

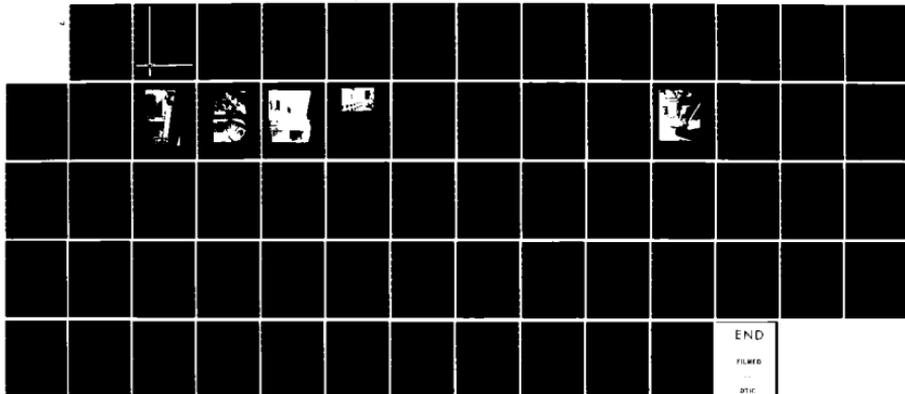
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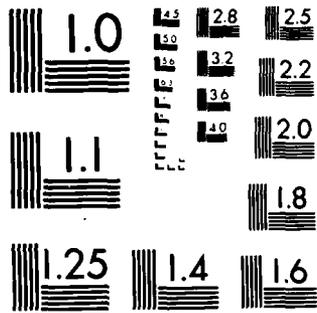
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Report 2408

PILOT PLANT DEMONSTRATION OF A SULFIDE PRECIPITATION
PROCESS FOR METAL-FINISHING WASTEWATER TREATMENT

May 1984

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United States Army
Belvoir Research & Development Center
Fort Belvoir, Virginia 22060

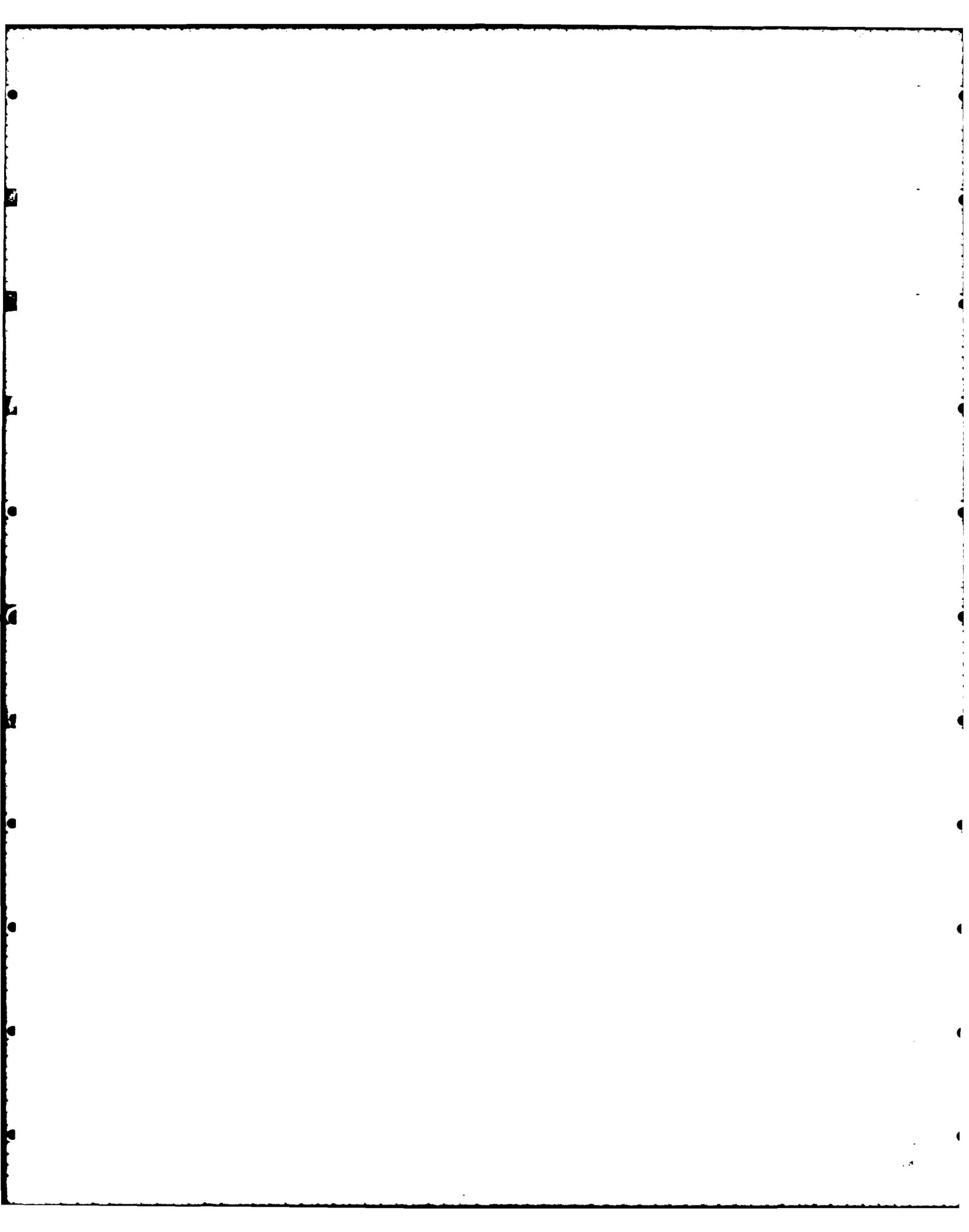
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The treatment process provides for cyanide destruction by alkaline chlorination, hexavalent chromium reduction by metabisulfite treatment, and metals-removal by the addition of sodium sulfide, ferrous sulfate, and an anionic polymer flocculant aid. The sludge produced is thickened in a gravity sludge thickener and dewatered in a filter press.

This report describes the unit processes and equipment used in the system and presents analytical, operating, and cost data obtained during an 11-month operating period.

This report concludes that:

a. The metal-finishing wastewater treatment system installed at the TOAD using cyanide destruction, chromium reduction, and metal sulfide precipitation by sodium sulfide addition is an effective process for the treatment of metal-finishing wastewaters.

b. The sulfide treatment system can produce an effluent complying with Federal regulations defined in "Final Rules, Electroplating and Metal-Finishing Point Source Categories, Effluent Limitations Guidelines, Pretreatment Standards and New Source Performance Standards, 48 *Federal Register* (FR) 32462, 15 July 1983."

c. The metal sulfide sludge produced by the sulfide treatment system can be dewatered to as high as 32 percent dry solids content. The average value determined was 22.4 percent.

d. The dewatered sludge produced at TOAD is minimal, amounting to 44 gal/100,000 gal of wastewater treated.

e. The sludge generated by the sulfide treatment process must be disposed of as a hazardous material as defined by Resources Conservation and Recovery Act regulations.

f. Costs for chemicals and sludge disposal add up to a combined cost of \$1.38/1000 gal of TOAD metal-finishing wastewater treated. Chemical costs average \$0.89/1000 gal and sludge disposal costs average \$0.49/1000 gal.

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PREFACE

The investigation covered by this report was conducted by the Petroleum and Environmental Technology Division, Logistics Support Laboratory, U.S. Army Belvoir Research and Development Center under Project 1L162720D048. The effort (Work Unit W-31, WBS No. P147.01.02, Sulfide Precipitation of Electroplating Wastes) was funded by the U.S. Army Toxic and Hazardous Material Agency (USATHAMA), Lead Laboratory for the DARCOM DO-48 Environmental Quality Program.

The investigation was conducted by the following Belvoir Research and Development Center personnel:

Mr. Maurice Pressman, Project Officer.

Ms. Gail Chesler, P.E., Environmental Engineer.

Ms. Janet Hall, Chemist.

Ms. Elizabeth Radoski, Chemist.

The cooperation of Dr. Mary Daly, Environmental Engineer, and the metal-finishing wastewater treatment plant operators at the Tobyhanna Army Depot is acknowledged. They furnished the wastewater and sludge samples for analysis and provided detailed system operating and chemical cost data.

The cooperation of Mr. John Resta, Army Environmental Hygiene Agency (AEHA), in supplying information on the AEHA survey and the results of the sludge leachate analyses is acknowledged.



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PILOT PLANT DEMONSTRATION OF A SULFIDE PRECIPITATION PROCESS FOR METAL-FINISHING WASTEWATER TREATMENT

I. INTRODUCTION

1. Subject. This report describes a program designed to evaluate the effectiveness of a metal-finishing wastewater treatment process based on the removal of heavy metals as metal sulfides by the addition of a soluble sulfide to the wastewater. The effectiveness of the process was demonstrated through the operation of a pilot demonstration system designed to treat 18,000 gal/d of toxic metal-bearing wastewater. The system was installed and operated at the Tobyhanna Army Depot (TOAD), Tobyhanna, Pennsylvania, where extensive electroplating and other metal-finishing operations are carried out for the Army.

2. Background. In September 1980, a contract was awarded by MERADCOM (now Belvoir R&D Center) to JRB Associates, McLean, Virginia, to design, fabricate, install, and start an electroplating wastewater treatment system at TOAD. The plant had to be designed to treat a daily flow of 18,000 gal of wastewater during an 8-h period. The wastewater would contain a number of commonly used complexing chemicals, such as phosphates, tartrates, EDTA and cyanide and one or more of the following metals: copper, nickel, chromium, zinc, lead, cadmium, tin, aluminum, and iron. Specifications called for the complete system to contain equipment for cyanide destruction, chromium reduction, metal sulfide precipitation by the addition of a soluble sulfide, and sludge dewatering. The process effluent discharged to the sanitary sewer had to meet proposed Federal Environmental Protection Agency (EPA) pretreatment standards. The sludge produced had to be dewatered to a minimum of 20 percent solids.

The process and design criteria evolved, in part, from the data developed in a previous treatability study of TOAD plating shop rinsewaters conducted in 1979.^{1 2}

II. INVESTIGATION

3. System Design Specification. The system had to be designed to fit into a space 15 ft wide, 13 ft high, and 65 ft long. It had to treat a total daily (8-h) flow of approximately 18,000 gal of wastewater composed of about 2,000 gal/d of chromium-bearing wastewater, 4,000 gal/d of cyanide-bearing wastewater, and 12,000 gal/d of acid/alkali rinsewater. Table 1 gives the effluent standards which had to be met. These standards were the proposed EPA Pretreatment Standards for Existing Sources, published in the *Federal Register*, 1 October 1979. Table 2 presents the major design specifications of the system which were developed from the information produced in the 1979 treatability study and preliminary design calculations.³

¹ "Engineering Analysis and Feasibility Study for Treatment of Plating Shop Rinsewaters at Tobyhanna Army Depot." prepared by Walden of Abcor, Inc., Wilmington, Massachusetts (31 Oct 79).

² "Design Criteria and Budgetary Cost Estimates for Treatment of Plating Shop Rinsewater at Tobyhanna Army Depot." prepared by Walden Division of Abcor, Inc., Wilmington, Massachusetts (20 Nov 79).

³ "Preliminary Design Calculations, Electroplating Wastewater Treatment Plant, Tobyhanna Army Depot." prepared by JRB, Associates, under USA MERADCOM Contract DAAK-70-80-C-0195 (12 Nov 80).

Table 1. Treatment Standards for System Effluent

Pollutant (mg/l)	Maximum For Any 1 d	Average of Daily Values of 10-d Consecutive Monitoring Shall Not Exceed:
Cyanide, Total	0.8	0.23
Copper	4.5	1.8
Nickel	4.1	1.8
Chromium	7.0	2.5
Zinc	4.2	1.8
Lead	0.6	0.3
Cadmium	1.2	0.5
Tin	2.5	1.0
Aluminum	1.0	0.5
Total Metal	10.5	5.0

pH Between 7.0 and 10.0.

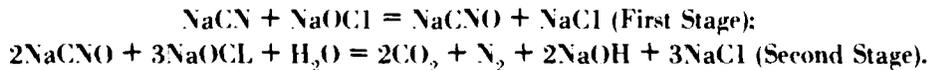
Table 2. Design Specifications

Unit Process	Design Flow (gal/min)	Detention Time (min)	Reactor Volume (gal)	Other Conditions
Cyanide Oxidation				
Stage I	8.3	15	125	pH > 11.00; ORP 375 ± 25 mv
Stage II	8.3	60	400	pH 8.0 ± 0.2 ; ORP 600 ± 20 mv
Chromium Reduction	4.2	100	420	pH < 2.5; ORP 275 ± 25 mv
Neutralization	37.5	12	150	pH 8.0 ± 0.2
Sulfide Addition	37.5	12	150	pH 8.0 ± 0.2 ; free sulfide = 1 mg/l
Ferrous Sulfate Addition	37.5	12	150	ph 8.0 ± 0.2
Flash Mixing	37.5	1.3	50	Anionic Polymer Dosage = 1 to 2 mg/l
Flocculation	37.5	6.9	260	N/A
Laminar Settling	37.5	64	2400	Surface Loading = 0.15 gal/min/ft ²
Polishing Filtration	37.5	N/A	N/A	Filtration Rate = 2.5 gal/min/ft ²
Sludge Thickening	8.3	265	2200	Thickened Solids Concentration = 3 to 10 percent
Filter Press Dewatering	N/A	N/A	N/A	15 gal capacity/cycle

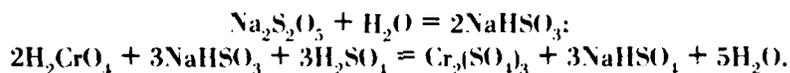
4. System Configuration. Based on the design specifications given in Table 2, a continuous flow-through treatment system was designed. A flow diagram of this system is shown in Figure 1. The system consists of segregated chromium wastewater and cyanide wastewater collection systems, an acid/alkali rinsewater sump; a unit for the two-stage oxidation of cyanide by alkaline chlorination, a unit for reducing hexavalent chromium by sodium metabisulfite addition; a surge tank to combine the three segregated wastewater streams, a 4-compartment section for pH adjustment followed by sulfide, ferrous sulfate, and anionic polymer additions; a flash mix tank, a flocculation tank; a laminar plate clarifier, a polishing filter, and a clear well equipped with a hydrogen peroxide feed system to oxidize any residual sulfide. A mud-well is provided for receiving the filter backwash water and filter press filtrate for recycling through the treatment system. The various items of equipment such as pumps, level controls, mixers, and pH and oxidation-reduction potential (ORP) measurement devices which make up the system are listed in Appendix C. Figures 2 through 6 show a section of the treatment system before installation and several components of the system.

5. Treatment Process Description. Following is a description of the unit processes and equipment comprising the system:

a. Cyanide Oxidation. Rinse water from the cyanide (CN) plating tanks flows to the cyanide sump. From this sump, the rinsewater is pumped to the first-stage tank of the cyanide oxidation unit. Sodium hydroxide (NaOH) is added to raise the pH to 11, and sodium hypochlorite (NaOCl) is added to oxidize the cyanide to cyanate (CNO). The NaOH addition is controlled by a pH controller. The NaOCl addition is controlled by an ORP controller, to produce a potential between 350 mv and 400 mv. The wastewater then flows to the second-stage tank where sulfuric acid (H_2SO_4) is added to lower the pH to 8.0 ± 0.2 , and additional NaOCl is added to convert the CNO to carbon dioxide and nitrogen. The ORP in the second-stage reaction is maintained between 580 mv and 620 mv. The chemical equations for these reactions are as follows:



b. Chromium Reduction. Rinsewater from the chromium (Cr) plating operations flows to the chromium sump. From here, the wastewater is pumped to the chromium reduction tank where H_2SO_4 is added to lower the pH to less than 2.5. Sodium metabisulfite ($Na_2S_2O_5$) is then added to reduce the hexavalent chromium (Cr(VI)) to trivalent chromium (Cr(III)). The ORP is maintained between 250 mv and 300 mv. The additions of the H_2SO_4 and $Na_2S_2O_5$ are controlled by pH and ORP controllers. It is necessary to reduce Cr(VI) to Cr(III) in order to make it amenable to precipitation as chromium hydroxide ($Cr(OH)_3$) later in the treatment. The following chemical equations show the reduction reaction:



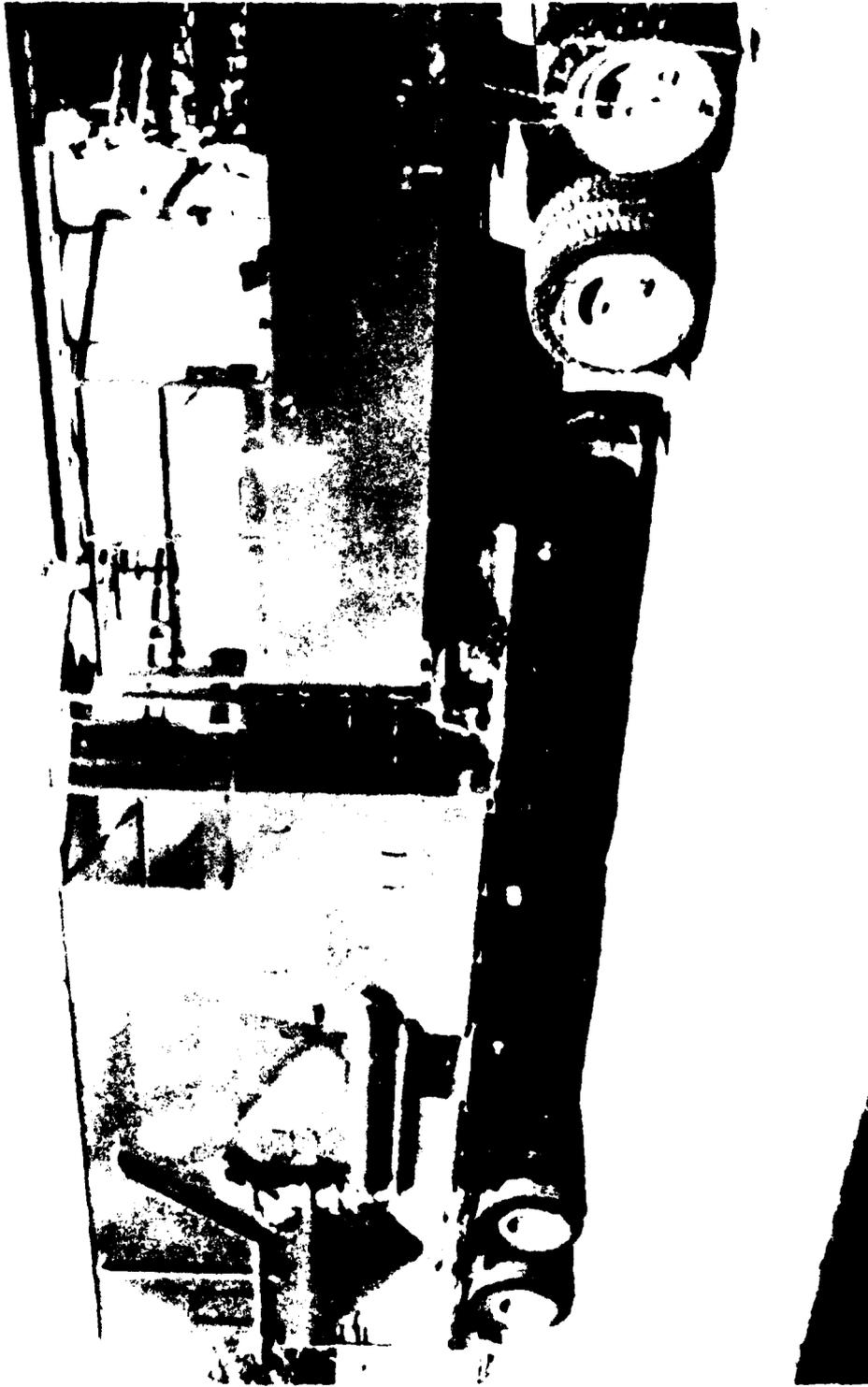


Figure 2. Section of TOAD metal-finishing wastewater treatment system.

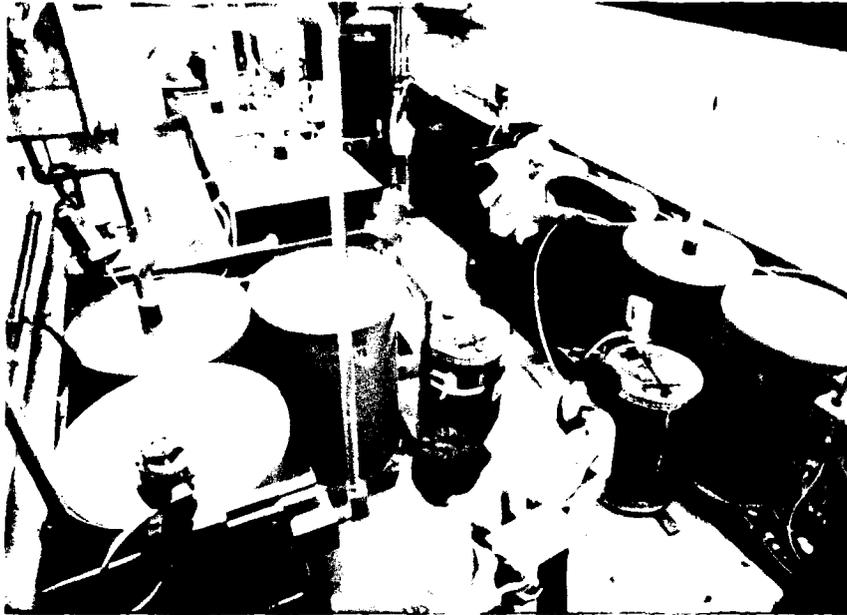


Figure 3. View of portion of treatment system.

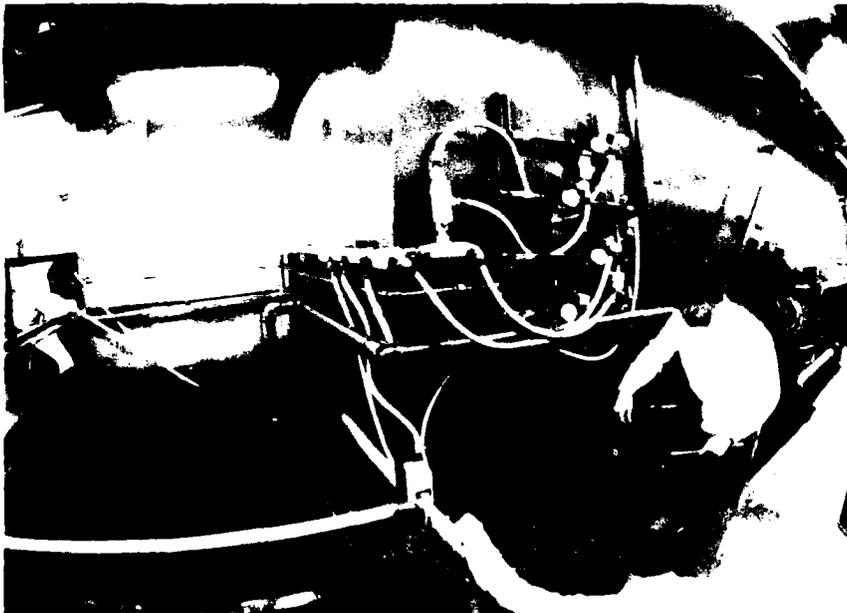


Figure 4. Section of treatment system, showing clearwell.



Figure 5. Filter press and air compressor.

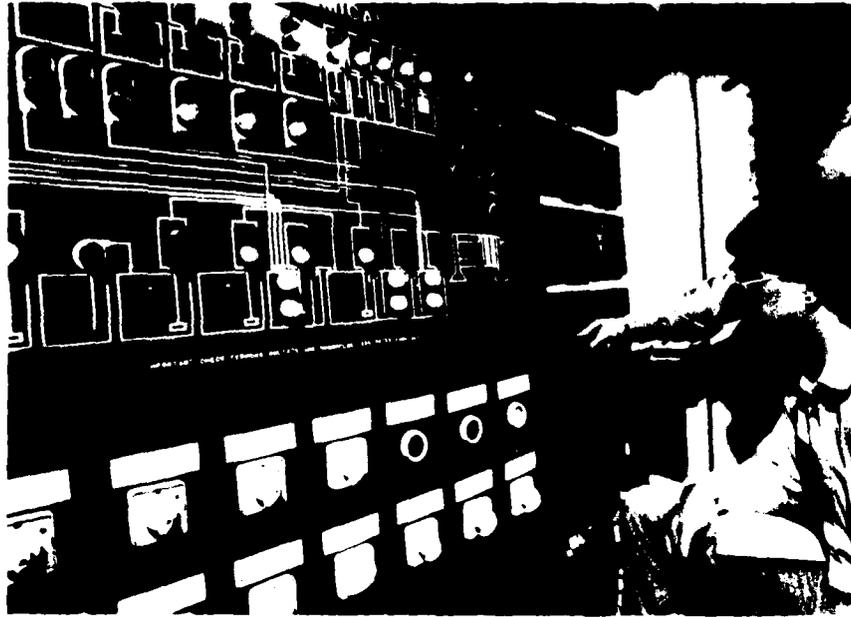


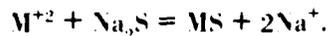
Figure 6. Control panel.

c. **Flow Equalization.** The effluents from the cyanide treatment unit, and the chromium reduction unit are combined in a surge tank with the acid/alkali rinsewater pumped from the acid/alkali sump. The acid/alkali wastewater, the largest volume of wastewater to be treated, is derived from such operations as surface preparation, chemical conversion coating operations, anodizing, and plating shop floor drains. Flow equalization serves to provide a steady, controlled flow of wastewater to the sulfide precipitation process.

d. **Metal Precipitation.**

(1) **pH Adjustment.** The combined wastewater is pumped from the surge tank to a neutralization tank where the pH is adjusted to 8.0 ± 0.2 . Control of pH at this point is very important for a number of reasons: (a) to prevent the generation of toxic hydrogen sulfide gas; (b) to insure the optimum removal of chromium hydroxide, which is amphoteric, and (c) to provide the proper pH for metal sulfide precipitation. It should be noted that chromium precipitates as an hydroxide and not as a sulfide.

(2) Sodium Sulfide Addition. Following pH adjustment, the wastewater flows to the sulfide addition tank where Na_2S is added to precipitate the heavy metals, other than chromium, as metal sulfides. The addition of the Na_2S is automatically controlled by a sulfide specific ion probe and controller to provide an excess of approximately 1 mg/l of sulfide ion. The following chemical equation illustrates the reactions:



The metal sulfides so produced are extremely fine non-settleable colloids which need to be conditioned by further treatment to insure their subsequent removal by sedimentation and polishing filtration.

(3) Ferrous Sulfate Addition. Following the addition of Na_2S , the wastewater flows to the ferrous sulfate (FeSO_4) addition tank. A solution of FeSO_4 is added to react with the excess sulfide ion to form insoluble ferrous sulfide (FeS). The FeSO_4 also aids in the agglomeration of the colloidal metal sulfides by forming an iron hydroxide floc. The ferrous ion can also serve as a chromium reducing agent as well as a catalyst in the reduction of hexavalent chromium to trivalent chromium by the sulfide ion, in the event that any unreduced chromium comes through the chromium reduction unit. The various parameters affecting these reactions have been investigated recently in laboratory and pilot-scale studies for the Air Force.⁴

(4) Polymer Addition. Following the addition of ferrous sulfate, the wastewater flows to a flash mix tank, where an anionic polyelectrolyte (Kronofloc) is added. After a 1-min flash mix, the wastewater flows to a flocculation chamber for gentle mixing. Here, the suspended solids are agglomerated into readily settleable floc particles for subsequent removal in the laminar plate clarifier.

e. Solids Removal.

(1) Laminar Plate Clarifier. Following flocculation, the wastewater flows to a laminar plate clarifier, where the suspended floc settles onto a stack of specially configured, inclined, parallel plates and then drops down to a hopper at the base of the clarifier.

(2) Polishing Filter. The overflow from the clarifier passes through a dual-media polishing filter for the removal of any residual suspended solids not removed in the clarifier. The filter media is composed of sand and anthracite. The filter is backwashed automatically with water from the clearwell. The backwash is discharged to the mud-well for storage and eventual discharge back to the flow equalization tank for recycling through the treatment system.

⁴ L. E. Higgins, and V. E. Sater, "Treatment of Electroplating Wastewater by Alkaline Ferrous Reduction of Chromium and Sulfide Precipitation," Report No. ESI-IR-83-21, College of Engineering and Applied Sciences, Arizona State University (Jun 83).

(3) **Clearwell.** The filter effluent flows to a clearwell where hydrogen peroxide is added to oxidize any residual sulfide. The treated water then flows by gravity to the sanitary sewer.

f. Sludge Handling.

(1) **Sludge Thickener.** Sludge from the bottom of the clarifier is pumped automatically to a sludge thickener to increase its solids content before dewatering. The decant from the thickener is returned to the mud-well for subsequent pumping to the equalization tank and recycling through the treatment system.

(2) **Filter Press.** Sludge from the bottom of the sludge thickener is automatically pumped to a filter press for dewatering. The filtrate is returned to the mud-well and then to the equalization tank for recycling through the treatment system. The dewatered sludge is discharged to a 55-gal drum and disposed of as a hazardous waste.

g. Safety Features. A number of safety features are included in the system design. The cyanide, chromium, and sulfide treatment tanks are covered and connected with a continuous ventilation system to exhaust any toxic gas such as chlorine, hydrogen cyanide, or hydrogen sulfide which could be generated through abnormal operation of the treatment system. Process control devices equipped with alarms have been provided to warn operators of hazardous conditions such as low pH in the cyanide tank, high or low pH in the neutralization tank, and low pH in the sulfide tank. Water level controllers and alarms have been included. Oxygen masks, fire-extinguishers, eye washer, and an automatic sprinkler system have also been provided.

6. System Tests. Testing of the system was conducted in three phases designated as follows: Start up Tests, Army Environmental Hygiene Agency (AEHA) Survey, and Belvoir R&D Center Monitoring Program. The start up testing was conducted by the contractor to demonstrate the system performance and to train the operators. The AEHA survey was conducted as Water Quality Engineering Special Study No. 32-24-0331-84. The Belvoir Monitoring Program was conducted to evaluate the system performance over an extended period of operation.

a. Start up Tests. The terms of the contract awarded to JRB Associates, Inc., called for the operation of the system over a period of 10 operating days following installation to demonstrate compliance with the contract specifications. Construction of the system was completed in October 1982. After initial start up, sampling and analysis of the system effluent being discharged to the sanitary sewer was begun on 9 November 1982. During this performance demonstration, equipment de-bugging and minor system modifications required that the system be shut down several times. These shut downs resulted in samples being taken over an extended period of time. Sampling and analysis were completed in January 1983, and a test report was submitted in February 1983.⁵

⁵ "Performance Test, Toluene Arms Depot Plating Shop Pretreatment System," prepared by JRB Associates, Contract No. DAAK 20004-0197-1-1-83.

b. Army Environmental Hygiene Agency (AEHA) Survey. During the period 30 March through 6 April 1983, a survey team from AEHA, Aberdeen Proving Ground, Maryland, conducted a water quality engineering study; the purpose was "to evaluate the recently constructed metal-finishing wastewater pretreatment plant (MFWPP) at the Tobyhanna Army Depot." Samples of the wastewater and sludge were taken at 14 sampling points shown in Figure 7. Samples of wastewater were analyzed for cyanide, heavy metals, oil and grease, suspended solids, sulfide, pH, ammonia-nitrogen and nitrite/nitrate-nitrogen. Samples of raw sludge and thickened sludge were analyzed for solids content. A sample of dewatered sludge was subjected to the standard EPA solid waste extraction procedure to determine whether the sludge should be considered hazardous according to Resources Conservation and Recovery Act (RCRA) standards. The analytical methods used were in accordance with EPA procedures.^{6 7}

c. Belvoir Monitoring Program. During the period between July 1983 and December 1983, a number of wastewater and sludge samples were taken at seven points in the treatment process and shipped to the Belvoir R&D Center for analysis. The samples were analyzed for cyanide, heavy metals, suspended solids, oil and grease, and sludge solids content. In addition, several samples of sludge from the filter press were subjected to the standard EPA and Battelle solid waste leaching procedure⁸ to determine the toxicity of the sludge. Samples were taken of the cyanide treatment unit influent and effluent, the chromium reduction unit influent and effluent, the acid/alkali rinsewater, surge tank effluent, and the clearwell water. Heavy metals were determined by flame atomic absorption using a Perkin-Elmer Model 503 atomic Absorption Spectrophotometer. Other analytical determinations were made in accordance with procedures given in *Standard Methods*.⁹ The apparatus used in the sludge leaching tests is shown in Figure 8.

III. RESULTS

7. Test Data. The results obtained in the start up tests of the system are given in Table 3 and Appendix A. The results obtained in the AEHA survey are given in Table 4 and in portions of Tables 7, 8, 9, and 11. The data for samples dated 30 March 1983 through 30 April 1983 given in Tables 7, 8, 9, and 11 were extracted from the AEHA survey report.¹⁰ The results obtained in the Belvoir R&D Center monitoring program are given in Tables 5 through 16, Appendix B, and Appendix D.

⁶ "Methods for Chemical Analysis of Water and Wastes," EPA, (Mar 79).

⁷ "Test Methods for Evaluating Solid Wastes," EPA (May 80).

⁸ "Solid Waste Leaching Procedures," Battelle Columbus Laboratories (1980).

⁹ "Standard Methods for the Examination of Water and Wastewater," American Public Health Association, American Water Works Association, Water Pollution Control Federation, New York, 15th edition (1980).

¹⁰ "Water Quality Engineering Special Study No. 32-24-0331-84, Metal Finishing Wastewater Treatment Plant Evaluation," Tobyhanna Army Depot, Tobyhanna, Pennsylvania, 30 Mar - 6 Apr 83, prepared by U.S. Army Environmental Hygiene Agency, Aberdeen Proving Ground, MD 21010.

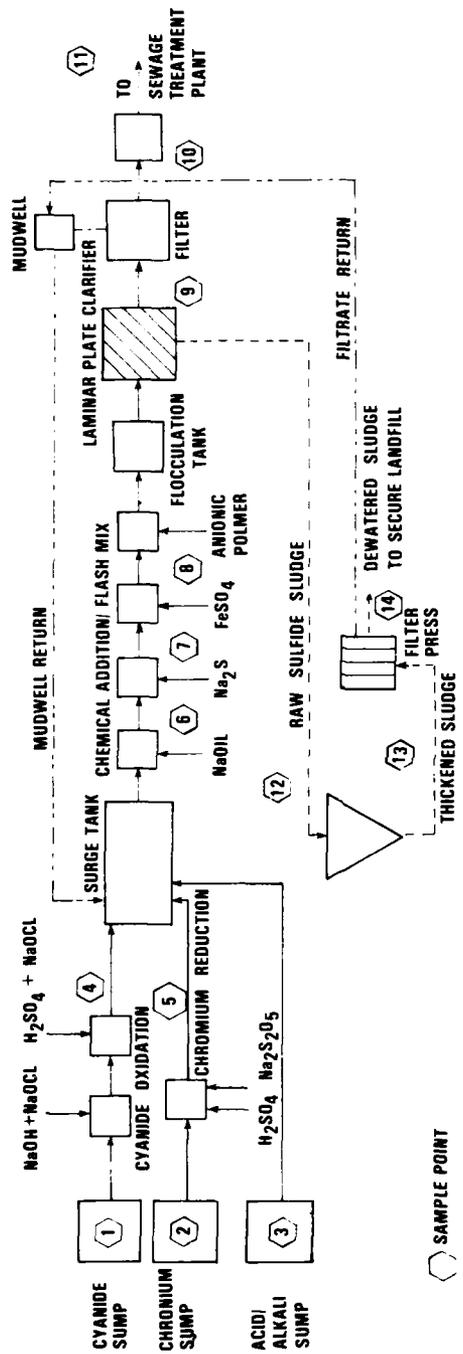


Figure 7. Sampling point locations.



Figure 8. Sludge extraction apparatus.

Table 3. System Effluent Analysis - Startup Test

Characteristic (mg/l)	System Maximum Concentration	Daily Maximum Limits		System 10-d Avg. Concentration	10-d Avg. Maximum Limits	
		Design*	EPA Std		Design*	EPA Std
Cadmium	0.65	1.2	0.69	0.17	0.5	0.26
Chromium, Total	0.31	7.0	2.77	0.16	2.5	1.71
Copper	0.56	4.5	3.38	0.24	1.8	2.07
Lead	0.20	0.6	0.69	0.15	0.3	0.43
Nickel	0.43	4.1	3.98	0.17	1.8	2.38
Silver	N.D.**	none	0.43	N.D.	none	0.24
Zinc	0.99	4.2	2.61	0.31	1.8	1.48
Cyanide, Total	0.37	0.8	1.20	0.08	0.23	0.65
Aluminum	4.73	1.0	none	2.17	0.5	none
Tin	0.006	2.5	none	<0.003	1.0	none

Note: Effluent pH Range = 5 to 9 during 10 d of test.

*Contract DAAK 70-80-C-0195 Specifications.

**N.D. = Not determined.

Table 4. System Effluent Analysis—AEHA Survey

Parameter (mg/l)	Sample Date (1983)					Daily Max Standard*
	30 Mar	31 Mar	1 Apr	4 Apr	5 Apr	
Al	7.9	3.2	20	6.3	3.4	none
Cd	0.54	0.023	0.017	0.023	0.012	0.69
Cr, Hex.	<0.025	<0.025	<0.025	<0.025	<0.025	none
Cr, Total	1.16	0.165	0.181	0.120	0.046	2.77
Cu	0.124	0.219	0.112	0.225	0.017	3.38
Pb	0.89	<0.20	<0.20	<0.20	<0.20	0.69
Ni	<0.10	0.12	0.17	<0.10	<0.10	3.98
Ag	<0.025	<0.025	<0.025	<0.025	<0.025	0.43
Su	<1.0	<1.0	<1.0	<1.0	<1.0	none
Zn	1.19	0.120	0.060	0.048	0.016	2.16
Cu, Total	<0.005	0.17	0.42	0.04	0.01	1.20
pH	9.3	9.0	9.9	10.0	10.3	6.0 to 9.0
Suspended Solids	31.0	18.0	4.0	8.0	1.0	60
Oil and Grease	1.0	<1.0	<1.0	<1.0	<1.0	52

*Final Rules, Electroplating and Metal-Finishing Point Source Categories; Effluent Limitations Guidelines, Pretreatment Standards and New Sources Performance Standards, 48 Federal Register (FR) 32642, 15 July 1983.

Table 5. Summary of System Effluent Analysis—Belvoir Monitoring Program
July 1983 through December 1983

Parameter (mg/l)	Maximum Effluent Concentration	Daily Maximum		Average Effluent Concentration	Average	
		Effluent Design	Effluent Limits EPA Std		Effluent Design	Effluent Limits EPA Std
Cadmium	0.25	1.2	0.69	0.09	0.5	0.26
Chromium	1.15	7.0	2.77	0.31	2.5	1.71
Copper	0.47	4.5	3.38	0.07	1.8	2.07
Lead	0.40	0.6	0.69	<0.19	0.3	0.43
Nickel	0.35	4.1	3.98	0.08	1.8	2.38
Silver	0.02	none	0.43	<0.01	none	0.24
Zinc	2.69	4.2	2.61	0.37	1.8	1.48
Cyanide	0.12	0.8	1.20	<0.04	0.23	0.65
Aluminum	18.0	1.0	none	4.3	0.5	none
Tin	<1.0	2.5	none	<0.01	1.0	none
Suspended Solids	152	none	60	18.8	none	31
Oil and Grease	22	none	52	12.8	none	26

Table 6. System Effluent Metal Content—Belvoir Monitoring Program

Sample	Metal Concentration (mg/l)													
	Cd	Cr	Cu	Pb	Ni	Ag	Sb	Zn	Al					
Date (1983)														
12 Jul	0.07	0.40	0.12	0.05	0.05	<0.01	<1.0	0.27	N.D.*					
19 Jul	0.06	0.13	0.03	0.09	0.02	0.01	<1.0	0.09	N.D.					
02 Aug	0.19	1.15	0.10	1.0	0.35	0.01	<1.0	2.69	N.D.					
09 Aug	0.04	0.04	0.03	<0.1	0.07	<0.01	<1.0	0.09	3					
23 Aug	0.06	0.36	0.05	<0.1	0.05	<0.01	<1.0	0.11	6					
30 Aug	0.05	0.22	0.05	<0.1	0.03	<0.01	<1.0	0.16	3					
06 Sep	0.10	0.15	0.05	<0.1	0.05	<0.01	<1.0	0.01	3					
20 Sep	0.25	0.50	0.04	0.2	0.07	<0.01	<1.0	0.94	18					
27 Sep	0.08	0.08	0.01	<0.1	0.01	<0.01	<1.0	<0.01	2					
18 Oct	0.04	0.15	0.05	<0.1	0.06	<0.01	<1.0	0.05	3					
25 Oct	0.14	0.37	0.05	0.3	0.10	<0.01	<1.0	0.41	4					
07 Nov	0.06	0.14	0.02	<0.1	0.04	<0.01	<1.0	0.06	4					
15 Nov	0.07	0.40	0.02	0.20	0.08	0.01	<1.0	0.28	3					
22 Nov	0.13	0.45	0.02	0.40	0.08	<0.01	<1.0	0.63	1					
06 Dec	0.05	0.32	0.04	<0.1	0.05	<0.01	N.D.	0.08	2					
13 Dec	0.05	0.17	0.47	0.1	0.12	0.02	<1.0	0.11	N.D.					
Average	0.09	0.31	0.07	<0.19	0.08	<0.01	<0.01	0.37	4.3					
EPA Limit	0.69	2.77	3.88	0.69	3.98	0.43	none	2.61	none					

*N.D. = Not determined.

Table 7. Cyanide Oxidation Data

Sample Date (1983)	Cyanide Oxidation Unit	
	Influent	Effluent (mg/l Total Cn)
04 April	7.3	0.01
05 April	9.9	0.12
06 April	16	< 0.15
19 July	17	< 0.008
26 July	40	0.016
02 August	50	0.026
09 August	56	0.012
18 October	< 0.005	< 0.005
15 November	17.5	< 0.005
06 December	0.01	< 0.005

Table 8. Hexavalent Chromium Reduction Data

Sample Date (1983)	Chromium Reduction Unit		Clearwell (mg/l Cr(IV))
	Influent (mg/l Cr (VI))	Effluent	
30 March	3.12	< 0.025	< 0.025
31 March	1.99	0.037	< 0.025
01 April	4.59	0.105	< 0.025
04 April	0.51	< 0.025	< 0.025
05 April	0.81	< 0.025	< 0.025
12 July	0.31	< 0.025	0.04
19 July	8.00	0.38	< 0.025
02 August	0.59	< 0.025	< 0.025
09 August	0.28	< 0.025	< 0.025
23 August	2.68	0.42	< 0.025
30 August	0.64	0.27	< 0.025
06 September	0.38	0.27	< 0.025
20 September	0.38	0.28	< 0.025
27 September	0.85	< 0.025	< 0.025
18 October	1.0	< 0.025	< 0.025
25 October	0.40	< 0.025	< 0.025
07 November	0.18	< 0.025	< 0.025
15 November	7.2	0.26	< 0.025
22 November	0.74	< 0.025	< 0.025

Table 9. Clearwell Effluent Suspended Solids

Sample Date (1983)	Suspended Solids* (mg/l)
30 Mar	31.0
31 Mar	18.0
01 Apr	4.0
04 Apr	8.0
05 Apr	1.0
22 Jul	8.8
09 Aug	6.0
23 Aug	6.4
30 Aug	5.9
06 Sep	6.7
27 Sep	152.0
10 Oct	1.9
20 Oct	21.5
25 Oct	6.9
11 Nov	3.3
22 Nov	53.0
06 Dec	2.0
13 Dec	1.5
Average	18.8

*EPA Limit = 60 mg/l—From "Proposed Rules, Best Conventional Pollution Control Technology, Effluent Limitations Guidelines, 47 FR 49176, 29 October 1982."

Table 10. Effluent Oil and Grease

Sample Date (1983)	Oil and Grease (mg/l)
01 Nov	22
08 Nov	5
10 Nov	0
15 Nov	9
17 Nov	14
22 Nov	12
29 Nov	21
02 Dec	7
06 Dec	8
08 Dec	20
13 Dec	20
15 Dec	16
20 Dec	12
22 Dec	16
28 Dec	10
29 Dec	12
Average	12.8

Table 11. Dewatered Sludge Solids

Sample Date (1983)	Suspended Solids Content (%)
06 Apr	22.9
23 Aug	30.3
30 Aug	18.3
09 Sep	32.2
20 Sep	16.1
27 Sep	21.3
25 Oct	22.0
07 Nov	22.5
22 Nov	21.1
13 Dec	11.2
Average	22.4

Table 12. Operating Time, Wastewater Flows, and Volume of Sludge Generated

Month (1983)	Operating Time (h)	Wastewater Flow		Dewatered Sludge (55-gal Drums)
		Total (gal)	Rate (gal/h) (Avg)	
February	180	279,835	1555	3.0
March	224	358,168	1599	3.5
April	209	378,156	1809	4.5
May	220	371,307	1688	3.5
June	216	366,046	1695	3.0
July	212	376,410	1776	2.5
August	268	471,613	1760	4.5
September	272	514,860	1893	3.5
October	196	373,436	1905	2.5
November	220	434,246	1974	2.0
December	231	417,141	1806	2.5
Total	2248	4,341,245		35.0
Monthly Average	223	394,659	1773	3.2

Table 13. Volumes of Segregated Wastewaters Treated

Month (1983)	Wastewater Treated (Gal)			
	Acid/Alkalie	Cyanide	Chromium	Total
February	259,980	0	19,855	279,835
March	319,630	0	38,565	358,195
April	309,964	34,342	33,850	378,156
May	312,012	33,132	26,163	371,307
June	322,164	29,694	14,188	366,046
July	322,280	29,810	24,320	376,410
August	389,753	42,086	39,774	471,613
September	414,980	41,657	58,223	514,860
October	303,716	31,458	38,262	373,436
November	338,940	49,607	45,699	434,246
December	344,596	30,976	41,569	417,141
Total	3,638,015	322,762	380,468	4,341,245
Monthly Average	330,729	35,862	34,588	394,659

Table 11. Chemical Usage and Cost

Month (1983)	Chemical									
	Na ₂ O ₂ (lb)	NaOH (gal)	NaOCl (gal)	H ₂ SO ₄ (gal)	FeSO ₄ (lb)	Na ₂ S (lb)	Polymer (pp)	H ₂ O ₂ (gal)		
February	31.0	61.0	0.75	1.85	116	5.25	3.30	-		
March	35.2	121.8	4.3	15.25	308	10.3	1.59	11.2		
April	38.0	96.0	112.0	27.0	101	22	2.0	10.0		
May	25.2	69.0	75.1	96.0	142	29.0	1.3	11.4		
June	18.1	79.1	102.3	19.1	117	51.9	1.2	10.8		
July	11.5	103.0	114	11.0	88	37.0	0.75	10.6		
August	12.6	112.0	99.3	19.1	44.5	57.1	1.7	13.4		
September	68.7	138.1	141.1	36.8	62.8	25.2	1.9	13.6		
October	37.8	79.6	130.1	20.2	14.9	23.5	1.25	9.7		
November	75.0	89.0	126.0	30.0	121.0	55.0	1.25	10.8		
December	17.3	79.1	52.2	21.6	66.5	46.8	1.3	12.0		
Total	500.1	1031.3	991.2	313.5	1511.7	366.05	17.54	113.5		
Monthly Average	45.5	93.8	90.1	28.5	137.1	33.3	1.59	10.3		
Cost (\$/1000 gal)	0.03	0.30	0.32	0.06	0.02	0.02	0.01	0.06		

Table 15. Treatment Chemicals and Sludge Disposal Costs

Month (1983)	Wastewater Treated (gal)	Dewatered Sludge 55-gal Drums)	Cost(\$)				Per 1000 gal Wastewater
			Chemicals	Sludge* Disposal	Total	Per 1000 gal Wastewater	
February	279,835	3.0	184.28	180.00	364.28	1.30	
March	358,195	3.5	280.85	210.00	490.85	1.37	
April	378,156	4.5	419.29	270.00	689.29	1.82	
May	371,307	3.5	356.95	210.00	566.95	1.53	
June	366,046	3.0	337.18	180.00	517.18	1.41	
July	376,410	2.5	362.44	150.00	512.44	1.36	
August	471,613	4.5	380.57	270.00	650.57	1.38	
September	514,860	3.5	495.48	210.00	705.48	1.37	
October	373,436	2.5	359.61	150.00	509.61	1.36	
November	431,246	2.0	414.72	120.00	534.72	1.23	
December	417,441	2.5	297.32	150.00	447.32	1.07	
Totals	4,341,245	35.0	3,888.69	2,100.00	5,988.69	1.38	

*Based on a disposal cost of \$600.00 per 55-gal drum paid by TOAD.

Table 16. Sludge Extraction Procedure Results

Metal (mg/l)	Procedure* and Sample Date (1983)		EPA		B		EPA/B		EPA/B	
	RCRA Limit		6 Apr	16 Jul	22 Jul	6 Sep	25 Oct	4 Nov		
Arsenic	5.0		<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	
Barium	100		<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	
Cadmium	1.0		32.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
Chromium, Total	5.0		<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	
Lead	5.0		3.87	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	
Mercury	0.2		<0.02	N.D.**	N.D.	N.D.	N.D.	N.D.	N.D.	
Selenium	1.0		<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	
Silver	5.0		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	

*Procedure: EPA = Environmental Protection Agency.

B = Battelle.

**N.D. = Not determined.

IV. DISCUSSION

8. General. The process upon which the TOAD metal-finishing wastewater treatment system is based is generally referred to as sulfide precipitation. It is one of a number of processes available for removing toxic, heavy metals from metal-finishing process wastewater. The most widely used process currently used for this purpose is the hydroxide process. This process uses 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 involved exhibit their minimum solubility. The metals are precipitated as metal hydroxides and are removed after flocculation, sedimentation, and filtration of any solids carried over from a sedimentation basin. In the case of the sulfide process, the metals are precipitated by the addition of a soluble sulfide such as sodium sulfide (Na_2S) or sodium bisulfide (NaHS), or an insoluble sulfide such as ferrous sulfide (FeS).

In comparing hydroxide precipitation with sulfide precipitation, a number of advantages of the sulfide process can be pointed out. Most heavy metal sulfides have lower solubilities than do corresponding metal hydroxides. In the case of metal hydroxides, the minimum solubilities of different metals occur at different pH values. Because of the amphoteric nature of some metal hydroxides where the minimum solubility is confined to a narrow pH range, the removal of metal from a mixed-metal wastewater by hydroxide precipitation is not always satisfactory. This can readily be seen by reference to Figure 9 which shows the solubilities of metal hydroxides and sulfides as a function of pH.

Other advantages can be cited. Sulfide precipitation, unlike hydroxide precipitation, is relatively insensitive to the presence of certain complexing and chelating agents often used in metal-finishing operations. Another is that hexavalent chromium can be reduced by the sulfide ion to trivalent chromium in the presence of ferrous ion. As noted under *Treatment Process Description*, paragraph 5, this advantage is incorporated in the TOAD system as a back up to insure that Cr (VI) is reduced to Cr (III), if for any reason the chromium reduction unit is performing abnormally. With regard to sludge produced in the two processes, the metal sulfide sludges are more readily dewatered to a higher solids content, and the volume of sludge generated/unit weight of metal removed is markedly less in the case of metal sulfide sludges.

The two processes using sulfide precipitation are generally referred to as the "soluble sulfide" process and the "insoluble sulfide" process. The main difference in the two processes is the manner in which the sulfide ion is added to the wastewater. In the insoluble sulfide process, a slightly soluble ferrous sulfide slurry produced by the in-situ reaction of ferrous sulfate and sodium sulfide is added to the wastewater to supply the sulfide ion needed for precipitation. In the soluble sulfide process, the sulfide ion is provided by the addition of a solution of sodium sulfide or sodium hydrosulfide.

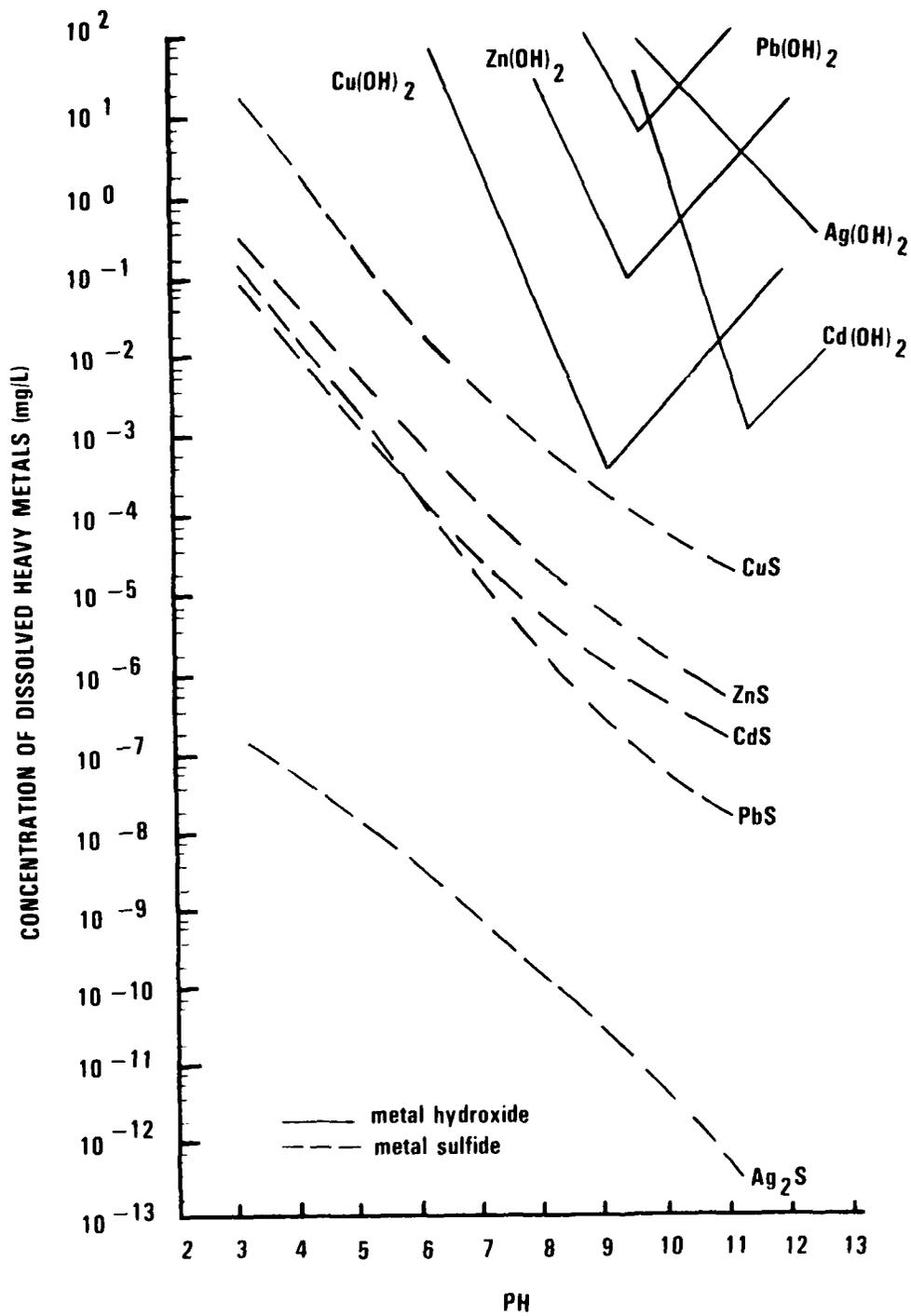


Figure 9. Heavy metal hydroxide and sulfide solubilities vs pH.

In the treatability study conducted in 1979, a number of advantages of the soluble sulfide process over the insoluble sulfide process were cited. This study was conducted with synthetic metal-bearing rinsewaters prepared with laboratory-grade reagents and with simulated wastewaters prepared by mixing and diluting samples from the actual plating and metal-finishing baths in use at TOAD. The study report indicated that although Na_2S , NaHS, and colloidal FeS are all effective in precipitating heavy metals, the use of colloidal FeS as the precipitating agent has several disadvantages. These include higher operating costs, more sludge generation, greater operational complexity, and problems of control with highly variable contaminant loadings. The report concluded that for an automatic system, the soluble sulfide process, using either Na_2S or NaHS should be designed for TOAD. It also recommended that: (1) a separate chromium reduction step using sodium metabisulfite be used; (2) an anionic polyelectrolyte flocculant be used as a flocculant aid; (3) a polishing filter be used following sedimentation; (4) a filter press be used for sludge dewatering.

9. System Start up. A review of the analytical data generated during the 10-day start up of the system indicates that the system was producing an effluent with pollutant concentrations well within design specifications in all cases except aluminum. This was due to unexpected high levels of aluminum in the influent to the system combined with some equipment problems which have since been rectified. It should be noted that the most recent Federal standards,¹¹ in contrast to earlier standards proposed at the time the TOAD system design specifications were prepared, no longer contain either a tin or an aluminum standard. The decision not to include an aluminum limit in the latest standards was probably based on the fact that any aluminum in the system effluent being discharged to the sanitary sewer would be settled out as aluminum hydroxide in the primary clarifier of the sewage treatment plant with no adverse effect. Therefore, any excursion of the aluminum concentration outside of the original design standards need not be considered significant.

10. Army Environmental Hygiene Agency (AEHA) Survey Findings. The essential findings of this 10-day survey taken from the survey report are as follows:

The MFWPP is meeting its design limitations, with the exception of the aluminum and lead limits. The high lead level was due to a temporary excursion that was corrected. The aluminum level was due to poor solids removal.

The MFWPP is complying with the newly promulgated Federal Metal-Finishing Categorical Effluent Limitations, with the exception of the lead and pH limits. The lead non-compliance was due to a temporary excursion and has been corrected. The pH non-compliance was due to overly concentrated caustic.

¹¹ "Final Rules, Electroplating and Metal Finishing Point Source categories: Effluent Limitations Guidelines, Pretreatment Standards and New Source Performance Standards," 48 Federal Register (FR) 32,462 (15 Jul 83).

A large volume of metal-finishing rinsewater is being discharged untreated to the sanitary sewer, because the current rinsewater flow exceeds the MFWPP design capacity. This untreated rinsewater has caused the sewage treatment plant to exceed the proposed cadmium limit in its discharge permit and has probably inhibited the STP's ammonia removal and anaerobic digestion.

The overall performance of the MFWPP is adequate. There are, however, several operation, maintenance, and design problems that are hindering the plant's reliability.

The operations and maintenance of the MFWPP needs to be improved. This is due mainly to inadequate training and a poor Operations and Maintenance (O&M) manual.

A number of deficiencies have been identified and various corrective actions recommended.

A review of the findings and the detailed analytical data presented in the survey report indicated that the treatment process, per se, was effectively accomplishing cyanide and metals removal. The average values of metal content for the five complete analyses of the plant effluent were all within design and Federal regulatory requirements, except for aluminum and lead. It should be noted that the lead non-compliance was observed in only the first sample taken. Very low levels of lead were determined in the remainder of samples taken during the survey. The high aluminum concentrations and pH values were caused by the use of an exceedingly high concentration of NaOH in the NaOH solution fed to the neutralization tank. The concentration of NaOH has been adjusted, and a pH of 8.0 is maintained to minimize or prevent the discharge of excessive amounts of aluminum from the system. The reason why the aluminum values are of little significance has been discussed in *System Start up*, Paragraph 9.

With regard to excessive flow from the plating shop, it should be noted that rinsewater flow control devices were installed in many of the rinse tanks before the wastewater-treatment system was installed. The maintenance of these devices, which are designed to reduce flows to well within MFWPP design specifications, is the responsibility of the plating shop personnel. Proper operation and maintenance of these rinsewater control devices can markedly reduce the volume of wastewater generated to well below the level on which the design of the treatment system was based.

The deficiencies noted in the survey report related to such rectifiable items as pipe leaks, a pump and air-operated valve malfunction, an inoperative hydrogen cyanide gas alarm, and missing self-contained emergency respirators. These deficiencies are being corrected.

As part of the survey, limited testing of sludge was carried out. A sample of dewatered sludge discharged from the filter press contained 23 percent dry solids. Another dewatered sludge sample was subjected to the standard EPA leaching test to determine the toxicity of the sludge. The leachate analysis showed a cadmium content of 32 mg/l Cd. This value far exceeds the permissible (RCRA) limit of 1 mg/l Cd for non-hazardous sludge and indicates that the sludge must be disposed of as a hazardous material in a controlled landfill.

The O&M of the system has improved considerably since the AEHA survey which was conducted shortly after the system was installed. The system operators are alternating sewage plant operators who were trained by the contractor during the system start up. With added experience, the operators are now operating and maintaining the system with ease. The O&M manual is a standard commercial manual which contains the following sections: General Description; Process; Equipment; Chemicals; Operations; Trouble Shooting; and Manufacturers' Manuals. The Manufacturers' Manuals section contains detailed installation, maintenance, and repair instructions for the system pumps, mixers, flow gauges, pressure regulators, pH and ORP meters, and controllers, and filter press. Although considerable information on the componentry of the system is presented, the O&M manual needs to be improved in the areas of safety, emergency operating procedures, and preventive maintenance.

11. Belvoir Monitoring Program. A review of the results of the analyses of the processed wastewater and the sludge samples taken during July through December 1983 indicated that the system performed very well and produced an effluent with pollutant levels well below the maximums specified in the EPA Pretreatment Standards for Existing Sources. The cyanide destruction unit, using alkaline chlorination, effectively destroyed the cyanide. The chromium reduction unit, using sodium metabisulfite and sulfuric acid, effectively reduced the hexavalent chromium to trivalent chromium. In a few cases when the hexavalent chromium concentrations in the feed water were below 1.0 mg/l and reduction was not complete, subsequent treatment with sodium sulfide and ferrous sulfide accomplished essentially complete reduction. The chromium was then removed as chromium hydroxide to undetectable levels as indicated in the analysis of water samples from the clearwell.

The low suspended solids found in the clearwell samples (except for one sample) indicated that the flocculant aid (Kronofloc) and ferrous sulfate were effectively agglomerating the colloidal metal sulfides so that they could be removed well in the laminar plate settler and the polishing dual-media filter.

The only metal not removed from the wastewater to the design specification level of 1.0 mg/l was aluminum. Specifications for the system design called for an effluent with characteristics conforming to federal standards proposed in 1979 specifying a maximum concentration of aluminum of 1.0 mg/l. Because aluminum in the treated water discharged to the sanitary sewer will have no adverse effect on the sewage plant operation, the recently published federal regulations (July 1983) no longer contain a standard for aluminum. Nine samples of acid/alkali wastewater were found to contain aluminum in concentrations ranging from 5 mg/l to 50 mg/l, with an average of 14 mg/l. The concentrations of aluminum found in the system effluent ranged from 1 mg/l to 18 mg/l with an average of 4 mg/l for the 12 samples analyzed. Although these aluminum concentrations in the effluent exceeded the design specified value of 1.0 mg/l, the effluent characteristics were in compliance with current federal regulations. The high aluminum concentrations in the system effluent regulations. The high aluminum concentrations in the system effluent samples were probably due to the pH of the effluent which was between 7 and 9. Aluminum hydroxide is an amphoteric compound with minimum solubility between 5.5 and 6. Current Federal regulations specify a pH between 6 and 9.

It should be noted that no odor problem was encountered. Maintaining the pH at 8, controlling the sodium sulfide addition with a reliable sulfide probe and controller, and adding ferrous sulfate prevented the generation of any hydrogen sulfide odor.

Sixteen samples of the system effluent, analyzed for oil and grease (Table 10) indicated an average value of 12.8 mg/l for these contaminants. The federal standard is 26.0 mg/l.

A summary of operating data for the months of February 1983 through December 1983 is given in Tables 12 through 15. The total volume of wastewater treated during this period was 4,341,245 gal. This volume consisted of 322,762 gal of cyanide bearing water, 380,468 gal of chromium bearing water, and 3,638,015 gal of acid/alkali water. During this monitoring period, the system was operated for 2,248 h and produced thirty-five 55-gal drums of dewatered sludge which averaged 22.4 percent in dry solids content. It should be noted that the volume of sludge generated is small, amounting to 44 gal/100,000 gal of wastewater treated. This has important implications regarding the cost of sludge disposal which is based on the volume of sludge handled. Sludge disposal cost is an important element in the overall treatment process evaluation. The low volume of dewatered sludge can be attributed to a relatively low concentration of metals in the system feedwater, probably resulting from excessive use of rinsewater, and the effective dewatering of sludge by the filter press.

The amounts of chemicals used during the 11-month monitoring period are given in Table 14. Calculations based on the total flow of wastewater treated and chemicals used in treatment indicate that chemical dosages of ferrous sulfate, sodium sulfide, and polymer were 41.3 mg/l, 10.0 mg/l, and 1.0 mg/l, respectively. The dosage of sulfide ion was, accordingly, 4.1 mg/l.

The costs for chemicals used in the treatment process and sludge disposal are given in Table 15 and Appendix D. Costs/1000 gal of wastewater treated each month are shown in Figure 10. The average chemical costs for the 11-month period was \$0.89/1000 gal of wastewater treated. Cost for the disposal of the thirty-five 55-gal drums of sludge generated during the 11-month period totaled \$2100.00 with an average cost/1000 gal of wastewater of \$0.49. These disposal cost calculations are based on the cost of \$60.00/55-gal drum currently being paid by TOAD. The combined costs for chemical and sludge disposal/1000 gal of wastewater treated during the 11-month period ranged from \$1.07 to \$1.82, with an average of \$1.38.

Five samples of dewatered sludges were subjected to leaching tests. Three of the samples were extracted by both the EPA and Battelle extraction procedures. The other two samples were subjected to the Battelle procedure only. Both procedures are essentially the same, except for pH of the extracting medium. The EPA procedure employs distilled water with pH adjusted to 5.0. The Battelle procedure uses distilled water without pH adjustment. Analysis of the leachates from all five samples indicated that all metal concentrations were below detectable limits. Mercury was not determined because of improper sample preservation. Table 16 shows the results of the sludge extraction tests. It should be noted that during the AEHA Survey, a single sample of sludge subjected to the EPA extraction procedure yielded a leachate containing 32 mg/l cadmium. All other metals were within RCRA limits. On the basis of the results of this single AEHA test, the sludge must be considered a hazardous material as defined by the RCRA regulations. However, in view of the results obtained in the tests of five sludge samples during the Belvoir monitoring program, where all metals were below detectable levels in the leachate, the question of whether the sludge is or is not hazardous warrants further investigation.

12. Summation. The successful operation of the metal-finishing wastewater treatment system at the Tobyhanna Army Depot has provided a full-scale demonstration of the effectiveness of a metal sulfide precipitation process using sodium sulfide. The combination of unit processing involving cyanide destruction, chromium reduction, pH adjustment, addition of sodium sulfide, ferrous sulfate, and an anionic polymer, followed by solids separation has consistently produced a treated effluent meeting Federal Metal-Finishing Categorical Effluent Limitations. Solids processing which included sedimentation in a laminar plate settler, sludge compaction in a gravity sludge thickener, and sludge dewatering in a filter press produced a dewatered sludge with an average of 22.4 percent dry solids content.

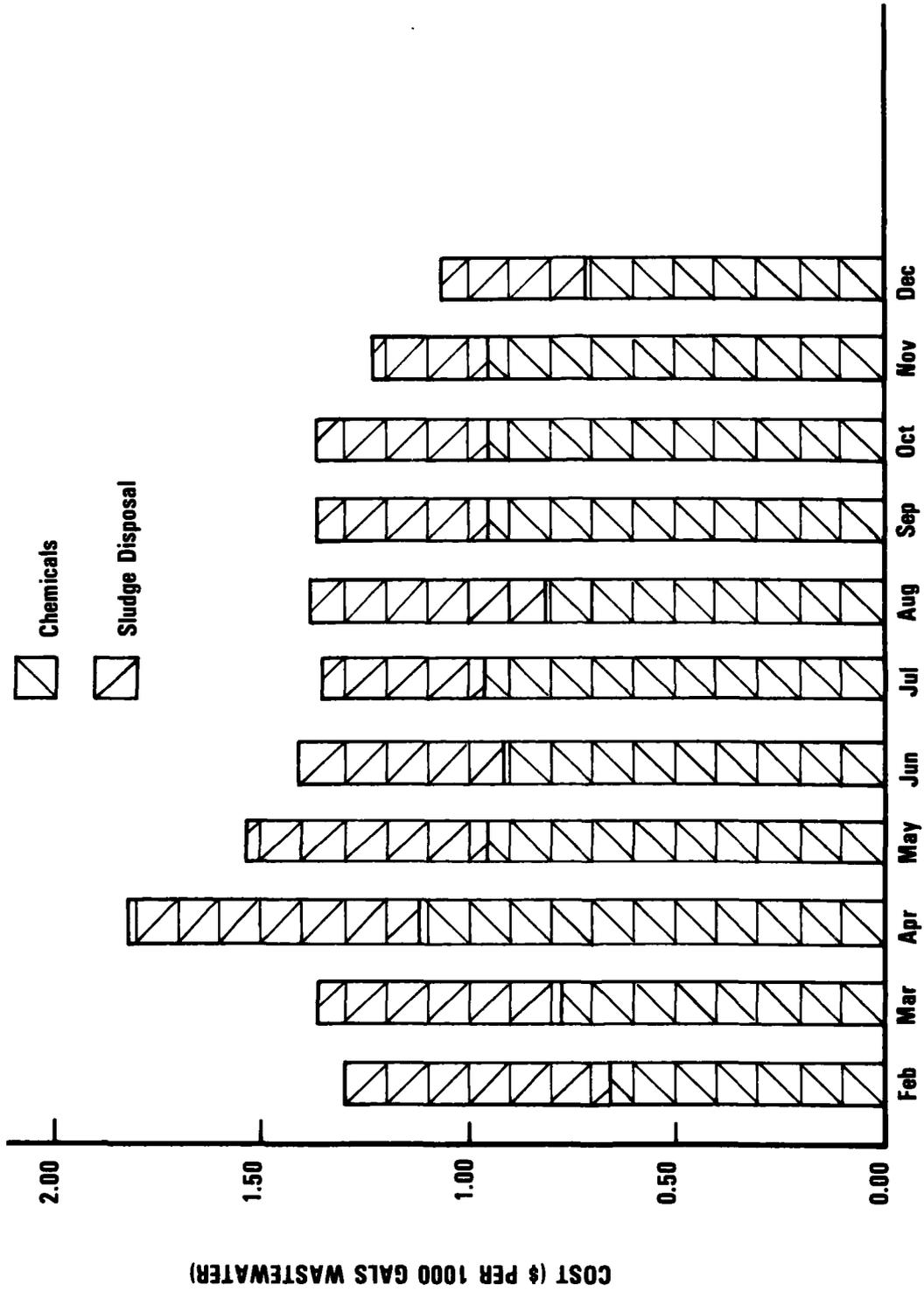


Figure 10. Chemical and sludge disposal costs.

The Tobyhanna Army Depot is the first Army installation engaged in metal-finishing using this sodium sulfide treatment process. In a recent survey¹² of 23 Army installations performing metal-finishing conducted by the U.S. Army Mobility Equipment Research and Development Command (now Belvoir R&D Center), it was determined that many of these installations use hydroxide precipitation. It is possible that some of these installations may be experiencing difficulties in meeting the recently promulgated federal or state pretreatment standards. If so, these installations could possibly upgrade their treatment systems with minimal cost by converting their hydroxide process to a sulfide process similar to the one used at the Tobyhanna Army Depot. This could be accomplished with minor changes in their existing equipment to provide for the addition of sodium sulfide, ferrous sulfate, and an anionic polymer, if such a polymer is not already being used. A survey of Army installations engaged in metal-finishing operations appears advisable to determine how the technology demonstrated at the Tobyhanna Army Depot could be used to upgrade treatment systems needing improvement.

V. CONCLUSIONS

13. Conclusions. Based on the results obtained in this investigation the following conclusions are drawn:

a. The metal-finishing wastewater treatment system installed at the Tobyhanna Army Depot using cyanide destruction by alkaline chlorination, chromium reduction with sodium metabisulfite, and metal sulfide precipitation by sodium sulfide addition is an effective process for the treatment of metal-finishing wastewaters.

b. The sulfide treatment system can produce an effluent complying with federal standards defined in "Final rules, Electroplating and Metal-Finishing Point Source Categories; Effluent Limitations Guidelines, Pretreatment Standards and New Source Performance Standards," *Federal Register* (FR) 32462, 15 July 1983."

c. The metal sulfide sludge produced by the sulfide treatment system can be dewatered to 32 percent dry solids content. The average value determined was 24.4 percent.

d. The dewatered sludge produced at TOAD is minimal, amounting to 44 gal/100,000 gal of wastewater treated.

e. The sludge generated by the sulfide treatment process must be disposed of as hazardous material as defined in the Resources Conservation and Recovery Act (RCRA) regulations.

f. Costs for chemicals and sludge disposal add up to a combined cost of \$1.38/1000 gal of TOAD metal-finishing wastewater treated. Chemical costs averaged \$0.89/1000 gal, and sludge disposal costs averaged \$0.49/1000 gal.

¹² P. Gail Chesler, P.E., "Plating Wastes Survey," AD A125230 (Nov 83).

APPENDIX A

SYSTEM STARTUP - ANALYTICAL DATA

Pollutant Parameter (mg/l)	Sample	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Day 9	Day 10	Avg.
Cyanide	INF.	1.00	0.50	1.17	8.0	1.70	1.57	1.04	1.48	0.624	0.654	1.08
	EFF.	0.048	0.011	<0.005	N.D.**	0.018	<0.005	0.18	0.041	0.37	0.043	0.08
Copper	INF.	6.19	3.57	2.53	1.35	1.50	1.80	*	1.42	2.25	0.56	2.35
	EFF.	0.26	0.13	0.56	0.31	0.04	0.48	*	0.17	0.12	0.12	0.24
Nickel	INF.	4.85	1.97	1.04	1.20	0.91	1.08	*	1.59	1.02	0.81	1.61
	EFF.	0.10	0.15	0.43	0.39	<0.04	0.11	*	0.12	0.10	0.07	0.17
Chromium (Total)	INF.	0.82	1.82	0.81	0.21	1.62	0.95	*	1.13	1.65	1.21	1.14
	EFF.	0.06	<0.05	<0.05	<0.05	0.12	0.11	*	0.31	0.17	0.12	0.16
Zinc	INF.	2.88	8.79	1.57	1.10	0.81	1.21	*	1.20	2.63	10.4	3.40
	EFF.	0.07	0.29	0.99	0.55	0.02	0.01	*	<0.01	0.57	0.27	0.31
Lead	INF.	0.40	0.56	0.48	0.31	0.24	0.65	*	0.33	0.68	0.21	0.43
	EFF.	0.14	<0.10	0.11	<0.10	0.11	0.20	*	0.15	0.31	0.14	0.15
Cadmium	INF.	1.99	1.65	0.84	2.23	0.82	2.07	*	1.26	0.65	0.57	1.34
	EFF.	0.03	0.09	0.56	0.65	0.01	0.02	*	0.02	0.06	0.06	0.17
Aluminum	INF.	3.90	5.64	3.43	3.54	6.50	7.96	*	10.1	14.4	4.54	6.67
	EFF.	1.49	0.91	0.68	0.31	2.79	3.80	*	4.73	3.68	1.10	2.17
Tin	INF.	0.067	0.042	0.061	.032	0.017	0.030	*	0.017	0.021	0.009	0.003
	EFF.	<0.002	<0.002	<0.002	<0.002	<0.002	<0.003	*	<0.002	0.006	0.003	<0.003
Sulfide	INF.	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
	EFF.	<0.03	11.7	<0.03	<0.03	0.20	0.30	*	1.00	0.92	<0.03	1.58
pH (units)	EFF.	7-8	6-9	5-6	5-6	8-9	8-9	8-9	8-9	8	N.D.	N.D.

*Samples taken but not analyzed due to equipment problems.

**N.D. - Not determined.

APPENDIX B
Belvoir Monitoring Program—Analytical Results

Sample* Point	Metal Concentration (mg/l)									
	Cd	Cr	Cu	Pb	Ni	Ag	Sn	Zn	Al	
12 July 1983 Samples										
1	N.D.	0.78	5.30	N.D.	N.D.	<0.01	N.D.	N.D.	N.D.**	
2	1.14	3.00	0.40	1.05	1.05	<0.01	0	0.17	N.D.	
4	2.60	0.34	1.47	0.20	0.20	<0.01	0	0.27	N.D.	
5	0.53	4.55	0.14	0.55	0.55	<0.01	0	0.14	N.D.	
3	0.81	1.50	0.44	3.90	3.90	<0.01	0	4.06	N.D.	
6	1.21	2.12	0.42	3.75	3.75	<0.01	0	3.75	N.D.	
10	0.07	0.40	0.12	0.05	0.05	<0.01	0	0.27	N.D.	
19 July 1983 Samples										
1	6.96	1.05	5.42	0.04	0.25	0.47	<1.0	0.06	N.D.	
2	0.74	16.22	0.74	0.02	0.12	0.08	<1.0	1.11	N.D.	
4	0.62	0.35	5.00	<0.01	0.08	0.07	<1.0	0.09	N.D.	
5	0.54	15.47	0.45	<0.01	0.12	0.04	<1.0	0.68	N.D.	
3	1.08	1.22	1.15	0.79	6.25	0.02	<1.0	5.67	N.D.	
6	1.32	7.68	1.07	0.62	4.45	0.05	<1.0	5.47	N.D.	
10	0.06	0.13	0.03	0.09	0.02	0.01	<1.0	0.09	N.D.	
02 August 1983 Samples										
1	8.11	0.70	6.08	0.1	0.40	0.16	<1.0	0.79	N.D.	
2	1.77	3.56	0.75	0.2	3.00	0.02	<1.0	0.69	N.D.	
4	2.90	0.23	1.75	0.1	0.35	0.02	<1.0	0.14	N.D.	
5	1.12	8.26	0.10	0.2	1.00	0.01	<1.0	2.18	N.D.	
3	1.15	0.30	2.00	0.7	4.55	0.01	<1.0	6.73	N.D.	
6	2.58	2.32	1.60	1.5	3.00	0.01	<1.0	7.59	N.D.	
10	0.19	1.15	0.10	1.0	0.35	0.01	<1.0	2.69	N.D.	

*Sample Code: (see Figure 7)

- 1 = Cn Unit Influent
- 2 = Cr Unit Influent
- 4 = Cn Unit Effluent
- 5 = Cr Unit Effluent
- 3 = Acid/Alkali Wastewater
- 6 = Surge Tank Effluent
- 10 = Clearwell Water

**N.D. = Not Determined.

APPENDIX B (cont'd)
Belvoir Monitoring Program—Analytical Results

Sample Point	Metal Concentration (mg/l)									
	Cd	Cr	Cu	Pb	Ni	Ag	Sn	Zn	Al	
09 August 1983 Samples										
1	5.65	0.44	4.96	<0.1	0.14	0.53	<1.0	0.39	N.D.	
2	0.48	3.00	0.17	<0.1	1.38	0.09	<1.0	0.21	N.D.	
4	4.03	0.43	2.62	<0.1	0.05	0.20	<1.0	0.27	N.D.	
5	0.43	1.86	0.18	<0.1	3.80	<0.01	<1.0	0.56	N.D.	
3	0.48	1.05	0.74	1.7	2.57	0.02	<1.0	5.47	N.D.	
6	4.48	3.05	4.62	2.0	7.28	0.13	<1.0	5.57	N.D.	
10	0.04	0.04	0.03	<0.1	0.01	<0.01	<1.0	0.09	3	
23 August 1983 Samples										
1	6.56	1.76	3.57	<0.1	0.13	0.05	<1.0	0.84	N.D.	
2	0.80	32.0	0.54	<0.1	0.53	0.01	<1.0	0.83	N.D.	
4	2.50	1.35	1.17	<0.1	0.06	0.05	<1.0	0.26	N.D.	
5	0.36	6.38	0.26	<0.1	0.40	0.02	<1.0	0.21	N.D.	
3	1.14	0.29	4.05	0.4	14.5	0.03	<1.0	2.37	N.D.	
6	1.00	0.94	3.05	0.1	7.70	0.02	<1.0	1.64	N.D.	
10	0.06	0.36	0.05	<0.1	0.05	<0.01	<1.0	0.11	6	
30 August 1983 Samples										
1	3.0	0.32	.022	<0.1	0.10	<0.01	<1.0	0.30	N.D.	
2	1.40	7.12	0.22	<0.1	0.22	<0.01	<1.0	0.29	N.D.	
4	0.58	0.94	1.44	<0.1	0.13	<0.01	<1.0	0.37	N.D.	
5	1.34	7.40	0.26	<0.1	0.30	<0.01	<1.0	0.32	N.D.	
3	0.68	1.23	1.24	2.8	2.33	<0.01	<1.0	6.59	N.D.	
6	1.66	2.33	0.77	0.1	0.98	<0.01	<1.0	3.08	N.D.	
10	0.05	0.22	0.05	<0.1	0.03	<0.01	<1.0	0.16	3	

APPENDIX B (cont'd)
Belvoir Monitoring Program—Analytical Results

Sample Point	Metal Concentration (mg/l)									
	Cd	Cr	Cu	Pb	Ni	Ag	Sn	Zn	Al	
06 September 1983 Samples										
1	—	Not Sampled	—	<0.1	—	—	<1.0	—	—	—
2	0.51	3.90	0.45	<0.1	0.15	0.01	<1.0	5.70	N.D.	3
4	0.13	0.30	0.02	<0.1	<0.01	0.07	<1.0	<0.01	N.D.	
5	0.67	8.10	0.22	<0.1	0.15	0.01	<1.0	0.71	N.D.	
3	1.50	0.20	1.45	0.2	3.50	0.03	<1.0	0.30	N.D.	
6	2.60	2.00	2.10	0.3	2.80	0.05	<1.0	5.20	N.D.	
10	0.10	0.15	0.01	<0.1	0.05	<0.01	<1.0	0.01	N.D.	
20 September 1983 Samples										
1	—	Not Sampled	—	<0.1	—	—	<1.0	—	—	—
2	1.20	4.80	0.55	<0.1	0.22	<0.01	<1.0	0.42	N.D.	
4	0.13	0.33	0.01	<0.1	<0.01	<0.01	<1.0	<0.01	N.D.	
5	0.88	3.60	0.27	<0.1	0.15	<0.01	<1.0	0.28	N.D.	
3	1.80	0.70	0.80	0.1	2.85	<0.01	<1.0	6.90	N.D.	
6	1.52	1.58	0.98	0.5	2.34	<0.01	<1.0	5.50	N.D.	
10	0.25	0.50	0.04	0.2	0.07	<0.01	<1.0	0.94	N.D.	18
27 September 1983 Samples										
1	—	Not Sampled	—	<0.1	—	—	<1.0	—	—	—
2	1.37	3.52	0.25	<0.1	0.30	<0.01	<1.0	0.65	N.D.	
4	0.05	0.42	<0.01	<0.1	<0.01	<0.09	<1.0	<0.01	N.D.	
5	1.19	7.10	0.20	<0.1	0.70	<0.01	<1.0	<0.72	N.D.	
3	2.35	0.64	2.35	1.0	2.20	<0.01	<1.0	14.60	N.D.	
6	2.82	0.28	1.65	<0.1	3.25	0.03	<1.0	8.90	N.D.	
10	0.08	0.08	0.01	<0.1	0.01	<0.01	<1.0	<0.01	N.D.	2

APPENDIX B (cont'd)
Belvoir Monitoring Program—Analytical Results

Sample Point	Metal Concentration (mg/l)									
	Cd	Cr	Cu	Pb	Ni	Ag	Sn	Zn	Al	
18 October 1983 Samples										
1	5.40	0.04	3.20	<0.1	0.15	<0.01	<1.0	<0.01	N.D.	
2	1.14	9.80	0.30	<0.1	0.85	<0.01	<1.0	<0.01	N.D.	
4	0.02	0.03	<0.01	<0.1	0.02	<0.01	<1.0	<0.01	N.D.	
5	1.14	8.10	0.23	<0.1	0.75	<0.01	<1.0	<0.01	N.D.	
3	1.11	0.45	3.00	0.1	2.65	<0.01	<1.0	3.10	N.D.	
6	2.75	3.00	4.30	0.9	4.62	0.03	<1.0	7.50	N.D.	
10	0.04	0.15	0.05	<0.1	0.06	<0.01	<1.0	0.05	N.D.	3
25 October 1983 Samples										
1	—	Not Sampled	—	—	—	—	—	—	—	—
2	0.70	2.10	0.20	<0.1	1.25	<0.01	<1.0	0.31	N.D.	
4	0.05	0.30	1.20	<0.1	0.03	<0.01	<1.0	<0.01	N.D.	
5	0.67	1.35	0.15	<0.1	1.30	<0.01	<1.0	0.22	N.D.	
3	0.18	0.21	0.40	0.2	0.95	<0.01	<1.0	0.87	N.D.	
6	0.42	0.92	0.42	0.2	3.45	<0.01	<1.0	0.88	N.D.	
10	0.14	0.37	0.05	0.3	0.10	<0.01	<1.0	0.41	N.D.	4

APPENDIX B (Cont'd)
 Belyoir Monitoring Program—Analytical Results

Sample Point	Metal Concentration (mg/l)									
	Cd	Cr	Cu	Pb	Ni	Ag	Sn	Zn	Al	
07 November 1983 Samples										
1	—	Not Sampled	—	—	—	—	—	—	—	—
2	0.41	1.00	0.12	<0.1	0.43	<0.01	<1.0	0.12	N.D.	
4	0.03	0.20	<0.01	<0.1	0.02	<0.01	<1.0	<0.01	N.D.	
5	0.45	2.50	0.14	<0.1	0.71	<0.01	<1.0	0.18	N.D.	
3	0.41	0.82	0.50	1.5	0.63	<0.01	<1.0	7.0	N.D.	
6	1.02	0.90	0.73	0.7	1.23	<0.01	<1.0	6.2	N.D.	
10	0.06	0.14	0.02	<0.1	0.04	<0.01	<1.0	0.06	N.D.	
15 November 1983 Samples										
1	—	Not Sampled	—	—	—	—	—	—	—	—
2	0.88	31.5	0.40	<0.1	0.19	0.03	<1.0	0.66	N.D.	
4	—	Not Sampled	—	—	—	—	—	—	—	—
5	0.75	19.3	0.23	<0.1	0.17	0.02	<1.0	0.43	N.D.	
3	0.76	0.40	0.26	0.6	0.37	0.01	<1.0	2.60	N.D.	
6	3.6	5.00	2.85	1.6	2.35	0.03	<M1.0	8.70	N.D.	
10	0.07	0.40	0.02	0.2	0.08	0.01	<1.0	0.28	N.D.	3
22 November 1983 Samples										
1	—	Not Sampled	—	—	—	—	—	—	—	—
2	0.19	6.70	0.04	0.1	0.14	0.01	<1.0	0.01	N.D.	
4	1.37	0.31	0.59	0.1	0.12	0.06	<1.0	5.20	N.D.	
5	0.17	7.00	<0.01	<0.1	0.36	<0.01	<1.0	0.05	N.D.	
3	0.18	4.00	0.39	7.6	0.22	0.01	<1.0	15.10	N.D.	
6	1.87	4.50	0.92	2.3	1.83	0.07	<1.0	11.3	N.D.	
10	0.13	0.45	0.02	0.4	0.08	<0.01	<1.0	0.63	N.D.	1

APPENDIX B (cont'd)
Belvoir Monitoring Program—Analytical Results

Sample Point	Metal Concentration (mg/l)									
	Cd	Cr	Cu	Pb	Ni	Ag	Sn	Zn	Al	
06 December 1983 Samples										
1	—	Not Sampled	—	<0.1	—	—	—	—	—	—
2	0.75	22.5	0.10	<0.1	0.18	<0.01	N.D.	0.35	N.D.	—
4	—	Not Sampled	—	—	—	—	—	—	—	—
5	1.10	26.1	<0.01	<0.1	0.26	<0.01	N.D.	0.38	N.D.	—
3	0.68	0.47	0.76	0.1	0.20	<0.01	N.D.	0.50	N.D.	—
6	2.40	2.50	2.15	2.0	2.90	0.07	N.D.	12.0	N.D.	—
10	0.05	0.32	0.04	<0.1	0.05	<0.01	N.D.	0.08	N.D.	—
13 December 1983 Samples										
1	—	Not Sampled	—	—	—	—	—	—	—	—
2	0.66	2.30	0.04	<0.1	0.05	<0.01	<1.0	0.01	N.D.	—
4	0.02	0.01	<0.01	<0.1	<0.01	<0.01	<1.0	<0.01	N.D.	—
5	0.77	1.68	0.05	<0.1	0.07	<0.01	<1.0	0.01	N.D.	—
3	1.26	0.58	25.8	0.7	1.65	0.27	<1.0	3.6	N.D.	—
6	3.70	3.12	19.0	1.9	3.32	0.25	<1.0	10.0	N.D.	—

APPENDIX C

PROCESS EQUIPMENT

Component	Description	Number
a. Pumps		
(1) Sump Area		
Cyanide rinse	Serfilco H-2x1 1/2 CE, CE 3V (M1xM1) D3	1
Chromate rinse	Serfilco H-2x1 1/2 CE, CE 3V (M1xM1) D3	1
General rinse	Serfilco H-2x1 1/2 CE, CE 3V (M1xM1) D3	1
Surge tank	Serfilco HB1 1/2 CE-5-CRL-48-90-H1 1/2	1
(2) Chemical		
Sodium hydroxide I	Marsch TES-MD	1
Sodium hydroxide II	Liquiflo 32FS6333J with Reliance ¼-hp Minpak DC motor	1
Sulfuric acid I	Marsch-TE 5-MD	1
Sulfuric acid II	Marsch-TE 5-MD	1
Sodium metabisulfite	Marsch-TE 5-MD	1
Sodium hypochlorite	Marsch-TE 5-MD	1
Sodium sulfide	Marsch-TE 5-MD	1
Sodium sulfate	Marsch-TE 5-MD	1
Ferrous sulfate	Marsch-TE 5-MD	1
Polyelectrolyte II	Liquiflo 32FS6333J with Zeromax drive	1

APPENDIX C (cont'd)
PROCESS EQUIPMENT

Component	Description	Number
a. Pumps (cont'd)		
(3) Sludge		
Clarifier to thickener	Wilden M4 WO NENENE-air operated	1
Thickener to filter press	Wilden M4 WO NENENE-air operated	1
(4) Filter backwash	Pacific—15 hp	1
b. Flow Timers	Signet Model 309	4
c. Level Controls		
(1) Concentrated chemical	B+W Type L Control +2 probes	2
(2) Chemical-low level reagent	B+W Type 2L	7
(3) Chemicals-low, low level reagent	B+W Type 2R	7
d. Mixers		
(1) Chemical reagents (poly-electrolyte, ferrous sulfate, sodium sulfide, sodium metabisulfite)	Lightnin NC 4, ¼ hp, 3.6-in. prop. 4-ft shaft	4
(2) Reaction tanks Cyanide oxidation I & II Chromium reduction. Neutralization	Lightnin 1A, ¼ hp, 9.4-in. prop. 4-ft shaft	4

APPENDIX C (cont'd)
PROCESS EQUIPMENT

e. pH and ORP Measurement System (Leeds & Northrup):

(1) Cyanide oxidation:

pH meter—Model 7773-10-2-22-2-000 (glass pH electrode) 2

ORP meter—Model 7773-10-2-24-1-000 (gold ORP electrode) 2

(2) Chromium reduction:

pH meter—Model 7773-10-2-22-2-000 (glass pH electrode) 1

(3) Neutralization:

pH meter—Model 7773-10-2-00-2-000 with 11790 pH electrode,
special reference electrode for sulfide addition. 1

Sulfide probe—Model 117408 1

**APPENDIX D
CHEMICAL COSTS**

Chemical	Form Received	Unit	Unit Cost (\$)
Sodium Metabisulfite	Solid	lb	0.28
Sodium Hydroxide	50 percent solution	gal	1.27
Sodium Hypochlorite	Solution — 12.5 percent Cl ₂	gal	1.39
Sulfuric Acid	66° Be-liquid	gal	0.90
Ferrous Sulfate	Solid	lb	0.17
Sodium Sulfide	Solid, 61 percent flake	lb	0.29
Polymer (Kronofloc)	Liquid	qt	9.00
Hydrogen Peroxide	35 percent solution	gal	2.35

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