	<1
Total chromium.....	1,700	109	39	187	17	20
Copper.....	21,000	1,300	367	2,250	169	11
Nickel.....	119,000	12,000	9,400	11,000	3,500	5,300
Zinc.....	13,000	625	10	192	8	5
Iron.....	NA	2	<2	5	<2	<2
Lead.....	13	7	5	4	3	3
Silver.....	6	NA	NA	NA	NA	NA

<sup>a</sup>LO-C = lime only, clarified; LO-CF = lime only, clarified, filtered; LWS-C = lime with sulfide, clarified; LWS-CF = lime with sulfide, clarified, filtered; LSPF = lime, sulfide polished, filtered; NA = not applicable.

<sup>b</sup>Qualitative tests indicated the presence of significant amounts of ammonium.

Note.—Wastewater by pilot test: 1—high-chromium rinse from aluminum cleaning, anodizing, and electroplating; 2—chromium, copper, and zinc rinse from electroplating; 3—high-zinc rinse from electroplating; 4 and 5—mixed heavy metal rinse from electroplating.

SOURCE: *Sulfide Precipitation of Heavy Metals*, EPA Grant 5805413, in preparation.

The data on effluent quality from this study suggest the following general conclusions about the treatment of wastewater with either hydroxide or sulfide precipitation for removal of heavy metals:

- In most cases, metal removal can be improved by precipitating metals as sulfides rather than as hydroxides.
- Some wastewaters can be effectively treated to low residual concentrations of all metals present by either hydroxide or sulfide precipitation processes; some wastewaters cannot be effectively treated by either hydroxide or sulfide precipitation.
- Consistent removal of metals to effluent concentrations of less than 1 mg/l requires filtration to remove residual suspended solids. Because fine particles (which include precipitated metals) are only minimally different in density from water, they cannot be effectively separated by clarification and therefore contribute to the effluent metal concentration.

Another significant finding of the study is the quantity of sulfide reagent consumed in precipitating the metals as sulfides. In the LWS processes, the bulk of the test runs consumed between 1.0 and 2.5 times the stoichiometric sulfide reagent demand based on the total mass of metals that form sulfides in the wastewater. This reagent demand factor supports the belief that all metals are precipitated as sulfides and that any metals initially precipitated as hydroxides are converted to metal sulfides.

In the LSPF process, the metals precipitated as hydroxides are separated by clarification before

addition of the sulfide reagent. The sulfide reagent demand for most of the LSPF process tests ranged from 2 to 6 times the stoichiometric sulfide reagent demand. The stoichiometric demand in this case can be calculated from the concentration of metals in the LO-C effluent. The study contained no conclusions as to the cause of the significantly higher sulfide reagent demand relative to the stoichiometric requirements.

### SSP System Description and Performance

Although only a few plants currently treat their wastewater with SSP, this process has proved effective for precipitation of many of the metals typically encountered in electroplating wastewater. At present, however, no commercial units are demonstrating the treatment of heavy metals at the high concentrations typical of metal finishing industry wastewater. The primary application of SSP has been for waste streams containing low concentrations of metals and complexing agents, which interfere with effective metal removal by hydroxide precipitation.

Figure 9a is a schematic of a continuous SSP system used to treat a heavy metal waste stream discharged from a large mechanical equipment manufacturer. Part of the wastewater results from electroplating and surface finishing operations. The wastewater pH is adjusted to 7.5 in the first-stage neutralizer and is maintained at approximately 8.5 in the second-stage neutralizer. If the pH falls below 7 in the first stage, a low-pH alarm sounds and the pump feeding the second-stage neutralizer is shut off. Consequently, a surge volume is required in the system to store the wastewater until the pH returns to the control set-point.

Sodium hydrosulfide is added in the second-stage neutralizer at a rate set to maintain a dosage of 5 to 10 mg of free sulfide per liter of wastewater. Automatic controls are not used to adjust sulfide reagent feed rate to account for changes in demand. The required sulfide reagent addition rate is determined by periodic testing.

The system shown in Figure 9a uses a separate hexavalent chromium reduction system, although the free sulfide can potentially accomplish the reduction. This approach was not evaluated because performing chromium reduction in the second-stage neutralizer would increase sulfide reagent demand to approximately 35 to 50 mg/l of feed (based on consumption equal to twice the stoichiometric reagent demand) and would make sulfide reagent demand considerably more variable. Without an automatic sulfide reagent addition system to match supply with demand, the increased variability in reagent demand would reduce the reliability of the treatment system. The existing chromium reduction unit, which uses sodium bisulfite ( $\text{NaHSO}_3$ ) as the reducing agent, reduced the hexavalent chromium to the required level. Therefore, sulfide precipitation was used only to achieve the superior metal removal required by the discharge permit.

The reduction in the metal solubility achieved by adding NaHS to this plant's wastewater is shown in Table 4. The data indicate that the metal solubility decreases as the sulfide reagent dosage increases.

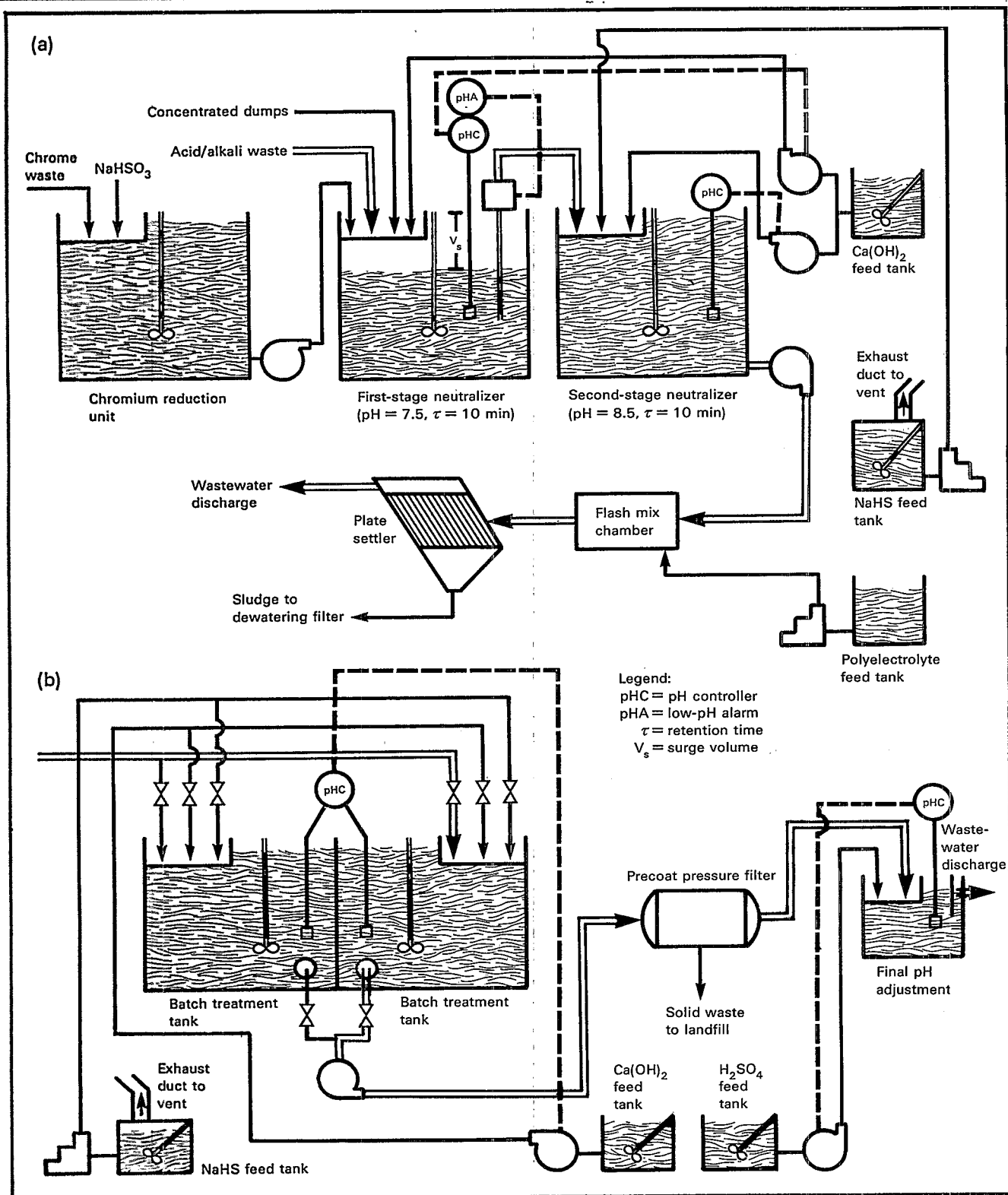


Figure 9.  
SSP Treatment Systems: (a) Continuous and (b) Batch

**Table 4.****Sulfide Precipitation of Cadmium, Zinc, and Mercury**

Metal (mg/l)	Raw waste	Hydroxide solubility at pH of 8.5	Supernatant <sup>a</sup>		
			Sulfide addition (mg/l)		
			1	5	10
Cadmium.....	2.1	2.0	1.6	0.39	0.06
Zinc.....	3.0	2.25	1.8	1.5	1.1
Mercury.....	0.006	0.0027	0.0013	0.001	0.0008

<sup>a</sup>Polyelectrolyte dose = 1 mg/l; settling time of 2 hours.

Note.—Stoichiometric sulfide requirement to precipitate mixture given is 2.1 mg/l of sulfide based on raw waste composition.

Table 4 also shows the solubilities of the metal hydroxides after pH adjustment to 8.5. Effective metal removal is achieved by this treatment system with a sulfide reagent in the sulfide dosage range of 5 to 10 mg/l.

Figure 9b shows a commercially operated batch wastewater treatment system using a soluble sulfide reagent. The system includes two batch treatment tanks, each sized to hold 1 day's wastewater flow. The sequence of treatment follows:

1. The pH of the full, off-stream tank is raised automatically to a value of 11 by the addition of hydrated lime.

2. Depending on the volume of wastewater in the tank, a quantity of NaHS is metered into the tank.
3. The tank is agitated for approximately 30 minutes and a sample is taken, filtered, and analyzed for the metal that is characteristically most difficult to remove.
4. If the metal concentration is low enough, the contents of the tank are pumped through a diatomaceous earth precoat pressure filter and, after final pH polishing (to 8), are discharged. If the reference metal level is not low enough, additional NaHS is added and Steps 3 and 4 are repeated.

The performance of the batch system in reducing the level of total metals in the wastewater discharge is presented in Table 5. As shown, the pH of the wastewater is raised to 11 before NaHS is added. Experimentally, it was found that the sulfide addition would reduce the dissolved metal concentration to equally low levels at a pH of 8.5. Removal of fluorides present in the plant's wastewater, however, required elevating the pH to 11.

The continuous and batch SSP systems described in this section

are located in segregated waste treatment areas. Despite careful control of the wastewater pH and sulfide addition rate, the H<sub>2</sub>S odor in the area was a nuisance. To reduce the ambient level of H<sub>2</sub>S, the open-top treatment tanks where the sulfide reagent is added to the wastewater were modified into closed-top, vacuum-evacuated tanks. In the batch system shown in Figure 9b, the final pH adjustment tank contributed to the odor problem and was modified similarly. The exhaust from these tanks, which contains a low level of H<sub>2</sub>S, is vented outdoors. These changes, plus rigid control of pH and sulfide dosage levels, have resulted in an almost undetectable H<sub>2</sub>S odor in the waste treatment area.

### SSP Polishing Treatment System

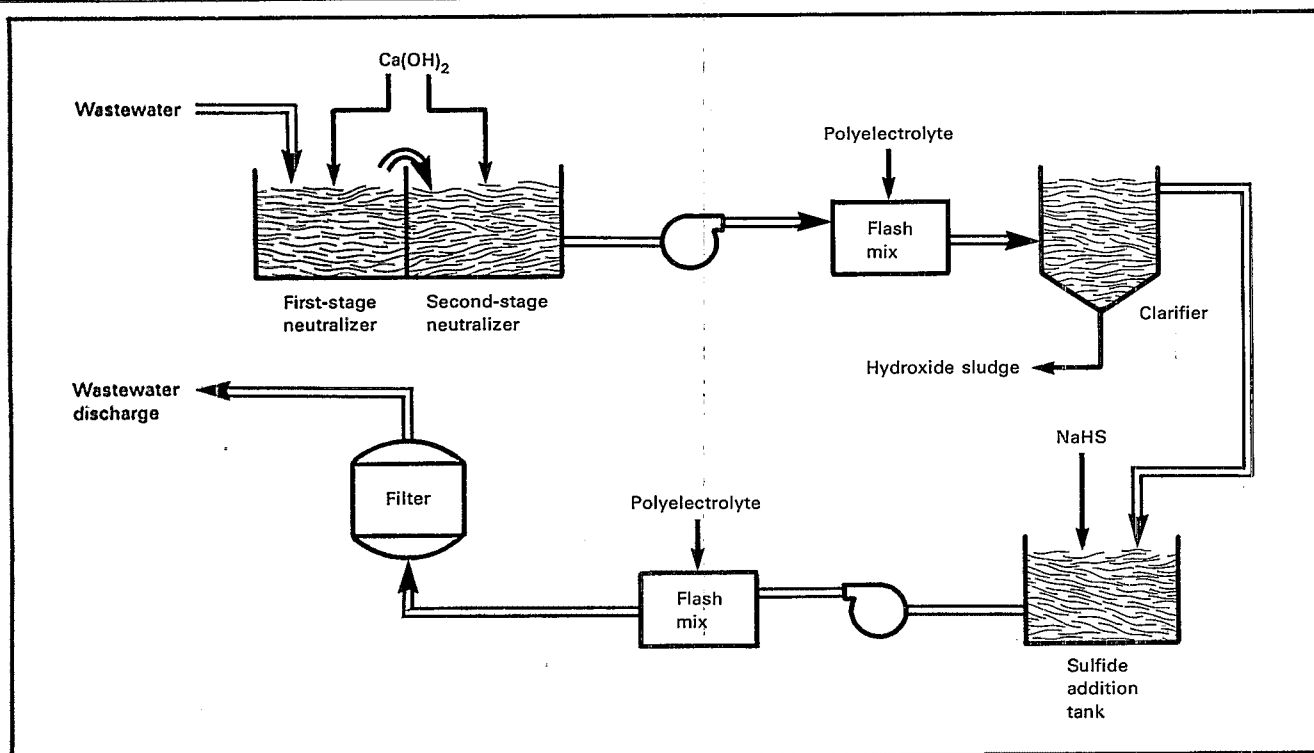
Sulfide reagent demand for the SSP treatment system shown in Figure 9a is a function of the total metal concentration of the raw wastewater. Sufficient reagent must be supplied to convert all entering metals to metal sulfides. In treating wastewater containing high metal loadings, significant sulfide reagent cost savings can be realized by using SSP to polish the effluent after a conventional pH adjustment/clarification treatment sequence (Figure 10). The LSPF process evaluated in the pilot studies discussed earlier simulated the use of SSP as a polishing system. There are no commercially operated SSP polishing systems currently in operation.

In addition to reducing sulfide reagent consumption, using sulfide precipitation as a polishing system will reduce the variability of reagent demand. The reagent demand for the polishing system will be a function of wastewater flow and the concentration of metals in the overflow from the first-stage clarifier. The metal concentration in the wastewater at this point

**Table 5.****Removal of Complexed Copper and Other Metals From Electroplating Wastewater**

Metal (mg/l)	Untreated wastewater	Filtrate
Copper.....	17	0.4
Nickel.....	0.3	<0.2
Lead.....	1.85	<0.2
Zinc.....	0.86	0.4
Tin.....	4.29	<1.0

Note.—Batch treatment sequence: lime added to pH of 11; NaHS added to equivalent sulfide ion concentration of 20 mg/l (stoichiometric requirement = 10 mg/l); filtered through diatomaceous earth filter; final pH adjustment to 8 before discharge.



**Figure 10.**  
SSP Polishing System

should not be subject to the wide variability that often characterizes the raw wastewater feed metal concentration. Without an automatic reagent addition control loop, dosing the wastewater with a predetermined amount of sulfide reagent would be considerably more reliable in a polishing treatment application.

The plant operating the treatment system shown in Figure 9a evaluated the use of SSP as a polishing treatment to reduce the variability of sulfide reagent demand. It was found that clarifying the wastewater before adding the sulfide reagent resulted in the formation of poor-settling particles that were difficult to remove from the wastewater. The current treatment sequence, in which the sulfide reagent is added in the second-stage neutralizer, removes precipitated metal more effectively. It was concluded that the presence of

the precipitated metal hydroxides and lime solids in the wastewater entering the second-stage neutralizer provided nucleation sites, which promoted the coagulation of the precipitated metal sulfides.

An SSP pilot study reports success in forming metal sulfide particles that were easily removed from the wastewater despite precipitation in a solution lacking nucleation sites. The researchers found that conditioning the colloidal metal sulfide precipitants with a cationic coagulant to increase the particle size and then adding an anionic flocculant to link the particles produced large, fast-settling particles when flocculated. In the pilot study discussed previously, the sulfide polishing process precipitated metals as sulfides after the

wastewater had been clarified to remove suspended solids. The study indicated that the metal sulfide solids were removed effectively by filtration.

The additional equipment requirements of a polishing treatment system include a second mixing tank to add the sulfide reagent and a second solids separation unit (using either a clarifier or a filter) installed downstream of the metal hydroxide clarification step. A second polyelectrolyte addition system also may be required to enhance the efficiency of the metal sulfide solids separation step.

#### Hydroxide System Modifications for SSP

Augmenting a hydroxide precipitation wastewater treatment system



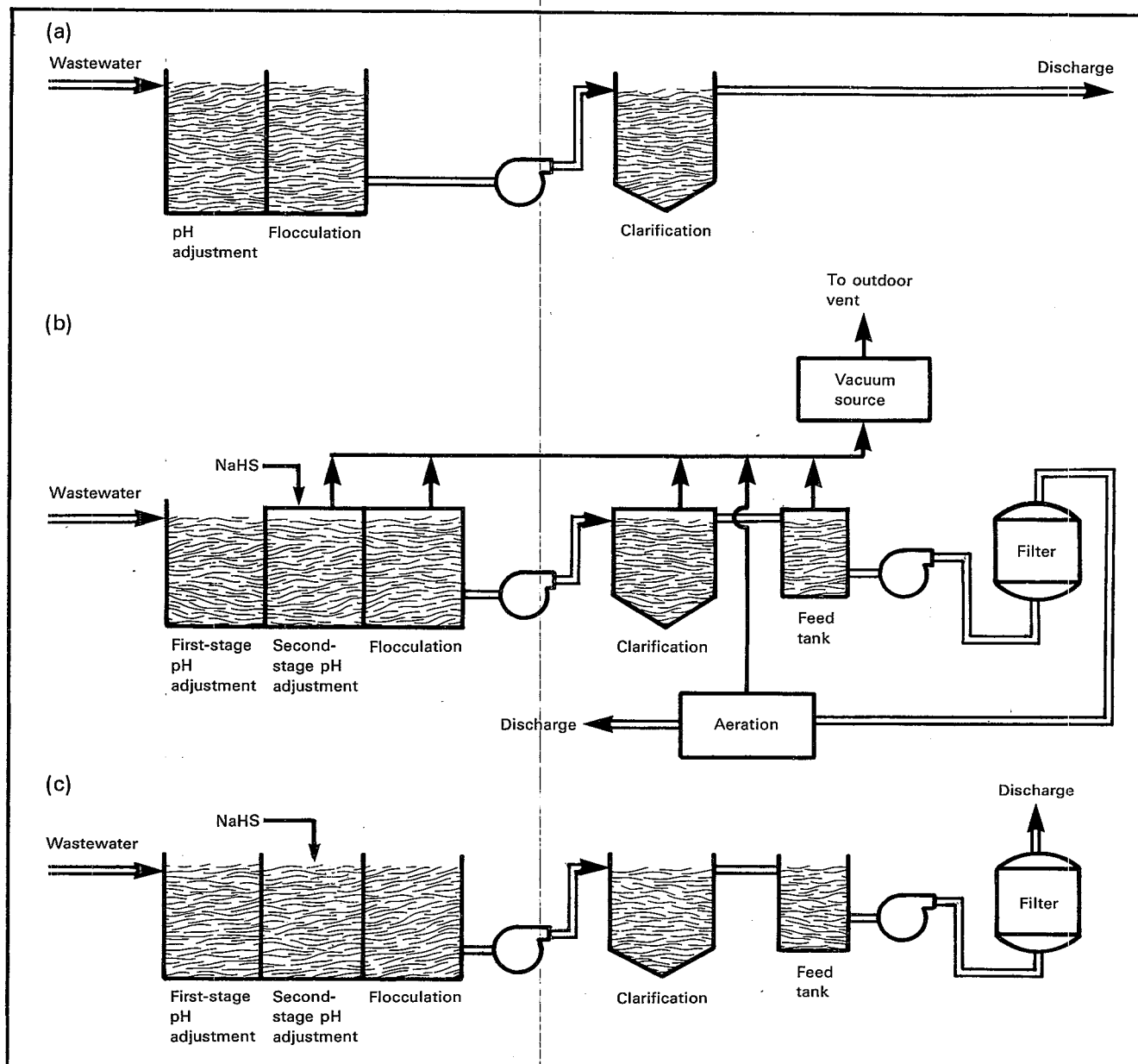


Figure 11.

Conversion of Hydroxide Treatment System To Use SSP: (a) Hydroxide Precipitation System, (b) SSP System, and (c) SSP System With Automatic Control of Sulfide Residual

with SSP to achieve a lower level of metals in the effluent can be a cost-effective means of achieving compliance. The cost of using soluble sulfide treatment will be significantly affected by the reliability and dependability of using the specific-ion sulfide reference electrode to control the sulfide reagent addition. If the

residual sulfide concentration can be maintained consistently at a level of 0.3 to 0.5 mg/l in the wastewater, it should not be necessary to modify existing treatment tanks to eliminate sulfide odor in the work area. Because the reliability of the control system has not been established, two alter-

native approaches emerge for converting a hydroxide system to use SSP.

With no automatic control of the level of residual sulfide in the wastewater, converting the conventional hydroxide precipitation system (Figure 11a) to an SSP system (Figure 11b) requires

several process modifications. The modifications, which are discussed in the following paragraphs, include:

- NaHS reagent feed tank and feed pump
- Second-stage neutralizer/soluble sulfide treatment tank
- Clarifier enclosure and vacuum evacuation
- Control system
- Sand filter or other polishing filtration unit
- Aeration system

The NaHS feed tank should have a closed top with a vent connecting to an exhaust system. In installations where venting any odor is considered a public nuisance, the vent can be connected to a scrubber system. Using a scrubber eliminates the discharge of any odor, whereas simply venting outdoors eliminates any hazard to the worker during reagent preparation. The feed pump should be a positive displacement pump with a variable stroke to facilitate the metering of reagent into the system.

The second-stage neutralizer/soluble sulfide treatment tank is used for adding the sulfide reagent to the wastewater. The tank also provides improved pH control to ensure that the sulfide reagent does not come into contact with acidic wastewater. The tank contents should be agitated. The tank should be sized to provide a minimum retention time of 20 min, and it should be equipped with a pH control loop and alkali neutralizing reagent feed system. To minimize any  $H_2S$  odor associated with the treatment, the tank should be totally enclosed and vacuum evacuated.

To convert the conventional hydroxide precipitation system to an SSP system, it is also necessary to totally enclose and vacuum evacuate the clarifier.

A control system is needed to avoid mixing of the sulfide reagent

with low-pH wastewater. An instrumentation loop that interrupts the wastewater feed to the sulfide treatment tank if the pH of this stream falls below set-point is one way of minimizing the potential hazard. Low-pH conditions also should sound an alarm and interrupt the sulfide feed to the system. This type of control will result in the need for surge volume upstream of the sulfide treatment tank to store the volume buildup until the pH is brought back above the set-point.

A sand filter or other polishing filtration unit that removes suspended solids in the clarifier overflow to very low levels is recommended for any treatment system that must achieve very low levels of metals in the effluent. The significance of reducing the solubility of a metal pollutant by means of sulfide precipitation will be lost unless the level of suspended solids, which include insoluble metals, is also controlled at a low level.

An aeration system may be needed to oxidize residual sulfide before wastewater discharge. If wastewater is discharged into a sewer system, precautions must be taken to ensure that the discharge does not contain high levels of sulfide. Discharge of wastewater containing significant quantities of sulfide could be hazardous to individuals working in a poorly vented sewer system. No specific limit exists for direct discharge of sulfide, but its presence contributes to the biochemical oxygen demand (BOD) of the wastewater. The easily oxidized sulfide compounds can be treated in an air-sparged tank with a retention time of approximately 30 min. If indoors, this tank also should be totally enclosed and vacuum evacuated.

For a process using automatic control of the sulfide reagent addition (Figure 11c), the required modifications to convert the hydroxide system to an SSP system would include the following:

- NaHS reagent feed tank and feed pump—identical to the tank and pump required for the previous case, except the feed pump is actuated by a signal from the sulfide reagent control system to maintain a constant residual sulfide concentration in the wastewater
- Second-stage neutralizer/soluble sulfide treatment tank—for addition of the sulfide reagent to the wastewater, but in this case the residual free sulfide ion concentration is maintained at a level below 0.5 ppm by means of a sulfide ion control loop
- Control system to avoid mixing of the sulfide reagent with low-pH wastewater
- Sand filter

The second-stage neutralizer/sulfide treatment tank and the downstream process tanks will not need to be enclosed and vacuum evacuated if careful control of pH (between 8 and 9.5) and sulfide ion concentration is maintained. Control of sulfide ion concentration also should eliminate the need to aerate the wastewater before discharge. The other elements of the sulfide system shown in Figure 11—first-stage pH adjustment, polyelectrolyte conditioning, and clarification—are common to hydroxide precipitation systems.

For batch treatment SSP systems, a two-tank system for alternately collecting and treating the wastewater would be required. The treatment sequence for a batch system was presented earlier. If the residual level of sulfide cannot be controlled, aeration of the wastewater after chemical treatment may be required in addition to enclosing and vacuum evacuating

the tanks during treatment. The wastewater could be aerated in the treatment tank before flocculation (if required) and solid/liquid separation.

Retrofitting a hydroxide system to use soluble sulfide polishing would require a mixing tank to add the sulfide reagent to the wastewater downstream of the existing clarifier and a second solids separation unit. Because the solids generation rate in the soluble sulfide polishing step should be low, a sand or mixed-media filter should be suitable for removing the suspended solids from the wastewater before discharge.

Polyelectrolyte conditioning and flocculation may be required between the sulfide reagent addition tank and the solids removal filter. Without instrumentation for reliable control of the residual sulfide concentration, the sulfide reagent mixing tank and downstream equipment would need to be enclosed and ventilated, and aeration of the effluent might be required.

### SSP Cost Estimating

Improving the performance of a hydroxide precipitation system through the use of SSP will require investment capital to modify the treatment system and will increase the cost to operate the system.

There is some uncertainty in predicting the extent of the modifications needed to convert a hydroxide system to use SSP. Demonstration of the reliability of automatic control of the sulfide reagent feed is needed to eliminate this uncertainty. Table 6 presents the costs (including hardware and installation) of the different

**Table 6.**

**Equipment Cost Factors for SSP Treatment Systems**

Equipment component	Installed cost (\$1,000), <sup>a</sup> by wastewater flow rate (gal/min)		
	30	60	90
Sodium hydrosulfide feed tank and metering pump .....	3.3	3.3	3.3
Automatic sulfide reagent addition control .....	3.5	3.5	3.5
Low-pH prevention control loop .....	1.5-2.0	1.5-2.0	1.5-2.0
Second-stage pH adjustment and sulfide reagent mixing tank:			
Open top .....	18	22	24
Totally enclosed and vented .....	23	28	30
Suspended solids polishing filter .....	24	33	41
Aerator .....	4	7	9

<sup>a</sup>March 1979 cost basis. Installed costs of different components are presented. Engineering and design costs, site preparation, and equipment freight charges are not included.

equipment components that may be required:

- NaHS feed tank and metering pump
- Automatic control of sulfide reagent addition
- Low-pH prevention control loop
- Mixing tank
- Suspended solids polishing filter
- Aerator

The cost for a sodium hydrosulfide feed tank is based on a 400-gal (1,514-l), closed-top, carbon-steel tank that has a removable lid, exhaust vent, and appropriate nozzles. The diaphragm metering pump is rated to deliver 0 to 20 gal/h (0 to 76 l/h).

A specific-ion sulfide reference electrode pair automatically controls the sulfide reagent feed pump. A control loop prevents low-pH conditions in the sulfide treatment tank by automatically shutting down the wastewater feed pump and sulfide reagent feed pump if the wastewater pH falls below the control set-point. The cost presented assumes the prior existence of a pH probe and a surge volume to hold the diverted flow.

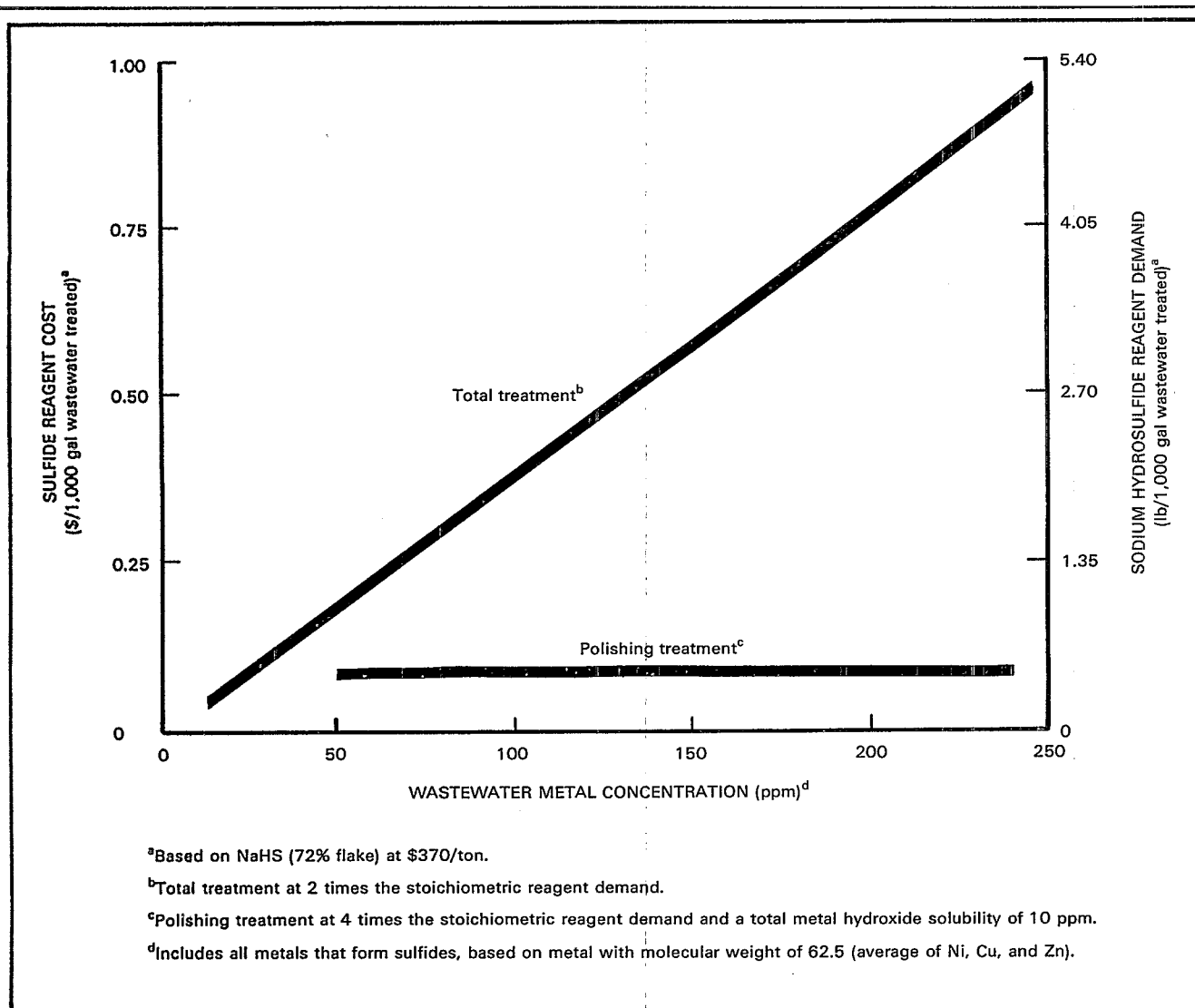
Second-stage pH adjustment and sulfide reagent addition occur in an agitated tank sized for 20-min

retention of wastewater. Costs are given for both an open-top and a totally enclosed and vented tank.

The suspended solids polishing filter costs presented are for dual mixed-media filters, skid mounted and sized so that one filter can process the maximum flow during backwash. The unit is equipped with a blower for low pressure air scouring, a backwash storage tank, and a pump to bleed the wash back into the treatment system.

The aerator cost is based on an enclosed, vacuum-evacuated tank sized for 30-min retention of wastewater and equipped with an air sparger.

Higher operating costs—for operating labor and treatment reagents—will result from incorporating SSP into an existing treatment system. Additional operating labor will be required to prepare sulfide reagent and to maintain and operate the additional equipment components. Additional expense will result from consumption of sulfide reagent. The consumption rate will depend on the volume of wastewater treated and the



**Figure 12.**

### Soluble Sulfide Reagent Cost

required dosage. The dosage per volume of wastewater treated will be a function of the wastewater metal concentration. Figure 12 presents the sulfide reagent cost per 1,000 gal (3,800 l) of wastewater treated as a function of metal concentration for an SSP system used to treat the total metal load as well as for polishing treatment.

Sludge generation rates will increase with the use of SSP com-

pared with a conventional hydroxide treatment system because of improved metal removal, but the increase should be insignificant. For example, precipitating an additional 5 ppm of dissolved metals from a waste stream will increase the clarifier underflow rate by less than 1 gal of sludge per 1,000 gal of wastewater treated, based on an underflow concentration of 1 percent solids by weight. Also, the dewatering properties of sulfide sludges are believed to be superior to those of hydroxide sludges,

although limited information is available to support this view.

If the pH of the neutralized wastewater is increased to minimize odor, more alkali will be consumed, causing an increase in cost. The increased cost of alkali should not be significant except for high-volume treatment systems. Use of a pH above 10 would necessitate a final adjustment to lower the pH to the acceptable discharge range.

## Insoluble Sulfide Precipitation

A commercially available ISP wastewater treatment system was developed to provide a treatment process that offers the superior metal removal of sulfide precipitation systems without the unpleasant  $H_2S$  odor often associated with soluble sulfide systems. Since the first commercial demonstration of the process in 1978, additional installations have become operational. The process is patented, and its use requires payment of a licensing fee to the patent holder. This section describes the process, presents performance data on three currently operating systems, and evaluates use of the process for treatment of electroplating wastewaters.

### Process Description

**Process Equipment Components.** A hydroxide neutralization/ISP treatment system for control of pH and precipitation of heavy metals is depicted in Figure 13. In this system, the hexavalent chromium is reduced to its trivalent state by the sulfide and ferrous ions present in the mixer/clarifier, thus eliminating the need for a separate chromium reduction unit. With the exception of chromium and iron, all other heavy metals in the wastewater precipitate as sulfides. The key elements of the system are:

- pH control
- Mixer/clarifier
- Reagent addition to mixer/clarifier
- FeS feed rate control
- Sand filter

Effective metal removal by sulfide or hydroxide precipitation requires that the pH of the wastewater be controlled within the neutral to slightly alkaline range. Although the dependence of metal solubility on pH is not critical for sulfide precipitation systems, it still affects metal removal (see Figure 3). It is more important to eliminate the danger of the FeS slurry coming into contact with acidic wastewater; FeS is soluble in acidic

solutions, and mixing it with low-pH wastewater would result in the emission of toxic  $H_2S$  fumes in the work area. The risk is minimized by installing a recycle control on the feed to the mixer/clarifier. If the pH of the feed stream drops below 7, valves automatically reroute the feed back to the second-stage neutralizer. For this reason, a surge volume, shown as  $V_s$  in Figure 13, is required to store the accumulated wastewater until the control set-point is reestablished.

The mixer/clarifier shown in Figure 13 serves two purposes. First, it provides the solid/liquid contact volume between the wastewater and the FeS slurry necessary to maintain the wastewater sulfide-ion concentration at its saturation point. As illustrated in Figure 6, both mixing time and sludge blanket density in the solid/liquid contact zone affect metal removal. Second, it clarifies the effluent of suspended solids.

To achieve low concentrations of dissolved metals, which are characteristic of metal sulfides, the liquid residence time in the solid/liquid contact zone of the mixer/clarifier must be sufficient for the metal precipitation reaction to reach completion. Proper agitation in the contact zone will enhance the degree of reaction completion achieved as well as promote particle growth of the precipitated metal sulfides. The formation of large, rapid-settling particles facilitates removal of the solids by clarification.

Reagent addition to the mixer/clarifier is controlled by a flow-measuring device that monitors the feed to the mixer/clarifier and sends a signal to a counter, which computes the cumulative flow. The additions of fresh FeS and polymer are controlled to provide a set quantity of each when

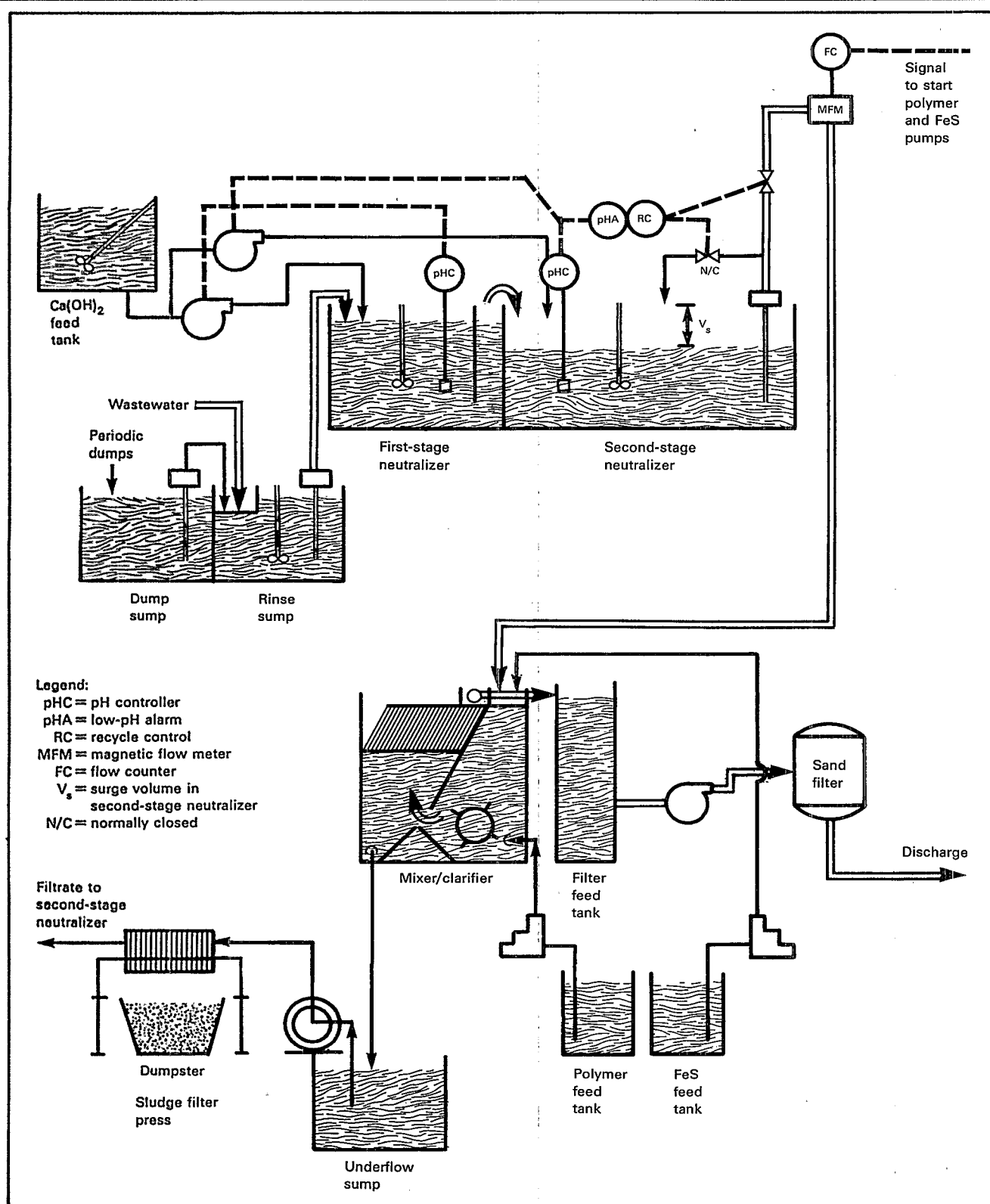
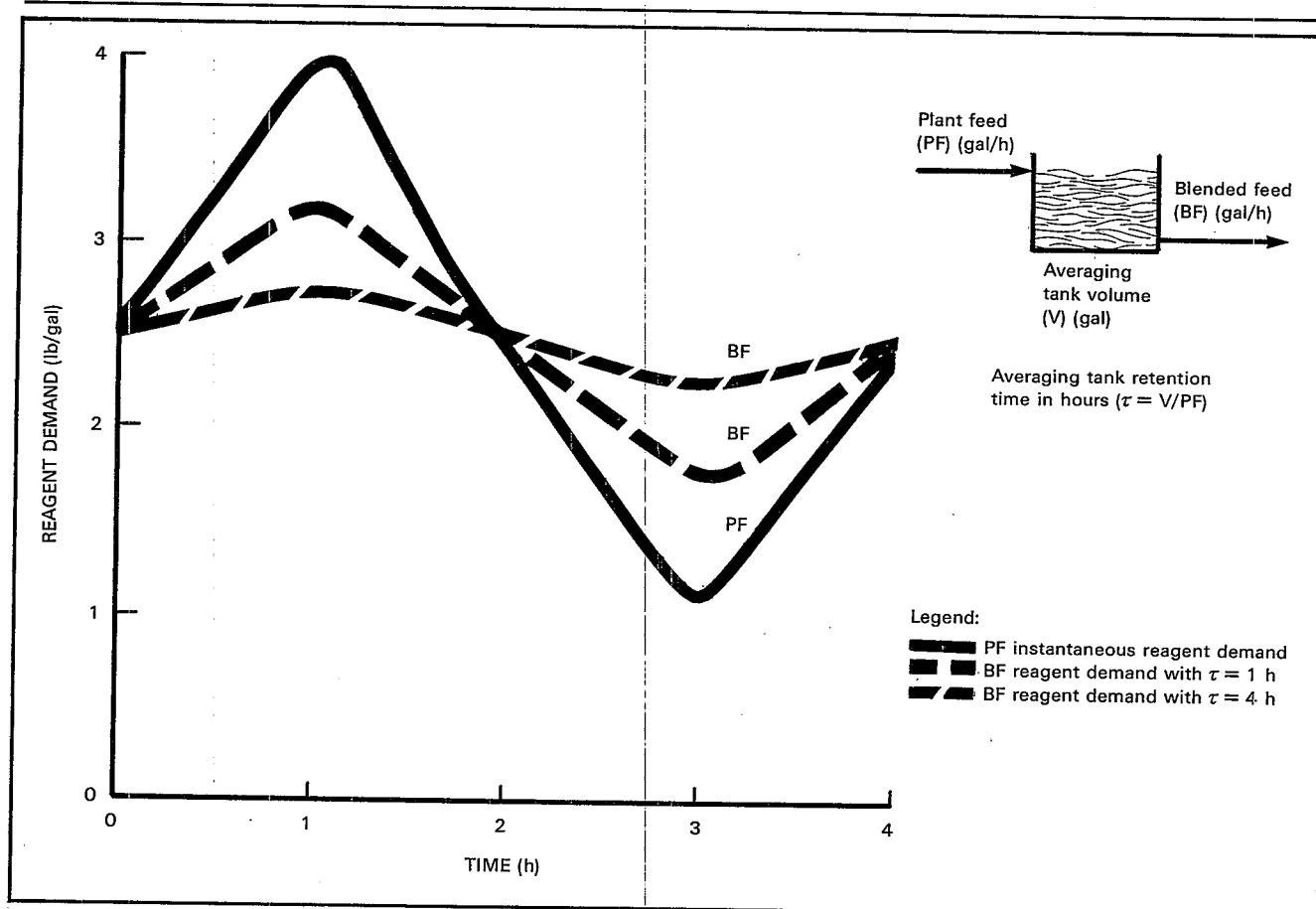


Figure 13.  
 Sulfex™ ISP Treatment System



**Figure 14.**

#### Impact of Averaging Tank Volume on Reagent Demand Variability

the counter records a set volumetric throughput. The dosage rate is determined for both reagents by performing a series of jar tests. A sample is taken from the second-stage neutralizer and tested to determine the required addition of FeS.

Jar tests are conducted on approximately four samples to determine the lowest FeS dosage that provides optimum metal removal. Because polyelectrolyte demand should be proportional to the demand for FeS, it is fed at a constant ratio of the demand for FeS. Jar tests normally are conducted once or twice per shift to determine the required addition rate.

The FeS feed rate control loop automatically adds a preset amount

of reagent each time an increment of wastewater enters the mixer/clarifier. The amount of reagent added is set manually based on the results of the jar tests. The inability to adjust the FeS reagent dosage automatically in response to changes in reagent demand complicates operation of ISP treatment systems. To compensate for the lack of automatic control, two features must be considered in design of the system:

- FeS reagent demand averaging
- Maintaining an inventory of unreacted FeS in the mixer/clarifier

Reagent demand averaging requires the elimination of sharp deviations in wastewater flow rate and pollutant concentration entering the treatment system. Flow variability normally is eliminated by providing a surge volume upstream of the treatment process and treating the wastewater at a constant average rate. The variability of pollutant concentration can be reduced by use of an averaging tank—an agitated tank that stores and blends the treatment system feed before processing. The impact of averaging tank volume and retention time on reagent demand variability is presented graphically in Figure 14. As shown, with 1 hour of retention time in upstream process tanks, the

variability of the mixer/clarifier (blended feed) reagent demand is equal to 54 percent of the plant feed reagent demand variability; with 4-hour retention time in upstream process tanks, the mixer/clarifier reagent demand variability is reduced to 15 percent of the plant feed variability. The graph presents an idealized situation of reagent demand fluctuating around a constant average demand. In actual practice, however, the deviations may be long term and may not average out to a constant demand rate. The relationship between retention time in upstream blending tanks and demand fluctuations is a key to operating any treatment process that does not adjust reagent supply to changes in demand automatically.

Maintaining an inventory of unreacted FeS in the mixer/clarifier is needed to provide the sulfide reagent when reagent demand exceeds supply. Because demand fluctuations are inevitable, an inventory of reagent is essential to consistently achieve maximum removal of metals. The quantity of FeS stored in the mixer/clarifier is proportional to the quantity of solids maintained in the unit and to the concentration of FeS in those solids.

A sand filter is included in the system to ensure that the wastewater discharge contains a minimum concentration of suspended solids. To meet strict metal discharge requirements, the level of dissolved and insoluble metals in the effluent discharge must be reduced to a minimum. For both sulfide and hydroxide precipitation systems, a sand filter ensures that upsets in the treatment system causing turbidity in the clarifier overflow will not jeopardize effluent quality.

*FeS Reagent Consumption.* As shown in Figure 6, precipitation of

dissolved metals to the low solubility level characteristic of metal sulfides normally requires 2 to 4 times the stoichiometric amount of FeS. The ratio of the amount of reagent added to the stoichiometric demand establishes the equilibrium concentration of FeS in the sludge blanket solids. The FeS added in excess of the stoichiometric demand provides the inventory of unreacted reagent that is consumed when reagent demand exceeds supply.

The concentration of FeS in the sludge blanket as a function of the ratio of reagent addition to stoichiometric reagent demand is shown in Figure 15. The quantity of reagent consumed as a function of this ratio also is shown. Because the underflow rate is set to balance the solids loading rate, the concentration of FeS in the sludge blanket also determines the amount lost in the sludge underflow.

By defining the volume of the solid/liquid contact zone and the density of the sludge blanket in this zone, the amount of FeS stored can be approximated. The larger the quantity of unreacted FeS maintained in the blanket, the greater the ability of the system to compensate automatically for increases in reagent demand. The FeS supply can be increased by:

- Increasing the FeS reagent feed rate
- Designing larger solid/liquid contact volume into the system
- Maintaining the maximum sludge blanket solids concentration in the solid/liquid contact volume that is compatible with

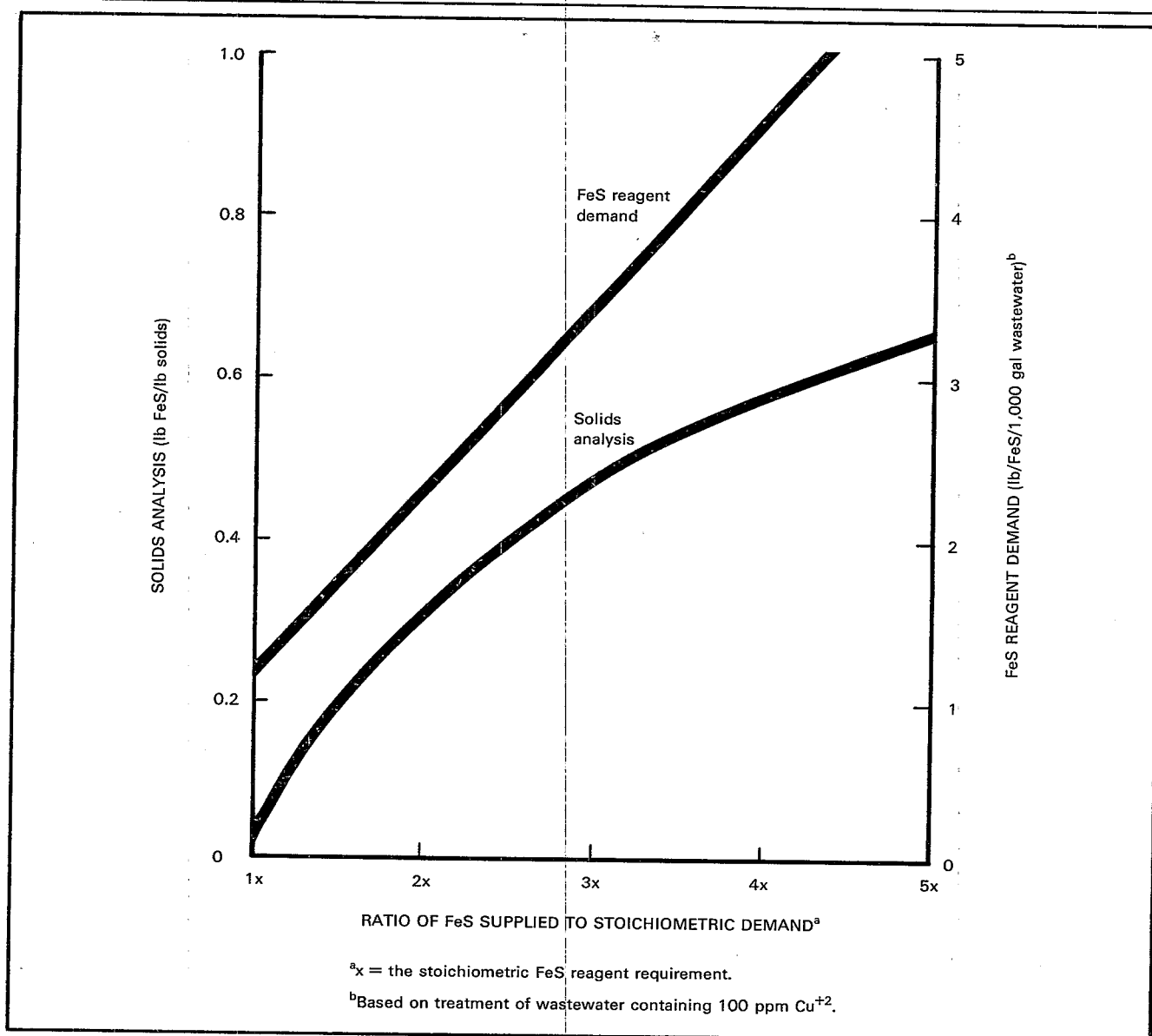
good clarification in the settling zone of the mixer/clarifier

The first two methods of increasing the FeS inventory have economic penalties: reagent cost and sludge volume rise as dosage is increased, and the initial cost and space requirements increase as larger mixing volume is designed into the system. Therefore, maintaining a dense sludge blanket in the mixing zone is the most efficient way to achieve good reagent use and to provide the inventory of FeS needed for reagent demand increases. In practice, this requires monitoring the blanket level and adjusting the sludge drawoff rate to match the solids accumulation rate in the system.

*Operating Procedure.* The ISP system shown in Figure 13 required a full-time operator during one shift and approximately 2 to 4 hours of operator attention during other shifts. Operator duties are as follows:

- Once each shift, a sample of mixer/clarifier feed is removed from the second-stage neutralizer for jar testing to determine the required FeS addition rate.
- Based on the jar test results, the FeS and polyelectrolyte addition control system is set to feed the needed quantity of reagents each time a set feed increment has entered the mixer/clarifier.
- The timer that controls the sludge blowdown is adjusted to reflect any change in the solids loading rate. (This relates to the jar test performed in the first step.)
- The level of solids in the mixer/clarifier is monitored periodically (normally every 1 or 2 hours) by performing a settling test on samples removed from the mixing zone of the mixer/clarifier. The sludge blowdown rate is adjusted to maintain the maximum solids concentration in the





**Figure 15.**

### Sludge Blanket FeS Concentration and Associated Reagent Demand

mixing zone that is compatible with low levels of turbidity in the clarified effluent.

Other operator duties generally required for operation of this system and most treatment systems include:

- Preparation of treatment reagents—in this case, reagents

include lime slurry, Sulfex™ reagent (Figure 16), and polyelectrolyte

- Operation of sludge dewatering filter

- Periodic back-flush cleaning of the sand filter
- Periodic calibration of pH probes
- Collection of samples required for discharge permit
- Regularly scheduled lubrication of system elements

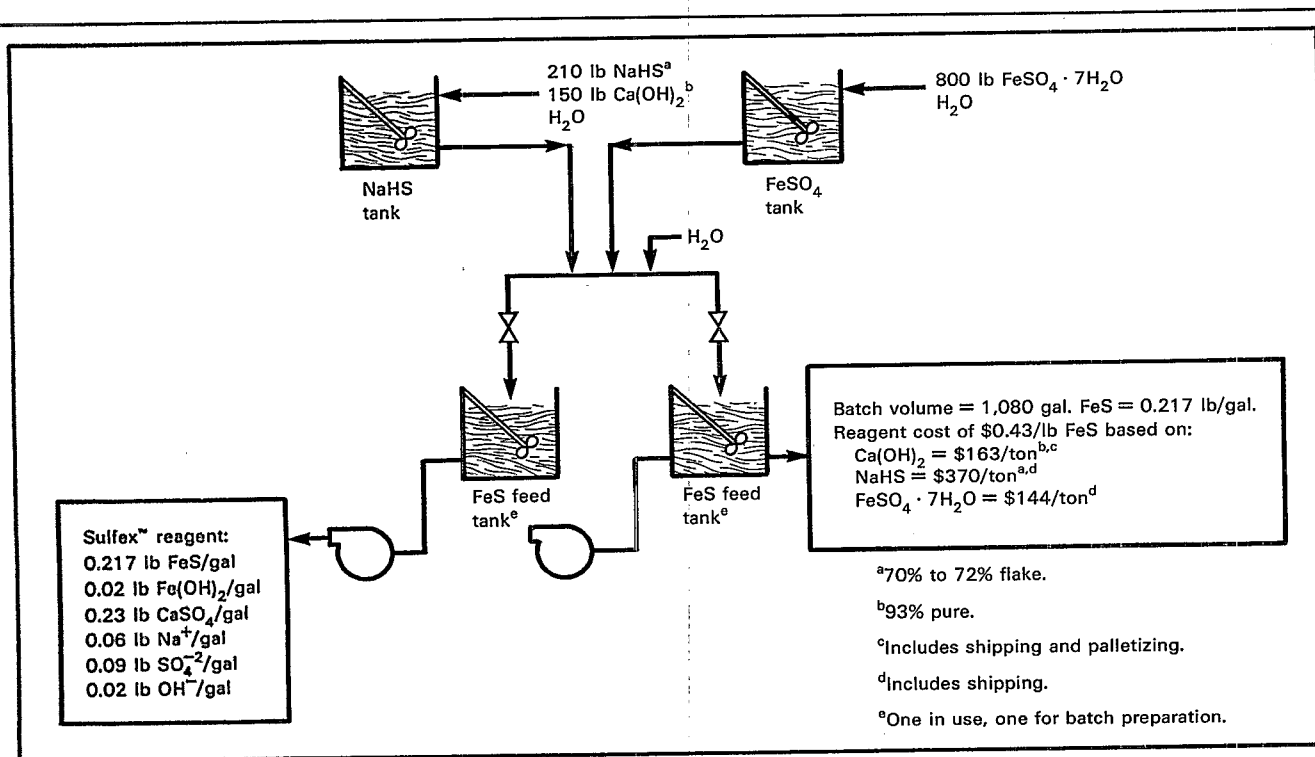


Figure 16.  
FeS Feed System

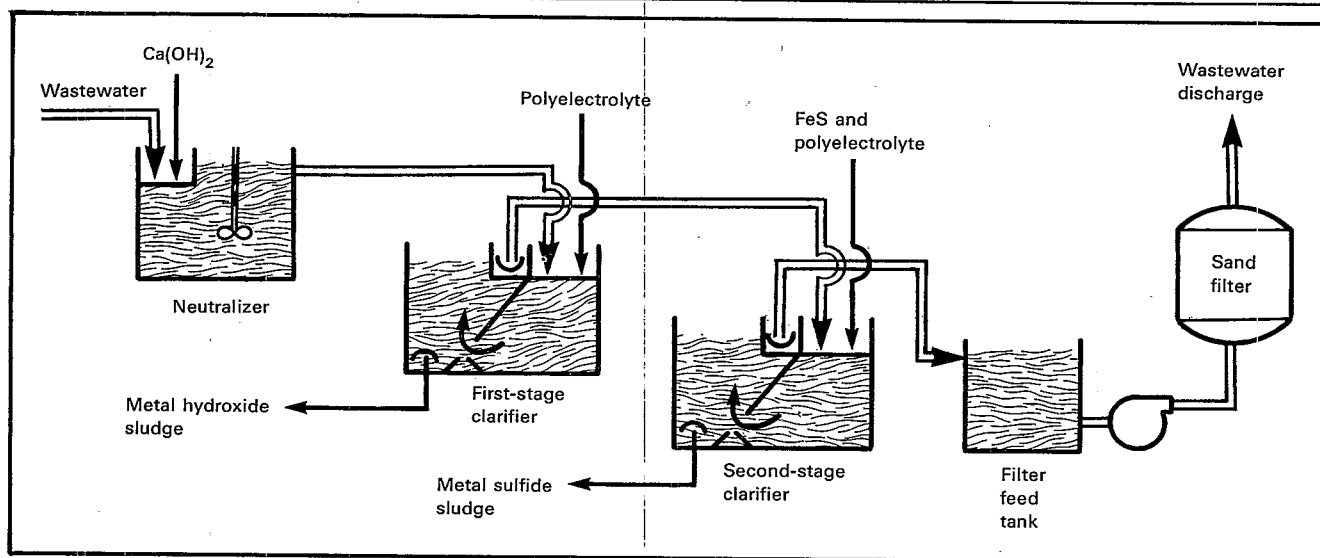
### ISP Polishing Treatment System

The FeS reagent demand for the system shown in Figure 13 is a function of the total metal load entering the mixer/clarifier. Sufficient FeS must be added not only to precipitate the dissolved metals but also to convert the precipitated metal hydroxides to metal sulfides. For treatment systems with a high mass flow of metals, FeS consumption will be high and considerable waste solids (a combination of metal sulfides, metal hydroxides, and unreacted FeS) will be generated. For these applications, the reduction in reagent consumption

and solid waste disposal charges may justify using ISP to polish the clarified overflow after a conventional hydroxide precipitation/clarification treatment sequence (Figure 17).

In this polishing system, the FeS demand is based on the metals contained in first clarifier overflow. If hexavalent chromium is present in the wastewater, it will be reduced in the second-stage mixer/clarifier and precipitated along with the dissolved metals. Two advantages of this approach, compared with the system shown in Figure 13, are reduced FeS reagent demand and reduced sludge generation, which is a function of metal loading and reagent consumption. Another advantage is that the concentration of metals in the first-stage clarifier overflow

will not be subject to the wide variation that often characterizes the wastewater feed metal concentration. The metal hydroxide equilibrium solubility will determine the concentration of dissolved metals in the overflow; this concentration will establish reagent demand. Again, because reagent supply is not adjusted automatically for changes in demand, this feature increases reliability. The concentration of hexavalent chromium, which is unaffected by the hydroxide treatment, will still be subject to variation, but the variability should be reduced because of the larger volume of upstream process tanks in a polishing treatment system.



**Figure 17.**

### ISP Polishing System

Identification of the optimum system—polishing sulfide precipitation or treatment of the total metal load—requires determining whether the operating cost savings of the polishing system offset the additional cost of a second mixer/clarifier and polyelectrolyte feeder.

### ISP System Performance

Three plants currently use the Sulfex™ system to remove heavy metals from wastewater discharge. All three systems were placed in plating shops where no wastewater treatment systems existed. Two of the plants (Plants A and B) treat the total metal load with FeS, whereas the third (Plant C) employs ISP as a polishing step after hydroxide precipitation/clarification.

Plant A performs copper, nickel, and chromium plating (both electroplating and electroless plating) of plastic components. The

**Table 7.**

**Plant A Discharge Permit Requirements**

Item	Discharge limits <sup>a</sup>			
	Mass (lb/d)		Concentration (ppm)	
	Average <sup>b</sup>	Maximum <sup>c</sup>	Average <sup>b</sup>	Maximum <sup>c</sup>
Suspended solids .....	35.3	53.0	NA <sup>d</sup>	NA <sup>d</sup>
Total copper.....	0.89	1.77	1.0	1.5
Total nickel.....	0.89	1.77	1.0	1.5
Total chromium .....	0.89	1.77	1.0	1.5
Hexavalent chromium .....	0.089	0.177	0.05	0.10

<sup>a</sup>Required pH level is between 6.0 and 9.5.

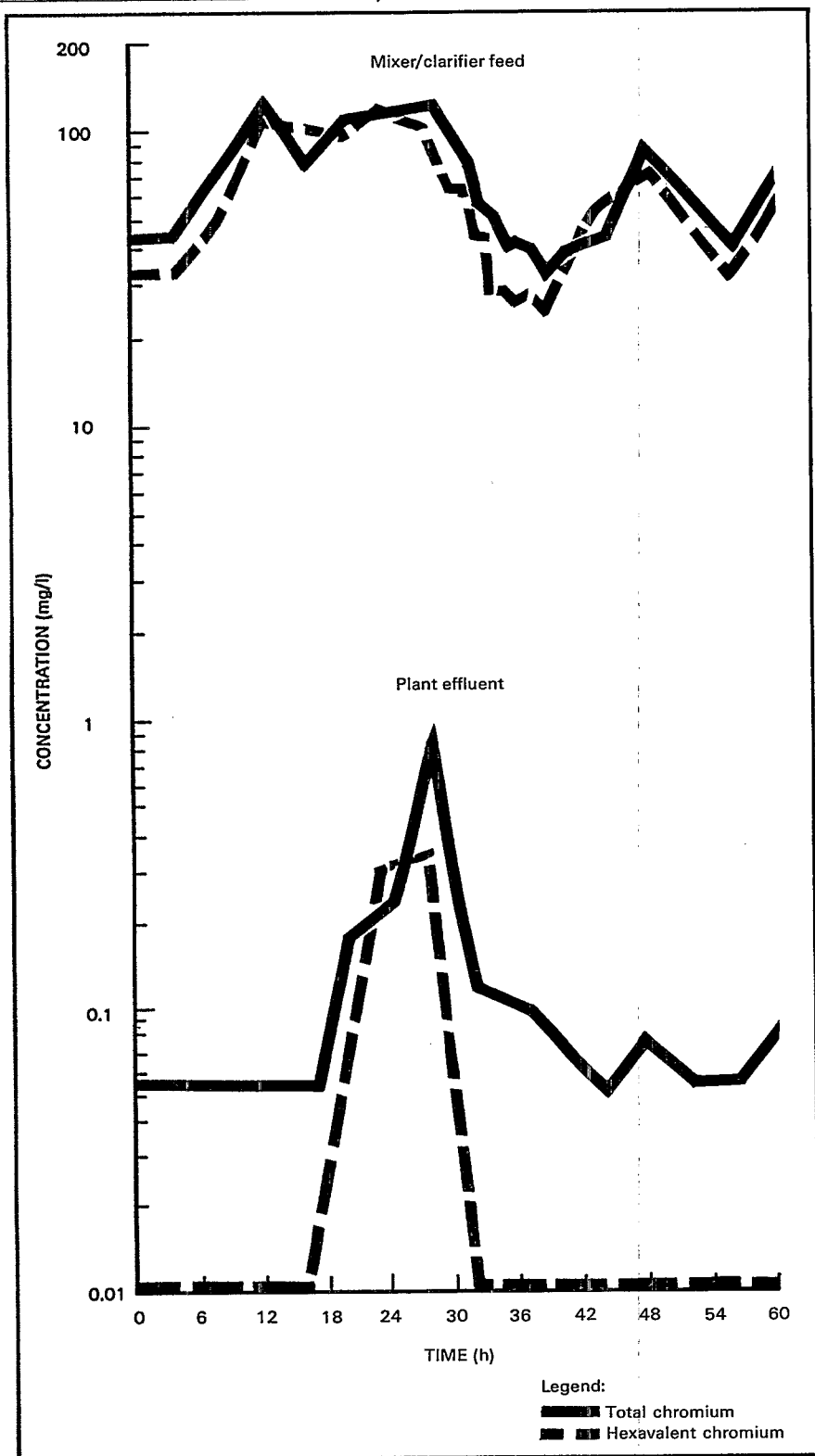
<sup>b</sup>Monthly average of daily 24-hour composite samples.

<sup>c</sup>Highest daily 24-hour composite in the month.

<sup>d</sup>Not applicable.

heavy metals in the wastewater are complexed with a variety of chelating agents. During the pilot evaluation, it was apparent that hydroxide precipitation would not remove

the metals to the levels required in the discharge permit (Table 7). After a pilot evaluation showed that ISP could achieve the required discharge limitations, the firm hired a vendor to design a treatment system using this technology. The vendor guaranteed that the system would meet all discharge regulations.

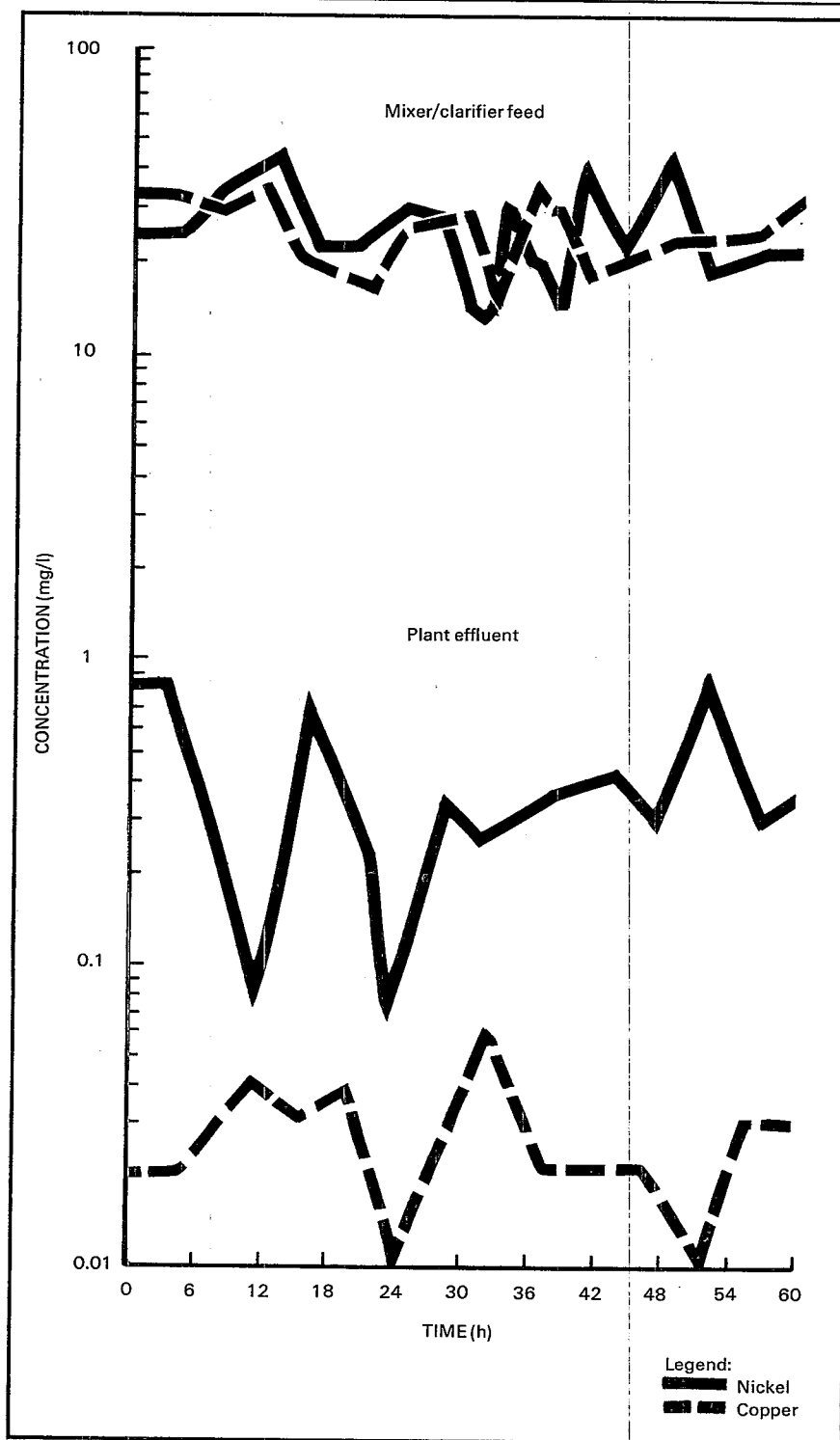


The system was designed to treat 40 gal/min (151 l/min) of wastewater and is essentially identical to the system shown in Figure 13. The performance of the system in removing copper, nickel, total chromium, and hexavalent chromium ( $\text{Cr}^{+6}$ ) during a 60-hour test period is shown in Figures 18 and 19. Figure 20 shows the corresponding sample point locations.

The performance in chromium removal shows a deviation from normal removal efficiency between hours 16 and 28 that corresponds to an increase in the level of hexavalent chromium in the mixer/clarifier feed during hours 8 through 28. By comparing the stoichiometric FeS demand with the quantity supplied and the associated mixer/clarifier removal efficiency (Figure 21), it is obvious that the FeS feed was not increased sufficiently to compensate for the increased demand. Consequently, the level of unreacted FeS in the sludge blanket was gradually depleted, and at hour 16 insufficient FeS was present in the blanket to achieve the normal high level of removal. This condition persisted until hour 28. The FeS stored in the sludge blanket maintained the high removal efficiency between hours 8 and 16, despite a low FeS reagent supply/demand ratio.

Figure 18.

Plant A's Performance in Removing Chromium



**Figure 19.**  
Plant A's Performance in Removing Nickel and Copper

Figure 21 shows that optimum removal efficiency for the chromium is achieved with an FeS dosage of approximately 3 times the stoichiometric demand. Stoichiometric demand was determined by laboratory analysis of mixer/clarifier feed samples. The removal efficiencies for nickel and copper were relatively constant and showed no discernible trends over the dosage ratios encountered during the test period.

Based on an FeS dosage rate of 3 times the stoichiometric demand and the observed consumption of other treatment reagents, the cost of treatment chemicals and sludge generation factors for the ISP system at this facility are shown in Table 8.

Plant B manufactures carburetors for the automotive industry. Wastewater from the metal finishing portion of the process contains varying quantities of chromium (hexavalent and trivalent), zinc, and iron in solution with phosphates, organic chelating agents, and assorted chemicals used in the process baths. The wastewater is treated in a neutralization/ISP/clarification treatment sequence similar to that shown in Figure 13. Then it is mixed with the remainder of the wastewater from the plant and is discharged to the city wastewater treatment system.

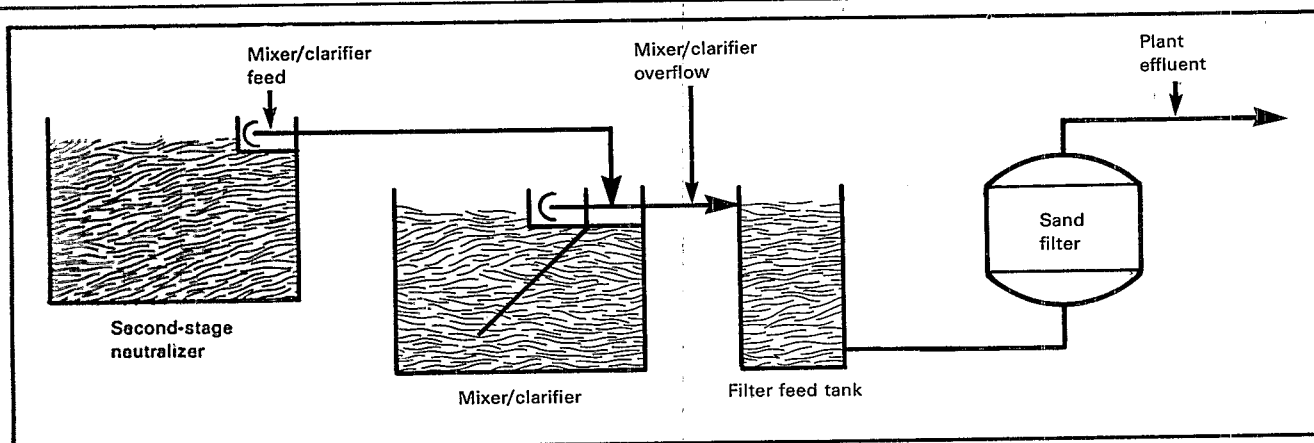
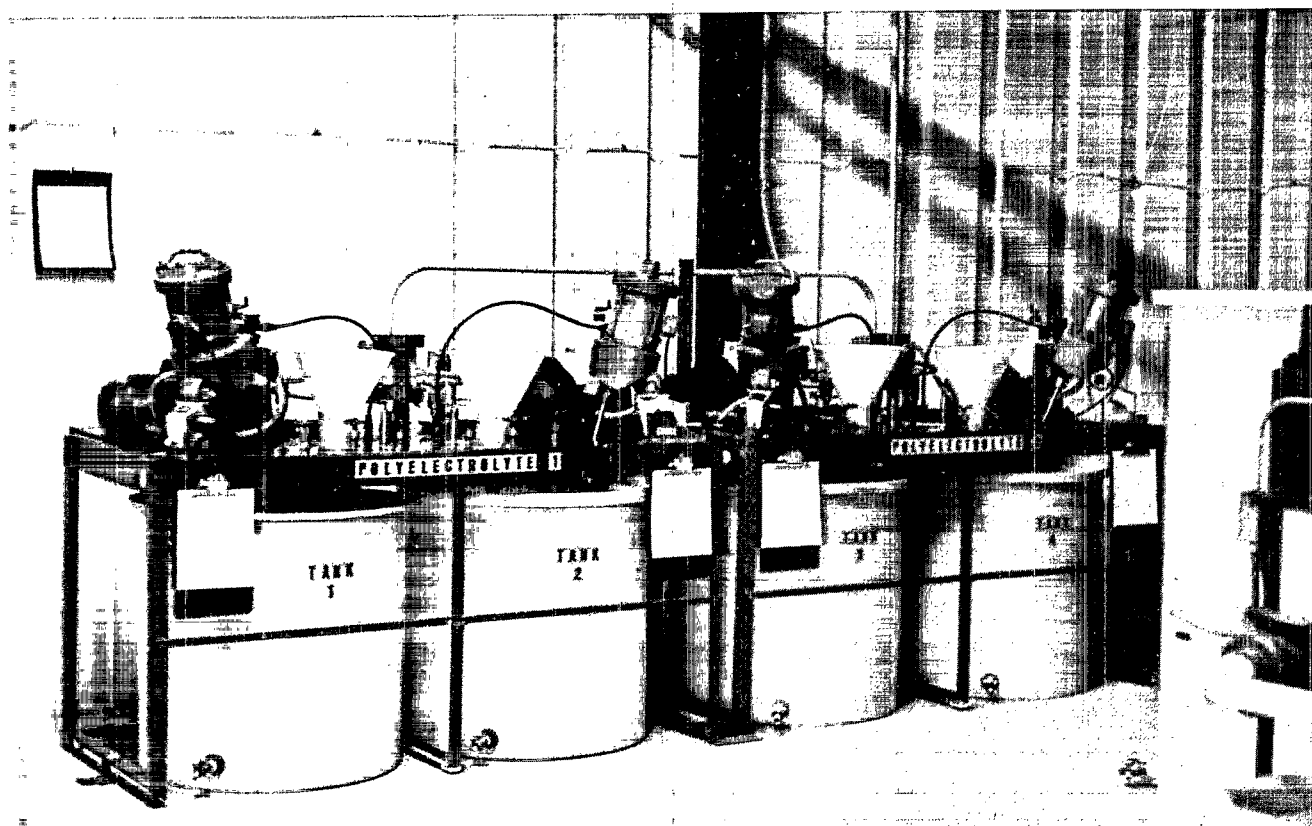


Figure 20.  
Sample Points

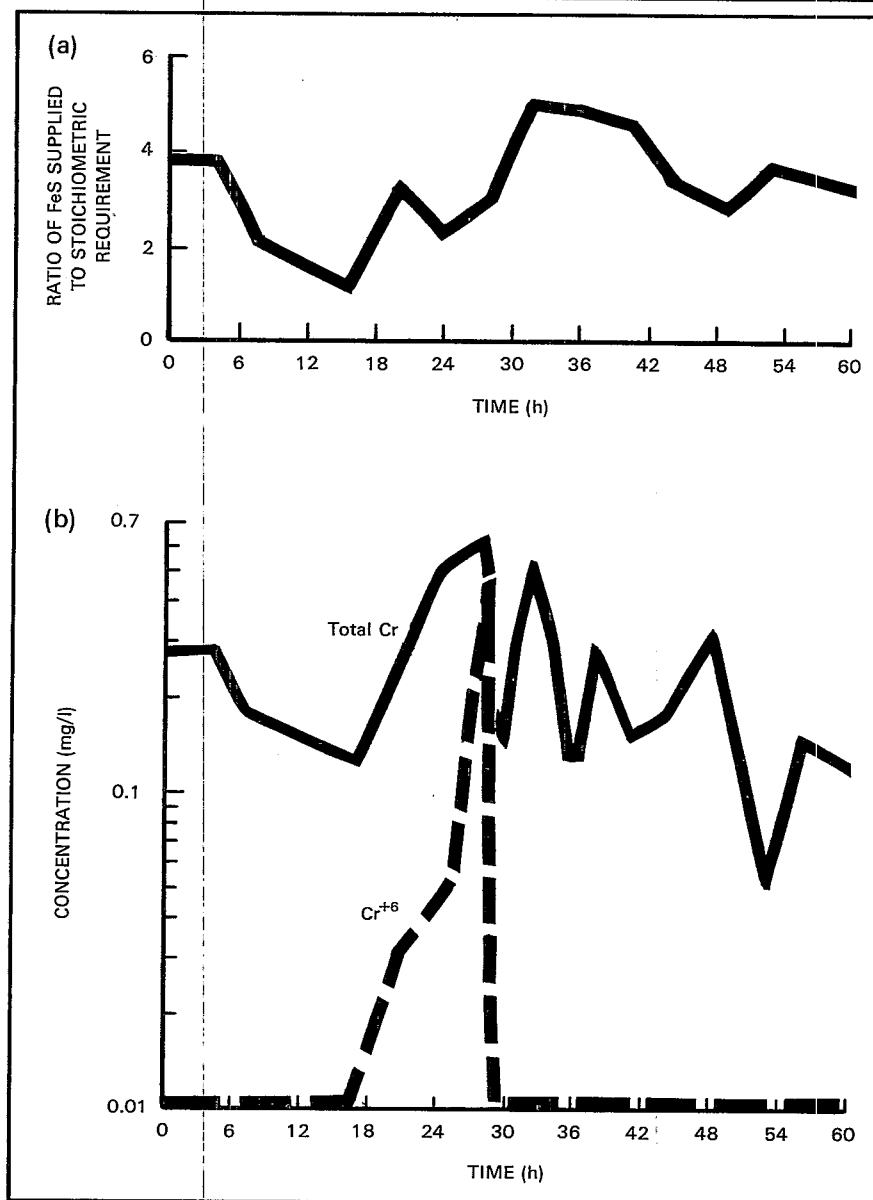


Anionic and cationic polymer feed systems

The wastewater flow rate to the system averaged 20 gal/min (76 l/min). The performance of the system during a 2-day test in removing chromium (total and hexavalent), zinc, and iron from the wastewater is shown in Figures 22 and 23. The same sample location designation used in Figure 20 applies. Figure 24 defines the ratio of FeS supply to stoichiometric demand for the same test period. The ratio varied from 3 to 5 times the stoichiometric demand during the test period. The quality of the effluent, which contained lower pollutant levels than those specified in both local and State guidelines, showed no discernible trends within this range of reagent supply/demand ratios.

The cost of treatment chemicals and the sludge generation factors for the ISP system at this facility are shown in Table 8. Chemical costs were approximately \$1.77/1,000 gal of wastewater treated.

Plant C uses the ISP process to polish the clarified overflow from a conventional hydroxide precipitation/clarification treatment sequence. The system treats approximately 15 to 18 gal/min (57 to 68 l/min) of wastewater from a programed, barrel-dip, zinc-phosphatizing plating line. The system is similar to the one shown in Figure 17; it has a second mixer/clarifier and polymer feed system, installed after the second-stage neutralizer, to remove the precipitated metal hydroxides and phosphates. Dual polyelectrolyte feed systems are needed because an anionic polymer is used in the hydroxide removal clarifier and a cationic polymer is used to enhance the settling of the precipitated metal sulfides. The sludge production and FeS consumption are reduced considerably compared with a system



**Figure 21.**

Impact of FeS Supply/Demand Ratio on Reduction of Hexavalent Chromium at Plant A: (a) FeS Supply vs. Stoichiometric Requirement and (b) Mixer/Clarifier Overflow Chromium Concentration

Table 8.

Wastewater Treatment Process Characteristics for Plants A, B, and C<sup>a</sup>

Characteristic	Value		
	Plant A	Plant B	Plant C
<b>Wastewater:</b>			
Average flow rate (gal/min) .....	39	21	16
pH:			
Feed .....	2.0-4.0	4.5-6.0	2.5-3.0
Effluent .....	9.0-10.0	8.5-9.5	7.5-8.5
Average feed concentration (ppm):			
Nickel .....	31	NA	NA
Copper .....	28	NA	NA
Hexavalent chromium .....	76	27	0.07
Total chromium .....	88	39	8
Zinc .....	NA	48	24
Iron .....	NA	1.4	127
Phosphorus .....	NA	NA	289
<b>Treatment chemicals:</b>			
Lime: <sup>b</sup>			
lb/h .....	8.8	2.0	8.1
\$/h .....	0.28	0.06	0.60
Calcium chloride (for phosphate removal): <sup>b</sup>			
lb/h .....	NA	NA	17.0
\$/h .....	NA	NA	1.70
Cationic polymer: <sup>b</sup>			
lb/h .....	0.1	0.17	0.02
\$/h .....	0.14	0.23	0.04
Anionic polymer: <sup>b</sup>			
lb/h .....	NA	NA	0.01
\$/h .....	NA	NA	0.03
Ferrous sulfide:			
lb/h .....	12.5 <sup>c</sup>	4.5 <sup>d</sup>	0.30 <sup>b</sup>
\$/h .....	5.37 <sup>c</sup>	1.94 <sup>d</sup>	0.11 <sup>b</sup>
Total chemicals (\$/h) .....	5.78	2.23	2.48
Chemical cost (\$/1,000 gal) .....	2.47	1.77	2.58 <sup>e</sup>
<b>Sludge generation factors:</b>			
Dry solids generation:			
lb/h .....	23.7	7.2	16.4
First stage .....	NA	NA	16
Second stage .....	NA	NA	0.4
lb/1,000 gal wastewater .....	10.1	5.7	17 <sup>a</sup>
Underflow volume (gal/h at 0.75% solids) .....	380	114	262
Filter cake volume (gal/h at 30% solids) .....	7.9	2.4	5.3

<sup>a</sup>All three plants use an ISP process to remove metals from wastewater, but Plant C uses ISP as a polishing system.

<sup>b</sup>Observed rates.

<sup>c</sup>Based on 3 times the stoichiometric requirement.

<sup>d</sup>Based on 4 times the stoichiometric requirement.

<sup>e</sup>Without the presence of phosphates, treatment cost equals \$0.81/1,000 gal, solids generation equals 6.4 lb/1,000 gal.

Note.—1979 cost basis, NA = not applicable.

treating the total metal load with sulfide precipitation. Less than 5 percent of the waste solids removed from the system are attributed to the sulfide precipitation step.

Table 8 presents the chemical consumption and sludge generation rates for Plant C. Treatment of the phosphates in the wastewater accounts for a large percentage of the treatment cost, and the phosphate solids constitute the bulk of the sludge generated. The chemical cost associated with removal of the heavy metals contained in the wastewater was estimated at \$0.81/1,000 gal. Without the presence of phosphates, the solids generation rate would equal 6.4 lb/1,000 gal (0.76 kg/m<sup>3</sup>) of wastewater.

Table 9 presents the pollutant concentrations in Plant C's raw waste and effluent discharge and shows the effluent quality required by the discharge permit.

In this polishing application, FeS is fed into the second-stage mixer/clarifier to yield a concentration of approximately 40 ppm in the wastewater. The dosage rates for the insoluble solids systems treating the total metal load for Plants A and B are approximately 640 ppm and 430 ppm, respectively.



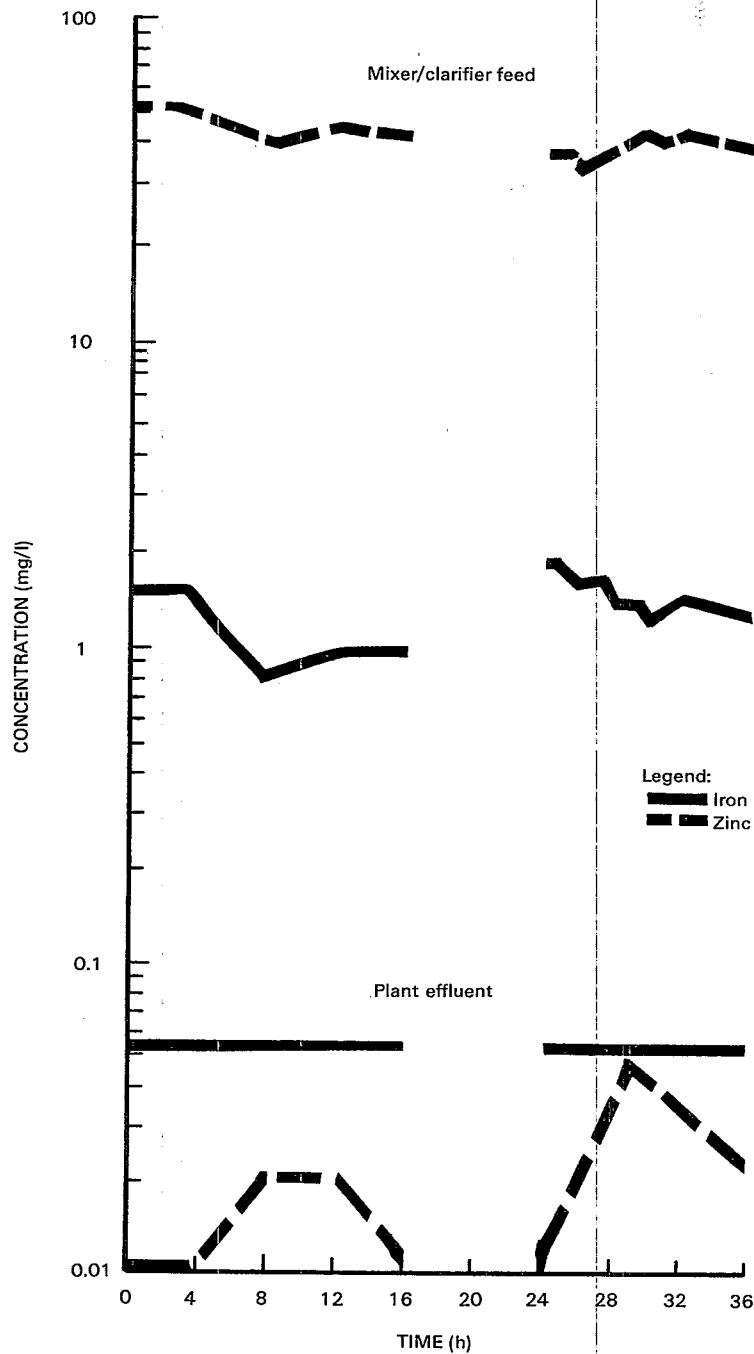
## Hydroxide System Modifications for ISP

The metal removal efficiency of a hydroxide precipitation system can be improved by incorporating ISP into the system. Sulfide precipitation can be used either to convert the metals to metal sulfides before the clarifier or as a polishing system to precipitate dissolved metals from wastewater after the insoluble metal hydroxides have been removed by clarification.

**Equipment Requirements.** The key component of an ISP system is the solid/liquid contact chamber where the wastewater is mixed thoroughly with the insoluble sulfide contained in the sludge blanket. Three design criteria must be addressed in specifying this piece of equipment:

- Liquid residence time in the mixing zone
- Sludge blanket volume and density
- Mixing efficiency

Figure 25 is a schematic of the mixer/clarifier designed specifically for this application. In the systems currently using ISP, the unit is sized to provide approximately 1 hour of liquid residence time in the mixing zone. Because the mixing zone volume is equal to the solids retention volume, a large inventory of unreacted FeS can be maintained in the unit. The agitator is designed to maintain a dense, fluidized sludge in the mixing zone. Sample ports are located in the different zones of the unit to check the sludge density. The unit also has a timed sludge drawoff valve that can be set to balance the blowdown to the solids accumulation rate automatically.



Note.—The plant operates two shifts per day; there was no wastewater flow between hours 16 and 24.

**Figure 22.**  
Plant B's Performance in Removing Iron and Zinc

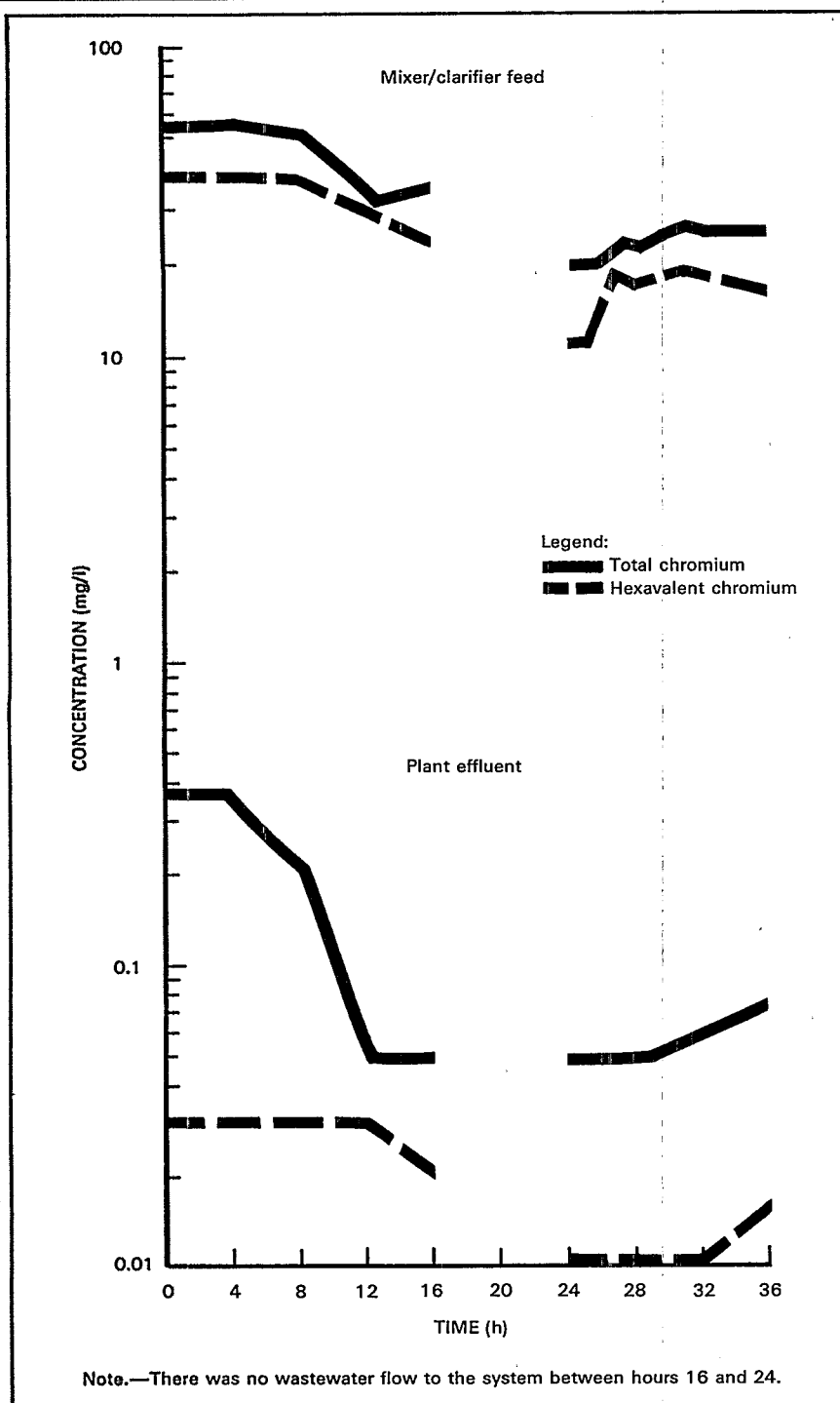


Figure 23.  
Plant B's Performance in Removing Chromium

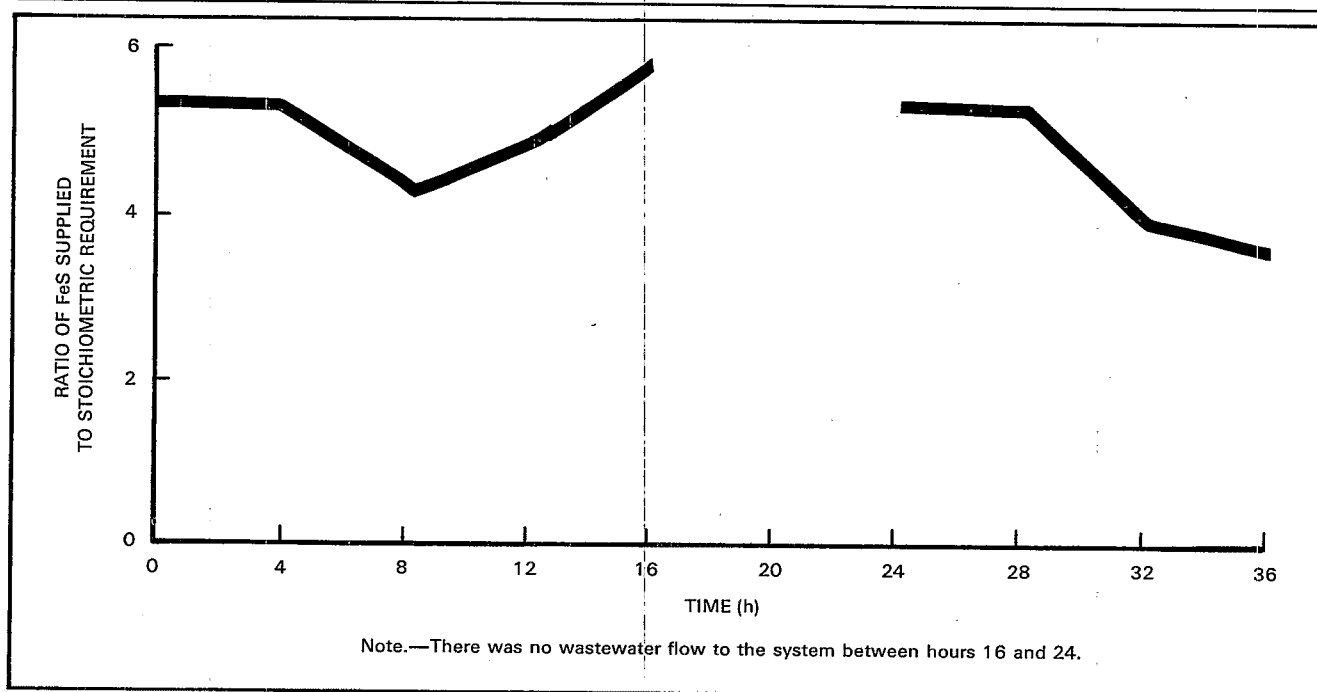
Other elements needed to augment a treatment system with ISP include:

- FeS reagent preparation tanks, reagent storage, and feed pumps
- A reagent feed control system that matches reagent dosage to wastewater flow rate
- A control loop to interrupt the wastewater feed during low-pH conditions

In converting a hydroxide system to use sulfide precipitation, the addition of a polishing filtration system to remove residual suspended solids from the clarifier overflow could significantly reduce effluent metal concentrations. Meeting strict effluent metal discharge limits will require an effluent with low levels of both suspended and dissolved metals.

**Treatment System Evaluation.** The cost advantages of using ISP as a polishing system must be weighed against the higher equipment costs and space requirements of a second clarifier. It might be more cost effective for plants with small metal loadings to incorporate ISP upstream of the existing clarifier and thus avoid the expense of a second clarifier.

Retrofitting a hydroxide treatment system that already has a flocculation zone to enhance the settling properties of the precipitated metals before clarification can be accomplished simply and with minimum investment. Many existing systems include a flocculation chamber either in a separate vessel or as part of the clarifier itself. As shown in Figure 26, sulfide precipitation can be incorporated



**Figure 24.**

FeS Supplied vs. Stoichiometric Requirement at Plant B

**Table 9.**

Influent and Effluent Wastewater Characteristics for ISP Polishing System

Item	Wastewater analysis		
	Influent	Effluent	Permit requirements <sup>a</sup>
pH.....	2.9	8.5	6.0-9.5
Phosphorus (mg/l).....	289	0.3	<1.2
Total suspended solids (mg/l).....	320	6	<23
Total chromium (mg/l).....	8	<0.10	<0.6
Hexavalent chromium (mg/l).....	0.07	<0.02	<0.06
Nickel (mg/l).....	0.77	<0.1	<0.6
Zinc (mg/l).....	24	0.12	<0.6
Iron (mg/l).....	127	0.60	<1.2

<sup>a</sup>Monthly average of daily composite samples.

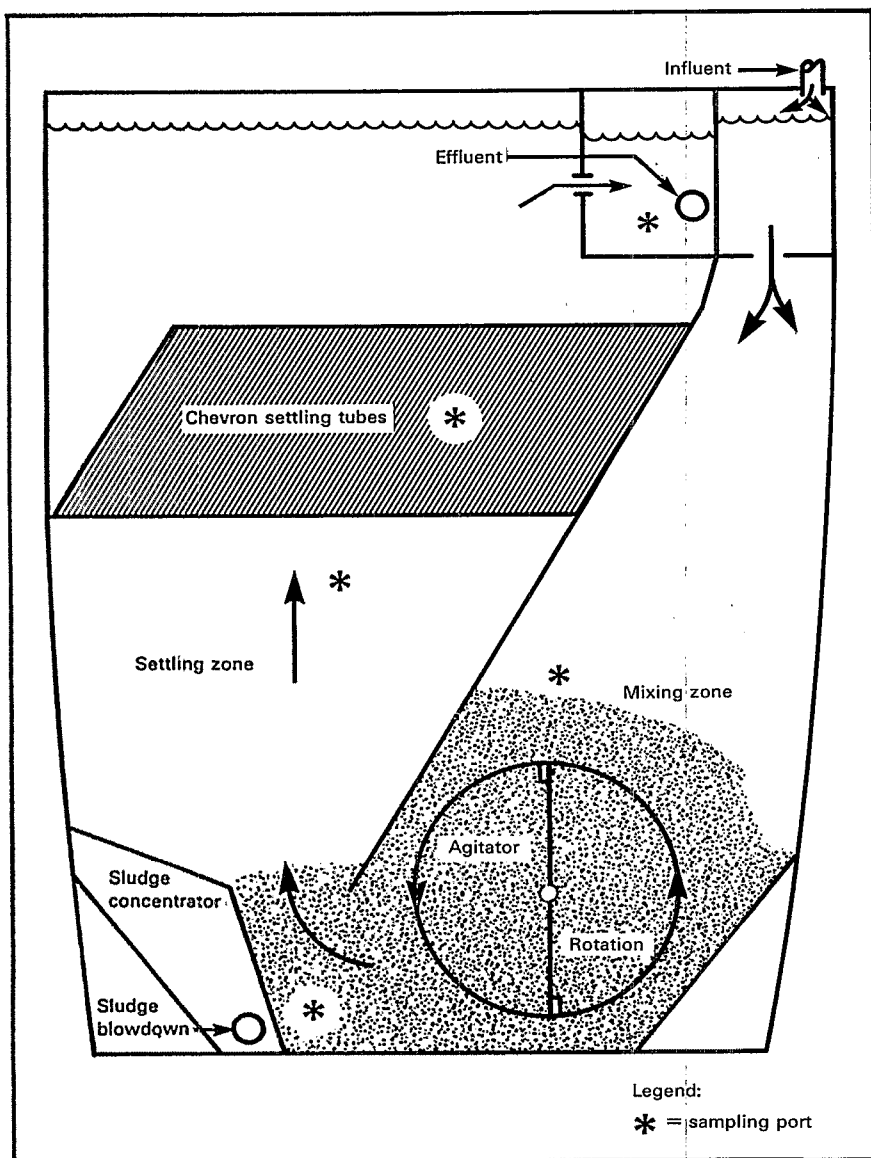
into this type of treatment system by installing:

- An FeS reagent addition system and feed control system to feed FeS into the flocculation chamber in proportion to the volume of wastewater processed

- A sludge recirculation loop (if not already existing) to recycle solids from the clarifier underflow back to the flocculator
- A low-pH feed interrupt control loop to stop the feed to the flocculator if the pH of this stream falls below the set-point

Pilot tests must be performed to determine if the residence time, agitation, and blanket density in the flocculation chamber are conducive to effective metal removal. Figure 6 defined the different variables for evaluation by pilot testing or jar testing. Deficiencies in the flocculator residence time, mixing efficiency, and the like can be tolerated, although they generally result in increased reagent consumption.

An approach for treatment systems that do not have flocculation zones is either to add a flocculator or to replace the existing clarifier with the mixer/clarifier designed for this application (Figure 25). The most reliable approach to using ISP as a polishing system would be to install a mixer/clarifier downstream of the existing clarifier.



**Figure 25.**  
Cross Section of Mixer/Clarifier

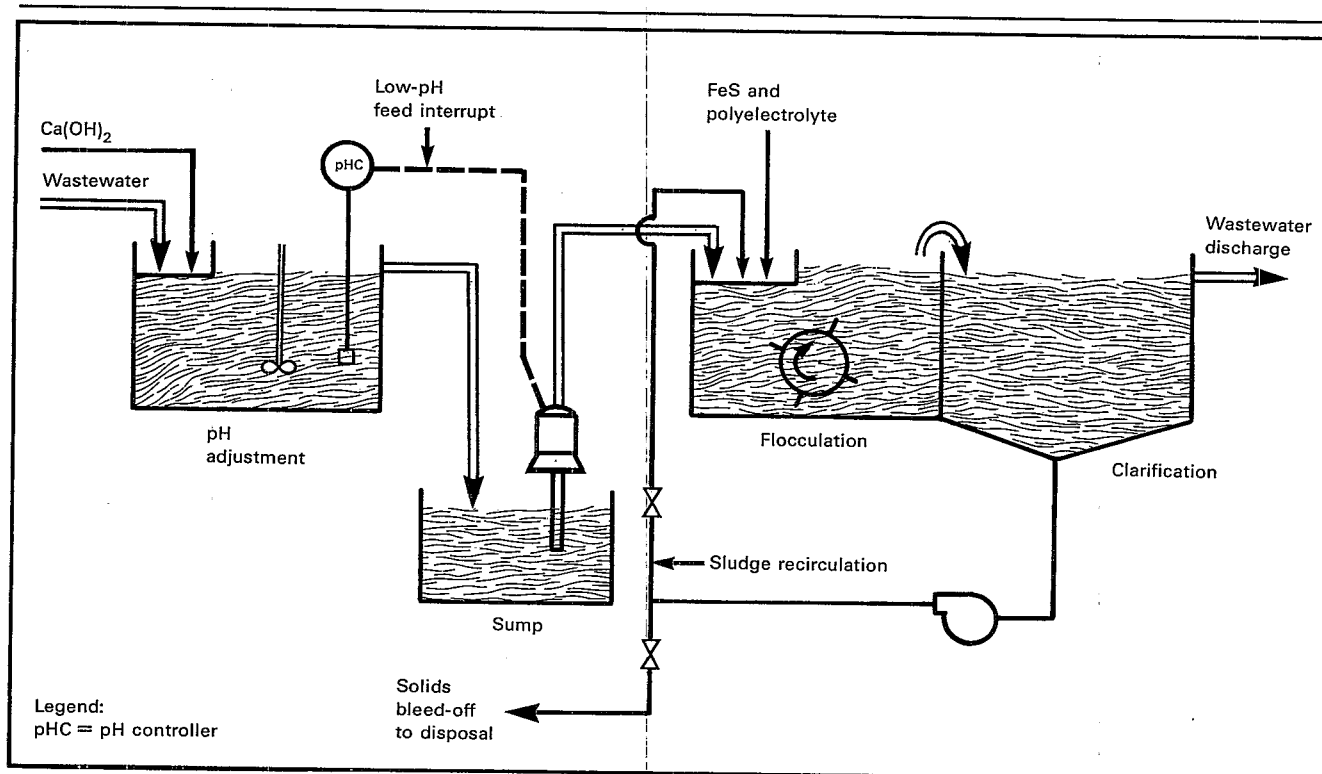
**ISP Batch Treatment Systems.** Batch treatment systems currently are not demonstrated for ISP. As with continuous treatment systems, batch treatment using ISP would require contact between the wastewater and a dense sludge blanket to achieve maximum metal removal. Consequently, a large volume of solids would be needed for each batch, necessitating storage of the settled sludge after batch treatment. Figure 27 shows a possible configuration of an ISP batch treatment system and the associated treatment sequence. The major process components of the system are:

- Two tanks equipped with mechanical agitation
- A precipitation tank
- Reagent storage and feed systems to add the lime (or caustic), FeS, and polymer

The two agitated tanks alternate as the wastewater collection tank and pretreatment tank. Pretreatment is required to neutralize the acidic wastewater before mixing it with the metal sulfide sludge. A precipitation tank is needed to bring the wastewater into contact with the FeS slurry and to provide storage volume for maintaining an inventory of sludge solids in the system. Gentle agitation is required to suspend the sludge solids during mixing and to promote particle growth of the precipitated solids.

#### ISP Treatment Costs

**Operating Costs.** The following costs associated with using ISP are in addition to the operating costs of



**Figure 26.**

#### Retrofit of a Hydroxide System With Insoluble Sulfide Treatment

a conventional hydroxide precipitation system:

- Reagent costs for FeS and polyelectrolyte
- Labor cost of additional operational duties described earlier
- Disposal cost of any additional solid waste generated
- Licensing fee charged by the patent holder to use the process

Reagent costs for FeS depend on the quantity of metals to be precipitated (or, in the case of hexavalent chromium, the quantity to be reduced chemically) and the ratio of reagent needed for

effective removal to the stoichiometric reagent requirement. Figure 28a shows the FeS consumption rates and reagent cost for various metal concentrations in the wastewater and typical ratios of reagent demand to stoichiometric requirement. The wastewater metal concentration is defined as the metals other than iron that will form sulfides. To compute reagent consumption rates, it was assumed that the metals have a "plus 2" valence and a molecular weight equal to the average

molecular weight of copper, nickel, and zinc. Although determination of the optimum dosage ratio requires testing, wastewaters with no heavy metal complexing agents generally require 1.5 to 2 times the stoichiometric reagent requirements, whereas wastewaters containing complexed heavy metals will require 3 to 4 times the stoichiometric reagent dosage. Figure 28b presents the FeS reagent demand and cost for wastewater treatment over a range of hexavalent chromium concentrations.

At the three plants currently operating, labor requirements for the ISP systems varied only slightly. Each plant employed a full-time operator for one shift and required 2 to 6 hours of operator attention on other shifts.

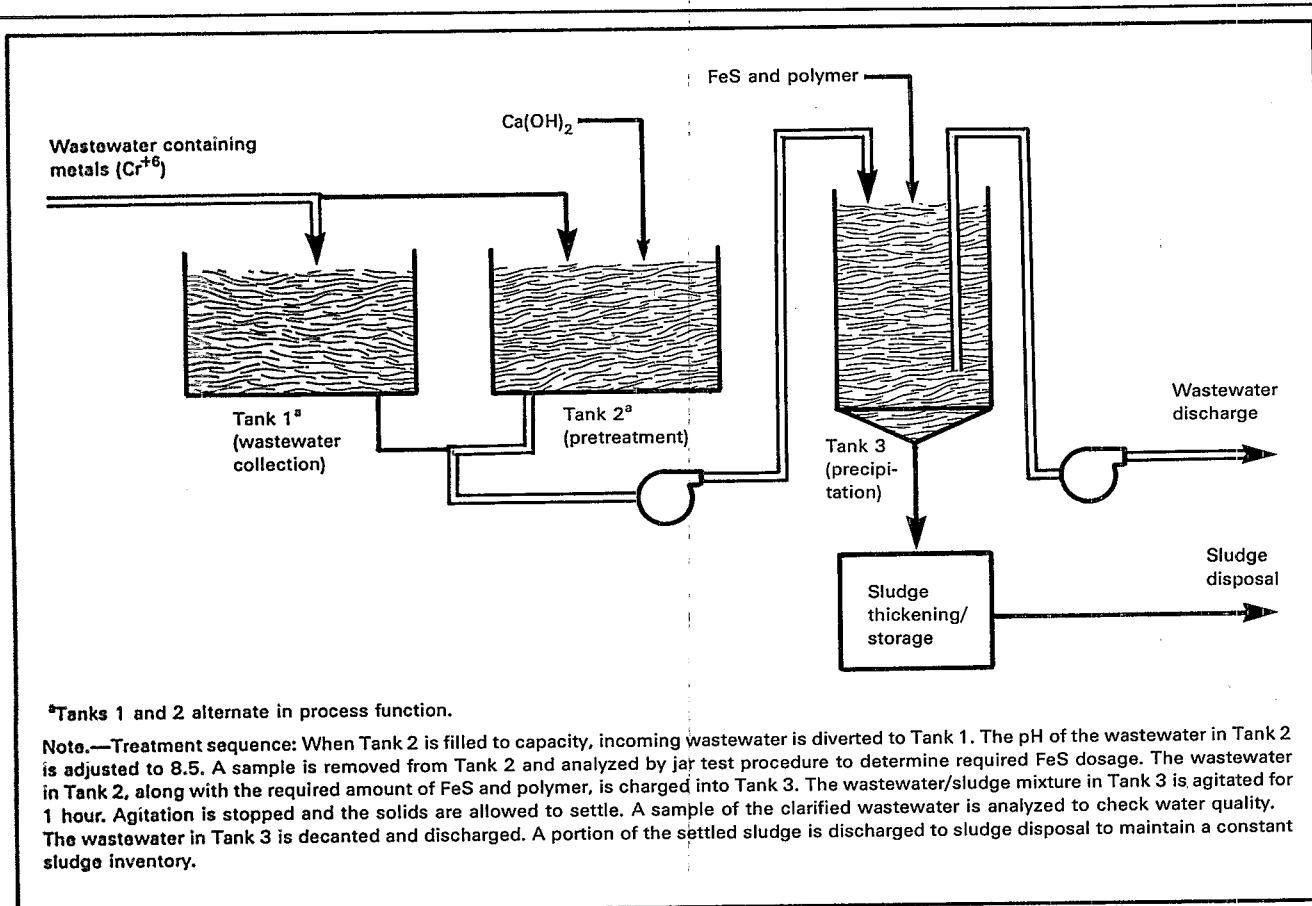


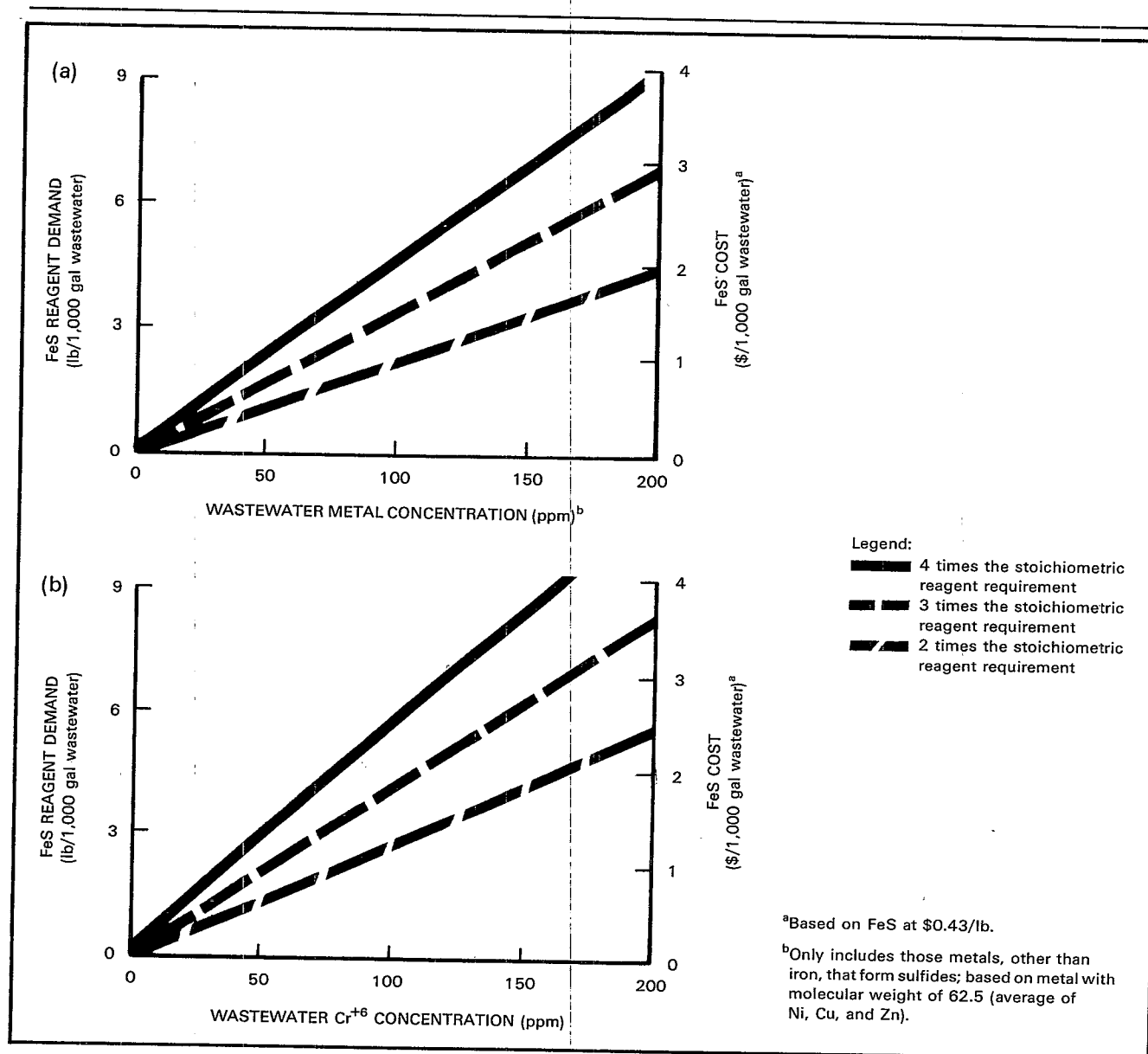
Figure 27.

#### Batch Wastewater Treatment Using ISP

The ISP systems generate considerably more sludge in treating a volume of wastewater than the conventional hydroxide precipitation scheme. The additional sludge results from precipitation as hydroxides of the ferrous and ferric ions liberated as the sulfide reagent is consumed and from the excess FeS that is used in treatment. Figure 29 compares the solids generation rates for ISP

systems with those for treatment systems using hydroxide precipitation for metal removal and sulfur dioxide ( $\text{SO}_2$ ) for chromium reduction. The graph also shows solid waste disposal charges, assuming the sludge is disposed of at 25 percent solids by weight and at a cost of \$0.10/gal. For plants with different sludge disposal cost formulas, the disposal cost can be calculated by multiplying the cost indicated in Figure 29 by the ratio of the actual disposal cost to the assumed rate of \$0.10/gal.

Owing to the high cost of sludge disposal—normally from \$0.05/gal to \$0.20/gal—it is cost effective to invest in mechanical dewatering equipment to reduce the sludge volume. At the three plants currently operating, recessed plate filter presses were installed



**Figure 28.**

FeS Consumption and Cost Factors for: (a) Precipitation of Metals and (b) Hexavalent Chromium Reduction

to dewater the sludge before transport to the disposal site. The presses dewatered the underflow from less than 1 percent solids by weight to 25 to 30 percent solids by weight.

Total sludge generation for both hydroxide and sulfide systems will be somewhat higher than the rates shown in Figure 29. The additional solids are caused by the presence of lime solids, suspended solids in the wastewater feed, and insoluble byproducts resulting

from neutralization. For treating waste streams to remove heavy metals, the additional solids should be approximately the same for

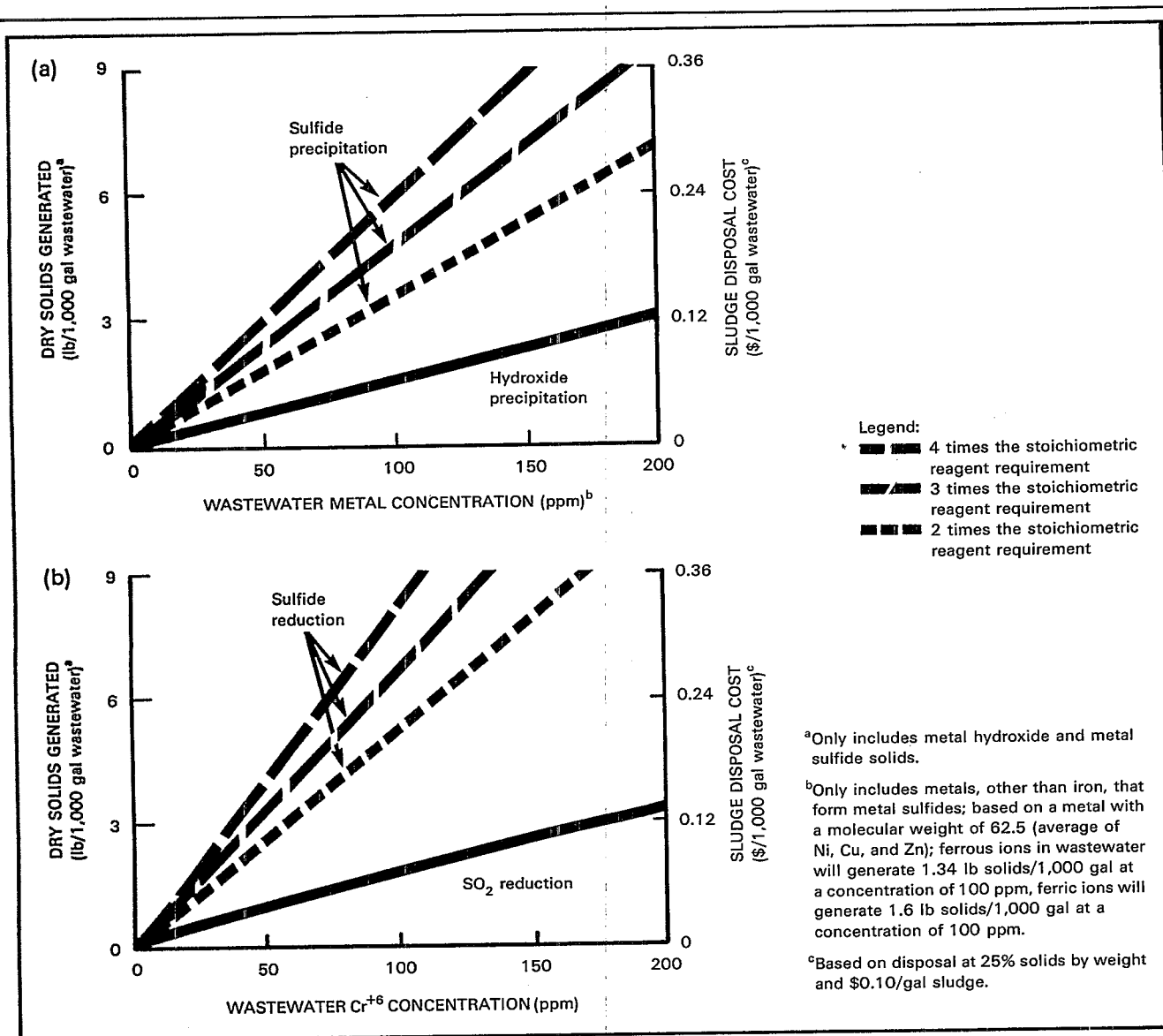


Figure 29.

Sludge Generation Factors for: (a) Precipitation of Metals and (b) Hexavalent Chromium Reduction

insoluble sulfide and hydroxide systems. For chromium reduction, SO<sub>2</sub> reduction systems often require the wastewater to be acidified, and the quantity of alkali for subsequent neutralization is larger than that required with

sulfide reduction. Consequently, the additional lime required for neutralization with SO<sub>2</sub> reduction will result in more lime solids in the sludge.

Licensing fees for the use of ISP to treat wastewater are charged annually and are determined by the flow rate of wastewater treated. This fee is small, however, compared with other costs typically associated with wastewater treatment.



**Equipment Costs.** The actual total installation costs for the three ISP treatment systems described earlier are presented in Table 10. All three systems were installed in plants that had no existing treatment systems. The systems in Plants A and B are similar to the one illustrated in Figure 13. The costs presented also include duplexing of many of the pumps and reagent storage tanks, a control panel, and additional instrumentation not shown on the flow diagram. Plant C is a sulfide polishing system similar to the one shown in Figure 17. The installed cost of this system includes the additional equipment required by a polishing system—a second clarifier (to separate the insoluble compounds resulting from hydroxide neutralization) and a second polyelectrolyte feed system.

Much of the equipment in an ISP system is common to hydroxide systems. Cost data on wastewater treatment equipment for the metal finishing industry are presented in the EPA report, *Economics of Wastewater Treatment Alternatives for the Electroplating Industry*. Converting a hydroxide system to use ISP in many cases will require only the installation of a mixer/clarifier downstream of the existing clarifier and a feed system to meter the FeS and polyelectrolyte into the wastewater.

Table 11 presents the cost (including installation and hardware) of installing the following ISP process

**Table 10.**

**Installation Costs for Three Sulfex™ ISP Treatment Systems**

Cost component	ISP system cost (\$1,000)		
	Plant A	Plant B	Plant C
Installation costs:			
Process equipment .....	175	92	NA
Underground tanks .....	36	48	NA
Shipping and installation .....	29	22	NA
Additional building space .....	20	NA	NA
Startup expenses .....	3	NA	NA
Engineering .....	NA	17	NA
Other .....	NA	1	NA
Total .....	263 <sup>a</sup>	180 <sup>b</sup>	155 <sup>c</sup>
Current installation costs <sup>d</sup> .....	303	195	169

<sup>a</sup>ISP system design flow = 40 gal/min; installed in September 1977.

<sup>b</sup>ISP polishing system design flow = 35 gal/min; installed in April 1978.

<sup>c</sup>ISP polishing system design flow = 15 gal/min; installed in March 1978.

<sup>d</sup>Costs escalated to March 1979 based on Chemical Engineering Plant Cost Index.

Note.—NA = not available.

**Table 11.**

**Equipment Cost Factors for ISP Treatment System Components**

Equipment component	Installed cost (\$1,000)
Mixer/clarifier:	
30-gal/min wastewater flow rate .....	18
60-gal/min wastewater flow rate .....	22
90-gal/min wastewater flow rate .....	24
Ferrous sulfide reagent preparation and feed system:	
5-lb/h FeS feed rate <sup>a</sup> .....	16
10-lb/h FeS feed rate .....	20
15-lb/h FeS feed rate .....	24
Polymer feed system .....	4-6
Control loops:	
Reagent addition system .....	4-5
Low-pH feed interruption control .....	1.5-2.5
Suspended solids polishing filters:	
30-gal/min wastewater flow rate .....	24
60-gal/min wastewater flow rate .....	33
90-gal/min wastewater flow rate .....	41

<sup>a</sup>For lower feed rates, less automated systems are available for approximately \$12,000.

Note.—March 1979 cost basis. Costs are basic installed costs of different components. Engineering and design costs, site preparation, and equipment freight charges are not included.

SOURCE: Equipment vendors.

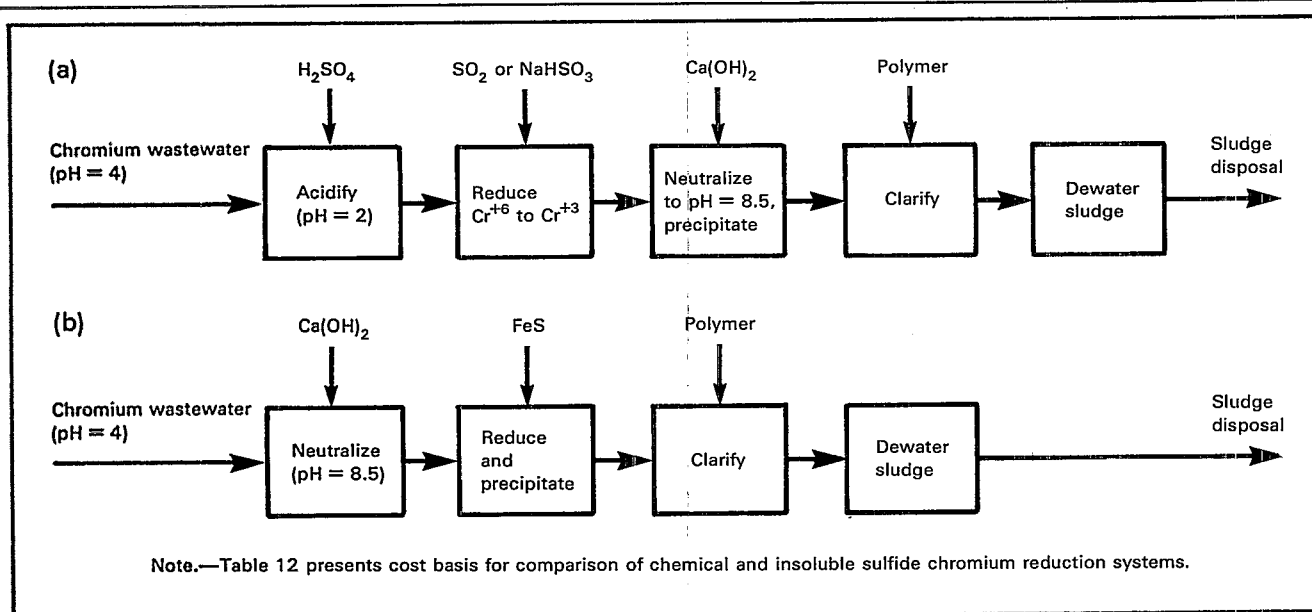


Figure 30.

Comparison of Chromium Reduction Treatment Sequences: (a) Chemical and (b) Insoluble Sulfide

equipment components in an existing treatment system:

- Mixer/clarifier
- FeS reagent preparation and feed system
- Polymer feed system
- Control loops
- Suspended solids polishing filters

The installed costs presented for a mixer/clarifier are for a preassembled, skid-mounted component requiring only piping and electrical connections for installation. The FeS reagent preparation and feed system includes two FeS feed tanks with low-level alarms, two reagent pumps, a mixing tank, and a transfer pump; the costs are for skid-mounted, preassembled units, constructed of carbon steel (see Figure 16).

The costs presented for the polymer feed system are based on a system with two plastic polymer feed tanks and two positive displacement pumps with adjustable stroke. The skid-mounted, preassembled components are equipped with a low-level alarm and dilution water-mixing apparatus. Costs are given for two control loops: a reagent addition control system with a magnetic flow meter and flow counter (to match the addition of FeS and polymer with wastewater volumetric throughput) and a low-pH feed interruption control. The costs for suspended solids polishing filters are for dual mixed-media filters, skid mounted and sized so that one filter can process the maximum flow during backwash. The filters are equipped with a blower for low pressure air scouring, a backwash storage tank, and a pump to bleed the wash back into the system.

*Cost Comparison of Conventional Chemical Reduction and ISP Chromium Reduction.* Replacing a conventional chromium reduction system with reduction by FeS can be advantageous. In some cases, an operating cost benefit will result. Another advantage of reducing chromium with FeS is that the hexavalent chromium wastewater does not need to be segregated for individual treatment; it can be treated in the common neutralization/precipitation treatment sequence. Figure 30 defines typical treatment sequences for reduction of chromium by chemical means and using FeS. The FeS treatment

process eliminates the need to lower and raise the pH of the wastewater and results in a significant saving in acid and alkali reagent. Table 12 presents treatment and sludge disposal costs for the two chromium reduction systems shown in Figure 30. The chemical consumption factors assume that lime consumption is twice the stoichiometric amount required to neutralize the wastewater and precipitate the dissolved metals. The excess lime is needed to overcome buffering normally encountered when neutralizing waste streams. It is further assumed that lime solids equal to 50 percent of the mass of lime used in neutralization are present in the sludge. These lime solids result from precipitation of insoluble byproducts in the neutralization reaction as well as from the tendency for some portion of the lime used not to dissolve and add to the sludge volume. Consequently, the lime required in the chemical reduction treatment sequence to raise the pH from 2 to 8 results in considerable sludge generation.

Figure 31 compares the cost of treatment chemicals and sludge disposal for the two chromium reduction systems shown in Figure 30 over a range of hexavalent chromium concentrations in the wastewater. A cost savings can be realized for FeS reduction compared with conventional chemical reduction. For wastewaters requiring twice the stoichiometric FeS dosage, a treatment cost advantage exists over treatment of wastewater containing less than 50 ppm  $\text{Cr}^{+6}$  by  $\text{SO}_2$  reduction and that containing less than 100 ppm  $\text{Cr}^{+6}$  by  $\text{NaHSO}_3$

**Table 12.**

Cost Basis for Comparison of Chemical and Insoluble Sulfide Chromium Reduction Treatment Systems Shown in Figure 30

Parameter	Cost <sup>a</sup>			
	Treatment <sup>b</sup>		Sludge disposal <sup>c</sup>	
	\$/lb $\text{Cr}^{+6}$	\$/1,000 gal wastewater	\$/lb $\text{Cr}^{+6}$	\$/1,000 gal wastewater
Chemical reduction:				
Sulfur dioxide.....	0.43	0.57	0.16	0.12
Sodium bisulfite.....	0.82	0.68	0.16	0.12
Insoluble sulfide reduction:				
Ferrous sulfide at dosage equal to 2 times stoichiometric requirement.....	1.58	0.03	0.21	0.01
Ferrous sulfide at dosage equal to 4 times stoichiometric requirement.....	3.12	0.03	0.33	0.01

<sup>a</sup>Total treatment cost is based on both mass of chromium reduced and volume of wastewater treated.

<sup>b</sup>Based on lime at \$0.035/lb, sulfur dioxide at \$0.15/lb, sodium bisulfite at \$0.20/lb, sulfuric acid at \$0.05/lb, and ferrous sulfide at \$0.43/lb.

<sup>c</sup>Based on disposal at 25 percent solids by weight at a cost of \$0.10/gal sludge.

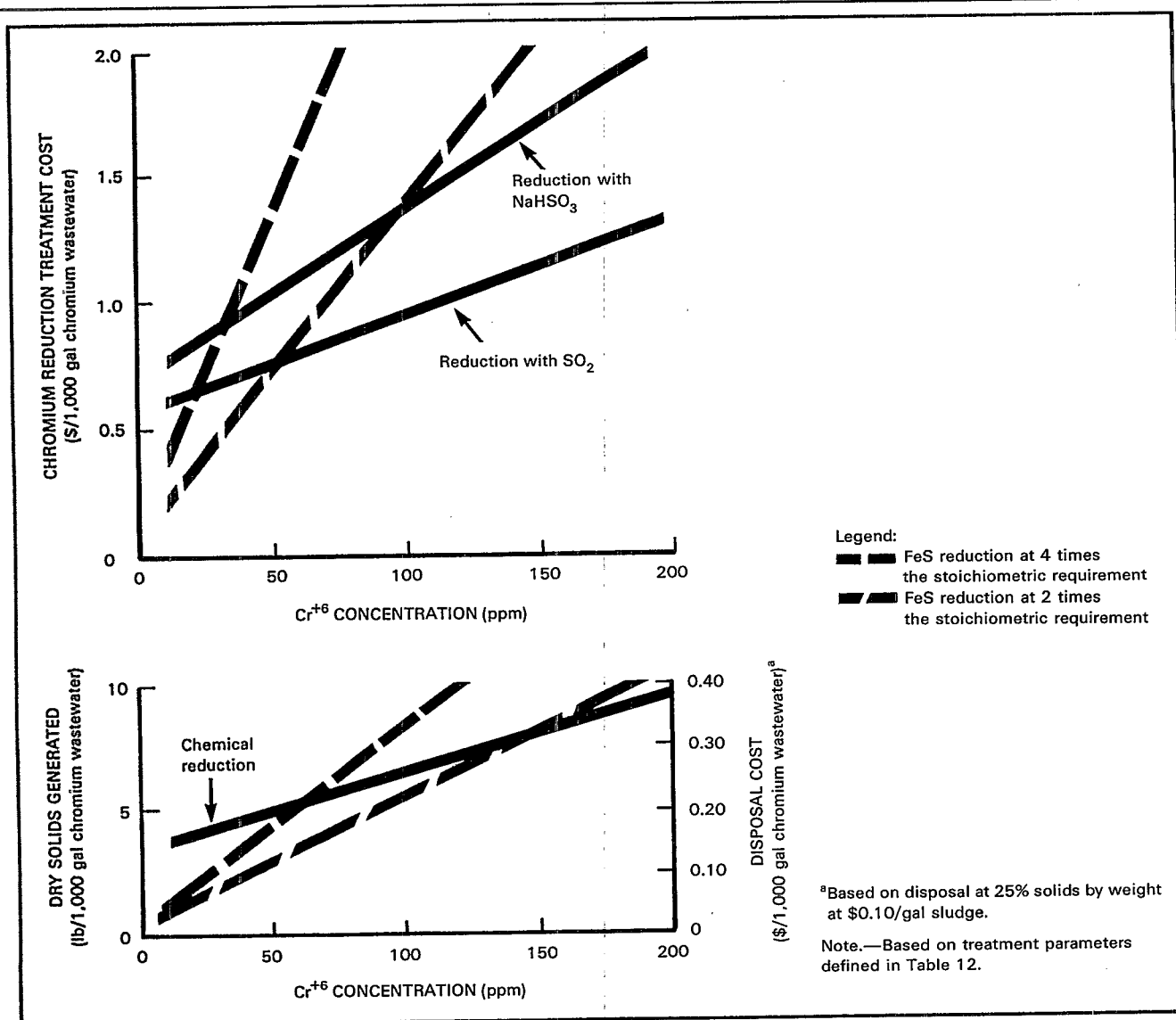
Note.—1979 cost basis. Sulfur dioxide and sodium bisulfite consumption is equal to 2 times the stoichiometric requirement at a hexavalent chromium ( $\text{Cr}^{+6}$ ) concentration of 50 ppm. Lime consumption is equal to 2 times the stoichiometric requirement for unbuffered waste streams. Lime solids are 50 percent of lime dosage and contribute to sludge volume.

reduction. For FeS reduction systems requiring twice the stoichiometric dosage rate, a savings in solid waste disposal costs also would be realized for treatment of wastewater containing less than 150 ppm  $\text{Cr}^{+6}$ . At higher FeS dosage requirements, such as 4 times the stoichiometric demand, chromium reduction using FeS is more economical for treatment of dilute chromium waste streams.

It is important to point out that the preceding comparisons are based on typical operating conditions and reagent costs; a comparative analysis for a specific plant should use actual operating data (e.g., reagent consumption and sludge generation).

#### *Cost Comparison of ISP Polishing and Total Metal Treatment.*

Converting all metals in a waste stream to metal sulfides via sulfide precipitation uses considerable FeS and results in a large volume of waste solids. Separation of the precipitated metal hydroxides from the wastewater before polishing with sulfide precipitation can reduce both reagent consumption and solid waste generation. In a polishing application, the FeS reagent demand is a function of the dissolved metal concentration in the wastewater after hydroxide precipitation/clarification. Conversion of a sulfide precipitation system



**Figure 31.**  
Costs of Treatment Chemicals and Sludge Disposal for Chemical and Insoluble Sulfide Chromium Reduction

to a polishing system requires installation of a second clarifier and polyelectrolyte feed system to separate the precipitated metal hydroxides from the neutralized wastewater before adding the sulfide reagent.

The reagent consumption and solid waste generation factors associated with treatment of the total metal load were presented in Figure 28. To estimate reagent requirements for a sulfide polishing system, it is necessary to determine the concentration of the metals in the wastewater after hydroxide neutralization/precipitation/clarification. Reagent consumption ranges between 1.5 and 4 times

the stoichiometric demand for polishing systems. Compared with the reagent consumption factors presented in Figure 28, the sulfide precipitation polishing system at Plant C required an FeS dosage rate of 40 ppm in the wastewater. Note, however, that this system did not have a significant level

Table 13.

## Potential Benefits for Use of ISP Polishing System at Plant A

Item	Value	
Wastewater characteristics:		
Average flow rate (gal/min)	39	
pH:		
Feed	2-4	
Effluent	9-10	
Average feed concentration (ppm):		
Nickel	31	
Copper	28	
Hexavalent chromium	76	
Total chromium	88	
	Current system	Polishing system
Treatment chemical costs (\$/h):		
Lime <sup>a</sup>	0.28	0.28
Polyelectrolyte <sup>b</sup>	0.42	0.35
Ferrous sulfide <sup>c</sup>	5.38	3.57
Total	6.08	4.20
Cost savings	NA	1.88
Sludge generation factors:		
Dry solids generation (lb/h):		
First stage	NA	6.2
Second stage	NA	13.1
Total	23.6	19.3
Sludge cake volume (gal/h at 30% solids)	7.9	6.4
Disposal cost at \$0.19/gal sludge (\$/h)	1.50	1.22
Disposal cost savings (\$/h)	NA	0.28
Net savings: treatment chemical cost savings plus disposal cost savings (\$/h)	NA	2.16
Annual savings based on 6,000-h/yr operation (\$/yr)	NA	13,000

<sup>a</sup>Observed rates.<sup>b</sup>Design rate.<sup>c</sup>Based on 3 times the stoichiometric requirement.

Note.—1979 cost basis, NA = not applicable.

of hexavalent chromium in the wastewater; hexavalent chromium is not removed by hydroxide precipitation, and reagent demand for chromium reduction will be the same for sulfide polishing or sulfide precipitation systems.

Plant A uses ISP for total treatment of the metals in the wastewater.

Table 13 presents the costs of wastewater treatment using ISP as a polishing step compared with its use to precipitate the total metal load at Plant A. The major cost saving results from reduced FeS consumption; the required FeS dosage is reduced

by separation of precipitated metal hydroxides before the addition of the sulfide reagent.

Based on the savings indicated in Table 13, a profitability analysis of the investment required to convert to a polishing system is presented in Table 14. The \$26,000 investment required for the conversion would have an average

Table 14.

Economics of Converting Plant A ISP Treatment System to ISP Polishing System Operating 6,000 h/yr

Item	Value
Installation costs (\$):	
Equipment:	
40-gal/min mixer/clarifier .....	18,000
Polyelectrolyte feeder .....	5,000
Total equipment installation .....	23,000
Additional installation: estimated freight, site preparation, and miscellaneous .....	3,000
Total installation costs .....	26,000
Additional annual operating costs (\$/yr):	
Labor (100 h/yr at \$8/h) .....	800
Supervision .....	0
Maintenance (6% of investment) .....	1,600
General plant overhead .....	800
Utilities:	
Electricity .....	200
Water (polymer feeder) .....	200
Total operating costs .....	3,600
Annual fixed costs (\$/yr):	
Depreciation (10% of investment) .....	2,600
Taxes and insurance (1% of investment) .....	260
Total fixed costs .....	2,860
Total operating and fixed costs (\$/yr) .....	6,460
Annual savings (\$/yr):	
Chemicals .....	11,280
Sludge disposal .....	1,680
Total annual savings .....	12,960
Net savings: annual savings minus operating and fixed costs (\$/yr) .....	6,510
Net savings after taxes, 48% tax rate (\$/yr) .....	3,380
After-tax average return on investment (%) .....	13.0
Cash flow from investment: net savings after taxes plus depreciation (\$/yr) .....	5,980
Payback period: total investment/cash flow (yr) .....	4.3

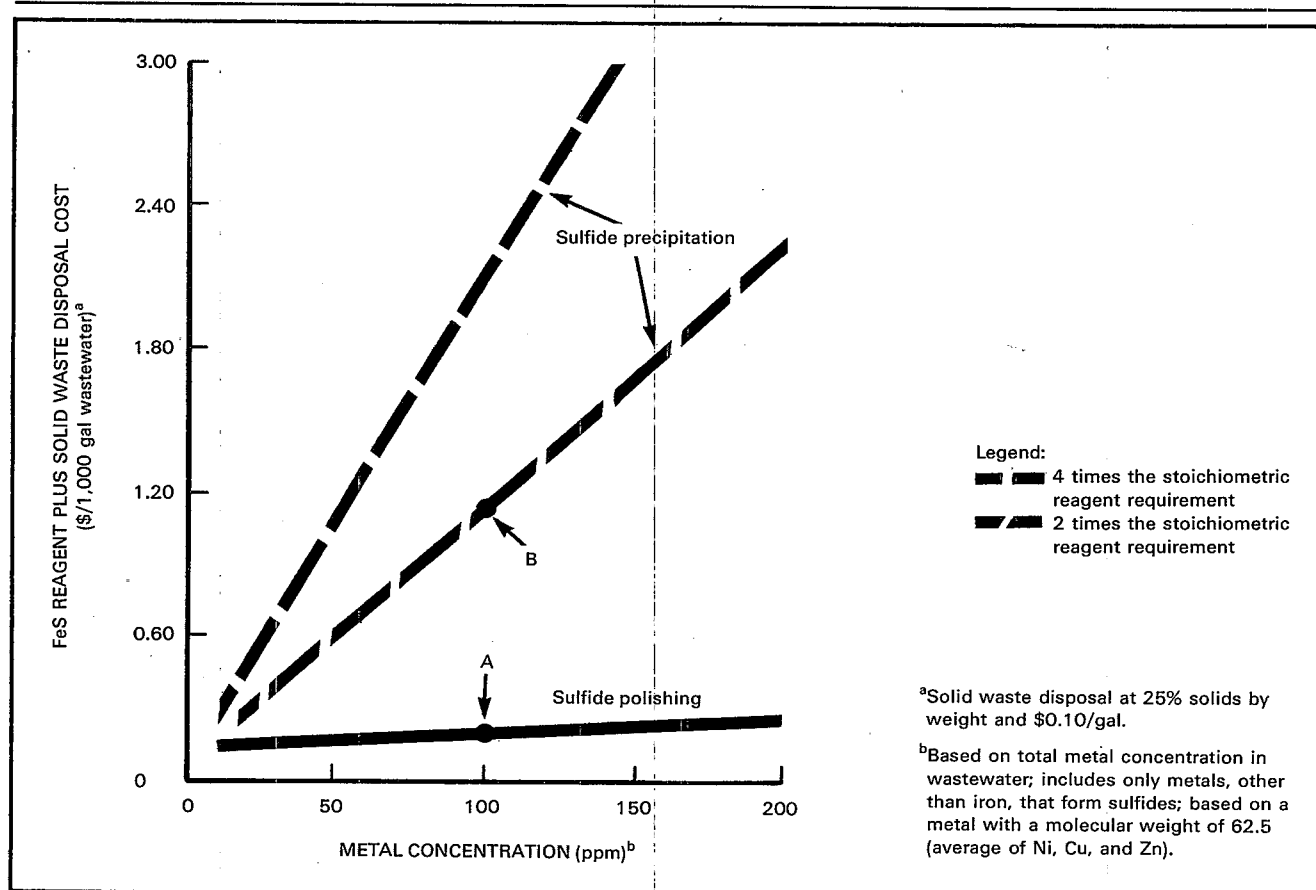
Note.—1979 cost basis.

after-tax return on investment of 13 percent.

The costs of FeS reagent and solid waste disposal for ISP systems and sulfide polishing systems are compared further in Figure 32 for each 1,000 gal (3,785 l) of wastewater treated at various metal concentrations. The solid

waste disposal cost estimate assumed disposal of the sludge at 25 percent solids by weight at a cost of \$0.10/gal of waste and that both sludges would dewater to the same level. The FeS reagent

cost for the polishing system was derived from a required FeS dosage rate of 40 mg/l of wastewater. Figure 32 presents the difference in cost, rather than total treatment costs, of sulfide reagent and solid waste disposal for sulfide precipitation and sulfide polishing systems. Other costs associated with treatment should be similar for both systems.



**Figure 32.**

Treatment Cost of ISP vs. Insoluble Sulfide Polishing

A polishing system can achieve significant savings at higher wastewater metal concentrations. As an example, Figure 32 reveals that a system treating 3,000 gal/h (11,340 l/h) with a metal concentration of 100 ppm and requiring twice the stoichiometric amount of FeS would save \$2.80/h—(B minus A) × 3,000 gal/h. At the

same flow rate and metal concentration, the savings would be \$5.70/h if the wastewater required 4 times the stoichiometric amount of FeS.

Using the savings shown in Figure 32, Figure 33 presents the return on investment for installing the additional treatment hardware needed for a polishing system over a range of metal concentrations and wastewater flow rates.

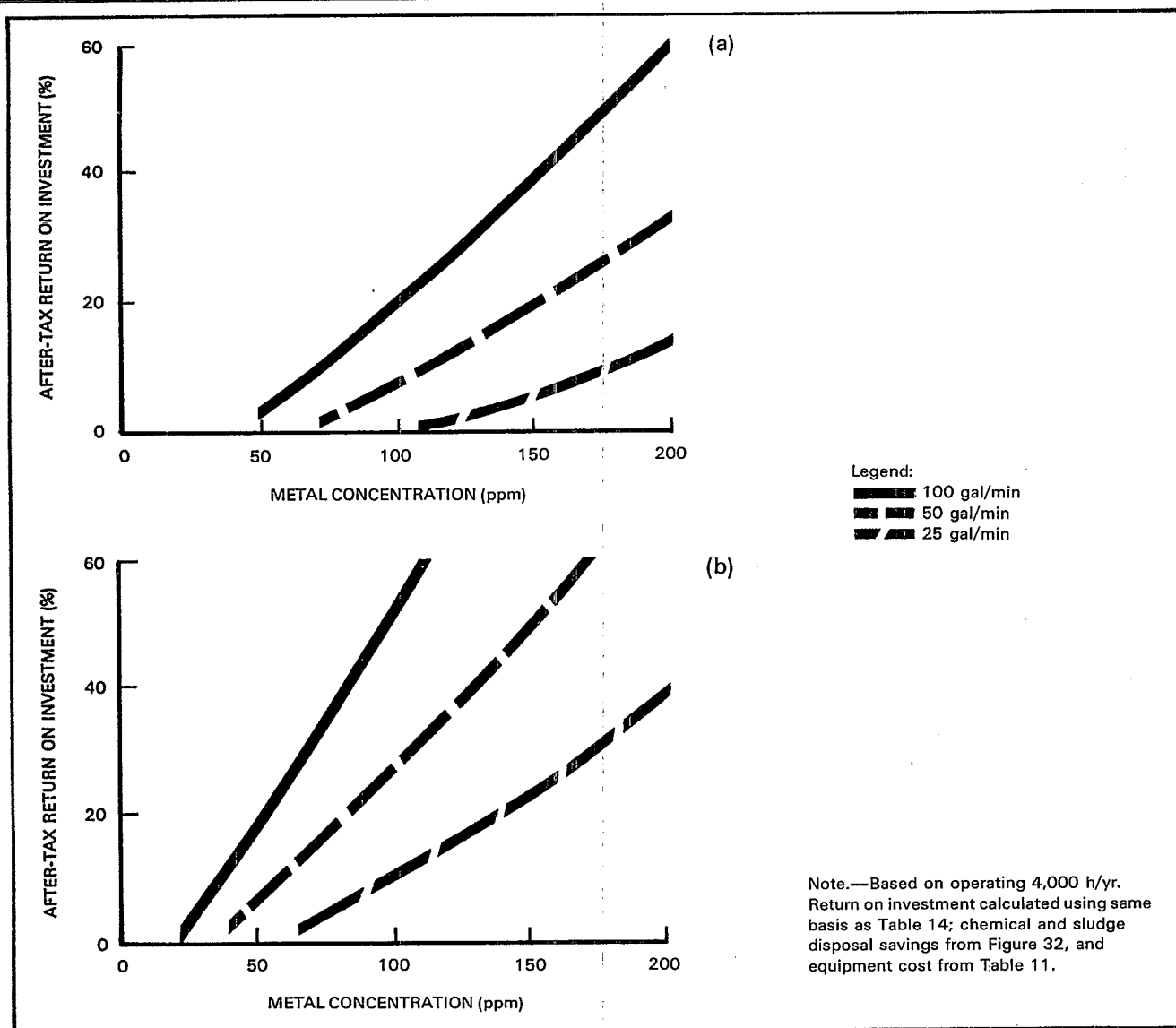


Figure 33.

Return on Investment of Additional Capital Required for Insoluble Sulfide Polishing System: (a) Treatment Requiring Two Times the Stoichiometric FeS Requirement and (b) Treatment Requiring Four Times the Stoichiometric FeS Requirement



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This report has been reviewed by the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati OH, and approved for publication. This summary report presents only one of many control alternatives for wastewater control. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use because other existing and future systems may be as acceptable as those mentioned in this document.

COVER PHOTOGRAPH: Sodium sulfide and sodium bisulfite mixing tanks