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PILOT FIELD VERIFICATION STUDIES OF THE SODIUM SULFIDE/FERROUS SULFATE TREATMENT PROCESS

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In a previous project, jar and dynamic testing showed that the sodium sulfide/ferrous sulfate process was a viable method for reducing hexavalent chromium and removing heavy metals from the Tinker AFB industrial wastewater with a significant decrease in sludge production and treatment costs. In this phase, pilot-plant field verification studies were conducted to evaluate the chemical and physical parameters of the chromium reduction process, the precipitation and clarification process, and the activated sludge system. Sludge production was evaluated and compared to the sulfuric acid/sulfur dioxide/lime process. The impact of and procedure for switchover to the sodium sulfide/ferrrous sulfate process were also investigated. In addition, the effects of orthophosphate, ethylenediaminetetraacetic acid, cyanide, additional metals, flow rate, and temperature on chromium reduction, metal removal, and the activated sludge system were evaluated.

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EXECUTIVE SUMMARY

The purpose of the project was to validate the sodium sulfide/ferrous sulfate method of reducing hexavalent chromium and removing heavy metals from electroplating rinsewater and industrial wastewater. In Phase I of this project, jar and dynamic testing showed the process to be viable for reducing hexavalent chromium and removing heavy metals from electroplating rinsewater and industrial wastewater (at Tinker AFB, Oklahoma) with a significant decrease in sludge production and treatment costs. In Phase II (reported here), pilot plant field verification studies were conducted to evaluate the chemical and physical parameters of the sodium sulfide/ferrous sulfate process, the precipitation and clarification process, and the activated sludge system.

A pilot-scale field verification unit was constructed at the Tinker AFB Industrial Waste Treatment Plant. The unit was designed as a scaled-down model of the Tinker AFB unit with the chromium reduction mixers, the solids contact clarifier, the activated sludge basin, and a final clarifier. The retention time and flow velocity were designed to represent 500,000 to 2,000,000 gal/day through the Tinker AFB Unit.

The process was optimized for sodium sulfide, ferrous sulfate, cationic polymer, and anionic polymer requirements, and pH requirements. The chemical requirements are listed in the following table. The pH of the influent had no effect on the process as long as it was maintained above 7.2. At lower pHs, hydrogen sulfide gas will be formed. The optimum pH after ferrous ion addition to mixer-2 was 7.2 to 7.5.

CHEMICAL REQUIREMENTS FOR THE TINKER AFB IWTP

Sodium Sulfide	2 mg/L S^{-2} per 1 mg/L Cr^{+6}
Ferrous Sulfate	1.5 mg/L Fe^{+2} per 1 mg/L Cr^{+6}
Betz 1195 Cationic Polymer	20 mg/L
Betz 1120 Anionic Polymer	0.5 mg/L
pH Mixer-2	7.2 - 7.5

The solids contact clarifier was optimized with the plant using the chemical feeds listed in the table. Clarification and metal removal could not be achieved unless the sludge depth was greater than the bottom of the intermediate ring of the solids contact clarifier so that the treated wastewater could be filtered through the sludge blanket to remove fine particulates. In addition, external sludge recirculation (10 to 20 percent of influent solid contact clarifier flow) is required, along with the internal sludge recirculation, to achieve 80 to 90 percent suspended solids in the inner mixer chamber (suspended solids was determined with a 5 minute settling test using 100 mL of the mixer chamber solution) in the mixing chamber, to achieve metal removal below NPDES permit requirements.

After the solids contact clarifier was operating at optimum conditions, the effect of orthophosphate (100 mg/L), ethylenediaminetetraacetic acid (50 mg/L), and mixed metal on chromium reduction was determined. With chemical feeds at the levels represented in the table and with the solids contact clarifier operated at optimum conditions, these additives had no effect on the chromium reduction, metal removal, or activated sludge. Influent wastewater temperatures from 41 to 95°F had no effect, nor did flows proportional to 500,000 and 2,000,000 gal/day.

Sludge production from the sodium sulfide/ferrous sulfate process was determined by filtering the sludge collected from the solids contact clarifier through a laboratory vacuum-drum filter and measuring the volume. In addition, the pilot unit was operated with the acid/sulfur dioxide/lime process for sludge production comparison between the two methods. There was an approximate 90 percent decrease in the sludge production with the sodium sulfide/ferrous sulfate process. The effect and procedure for the implementation of the sodium sulfide/ferrous sulfate process were determined.

Cost comparison of the sodium sulfide/ferrous sulfate process and the acid/sulfur dioxide/lime process shows a potential chemical treatment sludge removal savings of $317,781/yr if the sodium sulfide/ferrous sulfate process is implemented. These savings are based on the use of dry chemicals for the sodium sulfide/ferrous sulfate process and the treatment of 11,789 pounds of hexavalent chromium in 284,406,312 gallons of industrial wastewater at Tinker AFB in 1986 and the disposal of 2100 tons of sludge at $168/ton.

PREFACE

This report was prepared by Idaho National Engineering Laboratory, EG&G Idaho, Inc., P.O. Box 1625 Idaho Falls Idaho 83415 under Contract Number DE-AC07-76ID01570 for the Air Force Engineering and Services Center, (AFESC), Tyndall Air Force Base, Florida 32403-6001. Mr. Charles J. Carpenter was the Government technical program manager. This report summarizes work accomplished between 30 September 1987 and 30 May 1988.

This report has been reviewed by the Public Affairs Office and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical publication has been reviewed and is approved for publication.

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INTRODUCTION

A. OBJECTIVE

Electroplating facilities ranging from operations of three to four baths to those covering 40,000 square feet of floor space are operated by the United Stated Air Force (Reference 1). Principal contaminants in the wastewaters are chromium, nickel, copper, cadmium, lead and zinc. Engine cleaning and paint stripping processes also release heavy metals to the industrial wastewater. These wastes pose environmental hazards and must be treated to reduce the hexavalent chromium and precipitate the metals. The sludge from the treatment must be treated as a hazardous waste and thus, buried at chemical landfills. Conventional treatment methods result in large production of sludge. The purpose of this program was to determine the feasibility of the use of sodium sulfide and ferrous sulfate to reduce the hexavalent chromium, precipitate the metals, and decrease sludge production. Phase I investigated the use of this process in laboratory studies (jar tests and dynamic tests) on distilled water and Tinker Air Force Base (AFB) electroplating rinsewater and industrial wastewater. The purpose of Phase II was to determine the feasibility of the process in a pilot-scale field verification study using the influent to the Tinker AFB Industrial Waste Treatment Plant (IWTP).

B. BACKGROUND

The purpose of electroplating is to apply a protective metal coating to another metal. This requires surface preparation (degreasing, alkaline cleaning, electrocleaning, acidizing) and electrochemical deposition of the protective metal (Reference 2). Each step is followed by rinsing. As many as three metals may be applied to the same part. The final operation may include chromating, coloring, dying, and sealing or lacquering. The number and types of chemicals used vary from one plating shop to another, even for the same plating process. Concentrations of metals in plating baths may contain 100,000 to 200,000 mg/L of chromic acid. Others may contain 16,000 to 40,000 mg/L of copper, nickel, or zinc. The concentration of cyanide may be as high as the nickel or zinc (Reference 3). Nickel strip solutions are preserved using sodium metanitrobenzene sulfonate, sodium cyanide, and sodium hydroxide at a pH of 11 to 14 (Reference 2). Chromic plating solutions may contain fluoride as a catalyst and wetting agents (Reference 4). Complexing and chelating agents are universally added to metal finishing solutions for brightening, cleaning, and to inhibit or prevent precipitation of the heavy metals. These agents include tartrates, phosphates, ethylenediaminetetraacetic acid (EDTA), and ammonia (Reference 5).

These metals and other chemicals are carried into the rinsewater which must be treated at the Industrial Waste Treatment Plant (IWTP) at the Air Logistic Centers (ALCs). Additionally, the metals are carried into the industrial wastewater from engine cleaning and paint stripping processes. The discharge limits for the IWTP at Tinker AFB, Oklahoma, for the metals of concern are listed in Table 1. The effluent from the IWTP must meet these limits to comply with the National Pollutant Discharge Elimination (NPDES) Permit (Reference 6).

In 1980, regulations issued by the Environmental Protection Agency (EPA), classified metal-bearing sludges generated at the Air Logistics Center (ALC) IWTP as hazardous waste. The sludges, therefore, require costly disposal ($168/ton) in hazardous waste landfills and special handling (Reference 2). Disposal costs can be reduced by decreasing the amount of

TABLE 1. TINKER AFB NPDES PERMIT REQUIREMENTS (REFERENCE 6)

Constituent	Concentration (mg/L)
Cadmium, total	0.03
Chromium, total	1.0
Chromium, hexavalent	0.1
Copper, total	0.1
Lead, total	0.1
Nickel, total	1.0
Zinc, total	1.0

sludge produced. Methods of reducing the sludge include reduction in amount of wastewater, treatment optimization, plating chemical conservation, and sludge dewatering.

The common treatments for the industrial wastewater are oil and grease separation, destruction of cyanides, reduction of the hexavalent chromium, precipitation of the metal hydroxides, biological treatment for organic removal, and sludge disposal (Reference 4).

Although the other metals can be precipitated at alkaline conditions, hexavalent chromium cannot be precipitated without prior reduction to trivalent chromium. Conventional treatment of the mixed metal wastewater consists of reduction of the hexavalent chromium at acidic conditions (pH 2 to 3) with sodium sulfite, sodium bisulfite, or sulfur dioxide and subsequent precipitation of the trivalent chromium and other metals at alkaline pH using either lime or caustic. At present, the treatment chemicals used at Tinker AFB are sulfuric acid, sulfur dioxide, and lime. This treatment method requires acidic and alkaline controls and large quantities of chemicals, and produces a large amount of sludge.

Ferrous compounds can be used as an alternative for treatment of hexavalent chromium. Acid conditions or a large excess of ferrous are required for rapid reduction of the chromium by ferrous sulfate (Reference 1). The ferrous ion has only one electron available for reduction and this process requires a large ratio of iron to chromium for complete reduction and produces large amounts of sludge.

Reduction of hexavalent chromium with sulfide in the presence of the ferrous ion has been reported at alkaline pH with less sludge production than the conventional acidic sulfur dioxide/lime treatment process. Earlier studies by the Air Force have shown that the sodium sulfide/ferrous sulfate process can effectively reduce hexavalent chromium with removal of mixed metals at neutral and alkaline conditions. With upflow filtration, this method offers a potential cost saving treatment process for electroplating waste.

The report on Phase I of this program contains an extensive literature review describing the kinetics and chemistry of the reduction process of hexavalent chromium species and the metal precipitation processes (Reference 7).

Phase I was performed to validate the sodium sulfide/ferrous sulfate method of reducing hexavalent chromium and removal of the heavy metals from electroplating and industrial wastewater through clarifier operation. This method was validated by a large number of jar tests to investigate the extent of this reaction as a function of a number of variables similar to those experienced in a typical waste treatment process such as the process used at Tinker AFB. Dynamic tests were also conducted to evaluate this method in a continuous operation mode. The sodium sulfide/ferrous sulfate process was successful in hexavalent chromium reduction and total metal removal to less than NPDES permit requirements using distilled water, electroplating waste, and the influent wastewater to the Tinker AFB IWTP. The optimum reagent requirements, polymers, and pH for these wastes are listed in Table 2 (Reference 7). In addition, the sludge production from the sulfuric acid/sulfur dioxide/lime process was compared to the sludge production with the sodium sulfide/ferrous sulfate process. On a dry weight basis the relative dry weight difference was one to twelve. (These samples were dried in an oven at 104°C for 24 hours.) The results of Phase I indicated that sodium sulfide/ferrous sulfate process has significant

TABLE 2. LABORATORY STUDIES SUMMARY OF OPTIMUM CONDITIONS

	Distilled Water (20 mg/L Cr^{+6})	Electroplating Waste (55 mg/L Cr^{+6})	Influent Wastewater (9 mg/L Cr^{+6})
S^{-2} (mg/L)	24.7	56.0	12.4
Fe^{+2} (mg/L)	20.0	55.0	10.0
pH	7.2-9.0	7.2-8.1	7.2-7.5
Polymer	Betz 1120 (1.0 mg/L)	Betz 1120 (1.0 mg/L)	Betz 1195 (15 mg/L) with Betz 1120 (0.5 mg/L)

potential for reducing both chemical and sludge disposal costs. The purpose of Phase II of this program was to validate the process in a pilot-scale field-verification study using the influent to the Tinker AFB IWTP and to validate the decrease in sludge production.

C. SCOPE

The pilot-scale field-verification test unit was constructed at the Tinker AFB IWTP. Included with the plant was an analytical support trailer. Tests conducted at the pilot plant included determination of the optimum sulfide, ferrous, and polymer concentrations; determination of the effect of phosphate, cyanide, EDTA, and added metals on the reduction of hexavalent chromium and total metal removal; and determination of the optimum parameters for operation of the solids contact clarifier. The impact of flow rate and temperature were also investigated, as was the effect of the sodium sulfide/ferrous sulfate chromium reduction metal removal process on the activated sludge organic removal process. A comparison of the amount of sludge produced by the sodium sulfide/ferrous sulfate method to the acid/sulfur dioxide/lime method was obtained by operating the pilot plant using sulfuric acid, sulfur dioxide, and lime. In addition, a procedure was established for switching the present process to the sodium sulfide/ferrous sulfate process. This report describes the pilot plant, analytical procedures, the tests, and the results of the tests.

SECTION II
PLANT DESCRIPTION AND OPERATION

The pilot-scale field verification plant was designed to represent the flow characteristic and retention time of the Tinker AFB IWTP. The plant consisted of both heavy metal precipitation and the organic removal (Figure 1).

The unit consisted of the equalization tanks, the mixer tanks, the chemical feed tanks, the solid contact clarifier, the activated sludge bed, and the final clarifier (Figure 2). The influent to the pilot plant was pumped from the Tinker AFB IWTP equalization reservoir to a 500-gallon equalization tank (E-tank) equipped with a pH probe and mixer. Sulfuric acid and caustic were pumped to the tank to control the influent pH. The wastewater in the E-tank flowed by gravity (controlled from 2 to 10 gal/min) to a 50-gallon mixing tank where additional chemicals such as cyanide, EDTA, metals, or phosphate could be added. In addition, the E-tank contents could be pumped through the pilot plant to provide a feed of constant chemical composition during parameter tests. The influent flowed from the 50-gal/min mixing tank to a series of three mixer tanks. In the first tank sodium sulfide was added. This solution was fed at the center of the tank approximately 3 inches below the surface. The influent flowed into the bottom of this tank and over the top of a weir to the second tank. To prevent back mixing between the two tanks, the effluent flowed over the top of the Mixer-1 tank and down under a weir between the two tanks. The ferrous sulfate solution and sulfuric acid were added in the Mixer-2 tank. These solutions were fed near the mixer approximately 3 inches below the surface of the water. The effluent of Mixer-2 flowed to the third mixer tank where the cationic polymer (Betz 1195) was fed in the same manner as the other chemicals. The effluent flowed from the bottom of this mixer tank. The effluent piping was designed to maintain a constant volume in this tank. The effluent was split from the Mixer-3 tank with 1 to 4-gal/min flowing to the solid contact clarifier (SCC) with the anionic polymer (Betz 1120) and the excess going to the drain.

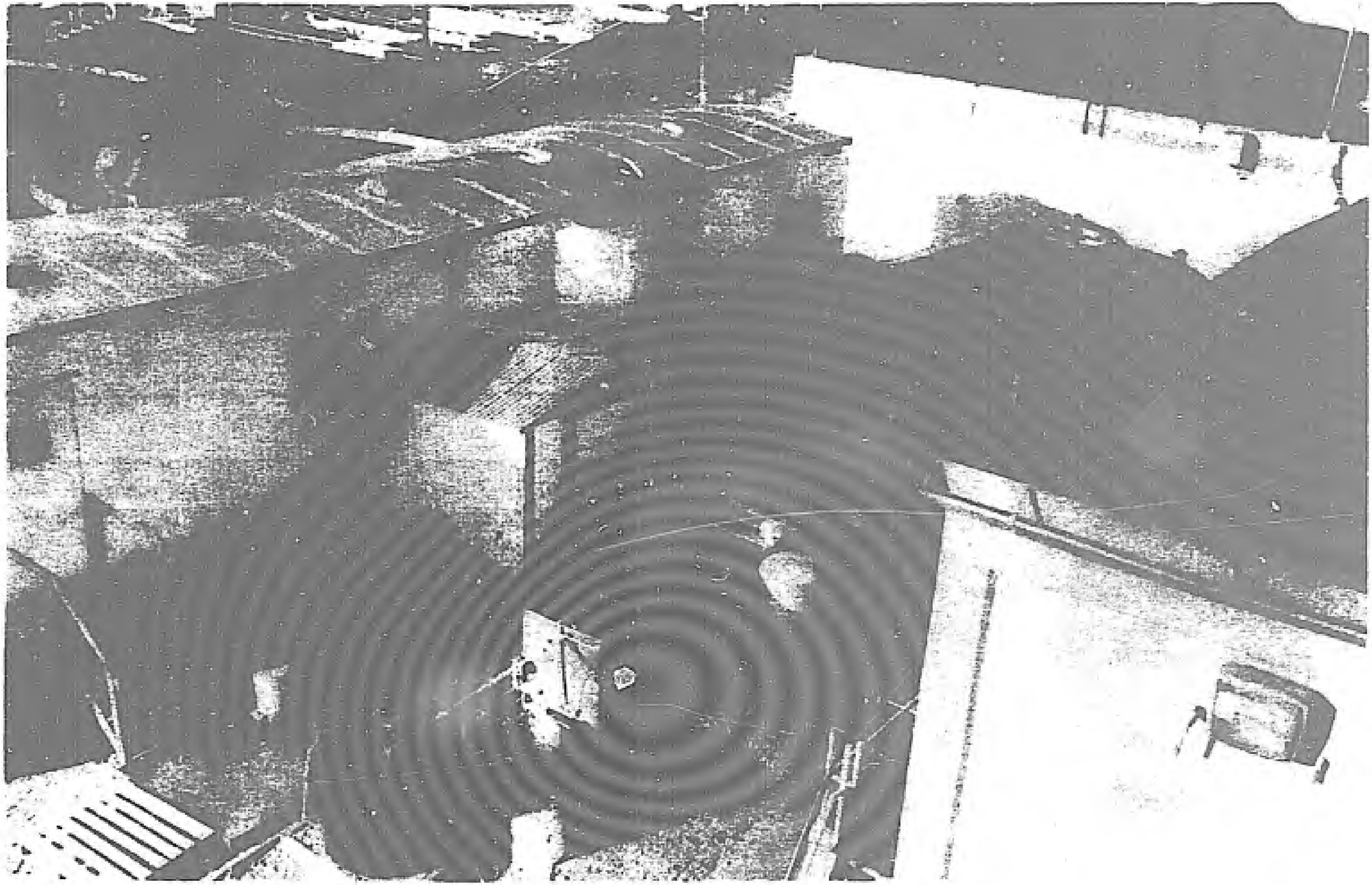

Figure 1. Photograph of the Pilot Plant.

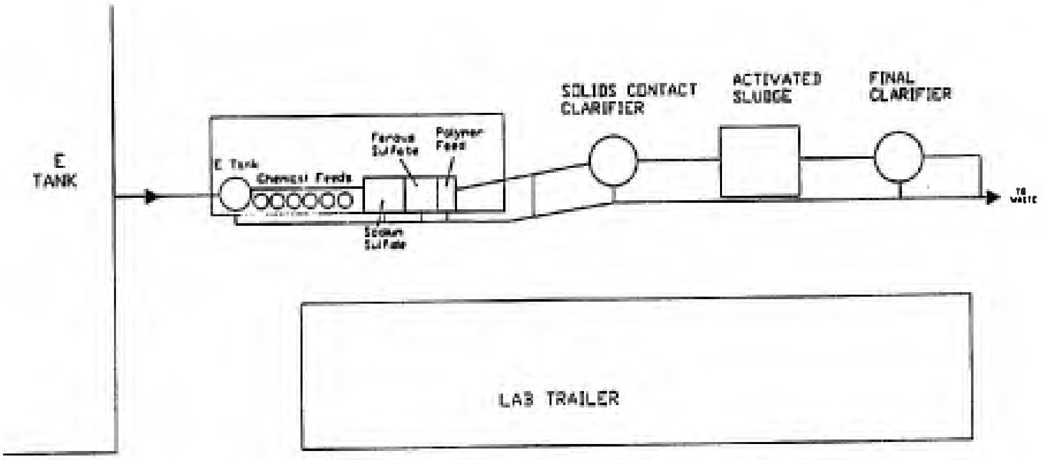

Figure 2. Schematic of the Pilot Plant.

The SCC (330-gallon) has a retention time of 2.75 hours at 2 gal/min. It was designed similar to the Tinker AFB SCC, which was designed by Walker Process Corp. A schematic of the pilot SCC is shown in Figure 3. The effluent of Mixer-3 flowed to the center pipe of the SCC, where it was mixed with an anionic polymer and an external sludge recirculation flow. The solution flowed from this pipe to a center well, which was equipped with a mixer to pull the sludge from the bottom of the SCC for internal sludge recirculation. The sludge was mixed in this centerwell as a seed or aid for flocculation. The mixture flowed from the top of the well to an intermediate settling ring or skirt. The solution flowed under the intermediate skirt through the sludge bed and up through an outer ring and over the weir to the activated sludge system. The SCC effluent could bypass the activated sludge system when upset conditions were being tested.

The activated sludge tank was designed for 0.5 to 2 gal/min of flow. Compressed air flowed through the pipes to the bottom of the activated sludge; each pipe was equipped with a valve so the air flow could be balanced across the activated sludge bed, which was seeded with activated sludge from the Tinker AFB system. Additional phenol and/or nutrients could be fed to the influent. In addition, domestic water could be fed to the system in place of SCC effluent when upset conditions were being tested. The effluent of the activated sludge flowed to the final clarifier.

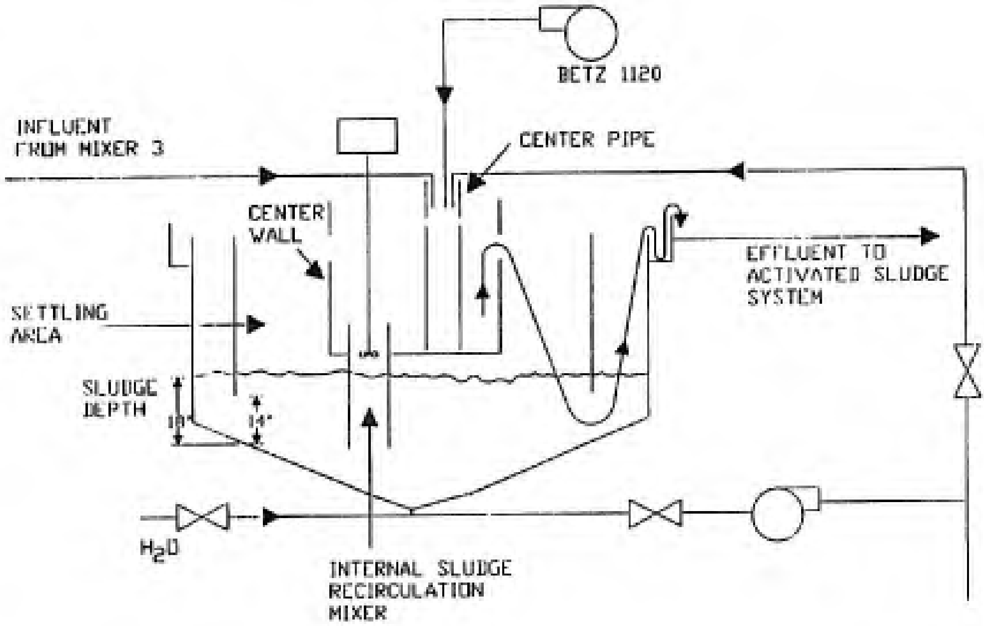

Figure 3. Schematic of Solids Contact Clarifier.

Influent to the final clarifier flowed into a center ring, which directed the stream to the bottom of the clarifier, where it flowed under the ring to the outer ring and up over the weir to the outlet. The effluent of the final clarifier flowed to the drain and the sludge could be recirculated to the inlet of the activated sludge or wasted to the drain. Polymer could be fed to the influent of the final clarifier.

The pilot plant was equipped with an IBM XT and the "Opto 22" program for controlling the influent flow, the influent pH, and the chemical feeds to the Mixer 1, 2, and 3 tanks. A Scientific Instrument Continuous Flow Analyzer (CFA) with a concentration range of 0 to 10 mg/L was installed at the influent to Mixer-1 tank to monitor the influent hexavalent chromium. The data were recorded by the computer and used to automatically set the sulfide and ferrous feed to the mixer tanks. The feeds were set proportionately (for example, if the influent hexavalent chromium concentration was 5 mg/L, the sulfide pump and the ferrous pump were set at 50 percent of the pump output; at 1 mg/L Cr^{+6} the pumps were set at 10 percent of output.) The pumps were calibrated, and the sulfide and ferrous solutions were made up to match the required feed concentration. The ferrous solution was made in 50-gallon batches using ferrous sulfate heptahydrate. Concentrated sulfuric acid (200 mL) was added to each batch to decrease the amount of ferrous oxidized to ferric iron and to prevent precipitation of the iron. A stock solution of sodium sulfide was prepared using sodium sulfide flake. (Sodium sulfide flake is 60 percent by weight sodium sulfide.) The stock solution was analyzed and the appropriate feed solution was made up.

A CFA with a concentration range of 0 to 1 mg/L was installed at the outlet of the SCC to monitor the hexavalent chromium in the effluent. The concentration was recorded by the computer. A Milton Roy Streaming Current Detector was installed at the outlet of Mixer-3 to monitor the charge and potential on the particles or floc formed by the precipitation process and, in conjunction with the computer, could be used to control the cationic polymer feed. The streaming current was recorded as a function of time.

A Techline on-line respirometer was used to monitor the respiration rate of the activated sludge bed. This provides a good indication of both the activity and health of the microorganisms and the degree of the degradation of the organic compounds to carbon dioxide. The respirometer set up to sample from the influent, middle, or effluent of the activated sludge, measures the oxygen consumed in a sample as a function of time. The respiration rate could be recorded on the computer or on a strip chart recorder.

The computer was also used to monitor, record, and control the influent pH and the pH in Mixer-2, and to monitor influent flow, system temperature, the dissolved oxygen through the activated sludge system, and the pH of the activated sludge. In addition, all the chemical feed pumps output were recorded. The pilot plant could be operated by setting a setpoint for influent and Mixer-2 pH, the streaming current, and letting the computer control the sulfide and ferrous feeds as a function of the influent hexavalent chromium concentration; or the pump output could be set separately either on the computer or at the pump for each chemical feed.

SECTION III
ANALYTICAL PROCEDURES

During testing, the influent to the plant and the effluent of the SCC, the activated sludge, and the final clarifier were sampled twice daily. In addition the influent, SCC, and activated sludge was sampled at least twice nightly. Sulfuric acid was added to the night samples to prevent degradation of the organic compounds. Hexavalent chromium was analyzed in the daytime influent and SCC samples. All of the influent and SCC samples were analyzed for total chromium, nickel, cadmium, copper, lead, iron, and zinc. The influent, SCC, activated sludge, and effluent samples were analyzed for chemical oxygen demand (COD). All SCC and activated sludge samples were analyzed for phenol. The day samples from the SCC, activated sludge, and final clarifier were analyzed for total carbon, phosphate, nitrogen, dry weights, and total solids. In addition, the feed and the effluent of Mixer-3 were analyzed for sulfide and ferrous iron.

All colormetric analyses were performed, using a Hach DR3000 spectrophotometer. Chemical oxygen demand was determined by using the Hach procedures for sulfuric acid potassium dichromate digestion and evaluating colormetrically. When less than 4 mg/L phenol was present, the Hach colormetric method for low-range phenol was used for analysis. At concentrations greater than 4 mg/L, samples were prepared for phenol analysis by adjusting the pH of 10 mL of the sample to less than 2 with concentrated sulfuric acid. This solution was extracted twice, using 20 mL of methylene chloride. Ten microliters of the combined methylene chloride extract were analyzed with a Flame Ionization Detector (FID) using a 2-meter, 80- to 120-mesh, 1240 DA Supelcoport glass column in a Perkin Elmer 2000 Gas Chromatograph equipped with an LCI 100 integrator. The gas chromatograph was temperature-programmed from 70 to 180°C at 8 degrees per minute with a 2-minute delay. The instrument was calibrated with a 250 mg/L phenol-in-methylene chloride standard. The peak acceptance width was 0.2 minutes. Nitrogen concentrations (ammonium) were determined by using the Hach colormetric procedure. Hardness (calcium) and alkalinity were determined using the Hach procedure for titration.

Dry sample weights were determined using 50 mL samples. The samples were filtered through preweighed filters, dried overnight at 103°C in an oven, and reweighed. Total residue was determined by drying 30 mL of the sample in a pre-weighed aluminum pan at 103°C overnight and reweighing the pan. ATP analyses were determined, using a Turner Design ATP photometer calibrated by the procedure for internal standard provided with the instrument.

SECTION IV
RESULTS

A. CHEMICAL PARAMETERS

The optimum sulfide and ferrous concentrations and the optimum pH were determined as follows: The IWTP plant influent contained in the 500-gallon E-tank was analyzed for hexavalent chromium, total metals, and phosphate. The pH of the influent was adjusted. Sulfide and ferrous feeds were adjusted based on the hexavalent chromium concentration. The pH in Mixer-2 was maintained at 7.2-7.5. For all chemical parameter tests the influent was 5 gal/min through the mixer tanks and split to 2 gal/min to the SCC with 3 gal/min going to the drain. The external sludge recirculation was 20 percent of the SCC flow, and the internal sludge recirculation was at 70 percent of the mixer speed.

Initial tests were conducted to determine the effect of the ratio of sulfide to hexavalent chromium on the chromium reduction in Mixer-1 with the influent pH at 7.5 and 8.0 (Figure 4). No ferrous ion was added during these tests. Samples were pulled at the effluent of the Mixer-1 tank for these tests. At pH 8, approximately 15 percent of influent hexavalent chromium is reduced at a ratio of 1 and 2.0 mg/L S^{-2} to 1 mg/L Cr^{+6}. However, at a 3 to 1 ratio, the reduction dropped to 4 percent. At the lower influent pH, 7.5, reduction was approximately 42 and 25 percent at the 2:1 and 3:1 ratio. The decrease in reduction at the 3:1 ratio at any influent pH is probably due to an increase in the pH in the Mixer-1 caused by the addition of the basic sodium sulfide solution and decreased reactivity of the sulfide at the higher pH. When the pH was adjusted in the Mixer-2 tank to 7.2 - 7.5 and the sample pulled at the effluent of Mixer-2, the hexavalent chromium was reduced by 70 percent at 2 and 3 mg/L S^{-2} to 1 mg/L Cr^{+6} (Figure 4). However, even at the higher sulfide to chromium ratios, the hexavalent chromium could not be reduced to less than NPDES permit requirements.

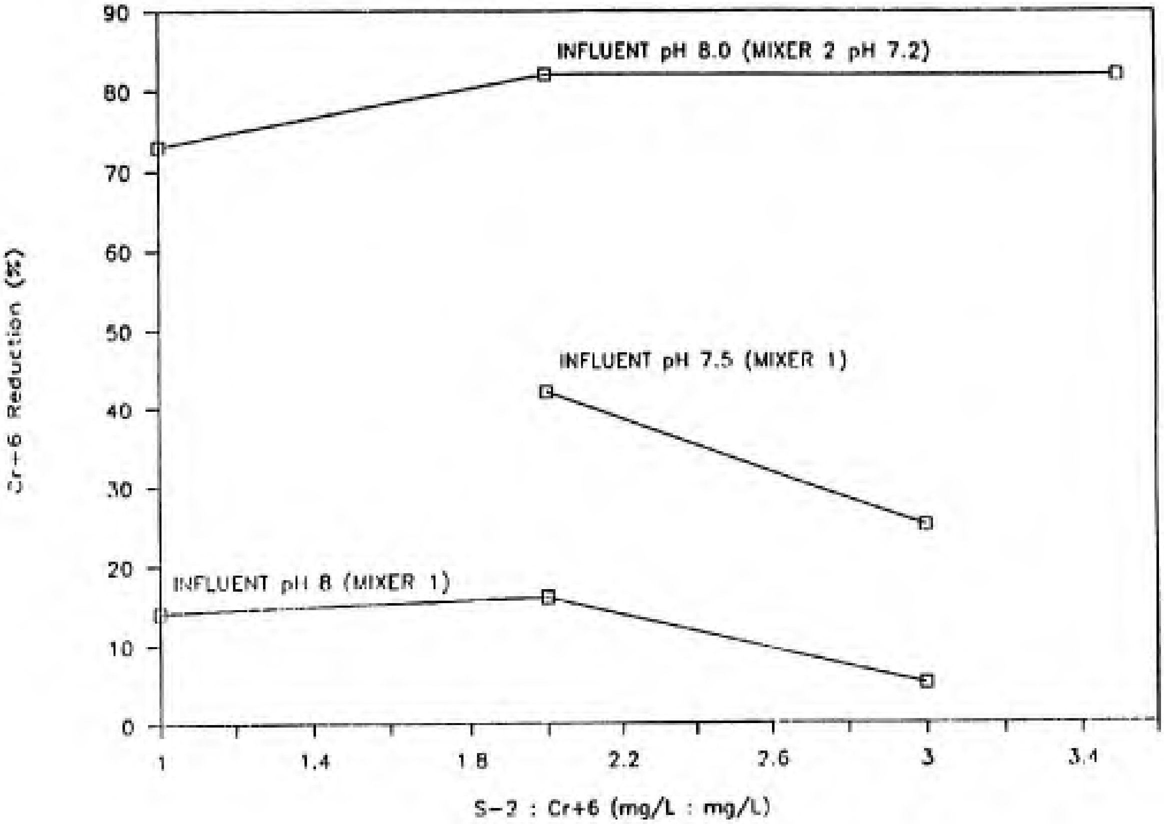

Figure 4. Chromium Reduction vs. Sulfide.

Figure 5 shows the chromium reduction as a function of the ratio of ferrous iron to hexavalent chromium at fixed ratios of 1 mg/L S^{-2} to 1 mg/L Cr^{+6}, 1.75 mg/L S^{-2} to 1 mg/L Cr^{+6} and 2 mg/L S^{-2} to 1 mg/L Cr^{+6}. In these tests, the influent pH was adjusted to 8.0 and the pH in Mixer-2 was adjusted to 7.2 - 7.5. Samples were taken at the effluent of Mixer-2 for hexavalent chromium analysis. As Figure 5 shows, there was a great deal of scatter in the reduction of the hexavalent chromium. The plant operated for 2 weeks at 1.75 S^{-2} to 1 Fe^{+2} to 1 Cr^{+6}, with complete reduction of the hexavalent chromium, before hexavalent chromium was detected in the effluent of Mixer-2. At 2 mg/L S^{-2} to 1.5 mg/L Fe^{+2} to 1 mg/L Cr^{+6}, the hexavalent chromium was reduced completely during the remainder of the test period. Although the chromium could be reduced at higher sulfide to ferrous ratios, clarity was difficult to achieve. Increasing the ferrous concentration to achieve clarity causes more sludge production and chemical usage and is therefore not economical. The 2 mg/L S^{-2} to 1.5 mg/L Fe^{+2} to 1 mg/L Cr^{+6} was selected as the optimum sulfide and ferrous feed for treatment of the hexavalent chromium.

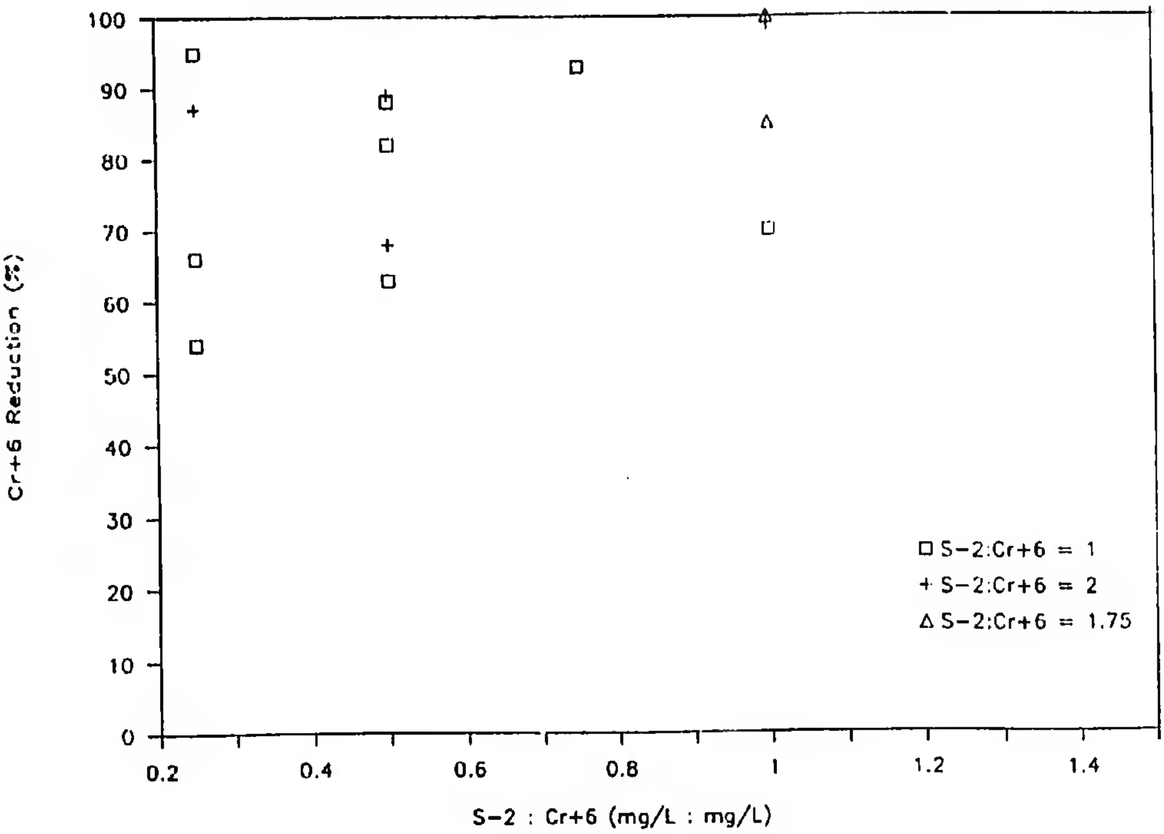

Figure 5. Reduction as a Function of S^{-2} concentration (pH 7.2 - 7.5).

The pH effect on chromium reduction was tested with the influent pH held at 8.0 while varying the pH in Mixer-2. The pH effect was tested with a 1.75 mg/L S^{-2} to 1 mg/L Fe^{+2} to 1 mg/L Cr^{+6} feed ratio and with a 2.0 mg/L S^{-2} to 1.5 mg/L Fe^{+2} to 1 mg/L Cr^{+6} feed ratio. The results are shown in Figure 6. At the 2 mg/L S^{-2} to 1.5 mg/L Fe^{+2} to 1 mg/L Cr^{+6}, the hexavalent chromium was reduced to less than NPDES permit requirements from a pH of 7.2 - 8.4; however, the hexavalent chromium was completely reduced only between pH 7.2 - 7.5. The hexavalent chromium was completely reduced only at pH 7.2 with a 1.75 mg/L S^{-2} to 1 mg/L Fe^{+2} to 1 mg/L Cr^{+6} ratio and was below NPDES permit requirements only below pH 7.6.

The effect of the influent pH on chromium reduction was tested with the pH in Mixer-2 maintained at 7.2 - 7.5 and a 2 mg/L S^{-2} to 1.5 mg/L Fe^{+2}

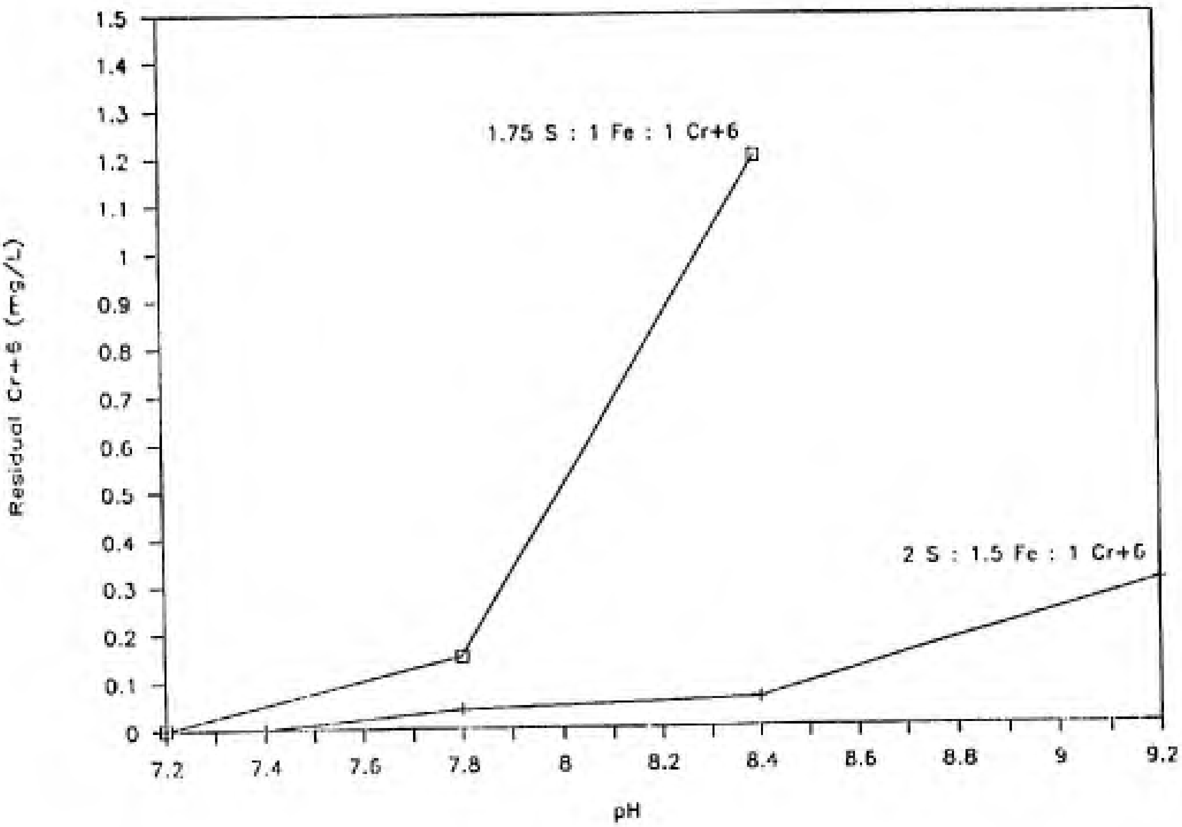

Figure 6. pH Effect on Chrome Reduction (Mixer-2).

to 1 mg/L Cr^{+6} ratio. The influent pH was varied from pH 7.2 to 11.0. In all cases the hexavalent chromium was completely reduced at the outlet of Mixer-2.

To determine the optimum cationic polymer feed, the plant was operated with an influent pH of 8, a Mixer-2 pH of 7.2 - 7.5, and a chemical feed of 2 mg/L S^{-2} to 1.5 mg/L Fe^{+2} to 1 mg/L Cr^{+6}. Six 1-L samples of the effluent of Mixer-3 were collected. The zeta potential was determined as a function of the concentration of Betz 1195. The effect of polymer concentration on the Zeta potential is shown in Figure 7. The zeta potential changed from a negative to positive charge when the Betz 1195 concentration was between 15 and 20 mg/L. Before the change in charge, a small addition of polymer caused a significant change in the zeta potential. Following the change in charge, the additions resulted in an insignificant change in the potential. These tests, as in Phase I (Reference 7) showed that good settling did not occur until the charge change occurred. An on-line Milton Roy Streaming Current Detector was

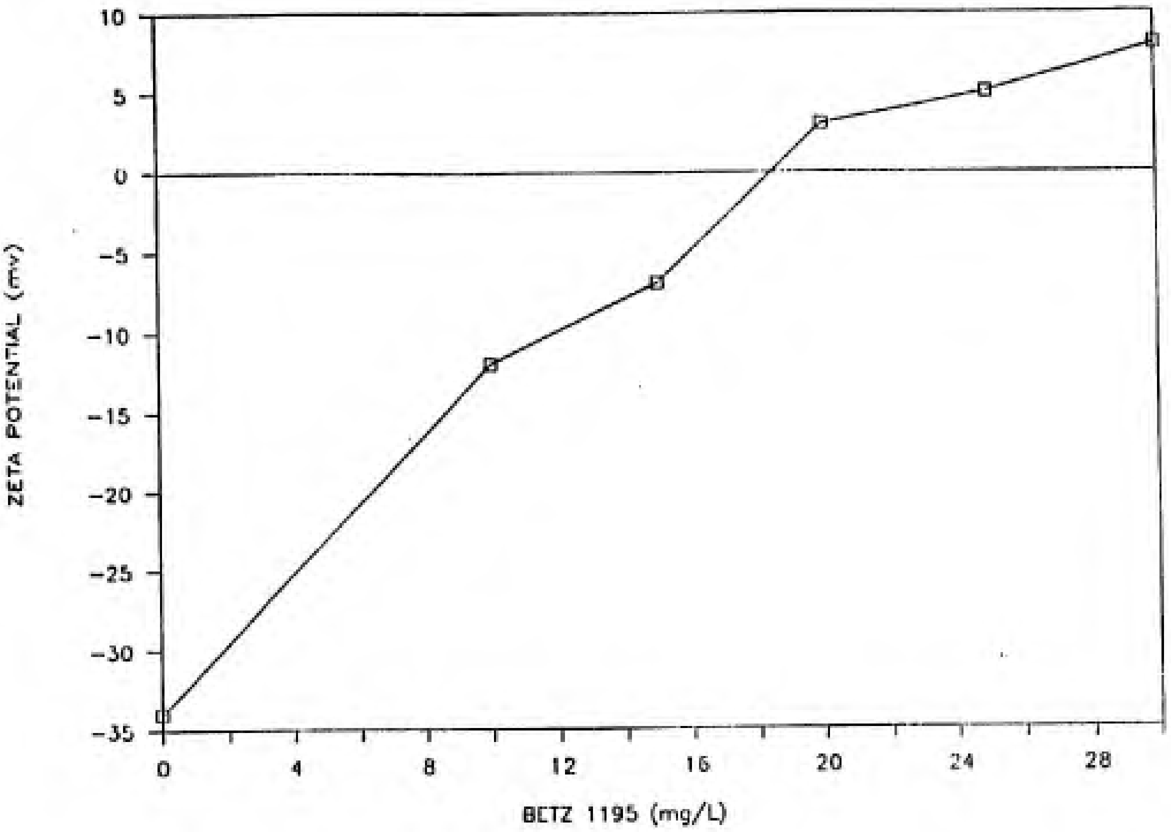

Figure 7. Zeta Potential vs. Betz 1195 Concentration.

installed at the effluent of Mixer-3 to monitor the charge and potential of the floc in the stream flowing to the SCC. The effluent flow rate to the instrument was 2 L/min. The streaming current tracks slightly less than the zeta potential such that a streaming current of -0.30 is equivalent to a zeta potential of +0.95 mL. The streaming current detector can be used to control the cationic polymer feed to Mixer-3. Generally, the cationic polymer concentration required to maintain the streaming current was 20 mg/L.

Jar tests were performed, using 20 mg/L of Betz 1195 as the optimum concentration of cationic polymer. These tests show that optimum settling and clarification occurred with 20 mg/L Betz 1195 and 0.5 mg/L Betz 1120. Tests conducted on the effluent of the SCC showed a decrease in floc settling with a decrease in anionic polymer concentration. This decrease in settling occurred over time (1 to 2 days) with a decrease of the anionic polymer concentration (0.5 mg/L to 0.2 mg/L). The sludge depth in the SCC expanded from 18 to 28 inches. Fines were carried over with the effluent, and the metals in the effluent increased. With the addition of the 0.5 mg/L anionic polymer, the bed expansion and fines carryover ceased within one retention time of the SCC (approximately 3 hours).

It was also found that if fresh solutions (less than 24 hours) of the cationic or anionic polymer were not used, increased polymer feed was required. Solutions 1 week old required an increase in the cationic polymer feed from 20 to 40 mg/L and the anionic feed from 0.5 mg/L to 2 mg/L.

In addition to testing the Betz 1195 cationic polymer, a Chemlink 6360 cationic polymer was tested in the pilot plant. The polymer had shown potential in the previous phase (Reference 7) in jar testing. The polymer was tested at 20 and 25 mg/L. The streaming current was positive at both of these concentrations. Although NPDES permit requirements were met, the effluent carried increased amounts of fines.

The remaining tests of the chemical parameters were conducted with the influent pH at 8.0, the Mixer-2 pH at 7.2 - 7.5, the chemical feed ratios at 2 mg/L S^{-2} to 1.5 mg/L Fe^{+2} to 1 mg/L Cr^{+6}, Betz 1195 at 20 mg/L, Betz 1120 at 0.5 mg/L, and the SCC operating at optimum conditions as discussed in Section IV-B. Samples were pulled from Mixer-2 to determine the effect on hexavalent chromium reduction and at the effluent of the SCC to determine the effect on metal removal and clarification. The chemical parameters used were orthophosphate, EDTA, cyanide, and additional mixed metals. These parameters were tested individually by feeding to the 50-gallon mixer tank a solution at the concentration and rate to give the desired concentration of the influent to Mixer-1. The parameters were tested for a minimum of 8 hours, allowing a flow of two retention times through the SCC.

1. Orthophosphate

In jar tests using distilled water, an increase in orthophosphate caused an increase in the remaining hexavalent chromium. However, no effect was found with the electroplating waste or the IWTP influent, (Reference 7). Therefore, the effect in the pilot plant of orthophosphate on the reduction of hexavalent chromium was tested using sodium phosphate (Na_3PO_4). The effect was tested at 50 mg/L and 100 mg/L additional orthophosphate in the influent stream. At both concentrations, the hexavalent chromium was completely reduced. In addition, during subsequent operation, the influent orthophosphate increased to 176 mg/L PO_4^{-3} and the chromium concentrations remained below NPDES Permit Requirements at the effluent of the SCC.

2. Ethylenediaminetetraacetic Acid

The effect of EDTA, one of the chelating agents added to the electroplating baths, was tested by adding Disodium Ethylenediaminetetraacetate (Na_2EDTA) to a final concentration of 50 mg/L EDTA. A method for analysis of EDTA in the influent is not available. As shown in Table 3, the EDTA caused no change in the effluent of the SCC quality, in contrast to the Phase I jar tests where 50 mg/L caused a significant increase in the metals remaining in the filtrate.

3. Cyanide

Cyanide is used for the metal stripping step in the electroplating process and normally is not present in the IWTP influent since it is drummed or treated at the electroplating shop. However, some spills do occur. When detected in the influent, cyanide is treated with sodium hypochlorite, before the chromium

TABLE 3. EDTA EFFECTS

Constituent	Influent (mg/L)	SCC Effluent With EDTA (mg/L)	SCC Effluent No EDTA (mg/L)
Cr^{+6}	4.60	0.00	0.00
Cr	5.15	0.30	0.28
Ni	1.25	0.25	0.20
Cd	0.88	0.02	0.02
Cu	0.07	0.00	0.02
Fe	1.65	3.67	--
Pb	0.38	0.06	0.06
Zn	0.18	0.04	0.03

reduction process, But, a certain amount may reach the chromium reduction process before detection and treatment. In the acid/sulfur dioxide/lime system, most cyanide entering the system is destroyed by the acid and does not reach the activated sludge. The sodium sulfide/ferrous sulfate process will not destroy the cyanide, but the cyanide may complex with the metals and, therefore, not be carried at full strength to the activated sludge. Cyanide, (to 10 mg/L CN^-) as potassium cyanide (KCN), was fed for 4 hours to the influent to simulate a spill or cyanide dump to the system. The cyanide and metals were monitored at the effluent of the SCC, and the effect on the respiration and phenol degradation was monitored at the effluent of the plant. Cyanide was decreased to 1.85 mg/L in the SCC and to 0.5 mg/L in the activated sludge system. Figure 8 plots the cyanide as a function of time in the SCC. Table 4 shows the metal remaining in the SCC. The 1.85 mg/L CN^- had no effect on the activity of the activated sludge. Cyanide would require prior removal at the influent to meet NPDES Permit cyanide limits, but its presence would not upset the activated sludge system.

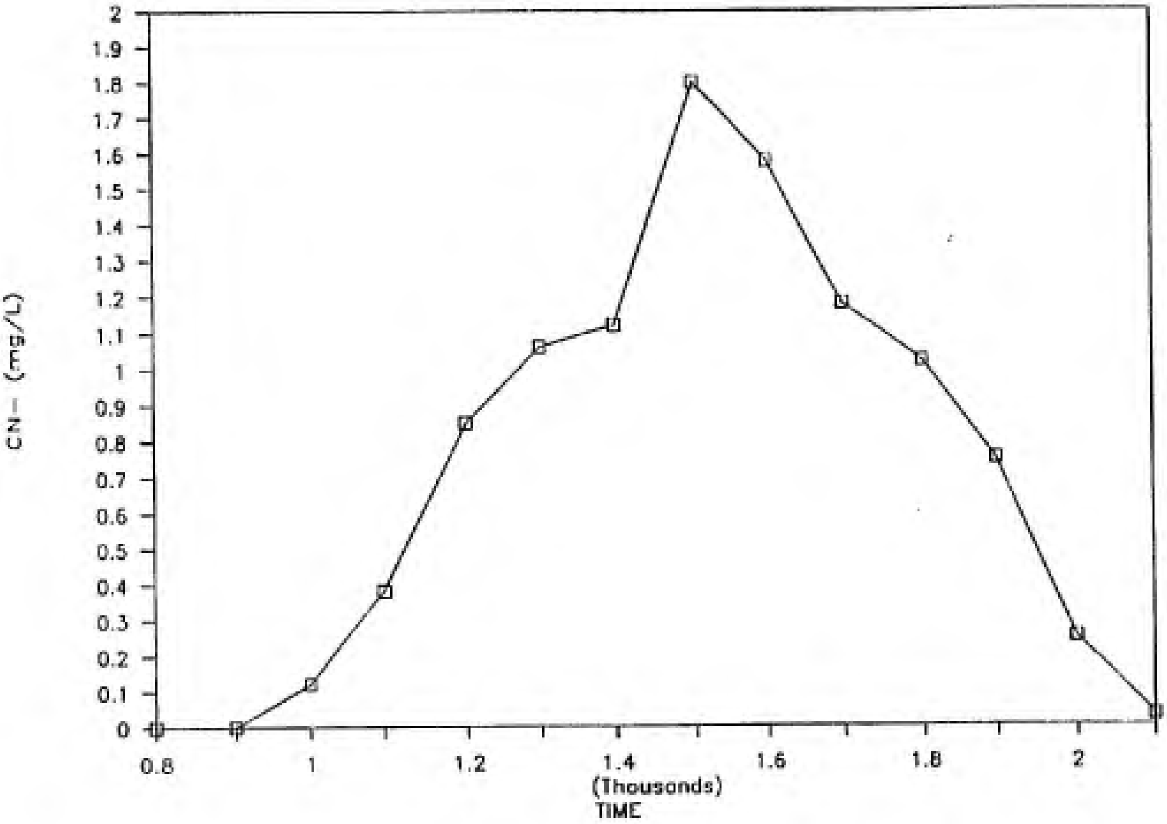

Figure 8. Cyanide vs. Time in the SSC.

TABLE 4. CYANIDE EFFECTS

Constituent	Influent (mg/L)	SCC Effluent Added Phosphate (mg/L)	SCC Effluent No Added Phosphate (mg/L)
Cr^{+6}	4.90	0.00	0.00
Cr	5.34	0.58	0.30
Ni	0.53	0.15	0.20
Cd	0.10	0.01	0.02
Cu	0.04	0.02	0.02
Fe	0.88	1.31	--
Zn	0.05	0.02	0.03

A mixture of metals was fed to the influent to a total metal (other than chromium) concentration of 5 mg/L. The initial concentration was 2 mg/L Ni, 1 mg/L Cu, 0.75 mg/L Pb, 0.75 mg/L Cd and 0.5 mg/L Zn. (The metal compounds used were cupric sulfate, cadmium chloride, nickel chloride, zinc chloride, and lead chloride.) Some of the metals precipitated in the mixer tank and the influent line. The precipitation, however, was insignificant. The influent concentration and the metal concentration at the effluent of the SCC is shown in Table 5. In all cases the metals were removed to below NPDES permit requirements.

B. PHYSICAL PARAMETERS

The physical parameters examined in the pilot plant included: (a) the optimization of the SCC and (b) the effect of flow and temperature on the chromium reduction process and the metal removal.

For proper metal removal, the solids contact clarifier (SCC) must operate at its optimum. The pilot plant SCC was a scale-down of the Tinker AFB SCC, a design patented by Walker Process Corporation of Aurora, Illinois. Although the pilot SCC was not built identically to the Tinker AFB, it incorporates the same retention time and flow characteristics. The pilot

TABLE 5. ADDED METALS EFFECTS

Constituent	Influent (mg/L)	SCC Effluent (mg/L)	SCC Effluent No Cyanide (mg/L)
Cr^{+6}	0.50	0.00	0.00
Cr	3.37	0.15	0.30
Ni	3.71	0.38	0.20
Cd	0.96	0.02	0.02
Cu	0.77	0.00	0.02
Fe	1.31	1.93	--
Zn	0.59	0.05	0.03

SCC (Figure 3), consists of an inner mixer chamber that receives the influent flow, the anionic polymer feed, and the external sludge flow. The external sludge was pumped from the bottom of the SCC. In addition, a variable-speed mixer is present in the mixer chamber to pull the sludge from the bottom of the SCC up into the mixer chamber. The liquid and floc flow from slits in the mixer chamber into an intermediate ring or skirt. The floc settles and the clear effluent flows under the skirt up through the outer ring and to the effluent weir. A rake, moving at 3 R/h around the bottom of the SCC, moves the sludge to the sludge outlet and prevents channeling of the sludge and/or effluent. The critical parameters of the SCC are the external sludge recirculation, internal sludge recirculation, sludge depth, and the solids in the mixer chamber. The effects were evaluated by monitoring the turbidity of the effluent of the SCC. Suspended solids were measured by pulling a 100 mg/L sample in a graduated cylinder and recording the solids level after 5 minutes (30 percent suspended solids means the solids have settled to 30 mL in 5 minutes). All optimization tests of the SCC were done with an influent flow of 3.5 gal/min, representing 1.75 million gal/day through the Tinker IWTP. This flow allowed more rapid changes in the SCC effluent (one retention time was 1.6 hours instead of 2.75 at 2 gal/min).

The sludge depth effect was an "all or none" effect. Normally, this type of SCC is operated with the sludge bed below the bottom of the intermediate skirt. With the type of floc formed in the sodium sulfide/ferrous sulfate process, clarity could not be achieved, no matter what the other parameters, if the sludge depth was not greater than the bottom of this skirt (the bottom of the skirt was 14 inches). This allowed the effluent to flow through the sludge bed, which acted as a filter to remove the pin floc (fines) associated with this process. The sludge depth was normally maintained between 18 and 24 inches. If the sludge depth dropped below 14 inches, the effluent became cloudy and carried excess floc or metals.

To determine the effect of the internal sludge recirculation on the turbidity of the effluent, the external sludge recirculation flow was set at approximately 7.5 percent of influent flow. The mixer speed was varied from 35 percent to 78 percent (this is the maximum mixer speed for the pilot system without excess vibration of the impeller), and the turbidity was monitored. The turbidity decreased from 70 Neophillic Turbidity Units (NTU) at 35 percent to 40 NTU at 78 percent mixer speed in (Figure 9).

The effect of suspended solids in the mixer chamber on the turbidity of the effluent decreased to less than 10 NTU near 95 percent of suspended solids (Figure 10). To increase the concentration of the suspended solids, external sludge recirculation rate was measured with the internal sludge recirculation rate set at a mixer speed of 78 percent. At the lower external sludge recirculation (Figure 11), there is a great deal of scatter in the suspended solids. With insufficient sludge recirculation it is difficult to maintain the sludge depth at 14 inches. At the higher recirculation rate the suspended solids can be maintained at 80 to 95 percent. Figure 12 shows the turbidity of the effluent of the SCC as a function of the external sludge recirculation flow. The turbidity decreases to near 0 NTU at the higher external sludge recirculation rate. This figure shows that an external sludge recirculation of 10 to 20 percent (1320 to 2640 mL/min) of the influent SCC flow is required to maintain the turbidity below 10 NTU and the metals below NPDES Permit requirements as shown in Table 6.

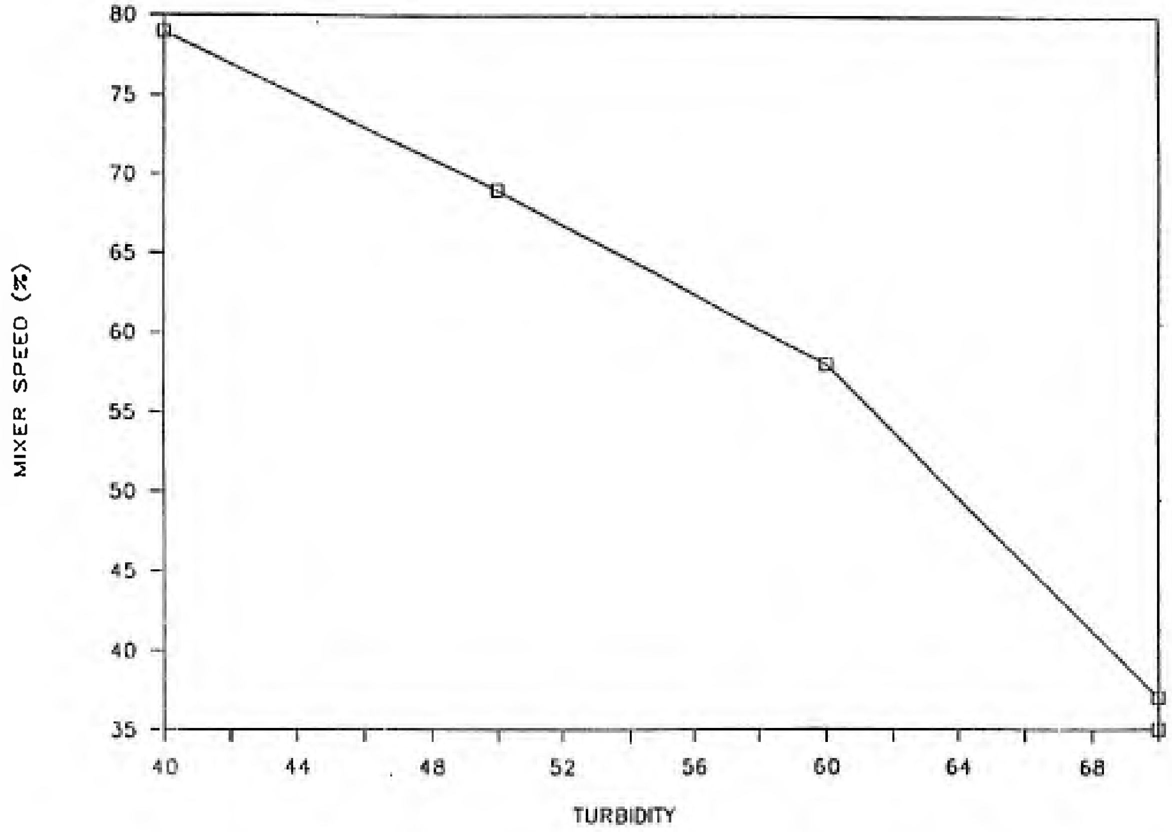

Figure 9. Internal Sludge Flow vs. Turbidity. Flow: 1000 - 1350 mL/min.

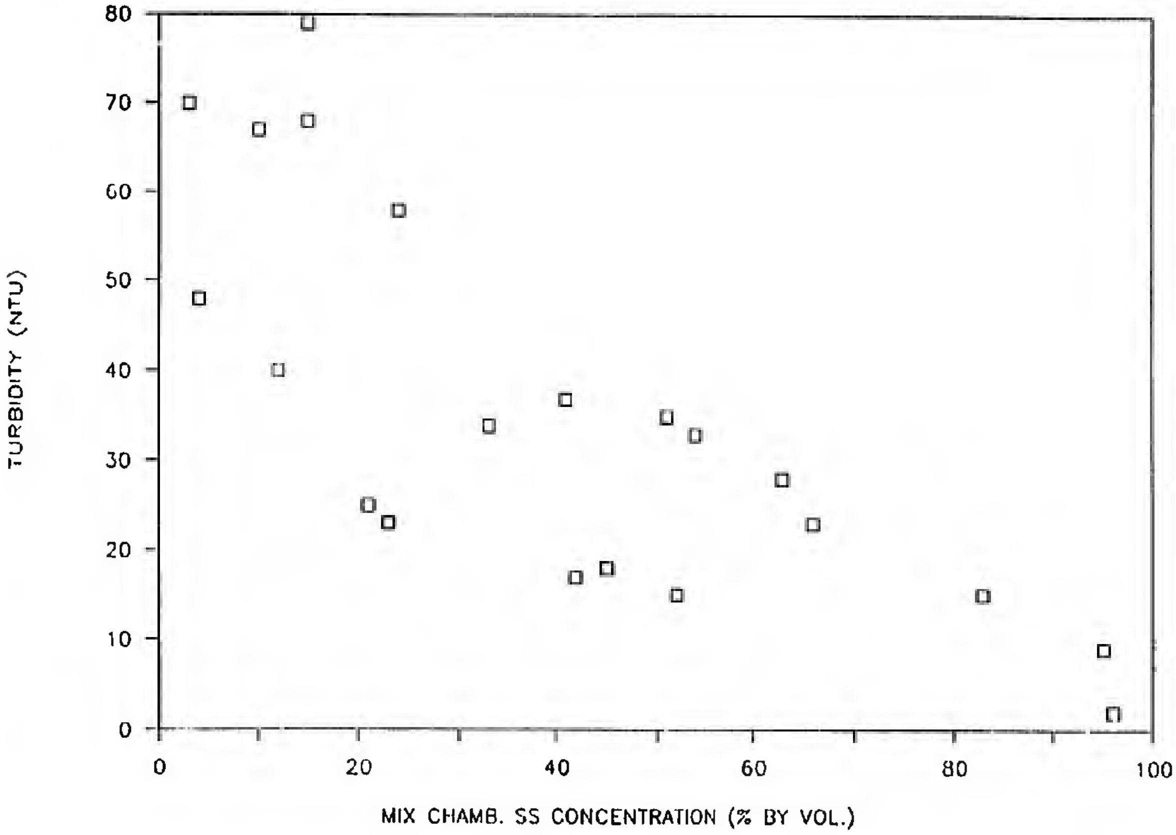

Figure 10. Mixing Chamber SS Concentration vs. Turbidity.

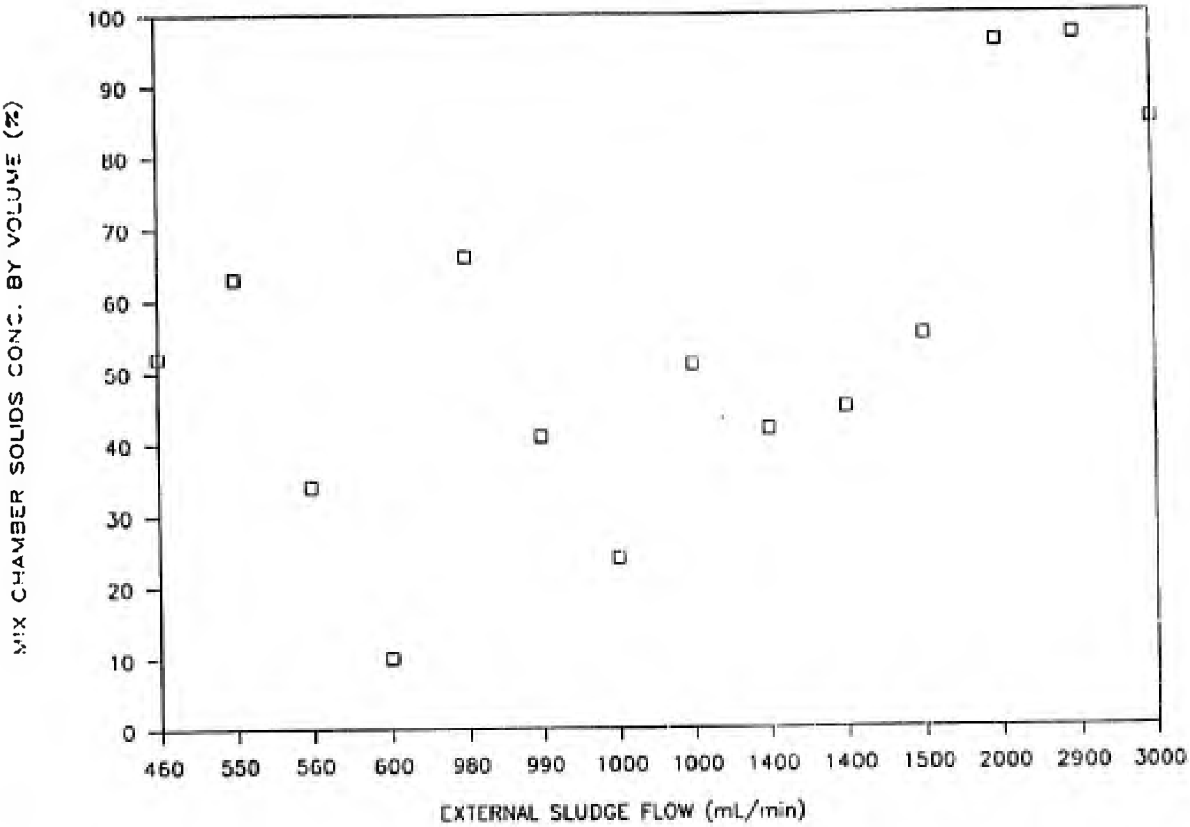

Figure 11. External Sludge Flow vs. Solids.

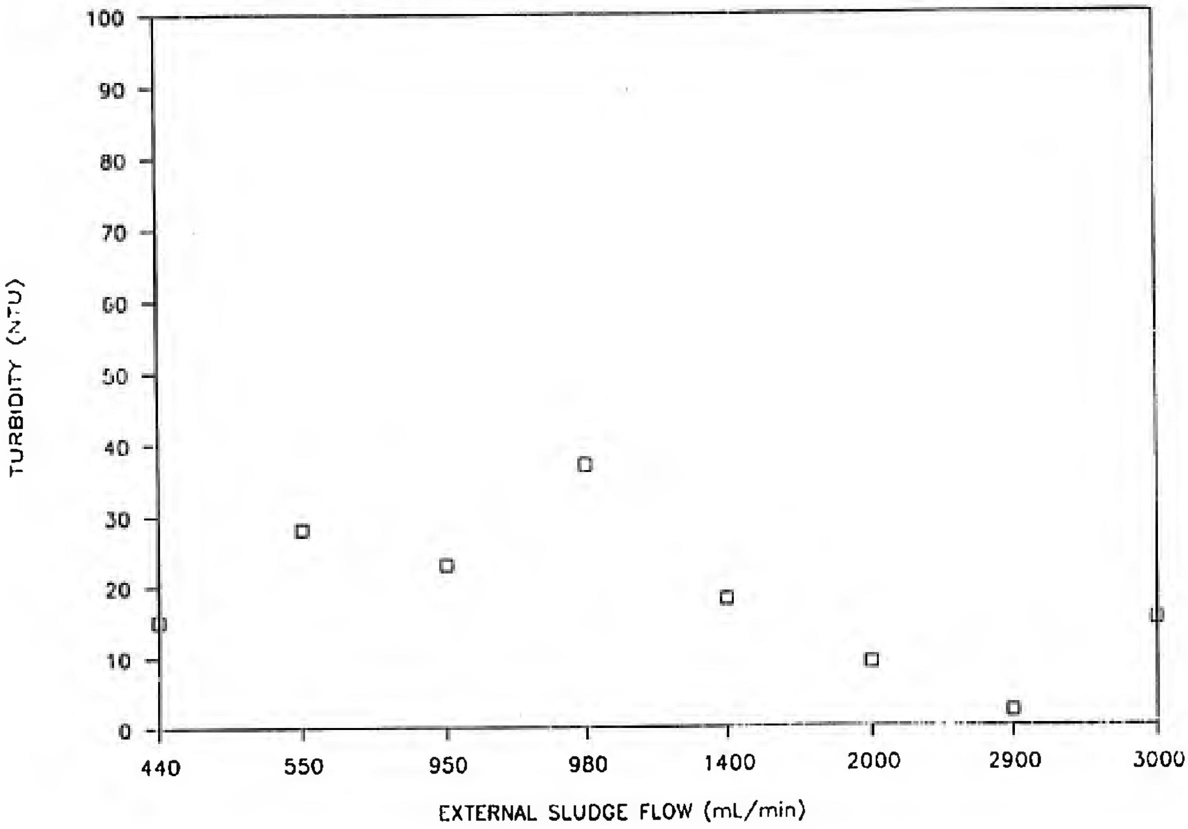

Figure 12. External Sludge Flow vs. Turbidity.

TABLE 6. SCC AT OPTIMUM OPERATING CONDITIONS (INFLUENT FLOW 3 GAL/MIN)

Constituent	Influent (mg/L)	SCC Effluent (mg/L)	NPDES (mg/L)
Cr^{+6}	3.30	0.00	0.10
Cr	6.20	0.28	1.00
Ni	2.01	0.20	1.00
Cd	0.27	0.02	0.03
Cu	0.12	0.02	1.00
Pb	0.17	0.06	1.00
Zn	0.20	0.03	1.00

The operation of the SCC was optimized at its maximum influent flow (3.5 gal/min); any decrease in the flow did not decrease the clarity or metal removal efficiency. During power outages and maintenance of the influent pump, flow to the SCC was stopped. If, before resuming flow, the rake, external sludge recirculation flow, and internal sludge recirculation had been started for 1/2 to 1 hour, there was no effect on the clarity or effluent quality. During long downtime (several days), the sludge and water would become septic and fines would be carried over for 4 to 8 hours.

Most clarifiers operate in the "slurry mode" or low sludge level during low flows, but in a sludge blanket mode during high flow.

During pilot plant operation, the sludge bed depth could be maintained in the SCC at flows near zero (0.5 to 1 gal/min) as long as the sludge recirculation was controlled. At these lower flows, more sludge had to recirculate through the external sludge recirculation to maintain the sludge depth.

The pilot plant influent flow rate was increased to a maximum of 7.5 gal/min and split to 3.5 gal/min to SCC influent as discussed in Section II with the chemical feeds adjusted accordingly. This influent flow represents the Tinker AFB IWTP maximum plant design flow of 1.5 million gal/day. At this rate, there was no effect on the efficiency of the chromium reduction.

The normal daytime operation temperature of the SCC was approximately 85°F with temperature spikes up to 95°F. These high temperatures had no effect on metal removal to below NPDES permit requirements. To test the effect of lower temperatures, ice was added to the 500-gallon E-tank to bring the temperature to 41°F. The influent was maintained at this temperature with ice for two retention times through the SCC. Influent flow was set at 5 gal/min and the SCC operated at 2 gal/min. The low temperature had no effect on the metal removal, as shown in Table 7.

C. SLUDGE PRODUCTION

Several batches of sludge from the SCC were filtered, using a bench-scale vacuum drum filter. The sludge was pumped down to 20 inches in the SCC. The pilot system was allowed to operate at 2 gal/min for a recorded period of time and the sludge again pumped down to 20 inches. The volume of water treated and the weight of the filtered sludge was recorded. Two such batches of sludge were filtered within 24 hours. A third batch, stored for approximately a week before filtering, became septic and was significantly heavier than the sludge filtered within 24 hours. It is assumed there was biological oxidation of the sludge with storage. Table 8 lists the filtered weight of each batch of sludge. This information was extrapolated to cover the volume of water treated at Tinker AFB IWTP in 1986. The table also shows the sludge disposed of at the Tinker AFB IWTP during 1986. This represents the amount of sludge produced in the treatment of 284,406,312 gallons of wastewater with 11,789 pounds of hexavalent chromium. The sludge volume also includes the sludge from the biological treatment process.

The pilot-scale system was drained, flushed, and operated using the acid/sulfur dioxide/lime process. Sulfuric acid was fed to Mixer-1, sulfur dioxide was bubbled into Mixer-2, and a lime solution was fed into Mixer-3. Chemlink 6360 cationic polymer (1 mg/L) was also fed to Mixer-3. The pilot

TABLE 7. EFFECT OF A 41°F TEMPERATURE

	(41°F) Influent (mg/L)	(41°F) SCC Effluent (mg/L)	(70°F) SCC Effluent (mg/L)
Cr^{+6}	5.40	0.02	0.00
Cr	7.00	0.30	0.28
Ni	1.15	0.20	0.20
Cd	0.13	0.02	0.02
Cu	0.05	0.01	0.02
Fe	1.77	1.99	--
Zn	0.11	0.02	0.03

system was operated both at pH ranges of 8 - 9 and 10 - 10.5. Metal removal to below NPDES Permit Requirement was achieved with either range, however, there was a significant decrease in sludge production at pHs 8.0 - 9.0 (Table 8). The sludge production at this pH was the same as that with the sodium sulfide/ferrous sulfate system when the sludge became septic. Sludge production was decreased by approximately 92 percent when the sulfide/ferrous process is compared to the acid/lime process at a range of 0 - 10.5. The IWTP at Tinker AFB normally operates at a pH range of 10 - 11. The amount of sludge produced various over different periods, with variations in characteristic of the influent water.

D. SYSTEM CHANGEOVER

The effects and procedure for changeover from the acid/sulfur dioxide/lime process to the sodium sulfide/ferrous sulfate process were evaluated to determine if any upsets will occur and to establish the procedures required to maintain an effluent which meets NPDES Permit Requirements.

Jar tests were conducted to determine the amount of ferrous required to reduce the hexavalent chromium in the wastewater to less than 0.1 mg/L Cr^{+6} at pH 7.2. It was found that 6 mg/L Fe^{+2} to 1 mg/L Cr^{+6} was required to reduce the chromium without the sulfide present.

TABLE 8. SLUDGE* PRODUCTION

Tinker AFB Existing System*	7.4 ton/MM gal	2,100 tons/yr
Pilot Plant Sulfuric Acid/Lime pH 10 - 10.5	10.0 ton/MM gal	2,844 tons/yr
Pilot Plant Sulfuric Acid/Lime pH 8.5 - 9	1.95 ton/MM gal	554 tons/yr
Pilot Plant Sodium Sulfide/ Ferrous Sulfate Sludge Septic	1.95 ton/MM gal	554 tons/yr
Pilot Plant Sodium Sulfide/ Ferrous Sulfate Filtered Within 24 h	0.75 ton/MM gal 0.45 ton/MM gal	213 tons/yr 128 tons/yr

* This sludge represents only the sludge from the acid/SO_2/time process and excludes the solids from the activated sludge system.

In the changeover test, the feed rate of the Betz 1195 and Betz 1120 were started at 20 mg/L and 0.5 mg/L, respectively, to Mixer-3 and the SCC. The acid, sulfur dioxide, and lime feeds were continued. With no polymer feed the lime floc was light and fluffy. Within 2 hours after starting the polymer feed, the sludge bed had compacted to a depth of less than 14 inches (the bottom of the intermediate skirt). The lime system is presently operated without external sludge recirculation at Tinker AFB; consequently, sludge recirculation was not used when treating the wastewater in the pilot plant with the acid and lime process. In the changeover test, after the polymer feeds were started, the external sludge recirculation was started at 20 percent of the SCC influent flow, which was at 2 gal/min. The system was operated with the acid, sulfur dioxide, lime, and Betz polymer feed until sufficient sludge had been produced to increase the sludge depth to 18 inches so that the SCC could operate with the sodium sulfide/ferrous sulfate process.

The ferrous sulfate feed was started at 6 mg/L Fe^{+2} to 1 mg/L Cr^{+6} to Mixer-2. The sulfuric acid and the sulfur dioxide feed solutions were turned off. The lime feed was continued to maintain the pH at 10 in

Mixer-3. The pH of Mixer-2 was allowed to increase to a pH of 7.2 with the influent wastewater, prior to starting the sodium sulfide feed to Mixer-1 at 2 mg/L S^{-2}:1 mg/L Cr^{+6}. (Sulfide feed could not be started at a lower pH because toxic hydrogen sulfide gases are produced.) Approximately 1.5 hours were required for the pH of Mixer-1 to equilibrate to 7.2. When the sulfide feed was started, the ferrous sulfate feed rate was decreased to 1.5 mg/L Fe^{+2} to 1 mg/L Cr^{+6} and pH control at 7.2 - 7.5 was started in Mixer-2, using sulfuric acid. When the changeover was completed in this manner, hexavalent chromium reduction was maintained, hydrogen sulfide was not produced and the metals were removed to NPDES Permit Requirements without upset to the activated sludge system.

E. THE ACTIVATED SLUDGE PROCESS

The data represented in the following graphs were obtained from two separate sources. The first figure (Figure 13) is based upon data gathered over the course of research during the summer of 1987. This comparison

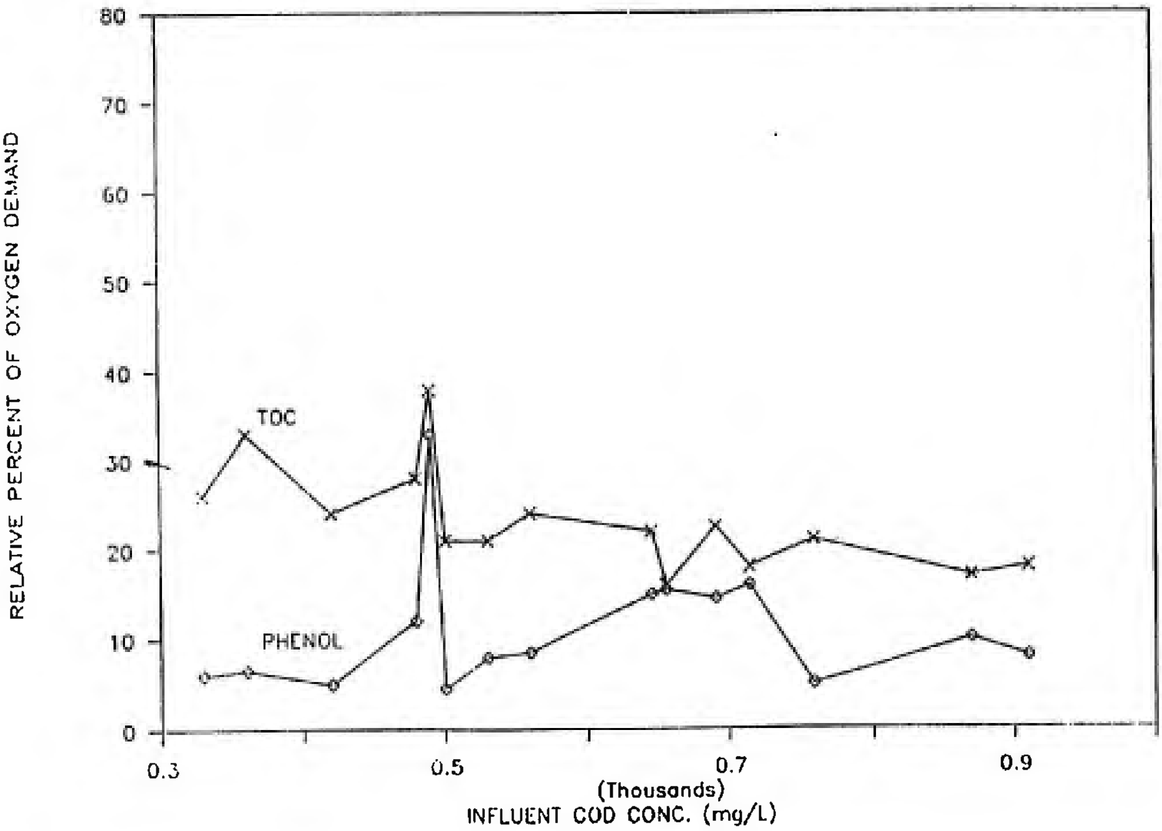

Figure 13. Comparison of Influent COD Sources.

indicated the known constituents of the wastewater which may contribute to the COD. These include phenol TOC (total organic carbon) and ammonium nitrogen. Phenol mirrors the TOC to a large extent in this figure. The data were assembled by using the pilot-plant influent data set and only points of this set where COD, TOC, phenol, and ammonium nitrogen measurements were available simultaneously. The data set was ranked according to increasing COD values; consequently, the data do not represent a consecutive daily order of analyses.

The remaining graphs are based upon data collected between September 28 and October 7, 1987. The data are presented in a consecutive order depicting changes occurring on a daily progressive basis. There are approximately four measurements per day. The data represent raw data that have not been fitted or smoothed to any statistical package.

Figure 14 compares measured COD levels in the activated sludge basin and the clarifier effluent. At the final point of discharge from the treatment system the effluent stream should be low in oxidizable material. The purpose of the activated sludge basin is to oxidize all organic material. The final clarifier should be designed to remove settleable solids from the effluent, hence producing a waste stream with no (or low) COD levels. This figure depicts the ability of the pilot plant's activated sludge basin and final clarifier to perform according to design criteria. Before these dates, an upset of steady-state conditions occurred in the influent of the activated sludge basin. It is believed that the upset was due to lime sludge leaving the SCC and discharged into the activated sludge basin. Consequently, the basin and clarifier conditions were altered. But, within three sample points (approximately one day) the activated sludge basin and the clarifier operations were restored, and once again COD levels were effectively reduced at the point of discharge.

Figure 15 exhibits similar trends depicted in Figure 14. During upset, the activated sludge basin was exposed to adverse conditions. Consequently, phenol degradation was reduced in the basin and phenol levels increased in the activated sludge basin and in the effluent stream discharged to the clarifier. As the activated sludge basin stabilized, the phenol

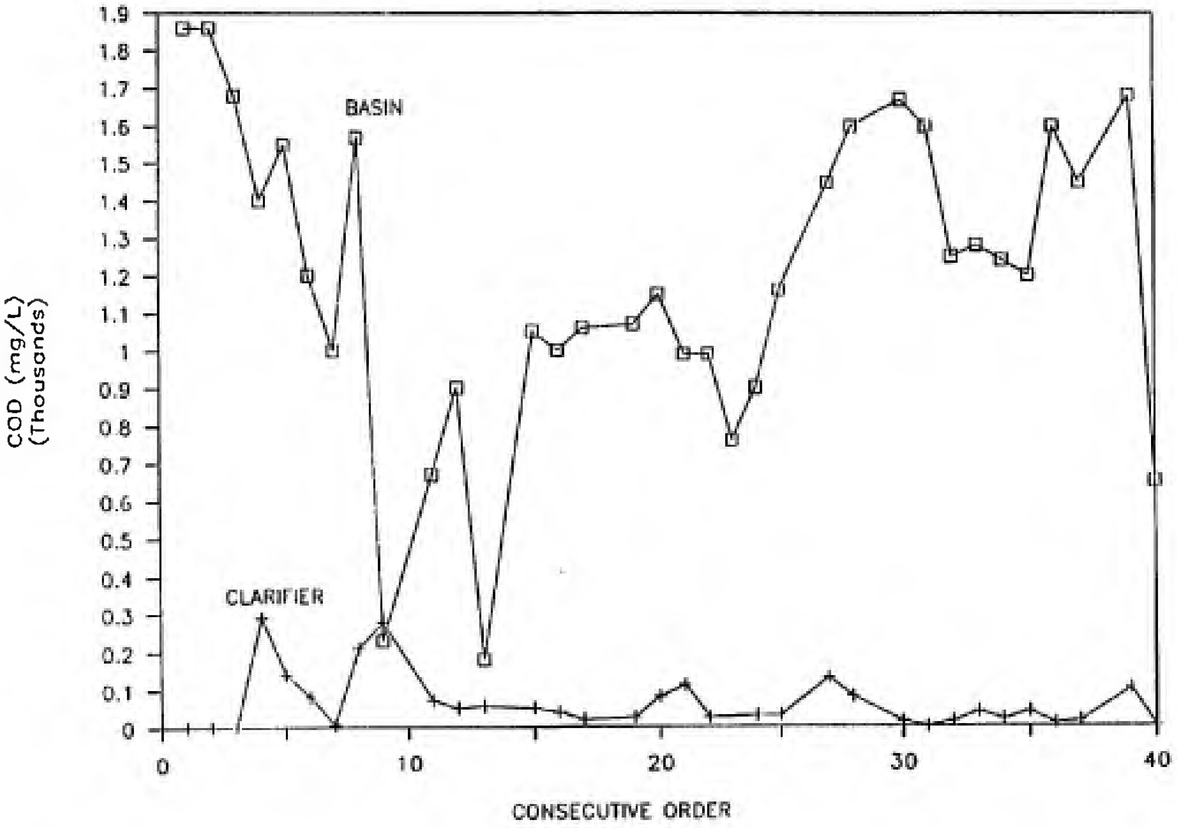

Figure 14. COD Through the AS Basin.

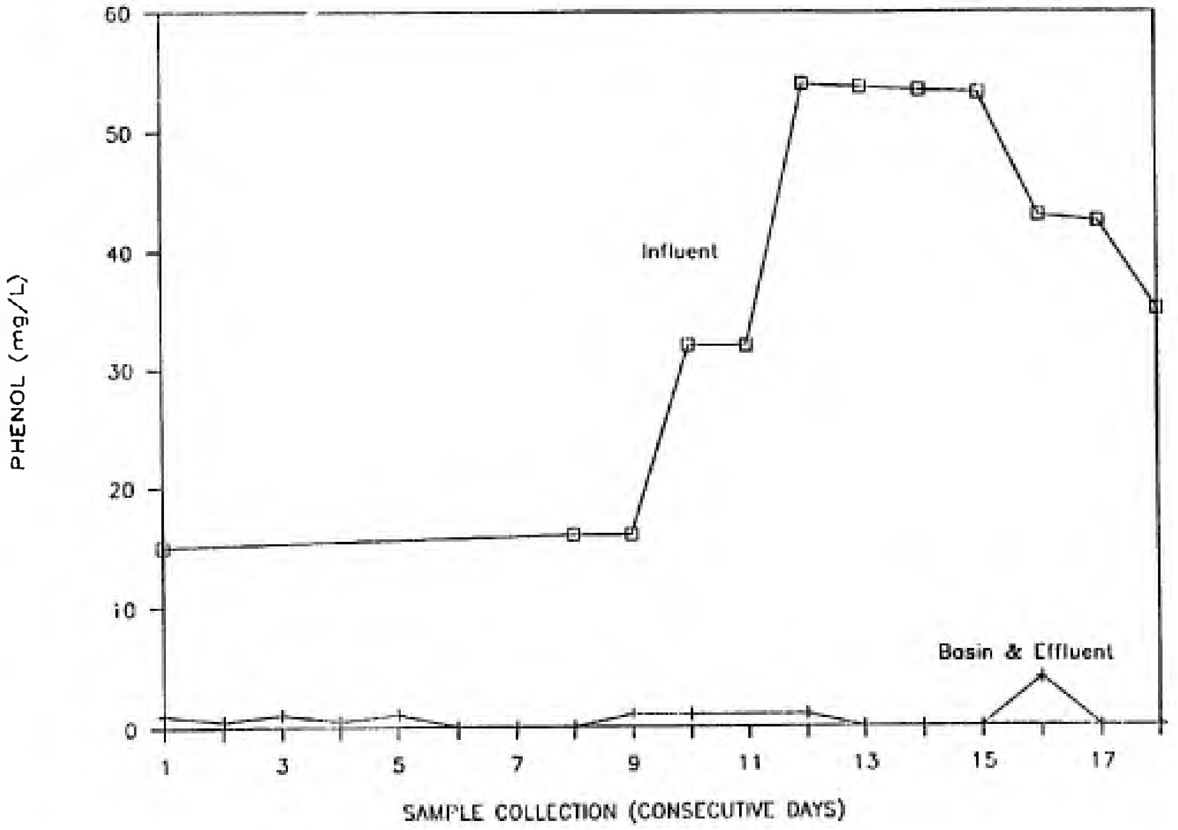

Figure 15. Phenol Through the AS Basin.

concentration decreased rapidly in the basin and in its discharge effluent. Phenol levels in the basin remained low even through tests to observe the effect of increased phenol feed rates to the activated sludge basin (Sample Points #20-30).

Figure 16 depicts orthophosphate levels through the activated sludge system during the same testing period. Orthophosphate levels remained low, even during the period of basin upset and increased phosphate additions.

Figure 17 shows the relationship of ammonium nitrogen in the influent, activated sludge basin, and the activated sludge basin effluent during the same testing period. Complete data were not available for the initial part of this testing period. At around Sample Point 25 the activated sludge basin seemed to be saturated with ammonium nitrogen, therefore, the influent activated sludge basin and activated sludge basin effluent ammonium nitrogen levels mirrored each other.

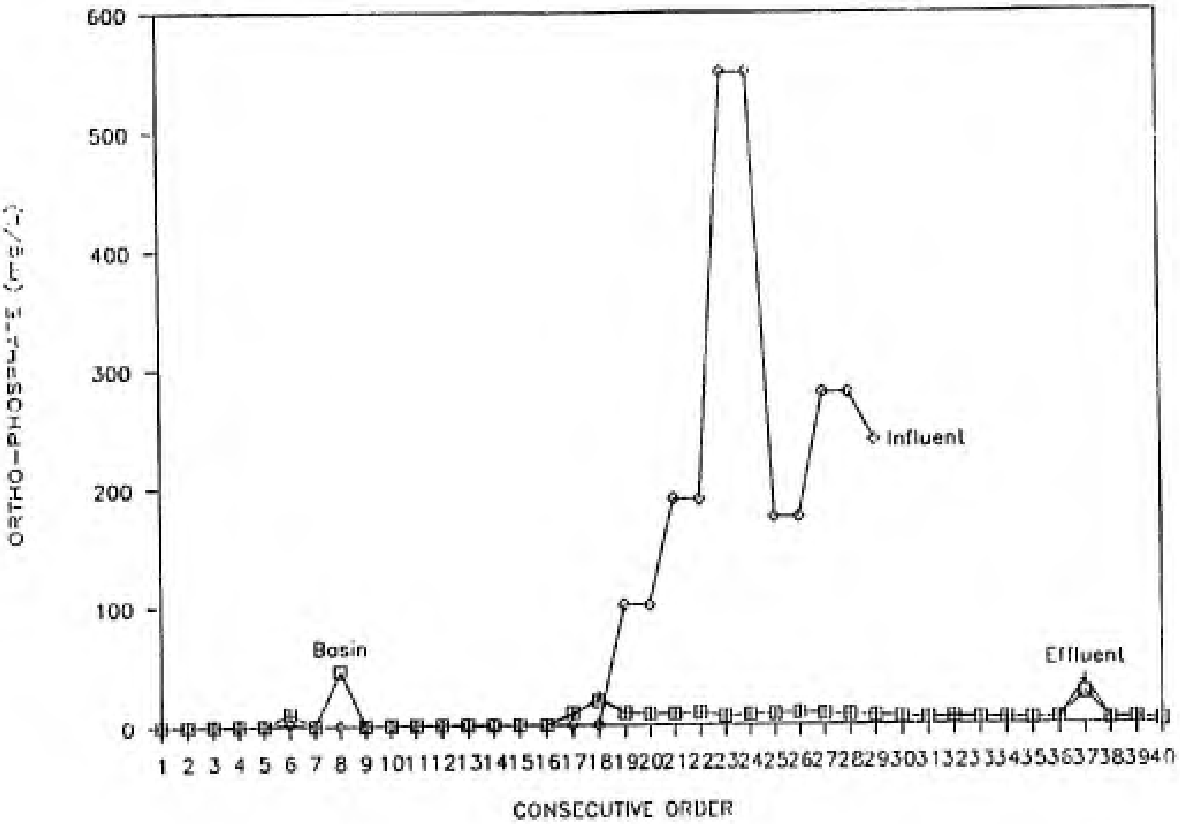

Figure 16. Phosphate Through the AS Basin.

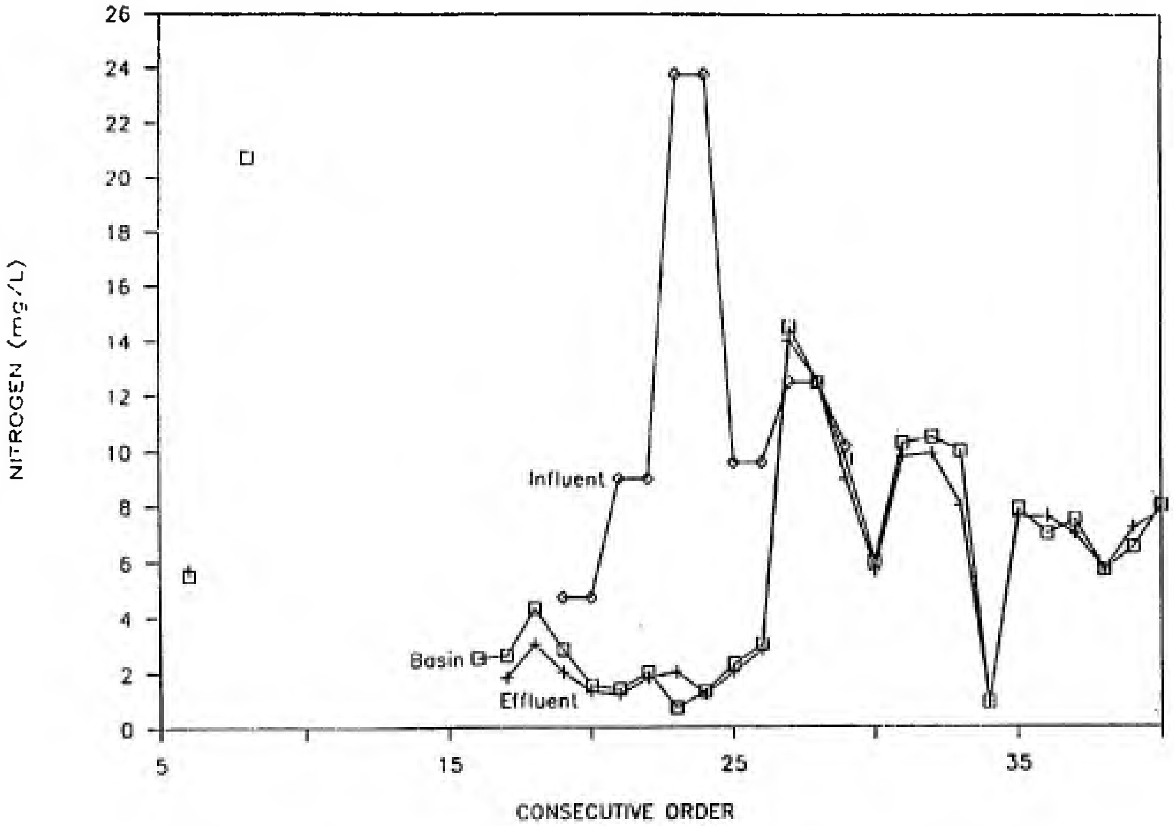

Figure 17. Nitrogen Through the AS Basin.

The comparison of ATP (adenosine triphosphate) levels in the activated sludge basin and the clarifier effluent (Figure 18) is a means of determining overall system performance. Similar to the logic associated with the COD in the activated sludge basin and final clarifier effluent, under normal operating conditions the activated sludge basin should have high concentrations of ATP, indicating a large and active microbial biomass. The effluent from the clarifier should be low in ATP, indicating the proper settling and removal of the biomass before discharge from the system. The activated sludge basin upset begins at Sample Point 7 with a drop in ATP in the activated sludge basin. A slow recovery over the remaining sample points indicates a gradual restoration of basin activity. Peaks in the clarifier discharge ATP levels indicate less than optimum settling conditions, resulting in a loss of biomass over the weir of the final clarifier.

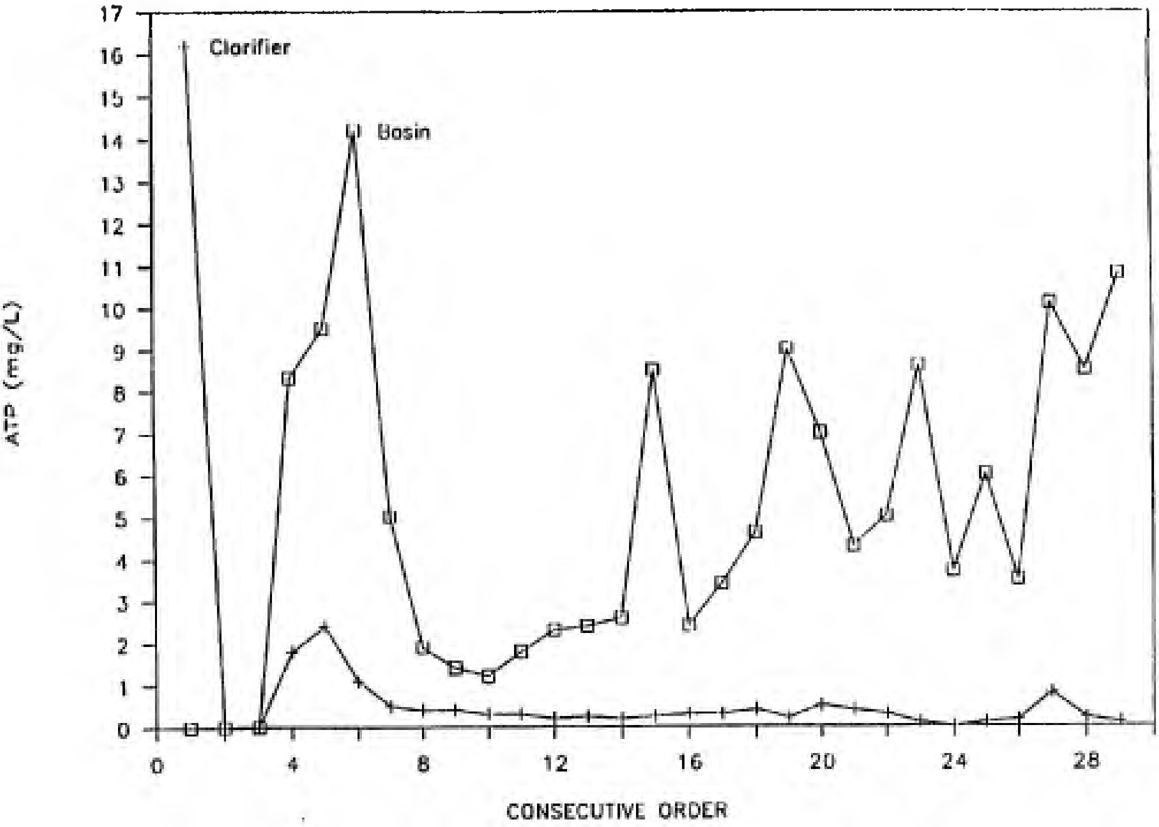

Figure 18. Influent and Effluent ATP Concentrations - AS.

Figure 19 exhibits similar information as Figure 18, however the relationship depicted is between suspended solids and ATP concentrations in the activated sludge basin. ATP levels decreased in response to the unfavorable upset conditions, and the suspended solids levels increased with the influx of inorganic materials to the activated sludge system. Over time, the solids decreased and ATP levels recovered.

F. INSTRUMENTATION

Following changeover, the pilot plant was operated with the ferrous sulfide process at optimum conditions for a number of weeks. During steady-state operation, the process removed metals and organics to the required limits.

The continuous flow analyzer (CFA) monitored the influent hexavalent chromium and could be used to control the sodium sulfide and ferrous sulfate feed. The influent wastewater carried a lot of solids, greases, and oils

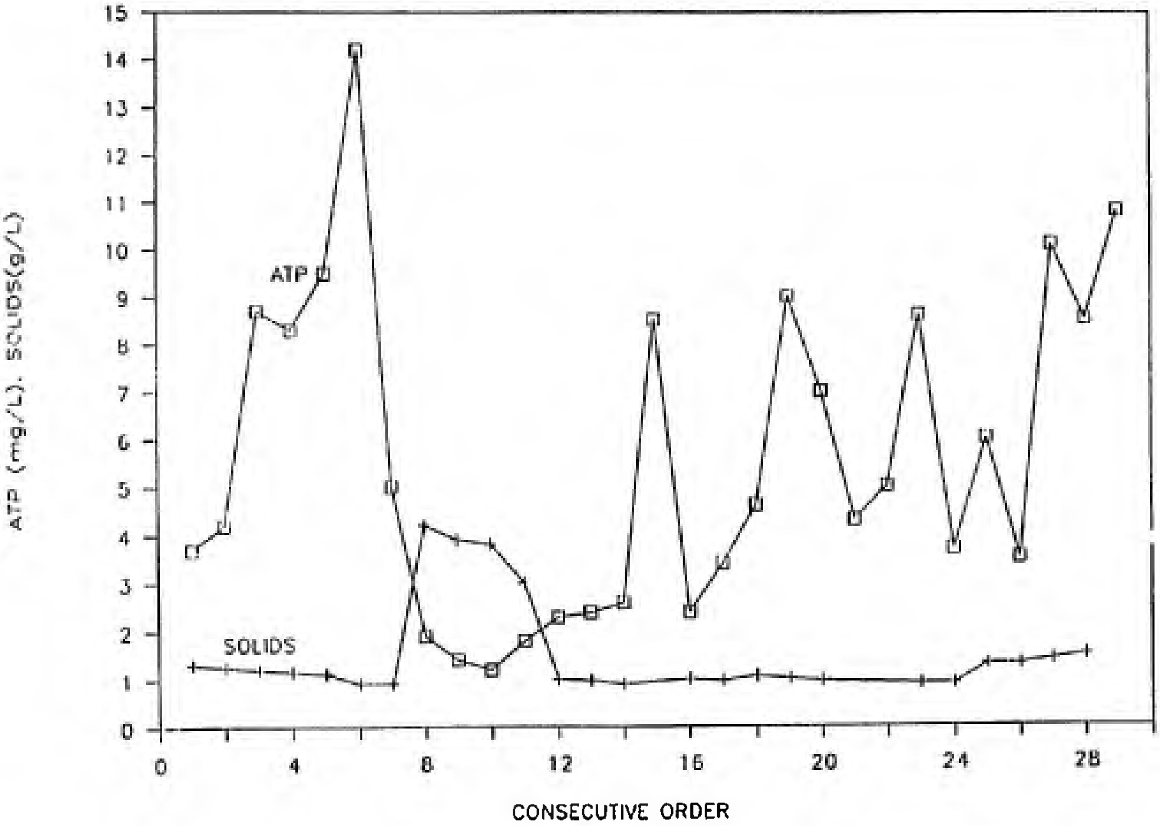

Figure 19. Comparison of the ATP and Solids in the AS Basin.

which plugged the sample lines to the CFA. Therefore, the pilot plant was operated in the manual mode by analyzing for chromium and manually setting the feeds to match this concentration. The Tinker AFB IWTP is operated in the batch mode with one equalization tank being filled while the other is being used. The pilot plant received its influent from only one of these tanks. The hexavalent chromium concentration did not change significantly during a given 6-hour period or while the tank was being filled. Figures 20 through 27 are plots of total chromium, hexavalent chromium, Cd, Cu, Pb, Ni, Zn, and phosphate concentration during the course of the pilot plant testing.

The CFA used for monitoring the effluent of the SCC for hexavalent chromium performed without plugging as long as the SCC was operating without carryover particulates. An increase in effluent hexavalent chromium concentration was a good indication of an upset.

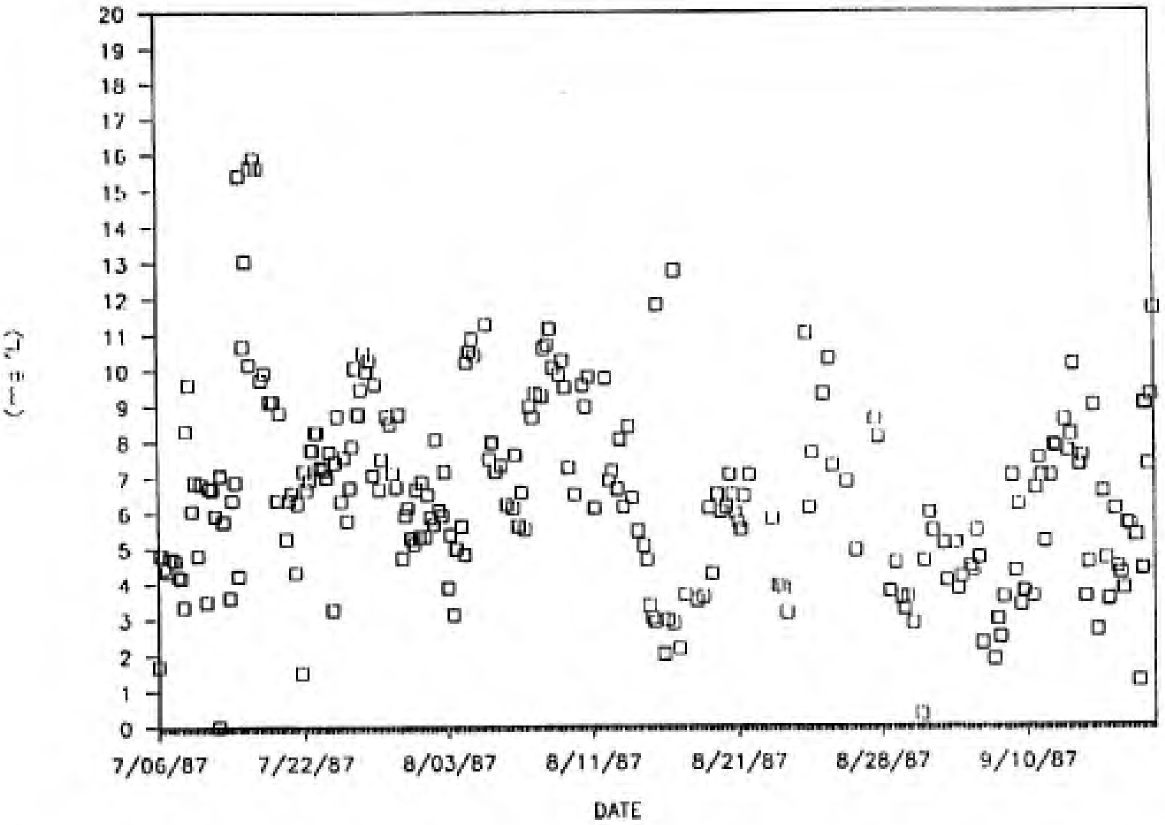

Figure 20. Influent (Total Chromium) Concentration.

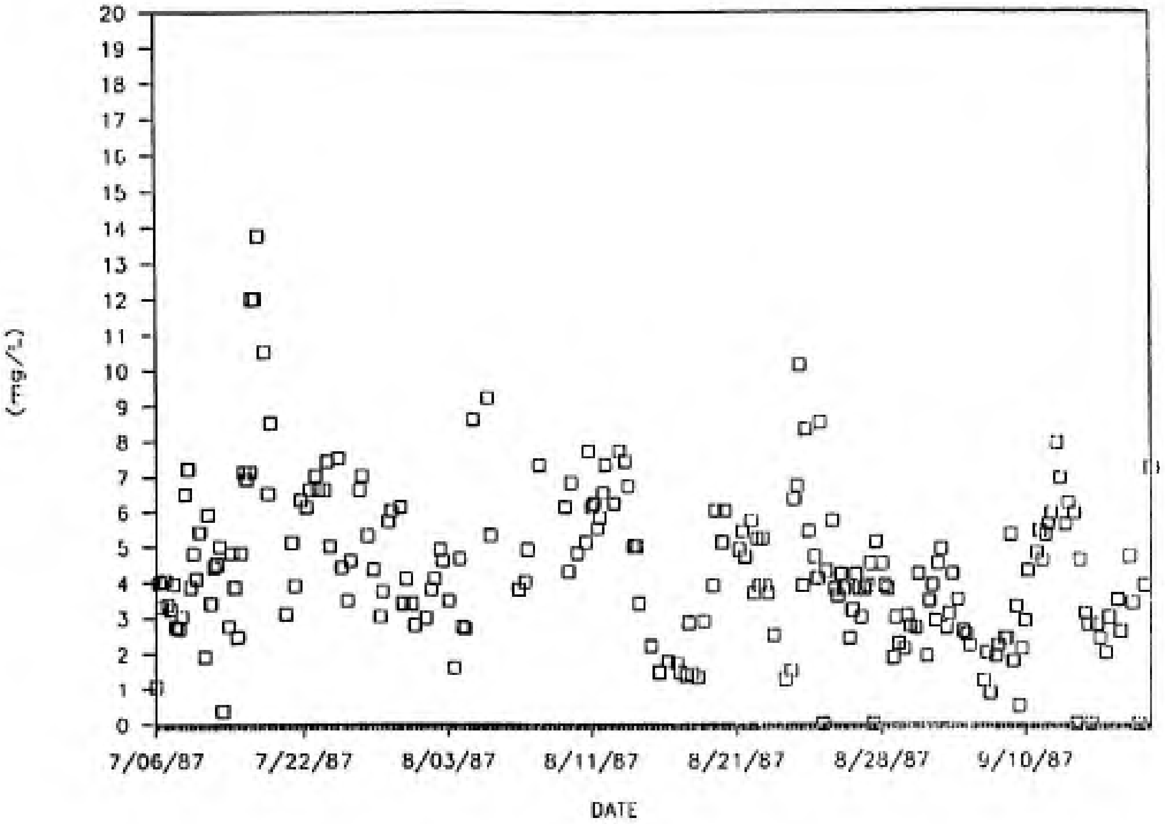

Figure 21. Influent (Cr_{+6}) Concentration.

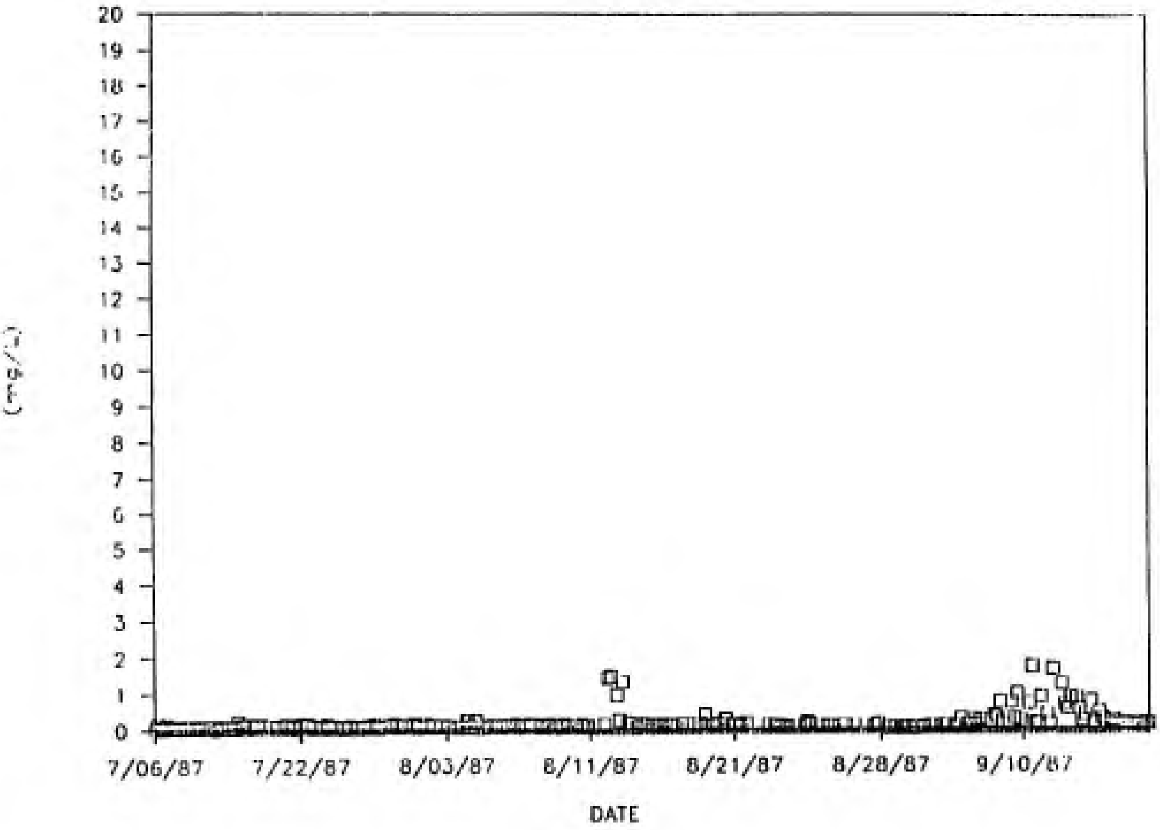

Figure 22. Influent (Cadmium) Concentration.

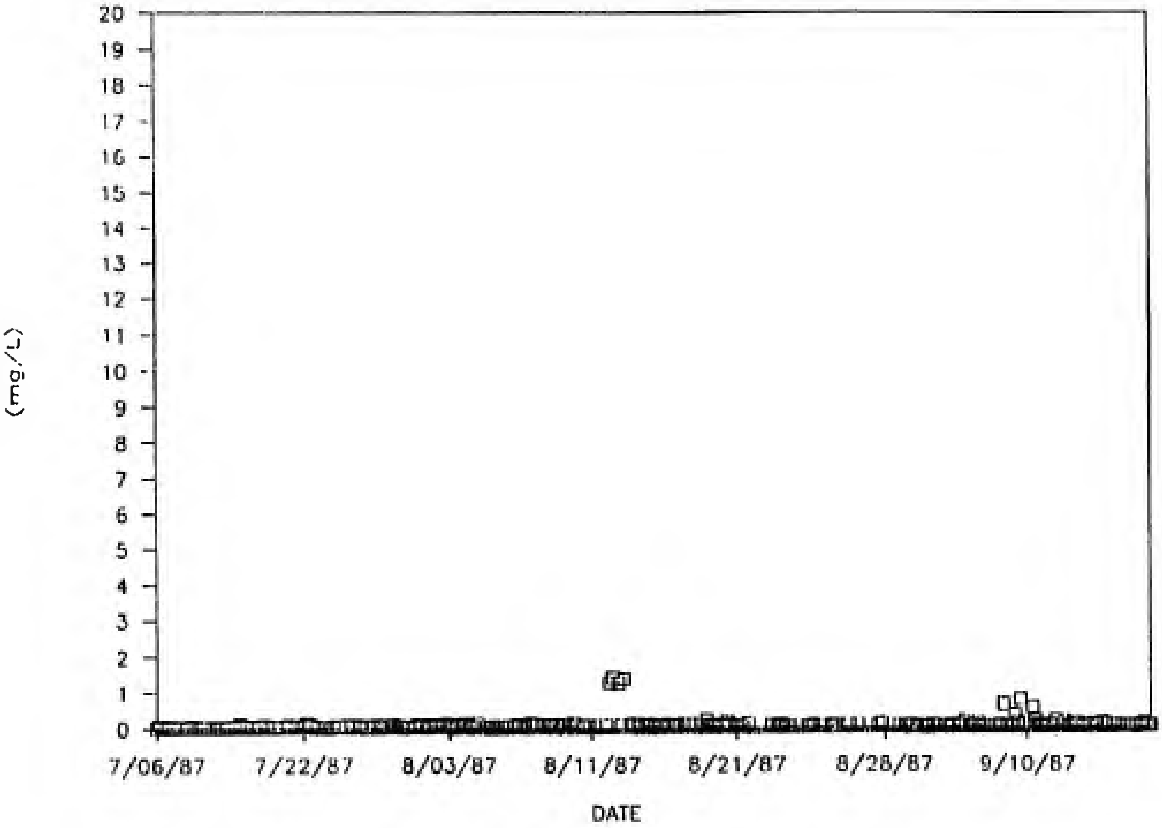

Figure 23. Influent (Copper) Concentration.

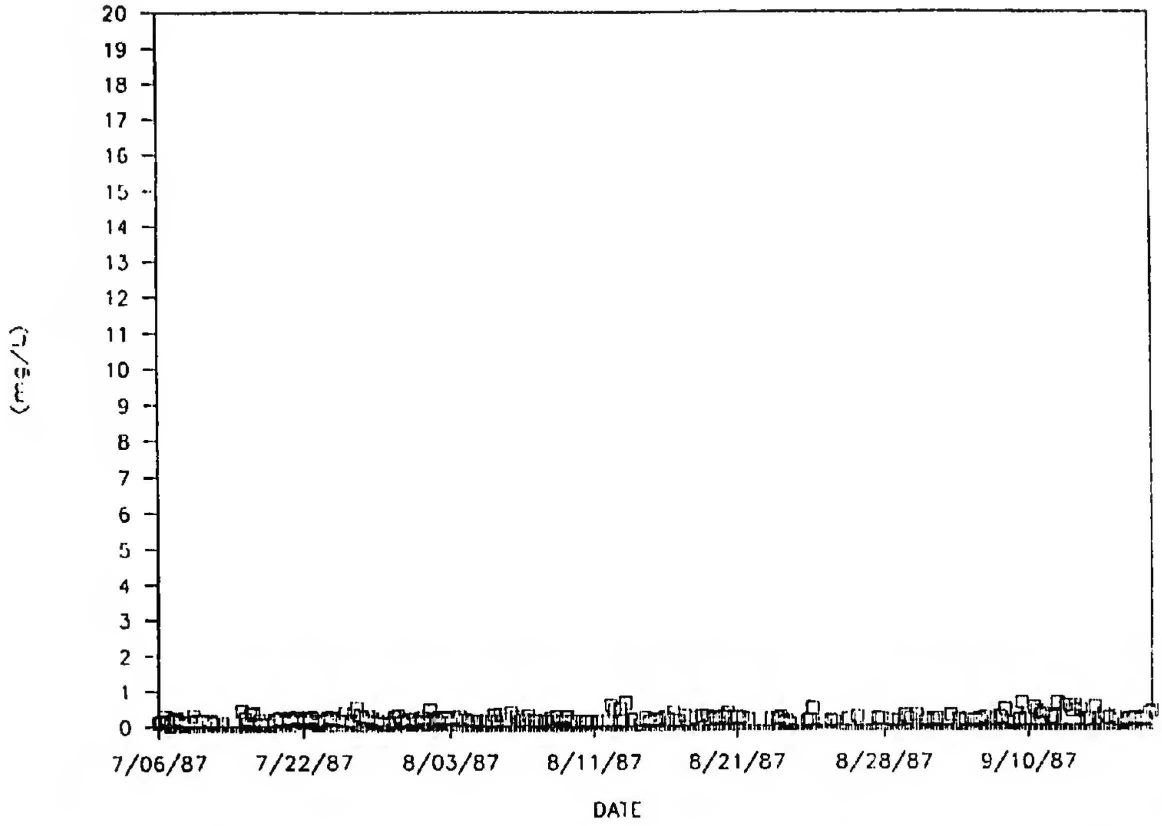

Figure 24. Influent (Lead) Concentration.

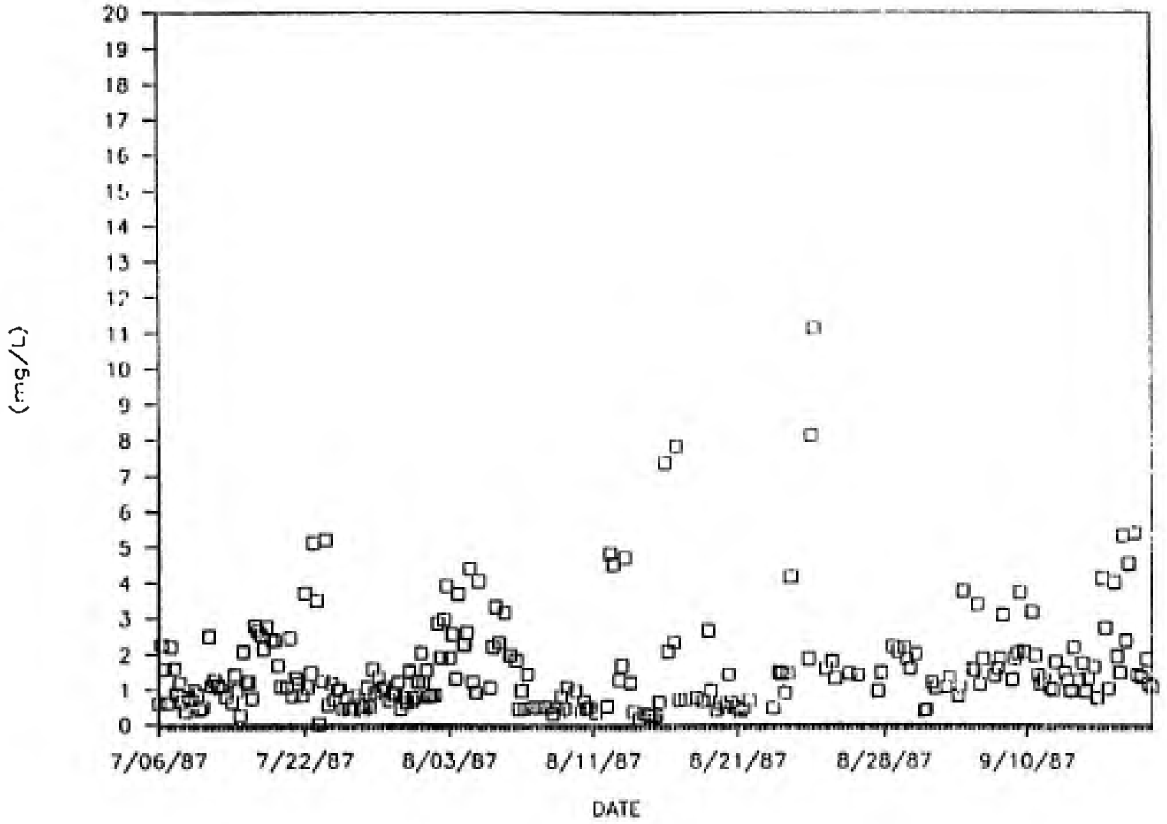

Figure 25. Influent (Nickel) Concentration.

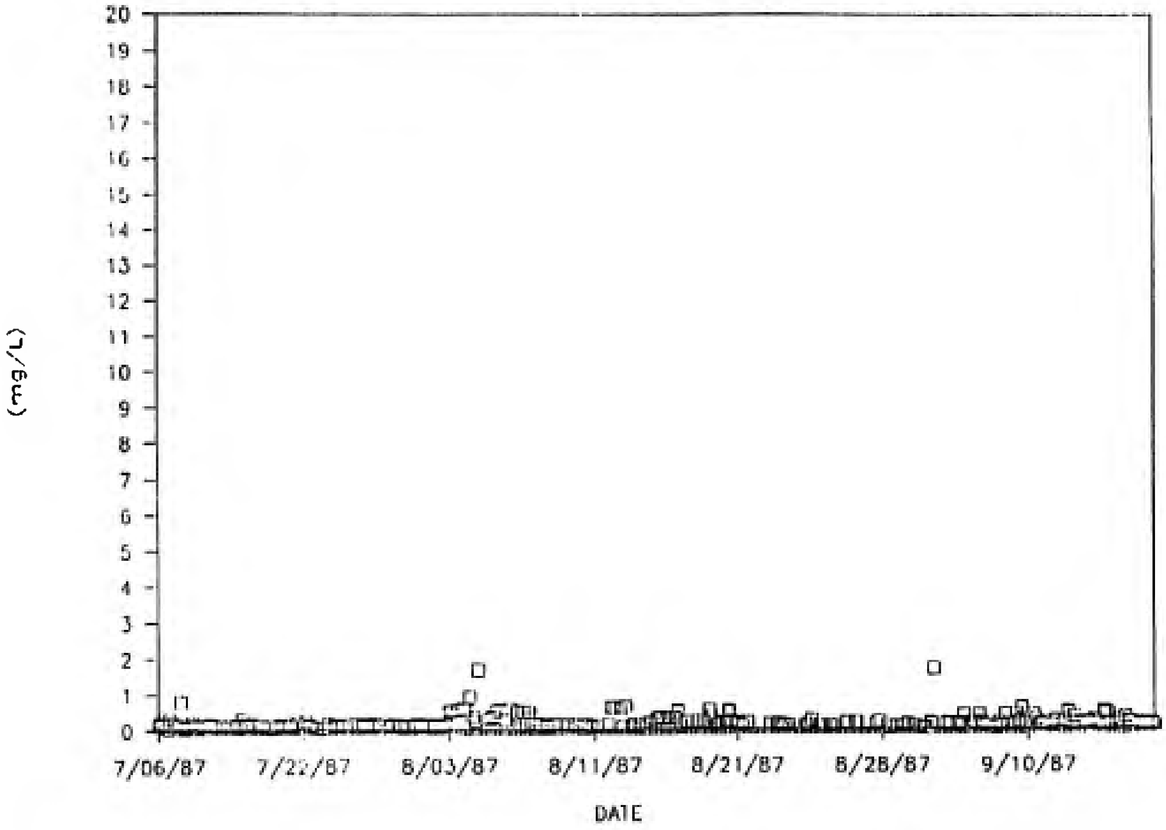

Figure 26. Influent (Zinc) Concentration.

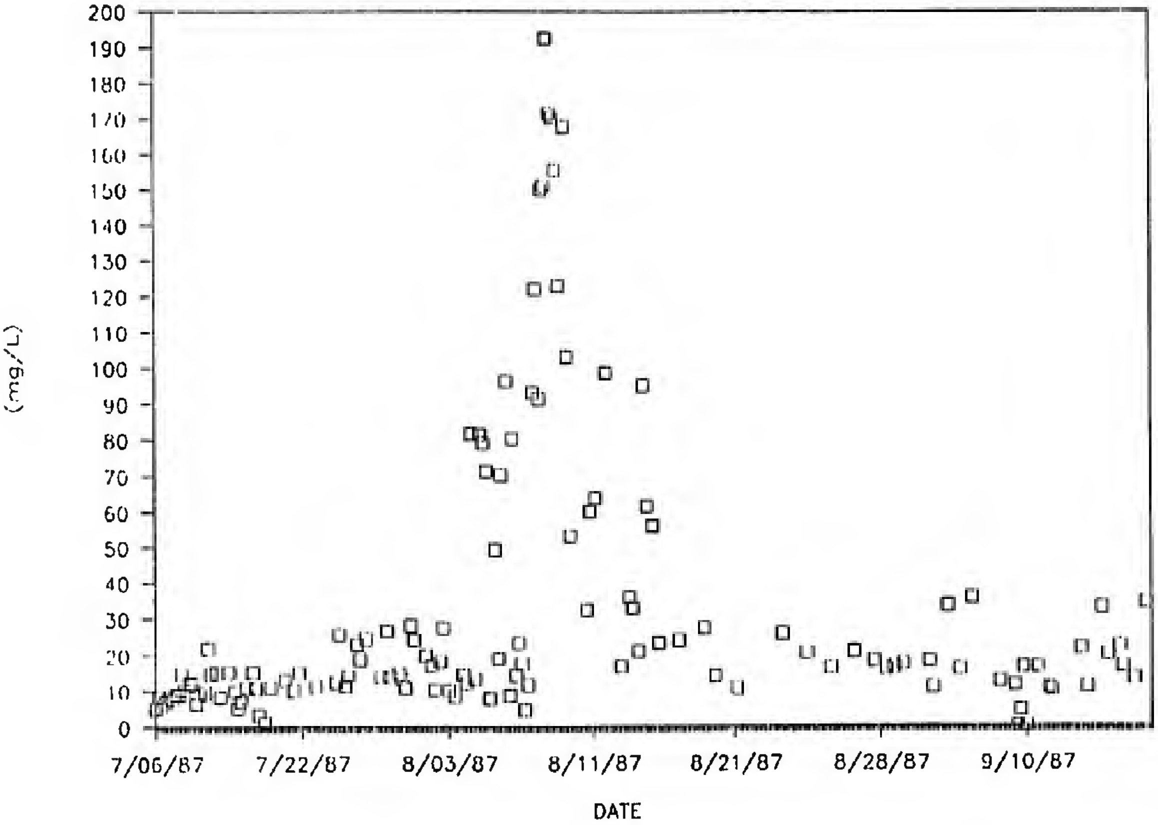

Figure 27. Influent (PO_4) Concentration.

The streaming current detector was used for monitoring the charge and potential of the floc from Mixer-3. The instrument was essentially maintenance-free; during a 4-month period, the pump was taken apart and cleaned monthly, and the line from Mixer-3 had to be flushed daily to prevent plugging. The flow rate in the line was 1 to 2 L/min by gravity flow, and the line was about 20 feet long. This detector can be used to control the streaming current with the on/off control to the polymer feed pump, thereby minimizing polymer use. The instrument was not set up to operate in this manner for the pilot plant operations.

Although the on-line respirometer was to be used to continuously monitor the respiration or activity of the activated sludge, the instrument was down for maintenance during most of the testing period. In general, respirometry is a good means of monitoring activated sludge activity and response to changes in the influent wastewater. However, the respirometer was not durable enough for continuous on-line operation in the pilot plant environment without excessive maintenance.

G. PROCESS CHEMISTRY

Goals of the process chemistry tests were to:

1. Define the chemical stoichiometry of the sodium sulfide/ferrous sulfate process
2. Identify the sulfur species produced in the reactions
3. Gain information on the Cr^{+6} reduction mechanism.

Jar tests were conducted on synthesized wastewater to evaluate the effects of Fe^{+2} and S^{-2} on the Cr^{+6} reduction rate and product distribution. The initial Cr^{+6} concentration was fixed at 20 mg/L as calculated on a per atom basis. In this report, all concentrations reported in mg/L are in reference to the individual species as though they existed separate from counter ions or complexing agents. Preliminary reactions indicated that a concentration range of S^{-2} and Fe^{+2} (narrower than originally proposed) should be controlled because solutions were produced

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with finely suspended particles and no increase in Cr^{+6} reduction. Thus, an equal number of reactions were run over a narrower concentration range.

The reactions were performed in 1-L beakers to which Cr^{+6} was added. The pH was adjusted to 7.2 - 7.5 with caustic. Solutions of S^{-2}, and Fe^{+2} were added sequentially before the pH was again adjusted to 7.2 - 7.5. The resulting 1.00-L solutions were then stirred for 5 min before aliquots were withdrawn, filtered, and analyzed. Reagent grade $K_2Cr_2O_7$, Na_2S, $FeSO_4$, NaOH, and H_2SO_4 from Fischer were used in the experiments. The reaction conditions and results are summarized in Table 9.

The ionic reaction can be written as:

$$CrO_4{}^{-2}(aq) + HS^{-1}(aq) + Fe^{+2}(aq) \;^{OH-}\; Cr(OH)_{3(s)} +$$

$$Fe^{+3}(OH)_{3(s)} + \text{sulfur species} \qquad (1)$$

The reaction is unbalanced since it is not known how many electrons are given up by the individual reductants in the Cr^{+6} reduction. Furthermore, the Cr^{+6}: HS^{-1} stoichiometry changes in a nonlinear inverse fashion with regard to the Fe^{+2} concentration. This is shown diagramatically in Figure 28. In the figure, the axes are labeled as mole ratios relative to the initial concentrations of the reagents. The initial concentrations of Cr^{+6} was 20 ppm, which is the common denominator for the ratios. Data are included for the jar tests where < 1 ppm Cr^{+6} remained after the reaction.

Analyses of the reaction solutions indicate that at least four sulfur species are formed: elemental sulfur, sulfite, sulfate, and sulfide. Elemental sulfur was detected in reaction solutions originally containing both Fe^{+2} and HS^{-1}.

Duplicates of several reaction solutions were extracted with toluene immediately after the pH adjustment. The toluene volume was then reduced to a thick slurry which was analyzed for sulfur by gas chromatography and mass

TABLE 9. REACTION CONDITIONS AND RESULTS OF JAR TESTS WITH HEXAVALENT CHROMIUM, SODIUM SULFIDE, AND FERROUS SULFATE

Initial Conditions[a,b,c]			Final Conditions[d]					
Run Number	S^{-2}	Fe^{+2}	Cr^{+6} [e]	Cr[f]	Fe^{+2} [g]	Fe[f]	S^{-2} [h]	floc[i] wt
1	0	0	21	22	0.0	0.0	0	None
2	0	10	18	21	4.4	7.8	0	100
3	0	20	13	9	0.1	6.0	0	660
4	0	30	11	11	0.2	6.3	0	--
5	0	40	8	7	0.0	2.3	0	250
6	10	0	19	22	0.0	0.0	10	None
7	10	10	8	1	0.0	2.0	1	470
8	10	20	2	4	0.2	0.8	1	750
9	10	30	0	3	0.2	1.0	1	970
10	10	40	0	3	0.0	0.8	1	1170
11	20	0	17	20	0.0	0.8	19	None
12	20	10	6	8	0.1	1.0	7	530
13	20	20	0	3	0.0	1.0	1	830
14	20	30	0	3	0.0	1.0	1	830
15	20	40	0	3	0.0	0.8	1	1280
16	30	0	15	22	0.0	0.0	16	None
17	30	10	3	7	0.0	2.3	8	620
18	30	20	0	1	0.0	0.8	5	820
19	30	30	0	1	0.3	2.7	2	1140
20	30	40	0	1	1.2	2.9	2	1250
21	40	0	12	11	0.0	0.0	22	240
22	40	10	0	3	0.5	1.2	15	640
23	40	20	0	2	0.2	2.8	11	870
24	40	30	0	1	0.9	4.4	5	1000
25	40	40	0	1	0.1	0.8	2	1400

TABLE 9. REACTION CONDITIONS AND RESULTS OF JAR TESTS WITH HEXAVALENT CHROMIUM, SODIUM SULFIDE, AND FERROUS SULFATE (CONCLUDED)

Initial Conditions[a,b,c]			Final Conditions[d]					
Run Number	S^{-2}	Fe^{+2}	Cr^{+6} [e]	Cr[f]	Fe^{+2} [g]	Fe[f]	S^{-2} [h]	floc wt[i]
26	50	0	13	15	0.0	0.0	41	200
27	50	10	0	4	0.0	2.0	22	620
28	50	20	0	17	2.2	16.8	16	560
29	50	30	0	22	2.1	27.8	3	560
30	50	40	0	16	3.0	35.4	2	990

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a. Concentrations are in ppm.

b. Initial Cr^{+6} concentration was 20.0 ppm

c. The pH was adjusted with H_2SO_4 or NaOH to $7.2 \leq 7.5$ after the Fe^+ was added.

d. After all the initial reagents had been mixed for 5 minutes.

e. As determined by Hach method for Cr^{+6} total chromium or iron.

f. As determined by AAS.

g. As determined by Hach method for Fe^{+2}.

h. As determined by Hach method for S^{-2}.

i. Dry weight of floc.

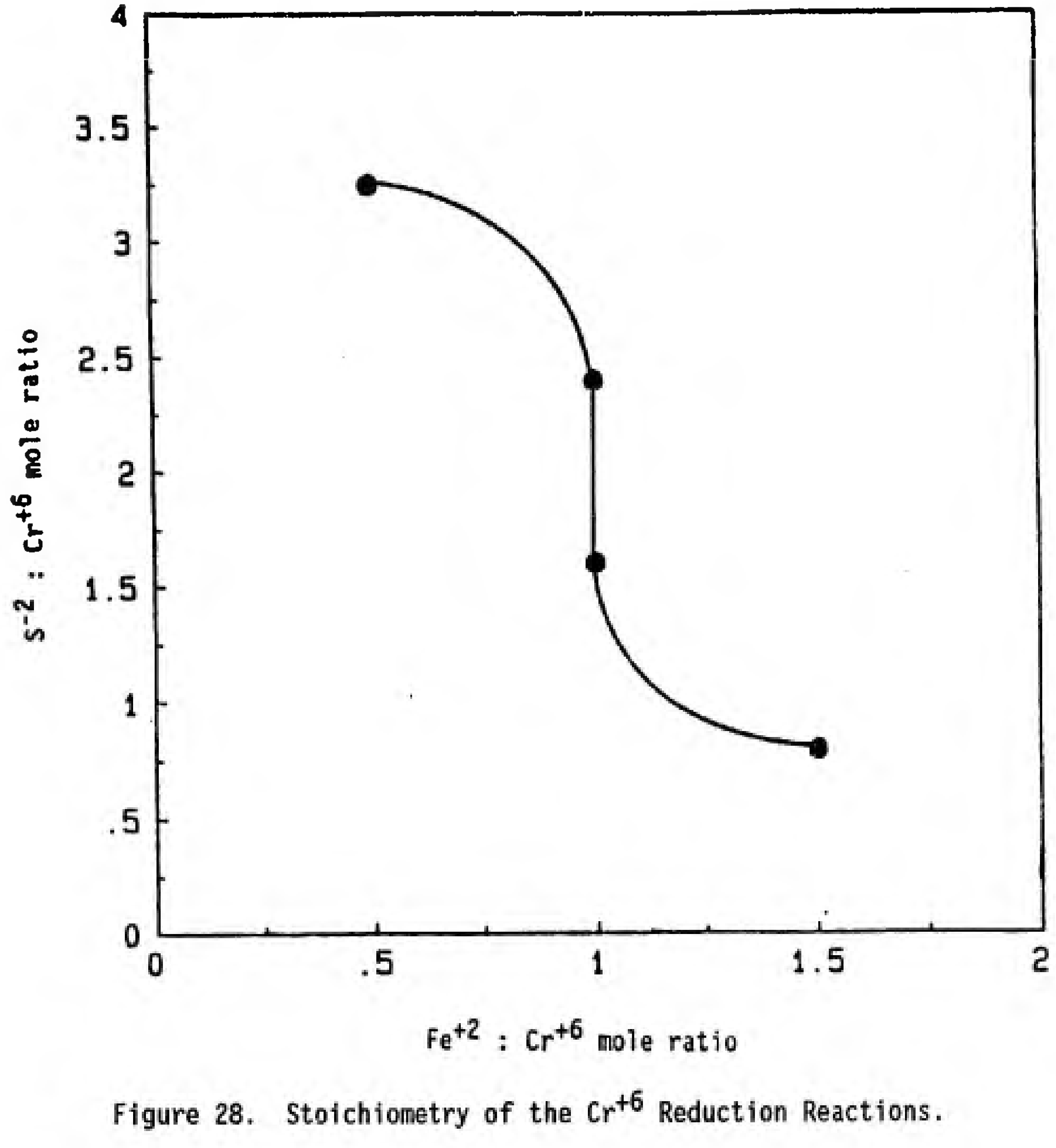

Figure 28. Stoichiometry of the Cr^{+6} Reduction Reactions.

spectroscopy. Analysis for sulfite was routinely performed using the Hach method, but produced ambiguous data due to interferences with other reagents in the mixture. Subsequent analyses of reactions (duplicate of those in Table 9) using ion chromatography clearly showed concentrations of sulfite exceeding 5 ppm. It is unclear if the sulfite is formed directly during the Cr^{+6} reduction or if it is strictly a product of the disproportion of elemental sulfur. Sulfur is thermodynamically unstable in base under these conditions and will disproportionate to form HS^{-1} and oxy-sulfur compounds. Complex interferences with the analysis methods used and problems with species precipitating with the floc precluded a rigorous mass balance and contributes to the uncertainty in determining the origin of the different sulfur species. Sulfate is readily formed as the oxidation product of the reactions of sulfite with Fe^{+3} and/or molecular oxygen. It cannot be concluded that sulfate is formed directly from the Cr^{+6} reduction reaction, only that it is formed in the overall process.

Several conclusions can be drawn from the data presented in Table 9. First, it is obvious that the mechanism of Cr^{+6} reduction to Cr^{+3} is complex and has many reaction pathways. Second, the reaction is concentration dependent for several species, particularly Fe^{+2} and HS^{-1}. This is further illustrated in Figures 29 through 31. In Figure 29, final Cr^{+6} is plotted vs. Fe^{+2} for six different concentrations of HS^{-1}. This clearly shows that high concentrations of HS^{-1} are more efficient at reducing hexavalent chromium. On the other hand, Figure 30 shows that although high HS^{-1} concentrations reduce hexavalent chromium, too-high a concentration hinders floccule precipitation. In Figure 30, the chromium includes all forms of soluble chrome plus fine particulates suspended in solution. These suspended fines are difficult to remove. Figure 31 is a plot of the total iron (including soluble forms and suspended fine particles of FeS) left in solution after the reactions vs. the initial amount of Fe^{+2} present. This illustrates that high Fe^{+2} and HS^{-1} concentrations, although effective at reducing hexavalent chromium, lead to black water. The black water is a fine

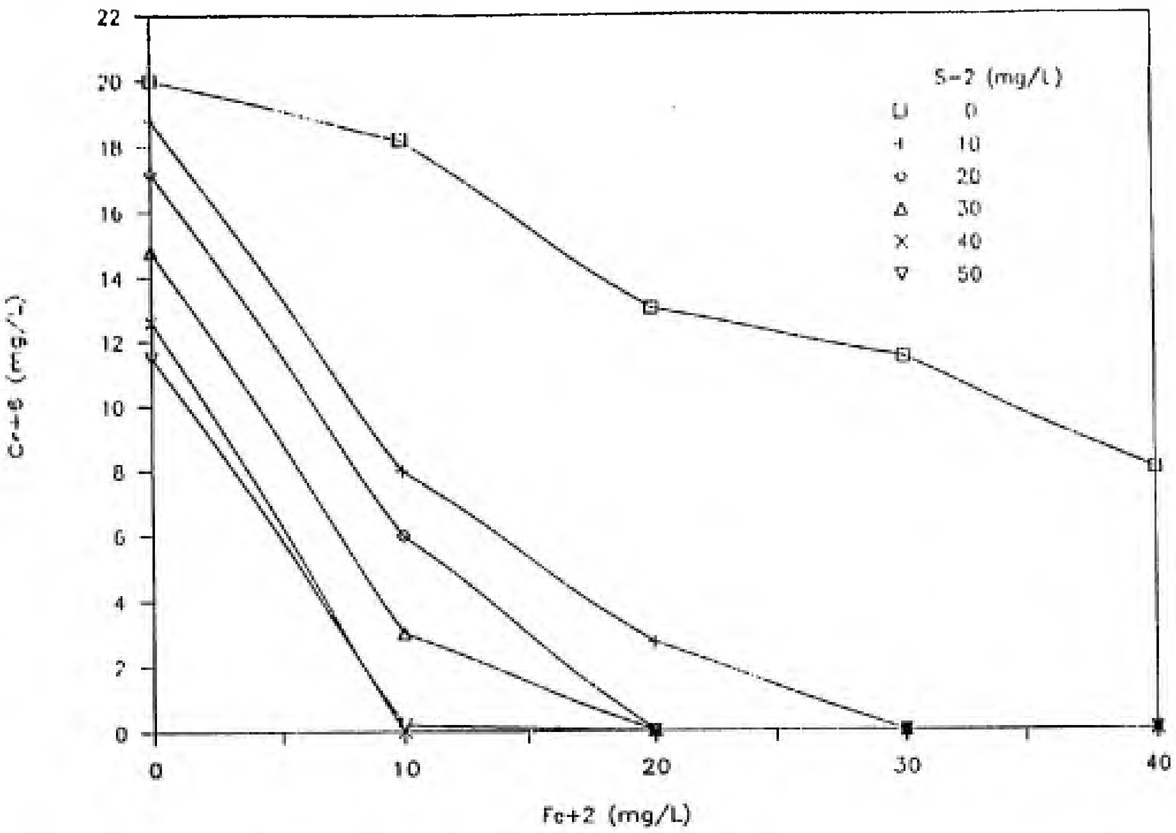

Figure 29. Final Cr^{+6} Concentration vs. the Initial Fe^{+2} Concentration for Different Sulfide Concentrations.

suspension of FeS that does not filter out well or precipitate with the floccules and leads to increased concentrations of soluble metals in the solutions.

To further investigate the mechanism of the hexavalent chromium reduction to Cr^{+3}, another series of test reactions were run with 10 mg/L Cr^{+6} solutions to evaluate the effect of bridging ligands. The reactions, conditions, and results are shown in Table 10. Run 31 illustrates that a reductant must be present to reduce hexavalent chromium. The reaction does not occur to any appreciable extent even in the presence of the bridging Cl^{-1} ligands. Run 33 tends to contradict this since significantly more Cr^{+6} reduction has occurred than should be expected from the amount of Fe^{+2} initially present. The results expected (if only rate enhancement and not a change in mechanism were assumed) are in accord with those obtained in Run 32. Similarly, Runs 34, 35, 36, and 39 yield final Cr^{+6}

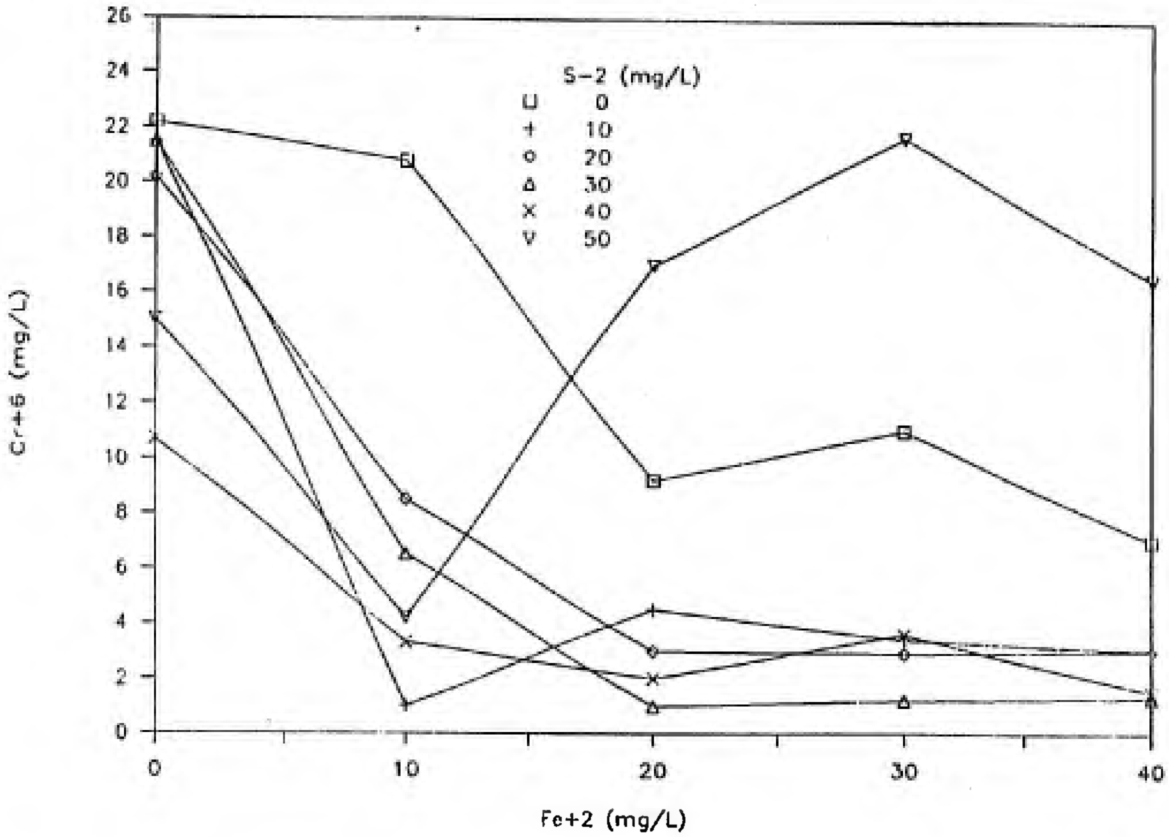

Figure 30. Total Chromium Left in Solution after the Reaction vs. the Initial Fe^{+2} Concentrations for Different Sulfide Concentrations.

concentrations differing by more than expected. Sulfide by itself is again shown to be ineffective at reducing Cr^{+6} but quite effective when in the presence of chloride. This later point is reinforced in subsequent runs, 36 and 40. For comparison, runs 37 and 42 show that different stoichiometries are possible for the Fe^{+2}, HS^{-1} system (in the absence of Cl^{-1} ligands), but a minimum atom ratio of Cr^{+6}:HS^{-2}:Fe^{+2} of 1:2:1 should be used. Run 41 remains an anomaly and is quite probably in error since the bridging ligand effect for SO_4^{-2} has not been previously demonstrated. It appears, therefore, that bridging ligands (Cl^{-1} or OSO_3^{-2} (SO_4^{-2}) in particular) are necessary in the Cr^{+6} reduction steps if Fe^{+2} is not present. In the presence of Fe^{+2}, bridging ligands are not necessary to effect electron transfer, presumably because the Fe^{+2} species can form an Fe-O-Cr bridge through which electron transfer can occur. Additionally, it is suggested that other reductants (HS^{-1}) can bridge through the iron and effectively reduce the Cr^{+6}. In the absence

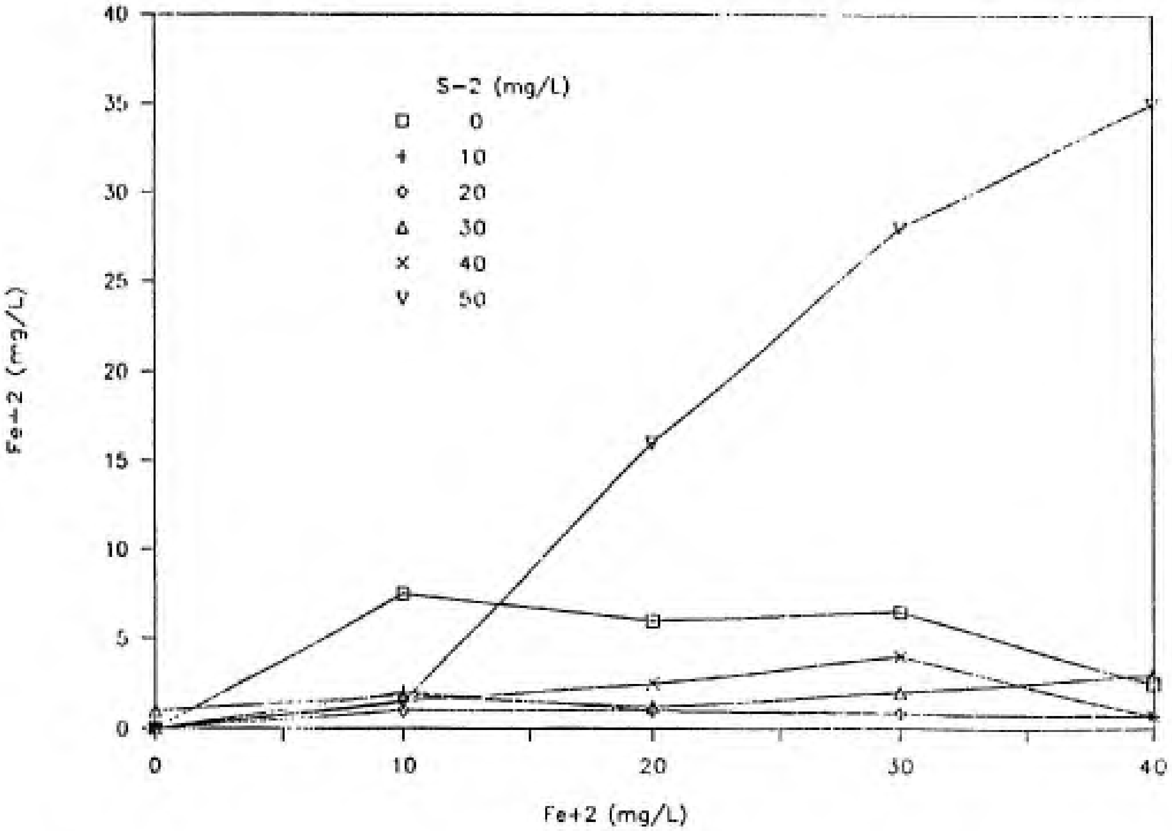

Figure 31. Total Iron Remaining in the Supernate After the Reaction vs. the Initial Fe^{+2} Concentration for Different Sulfide Concentrations.

of Fe^{+2}, bridging ligands like Cl^{-1} may form the electron transfer bridge by either joining to an oxygen, as does Fe^{+2}, to form Cl-O-Cr where the reductant can then bond through the Cl^{-1}, or by displacing an oxygen from the chromium to yield a Cl-Cr bridge. The implications here are that several different reaction mixtures will be effective. In practice, when dealing with real electroplating wastewater, both Fe^{+2} and HS^{-1} are necessary for efficient hexavalent chromium reduction and other metals precipitation. The effective concentration range (for the scaleup work) for these materials is also narrower than that determined by the jar tests.

TABLE. 10. REACTION CONDITIONS AND RESULTS OF JAR TESTS WITH AND WITHOUT BRIDGING LIGANDS

Initial Concentration[a] (mg/L)					Final Concentration (mg/L)
Run [b] Number	S^{-2}	Fe^{+2} ($FeSO_4$)	Fe^{+3} [c] (Source)	pH Adjust[d]	Cr^{+6}
31	0	0	20 ($FeCl_3$)	H_2SO_4	10
32, 33	0	10	0	H_2SO_4, HCl	7, 0.7
34, 35	10	0	0	H_2SO_4, HCl	9, 0.9
36	10	0	10 ($FeCl_3$)	H_2SO_4	2
37	10	10	0	H_2SO_4	0.1
38,39	20	0	0	H_2SO_4, HCl	7, 0.7
40,41	20	0	10 ($FeCl_3$, Fe_2,[SO_4]3)	H_2SO_4	0.1
42	20	10	0	H_2SO_4	0.1

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a. Initial hexavalent chromium concentration was 10 mg/L.

b. First number refers to first set of conditions listed, second number refers to second set of conditions.

c. Sources of iron (III); separated by a comma when multiple reactions were run using different sources.

d. Acids used to adjust the pH; separated by a comma when multiple reactions were run using different acids.

SECTION V
CONCLUSIONS

The sodium sulfide/ferrous sulfate process with the activated sludge process was successfully used on the pilot scale to treat Tinker AFB IWTP influent for reduction of hexavalent chromium, total metal removal and organic removal to less than NPDES permit requirements. The sulfide, ferrous and polymer requirements were optimized as well as the pH for this process, and the SCC operation. The optimum operating conditions are summarized in Table 11. The effects of chemical and physical parameters on the process operation were also investigated in the pilot plant. The general conclusions from these investigations are:

1. Control of pH is required in Mixer-2 after the addition of the ferrous sulfate. Although the hexavalent chromium was reduced to less than 0.1 mg/L Cr^{+6} in a pH range of 7.2 to 8.4, there was less scatter and less chance of exceeding NPDES permit requirements if the pH was controlled between 7.2 and 7.5.

2. Control of the influent pH is not required to maintain chromium reduction, but pH must be controlled to greater than 7.2 to prevent off-gassing of hydrogen sulfide gas.

3. The process will produce an effluent at the SCC that will meet the NPDES permit metal requirement as long as the chemical feed requirements are met and the SCC is operated at the optimum conditions.

4. Optimum operating requirements for the SCC include maintaining a sludge depth greater than the bottom of the intermediate ring so that the effluent is filtered through this sludge to remove fines. An external sludge recirculation rate of 10 to 20 percent of the influent flow with an internal sludge recirculation maintains the required high suspended solids concentration in the inner mixer chamber (80 to 90 percent suspended solids by volume). Operation

TABLE 11. CHEMICAL REQUIREMENTS FOR THE TINKER AFB IWTP

Sodium Sulfide	2 mg/L S^{-2} per 1 mg/L Cr^{+6}
Ferrous Sulfate	1.5 mg/L Fe^{+2} per 1 mg/L Cr^{+6}
Betz 1195 Cationic Polymer	20 mg/L
Betz 1120 Anionic Polymer	0.5 mg/L
pH Mixer-2	7.2 - 7.5

of the SCC at low flow, indicate the sludge bed can be maintained at these flows.

5. Even though cyanide, at 10 mg/L, was carried through the SCC at 1.81 mg/L, this concentration did not effect the activated sludge system and was reduced to 0.5 mg/L at the effluent of the final clarifier. In addition, cyanide did not affect the metal removal at the SCC.

6. Orthophosphate concentrations of 100 mg/L, and EDTA concentrations of 50 mg/L had no effect on hexavalent chromium reduction or total metal removal in the SCC.

7. Addition of 5 mg/L metal ions in addition to those present in the influent had no effect on the hexavalent chromium reduction or the total metal removal in the SCC.

8. If the SCC is operated at optimum conditions, the activated sludge system will not be affected by the sodium sulfide/ferrous sulfate system.

9. The activated sludge system will perform best if sound basin management is followed. This includes control of the oxygen feed, organic loading, flow, and the solids inventory.

10. Flow proportional/equivalent to 1.75 million gal/day through the Tinker AFB IWTP had no effect on the pilot-scale system's ability to meet NPDES permit requirements. Low flows (0 to 0.5 gal/min) through the SCC did not decrease the sludge blanket level to below the intermediate skirt and did not affect the effluent quality.

11. Temperature from 41 to 95°F did not affect the pilot-scale process.

12. The continuous flow analyzer works well to monitor the SCC effluent for hexavalent chromium, but requires excessive maintenance (due to plugging by dirt and greases in the influent wastewater) when used to control the feeds by monitoring the influent hexavalent chromium.

13. The streaming current detector is an effective method of measuring the current at the effluent of Mixer-3, and its operation is relatively maintenance-free. It appears to be a good method for controlling cationic polymer feed.

14. Although respiration monitoring is a good indication of the health (activity) of the activated sludge system, the respirometer was not rugged enough in the pilot plant for use without excessive maintenance.

15. The mechanics for chromium reduction with the sodium sulfide ferrous sulfate process is complex with multiple reaction pathways. The reaction is concentration dependent on several species (i.e., S^{-2}, Fe^{+2}, and bridging ligands). There is an inverse-concentration dependence on S^{-2} and Fe^{+2} with several sulfur species formed in the process.

SECTION VI
PRELIMINARY COST COMPARISONS

The cost comparisons between the acid/sulfur dioxide/lime process and the sodium sulfide/ferrous sulfate process (Table 12) are based on 1986 operating logs at Tinker AFB. During this time 11,789 pounds of hexavalent chromium and 284,406,312 gallons of industrial wastewater were treated, 2100 tons of sludge were produced, excluding any solids from the activated sludge system. The sludge included the sludge from the metal removal and the organic treatment process; it is assumed that most of the sludge is produced in the metal removal process. Tinker AFB is considering recycling the treated industrial waste back to their cleaning and electroplating processes. With the lime process, the wastewater requires softening to remove calcium to 150 mg/L calcium carbonate. Jar tests were run to determine the volume of soda ash (Na_2CO_3) required for softening. Approximately 709 tons/year of soda ash would be required and would produce approximately 709 tons of sludge. These costs are included in the cost comparison. The cost for the sodium sulfide/ferrous sulfate process is based on the use of dry chemicals and treatment of the same volume of water and hexavalent chromium as in the acid/lime process. Potential savings for the process is $382,995/year if the treated water is discharged as it is presently. If the treated water were to be recycled back to the industrial processes, the potential savings would be $590,023/year.

TABLE 12. SODIUM SULFIDE/FERROUS SULFATE PROCESS COST COMPARISON

Treatment Cost for Sulfuric Acid/Lime System	
Sulfur dioxide (3000-lb cylinders; 42 cylinders @ \$460/CY)	\$ 19,320
Sulfuric acid (2,000,000 lb @ \$0.04/lb)	\$ 80,000
Calcium hydroxide (675 tons @ \$66/ton)	\$ 44,500
Sludge disposal cost (2100 tons @ \$168/ton)*	\$352,800
Total Costs	\$496,620
Softening to 150 mg/L $CaCO_3$	
Soda ash (709 tons @ \$124/ton)	\$ 87,916
Sludge disposal (709 tons @ \$168/ton)	\$119,112
Total Costs	\$207,028
Total Treatment Costs	\$703,648
Treatment Cost for Sodium Sulfide/Ferrous Sulfate System	
Sodium sulfide ($Na_2S.9H_2O$) (88.34 tons @ \$495/ton)	\$ 43,727
Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) (43.9 tons @ \$195/ton)	\$ 8,559
Sulfuric acid (250,000 lb @ \$0.04/lb)	\$ 10,000
Betz 1195 cationic polymer (20 mg/L) (47,302 lb @ \$1.60/lb)	\$ 75,683
Betz 1120 anionic polymer (0.5 mg/L) (1,183 lb @ \$4.30/lb)	\$ 5,086
Sludge disposal (213 tons @ \$168/ton)	\$ 35,784
Total Costs	\$178,839
Potential Savings (without softening)	\$317,781
Potential Savings (with softening)	\$524,809

* Sludge disposal cost is for 2100 tons of sludge from the Acid/So_2 Process only, not from the activated sludge system.

SECTION VII
RECOMMENDATIONS

The sodium sulfide/ferrous sulfate process was used to treat the Tinker AFB IWTP influent wastewater on the pilot scale with the effluent meeting NPDES Permit Requirements. The process requires control of the chemical feeds and proper operation of the SCC, which includes maintaining a sufficient sludge depth and external sludge recirculation. When operated properly, the process can result in a substantial cost savings. The process should be implemented in the Tinker AFB IWTP and its operation demonstrated. An operation and maintenance manual should be prepared to describe the process operation. Implementation will require installation of an external sludge recirculation pump and pH controls.

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