ESL-TR-83-21

12

TREATMENT OF ELECTROPLATING WASTEWATERS BY ALKALINE FERROUS REDUCTION OF CHROMIUM & SULFIDE PRECIPITATION

THOMAS E. HIGGINS, PhD, VERNON E. SATER, PhD
COLLEGE OF ENGINEERING & APPLIED SCIENCES
ARIZONA STATE UNIVERSITY
TEMPE, ARIZONA 85287

JUNE 1983

FINAL REPORT
OCTOBER 1981 - MARCH 1983

AFESC

ENGINEERING & SERVICES LABORATORY
AIR FORCE ENGINEERING & SERVICES CENTER
TYNDALL AIR FORCE BASE, FLORIDA 32403

NOTICE

PLEASE DO NOT REQUEST COPIES OF THIS REPORT FROM HQ AFESC/RD (ENGINEERING AND SERVICES LABORATORY). ADDITONAL COPIES MAY BE PURCHASED FROM:

NATIONAL TECHNICAL INFORMATION SERVICE
5285 PORT ROYAL ROAD
SPRINGFIELD, VIRGINIA 22161

FEDERAL GOVERNMENT AGENCIES AND THEIR CONTRACTORS REGISTERED WITH DEFENSE TECHNICAL INFORMATION CENTER SHOULD DIRECT REQUESTS FOR COPIES OF THIS REPORT TO:

DEFENSE TECHNICAL INFORMATION CENTER
CAMERON STATION
ALEXANDRIA, VIRGINIA 22314

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ESL TR 83-21	2. GOVT ACCESSION NO. A131079	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) TREATMENT OF ELECTROPLATING WASTEWATERS BY ALKALINE FERROUS REDUCTION OF CHROMIUM AND SULFIDE PRECIPITATION		5. TYPE OF REPORT & PERIOD COVERED Final October 1981 - March 1983
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Thomas E. Higgins, Ph.D. Vernon E. Sater, Ph.D.		8. CONTRACT OR GRANT NUMBER(s) F08635-82-K-0089
9. PERFORMING ORGANIZATION NAME AND ADDRESS College of Engineering and Applied Sciences Arizona State University Tempe, Arizona 85287		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS JON: 19007018 PE: 62601F
11. CONTROLLING OFFICE NAME AND ADDRESS Headquarters Engineering and Services Center Tyndall Air Force Base, Florida 32403		12. REPORT DATE June 1983
		13. NUMBER OF PAGES 112
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

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

18. SUPPLEMENTARY NOTES

Availability of this report is specified on reverse of front cover.

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

Electroplating	Cyanide interferences
Electroplating wastes	Nickel waste treatment
Heavy metals treatment	Mixed metals treatment
Cadmium waste treatment	Ferrous reduction
Chromium reduction	Sulfide reduction
	Sulfide precipitation

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

The Air Force operates a number of electroplating facilities in support of weapons systems maintenance. These range from small, three-to four-bath operations to very large, 40,000-square foot, shops. This laboratory and pilot scale research effort was undertaken to develop simple treatment operations applicable to the small Air Force plating shops and improve the waste treatment at the large facilities. Treatment of wastewaters containing chromium, nickel, and cadmium was investigated using both synthetic and actual plating baths. The major results of this effort are as follows:

(Continued on reverse)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

1. Hexavalent chromium can be rapidly reduced and precipitated at alkaline pH levels, by stoichiometric, point-source additions of ferrous sulfate and sodium sulfide.
2. Background sulfide lowers the solubility of cadmium and nickel in solution except when cyanides are present. Due to complexing, cyanides blocked nickel, removed completely, and reduced the effectiveness of chromium and cadmium removal.
3. When dilute wastes were treated, the only unit processes required were in-line chemical addition for chromium reduction and upflow sand filtration. For concentrated wastes, a clarification step was included to ease the solids loading on the filter.
4. The process was adaptable to automatic control using colorimetric methods of chromium (VI) measurement.

The data generated, methods and procedures used, and full explanation of theory are included in the report.

PREFACE

This report was prepared by the Department of Civil Engineering, Arizona State University, Tempe, Arizona 85287, under Contract F08635-82-K-0089 for the Air Force Engineering and Services Center, Engineering and Services Laboratory (AFESC/RD), Tyndall Air Force Base, Florida 32403.

Work was performed between October 1981 and March 1983. The principal investigator was Dr. Thomas E. Higgins. Senior faculty involved with the project were Dr. V. E. Sater and Dr. J. W. Klock. AFESC/RDVW project officers were Major Stephen G. TerMaath and 2nd Lt James R. Aldrich.

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

This report has been reviewed and is approved for publication.

James R Aldrich
JAMES R. ALDRICH, 2nd Lt, USAF
Project Officer

Michael J. Ryan
MICHAEL J. RYAN, Lt Col, USAF, BSC
Chief, Environics Division

Robert F. Olfenbuttel
ROBERT F. OLFENBUTTEL, Maj, USAF, BSC
Chief, Environmental Engineering Branch

Robert E. Boyer
ROBERT E. BOYER, Col, USAF
Director, Engineering and Services Laboratory

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF FIGURES (Concluded)

LIST OF TABLES

LIST OF SYMBOLS

A = Absorbance
A_∞ = Steady-state absorbance
A = Area of filter (m^2)
A = K_1/K_2
B = [Fe(II)]e/3
b = Slope of E/V vs. V (sec/m^6)
C = Plating baths with Cd
c = Weight of solids per unit volume of filtrate (Kg/m^3)
Cl = Clarifier used
Cr_T = Total chromium concentration
D = Distilled water
D = A-B
F = Filter used
Fl = Flocculator used
(Fe) = Concentration of ferrous iron (mg/l)
[Fe(II)]e = Excess ferrous ion concentration (moles/l)
K_{sp} = Solubility product
Kw = Dissociation constant for water
k_1 = Reaction rate constant
k_2 = Reaction rate constant
P = Test pressure (N/m^2)
P = Plating baths
R = Specific resistance (m/Kg)
S = Synthetic
(s) = Denotes a solid precipitate
T = Tempe tap water
T = Percent transmittance
t = Time
V = Volume of filtrate collected (m^3)
x = [$HCrO_4$]
μ = Dynamic viscosity ($N\text{-}sec/m^2$)
[ ] = Molar concentration

(The reverse of this page is blank)

SECTION I

INTRODUCTION

The United States Air Force electroplating facilities range from the small, three- to four-bath operation to the very large operation with over 40,000 square feet of floor space. These shops plate a variety of metals in support of both local maintenance, and periodic, major overhaul of engines and aircraft at Air Logistics Centers. Although recovery and reuse are used to the extent economically feasible, low concentrations of mixed metals are present in the wastewater from electroplating facilities. The variety of metals and the normally low flow rates make total segregation and treatment of the waste streams impractical.

This research was undertaken to develop simple treatment operations applicable to small Air Force plating facilities and improve treatment already being accomplished at large plating shops. Variable workloads generate mixed metal-bearing wastewaters which are difficult to treat with conventional hydroxide precipitation. This is further complicated at small plating shops where full-time treatment plant operators are not practical; thus, an efficient and simple treatment methodology was desired.

Past Air Force successes with ferrous reduction of hexavalent chromium at near-neutral pH, coupled with the lower solubilities of sulfide precipitation, were judged to be candidate processes. Upflow filtration offered additional potential to eliminate rapid mixing and flocculation steps. Therefore, a single process was conceived where chemicals to reduce hexavalent chromium and precipitate metals are added just ahead of an upflow filter. Before such a process could be instituted, ferrous reduction of hexavalent chromium at neutral and alkaline pH had to be proven, since the literature reported reduction as essentially nonexistent above pH 3. This proof was provided in earlier studies by the principal investigator under grants from the Air Force. This study was initiated to develop a pilot plant and test the feasibility of the process.

We reviewed the theoretical basis for previous contentions that chromium reduction by ferrous iron at neutral and alkaline pH was infeasibly slow. Studies were performed to determine the kinetics of the reactions with varying pH.

In early studies, difficulties were encountered in removal of nickel from a mixed-metal waste. Studies were performed to determine the cause of this interference.

A pilot plant was designed and built, incorporating the potential unit processes (flocculation, clarification, upflow filtration) most likely to be incorporated in a final treatment system. The pilot plant was tested, under varying operating conditions, to determine the effectiveness of each process and to determine design criteria for a full-scale system.

Candidate methods were investigated for monitoring and control of the treatment process and colorimetric analysis of hexavalent chromium was selected as the most promising control method.

Residuals produced by the pilot plant were collected and analyzed to determine: quantities produced by plant operation; dewaterability by vacuum filtration; relative concentrations of the different metals; and toxicity, as evaluated by the "E.P." Toxicity Method.

SECTION II

LITERATURE AND THEORY

A. CHROMIUM REDUCTION

Conventional treatment of a mixed-metal wastewater consists of hydroxide precipitation of the metals at an alkaline pH, followed by removal of the resulting solids by plain sedimentation and sometimes filtration. Hexavalent chromium is very soluble, and thus is not removed by the above processes, unless preceded by reduction to the less-soluble trivalent chromium. Sulfur compounds (sodium sulfite, sodium bisulfite, sulfur dioxide) are commonly used as reducing agents for this process. Since these reactions are slow at neutral and alkaline pH, chromium reduction is usually carried out in a reactor maintained at the optimum pH (2 to 3).

Treatment complexity results from the need to purchase and control separate acidic and alkaline reactors. It also can result in excessive chemical usage due to the need to add acid to the first reactor, then neutralize it with base in the second. Efficient alkaline reduction of hexavalent chromium would consolidate these two processes, simplify the treatment of mixed-metal wastewaters, and reduce acid and base usage.

1. Alkaline Chromium Reduction by Ferrous Iron

Ferrous compounds are used as alternate reducing agents for chromium reduction. Bennet (Reference 1) and Watson (Reference 2) stated that an acidic pH (less than 3) is required for reasonably rapid reduction of chromium by ferrous sulfate. That acidic pH is necessary is commonly accepted in the field of sanitary engineering (References 3 and 4). In contrast, Germaine et al., (Reference 5) and Sorg (Reference 6) reported that ferrous sulfate had effectively reduced hexavalent chromium at other than acidic pH. Recent studies by Higgins (References 7-11) have demonstrated that hexavalent chromium can be rapidly reduced at neutral and alkaline pH.

The use of ferrous iron as a reducing agent has both advantages and disadvantages. The oxidized ferric iron is an excellent coagulant and its use could improve removal of the resulting solids and reduce the need for a separate coagulant. The ferric iron precipitates as a hydroxide. Jenne (Reference 12) reported that ferric hydroxides have a significant capacity to remove metals from solution. The use of ferrous iron for reducing chromium can result in more complete removal of a mixture of metals than predicted by solubility. Other metal hydroxides can be included in the resulting heterogeneous, amorphous ferric hydroxide precipitate. A disadvantage of ferrous iron is the small valence charge of one electron per ion, necessitating a large iron-to-chromium dose ratio (3.2:1 by weight) and a resulting high-sludge production. Due to these characteristics, the use of ferrous iron would probably be most advantageous in the treatment of wastewaters having low hexavalent chromium concentrations and requiring a high-removal efficiency for this and other metals (e.g. a mixture of plating bath rinse waters or cooling tower blowdown).

Since there are these potential advantages to the development of a process employing alkaline ferrous reduction of chromium as well as treatment of mixed-metal wastewaters, it is useful to further investigate the theoretical bases for the published differences on the effects of pH on reaction rates.

2. Reaction Rates of Ferrous Reduction of Chromium

Hexavalent chromium is a weak acid anion, with the predominant form dependent on pH and total chromium concentration. Figure 1 is the distribution diagram for the various species of hexavalent chromium for concentrations of total chromium commonly encountered in plating rinse waters (5.2 and 104 mg/l).

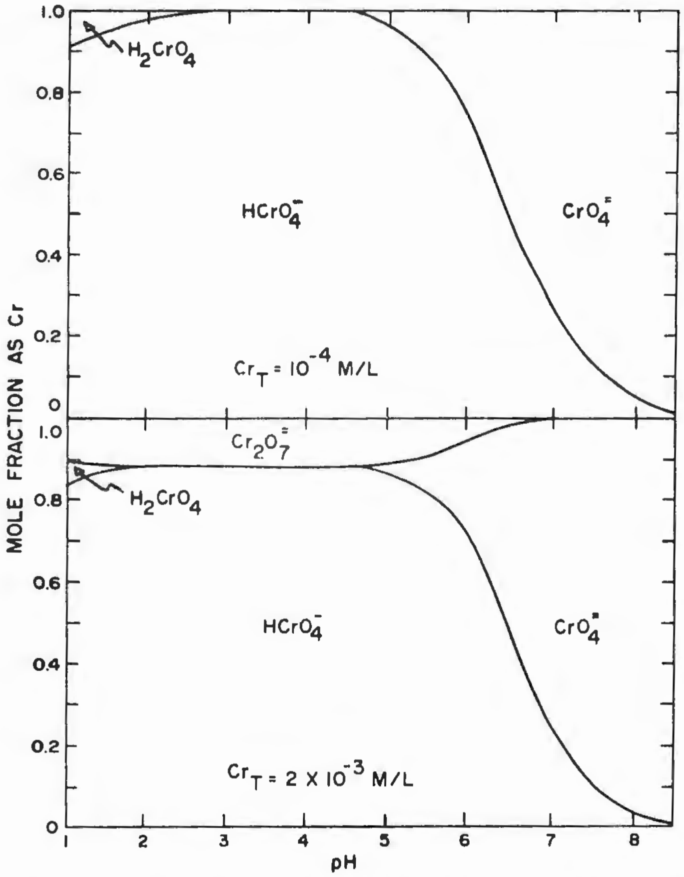

Figure 1. Distribution of Hexavalent Chromium as a Function of PH, After Thomas (Reference 15).

For acidic pH commonly used for hexavalent chromium reduction, the predominant species is $HCrO_4^-$. The assumed reaction for acidic ferrous iron with hexavalent chromium is

$$3Fe(II) + HCrO_4^- + 7H^+ = 3Fe(III) + Cr(III) + 4H_2O \qquad (1)$$

Increasing the pH by adding base results in the precipitation of the metals as hydroxides,

$$3Fe(III) + Cr(III) + 12(OH^-) = 3Fe(OH)_3(s) + Cr(OH)_3(s) \qquad (2)$$

which are then removed from suspension. Intuitively, the rate of Reaction(1) would be increased by increasing the concentration of any one of the reactants.

In treatment, this can be accomplished by increasing the dose of ferrous iron or lowering pH (increasing H^+). The chromium concentration is usually not under the control of the treatment plant operator. However, one would expect that the reaction rate would be high in a concentrated waste and lower in a weaker waste. The rate of a reaction is normally inversely proportional to the concentrations of the reaction products. At acidic pH, the trivalent iron and chromium can remain in solution, slowing Reaction (1) until an equilibrium is achieved between products and reactants. Reaction (2) is speeded up by an alkaline pH.

Combining Reactions 1 and 2 reaction would be:

$$3Fe(II) + HCrO_4^- + 8\ H_2O = 3Fe(OH)_3(s) + Cr(OH)_3(s) + 5H^+ \qquad (3)$$

This assumed reaction would be favored by increased pH, thus reducing the concentrations of the end products in solution. A discussion of the solubility of trivalent chromium is included later.

Rate studies of the reduction of hexavalent chromium by ferrous iron were performed by Espensen (References 13 and 14). Hexavalent chromium was analyzed spectrophotometrically. If the reaction is carried out at neutral or alkaline pH, the resulting solid iron and chromium hydroxide would interfere with the analysis. Thus, Espensen's work was performed under very acidic conditions so that the resulting trivalent iron and chromium could be kept in solution. The following rate equation was derived by Espensen:

$$\frac{d[HCrO_4^-]}{dt} = \frac{-\ [Fe(II)]^2[H^+]^3(k_1[HCrO_4^-] + k_2[HCrO_4^-]^2)}{[Fe(III)]} \qquad (4)$$

where

$k_1 = 2.1 \times 10^{-8}$ Moles^{-4} liters^4 seconds
$k_2 = 7.3 \times 10^{-11}$ Moles^{-5} liters^5 seconds

This rate equation is significant in that it is the basis for claims that ferrous reduction of chromium is slow at all but very acidic pH (Reference 15). Rate Equation (4) is third-order with respect to hydronium ion concentration. This means that each unit increase in pH (decrease of H^+) would result in three orders of magnitude decrease in reaction rate. Using this reaction rate equation, Thomas (Reference 15) calculated that, using a dose of ferrous iron 50 percent over stoichiometric, it would take 5 seconds for 99 percent reduction of 100 mg/l of chromium at pH 2, but 90 minutes at pH 3, and impractically slow at higher pH.

This analysis assumed that the concentration of ferric iron (Fe(III)) is independent of pH. Espensen (Reference 13) maintained a large (therefore reasonably constant) concentration of ferric iron in the reactor. This is possible at low pH. At alkaline and neutral pH, the solubility of ferric iron is controlled by hydroxide,

$$Fe(III) + 3OH^- = Fe(OH)_3(s) \qquad (5)$$

with an equilibrium solubility equation:

$$K_{sp} = [Fe(III)][OH^-]^3 \qquad (6)$$

Including the dissociation equation for water,

$$K_w = [H^+][OH^-] \qquad (7)$$

results in Equation(6)being reduced to

$$[Fe(III)] = \frac{K_{sp}}{K_w^3}[H^+]^3 \qquad (8)$$

Substituting into Rate Equation(4)results in:

$$\frac{d[HCrO_4^-]}{dt} = \frac{-[Fe(II)]^2 K_w^3 (k_1[HCrO_4^-] + k_2[HCrO_4^-]^2)}{K_{sp}} \qquad (9)$$

It is thus seen by our analysis that Espensen's (Reference 13) Rate Equation (4) is independent of pH for conditions in which the Fe(III) concentration is controlled by hydroxide solubility. At a pH of 3 the equilibrium solubility of Fe(III) is approximately 0.1 mg/l, using a K_w of 10^{-14} and a K_{sp} of 2×10^{-39}, as taken from Stumm and Morgan (Reference 16). The solubility of ferric iron decreases as a third-order with increased pH. Since doses of ferrous iron greater than 0.1 mg/l are required for chromium treatment, Espensen's Rate Equation is independent of pH for the pH region of around 3 and above.

Carrying our analysis further, equations were developed to relate time and degree of treatment for various initial conditions.

Assuming that a stoichiometric dose of ferrous iron is used, the concentration of unreacted ferrous iron remaining at time t would be:

$$[Fe(II)] = 3[HCrO_4^-] \qquad (10)$$

Rate Equation(9)is reduced to

$$\frac{d[HCrO_4^-]}{dt} = \frac{-9K_w^3[HCrO_4^-]^3(k_1 + k_2[HCrO_4^-])}{K_{sp}} \qquad (11)$$

Rearranging and integrating with respect to chromium and time results in the equation

$$t - t_o = \frac{K_{sp}}{9K_w^3 k_1^3}\left(k_2^2 \ln X - 2k_2 X + \frac{X^2}{2}\right) \qquad (12)$$

where:

$$X = \frac{k_1 + k_2[HCrO_4^-]}{[HCrO_4^-]} \qquad (13)$$

If excess ferrous iron is used to speed up the reaction, then the Fe(II) remaining at any time t would be:

$$[Fe(II)] = [Fe(II)]_e + 3\ [HCrO_4^-] \tag{14}$$

where

$$[Fe(II)]_e = \text{excess ferrous dose}$$

Substitution into Rate Equation (9) results in:

$$\frac{d[HCrO_4^-]}{dt} = \frac{-K_w^3([Fe(II)]_e + 3[HCrO_4\ ])^2(k_1[HCrO_4^-] + k_2[HCrO_4^-]^2)}{K_{sp}} \tag{15}$$

Substitution of the following equations:

$$A = \frac{k_1}{k_2} \tag{16}$$

$$B = \frac{[Fe(II)]_e}{3} \tag{17}$$

$$D = A - B \tag{18}$$

$$x = [HCrO_4^-] \tag{19}$$

and rearranging, reduces Equation(15) to:

$$\int_{t_o}^{t} dt = \frac{-K_{sp}}{9K_w^3 k^2} \int_{x_o}^{x} \frac{dx}{x(A+x)(B+x)^2} \tag{20}$$

Integrating Equation(20) yields:

$$t-t_o = \frac{-K_{sp}}{9K_w^3\ k_2\ B\ D^2}\left(\frac{D^2\ \ln x}{A\ B} - \frac{B}{A}\ \ln(A+x) - \frac{(D-B)}{B}\ \ln(B+x) + \frac{D}{B+x}\right)\Bigg|_{x_o}^{x} \tag{21}$$

Equations (12) and (21) are represented in Figure 2 for an initial hexavalent chromium concentration (60 mg/1) and various excess doses of iron, $[Fe(II)]_e$. For moderate to high concentrations of chromium the reaction is rapid, with the chromium concentration reduced to less than 5 mg/1 in less than a minute, for all doses (stoichiometric or greater) of ferrous iron. For the stoichiometric dose of iron ($[Fe]_e = 0$), the reaction slows considerably with lower concentrations of chromium. An hour is required to reach 0.65 mg/1 and 200 hours to reach 0.05 mg/1 (the U.S. EPA Maximum Contaminant Level for drinking water). The reaction rate can be greatly increased by the addition of excess ferrous iron. The addition of 10 mg/1 excess iron (a 17-percent increase over stoichiometric for an initial chromium concentration of 60 mg/l) would reduce the reaction time to reach 0.05 mg/l to 14 minutes.

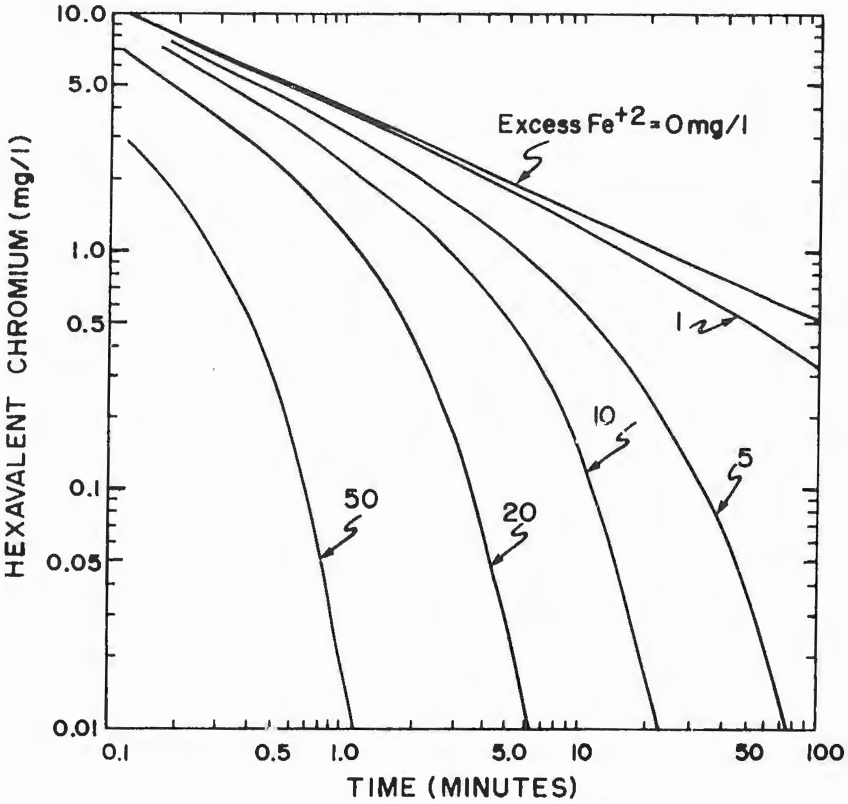

Figure 2. Rate of Hexavalent Chromium Reduction by Ferrous Iron (Initial Chromium = 60 mg/l).

In summary, what appeared to be experimental and theoretical bases for concluding that chromium reduction by ferrous iron was pH-dependent and impractically slow at neutral and alkaline pH, were shown to support the contention that chromium reduction by ferrous iron is not dependent on pH where the solubility of the end products is controlled by hydroxide solubility. In addition, the reaction can be accelerated, if necessary, by a modest excess dose of ferrous iron.

One additional comment is in order. The rate equation used was based on the reaction of $HCrO_4^-$. This is the predominant hexavalent chromium species at acidic pH. At neutral and alkaline pH CrO_4^{-2} predominates. The reduction of this species, with precipitation included, would be:

$$3Fe(II) + CrO_4^{-2} + 4H_2O + 4OH^- = 3Fe(OH)_3(s) + Cr(OH)_3(s) \qquad (22)$$

This chromium species probably has a different reaction rate equation than that of $HCrO_4^-$. A faster rate for CrO_4^{-2} reduction would account for the rapid removal of hexavalent chromium experienced with stoichiometric doses of ferrous sulfate at pH levels from 7 to 10 (Reference 8).

3. Chromium Reduction by Sulfide

It is well established that reduction of hexavalent chromium by reduced sulfur (valence +4) compounds is reasonably rapid at acidic pH (less than 3), and that the rate slows logarithmically with increased pH (References 15 and 17). Sulfides (valence −2) are also reported to be effective at reducing hexavalent chromium at acidic pH (References 8 and 18). Sulfide is a weak acid, with distribution of species with pH shown in Figure 3. H_2S, the predominant species at acidic pH, is a noxious, toxic gas.

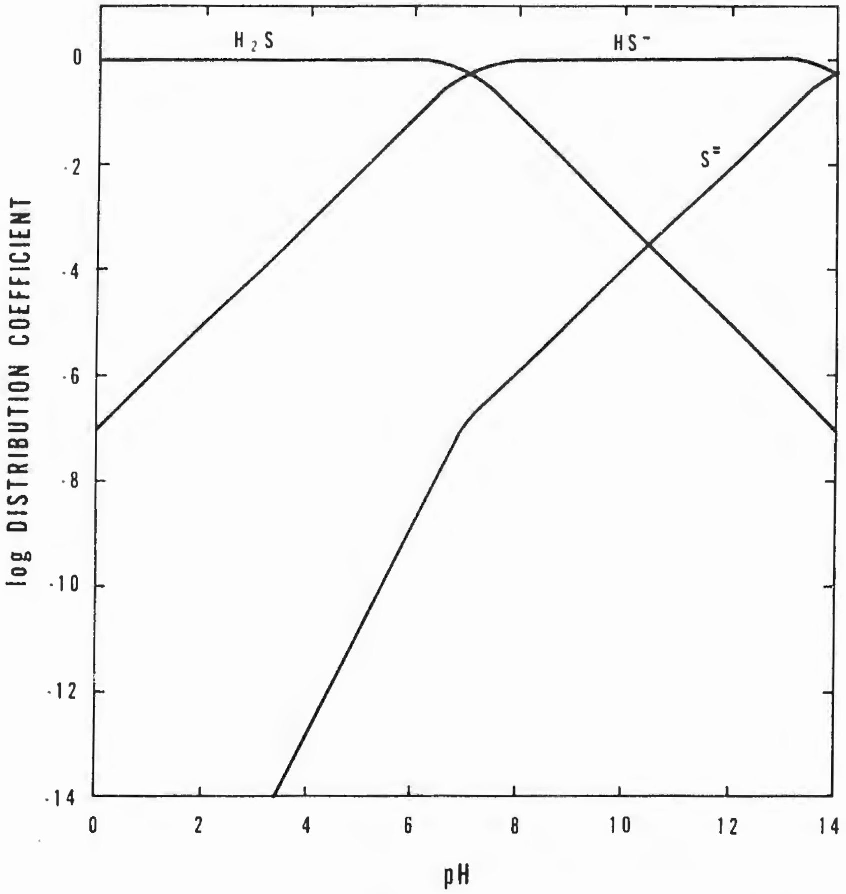

Figure 3. Distribution of Sulfide Species with pH.

The reaction of sulfide with hexavalent chromium at acidic pH is probably:

$$3H_2S + 2HCrO_4^- + 2H^+ = 3S^0(s) + 2Cr(OH)_3(s) + 2H_2O \qquad (23)$$

This reaction consumes hydronium ions and, therefore, would be expected to be aided by increased acidity. In the neutral pH range, the predominant species of sulfide and chromium shift, and the reaction shifts to the more acid-consuming (or alkalinity-producing) reaction.

$$3HS^- + 2CrO_4^{-2} + 5H_2O = 3S^0(s) + 2Cr(OH)_3(s) + 7OH^- \qquad (24)$$

This reaction would be expected to be drastically slowed at alkaline pH. Our experience (Reference 8) has been that sulfide, by itself, is ineffective in reducing chromium at neutral and alkaline pH. Figure 4 shows the removal of chromium by sulfide in batch studies using a 2-minute reaction time and solids removal by membrane filtration.

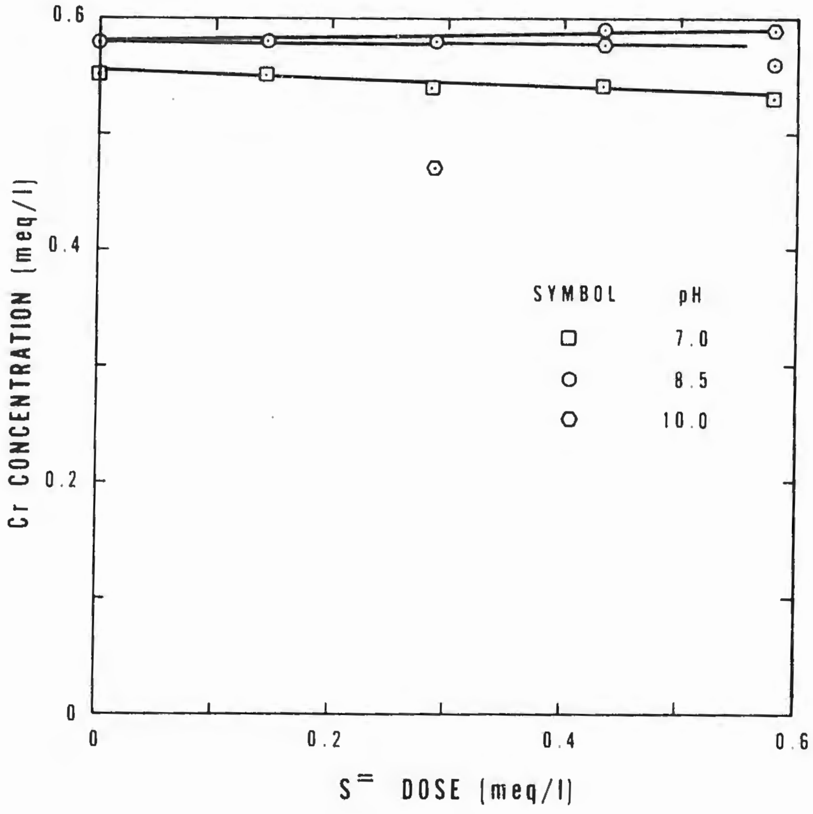

Figure 4. Chromium Reduction by Sulfide.

However, it has been reported that, when ferrous iron was used as a coagulant in conjunction with sulfide, hexavalent chromium was reduced (Reference 19). It has also been claimed that freshly precipitated ferrous sulfide effectively reduces hexavalent chromium at alkaline pH (Reference 20).

Our studies have shown that ferrous iron rapidly and effectively reduces hexavalent chromium at neutral and alkaline pH (References 8, 10 and 11). Figures 5 through 7 show that ferrous sulfate stoichiometrically reduced hexavalent chromium at pH from 7 to 10 (the circles represent treatment with just ferrous sulfate). When sodium sulfide was added, along with the ferrous sulfate, additional chromium reduction and removal were realized, with the ferrous iron appearing to catalyze the sulfide reaction. The effectiveness of the sulfide is seen to be reduced at pH 8.5 and 10. The assumed reaction for equivalent doses of ferrous iron and sulfide at neutral pH is:

$$3HS^- + 6Fe(II) + 4CrO_4^{-2} + 13H_2O + OH^- = 3S^0(s) + 6Fe(OH)_3(s) + 4Cr(OH)_3(s) \quad (25)$$

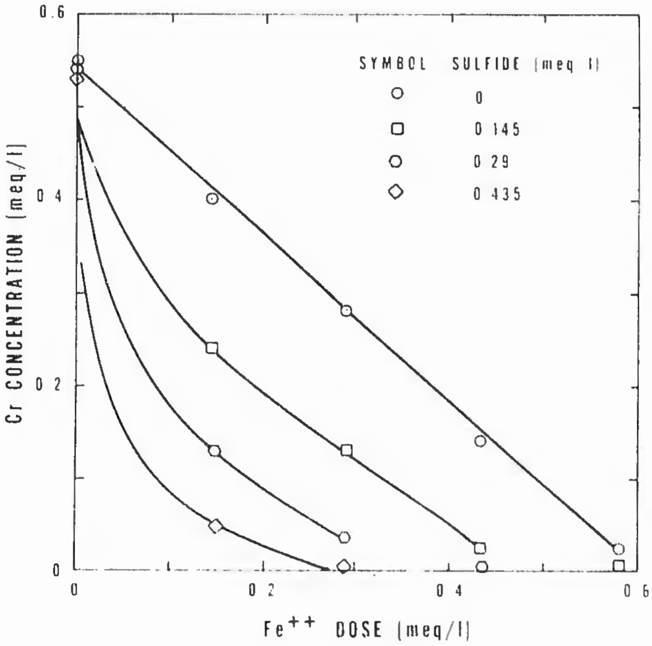

Figure 5. **Chromium Reduction by Ferrous** Sulfate and Sodium Sulfide at pH 7.

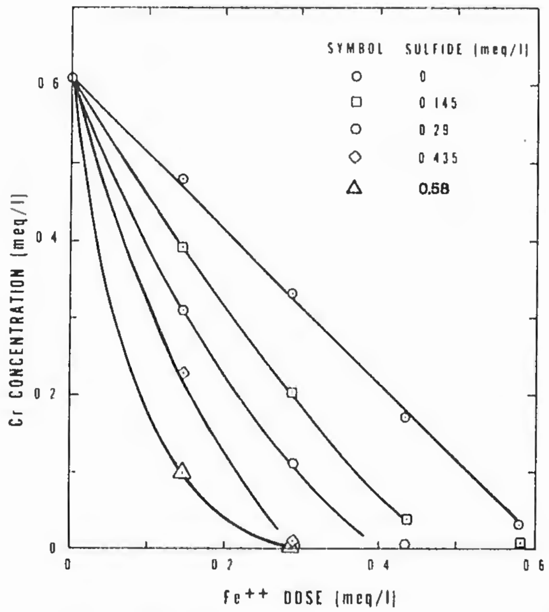

Figure 6. **Chromium Reduction by Ferrous** Sulfate and Sodium Sulfide at pH 8.5.

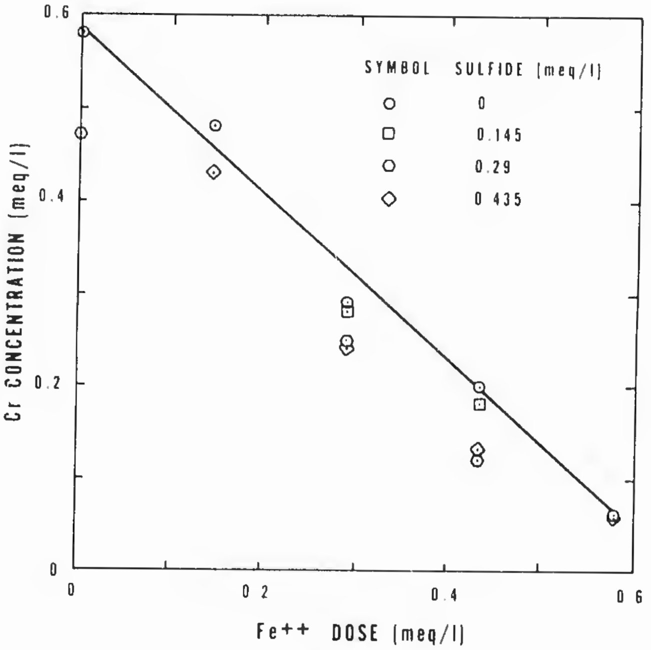

Figure 7. Chromium Reduction by Ferrous Sulfate and Sodium Sulfide at pH 10.

This reaction appears to be slightly favored by increased alkalinity (OH^-). This advantage is lost for higher ratios of sulfide to iron. For a reaction where two equivalents of sulfide are combined with one equivalent of ferrous iron to reduce chromium the following reaction results at alkaline pH:

$$HS^- + Fe(II) + CrO_4^{-2} + 3H_2O =$$
$$S^0(s) + Fe(OH)_3(s) + Cr(OH)_3(s) + OH^- \quad (26)$$

One would expect this reaction to be favored at acidic pH.

The use of sulfide complements the use of ferrous iron in the reduction of hexavalent chromium. Ferrous iron is not efficient in that only one electron is exchanged per iron atom and a large quantity of iron hydroxide sludge is produced when ferrous iron is used as the sole reducing agent. Iron is effective by itself at alkaline pH, acts as its own coagulant, and is necessary for sulfide to be effective. Sodium sulfide has a much lower equivalent weight than ferrous sulfate (39 vs. 151.9) and a lower equivalent dry sludge production (16 vs. 106.9). Sulfide is inefficient by itself and is less efficient at high sulfide-to-iron ratios. A combination of ferrous and sulfide at neutral pH would appear to be most effective for hexavalent chromium reduction and removal.

B. SOLUBILITY CONSIDERATIONS

The ability to meet increasingly stringent effluent standards for heavy metals has been limited by the relatively high solubility of most metal hydroxides. The formation of soluble metal hydroxide complexes at high pH levels increases solubility and prevents the optimum removal of a mixed-metal solution at a common pH. Figure 8 shows that the minimum hydroxide solubilities of cadmium, chromium and nickel are not achieved at a common pH, and the EPA drinking water standards for these metals theoretically cannot be achieved by hydroxide precipitation.

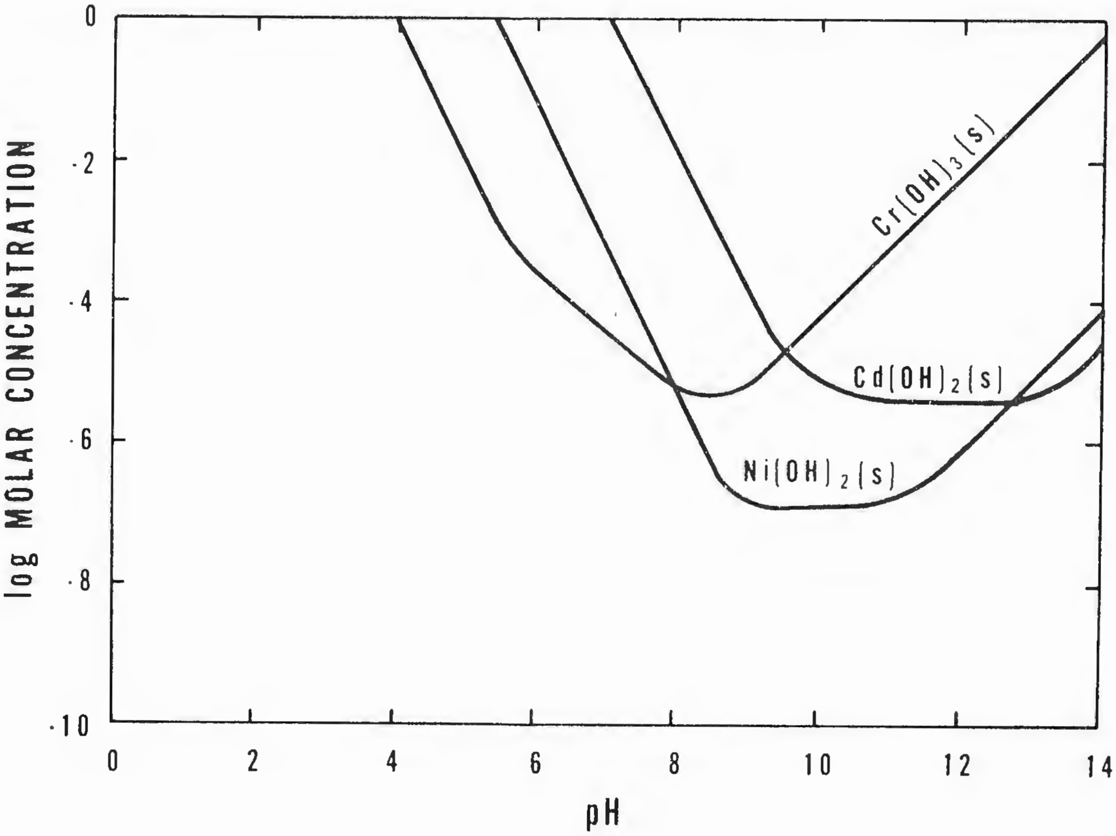

Figure 8. Solubilities of Cd, Cr and Ni as a Function of pH.

1. Sulfides Reduce Metal Solubilities

It has been reported (References 21 and 22) that, since the solubilities of metal sulfides are considerably less than corresponding metal hydroxides, improved removal efficiencies can be achieved by sulfide precipitation. Figure 9 shows the solubility of chromium (III), nickel (II) and cadmium (II) in the presence of 10^{-6} M total sulfide. A total sulfide concentration of 10^{-6} M was chosen because it was an order of magnitude lower than that found to cause a minimal odor problem (Reference 21) but still sufficient to limit metal solubility. Solubility data for chromium (III) sulfide are not reported (References 23-25). It has been assumed that solubility of this metal is controlled by hydroxide. Minimum solubilities for these three metals of interest are achieved at a pH between 8 and 9. Increasing the pH beyond 9 results in increased solubility due to formation of metal hydroxide complexes.

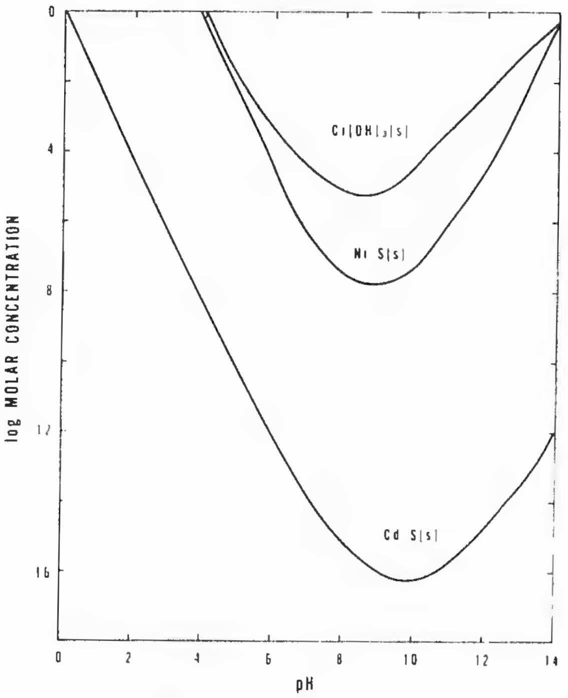

Figure 9. Solubilities of Cd, Cr and Ni with 10^{-6}M Total Sulfides.

Sulfide is a weak acid anion. The pH - sulfide species distribution diagram was shown as Figure 3. Below pH 7, the principal species is H_2S, a slightly soluble, noxious and toxic gas. Use of sulfide compounds under acidic conditions can result in the release of toxic quantities of this gas, and is not normally recommended. However, one researcher (Reference 19) tested an acidic sulfide process where the units were enclosed to prevent release of H_2S gas. Peroxide was used in a final stage for oxidation of residual sulfide before discharge of the effluent.

Sulfex (References 20, 26 and 27) is another process developed to utilize sulfide to precipitate metals. It has a unique method of controlling sulfide concentrations in solution and minimizing H_2S formation. Freshly precipitated ferrous sulfide is mixed with the wastewater in a reactor. The ferrous sulfide is more soluble than most other heavy metal sulfides. The soluble sulfide concentration is limited and yet sufficient to limit the solubilities of less soluble metals (than ferrous iron).

Higgins et al. (References 7-11) have been developing a process where soluble sulfide and ferrous iron are added independently to a reactor with the wastewater. This has the advantages of the sulfex process, eliminates the need for a separate ferrous sulfide precipitation reactor, and allows separate control of ferrous and sulfide doses for optimal treatment.

2. Complexing Agents and Metals Removal

In a previous study (Reference 9), the use of soluble sulfide and ferrous iron was found to be effective for the treatment of a mixed-metal (chromium, cadmium and nickel) synthetic waste, prepared from laboratory chemicals. When actual plating baths were used to prepare a mixed-metal waste, the process effectively removed chromium and cadmium, but nickel remained in solution.

A plating bath is formulated to maintain a high concentration of the plating metal in solution. Complexing agents are commonly added to accomplish this. Cyanide is frequently used in cadmium baths, and it was postulated that cyanide from the cadmium bath interfered with nickel removal. Cyanide destruction is normally required prior to mixing these wastes with other wastes. Some metal-cyanide complexes (e.g., ferrocyanide) are hard to break down and strongly interfere with subsequent cyanide destruction. Nickel, being in the same period and group on the periodic table and same normal valence (+2) as ferrous iron, would be expected to form a strong cyanide complex which would interfere with their mutual removal.

Thomas and Theis (Reference 28) reported that carbonates and phosphates, found in combined plating wastes due to their use in cleaning baths, interfere with coagulation and removal of chromium hydroxide precipitates. These interferences were reduced or eliminated by the use of ferrous iron as the reducing agent or the use of lime for pH adjustment.

In a previous study (Reference 9), no interferences were found for removal of hexavalent chromium by ferrous reduction. The interferences of hardness, carbonate alkalinity, and the complexing agents EDTA and cyanide were investigated.

C. SOLIDS REMOVAL

Following precipitation, solid metal hydroxides are typically flocculated with the aid of coagulants such as polymers, and removed by sedimentation. To improve removal of the suspended metal hydroxide solids, filtration is frequently added as a polishing step. Where pumping is required between sedimentation and filtration, shearing of the hydroxide floc usually results in the need for further addition of polymers.

In a study, TerMaath (Reference 29) found that mercury sulfide could be precipitated and effectively removed by direct upflow filtration. In a study by Higgins and TerMaath (Reference 8), effective treatment of a mixed-metal waste was accomplished by ferrous sulfate and sodium sulfide addition and direct upflow filtration. They found that the upflow filter combined the traditionally separate unit processes of chemical mixing, flocculation and filtration and has the potential of reducing the size and complexity of mixed-metal treatment over conventional techniques.

The main disadvantage of conventional downflow sand filters is that the finest material is encountered first, and the greater portion of the solids removal occurs in the top layer of the bed. As a result, high head losses develop in a short period of time, and the bottom portion of the bed is poorly utilized. The coarse-to-fine gradation in an upflow filter would contribute to good removal without the head loss problems of conventional sand filters. Diaper and Ives (Reference 30) conducted a study on upflow filtration and concluded that for a given head loss, upflow filtration allowed longer runs due to a more even distribution of solids, and upflow filtration has some disadvantages which include: (a) a tendency for the bed to expand as pressure differences overcome the weight of the media; (b) difficulty in backwashing layers of materials which tend to accumulate; (c) the possibility of deposits in the underdrain which may be difficult to remove; and (d) size-graded media are best used with high flows and high concentration of solids.

Hamaam and McKinney (Reference 31) reported similar advantages of upflow filtration. They also describe additional advantages: (a) a reduction in the size of the physical plant since flocculation and sedimentation facilities are not required; and (b) a reduction in the amount of chemical coagulant is required because a large, easily settling floc is not needed. They found that effectiveness improved with bed depth.

Upflow filters have been found to perform as well or better than downflow filters for removal of turbidity (Reference 31). Average reductions in bacteria have also been found to be approximately equivalent to those in a conventional plant (Reference 32).

If there is a more uniform distribution of solids with upflow filtration than with downflow, upflow should have less tendency to cake or form mudballs and therefore be easier to clean (Reference 33). However, the studies by Diaper and Ives (References 32 and 34) and Hamaam and McKinney (Reference 31) have found difficulties with backwash. Bands of deposits tend to form within the bed (References 32 and 34). During backwash the bands of deposits are pushed into finer sand where the clogged media formed an impervious barrier. The barriers caused an arching effect which lifted the bed in layers (References 35 and 36). Compressed air was found necessary to break up the bands of deposits and adequately clean the entire bed (References 35-37).

D. INSTRUMENTATION AND CONTROL

The waste treatment process uses the reduction of Cr(VI) to Cr(III) with ferrous iron, Fe(II), as the reducing agent. The reduced CR(III) is immediately precipitated as $Cr(OH)_3$ at high pH. The ferric iron, FE(III), produced also precipitates (as $Fe(OH)_3$). Since the solubility of $Cr(OH)_3$ is so small, it can be assumed that any chromium still in solution is in the Cr(VI) state. Therefore, monitoring that particular ion would indicate the concentration of dissolved chromium in the effluent. This data would then be used to indicate the effectiveness of the process and also to regulate the amount of chemical reagents to be added.

If it is assumed that the oxidation-reduction reactions are fast and that the Fe(II) is fairly soluble, another approach would be to monitor the Fe(II) concentration in the effluent stream and assume that the presence of Fe(II) in the stream would indicate an excess of reducing agent. Therefore, all Cr(VI) had been reduced and precipitated. While such a scheme would probably be adequate for control purposes, direct measurement of the Cr(VI) in the effluent would be necessary to verify the degree of removal of chromium.

Because the monitoring data are to be used for automatic control of the process, any methods used have to be continuous, fast, and make use of relatively inexpensive but rugged instrumentation.

1. Automated Analysis of Chromium (VI)

A review of the literature and examination of vendors' literature indicates that the prevalent technique for continuous measurement of Cr(VI) in the mg/l range is to use colorimetric methods. An excellent source of state-of-the-art instrumentation methods is a survey published periodically by the Lawrence Berkeley Lab (References 38 and 39). The emphasis of this work is on laboratory instruments and not necessarily continuous monitoring techniques.

Technicon (Reference 40), Hack (References 41 and 42) and Lachat (Reference 43) manufacture continuous monitoring equipment based on colorimetric measurements. Alpkem (Reference 44) sells Technicon hardware but will also do custom method development. They all use peristaltic pumps to accurately meter both reagents and the sample stream before mixing. Sufficient reaction time is obtained using coils through which the mixed stream passes before entering a flow cell in a colorimeter equipped with filters to isolate the desired wave length. The chemistry is similar in each case and based on the Standard Method for Cr(VI) (Reference 45).

Gorringe (Reference 46) reported the use of a Technicon Monitor IV to monitor Cr(VI) in the effluent of an electroplating wastewater treatment plant using Technicon's standard method. The information was not used for automatic control purposes but rather to determine when incidents of exceeding maximum levels in effluents had occurred.

Saltzman and Bonam (Reference 47) present an interesting method for determining Cr(VI) in the 0-100 ppb range in the presence of interfering materials. The scheme compares the absorbance at 365 nm of the waste stream with the absorbance of the same stream after the Cr(VI) has been reduced with SO_2. With elaborate valving, the output signal consists of alternating values for the two absorbances with approximately a 10-minute cycle. To use the signal for control purposes would require some way of measuring the difference between the alternating values and generating a continuous signal based on this difference. The method does not require the metering of complexing chemicals but does require close control of pH. They report good success during in-plant tests.

2. Automated Analysis of Fe(II)

The colorimetric analyzers described above for the on-line determination of Cr(VI) can be adapted for Fe(II) analysis (References 41, 43 and 48). The methods all use phenanthroline as the color-producing reagent as described in Standard Methods. Potential problems such as color development time and in-line filtration of the sample are common to those discussed in the previous section.

3. Electrode Methods

No mention of selective ion electrodes for Cr(VI) or Fe(II) could be found in the literature or vendors' materials.

Because of the oxidation-reduction reactions taking place, redox electrodes have been used to measure the Cr(VI)/Cr(III) ratio with some success. Mracek and Greenberg (Reference 50) report the use of an Oxidation Reduction

Potential (ORP) electrode to measure the extent of the reduction reaction in a process using SO_2 as the reducing agent at a pH close to 2. Under these conditions, the electrode potential drops sharply at the end point during their batch process. The potential developed is also a function of pH but at a low pH, small changes have a negligible effect. They report a 4-year life of their self-cleaning flow-through electrode. Bennett (Reference 51) reports similar success using ORP measurements with essentially the same process conditions.

These batch processes carry out the reduction phase at low pH followed by an increase in pH and subsequent precipitation of the hydroxides. No references were found on the use of ORP electrodes in processes at high pH with simultaneous precipitations.

E. RESIDUALS MANAGEMENT

The quantities and characteristics of sludges produced by a treatment process have a considerable impact on the feasibility of the process. The ability to concentrate this sludge easily can reduce this impact. Analysis of the composition of the sludge can provide insights into the treatment process as well as affect the methods used for its disposal. Classification of a sludge as hazardous or toxic can significantly increase the costs of disposal.

1. Sludge Dewaterability

Treatment plant sludges are dewatered to reduce the volume of sludge to be handled and to facilitate disposal. Mechanical devices for dewatering sludges include belt presses, centrifuges, filter presses and vacuum filters. Natural methods include the use of outdoor drying beds and lagoons, which rely on evaporation and percolation or decanting. Sludge dewatering can often be increased by the addition of conditioning agents such as ferric chloride, lime, aluminum sulfate or organic polyelectrolytes.

Attempts have been made to characterize the dewaterability of a given sludge with simple laboratory tests. The Specific Resistance concept was first developed by Carmen (Reference 52) and refined by Coakley and Jones (Reference 53). Specific Resistance represents the relative resistance a sludge offers to drainage of its liquid component. A review of the development of the Specific Resistance Equation is provided by Adrian (Reference 54). A detailed description of the method used to determine the Specific Resistance of a sludge is included in section IIIE.

Typical values of Specific Resistance for various sludges are listed in Table 1.

TABLE 1. TYPICAL SPECIFIC RESISTANCE VALUES FOR SLUDGES (Reference 55)

Sludge	Specific Resistance (m/k_g)
Primary Sewage	$1.5 - 5.0 \times 10^{14}$
Activated Sewage	$1.0 - 10.0 \times 10^{13}$
Digested Sewage, Unconditioned	$1.0 - 6.0 \times 10^{14}$
Digested Sewage, Conditioned	$3.0 - 40.0 \times 10^{11}$

2. Sludge Composition

In ferrous and sulfide reduction of hexavalent chromium, and the resulting precipitation of trivalent chromium and other metals, it has been postulated that the end products would consist of metal hydroxides and sulfides, along with elemental sulfur. Analysis of the composition of the sludge would be useful to test the assumed reactions.

Disposal of a waste can be complicated by its composition. The EPA has not established guidelines on the disposal of wastes based on content but rather on potential leachability of metals. The State of California, however, has established standards that classify wastes as hazardous, and require their disposal in special, secure landfills if they contain chromium, cadmium or nickel in concentrations greater than 0.25, 0.01 and 0.20 percent, respectively (Reference 56).

3. Extraction Procedure (EP) Toxicity

The EPA (Reference 57) has developed a method for classifying wastes as hazardous based on the relative leachability of selected metals from a waste under conditions simulating the disposal of the waste in a municipal landfill. The procedure used assumes that the waste could come in contact with acidic percolating water, produced by the decomposition of organic wastes to organic acids. The contaminated water could escape an unsecure landfill, percolate through the underlying soils and contaminate a groundwater supply. A waste is classified as hazardous if the leachable concentration exceeds the maximum contaminant level for drinking water by a factor of 100 or more. This somewhat arbitrary factor was selected to account for dilution and attenuation of the metal content of percolating waters through soils.

(The reverse of this page is blank)

SECTION III

METHODS AND MATERIALS

A. WASTE SYNTHESIS AND TREATMENT CHEMICALS

Wastes were prepared to simulate the wastewaters typically discharged from electroplating shops on Air Force bases. The bulk of these wastes consists of overflows from rinsewater tanks used to remove residual plating solutions "dragged out" from plating baths on finished parts. Metals commonly plated are chromium, cadmium and nickel. The composition of plating baths from the plating shop at Tinker Air Force Base is presented in Table 2. Also included

TABLE 2. (References 58-60)

COMPARISON OF PRETREATMENT EFFLUENT GUIDELINES, WATER QUALITY CRITERIA, AND NPDES DISCHARGE LIMITS FOR SELECTED METALS.

Pollutant	Cd	Cr(VI)	Cr(T)	Cu	Ni	Pb
EPA Pretreatment						
Guidelines (mg/l)						
Small Discharges (a)						
1-Day Maximum	1.2	-	-	-	-	0.6
4-Day Average	0.7	-	-	-		0.4
Large Discharges (b)						
1-Day Maximum	1.2	-	7.0	4.5	4.1	0.6
4-Day Average	0.7	-	4.0	2.7	2.7	0.4
EPA Water Quality						
Criteria	0.12	0.1	0.1	1.0	-	0.05
NPDES Permit, Ind.						
Waste T.P., Tinker						
AFB, OK (c)	0.019	0.05	0.11	0.01	0.22	0.06
Tinker Electroplating						
Waste (d)						
Maximum	0.23	55	156	0.42	170	0.25
9-Day Average	0.14	28	43	0.09	37	0.06

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

are EPA plating waste pretreatment and water quality standards and the NPDES permit standards for Tinker AFB for comparison.

Synthetic wastewaters were prepared using reagent-grade potassium dichromate ($K_2Cr_2O_7$), cadmium chloride ($CdCl_2$) or cadmium oxide (CdO) and nickel chloride ($NiCl_2$). Concentrated stock solutions of these chemicals were made in deionized distilled water and synthetic wastewaters were prepared by dilution with Tempe tap water or distilled water (Table 3). Air Force plating shops use various amounts of demineralized and local tap water for rinsing needs. Tempe tap water is characterized as being a hard, alkaline water with a high dissolved solids content. Distilled water was supplied in small quantities for batch studies by a laboratory still and in larger quantities for pilot plant use from a central distillation plant. Both supplies are of good quality.

TABLE 3. TAP WATER ANALYSES, CITY OF TEMPE, ARIZONA

Constituent	Concentration (mg/l except pH)				
	City of Tempe Reservior Analysis		ASU Laboratory Tap Water Analysis		
	June/July	Aug./Sept.	Jan.	June.	Aug.
Hardness (a)	152-172	168-204	222	175	161
Calcium (a)	103-128	108-138	112		
Magnesium (a)	45-66	45-103	110		
Sodium (b)	12-84		52		
Alkalinity (a)	100-118	110-128	188	119	127
Sulfate (b)	0-250		70		
Chloride	114-154	130-230	44		
pH	7.5-7.9	7.6-7.8	7.6		
TDS	376-508	427-636	382		

Notes: a. As $CaCO_3$.
b. Year's range.

For some studies, wastewaters were prepared using plating baths received from Williams Air Force Base (Table 4 for composition) and diluted with tap or distilled water to more closely simulate rinsewaters from a plating shop.

TABLE 4. COMPOSITION OF PLATING BATHS FROM WILLIAMS AFB, AZ

Bath	Constituent	Recommended Composition (oz/gal)	Batch Analysis (g/l)	Batch Analysis oz/gal
Chromium	Chromium (as Cr)	15.6-18.7	142	18.9
	(as CrO_3)	30-36		
	Sulfuric Acid	0.3-0.36		
Cadmium	Cadmium (as Cd)	3.1	23.1	3.1
	(as CdO)	3.5		
	Sodium Cyanide	12-16		
	Sodium Hydroxide	1.0		
	Sodium Carbonate	1.0-1.8		
Nickel (a)	Nickel		195	26

Note: a. Roplate Electroless Nickel Concentrate, composition proprietary - recommended dilution;1 part concentrate to 3 parts water.

Treatment chemicals used in this study were reagent grade ferrous sulfate ($FeSO_4 \cdot 7H_2O$), sodium sulfide (60 percent Na_2S), and liquid sodium hydroxide (50 percent NaOH). Stock solutions of these chemicals were prepared in distilled water. Operation of the pilot plant through Run 21 was affected by the use of stock solutions of ferrous sulfate and sodium sulfide that were partially oxidized by atmospheric oxygen in storage. After Run 21 these reagents were prepared fresh before each run. All batch studies were performed using fresh reagents.

B. BATCH REACTOR STUDIES

Batch reactor studies were performed as outlined in Figure 10. A 2-liter

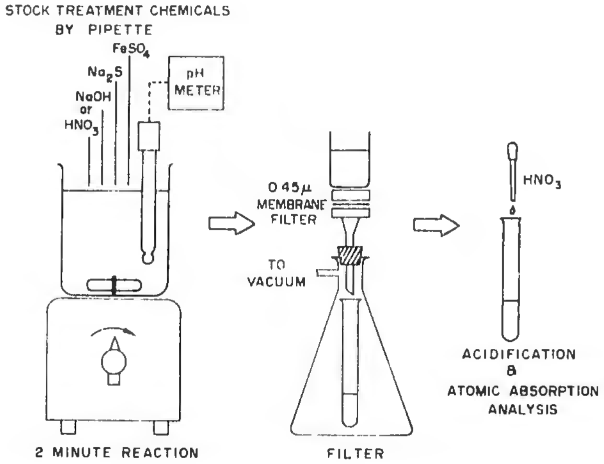

Figure 10. Experimental Procedure for Batch Reaction Studies.

batch of simulated waste was prepared by dilution of stock solutions of reagent chemicals or plating baths with tap or distilled water, as required. A 100 ml aliquot of waste was transferred to a 250 ml borosilicate glass beaker for batch treatment. The waste was stirred at a moderate speed on a magnetic stirrer using a Teflon®-coated stirring bar. The pH was monitored using a combination glass and reference electrode, and manually adjusted by dropwise addition of dilute sodium hydroxide or acid (acetic or nitric). Treatment chemicals were transferred by pipet from fresh stock solutions to the beaker while the pH was monitored and controlled. Following approximately 2 minutes for reaction, the mixture was settled for 3 minutes and the supernatant filtered through a 0.45 micron cellulose acetate filter. The filtrate was collected in a 50 ml polypropylene stoppered centrifuge tube. Samples were acidified with nitric acid (approximately 1 drop per 20 ml) and analyzed for metals by atomic absorption spectrophotometry.

C. CONTINUOUS FLOW REACTOR (PILOT PLANT) STUDIES

1. Pilot Plant Design

A flow diagram of the bench scale pilot plant, used to develop the proposed treatment process, is shown as Figure 11. Design criteria for the pilot plant are listed in Table 5. Photographs of the individual units are shown as Figures 12 through 17.

A treatment scheme tested previously (Reference 7) consisted of in-line injection of treatment chemicals followed by direct upflow filtration. The high solids loading used in the process resulted in a rapid buildup of solids in the filter and short run times between backwashing (less than 4 hours for the treatment of 10 mg/l each of chromium and cadmium). Pretreatment for solids removal was felt to be necessary to make the treatment of plating wastes viable. The pilot plant was designed to include flocculation, clarification and filtration.

2. Unit Processes

A pilot plant was designed as a test bed to develop a treatment system utilizing alkaline ferrous reduction and precipitation of hexavalent chromium. Unit processes incorporated into the pilot plant included waste synthesis, chemical feed and rapid mix, flocculation, sedimentation, and upflow filtraion. Flexibility was provided so that combinations of unit processes could be easily tested. The size of the system was controlled by the availability of water supply (~ 5 gpm) and laboratory space. One goal was to minimize the size of the units due to restrictions on space available in existing plating shops. Units were enclosed and pressurized so that one pump would provide the flow through all of the units. This eliminated floc breakup caused by intermediate pumping.

a. Waste Synthesis System

A continuous-flow waste synthesis system was designed to simulate the operation of a metal plating rinse tank. Concentrated wastes were prepared in batch by dilution with distilled water and stored in concentrated waste tanks. The cadmium plating bath contained cyanide at an alkaline pH. Combining it with an acidic bath to form a combined concentrated waste would have resulted

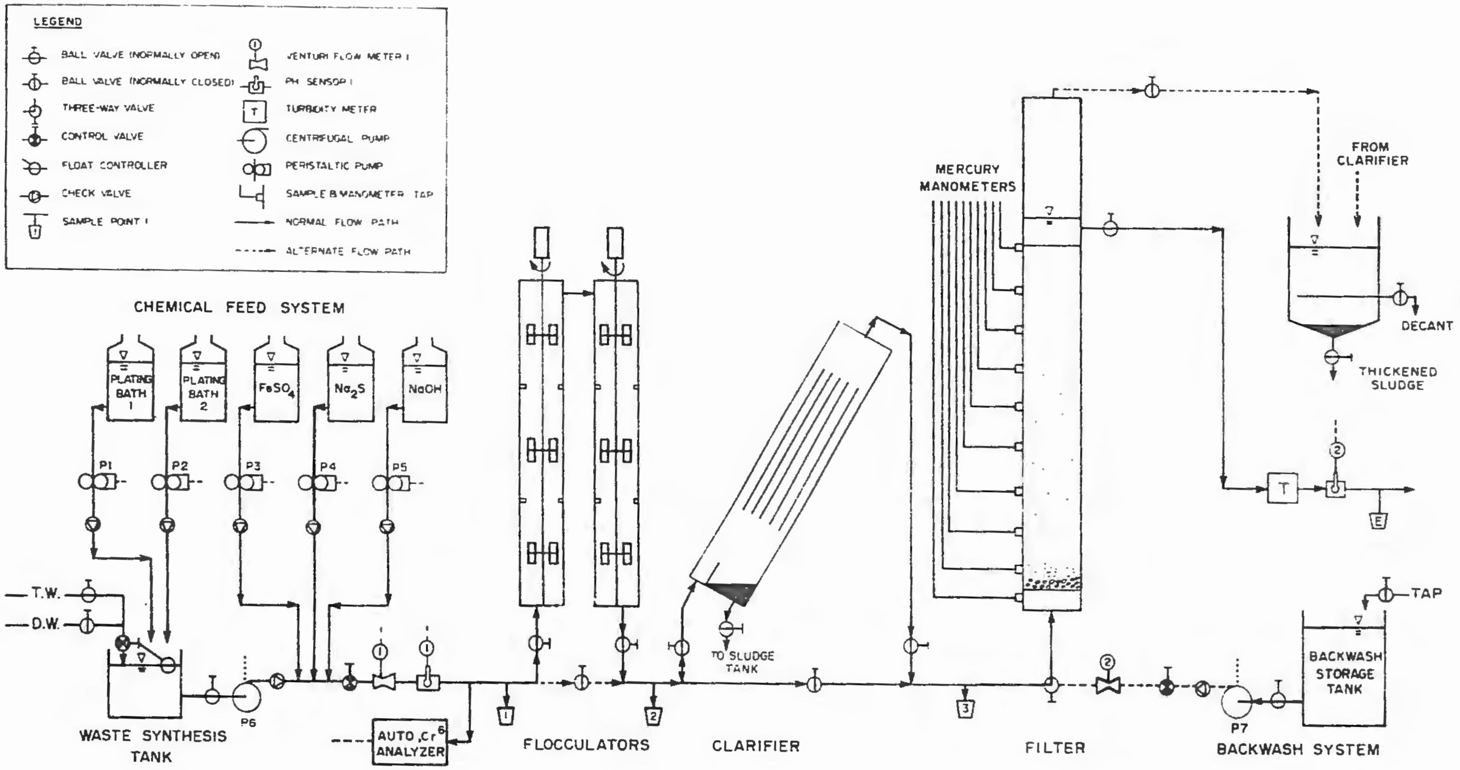

Figure 11. Schematic of Pilot Plant

TABLE 5. PILOT PLANT DESIGN CRITERIA

Unit Process	Parameter	Criteria
Waste Synthesis	Production capacity	0-5 gpm
	Waste mixing tank volume	20 gallons
	Dilution water	Tap or distilled
	Dilution water control	Float
	Concentrated waste tanks	2
	Volume, each	5 gallons
	Concentrated waste pumps	2
	Types	Peristaltic
	Capacity	1-25 ml/min
	Process pump	Centrifugal
	Rating	10 gpm at 25' head
	Control	Diaphragm valve
	Flow measurement	Venturi meter
Chemical feed	Chemicals	$FeSO_4$, Na_2S, NaOH
	Storage tanks	3
	Volume, each	5 gallons
	Chemical feed pumps	3
	Type	Peristaltic
	Capacity	1-25 ml/min
	Mixing	In-line
Flocculators	Number of units	2
	Dimensions, each	10" diameter x 6.5' long
	Detention time	10 min
	Mean velocity gradient	50 sec^{-1} (20-70 sec^{-1} range)
	Paddle area, each	31.5 in^2
	Rotating speed	41 rpm (17-66 rpm range)
	Horsepower, each	1/8 hp
Clarifer	Flow	5 gpm (2-8 gpm range)
	Dimensions	5.5' x 1' x 1'
	Overflow rate required	1.5-3.0 gpm/ft^2
	Overflow rate provided	2.5 gpm/ft^2
	Projected horizontal surface area	2 ft^2
	Number of plates	5
	Effective horizontal surface area	9.5 ft^2
	Effective overflow rate	0.53 gpm/ft^2
	Cross-sectional area	1 ft^2
	Horizontal velocity required	21.5 fpm
	Horizontal velocity provided	0.7 fpm
	Inclination from horizontal	60°

TABLE 5 (Continued)

Unit Process	Parameter	Criteria
Filter	Type	Upflow
	Loading rate required	3-15 gpm/ft^2
	Loading rate provided	5 gpm/ft^2
	Dimensions	12' x 1' x 1'
	Cross-sectional area	1 ft^2
	Sand depth	6-8 ft
	Gravel depth	6"
Filter Backwash	Backwash rate	15-22 gpm/ft^2
	Time	3-15 min
	Volume of water required	66-225 gal
	Storage tank	275 gal
	Pump	Centrifugal
	Pump rating	37 gpm at 40 ft of head
	Sludge storage and decant tank	500 gal

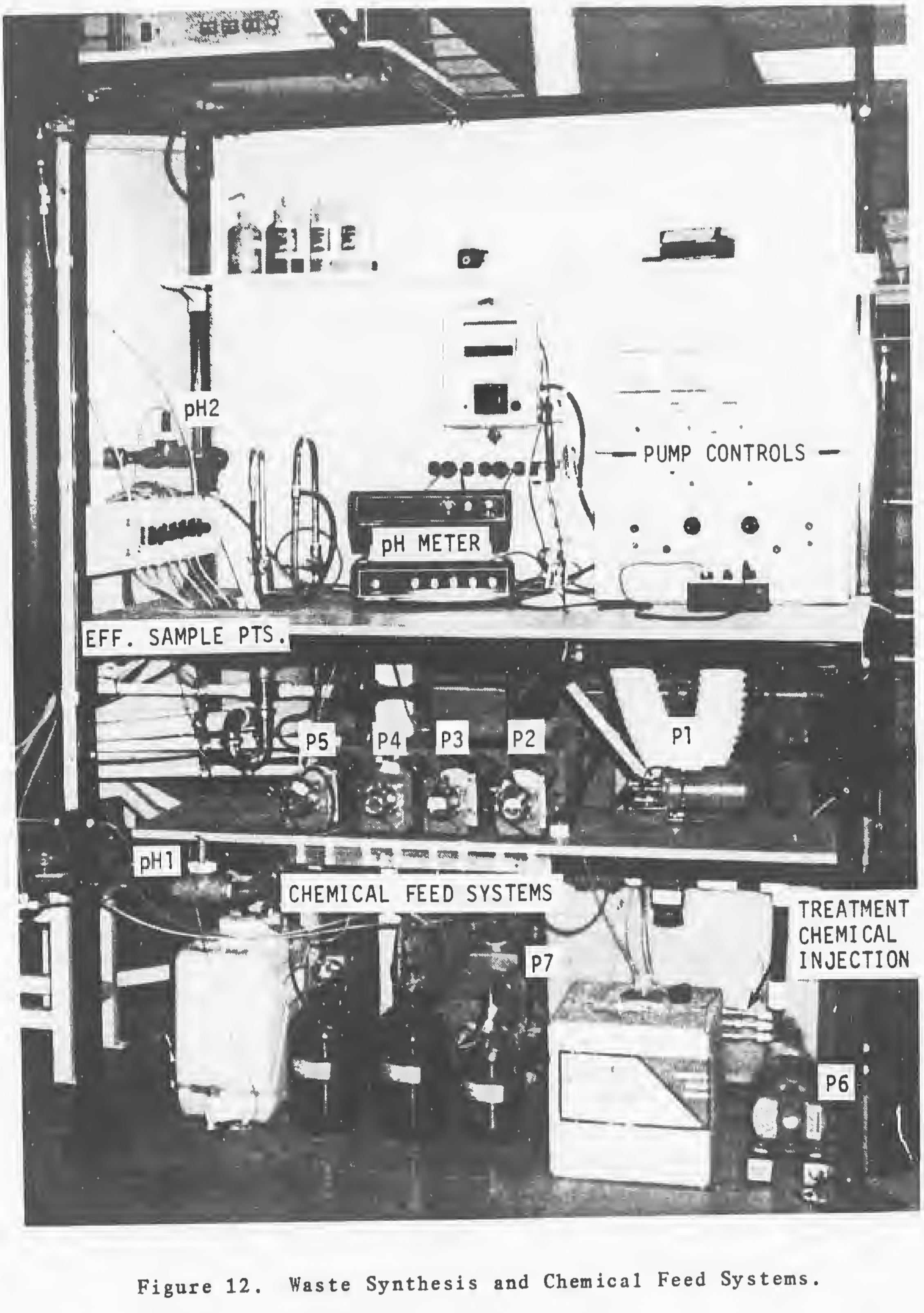

Figure 12. Waste Synthesis and Chemical Feed Systems.

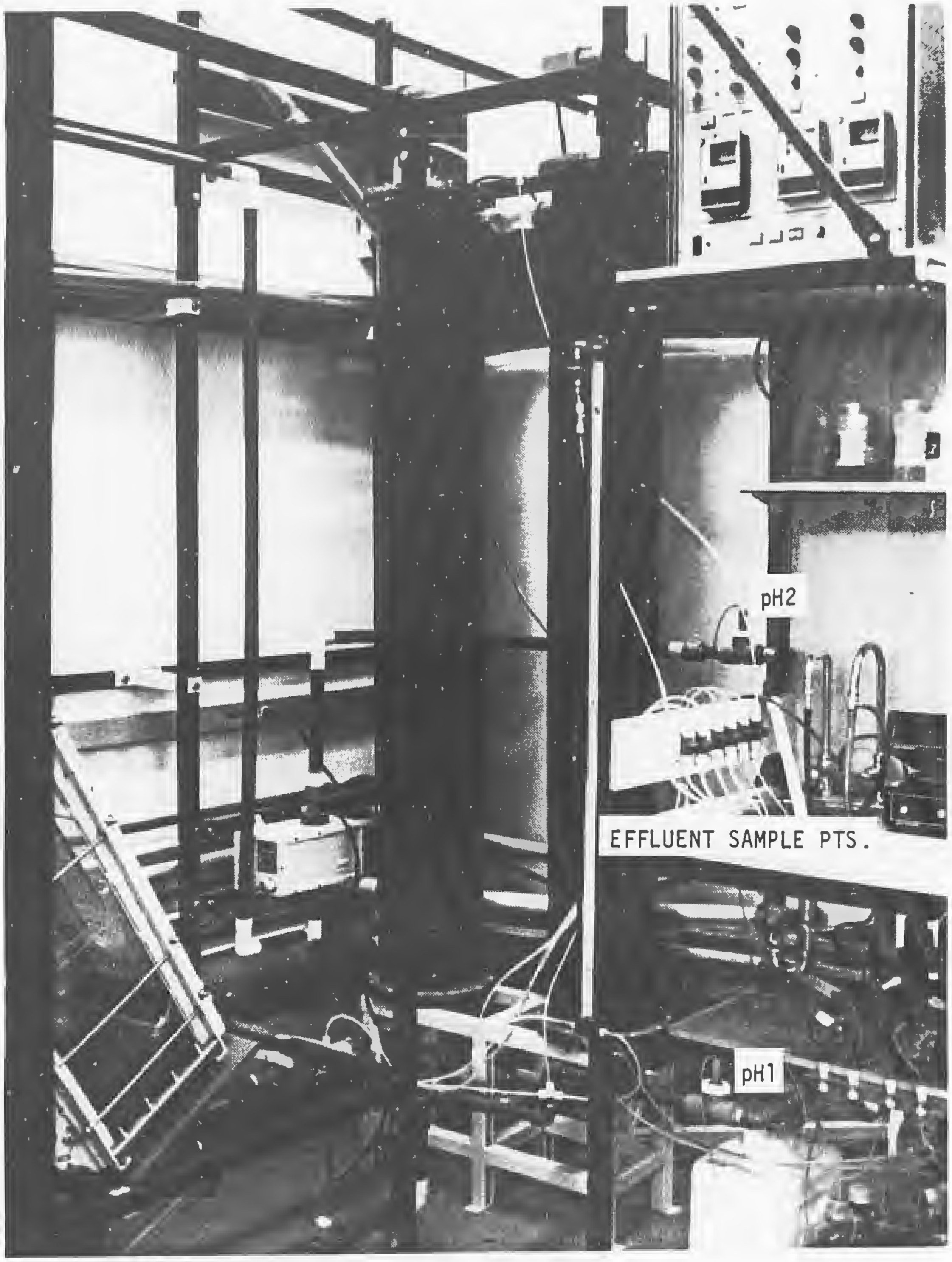

Figure 13. Flocculators.

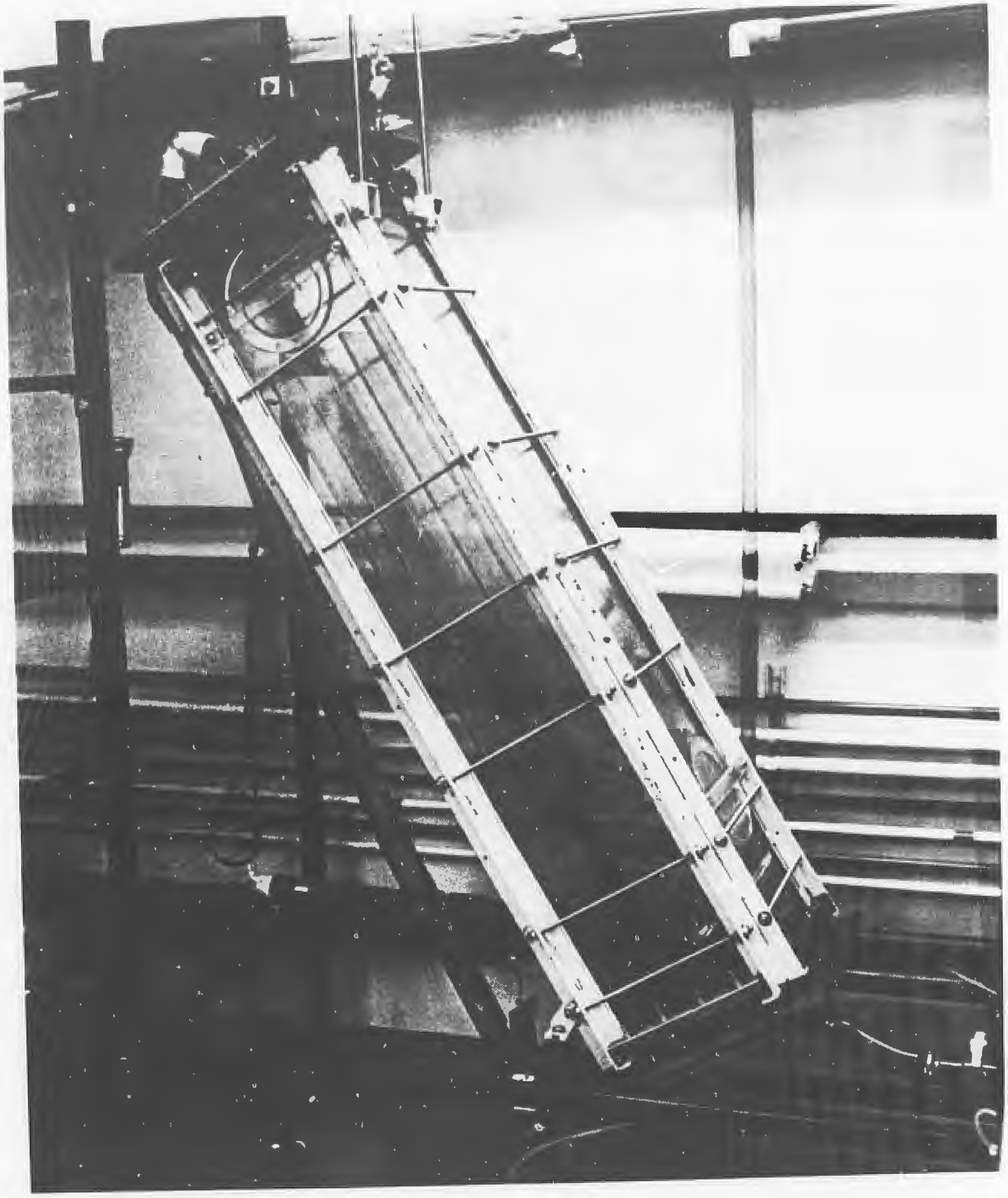

Figure 14. Clarifier.

Figure 15. Filter.

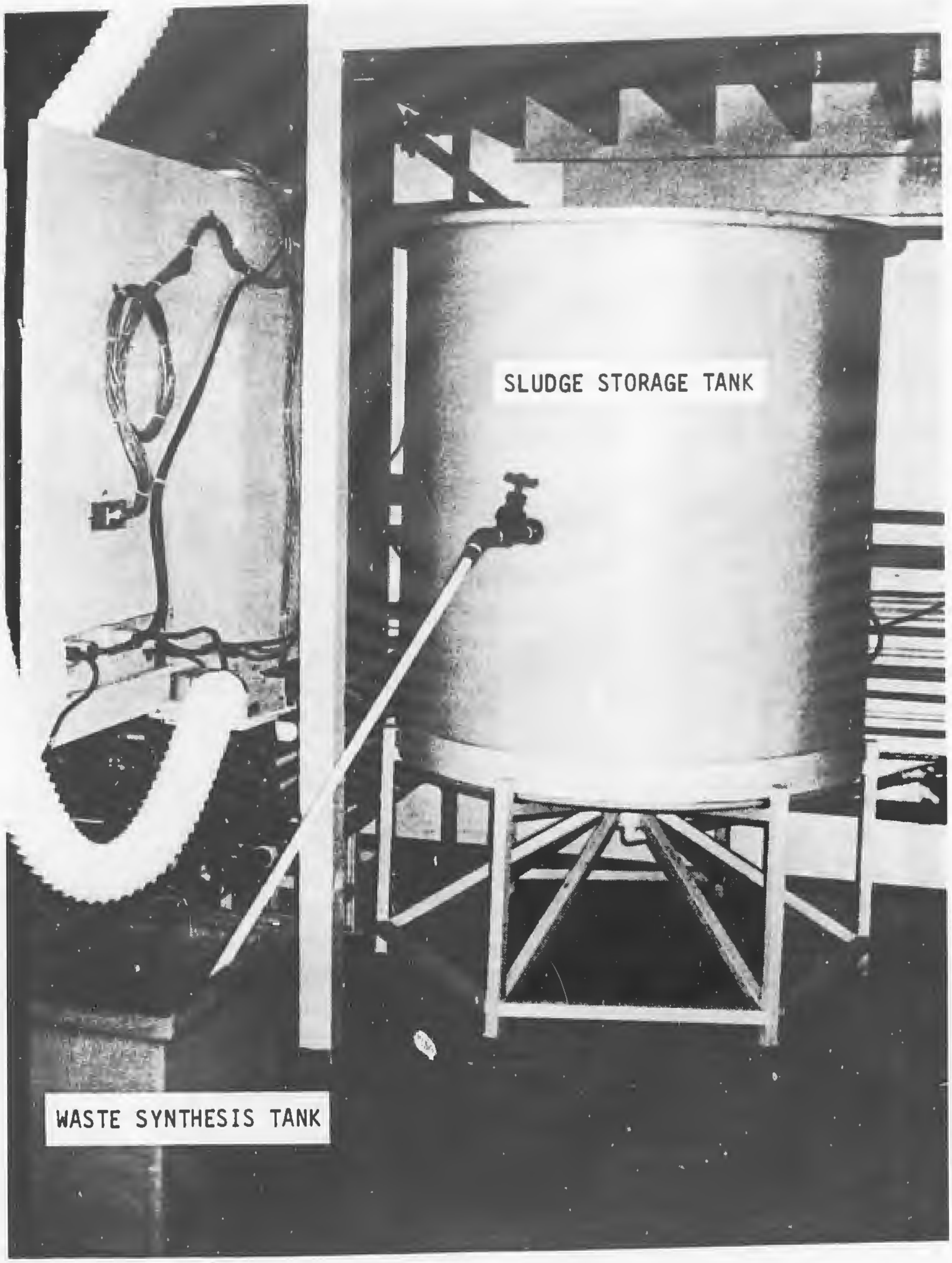

Figure 16. Sludge Holding Tank.

in the release of hydrocyanic gas, a dangerous condition. Two concentrated waste tanks and pumps were used to separate the cyanide containing cadmium bath from the other baths. A third peristaltic pump was used to pump concentrated nickel directly from its commercial container.

The concentrated wastes were metered into the waste mixing tank by calibrated peristaltic pumps. The water level in the mixing tank was maintained by a float-operated control valve, metering dilution water (tap or distilled) to the rate of outflow.

The synthetic wastewater was pumped through the treatment plant by a centrifugal pump. The flow rate was measured,using a bronze venturi meter with a water manometer,and controlled with a manually operated diaphragm valve.

b. Chemical Feed and Rapid Mix

Earlier studies (References 8 and 9) demonstrated that chromium reduction and precipitation, using ferrous iron, is rapid and that on-line addition of treatment chemicals provided sufficient time for mixing and reaction. To increase mixing intensity, the treatment chemicals were fed on-line just before the process flow pump, thus utilizing the centrifugal pump as a rapid mixer. Early test runs resulted in poor treatment due to shearing of flocs by the centrifugal pump. Relocating chemical additions to after the pump resulted in greatly improved floc formation and treatment efficiency. Mixing was promoted by turbulent flow through valves and fittings.

Flow integrators were installed in the chemical feed lines to smooth the pulsating flow from the peristaltic feed pumps. They amplified the pulsing and were removed. Sinusoidal fluctuations were noted in the chromium concentration at the autoanalyzer (discussed later under Automation and Control), located on-line, a few feet after chemical addition, probably caused by pulsing of the chemical feed pumps. Fluctuations were not noted in effluent chromium concentrations, since the treatment system is well-buffered by longitudinal dispersion.

The pH was monitored at a location just after chemical addition (pH1 - Figure 10) and at the effluent from the filter (pH2 - Figure 10). On-line, self-cleaning, combination pH electrodes (Sensorex model S645C) were used with an Orion model 605 electrode switch, and an Orion model 701A digital pH meter.

Taps were installed in the pipes connecting each of the treatment processes so that samples could be continuously withdrawn from the influent and effluent of each.

c. Flocculation

In previous studies of the proposed treatment system, a separate flocculator was not employed. In direct upflow filtration, the circuitous flow of the liquid through the coarse media at the bottom of the filter causes a gentle mixing that results in flocculation. Since a clarifier was included in the pilot plant to reduce solids loading on the filter, a separate flocculator was considered. Preliminary tests showed that 10 to 15 minutes of slow mixing significantly improved the removal of the precipitated metal hydroxides by plain settling (Figure 17). Separate flocculation was included in the pilot plant design.

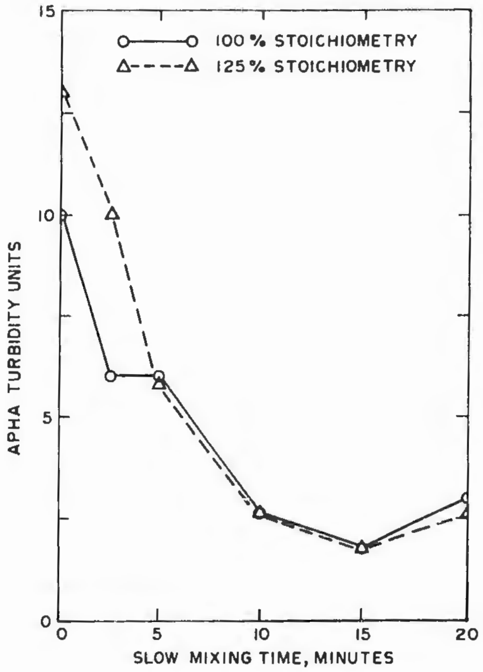

Figure 17. Flocculation Effects on Settled Turbidity.

d. Sedimentation

Gravity sedimentation was included to reduce the solids loading on the upflow filter, and thus increase run times between filter backwashes. Upflow filters can handle more solids loading than traditional downflow filters, so maximum solids removal was not required of a candidate clarifier. Minimum size was important, due to the decision that all processes be pressurized (to eliminate intermediate pumping); therefore, a parallel plate settler was incorporated in the treatment system.

e. Filtration

Previous studies, utlizing a small (1 3/4-inch diameter) filter, demonstrated that upflow filtration effectively removed the solids produced by alkaline ferrous reduction of hexavalent chromium. Significant wall effects were noted in its operation, which precluded its use in determining loading rates of larger filters. A 1-foot square filter was incorporated in the pilot plant. This larger size was a compromise between the need to limit wall effects and the limitations of a laboratory water supply to provide water for waste synthesis.

A coarser filter media is recommended for upflow filters than that commonly used in conventional downflow filters. Effective sizes of media recommended range from 0.55 to 0.65 mm (Reference 31) up to 0.95 mm (Reference 29). The larger effective size allows a greater hydraulic loading and solids loading without uplift, and the disadvantage of poorer removal of fine suspensions. Previous studies (Reference 7) utilized a sand with an effective size of 1.0 mm and a uniformity coefficient of 1.5. Three sands were selected for testing in the pilot plant filter. Their characteristics are shown in Table 6. The coarse and fine sands were available commercially. The medium sand was obtained by sieving a sand collected from a sand bar in the normally dry Salt River bed at Tempe, Arizona.

TABLE 6. FILTER MEDIA DATA

Media	Effective Size (mm)	Uniformity Coefficient
No. 20 Silica Sand	0.44	1.48
Sieved Salt River Sand	0.70	1.5
Monterey Sand	1.10	1.41

The filter media was supported by washed graded filter gravel (1/16 to 1/8 inch, 1/8 to 1/4 inch, and 1/4 to 1/2 inch) in three layers. The gravel was supported by a 3/16 -inch stainless steel plate which formed a false floor at the bottom of the filter. Holes were drilled in the plate in a grid pattern, 1 inch on center and 3/16th-inch diameter, to provide even distribution of incoming water.

Rubber-septum covered access ports were provided at 1-foot intervals along the length of the filter. Samples were drawn from the filter at these points using a syringe fitted with a hypodermic needle. Head loss measurements were made using hypodermic needles connected by tubing to mercury manometers.

Filter cleaning was accomplished by upflow backwash of the media using clean water. Backwash water was pumped from a storage tank through a three way valve into the inlet at the base of the filter. Flow rate was measured by a 1 1/2-inch brass venturi with a water manometer, and controlled with a diaphragm valve. Compressed air could be added to the backwash water line to aid in the baskwash. Head space was provided in the filter for 50-percent expansion of the media during backwash. Backwash water was discharged to a 500-gallon sludge storage tank for concentration and disposal.

D. INSTRUMENTATION AND CONTROL

Emphasis was placed on the on-line determination of hexavalent chromium and ferrous iron, using instrumentation that would be rugged and relatively inexpensive, require minimal maintenance, and give reproducible and fast results. Both colorimetric and redox potential methods were examined.

1. Colorimetric Analysis of Hexavalent Chromium

Laboratory work was undertaken to become familiar with the chemistry of the colorimetric methods as described in Standard Methods. Modification of an available colorimeter system was also undertaken to satisfy our needs.

a. Background Studies

The diphenylcarbazide (DPC) for hexavalent chromium analysis, Method 307 in Standard Methods, was studied with a Varian Model 635 LC spectrophotometer using a wavelength of 540 nm. When eliminating the steps for oxidation of trivalent to hexavalent chromium and removing interfering metal ions (from Step b directly to Step e), the development of color with the addition of diphenylcarbazide did not occur. Other procedures (References 42 and 43) refer to diphenylcarbazide "in acid", without directly specifying the acid or concentration. Both Alpkem (Reference 44) and Technicon (Reference 40) recommend the use of sulfuric acid. Because of the vagueness of the method it was decided to determine the effects of both the type and quantity of acid used in the analysis. Hydrochloric acid gave poor color development. Both phosphoric and sulfuric acids (5 drops of concentrated acid in 100 ml of sample) gave essentially the same sensitivity when allowing sufficient time for the color to completely develop. However, the use of sulfuric acid resulted in a faster attainment of steady state (Figure 18). Because of the shape of the curves on Figure 18, it was assumed the rate of color development, as measured by absorbance, is first-order and could be modeled by:

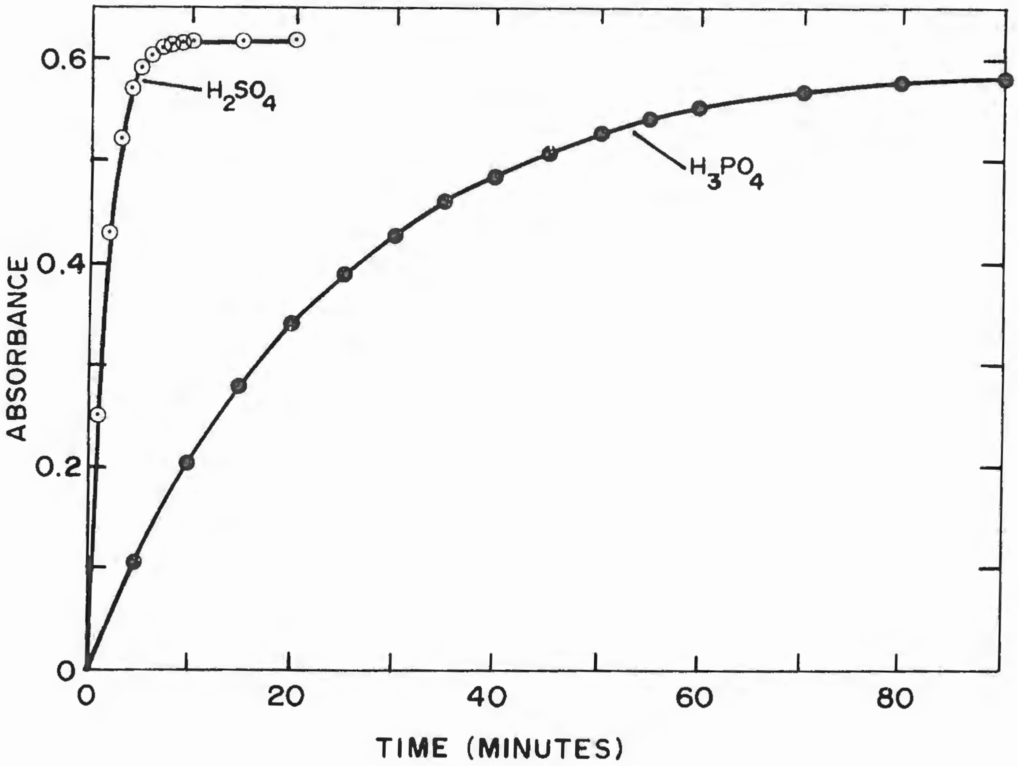

Figure 18. Effect of Acid Used on Cr(VI)-DPC Response Time.

$$\frac{d(A_\infty - A)}{dt} = -k(A_\infty - A) \qquad (27)$$

where A is the absorbance at any time, t, and A_∞ represents the final steady-state value of the absorbance. The concentration of hexavalent chromium ion not yet complexed with the DPC is proportional to A_∞-A. When plotting the transients on semilog paper (Figure 19), the resulting straight lines verify the suggested model and show that the rate of color development using sulfuric acid (k = 0.042 min^{-1}) is approximately 14 times faster than the rate using phosphoric acid (k = 0.60 min^{-1}).

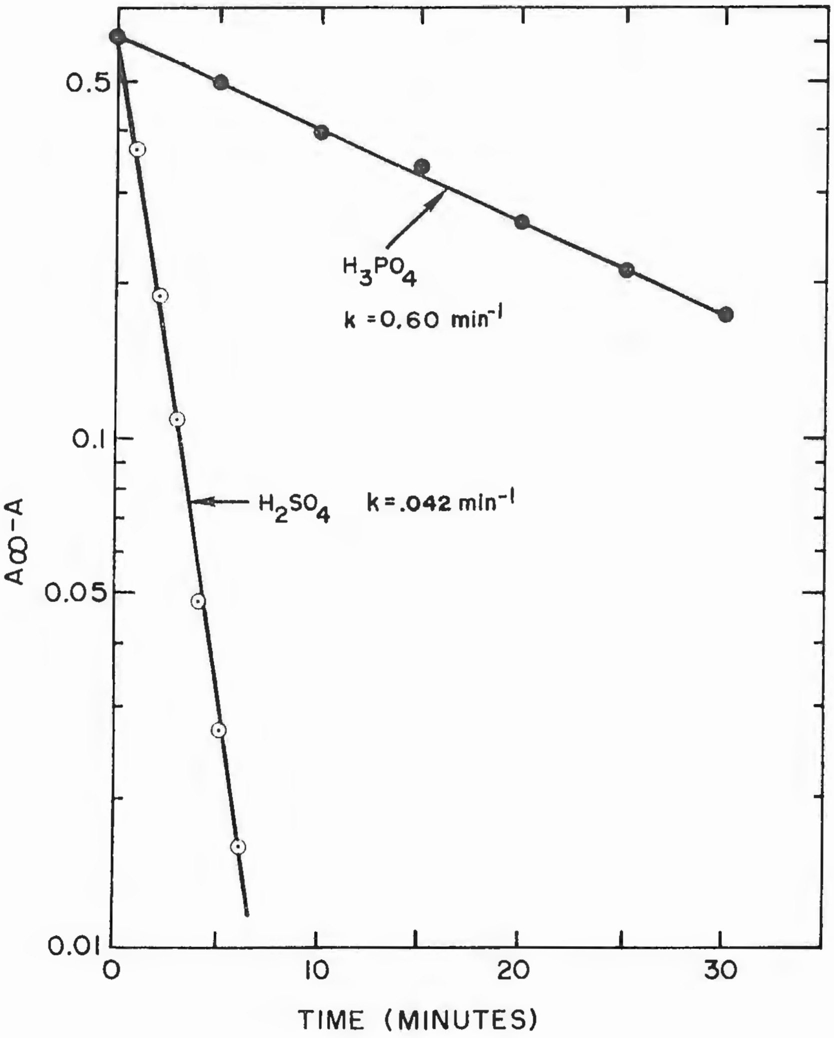

Figure 19. Effect of Acid Used on Cr(VI)-DPC Reaction Rate (Cr(VI) = 0.8 mg/l, T = 25°C).

Since the steady-state absorbance was essentially the same regardless of the type of acid used, it would imply that the amounts of the acids used were in excess and sufficient. As a check, the amount used (5 drops phosphoric acid per 100 ml sample) was increased to 1 ml acid and the steady-state absorbance did not change. Therefore, it can be assumed that 5 drops of concentrated phosphoric acid are sufficient for a 100 ml sample. Runs were also made using 10 drops of sulfuric acid in a 100 ml sample with no change in steady-state values or the rate of reaction. Figure 20 shows that absorbance conforms to Beer's Law up to 1.0 mg/l concentration.

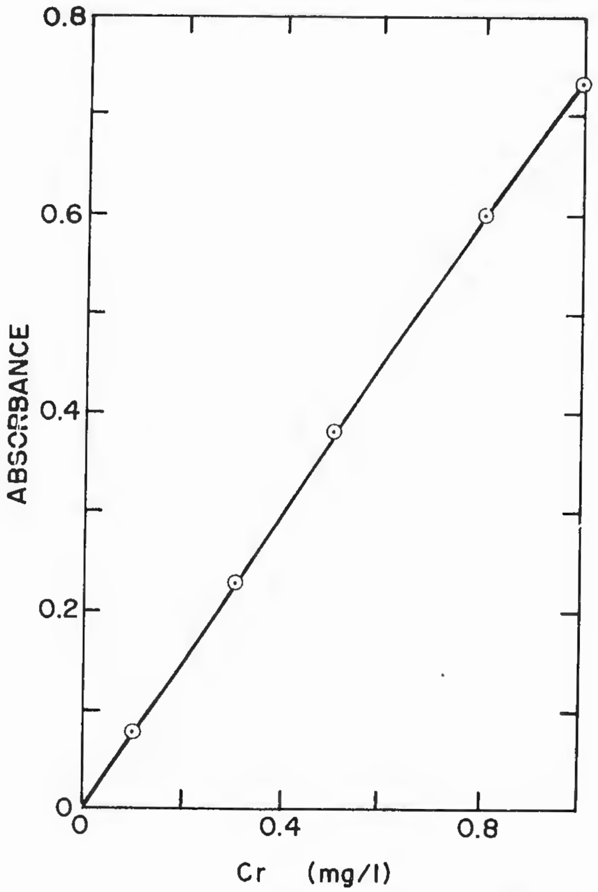

Figure 20. Calibration Curve for Cr(VI)-DPC (540 nm, 25°C, H_3PO_4).

To determine the effect of temperature on the rate of color development, absorbance-time curves were determined for 0.4 and 0.8 mg/l solutions using phosphoric acid and maintaining the solutions at 25°C or 50°C during the analysis (see Figure 21). An analysis at 90°C was also performed. Increasing

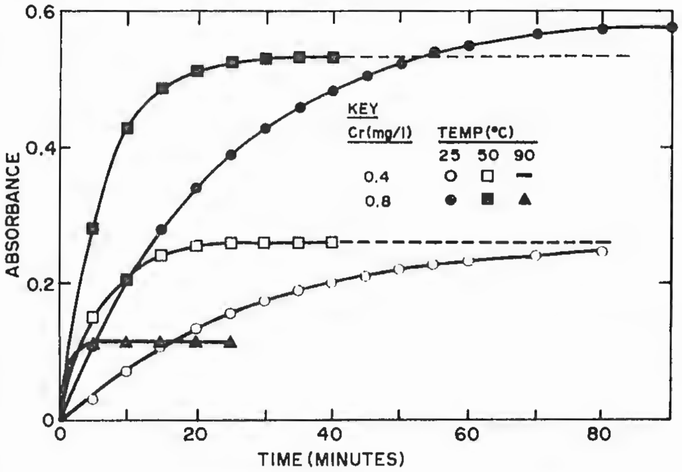

Figure 21. Effect of Temperature on Cr(VI)-DPC Reaction Rate (H_3PO_4).

the temperature increased the rate of reaction but reduced the steady-state final absorbance for a lower concentration. Appreciable liquid was vaporized at 90°C so the final value is suspect. However, nothing unusual happened during the 50°C run and yet it still gave a lower steady-state value. It was suspected that the differences were the result of absorbance being measured at different temperatures, and that temperature was affecting absorptivity of the complex and perhaps the absorption cell itself.

To check this out, a 0.8 mg/l solution was prepared and left overnight. The absorbance was measured at 25°C and again after heating to 50°C with resulting absorbances of 0.589 and 0.581, respectively, as compared to values of 0.587 and 0.535. This indicated that temperature affects the degree of complexing that occurs but does not affect the absorptivity of a given solution.

Neither Technicon, Hach or Alpkem used a heating coil in their schemes. Therefore, because of the temperature shift in steady-state value absorbance it was decided not to increase the rate of color development by raising the temperature.

It was postulated that the response rate could be increased by increasing the amount of DPC used. To check this, the amount of DPC used was doubled, resulting in doubling the response rate but giving the same steady-state absorption (Figures 22 and 23). A calculation shows that with the standard amount of DPC added to a 0.8 mg/l sample, there are approximately 135 moles of DPC per mole of Cr(VI). With this large excess, one would expect the rate to be proportional to the amount of DPC used but the final reading should depend on the limiting component, Cr(VI), only.

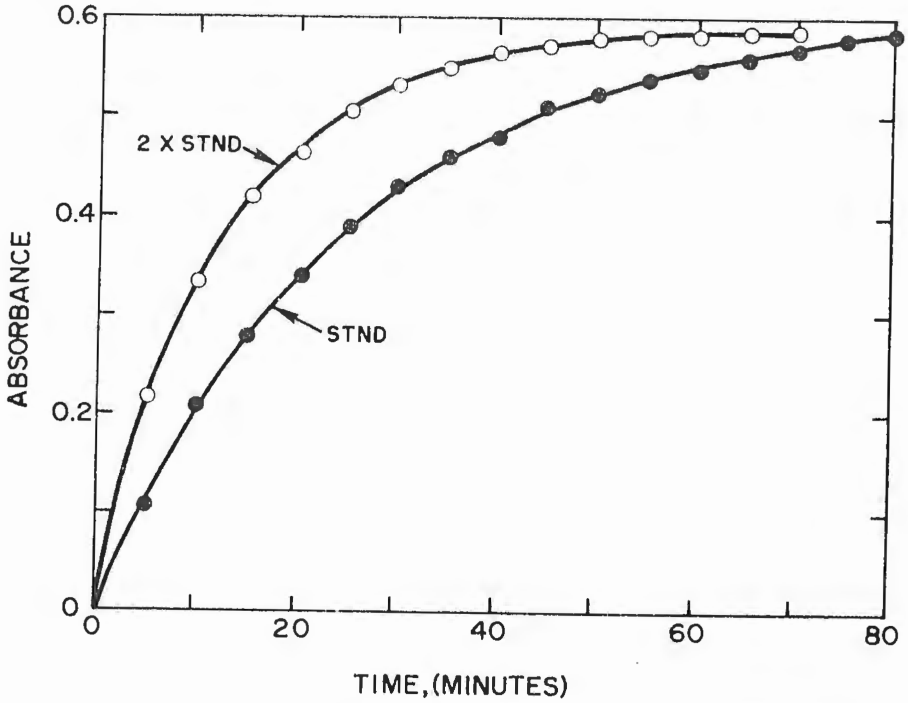

Figure 22. Effect of Varied DPC on Cr(VI)-DPC Reaction.

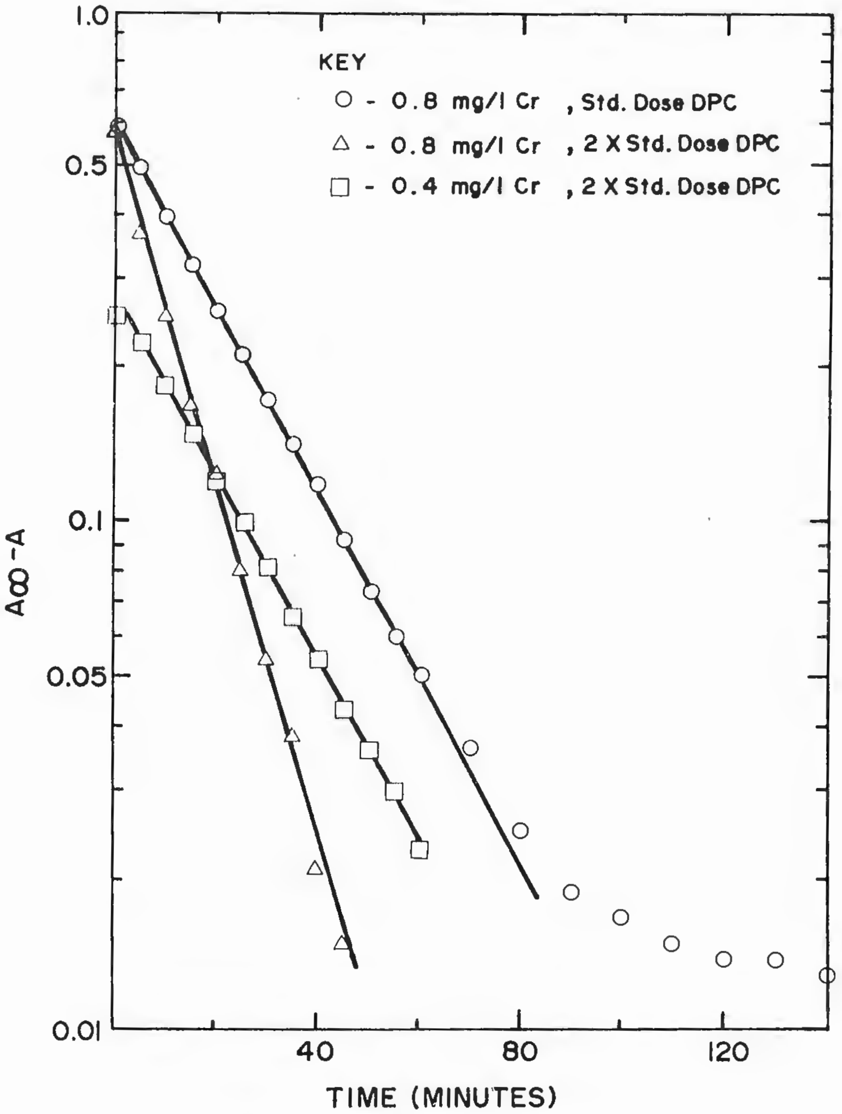

Figure 23. Effect of DPC on Cr(VI)-DPC Reaction Rate.

In summary, sulfuric acid should be used with the Standard Method to give a rapid color development. The rate is first-order with respect to free Cr(VI) concentration where the rate constant is proportional to the amount of DPC used and increases with temperature.

b. On-Line Colorimeter, Cr(VI)

Two Model I colorimeters and a Model II pump, manufactured by Technicon as part of their Auto-Analyzer line, were made available to the project. Cartridges (tubing, mixing tees, mixing coils, procedures, etc.) for both hexavalent chromium, Cr(VI), and ferrous iron, Fe(II), determinations were purchased from Alpkem, a company specializing in the design of systems compatible with Technicon's equipment and procedures. The schematic for the

Cr(VI) cartridge and method of reagent preparation is shown as Figure 24. The procedure is similar to that described in Standard Methods, but differs in reagent preparation.

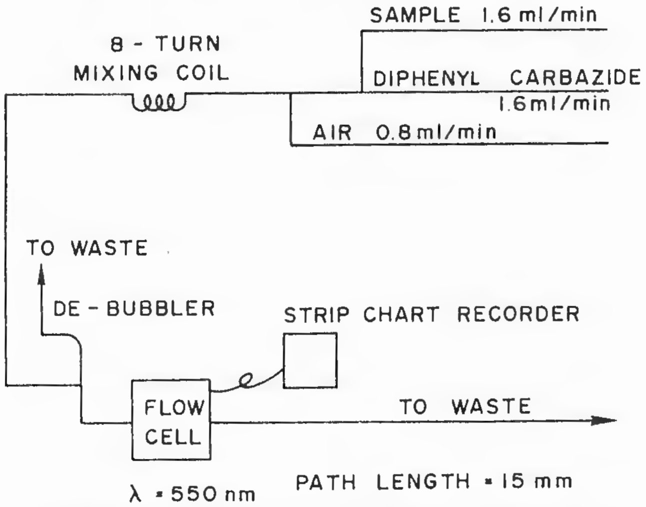

Figure 24. Schematic for Cr(VI)-DPC Colorimetric Cartridge.

Alpkem recommended the use of a 540 nm filter. A 550 nm filter was the closest wavelength filter available. A solution was made of equal parts of a 0.8 mg/l Cr(VI) solution and the DPC reagent, the ratio used in the Alpkem cartridge, and, after a suitable time for color development, a scan was made of absorption versus wavelength using a Varian 635LC spectrophotometer. Figure 25 shows the results. In the 540 to 550 nm wavelength range the absorptivity is essentially constant, and since the wavelengths passed by a particular filter

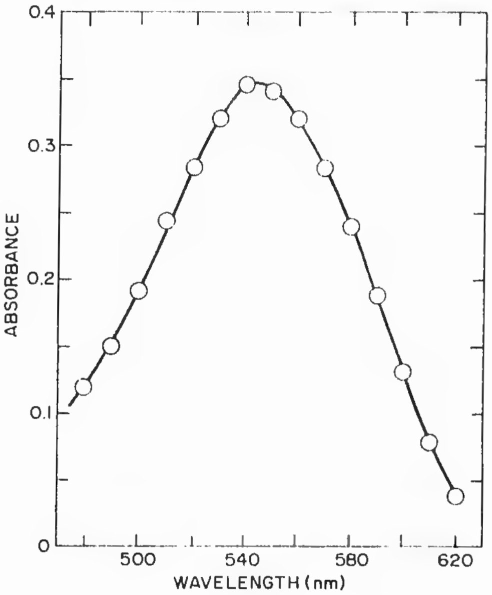

Figure 25. Wavelength Scan of Cr(VI)-DPC Absorbance.

are fixed, the use of the 550 nm filter should not affect the accuracy of the analysis.

The effect of changing the reagents on the time required to develop a steady-state color was investigated. A solution was prepared, as described above, for the wavelength scan and quickly placed in the spectrophotometer. The fastest a reading could be obtained was 1 minute, by which time absorbance had reached a steady-state value. This was considerably faster than the procedure from Standard Methods described in IIIB1a, probably due to the higher concentration of acid used in the Alpkem method.

Attention then turned to a study of the on-line colorimeter itself. The signal from the colorimeter (0-10 mv) displayed on a strip-chart recorder was determined to be proportional to transmittance. With a shutter in the light path, the output was set to 0 mv (corresponding to zero transmittance). With the shutter replaced with an aperture plate and the sample line in a beaker of distilled water, the output was arbitrarily adjusted to give a recorder reading between 75 and 100 percent of full scale. This reading corresponded to 100-percent transmittance. For a sample, the transmittance could then be calculated as the deviation from zero reading relative to the 100-percent span. The percent transmittance, T, was then converted to absorbance, A, using:

$$A = -\log (T)(100) \qquad (28)$$

Figure 26 shows the effect of slot size used and color development time

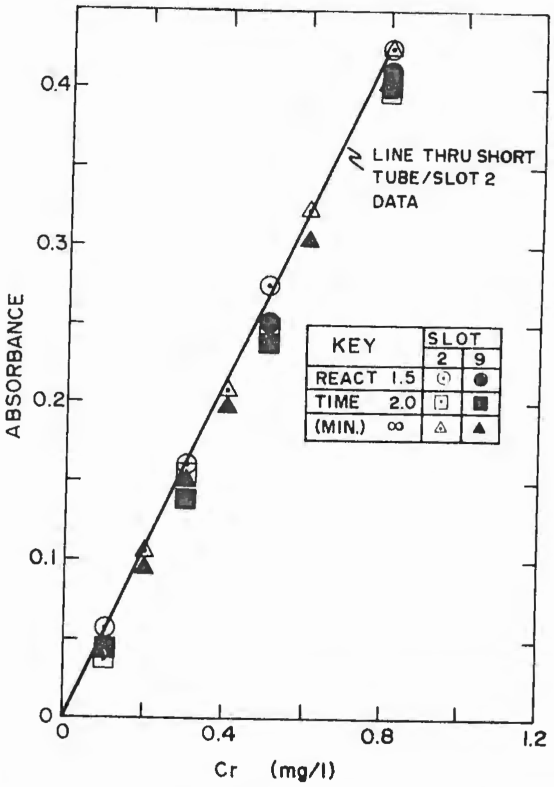

Figure 26. Analysis of Cr(VI) Using Alpkem Cartridge.

(residence time between mixing tee and flow cell) on the absorbance reading for different Cr(VI) concentrations. Slots 2 and 9 have aperture sizes of 7 mm and 14 mm, respectively. The reaction time of infinity represents data taken on a batch sample prepared using ratios of sample/reagent identical to the ratio of flow rates in the cartridge. These solutions were then allowed to sit overnight before being pumped through the flow cell. Using the length of tubing supplied with the cell resulted in a 2-minute reaction time. When the colorimeter was placed immediately next to the pump and the shortest tubing was used, the reaction time was reduced to 1.5 minutes.

Analysis of the data showed that the results were independent of both slot size and development time. This led to the conclusion that a development time of 1.5 minutes was sufficient and could possibly be reduced further. Alpkem recommended that the smallet slot (Slot 2) be used to reduce the amount of stray light reaching the cell. (As long as the amount of light reaching the cell provides a high signal/noise ratio, a small aperture should be used.)

A line was drawn through the 1.5 min/slot data for calibration purposes and is described by:

$$A = 0.535(Cr) \tag{29}$$

where (Cr) is the concentration of hexavalent chromium in mg/l.

2. Colorimetric Analysis of Ferrous Iron

Studies similar to those described above were done to become familiar with the colorimetric method for Fe(II) as described in Standard Methods. Modification of the colorimeter system was also undertaken to handle Fe(II) analysis.

a. Background Studies, Fe(II)

The phenanthroline method for ferrous iron (Method 310 in Standard Methods) was investigated using a Beckman Model DU Spectrophotometer. A scan of absorbance vs. wavelength for a 0.5 mg/l Fe(II) solution is shown as Figure 27. Peak absorbance was found at 508 nm. (Standard Methods specifies a 510 nm wavelength.) Figure 28 is the calibration curve run at 508 nm for 0-0.5 mg/l of ferrous iron. This concentration range resulted in absorbances less than 0.11 over which the data followed Beer's Law. Samples were allowed 10 minutes for color development prior to absorbance readings.

Before other basic tests were performed, the on-line colorimeter became available and its use was incorporated in further development of this procedure.

b. On-Line Colorimeter, Fe(II)

The pump and colorimeters are described in IIID1b. The procedure used is shown in Figure 29 and, in general, follows the Standard Method. Reagent preparation is described in Figure 29.

Both the Standard Methods and Alpkem's procedure recommend a 505 nm filter. A 484 nm wavelength filter was available. A scan of absorbance,

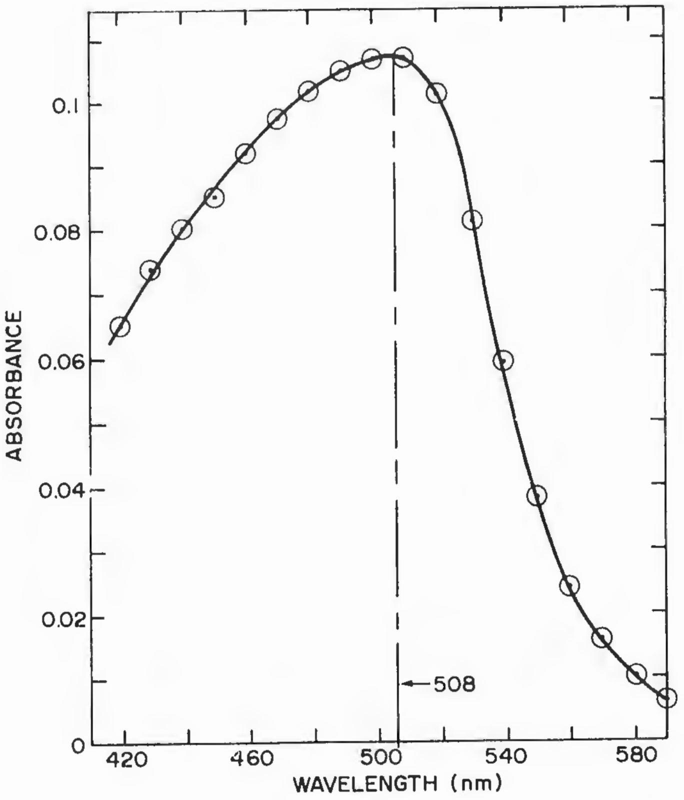

Figure 27. Wavelength Scan of Fe(II) – Phenanthroline Absorbance.

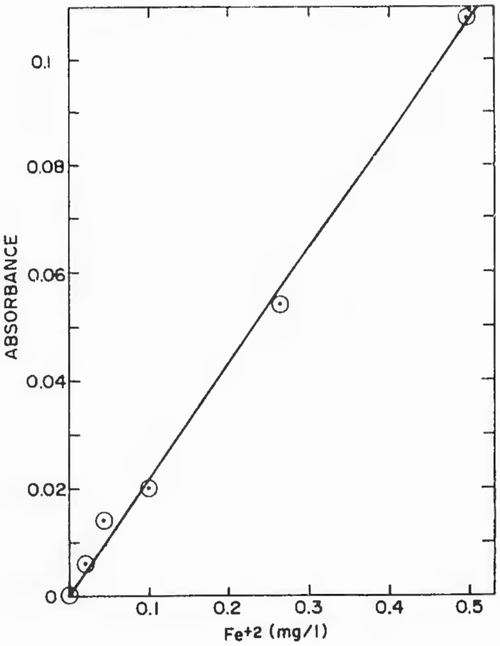

Figure 28. Calibration Curve for Fe(II) at 508 nm.

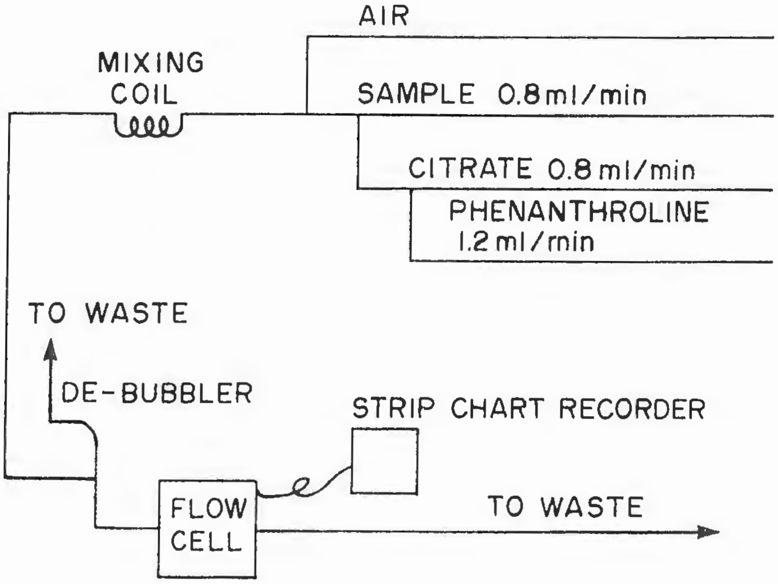

Figure 29. Schematic for Fe(II)-Phenanthroline Colorimetric Cartridge.

Figure 27, shows that the absorbance at 484 nm is approximately 95 percent of the peak value of 505 nm. A 5-percent loss in sensitivity is acceptable, since it has no effect on accuracy.

Calibration of the colorimeter was done as described in IIID1b, using distilled water to establish 100-percent transmittance.

Figure 30 shows that reducing color development time from 1.3 minutes to 1

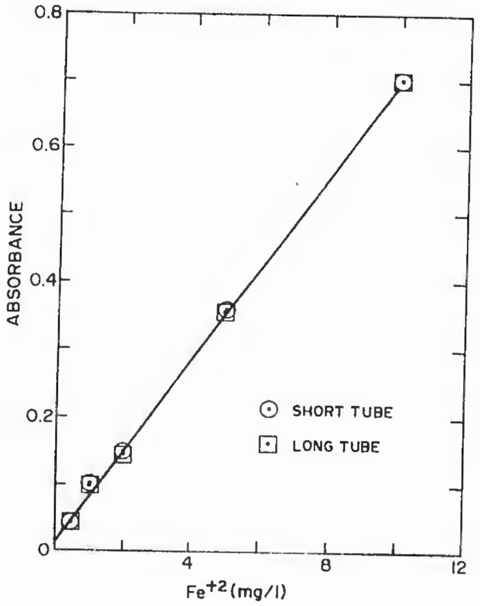

Figure 30. Analysis of Fe(II) Using Alpkem Cartridge (Effect of Tube Length).

minute had no effect. (This was done by placing the colorimeter close to the pump/cartridge and reducing the lengths of connecting tubing. The mixing coil supplied with the cartridge was retained.) The effects of slot or aperture size are shown in Figure 31. No significant difference was apparent, so a straight line was drawn, utilizing the smaller slot (2) data and used for calibration:

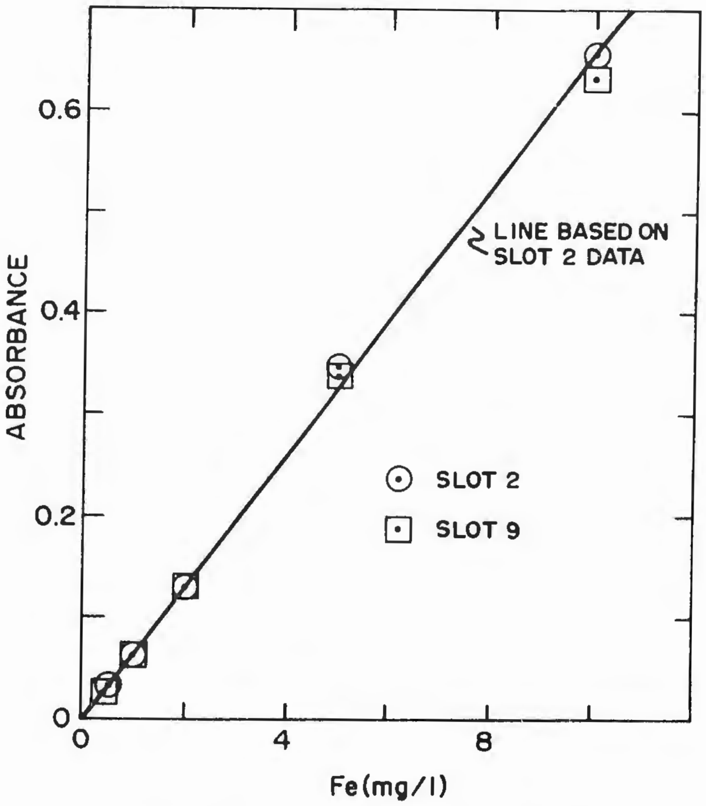

Figure 31. Analysis of Fe(II) Using Alpkem Cartridge (Effect of **Slot** Size).

$$A = 0.666(Fe) \qquad (30)$$

where (Fe) is the concentration of ferrous iron in mg/l.

3. Interferences

It was concluded that on-line colorimeters would give accurate measurements of Cr(VI) or Fe(II) concentrations with lag times less than 1 minute. The earlier tests were performed using solutions containing only one and not both of the ions. This section describes experiments that were run to determine the effects of having both ions present.

Table 7 shows the results of experiments in which Fe(II) and Cr(VI) solutions were mixed and the pH adjusted to the 9-10 range using 0.1 N NaOH solution. In Run 1, the solution was clear to the eye with a straw-like color. An analysis was run on this solution without filtering and using the procedure outlined in Standard Methods and the Varian spectrophotometer as described in sections IIID1a and IIID2a. After a few hours, a brownish precipitate collected at the bottom of the flask. The color of the solution became lighter. The results of the analysis were therefore suspect and the analysis was repeated after filtering with a 0.45-micron filter. The absorbance readings decreased, as shown in Table 7. The second run was done under essentially the same conditions.

TABLE 7. RESULTS OF INTERFERENCE TESTS UNDER BASIC CONDITIONS

Run	Filter	Ion	Initial			Final			Reacted	
			Vol, ml	conc., mg/l	meq. x10^3	Vol. ml	conc., mg/l	meq. x10^3	meq. x10^3	%
1	None	Cr(VI)	50	10	28.8	100	.145	.837	28.0	97.2
		Fe(II)	50	30.9	27.7		.134	.239	27.5	99.3
	.45 m	Cr(VI)	same as above			100		.051	.294	28.5
		Fe(II)					.021	.037	27.7	100
2	.45 m	Cr(VI)	100	10	57.7	205	.168	1.98	57.0	96.6
		Fe(II)	105	30.9	58.1		.075	.275	57.8	99.5

Since the redox reactions take place, the actual concentrations of Fe(II) and Cr(VI) in the filtrate are not known and direct confirmation of the accuracy of the analyses is not possible. An indirect check can be made by comparing the differences between ions initially in the stock solutions and the residual remaining in the solution after the reaction (as measured with the analysis). Assuming no other reactions occur, there should be stoichiometric agreement between the amounts reacted. Examination of Table 7 shows excellent agreement. A word of caution is in order here. Since the reacting solutions contain essentially stoichiometric amounts of the two ions and the reaction approaches 100-percent completion, the amount reacted is not sensitive to the accuracy of the low final concentration reading (i.e., the concentrations in the final solutions could vary by 100 percent and yet yield only a 1-percent error in amount reacted). Therefore the results of these tests, even while showing agreement, are not sufficient to prove the analyses are accurate.

Another series of runs was made, using the two-channel colorimeter and its related chemistries for the analyses. Table 8 shows the results when stock solutions of Cr(VI) and acidified Fe(II) are mixed and analyzed without adding

NaOH. Because of the low pH (~3), no visible precipitates were formed. In the series, the three runs were based on different ratios of reactants ranging from an excess of Cr(VI) to an excess of Fe(II). Because of this and the fact that the reaction is not as complete at low pH, the resulting agreement between the amounts of the two ions reacted gives more confidence in the analysis than the data shown in Table 7.

TABLE 8. RESULTS OF INTERFERENCE TESTS UNDER ACIDIC CONDITIONS (pH 3)

		Initial			Final			Reacted	
Run	Ion	Vol, ml	conc., mg/1	meq x10^3	Vol, ml	conc., mg/1	meq x10^3	meq x10^3	%
1	Cr(VI)	50	0.8	2.31	70	0.37	1.48	.83	40
	Fe(II)	20	5	1.79		.74	.93	.86	48
2	Cr(VI)	38.7	0.8	1.79	58.7	.29	.98	.81	45
	Fe(II)	20	5	1.79		.83	.87	.92	51
3	Cr(VI)	20	0.8	0.924	40	.085	.196	.73	79
	Fe(II)	20	5	1.79		1.39	1.0	.80	45

An in-line filter was then added to each feed line of the colorimeter pump. Solutions containing stoichiometric amounts of Cr(VI) and Fe(II) were mixed and the pH was adjusted to 8.5. The resulting solution was divided in two and one was acidified as would be done with a standard ferrous ion sample. The two solutions were then fed to the two-channel colorimeter through the filters. Table 9 shows the results. Good agreement is shown in the amounts reacted. Using a 0.45-micron filter resulted in higher absorbance readings than the coarser No. 4 filter. This was not expected since the interference from the precipitates should be higher for the coarse filter and give a higher absorbance. In the case of the basic solution fed to the Cr(VI) cartridge, the relative small difference, .0886 mg/1 compared to 0.068 mg/1, is probably due to experiment error. In the case of the Fe(II) analysis, the acidified solution cleared with time, indicating the precipitate formed during the basic reaction was redissolved in acid. This may account for the difference since the 0.45-micron filter runs were made first.

TABLE 9. EFFECT OF FILTER POROSITY ON COLORIMETRIC READINGS (pH = 8.5)

Filter	Ion	Initial			Final			Reacted	
		Vol, Ml	Conc., mg/l	meq x10^{3}	Vol, ml	Conc., mg/l	meq x10^{3}	meq x10^{3}	%
.45 micron	Cr(VI)	100	10	57.7	200	.0886	1.0	57.6	99.8
	Fe(II)	100	30.7	55.0		.208	0.7	54.3	98.7
No. 4	Cr(VI)	same as above			200	.068	0.8	56.9	98.6
	Fe(II)					.124	.4	54.6	99.3

To determine if the acidifying step would affect the degree of reduction of the Cr(VI), the inlet lines were reversed. No difference was detected in the reading on the Cr(VI) colorimeter indicating that acidifying the solution would not affect the amount of Cr(VI) present event though the Cr(OH)$_3$ was redissolved, putting more Cr(III) into solution.

Even though the above results do not directly verify the accuracy of the proposed analysis scheme, they imply that the presence of Fe(II) and precipitates will not affect the Cr(VI) analysis as long as the sample is filtered. It was concluded that the on-line colorimeter and cartridge, as described in Figure 24, would be adequate for on-line control purposes.

In the case of the measurement of the Fe(II) ion, the results are not as clear. When the inlet streams were reversed, as described above, the solution, which was not acidified and was at a pH of 8.5, gave no reading at all. This indicated either that the color development chemistry would not work on the high pH sample or that the ferrous ion was oxidized to ferric ion by atmospheric oxygen.

Because of the success in monitoring Cr(VI), it was decided to suspend work on the Fe(II) analysis and install the Cr(VI) cartridge and colorimeter in the pilot plant and use the resulting Cr(VI) readings to monitor the process.

4. Redox Electrode Measurements

Both the Fe(II)/Fe(III) and Cr(III)/Cr(VI) pairs have relatively high oxidation-reduction potential. Redox electrodes have been used to monitor the concentrations of these ions in solution. Experiments were performed to determine the effectiveness of redox measurements on solutions containing both of these pairs. An Orion 96-78-00 combination redox electrode was used with an Orion Digital Ionalyzer. The electrode was calibrated, using solutions of potassium ferrocyanide and potassium ferricyanide, according to the instructions supplied with the electrode.

In an initial experiment, 100 ml of a 10 mg/l Cr(VI) solution were mixed with 100 ml of a 30.9 mg/l Fe(II) solution and the pH adjusted to ~9 by the addition of a small amount of 0.1 N NaOH. Figure 32 shows that it takes over 10 minutes to approach a steady-state value. Possible reasons for the lag are: (1) the electrode response time was slow; (2) the reaction itself was slow; (3) the presence of a fine precipitate caused a drift in the electrode output; or (4) the reacting solutions contained an excess of Fe(II) ions which were gradually oxidized by dissolved oxygen, increasing the redox potential.

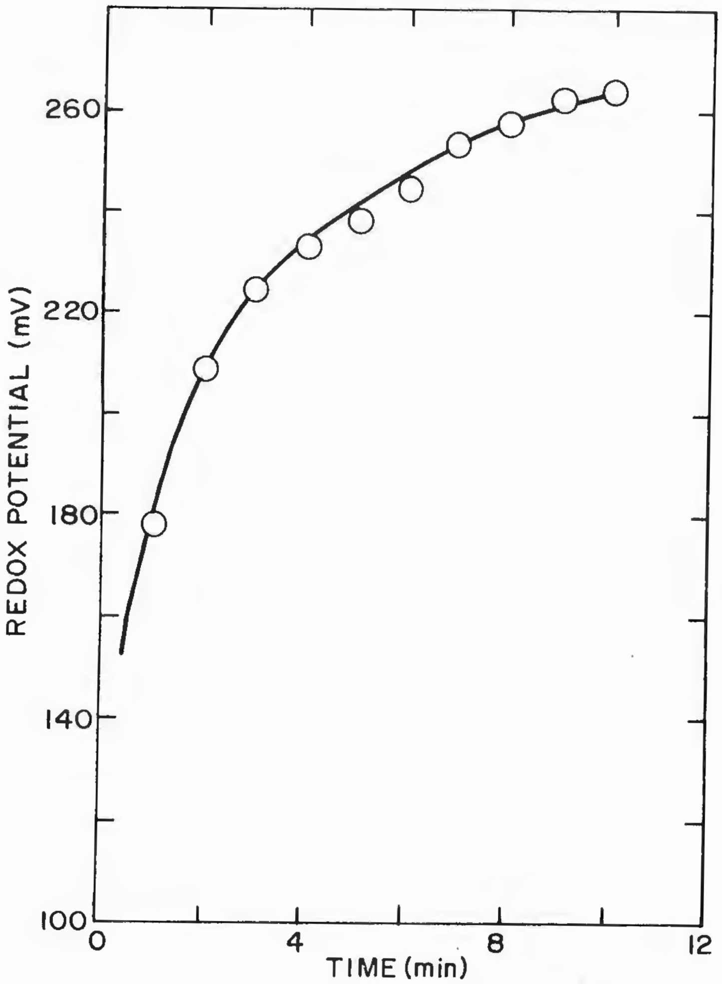

Figure 32. Redox Electrode Response to Batch Mixing of Fe(II) and Cr(VI) at pH ≈ 9.

The solution was clear with a straw color. Upon standing for a period of time, a precipitate settled to the bottom of the flask and the color lightened.

To determine the electrode response time, the redox electrode was rapidly placed in a 0.8 mg/l Cr(VI) solution after coming to steady state in a 0.4 mg/l solution. A new steady state was reached within 30 seconds indicating that a slow electrode response time was not responsible for the lag.

A titration of 100 ml of a 10 mg/l Cr(VI) solution with 75 mg/l Fe(II) was performed holding the pH to ~9 by addition of 0.1 N NaOH. Figure 33 is the result. Up to the stoichiometric end point (43.1 ml of Fe(II) solution), the redox potential dropped slowly, indicating the reduction of Cr(VI) to Cr(III). The readings quickly came to steady state during this titration, after the addition of each 5 ml aliquot. However, when the end point was reached, the addition of a 5 ml aliquot of the ferrous ion resulted in a rapid reduction in potential followed by a slow increase. This seemed to indicate that the excess iron was being oxidized by dissolved oxygen and that the appreciable lags described in the first experiment were caused by this reaction and not due to precipitate fouling or a slow reaction between Cr(VI) and Fe(II).

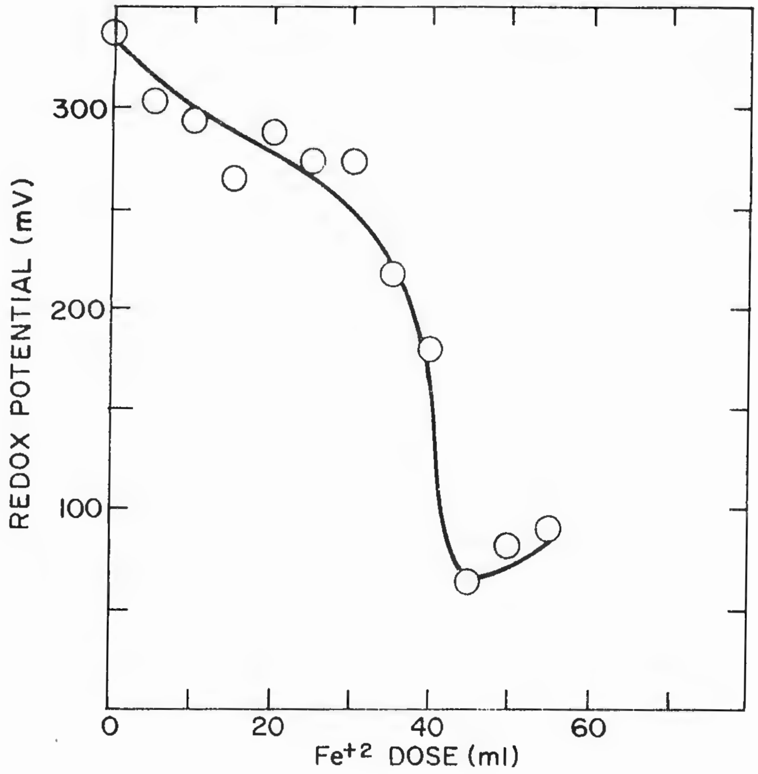

Figure 33. Redox Response to Cr(VI) Titration by Fe(II) at pH ≈ 9.

Examination of the response curve showed a clear breakpoint in the neighborhood of the end point. The method then could be used for control purposes if sufficient Fe(II) were added to maintain the redox potential below 100 mv. This would ensure adequate reduction of Cr(VI). A problem arises in not knowing exactly how much excess Fe(II) has been added since the curve flattens out past the end point. For this reason, the use of redox measurements was abandoned in favor of the colorimetric methods described earlier.

Figure 34 shows the curve resulting from a similar titration where the pH of the Cr(VI) solution was initially adjusted to 0.28 with sulfuric acid. No further adjustment of pH was made during the titration. The pH slowly rose to 0.42 during the titration. The end point under these conditions was very sharp but less than the 43.1 ml expected. The sharp end point is a reason why titration of Cr(VI) using Fe(II) at low pH is a recommended method (Reference 63) for measuring Cr(VI) concentrations in dilute solutions.

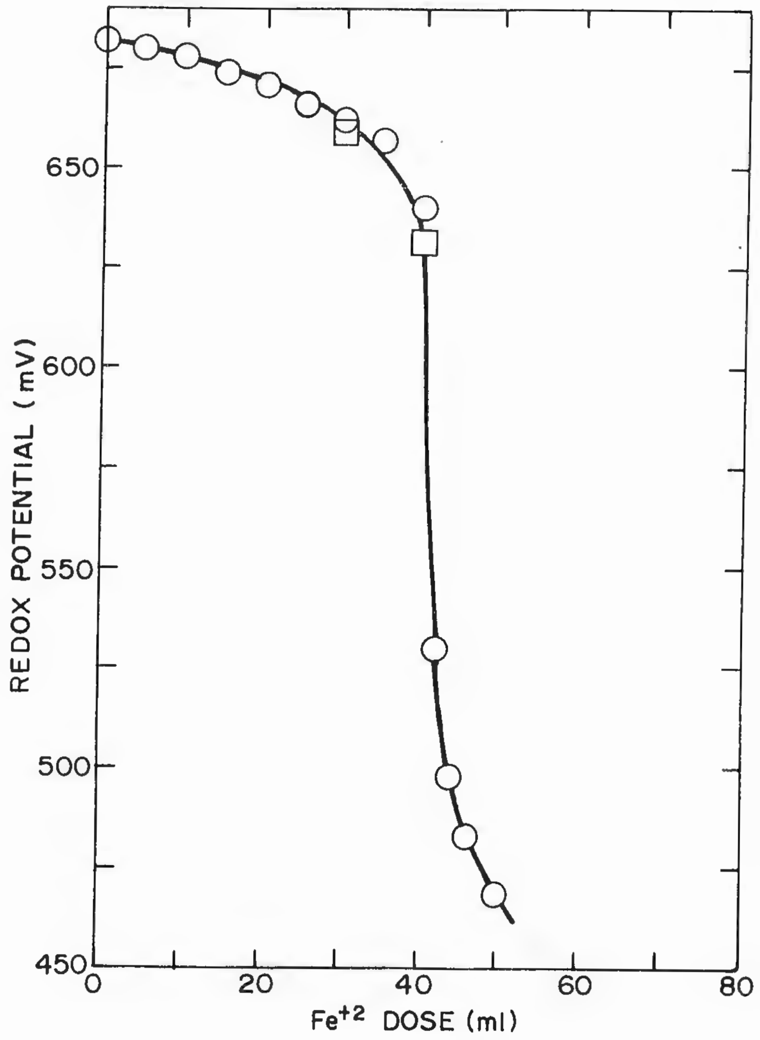

Figure 34. Redox Response to Cr(VI) Titration by Fe(II) at pH ≈ 0.3.

E. RESIDUALS ANALYSIS

1. Sludge Dewaterability

The sludges produced during pilot plant operation were collected and analyzed for specific resistance using a Buchner Funnel Test, described by Vesilind (Reference 61). The apparatus used in the test is shown in Figure 35. A 100 ml portion of sludge is placed in the funnel, and while a constant vacuum is maintained, the volumes of filtrate (V) and time (t) are recorded until the sludge cake cracks. Specific resistance is calculated from Equation (31).

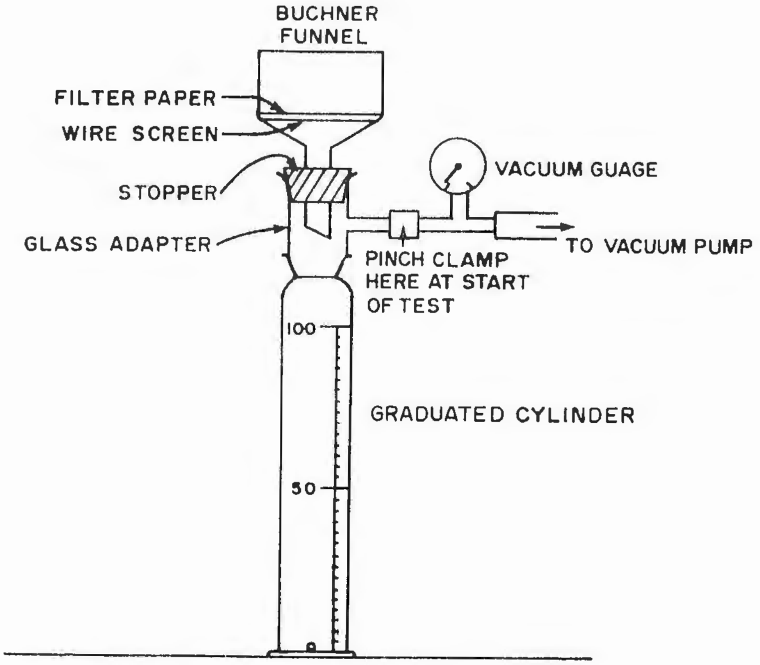

Figure 35. Buchner Funnel Apparatus.

$$R = \frac{2\ b\ A^2\ P}{\mu\ c} \tag{31}$$

where: R = Specific Resistance (m/kg)
b = Slope of t/V vs V (sec/m^6)
A = Area of filter (m^2)
P = Test pressure (N/m^2)
μ = Dynamic viscosity (N-sec/m^2)
V = Volume of filtrate collected (m^3)
t = Time from start (sec)
c = Weight of solids per unit volume of fitrate (kg/m^3)

Specific Resistance measurements were made of unconditioned and conditioned sludges. Lime and ferric chloride were tested as conditioners.

2. Sludge Composition

Sludges were digested with concentrated nitric acid on a steam table for 4 hours. The resulting mixture was filtered through a membrane filter, and the various metal concentrations of the filtrate analyzed by atomic absorption spectrophotometry. A more detailed outline of the digestion procedure is included as Appendix B.

A portion of the sludge was not dissolved in the hot nitric acid. Elemental sulfur was theorized as the end product when sulfide was used to reduce hexavalent chromium. Elemental sulfur is insoluble in nitric acid, but soluble in carbon disulfide (CS_2) (Reference 62). The solid residue from the sludge digestion was mixed with CS_2 and filtered. The CS_2 was vaporized and the residue was placed in a closed capillary tube and analyzed for melting point, using a calibrated heated oil bath.

3. Extraction Procedure (EP) Toxicity Analysis

Two variations of the EP Toxicity Test were used in analyzing the pilot plant sludges. Method 1 was used to analyze the cake produced by filtering the sludge. Method 2 was used to test settled decanted sludge. These methods are outlined in Appendix B and summarized below. Both tests consisted of diluting the sludge with 16 times its weight in distilled water, adjusting the pH to 5.0 ± 0.2 with 0.5 N acetic acid, and agitating the mixture for 24 hours. The pH was adjusted at set time intervals to 5.0 with a maximum of 4 ml of 0.5 N acetic acid per gram of sludge. At the end of the agitation period, the samples were diluted to 20 times their original weight with distilled water and filtered. The filtrate was analyzed by atomic absorption spectrophotometry. These metal concentrations were compared with the EPA standards. The original filtrates obtained from the filtered sludge samples were also analyzed.

F. CHROMIUM REDUCTION RATE STUDIES

Batch studies were performed to determine the effects of ferrous iron dose and pH on the rate of hexavalent chromium reduction. Methods used were as outlined in section IIIB of this report. The Auto-Analyzer, using the colorimetric method, was utilized to monitor reaction progress. Hexavalent chromium concentrations and pH were recorded on a dual-pen strip-chart recorder.

One-hundred ml aliquots of 5.0 mg/l hexavalent chromium were treated with ferrous sulfate (stoichiometric and twice stoichiometric doses). Iron doses were from stock solutions, sufficiently concentrated to minimize dilution effects and added from beakers to approximate instantaneous addition. The pH was controlled by manual addition of dilute sodium hydroxide or nitric acid by eyedropper. Reactions were monitored until steady state was achieved.

Responses were compared with responses of the Auto-Analyzer to step-changes in solutions fed to Auto-Analyzer. The Analyzer feed line was switched from a 5.0 mg/l Cr(VI) solution to solutions containing 1.6, 1.0, 0.5 and 0.1 mg/l of Cr(VI) respectively to determine the response curves for these step-changes in concentration. The rate for the chromium reduction reaction is responsible for the difference between responses in reaction studies and responses due to step-changes.

G. ANALYTICAL PROCEDURES

Metal analyses were performed by atomic absorption spectrophotometry, using a Varian Model 1250 AA and methods recommended by the manufacturer. Samples were collected in 50 ml polypropylene centrifuge tubes, acidified with nitric acid (1 drop per 20 ml), then stoppered and stored at room temperature for analysis. Samples analyzed for chromium were aspirated into a reducing nitrous oxide-acetylene flame; cadmium and nickel into an oxidizing air-acetylene flame. Trace concentrations (below flame limits) of these metals were measured using a Varian Carbon Rod Atomizer attached to the AA.

Other chemical analyses (hardness, alkalinity, sulfate, etc.) were performed in accordance with Standard Methods.

(The reverse of this page is blank)

SECTION IV

RESULTS AND DISCUSSION

A. BATCH REACTOR STUDIES

In previous studies (Reference 9) utilizing the proposed process for the removal of chromium, cadmium and nickel from plating wastewaters, satisfactory removal of chromium and cadmium was achieved, but problems were encountered with nickel removal. When a synthetic waste composed of potassium dichromate ($K_2Cr_2O_7$), cadmium chloride ($CdCl_2$), and nickel chloride ($NiCl_2$) was treated, all three metals were removed, but when a mixture of actual plating baths was treated, the nickel remained unaffected by treatment.

Plating baths commonly contain complexing agents to keep metals in solution, so it was postulated that something in the plating baths was preventing nickel precipitation as nickel sulfide (NiS) or nickel hydroxide ($Ni(OH)_2$). In particular, it was known that cadmium plating baths usually contain cyanide as a complexing agent, and it was suspected that cyanide was interfering with nickel removal.

The objectives of this study were to determine if nickel can be removed from plating wastewaters by the proposed treatment method, to isolate what is interfering with nickel removal, and to investigate methods of compensating for the interfering agent in the treatment method.

1. Solubility of Nickel

Experiments were performed to determine the practical solubility of nickel in tap and distilled waters with varied hydroxide and sulfide concentrations. A 10 mg/l (0.17 mM) solution of nickel (plus 0.17 mM sulfide, as appropriate) was made up in the test water, the pH adjusted and the mixture filtered. The 10 mg/l of nickel was selected as being close to those encountered in mixed plating rinsewaters, although it is less than the theoretical solubility of nickel at acidic pH.

Figure 36 shows how much of the initial nickel concentration remained

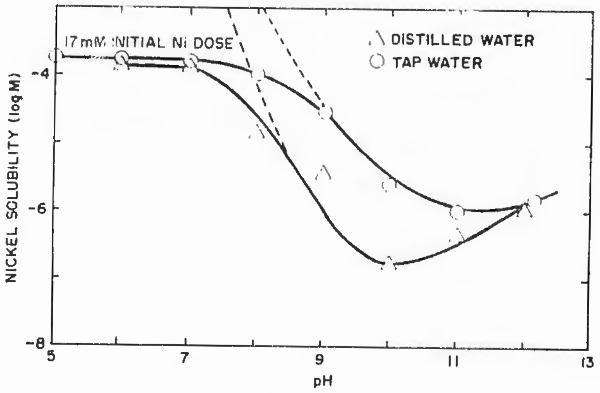

Figure 36. Nickel Solubility in Tap and Distilled Waters.

soluble at the indicated pH levels. At pH 7 and below, insufficient nickel was present to indicate solubility. The estimated solubilities are projected by dotted lines. This experimentally determined solubility of nickel in distilled water is in close agreement with that developed from theory and shown in Figure 8. The solubility of nickel in the tap water is seen to be an order of magnitude greater than in distilled water, probably due to complexation of the nickel with anions.

The addition of a stoichiometric amount of sodium sulfide has little effect on nickel solubility (Figure 37), as compared to that predicted (Figure 9). Again, nickel is appreciably more soluble in the tap water. This result agrees with an earlier study (Reference 9) which showed poor removal of nickel from a mixed-metal waste prepared in this tap water when compared with one prepared in distilled water.

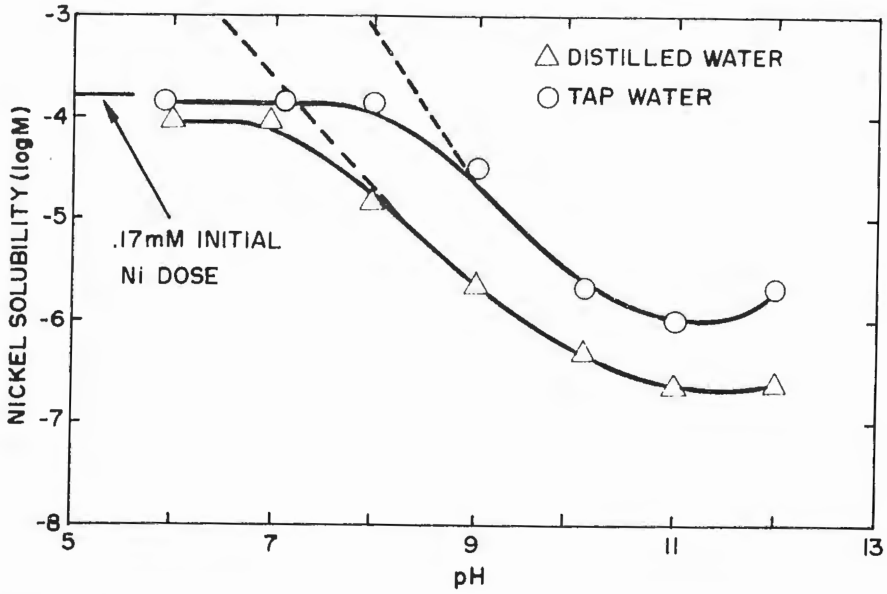

Figure 37. Nickel Sulfide Solubility (Initial Sulfide = 0.17 mM).

Increasing the sulfide dose to twice the stoichiometric requirement for nickel sulfide precipitation did not reduce the solubility of nickel. With a sulfide dose 100 times stoichiometric, 10 mg/1 of nickel remained soluble at all pH levels. This result was similar to an earlier study (Reference 9) on cadmium solubility which showed that cadmium solubility was increased by sulfide in concentrations greater than stoichiometric.

2. Nickel Solubility in Plating Bath Solutions

Next, the solubility of nickel from nickel plating baths was investigated. A comparison between nickel solubility for solutions prepared in distilled water from (1) nickel chloride and from (2) nickel plating bath, with a sulfide concentration twice stoichiometric, is shown as Figure 38. The nickel solution prepared from nickel plating bath was completely soluble in the distilled water for all pH ranges. The complexing agent(s) present in the plating bath were sufficient to maintain this high solubility, in spite of the high concentration of sulfide and hydroxide at the higher pH range.

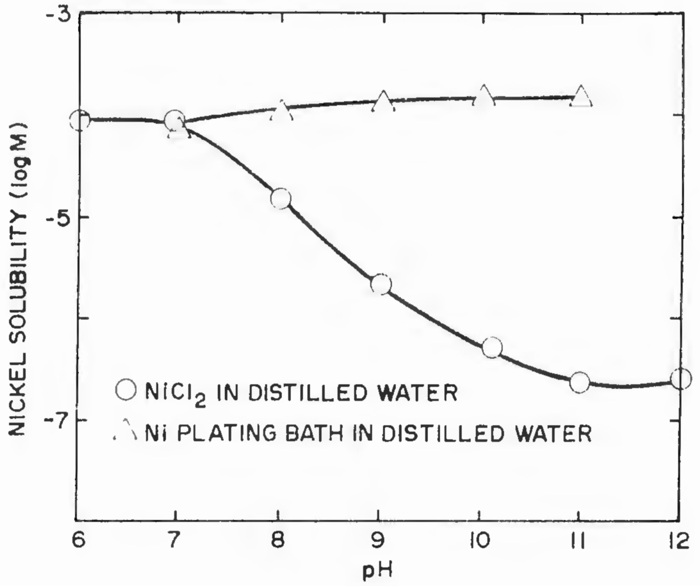

Figure 38. **Nickel Sulfide Solubility Using Nickel Chloride and Nickel** Plating Bath in Distilled Water (Initial Sulfide = 0.34 mM).

In tap water (Figure 39), significant nickel precipitation occurred. The solubility of the nickel (prepared from nickel chloride) is greater in the tap water than in distilled water, but the solubility of the plating bath nickel in tap water is greatly reduced, probably due to competition for the complexing agent by other cations (hardness) present in the tap water.

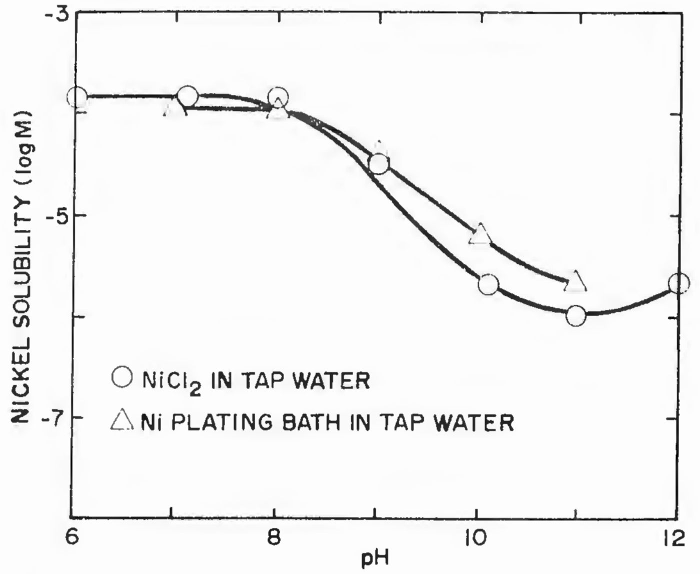

Figure 39. **Nickel Sulfide Solubility Using Nickel Chloride and** Nickel Plating Bath in Tap Water (Initial Sulfide = 0.34 mM).

This indicates that whatever nickel complexes are present in nickel plating bath are weak enough that the ions present in tap water can break them and allow nickel sulfide precipitation at an alkaline pH. Thus the nickel plating bath itself should not present a significant obstacle to nickel removal by the proposed treatment.

When sulfide (1.3 times stoichiometric) was added to a mixture of nickel and cadmium plating baths (10 mg/l Ni and 10 mg/l Cd) no nickel was removed by precipitation and filtration from either tap water or distilled water at pH 7 through 11. Essentially, all the cadmium was removed at each tested pH. Complexing agents in the cadmium plating bath were apparently complexing the nickel more strongly than the cadmium so that NiS could not form. Cadmium plating baths often contain cyanide, so the effects of cyanide on nickel solubility were investigated.

3. Cyanide Effects on Nickel Solubility

Nickel cyanide tetrahydrate, $NiCN_2 \cdot 4H_2O$ is described as being a pale, green, insoluble powder (Reference 62), suggesting that cyanide should not interfere with nickel precipitation. When a solution of 0.34 mM sodium cyanide and 0.15 mM (8.8 mg/l) nickel (from plating bath) was prepared in tap water at pH 9.5, a pale green precipitate formed, and soluble nickel was reduced to 3.2 mg/l. Comparable results were observed when 0.34 mM sodium sulfide was added to the solution. However, with increased cyanide concentration, nickel solubility was found to increase, as shown in Figure 40. This suggests that

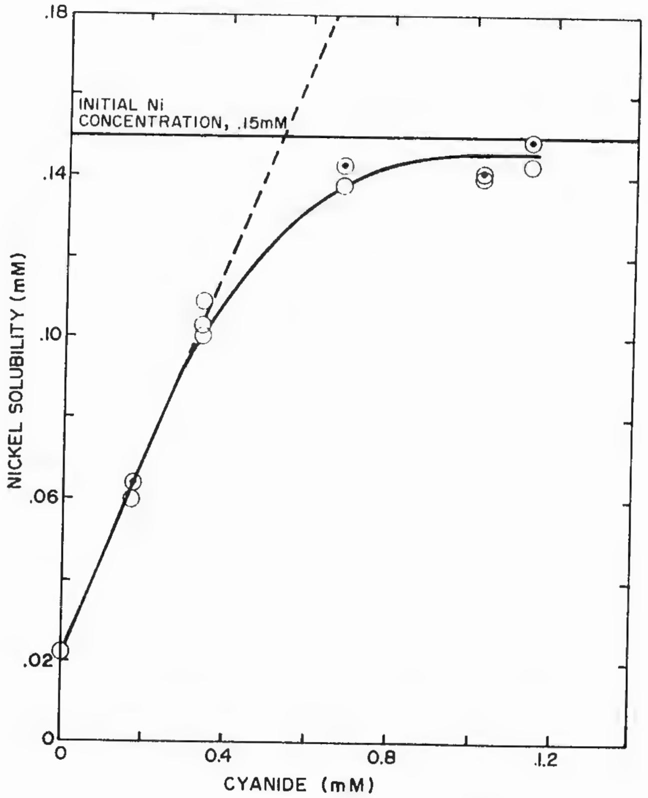

Figure 40. Nickel Sulfide Solubility with Varying Cyanide at pH 9 (Initial Sulfide = 0.34 mM).

excess cyanide causes formation of ions such as $Ni(CN)_3$ which remain in solution, rather than the formation of insoluble $Ni(CN)_2$.

The recommended concentrations of cyanide in a cadmium plating bath from Williams Air Force Base is three times the cadmium concentration on a weight basis, so a cadmium plating bath diluted to 10 mg/1 Cd would have 30 mg/1 cyanide. This corresponds to 1.14 mM or 6.7 times the molar concentration of nickel at 10 mg/1 (0.17 mM). The solubility curve developed for nickel sulfide-varying concentrations of cyanide indicates that this high concentration of cyanide(relative to nickel)would interfere with any removal of nickel sulfide.

4. Effects of Increasing Doses of Treatment Chemicals

The effects of varying ferrous iron and sulfide doses on metal removal from mixed chromium (10 mg/1) and cadmium (10 mg/1) plating baths in distilled water, and mixed chromium (10 mg/1), cadmium (10 mg/1), and nickel (5 mg/1) plating baths in tap water were studied.

Work done with mixed cadmium and chromium baths at pH 8 showed that cadmium plating bath does not interfere with chromium removal. Figure 41 shows that chromium removal was directly proportional to the iron dose, and the presence of sulfide-improved chromium removal, in agreement with earlier studies (Reference 9). Cadmium removal was directly proportional to sulfide

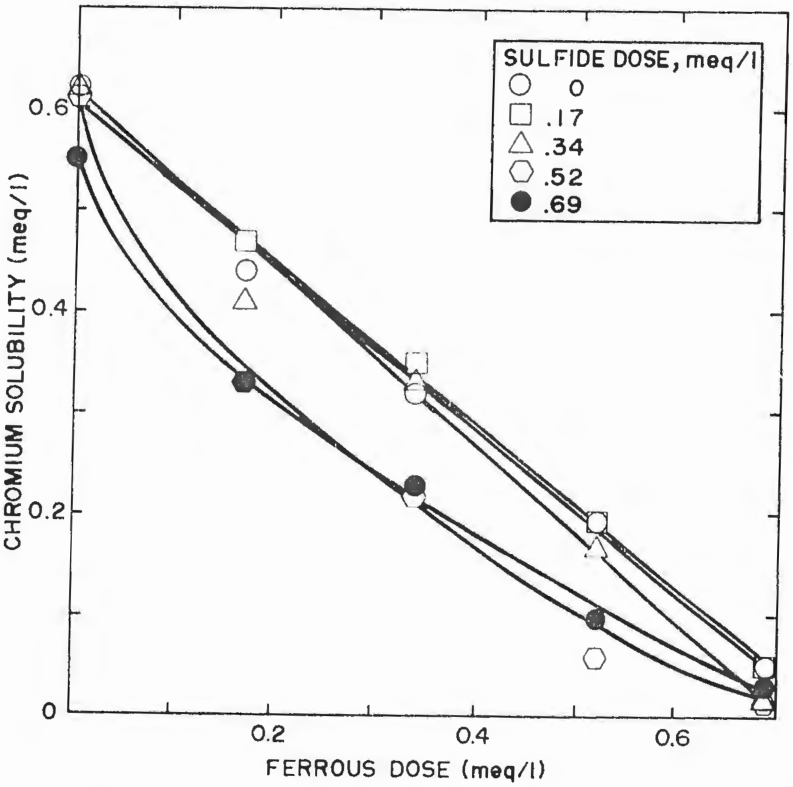

Figure 41. Chromium Removal from Chromium and Cadmium Plating Baths in Distilled Water.

dose and essentially independent of the iron dose as shown in Figure 42. This

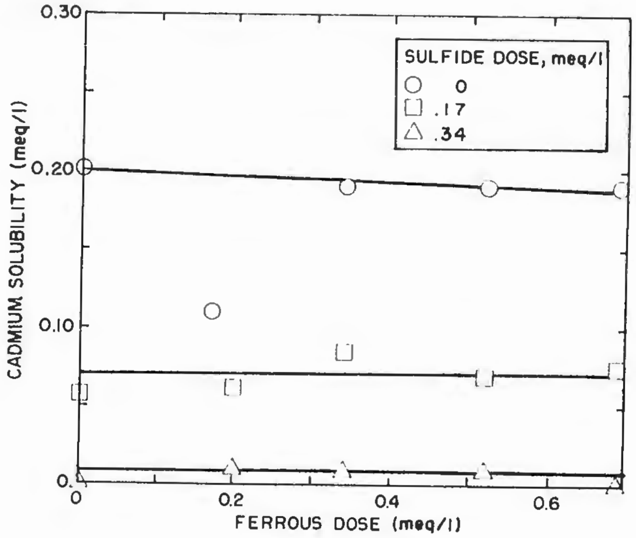

Figure 42. Cadmium Removal from Chromium and Cadmium Plating Baths in Distilled Water.

is what would be expected since cadmium precipitates as CdS. At sulfide doses above 0.34 meq/1, residual cadmium concentrations were below detectable limits.

From mixed cadmium, chromium and nickel plating baths in tap water at pH 8, similar trends were observed in chromium removal (Figure 43). The effects

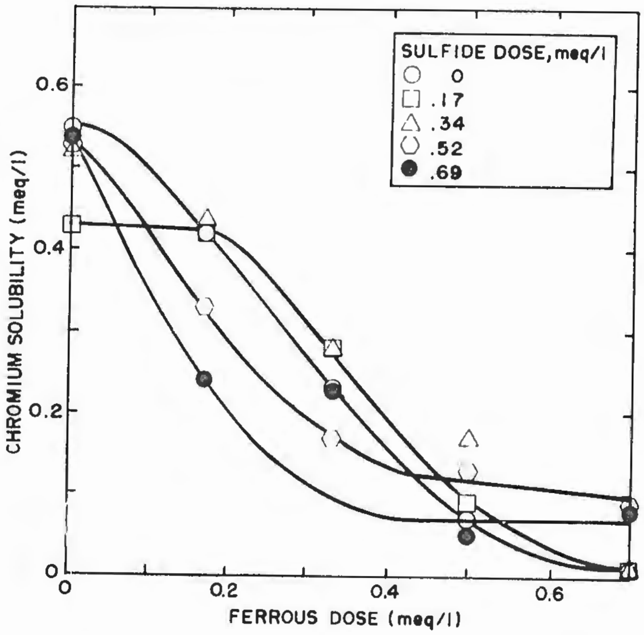

Figure 43. Chromium Removal from Chromium, Cadmium and Nickel Plating Baths in Tap Water.

of increased sulfide doses were more marked than in the previous case. This also agrees with earlier work. Cadmium removal (Figure 44) was proportional to sulfide dose as in the previous case, but in tap water, cadmium removal was also improved by the presence of iron. Nickel concentrations remained unaffected by iron or sulfide doses, as would be expected with the high concentration of cyanide present in the cadmium bath. Figure 39 shows that 5 mg/l (log molar concentration of -4.07) is soluble in a nickel plating bath at pH 8, without cyanide present.

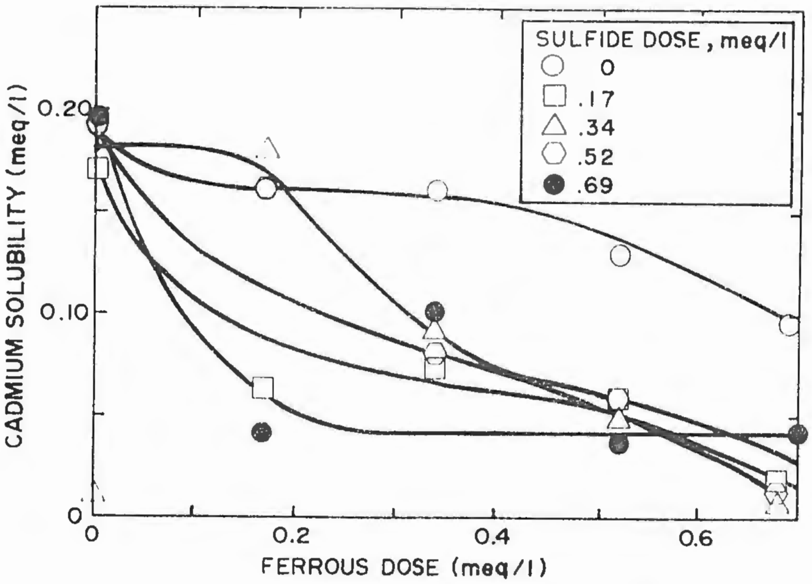

Figure 44. Cadmium Removal from Chromium, Cadmium and Nickel Plating Baths in Tap Water.

Mixed chromium (10 mg/l), cadmium (10 mg/l) and nickel (10 mg/l) plating baths were treated with excess iron, anticipating that the formation of iron cyanide complexes would prevent the nickel cyanide complexes from forming, and would allow nickel removal as NiS. Excess doses of iron up to five times stoichimetric to the chromium did not significantly improve nickel removal. Also, the effluent showed consistently low concentrations of iron, indicating that iron-cyanide complexes were not formed. This conclusion is supported by the fact that cadmium bath does not interfere with chromium removal, because iron would not be available to reduce the chromium if it were complexed by cyanide.

When a cadmium plating bath (10 mg/l Cd) was mixed with nickel plating bath at 83 mg/l (3.4 meq/l) and 3.4 meq/l sulfide, resulting nickel solubility was 39 mg/l. This indicates that cyanide significantly increases nickel solubility.

B. CONTINUOUS FLOW REACTOR (PILOT PLANT) STUDIES

The pilot plant operating conditions and data are summarized in Table 10. The runs listed in this table are grouped into several broad categories for

TABLE 10. SUMMARY OF DATA FOR PILOT PLANT RUNS.

Run #	Flow (gpm)	Units Used	Water	Waste	Influent Waste (mg/l)			Feed (mg/l)		Fe/Cr	S/Cr	pH1	pH2	Effluent (mg/l)			Breakthrough Time (min)	Head Loss (ft)
					Cr	Cd	Ni	Fe^{+2}	S^{-2}	(meq/meq)				Cr	Cd	Ni		
3[1]	4.9	F	T	S	15.4	–	–	33.0	–	0.65	–	8.9	8.3	4.5	–	–	–	–
4	5.3	F	T	S	14.0	–	–	30.7	–	0.72	–	7.9	7.5	0.08	–	–	<20	–
5	3.1	F	T	S	9.3	–	–	31.3	–	1.0	–	8.5	8.2	1.0	–	–	53	–
6	3.0	F1,F	T	S	10.4	–	–	32.4	–	0.97	–	8.8	8.2	2.0	–	–	59	–
7	3.1	F	T	S	8.3	–	–	31.3	4.5	1.11	0.58	9.0	8.9	0.13	–	–	50	–
9[2]	3.3	F	T	S	6.5	–	–	29.6	4.3	1.39	0.71	8.9	8.5	0.1	–	–	39	–
11[3]	3.0	F	T	S	6.4	–	–	32.4	4.6	1.57	0.5	8.9	9.0	<0.1	–	–	87	–
12	3.0	C1,F	T	S	9.1	–	–	32.4	4.6	1.09	0.55	8.6	7.9	<0.1	–	–	408	–
13	2.9	F	T	S	6.7	–	–	34.0	4.8	1.51	0.77	–	–	0.2	–	–	146	–
14	5.1	F	T	S	6.1	–	–	31.8	4.5	1.63	0.80	–	–	1.2	–	–	43	–
15	2.9	F	T	S	4.4	–	–	33.0	4.8	2.27	1.15	7.0	7.2	<0.1	–	–	192	–
16	3.1	F	T	S	10.2	–	–	24.0	4.6	0.73	0.49	7.1	7.0	0.5	–	–	79	–
17	2.9	F	T	S	8.9	–	–	33.0	4.8	1.13	0.58	7.1	7.1	0.3	–	–	85	–
18	2.9	F1,F	T	S	10.4	–	–	33.5	4.8	1.0	0.5	7.0	7.2	<0.1	–	–	52	–
19	2.8	F1,F	T	S	9.7	–	–	53.1	9.3	1.69	1.04	7.7	7.5	<0.1	–	–	79	–
20	3.0	C1,F	T	S	7.8	–	–	~32.	4.6	~1.	~0.5	7.2	7.1	<0.1	–	–	303	–
21	3.0	F	T	S	10.3	4.7	–	32.4	4.6	0.97	0.48	8.3	7.8	1.5	0.01	–	64	–
22[4]	3.0	F	T	P	8.6	–	–	43.7	4.6	1.6	0.58	7.8	7.6	<0.1	–	–	49	–
23	3.0	F	T	P	7.7	4.1	–	24.8	4.6	0.98	0.64	8.2	7.9	0.2	0.04	–	87	–
24	3.0	F	T	P	7.8	–	7.4	15.6	4.6	0.62	0.64	8.0	7.7	0.4	–	1.8	123	–
25	2.9	F	T	S	8.9	–	–	23.3	4.8	0.81	0.58	8.1	7.8	0.2	–	–	100	–
26[5]	2.9	F	T	S	8.7	–	–	20.7	4.8	0.74	0.60	8.1	8.0	<0.1	–	–	102	–
27[6]	2.9	F	T	S	8.5	–	–	21.6	4.8	0.80	0.61	8.0	7.9	<0.1	–	–	126	–
28[7]	3.0	F	T	S	7.9	–	–	18.8	4.6	0.74	0.63	8.0	7.8	<0.005	–	–	189	–
29[7]	3.0	F	T	S	8.0	–	–	21.9	4.6	0.85	0.63	8.0	–	<0.1	–	–	212	–
30	3.0	F	T	S	7.7	–	–	36.6	4.8	1.46	0.67	8.1	–	<0.1	–	–	163	–
31[8]	2.9	F	T	S	8.0	–	–	~22.	~4.6	0.84	0.63	8.0	–	–	–	–	243	–
32	2.9	F	T	P	8.7	–	–	23.	4.8	0.82	0.6	8.0	–	<0.1	–	–	213	4.1
33	3.1	F	T	P	23.6	–	–	39.6	9.0	0.52	0.41	8.0	–	1.4	–	–	61	2.4
34	3.3	F	T	P	21.5	–	–	69.6	4.2	0.98	0.21	8.0	7.6	0.96	–	–	61	3.1
35	3.4	F	T	P	20.9	–	–	64.3	5.0	0.94	0.26	8.0	7.6	<0.05	–	–	60	2.6
36	3.3	F	T	P	19.1	–	–	42.2	9.3	0.68	0.52	8.0	7.9	0.08	–	–	82	2.3
37	3.1	F	T	P	21.6	–	–	30.7	14.4	0.44	0.71	8.0	8.1	<0.05	–	–	88	2.3
38	3.1	F	D	P	20.6	–	–	40.8	9.9	0.61	0.52	8.0	8.5	<0.05	–	–	269	7.1
39	3.0	F	D	P	54.5	–	–	66.6	34.7	0.37	0.69	8.1	8.0	<0.05	–	–	94	4.0
40	3.2	F	T	C	38.8	11.5	8.9	61.4	43.0	0.48	1.19	8.5	7.7	<0.1	<0.05	0.33	32	1.4
41	3.2	F	D	C	48.6	15.1	8.8	62.8	42.4	0.39	0.94	8.0	8.1	1.2	<0.05	0.14	65	3.0
42	3.4	F	D	C	50.2	14.8	8.7	54.7	42.4	0.33	0.91	7.9	7.8	<0.01	<0.05	<0.01	57	2.2
43[9]	3.3	C1,F	T	C	47.1	13.7	8.5	54.7	42.4	0.36	0.97	8.0	7.1	1.8	<0.05	0.22	>195	>1.3
44	3.4	F	D	C	19.5	7.2	4.4	45.4	9.4	0.72	0.52	8.0	8.1	<0.1	<0.05	0.22	139	3.6
45	3.3	F	T	P	11.1	11.7	4.8	48.8	3.8	1.34	0.38	7.5	7.8	0.4	0.11	4.1	83	2.5
46	3.3	F	D	P	10.1	11.5	4.6	51.0	3.8	1.55	0.41	7.7	7.9	0.25	0.10	4.9	340	8.5

Symbols:

F – Filter used	T – Tempe Tap Water	S – Synthetic (from laboratory chemical(s))
F1 – Flocculator used	D – Distilled Water	P – Plating Baths (from WAFB)
C1 – Clarifier used		C – Plating Baths with Cd (as CdO)

Notes:

1. Filter consisted of 7 feet of medium coarse sand – effective size 0.71 mm and uniformity coefficient of 1.8.
2. Filter changed to 16 inches of Monterey sand; 12 inches of river sand and 12 inches of #20 silica sand.
3. Treatment chemicals introduced at outlet side of waste pump.
4. Before Run 22, iron doses are estimates. Lower doses probable due to oxidation by atmospheric oxygen of the ferrous ion to ferric and percipitation as ferric hydroxide.
5. Filter changed to 3 inches of coarse (1.1 mm), 2 feet of medium (0.7 mm) and 1 foot of fine (0.45 mm) sand.
6. Filter modified by the additions of 16 inches of medium sand.
7. Filter modified by the addition of 1 foot of medium sand.
8. Filter modified by the addition of 8 inches of fine sand.
9. Clarifier used; run shut down before filter breakthrough.

detailed discussion below.

1. Pilot Plant Starting (Runs 3-17).

Results from early pilot plant operations were erratic. The filter was initially loaded with 7 feet of Monterey sand (effective grain size of 1.10 mm) which proved to be too coarse for effective removal of the precipitated metal hydroxides produced by the treatment process. Starting with Run 3, this coarse media was replaced by 7 feet of sieved Salt River sand (0.71 mm effective grain size). This new media was more effective in removing chromium, but failed to produce run times that were acceptable (Runs 3 and 4).

Reduction of the flow rate to 3 gpm (filter loading of 3 gpm per square foot), starting with Run 5, improved run times. However, these run times were considerably less than those experienced with the smaller filter column previously tested. Use of the flocculator did not significantly improve filter performance. With Run 9, a shorter filter was prepared using a mixture of sands (Figure 45) to evaluate the relative effectiveness of the three sand sizes described in Table 6. A reduced run time is noted due to the reduced height of the filter.

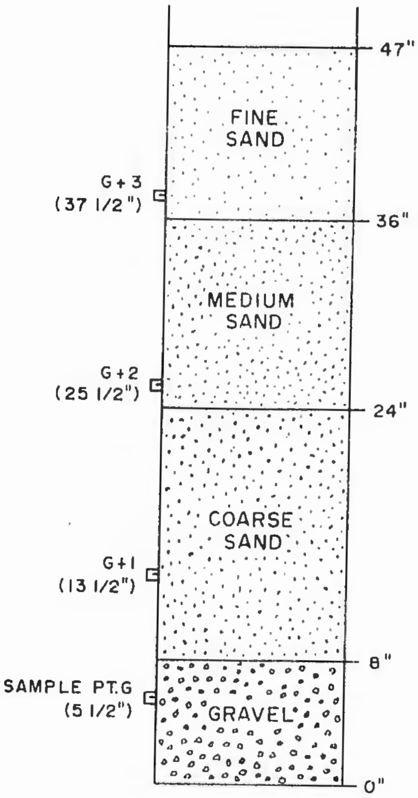

Figure 45. Filter Composition for Runs 9-25.

It was postulated that the poor performance of the process was caused by floc breakup (and subsequent loading of only the finer sand) in the process pump. Starting with Run 11, the injection point for treatment chemicals was shifted to a point following the process pump. This improved removal efficiency and more than doubled the time to breakthrough. Use of the clarifier (Run 12) produced another significant increase in run time.

Starting with Run 12, samples were taken from sampling ports (Figure 45) located at 1-foot intervals through the depth of the experimental mixture of sands. Using a long hypodermic needle and syringe, samples were collected from points in the sand approximately 1 inch away from the wall of the filter. Results for Run 12 are illustrated in Figure 46. It is apparent that the chromium rapidly penetrated the gravel and coarse sand to G+1 and that the coarse sand between G+1 and G+2 had little additional capacity for chromium removal. The medium sand removed the bulk of the chromium, as demonstrated by the longer time needed to reach G+3. This fine material, however, had a low capacity for solids storage before breakthrough. The medium sand continued to store more solids (as measured by the difference in concentrations at G+3 and G+2) after breakthrough than were retained in the fine sand.

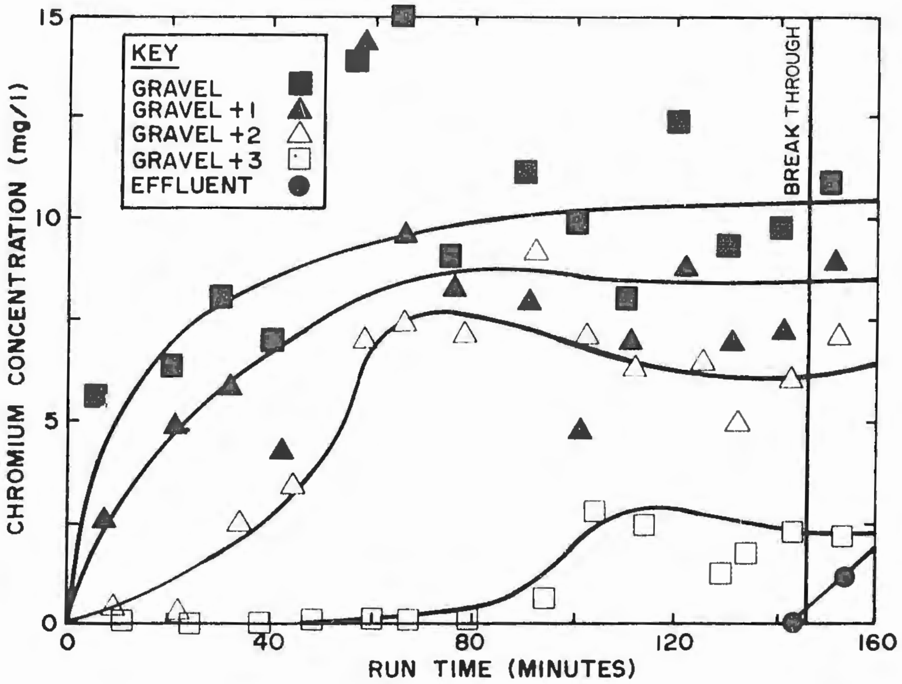

Figure 46. Chromium Breakthrough Curves for Run 13.

Use of the clarifier in Run 12 reduced the loading on the filter and extended the run time proportionally (Figure 47). Sample Point 3 is located between the clarifier and the filter. The clarifier was approximately 70 percent efficient in removing the chromium. The removal characteristics of the filter were unaffected by the use of the clarifier, with the medium sand (G+2 to G+3) removing the bulk of the chromium. Further testing was performed, using this configuration of filter media, to see how varied operating conditions affected the removal efficiencies of the different sands.

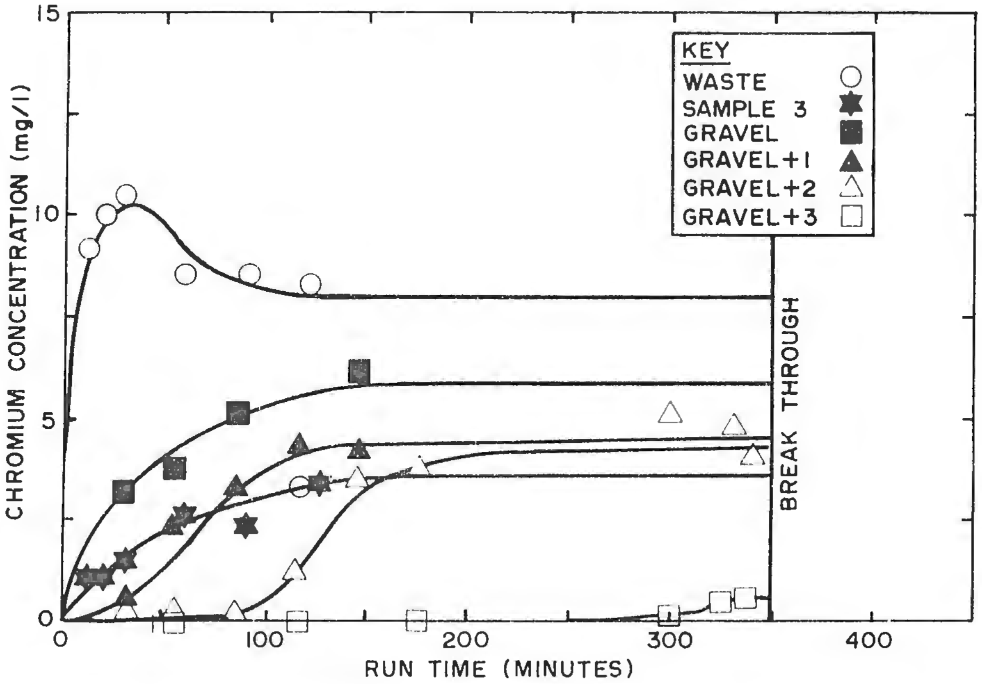

Figure 47. Chromium Breakthrough Curves for Run 12.

Increasing the loading rate on the filter to 5.1 gallons per minute in Run 14 greatly reduced the time to breakthrough (Figure 48), although it had little

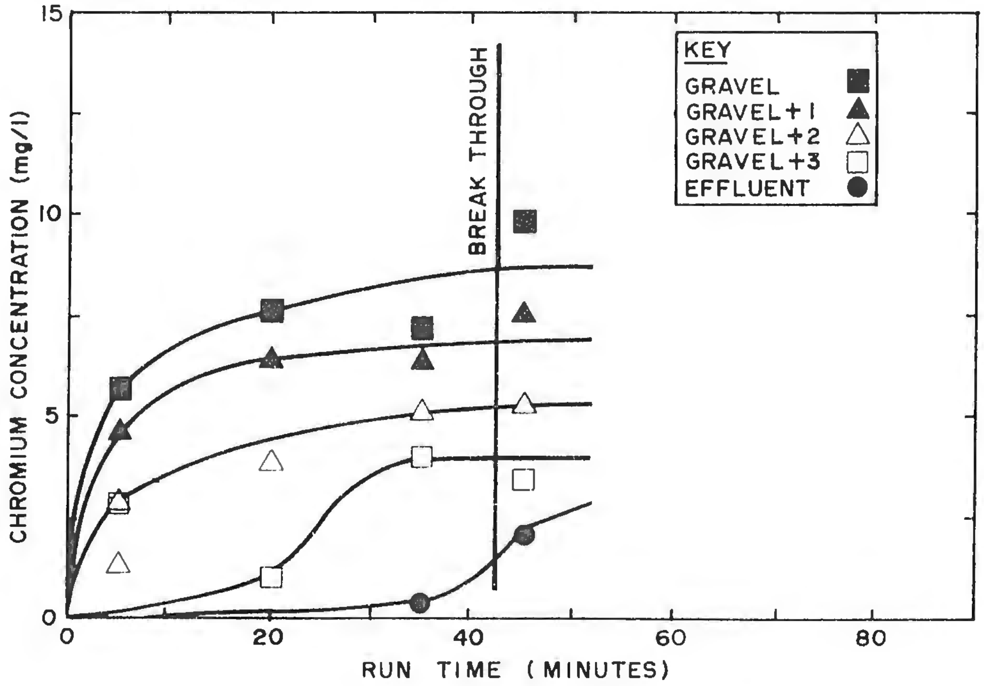

Figure 48. Chromium Breakthrough Curves for Run 14.

effect on the region of the filter that removed the bulk of the chromium.

Varying the chromium concentration of the waste in Runs 15 through 17 (Figures 49 through 51) resulted in a change in run times inversely

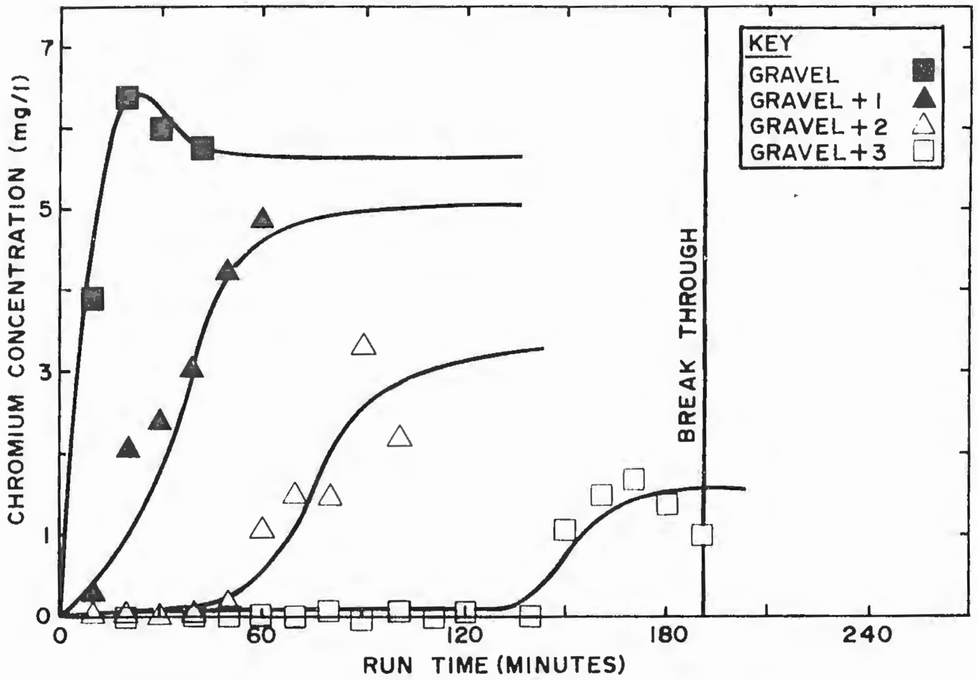

Figure 49. Chromium Breakthrough Curves for Run 15.

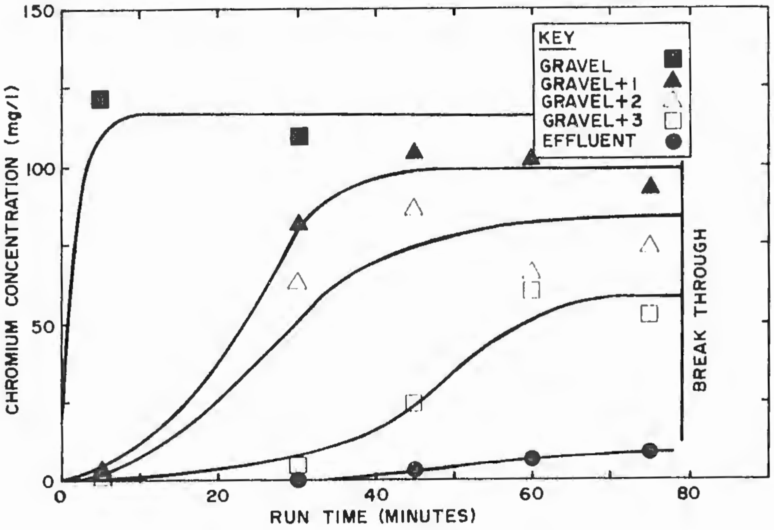

Figure 50. Chromium Breakthrough Curves for Run 16.

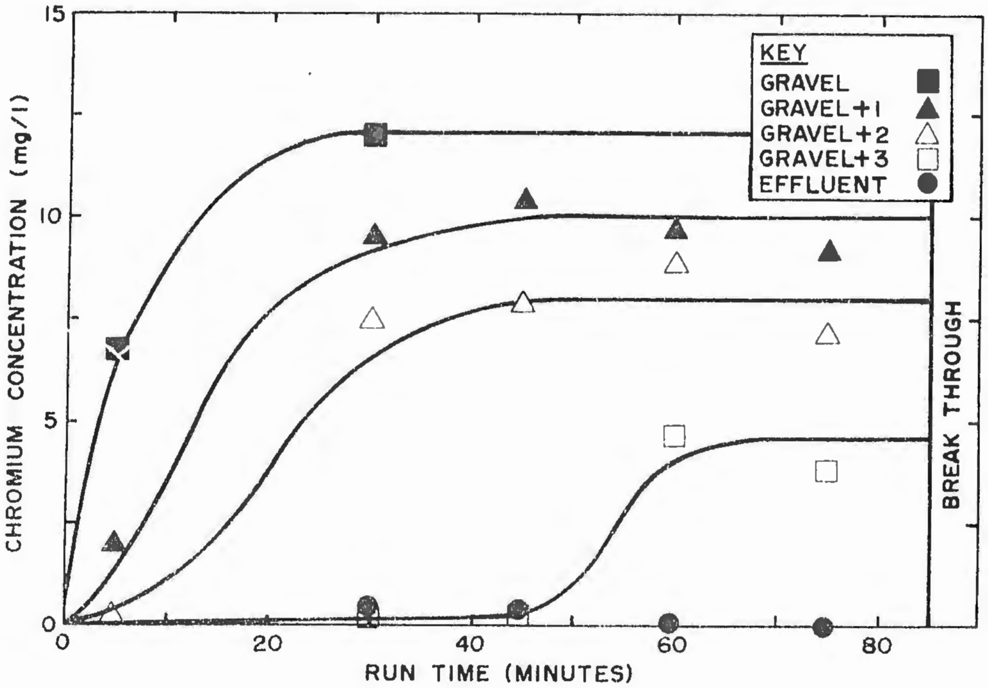

Figure 51. Chromium Breakthrough Curves for Run 17.

proportional to the concentration of chromium treated. The relative effectiveness of the different layers of filter media was unaffected by these different concentrations, with the bulk of the removal occurring in the medium coarse Salt River sand.

Problems resulted in these runs from degradation of treatment and waste synthesis chemicals. A saturated potassium dichromate solution, used for waste synthesis, degraded with storage, resulting in decreasing influent waste concentrations. The ferrous sulfate and sodium sulfide stock solutions likewise degraded with storage, probably due to oxidation by atmospheric oxygen. Starting with Run 22 these solutions were prepared fresh prior to each day's runs. Also, the concentration of iron added was measured, starting with Run 22, rather than calculated.

2. Filter Media Optimization (Runs 26-31)

The experiments with a mixture filter media sizes led to a number of conclusions. The medium Salt River sand was most effective. The fine number 20 silica sand was effective in polishing the material that penetrated the coarser sand below, although this finer sand has little capacity for solids storage. The coarse sand at the bottom provided support for the media above it and aided in flow distribution and particle flocculation but had little capacity for solids storage.

The filter was therefore modified before Run 26 to increase the proportion of medium Salt River sand. The new media consisted of 3 inches of Monterey sand, (1.1 mm), 2 feet of Salt River sand (0.7 mm) and 1 foot of number 20 silica sand (0.45 mm). The resulting breakthrough of chromium (Figure 52)

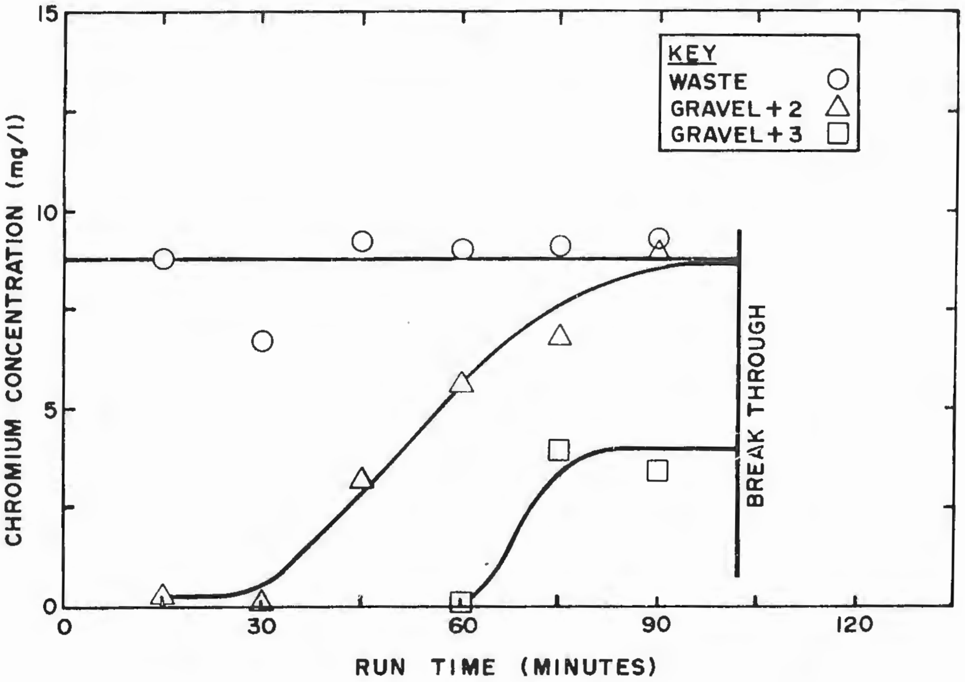

Figure 52. Chromium Breakthrough Curves for Run 26.

shows a more even distribution of chromium solids in the filter and an increase in run time.

The filter was modified by the addition of 16 inches of Salt River sand before Run 27. The resulting chromium breakthrough curves (Figure 53) were

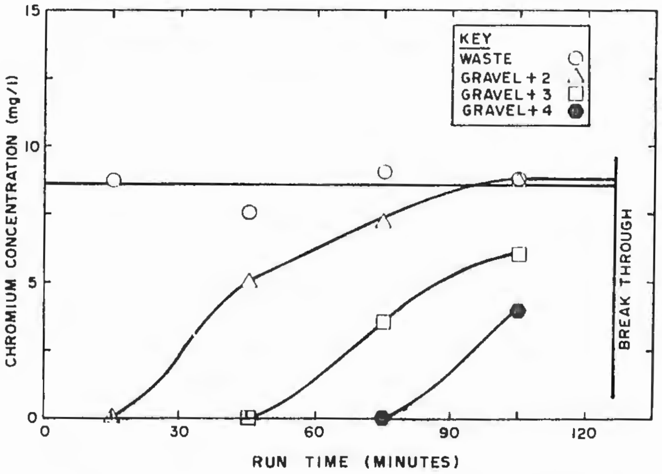

Figure 53. Chromium Breakthrough Curves for Run 27.

essentially identical to Run 26 below Gravel +3. An increased run time was the result of additional storage provided between Gravel +3 and Gravel +4. Increasing the depth of Salt River sand further improved the run times, with chromium removal spread throughout the filter (Figures 54 and 55). An over-

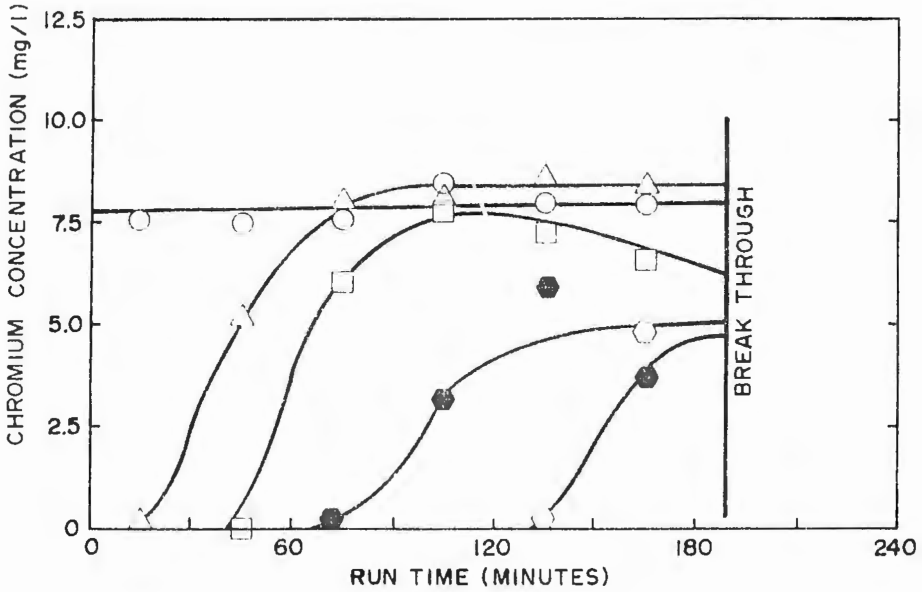

Figure 54. Chromium Breakthrough Curves for Run 28.

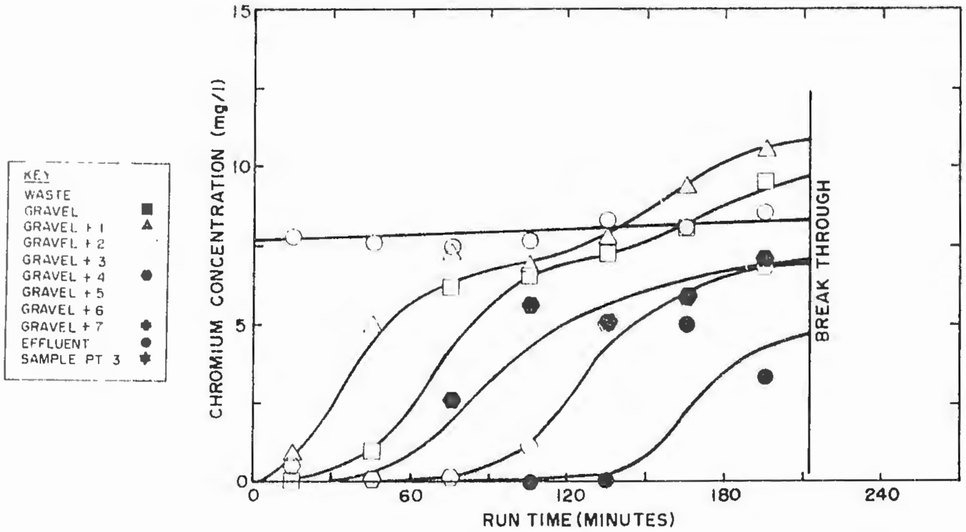

Figure 55. Chromium Breakthrough Curves for Run 29.

dose of $FeSO_4$ was used in Run 30 to determine if the resulting larger floc would extend run time. The increased solids productions, however, resulted in a decreased run time.

The relationship between filter run times and filter sand depth is shown as Figure 56. It is proposed that increasing the depth of filtration media improves run times by two mechanisms. First, increased depth provides additional storage space for solids, with breakthrough occurring at a given depth in the media when all potential sites for storage are filled. This appears to be the mechanism for breakthrough under the operating conditions used in Runs 25 through 31, as indicated by the linearity of Figure 56. A second mechanism occurs when head loss through the filter exceeds the submerged weight of the filter media and breakthrough results from lifting of the bed. Run times could be increased in this case by increasing depth and weight of media. This appears not to be the mechanism involved here, however.

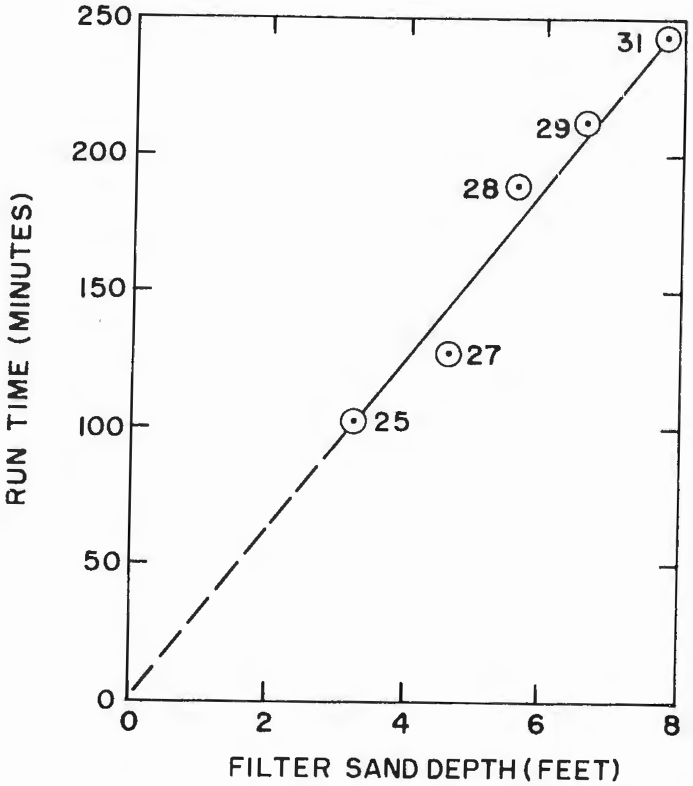

Figure 56. Effect of Media Depth on Filter Run Times.

3. Treatment of Chromium Plating Wastes (Runs 32-39)

Plating baths were used for waste synthesis and head losses were measured, starting with Run 32. No significant differences were noted in treatment of wastes made from plating baths and those made from laboratory chemicals. Figure 57 shows the chromium breakthrough curves and Figure 58 the head loss curves for Run 32. As the chromium broke through a particular layer of the filter (Figure 57), the head loss began to increase in that layer due to plugging of the pores above. At breakthrough, the head losses were distributed fairly evenly through the bed. The coarse material at the bottom was capable of storing material in its larger pores without causing appreciable head loss. However, these large pores were not efficient at retaining the solids in the

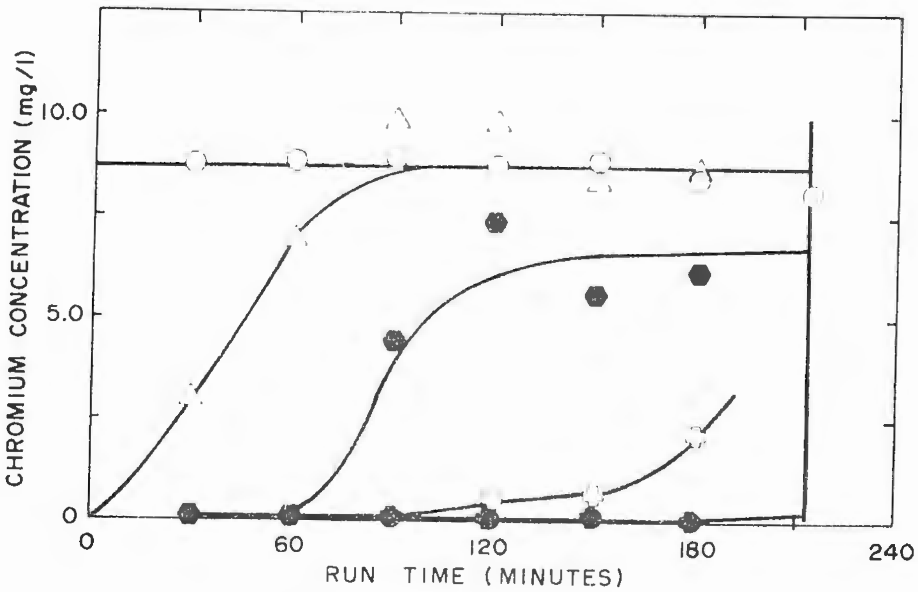

Figure 57. Chromium Breakthrough Curves for Run 32.

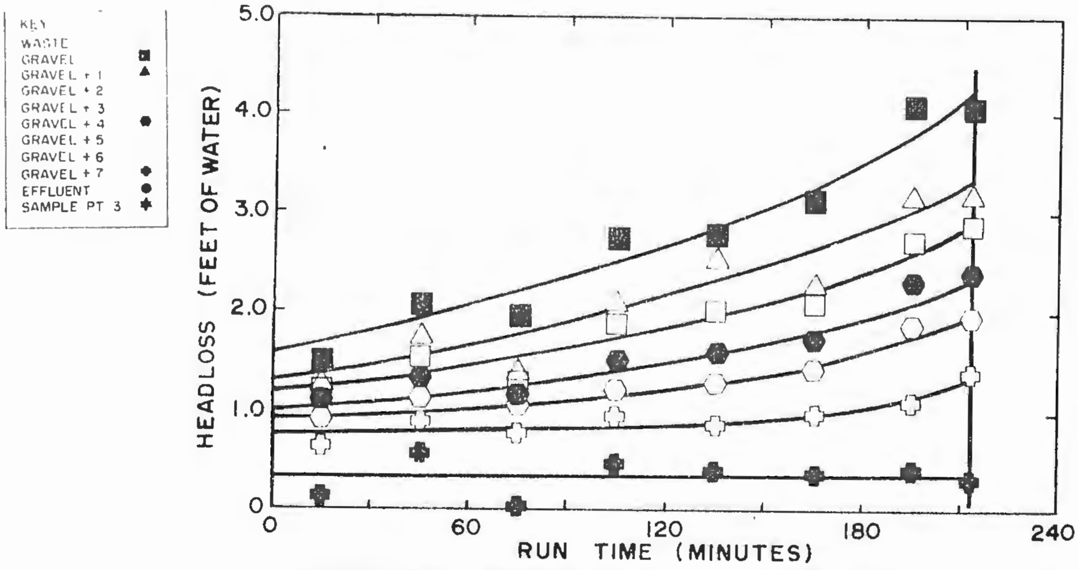

Figure 58. Head Loss Curves for Run 32.

increased turbulence resulting from pore plugging. The medium sand was more effective at both providing storage without appreciable head loss and solids retention in the diminishing pores. The fine sands at the top provided little storage volume in the sand's small pores before this constriction resulted in appreciable head loss and breakthrough, usually the result of lifting and fluidizing these fines.

Increasing the chromium concentration in the waste to 23.6 mg/l resulted in a proportionate decrease in run time, but had no effect on the relative removal efficiencies of the different filter layers (Figure 59). The head loss

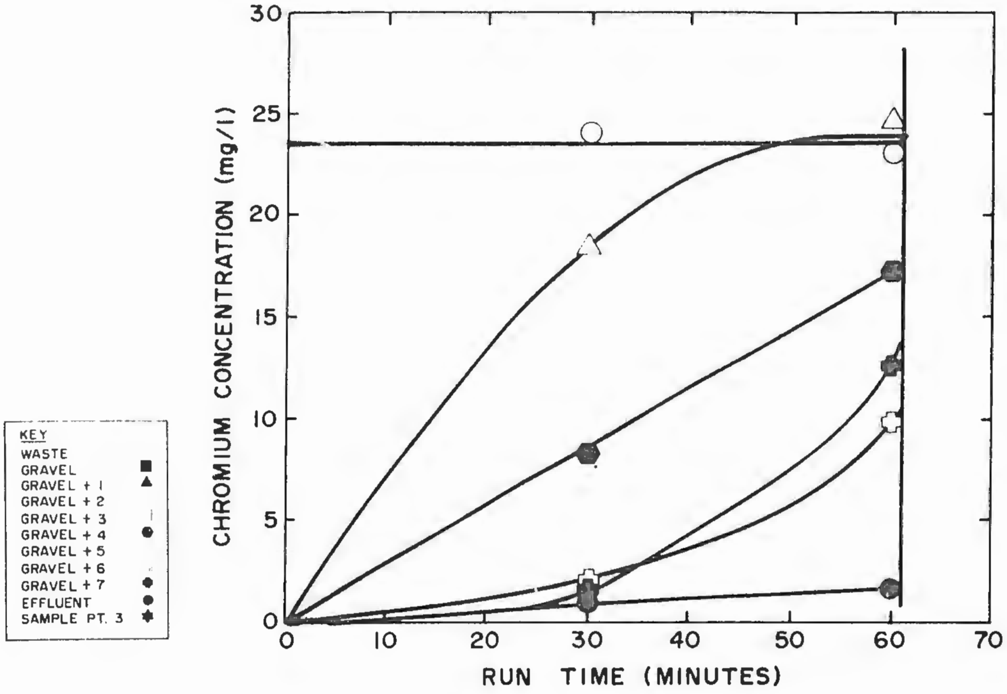

Figure 59. Chromium Breakthrough Curves for Run 33.

trends (Figure 60) are similar to those in Run 33, except that final head loss is reduced.

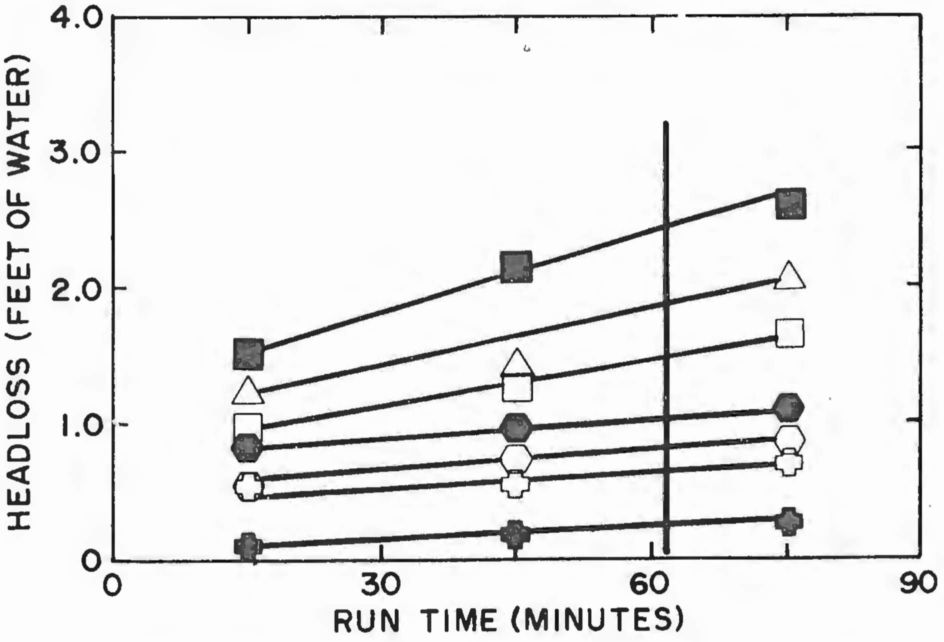

Figure 60. Head Loss Curves for Run 33.

a. Effects of Varying Ferrous Iron and Sulfide Doses (Runs 34-37)

Tests were performed to evaluate removal of higher chromium (20 mg/1) concentrations with varying $FeSO_4$ and Na_2S doses. Since Na_2S has a much lower equivalent weight (39) than $FeSO_4$ (152) and produces approximately 1/7 of the solids residue, one would like to maximize the sulfide dose for equivalent treatment. Ferrous sulfate is required as a catalyst and is desirable to control sulfide odors by precipitation of excess sulfide. Increasing sulfide replacement of iron (Figures 61 through 64) resulted in increased run times.

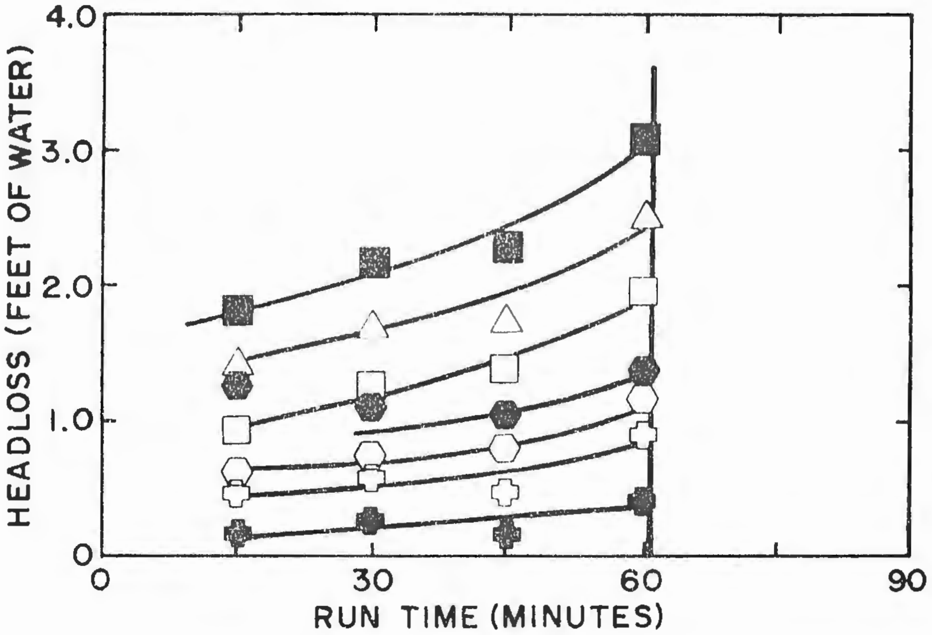

Figure 61. Head Loss Curves for Run 34.

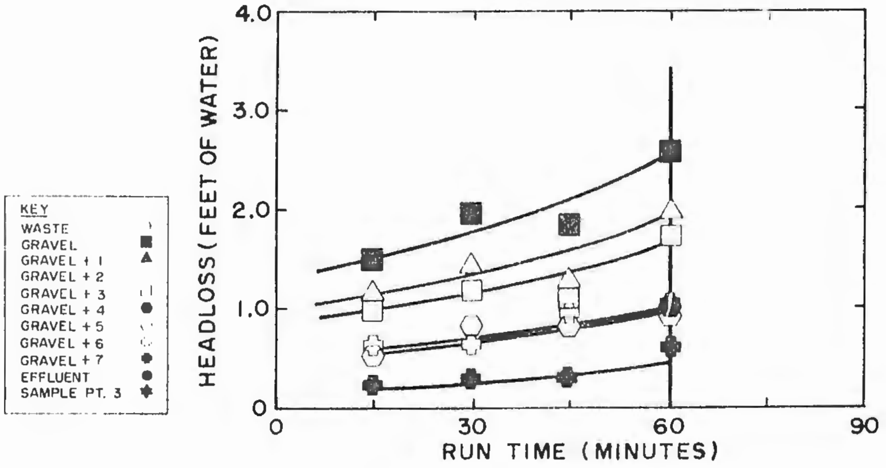

Figure 62. Head Loss Curves for Run 35.

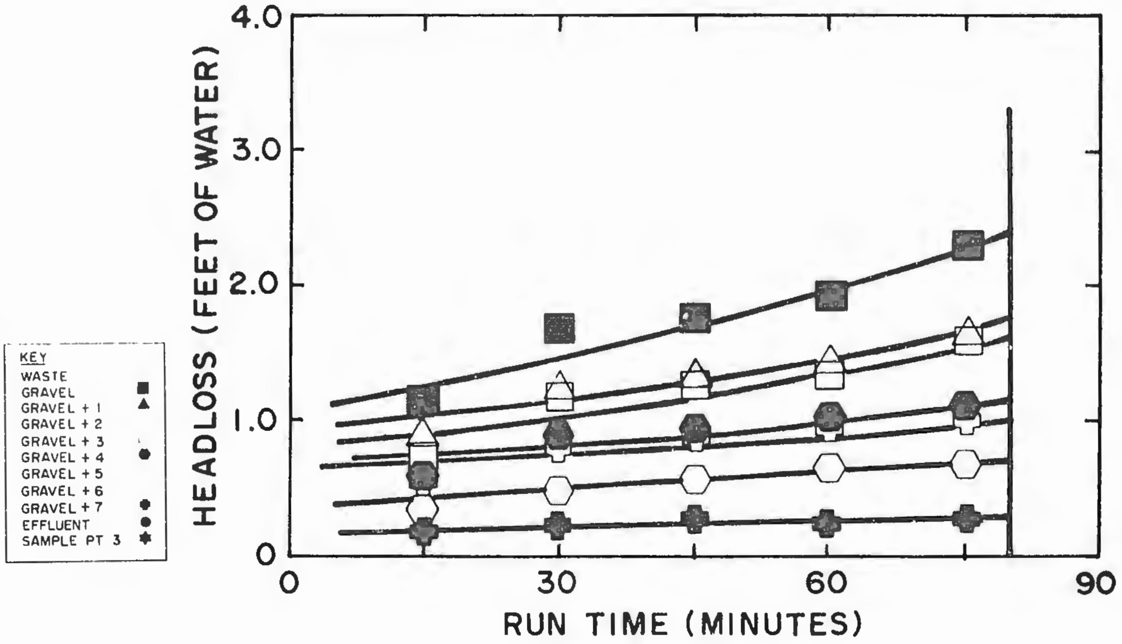

Figure 63. Head Loss Curves for Run 36.

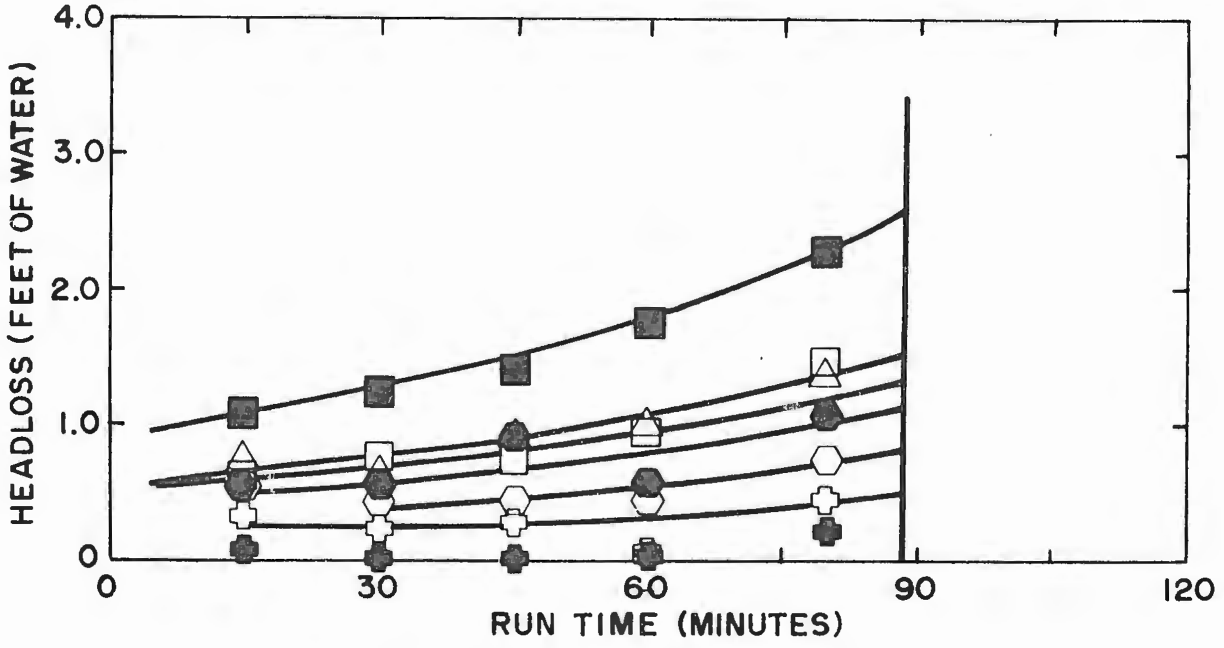

Figure 64. Head Loss Curves for Run 37.

Decreased head losses indicated that less solids were produced by sulfide than iron. However, sulfide precipitation resulted in a finer solid that more easily penetrated the filter. Final head losses were lower for the high-sulfide doses. A sulfide odor was noted.

b. Effects of Distilled Water (Runs 38 and 39)

Treatment of a waste in distilled water (Figure 65) resulted in a significant increase in run time (269 minutes as compared to 82 minutes for a waste in hard tap water). Head losses at breakthrough were proportionally increased, indicating that a similar solids production occurred as in tap water, but that the solids were more easily retained in the filter. Pores were visibly more packed with solids. A stronger floc is apparently produced in distilled water than in tap water. This opposed the conventional wisdom that hardness improves flocculation. Breakthrough was by bed uplift due to high head loss.

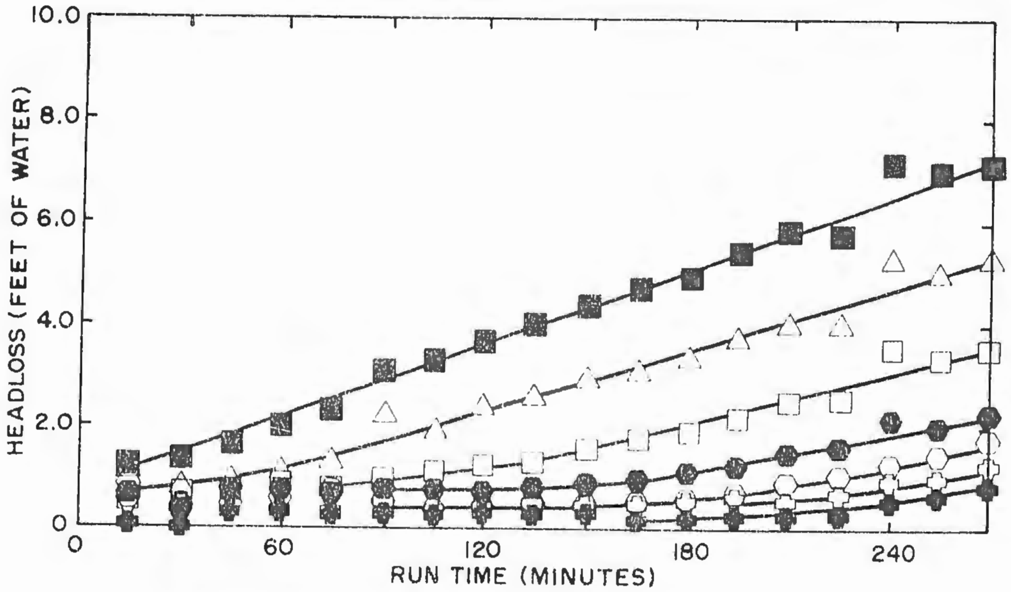

Figure 65. Head Loss Curves for Run 38.

Increasing the chromium concentration to 54.5 mg/l resulted in a portional decrease in run time (Figure 66). A lower head loss at breakthrough was noted

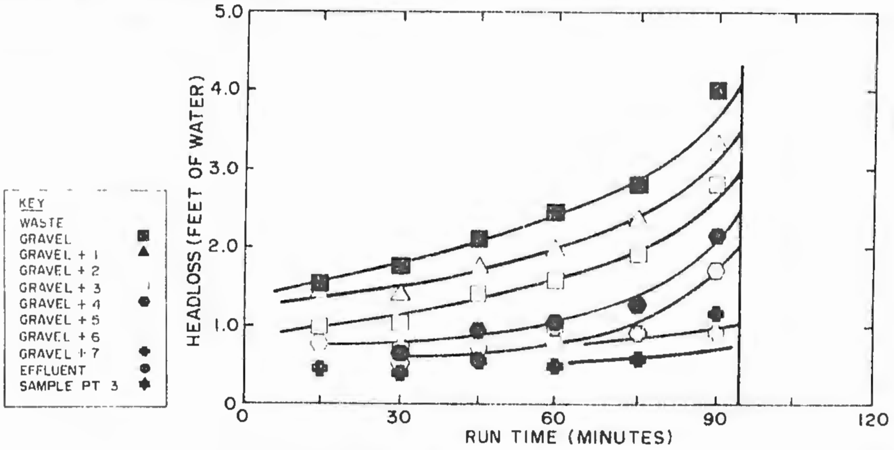

Figure 66. Head Loss Curves for Run 39.

in this run, due to the higher proportion of sulfide used for chromium reduction.

Figure 67 was prepared to relate run time to solids production (as measured by the sum of chromium removed and iron added). Run times decrease in inverse proportion to increased metal concentrations. It is evident that it would be infeasible to treat high concentrations of chromium in a hard water by direct filtration. Using high sulfide - low iron doses would be advisable. Adding clarification (Run 43) greatly increased the run time. High concentrations of chromium were efficiently treated where the waste was in distilled water (Runs 38 and 39).

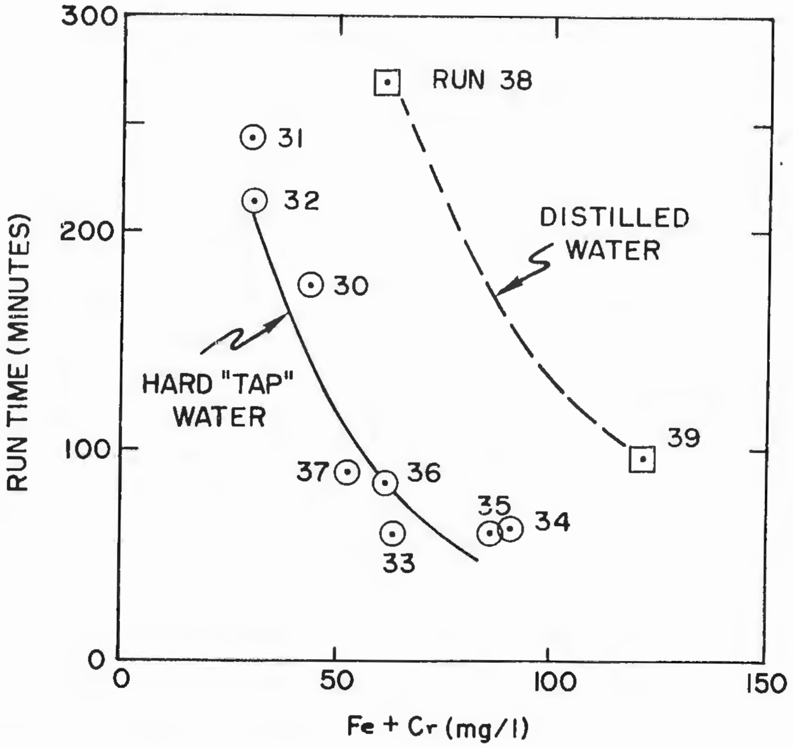

Figure 67. Effects of Metal Concentrations on Run Times.

4. Treatment of Mixed-Metal Wastes (Runs 21, 23, 24, 40-46)

Problems had been encountered in bath studies with removal of nickel from a mixture of metal plating wastes. Pilot plant treatment of wastes consisting of mixtures of metals was, therefore, investigated. In Run 21 a mixture of 10.3 mg/l of chromium and 4.7 mg/l of cadmium, prepared from reagent grade chemicals in tap water was treated. Good cadmium removal was noted (Table 10), although chromium removal was incomplete. This run was performed prior to the establishment of a policy of preparing treatment reagents fresh daily. The lower concentration of active chemical actually added, as well as competition for sulfide between the two metals, removed may explain this reduced treatment effectiveness. Run 21 was performed using a mixed filter media described in

Figure 45. Figure 68 shows that the bulk of the chromium was removed in the

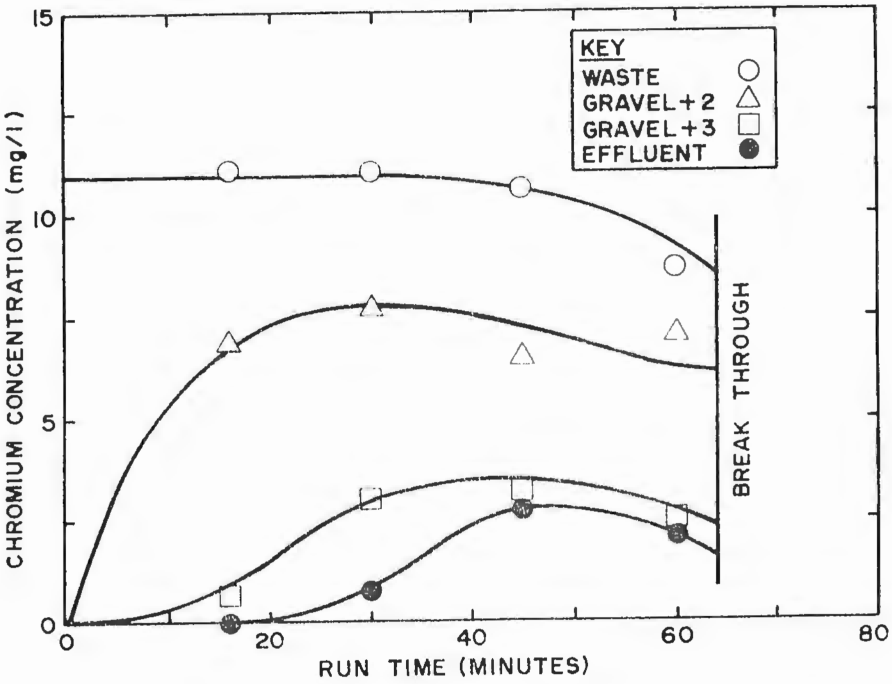

Figure 68. Chromium Breakthrough Curves for Run 21.

medium coarse Salt River sand, showing that the particle removal characteristics are similar to previous runs where chromium alone was treated. Removal of cadmium (Figure 69) closely resembles removal of chromium,

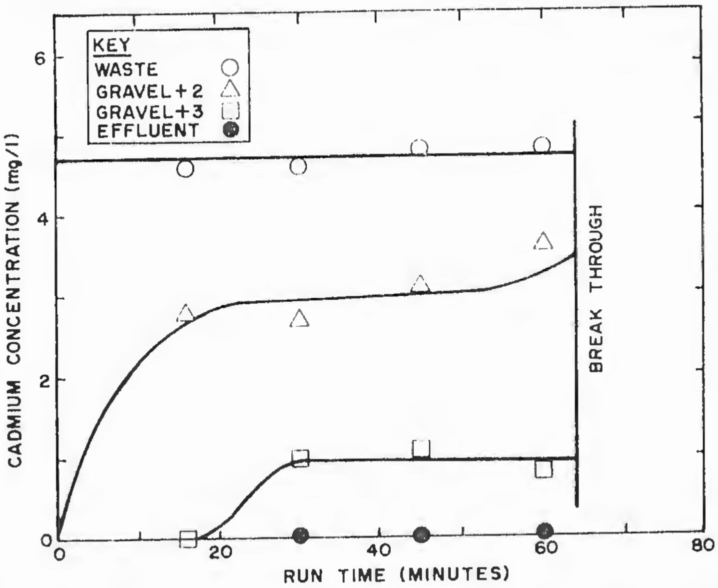

Figure 69. Cadmium Breakthrough Curves for Run 21.

indicating that they are co-precipitated and removed together. The chromium in the effluent was observed to be soluble, due probably to underdosing of the chemicals.

After a policy of preparing reagents fresh daily was established, a similar run was performed,using a mixture of chromium and cadmium plating baths (Figure 70 and 71). Again, chromium and cadmium removals paralleled each

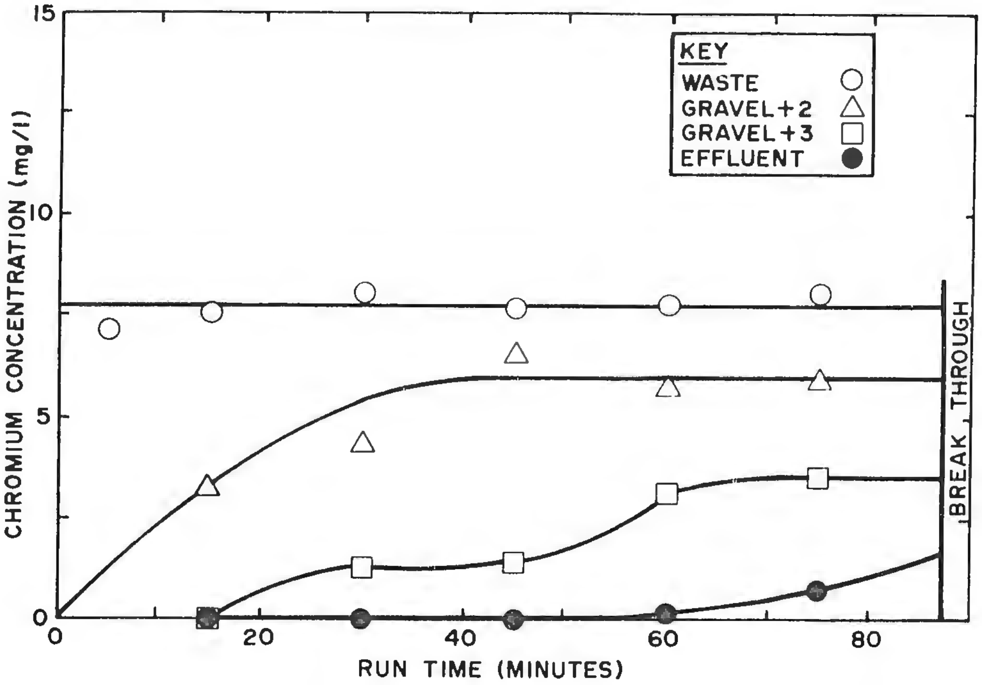

Figure 70. Chromium Breakthrough Curves for Run 23.

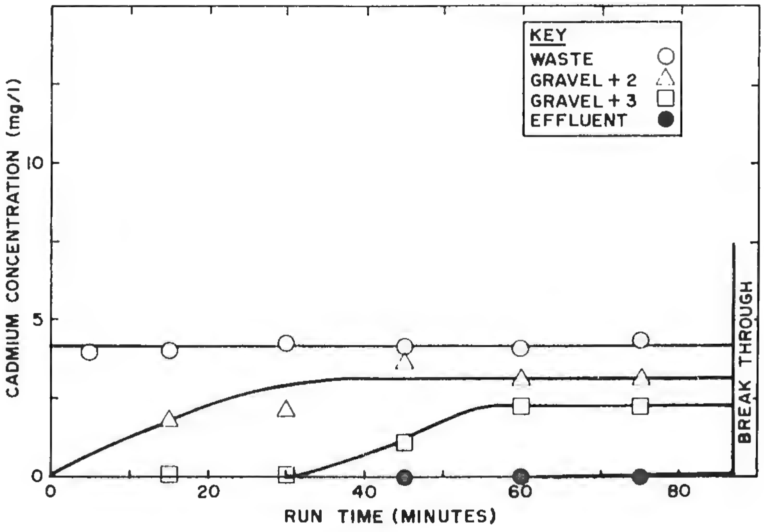

Figure 71. Cadmium Breakthrough Curves for Run 23.

other, with the medium coarse Salt River sand most effective in precipitate removal. Good chromium removal was accomplished, using fresh reagents. The cadmium concentration in the effluent was higher than in Run 21, probably due to the cyanide contribution from the cadmium bath. Run time was comparable to that encountered in the treatment of a synthetic chromium bath of equivalent concentration.

Treatment of a mixture of chromium and nickel plating baths (Run 24) in tap water had little effect on chromium removal (Figure 72), with a significant increase in run time noted. Nickel was quite soluble, with only about 75 percent of the nickel precipitated and removed (Figure 73). In batch studies

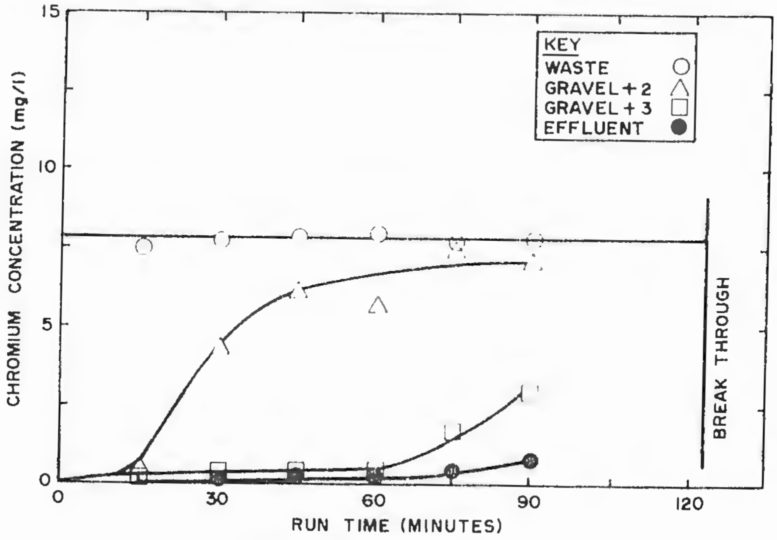

Figure 72. Chromium Breakthrough Curves for Run 24.

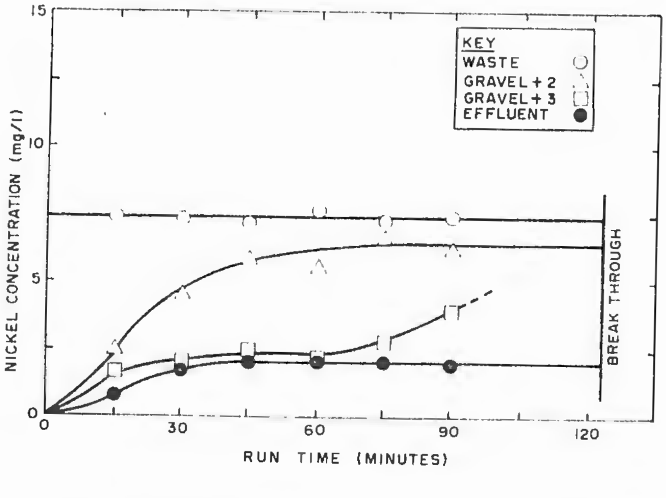

Figure 73. Nickel Breakthrough Curves for Run 24.

(Figures 38 and 39) it was difficult to remove nickel from solutions prepared from nickel plating baths. Treatment of nickel in a mixed-metal waste appears to improve nickel removal. Again the two breakthrough curves are seen to parallel each other, indicating that the two metals are co-precipitating.

Following development of the filter to its full height by the addition of Salt River sand, the pilot plant was tested using all three metals. Since batch studies confirmed that cyanide prevented removal of nickel from solution and since cadmium plating baths are commonly prepared with cyanide, a synthetic cadmium solution was used for runs with mixed metals. The solution was prepared using cadmium oxide, the salt commonly used in cadmium plating baths, without sodium cyanide. The chromium and nickel were from plating baths obtained from Williams Air Force Base.

In Run 40, high concentrations (38.8, 11.5 and 8.9 mg/l) of chromium, cadmium and nickel were treated in tap water. Good removal of all three metals was the result, although the run time was short (Figure 74). A high dose of sodium sulfide was used relative to ferrous iron, as recommended previously to reduce solids production. Breakthrough occurred at low head loss due to breakthrough of fine flocs, the result of high concentrations of sulfides.

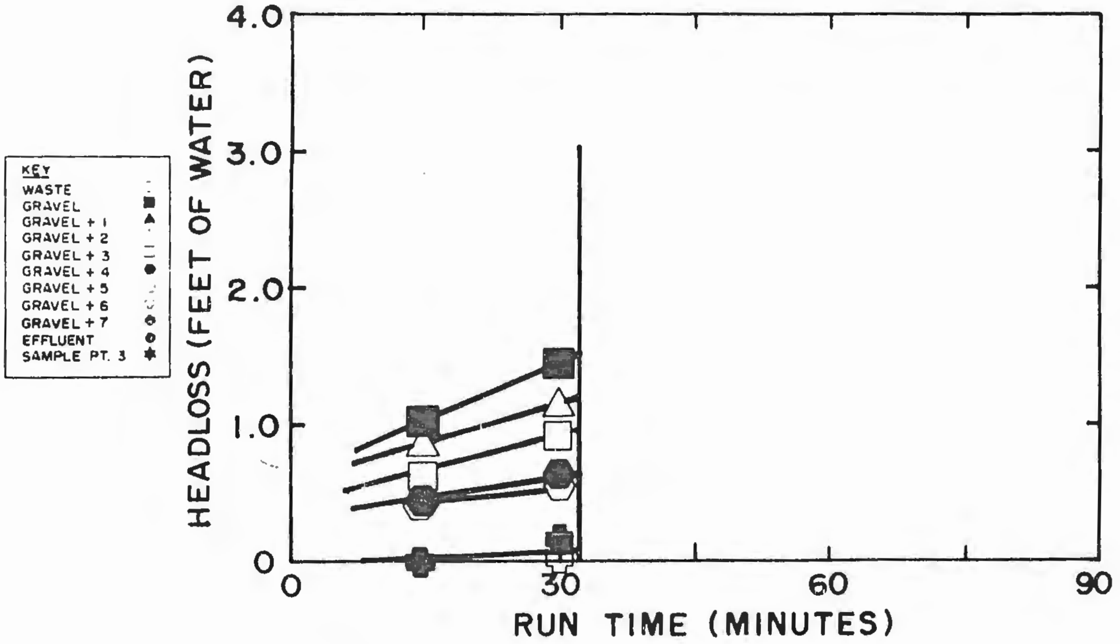

Figure 74. Head Loss Curves for Run 40.

Treatment of higher concentrations of these three metals in distilled water (Runs 41 and 42) resulted in a significant increase in run times and head loss at breakthrough (Figures 75 and 76) compared with runs performed in hard tap water.

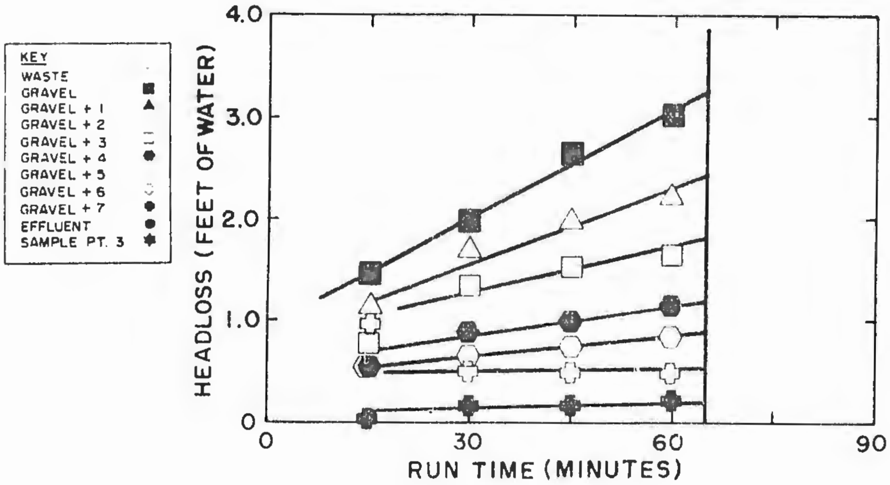

Figure 75. Head Loss Curves for Run 41.

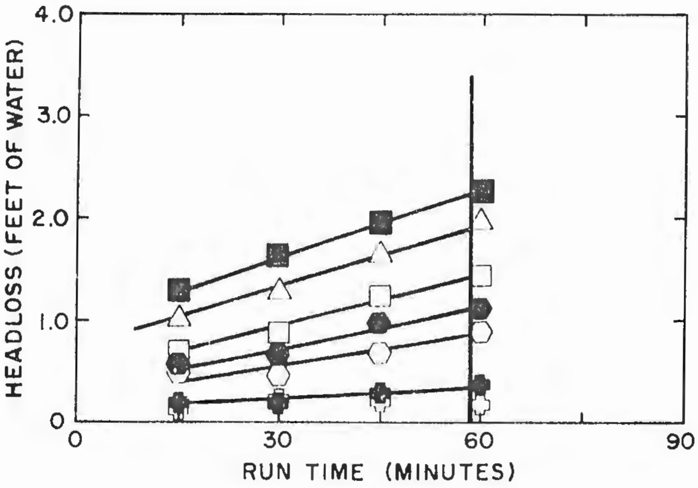

Figure 76. Head Loss Curves for Run 42.

A comparison of run times with mixed metal wastes (solid symbols) results in Figure 77 (an expansion of Figure 67). Treatment of mixed metals is similar to treatment of chromium alone. Good chromium removal resulted in good removal of cadmium and nickel. Run times for wastes in distilled water are significantly longer than for similar wastes in hard tap water.

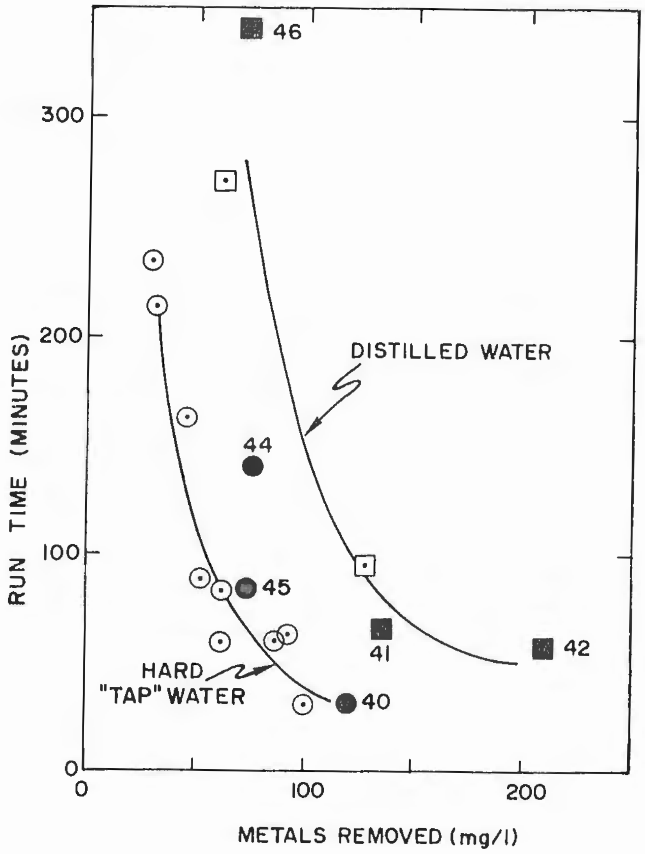

Figure 77. Effect of Metals Removed Concentrations on Run Times (Solid Figures are for Mixed Metal Wastes).

Treatment of wastes containing cyanide (Runs 45 and 46) resulted in reduced effectiveness of chromium and cadmium removal and no removal of nickel. High iron concentrations were used in an attempt to compete for the cyanide. Distilled water increased run times but did not improve nickel removal. These runs fall on the predictive curves prepared for non-cyanide-containing wastes (Figure 77), indicating that the solids phase was not interfered with by the cyanide. The cyanide apparently only increased the metals' solubility by complexation.

5. Use of the Flocculator and Clarifier (Runs 6, 12, 18-20, 43)

Use of the flocculator resulted in no improvement in the removal efficiency of the process. Visually, it was noted that the floc size leaving the flocculators was smaller than when the flocculators were bypassed. The chromium breakthrough curves for Runs 18 and 19 are included as Figure 78 and 79. No improvement in run times was noted, compared to operation without flocculation. It was noted that significant flocculation was taking place in the turbulent area at the inlet to the filters, precluding the need for separate flocculation.

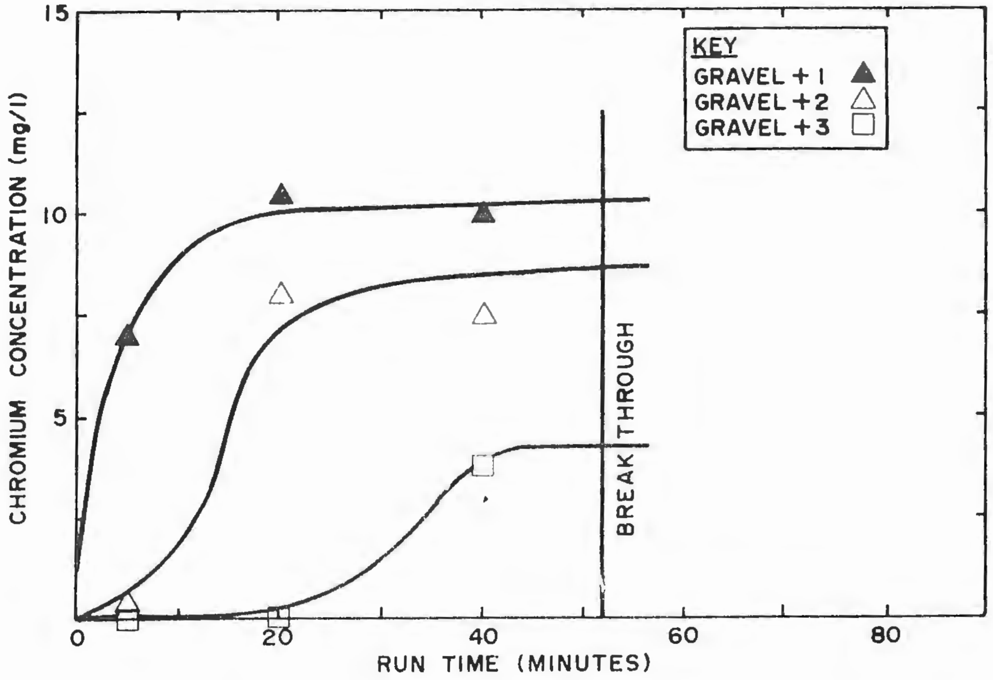

Figure 78. Chromium Breakthrough Curves for Run 18.

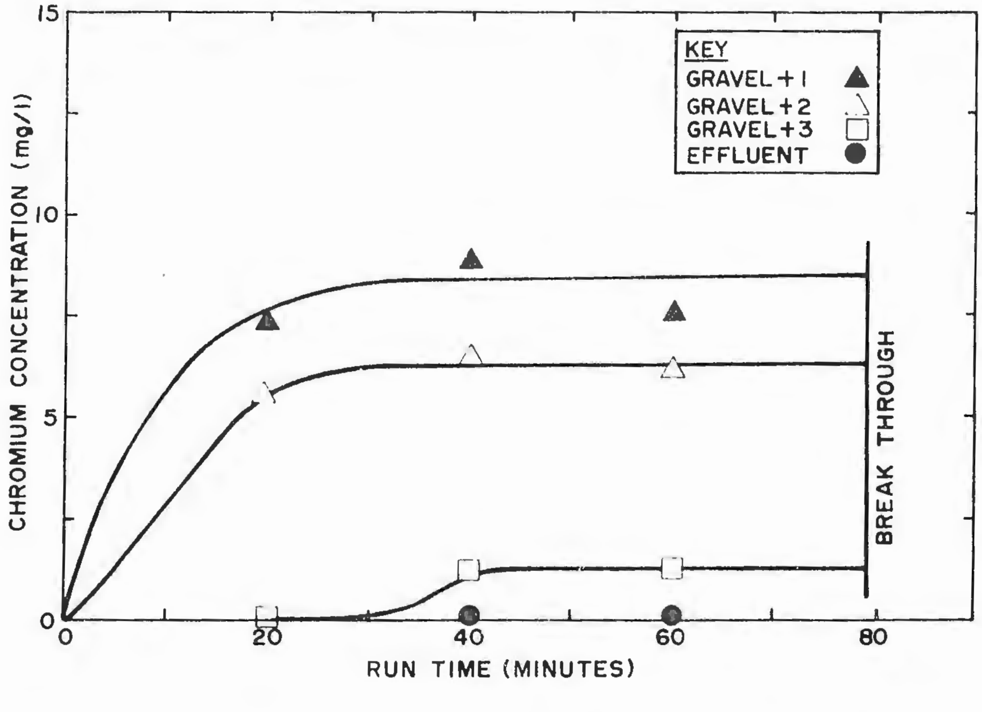

Figure 79. Chromium Breakthrough Curves for Run 19.

Use of the clarifier, on the other hand, significantly improved the effectiveness of the process. It was previously shown (Figure 47) that use of the clarifier in Run 12 greatly increased the run time by decreasing the solids loading on the filter. A similar improvement in run time was noted for Run 20 (Figure 80). Approximately two-thirds of the chromium was removed by the clarifier during this run. It was noted that the clarifier acted as a solids contact clarifier, providing intimate mixing of the freshly treated waste with a blanket of sludge descending along the plates, promoting particle growth. The bulk of the solids remaining after clarification was removed by the Salt River sand, located between G+2 and G+3. The particles remaining following clarification thus are seen to behave similarly to particles produced without clarification. Since the principal effect of the clarifier was to increase the run time by a factor of about 3 to 4, but not affect the apparent removal characteristics of the particles in the filter, most runs were made with just the filter to more rapidly assess the effects of operating parameters on filter performance.

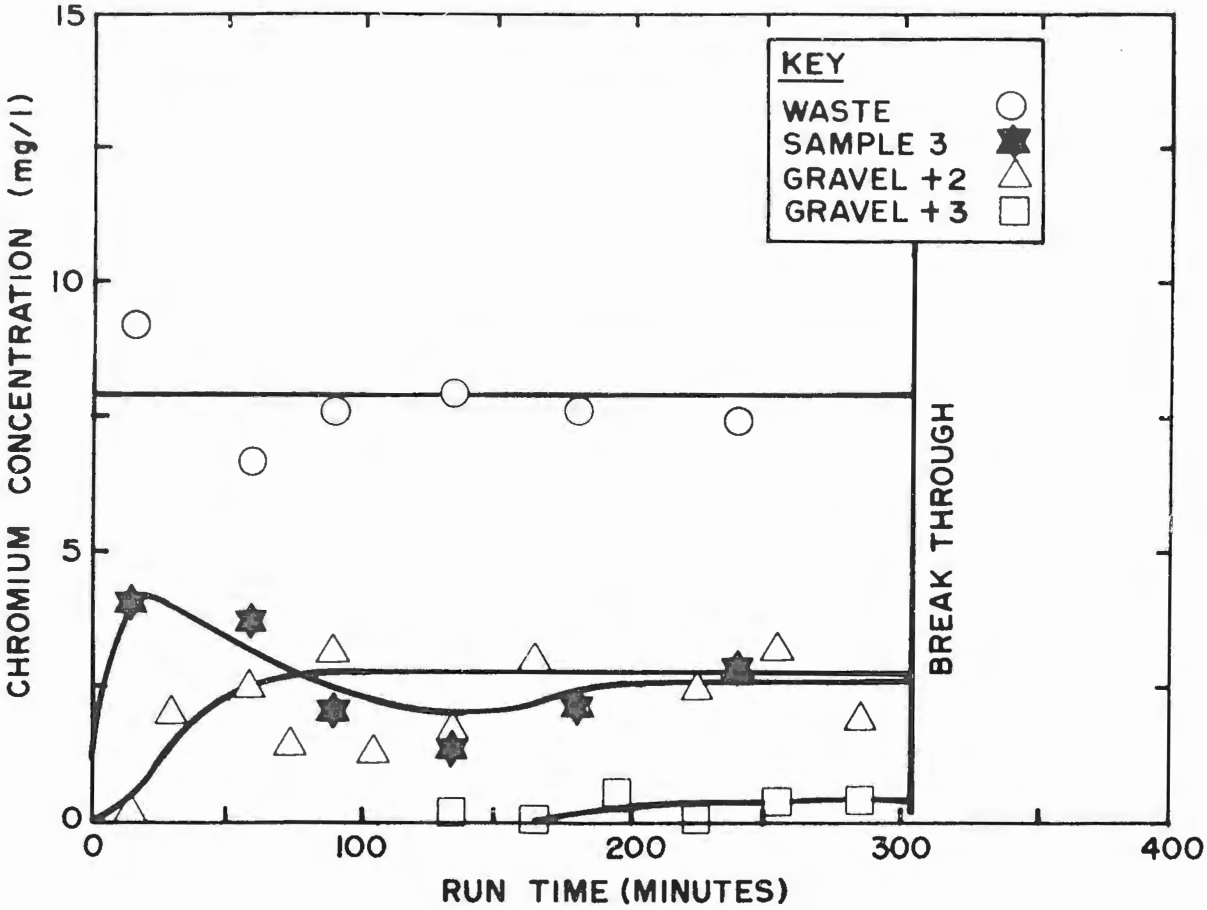

Figure 80. Chromium Breakthrough Curves for Run 20.

Run 43 was performed to assess the effect of clarification on removal of a mixed metal waste prepared with tap water. Figure 81 shows the head loss curves for this run. Breakthrough was not reached due to time limitations on the experiment.

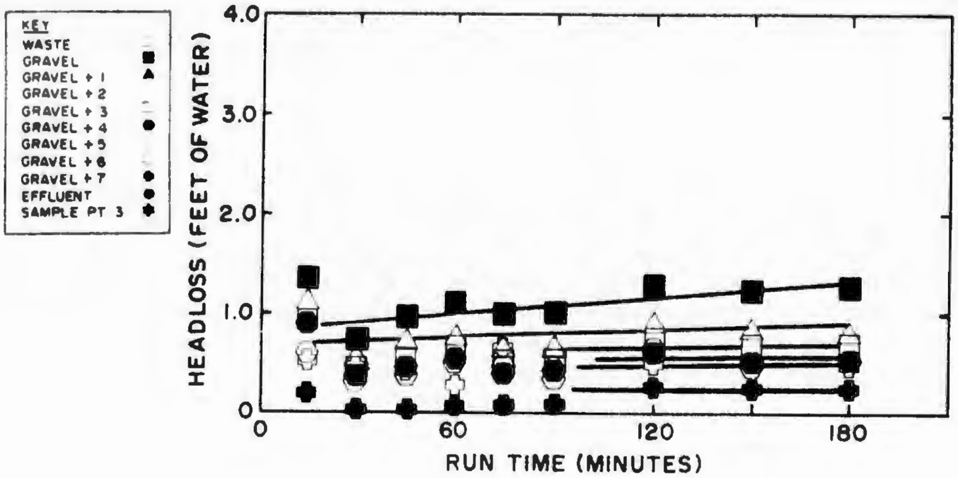

Figure 81. Head Loss Curves for Run 43.

C. INSTRUMENTATION AND CONTROL

Evaluation of the performance of the pilot plant, as discussed above, was based on analysis of samples taken from the process and analyzed with an atomic absorption spectrophotometer. In order to evaluate the on-line colorimetric method for Cr(VI) as described in Section IIID, the colorimeter, beginning with Run 47, was connected to a sampling port as shown in Figure 11. The colorimeter was placed as close to the sampling port as possible, decreasing dead time (the transport time for the sample to pass from the sample point to the flow cell) in the sampling line. The system was modified by replacing the original mixing coil in the cartridge with one having a shorter residence time as shown in Figure 82. An additional sample line to a container of distilled

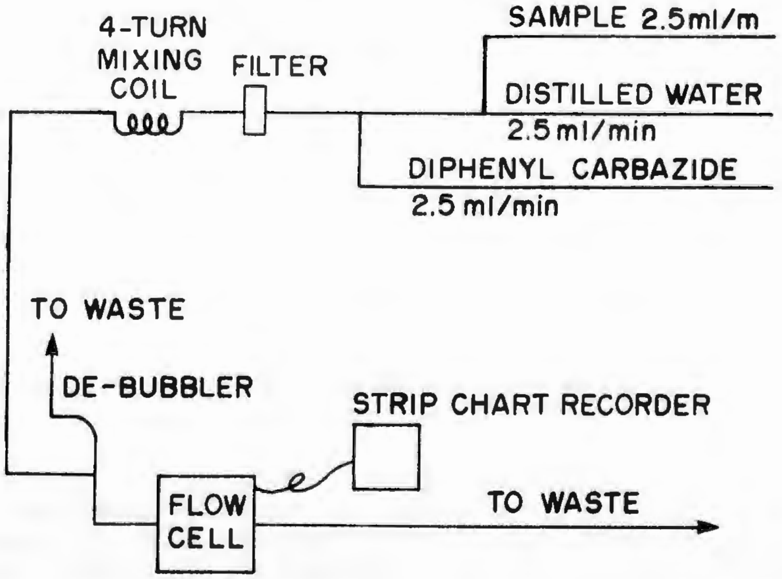

Figure 82. On-Line Colorimetric Determination of Cr(VI).

water was added to allow dilution of the sample to the 0-1 mg/l Cr(VI) level. This also decreased the residence time between mixing tees and the flow cell because of the increased flow rate through the same tubing.

To determine the dynamics of the colorimeter, the system was allowed to reach steady state using a 5 mg/l Cr(VI) standard as the sample. The sampling tube was quickly switched to a 1.0 mg/l standard and the response measured. This procedure was repeated,using 0.5, 0.1, 0.05, and 0.01 mg/l standards. The dead time was found to be approximately 33 seconds. Because of the storage volumes associated with the filter chamber and the flow cell itself, the response to the step change in input was not sharp but had the characteristics of a first-order reaction with a time constant of 13 seconds (time to reach 63 percent of steady state). Figure 83 shows the good agreement between the five runs in terms of the response curves. The time for the colorimeter to reach the new steady state after a change was made was around one minute. However, since the time allotted for color development in the colorimeter cartridge was significantly reduced from the times used in the studies reported in Section IIID1, it was questionable as to whether the color development reaction between the Cr(VI) and diphenylcarbazide had come to steady state by the time the solu-

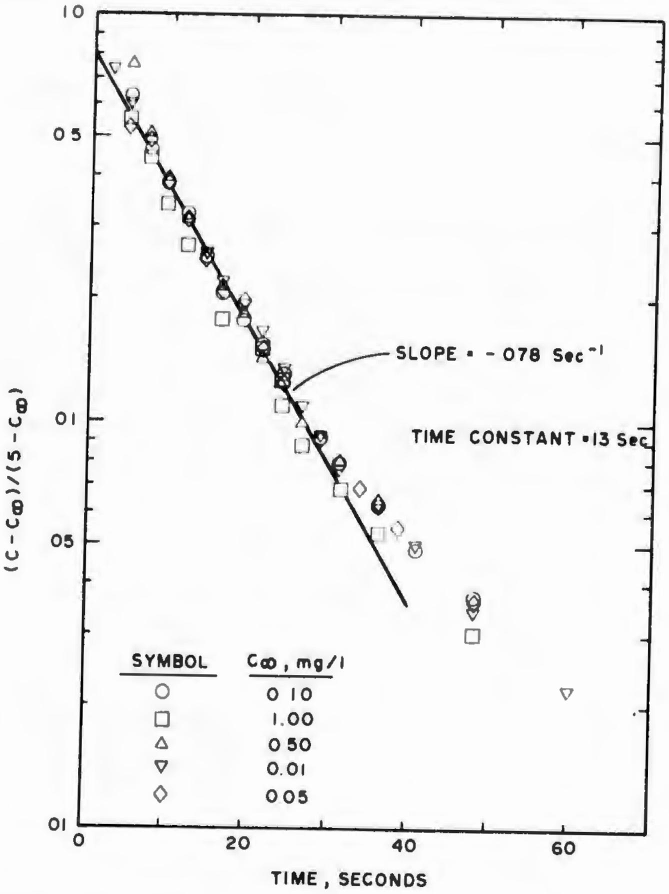

Figure 83. Determination of Time Constant for On-Line Colorimetric Method for Cr(VI).

tion reached the flow cell. The absence of steady state would not be a problem, however, if the reaction was first-order as shown in Section IIID1. The fraction of the Cr(VI) that had been complexed would be fixed if the reaction time was fixed and therefore the absorbance reading would be a fixed fraction of the reading that would occur under steady-state conditions, for example, if the time was such that only 75 percent of the reaction was complete, for all concentrations the absorbance readings would be only 75 percent of the readings based on steady state. This factor would be constant and, thus, a calibration curve could be generated and used just as effectively as a curve based on steady-state data.

A calibration curve of absorbance vs. concentration for the colorimeter was prepared using Cr(VI) standard solutions and is shown in Figure 84. Note that deviations from Beer's Law occur at concentration levels greater than 2.5 mg/l. Below, this value

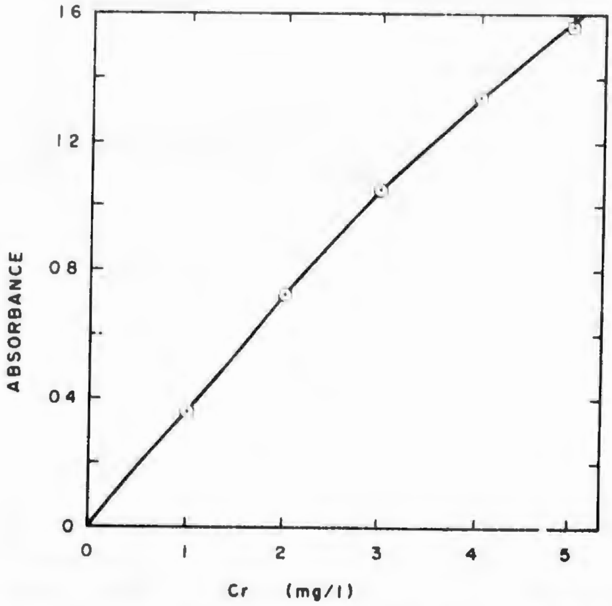

Figure 84. Calibration of On-Line Colorimetric Method for Cr(VI).

Absorbance = 0.360 (Cr(VI))

where (Cr(VI)) = concentration of hexavalent chromium (mg/l).

Three runs (47,48,49) were conducted using on-line colorimetric analysis of hexavalent chromium to monitor pilot plant performance. Comparisons were made between on-line measurement and atomic absorption analysis of the plant effluent.

The waste treated during Run 47 consisted of 20 mg/l of Cr(VI), 10 mg/l of Cd(II) and 5 mg/l of Ni(II). Figure 85 shows the effects of varying doses of ferrous iron and sulfide. In general, the Cr(VI) concentration varied inversely with iron and sulfide doses, as expected. The chromium concen-

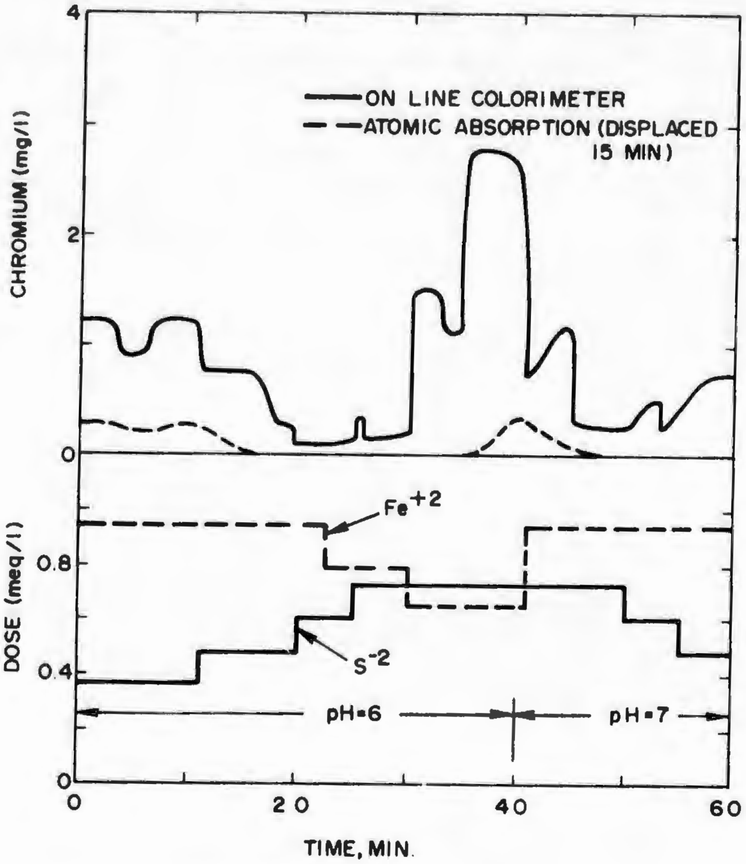

Figure 85. Results for Run 47.

trations determined by the two methods are included on this figure. There is a residence time of about 15 minutes between the sampling point used for the on-line colorimeter and the filter effluent. The filter effluent times were therefore adjusted by subtracting 15 minutes so the two methods are compared for approximately the same solution.

The two methods parallel each other, with peaks and valleys coinciding. However, the colorimeter showed consistently higher concentrations of chromium than found by atomic absorption analysis of the effluent. One possible explanation would be that the reaction is slow at a pH less than 7 and that treatment of the wastes had not gone to completion before colorimetric analysis. (The rate of reaction was investigated separately and will be discussed later in the report.) Another possible explanation is the use of peristaltic pumps for chemical feed, with their inherent pulsing, resulting in insufficient longitudinal mixing of treatment chemicals in the piping and incomplete reaction. In the filter or clarifer, longitudinal mixing is sufficient to remedy this deficiency before the filter effluent.

Run 48 treated a waste with 10 mg/1 Cr(VI), 5 mg/1 Cd(II) and 2 mg/1 Ni(II). The pH was varied between 7 and 9. As seen in Figure 86, there is close agreement between readings of the two instruments for a pH of 8 or greater. However, at a pH of 7, the on-line colorimeter gave much higher

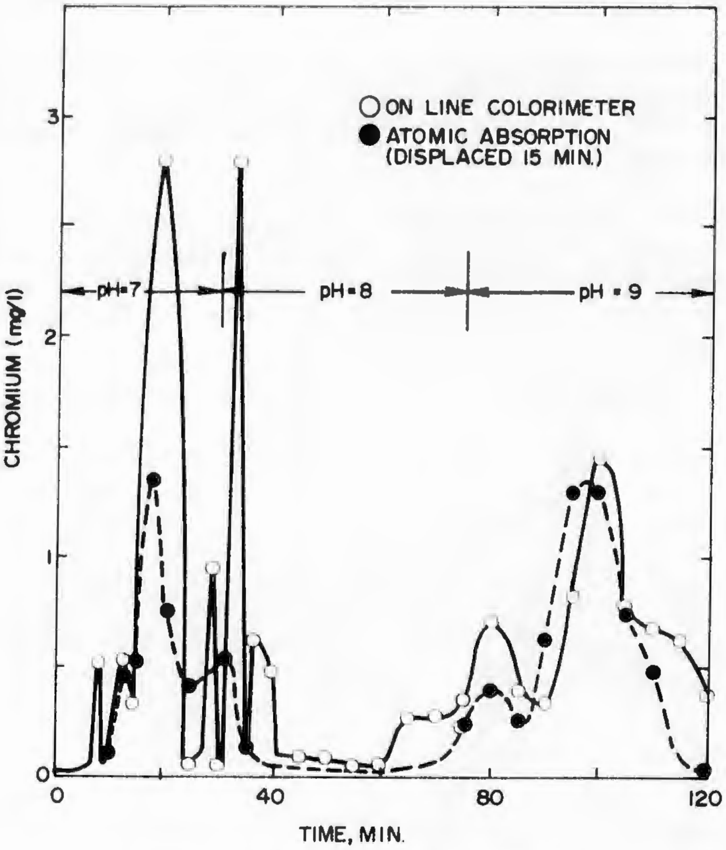

Figure 86. Results for Run 48.

readings than the atomic absorption analysis of the filter effluent as occurring during Run 47 at pH less than 7.

Run 49 utilized sufficient doses of reagents to maintain minimal Cr(VI) concentration using Fe(II) only. The A.A. readings showed < .05 mg/1, while the colorimeter readings drifted randomly in the 0.05 mg/1 Cr(VI) to 0.20 mg/1 range.

In summary, the colorimeter can be used to rapidly and continuously measure Cr(VI) on-line and would be a suitable way of measuring Cr(VI) concentrations for automatic control purposes.

D. RESIDUALS ANALYSIS

1. Sludge Dewaterability

Sludge samples were collected from Runs 32 and 33 and from Runs 40 and 41 for determination of Specific Resistance. Solids content of the filter backwash water was quite dilute. Following settling overnight, approximately 95 percent of the water was readily decanted, producing a sludge with a solids content ranging from 0.9 to 1.4 percent by weight. These sludges rapidly were dewatered to a solids content of 16 to 20 percent by vacuum filtration on the Buchner Funnel apparatus.

The Specific Resistance of these sludges ranged from 7.5 to 9.5 x 10^{12} m/kg, somewhat lower than values quoted previously for municipal wastewater sludges (Table 1), indicating that the sludges from the proposed process would be more readily dewatered.

The effects of conditioning chemical (lime and ferric chloride) on Specific Resistance of the sludge were investigated. The conditioning of the sludge from Runs 32 and 33 with a 5-percent lime (CaO) slurry is illustrated in Figure 87. Addition of lime reduced the Specific Resistance with a minimum at about 1-percent lime dose to the sludge. This was approximately equivalent to the solids content of the sludge. Powdered lime was used to condition the sludge from Runs 40 and 41 (Figure 88). This second test was virtually identical to the first, with minimum Specific Resistance produced by a 1-percent dose of lime.

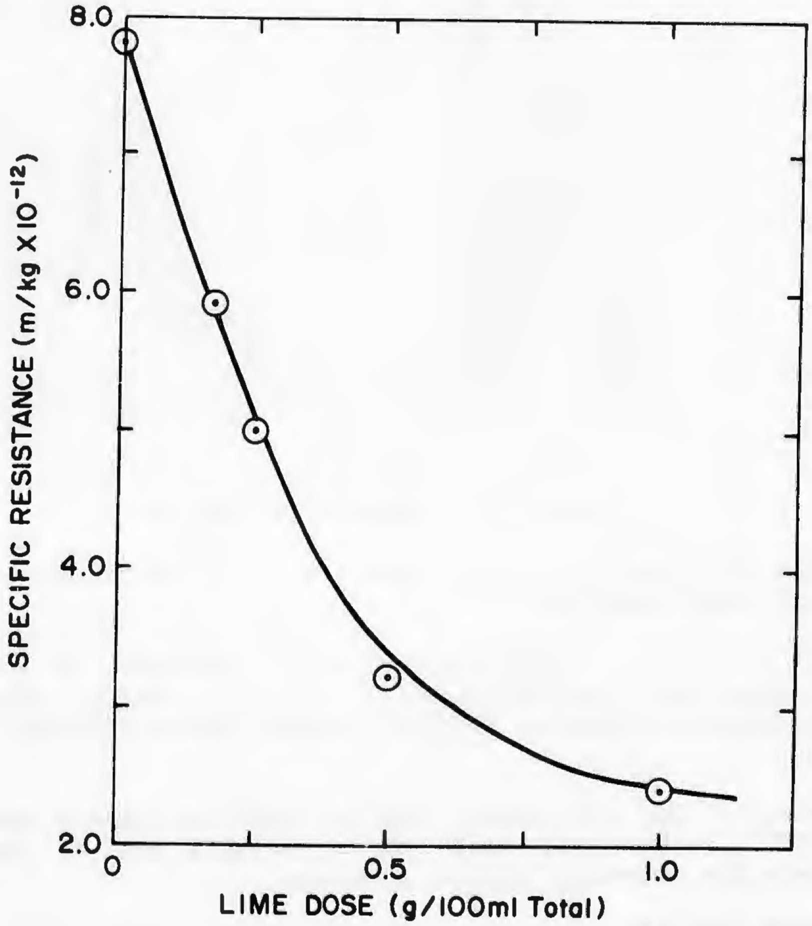

Figure 87. Effects of Slurried Lime (5 Percent) Conditioning on Sludge Specific Resistance (Runs 32 and 33).

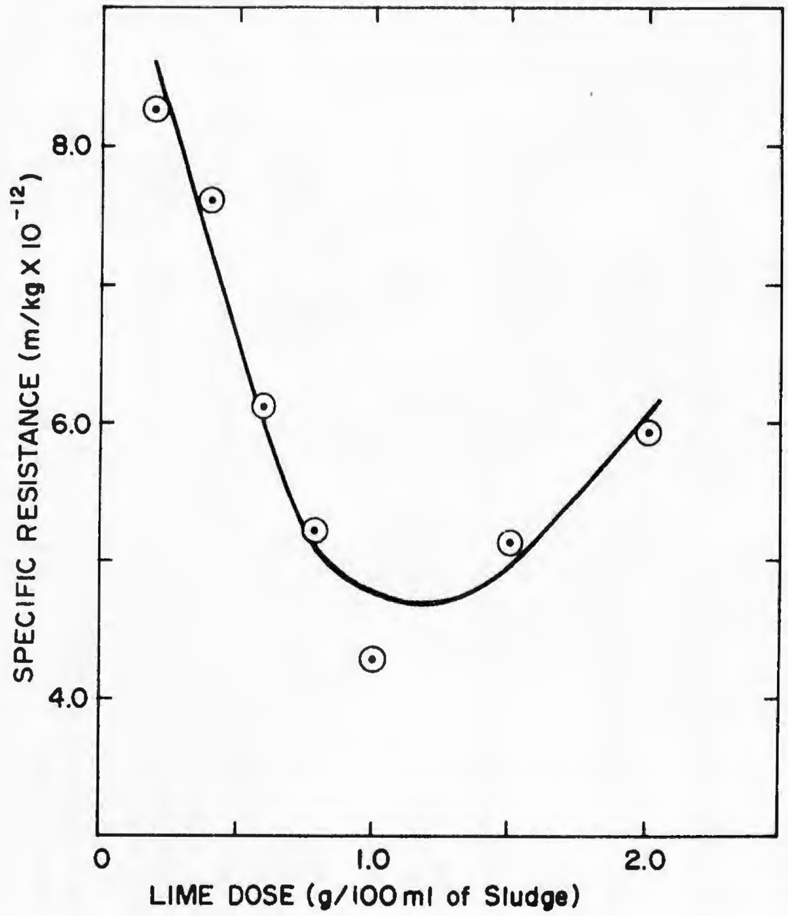

Figure 88. Effects of Powered Lime Conditioning on Sludge-Specific Resistance.

Conditioning of the sludge from Runs 32 and 33 with ferric chloride resulted in dispersion of the solids and excessive bleeding of solids through the filter paper without improvement in Specific Resistance. Combining ferric chloride with lime improved the solids retention on the filter but produced no improvement in Specific Resistance.

2. Decant and Filtrate Quality

The decant from the sludge storage tank and filtrate from Buchner Funnel tests were analyzed to determine if these by-product streams would require treatment prior to discharge (Table 11). The decants from the sludge tank were considerably better than the untreated waste, but retreatment may be required depending upon effluent limits at a specific site.

The filtrates from the Buchner Funnel tests contained higher concentrations of chromium and cadmium compared to the decant. Use of lime as a conditioner prior to filtration of the sludge reduced the concentrations of chromium and cadmium in the filtrate but increased the solubility of nickel. Storage of the conditioned sludge increased the solubility of cadmium and nickel and slightly decreased the solubility of chromium.

TABLE 11. SLUDGE DECANT AND FILTRATE COMPOSITIONS

		Concentrations			
Run #	Sample Description	Cr (mg/1)	Cd (mg/1)	Ni (mg/1)	Fe (mg/1)
–	National Drinking Water Standards.	0.05	0.01	–	–
–	NPDES Effluent Permit for Tinker AFB.	0.05	0.019	0.22	–
32	Decant from Sludge Tank.	0.2	–	–	–
41	Decant from Sludge Tank.	0.1	0.05	6.3	–
40, 41	Filtrate from Unconditioned Sludge.	0.4	.012	<0.1	0.6
46	Filtrate from Unconditioned Sludge.	1.0	.07	<0.1	0.4
40, 41	Filtrate from Sludge Conditioned with 1.0 g CaO per 100 ml Sludge: Filtered Immediately	0.3	<.01	<0.1	0.7
40,41	Filtrate from Sludge Conditioned with 1.5 g CaO per 100 ml Sludge: Filtered Immediately	0.2	<.01	0.2	1.0
40, 41	Filtrate from Sludge Conditioned with 1.0 g CaO per 100 ml Sludge: Filtered After 2 Days	0.2	0.7	1.2	1.0
40, 41	Filtrate from Sludge Conditioned with 1.5 g CaO per 100 ml Sludge: Filtered After 2 Days.	0.1	0.3	0.2	0.2

From these results it is apparent that provisions will have to be made for treatment of these side streams in the design of the full-scale treatment plant.

3. Sludge Composition

Samples of sludge were digested with nitric acid,using the stream table digestion procedure outlined in the appendix. The results of analyses of four representative sludges are presented as Table 12.

TABLE 12. COMPOSITION OF SLUDGES (% DRY WEIGHT)

Run #	Cr	Cd	Ni	Fe	$Cr(OH)_3$	CdS or $Cd(OH)_2$	NiS or $NI(OH)_2$	$Fe(OH)_3$	Other
(a)	0.25	0.01	0.20	-	-	-	-	-	-
21	8.0	4.0	-	28.0	16.0	5.0	-	53.0	26.0
24	9.0	-	7.0	26.0	18.0	-	11.0	49.0	22.0
40, 41	13.5	5.6	3.9	17.0	26.7	7.2	3.9	32.7	29.5
46	10.0	10.9	0.05	41.0	19.9	14.0	0.7	78.4	-

(a) California Hazardous Waste Limits on Total Metal Content.

No Federal standards exist for classifying a waste as hazardous, based on its composition. However, California recently proposed standards based on metals content (Reference 56). These standards are included in Table 12.

The composition of the sludges closely compares with the composition of the wastes treated and the iron added. Iron is the predominant metal in all of the sludges since high concentrations of ferrous iron are needed for chromium reduction. Replacement of some ferrous iron by sulfide (Runs 40 and 41) reduces the relative amount of iron (and decreases the sludge production).

Also included in Table 12 are the various metals expressed as concentrations of their expected precipitates (hydroxides or sulfides). Solids not accounted for are included under the heading Other. This category includes metals not dissolved in the digestion, waters of hydration, elemental sulfur produced by oxidation of the sulfide and some sand carried over from the filter during backwash.

a. Sulfur Analysis

It has been postulated that sulfide affects reduction of hexavalent chromium by being reduced to elemental sulfur. Earlier studies showed that a stoichiometric dose of sulfide corresponded to a change of two valence units indicating a change from sulfide to elemental sulfur.

There are three forms of elemental sulfur, all of which are pale yellow, which dissolve in carbon disulfide and melt at between 112.8 and 120°C (Reference 62). The residue from the nitric acid digestion was analyzed for the presence of elemental sulfur. The residue was dissolved in carbon disulfide and filtered. When the filtrate was evaporated, a pale yellow solid remained. The solid was determined to have a melting point of 118°C, confirming the presence of elemental sulfur in the sludge. This confirmed that elemental sulfur was the end product when sulfide was used to reduce hexavalent chromium.

5. Sludge Volume

An important consideration in determining the economics of a process is the amount of sludge that must be handled, dewatered and eventually disposed of. Experiments have shown that the sludge produced by the candidate process can be readily decanted to about 1 percent solids and dewatered to about 20 percent solids. Table 13 lists calculated volumes of sludge production for the runs that sludge analysis was performed on. Sludge production is reported as a fraction of the volumes of waste treated during these runs. The 1-percent solids content is useful in sizing sludge dewatering equipment and the 20 percent should be used to calculate disposal costs.

TABLE 13. SLUDGE PRODUCTION

	Sludge Production (Fraction of Waste Treated)	
Run Number	1% Solids	20% Solids
21	0.012	0.0006
24	0.0096	0.0005
40,41	0.028	0.0014
46	0.01	0.0005

Figure 89 shows the volume of sludge produced (1 percent solids) as a function of total concentration of metals removed from the waste,plus ferrous iron added in treatment. Sludge volume is shown as a function of wastewater treated. Volume of sludge production increases as concentrations of metals in the waste increases and as iron doses are increased to treat these increased waste concentrations. Due to the high use of iron in this process, it is anticipated that use of the process would be limited to wastes containing low concentrations of chromium (dilute mixed-metal rinsewater wastes).

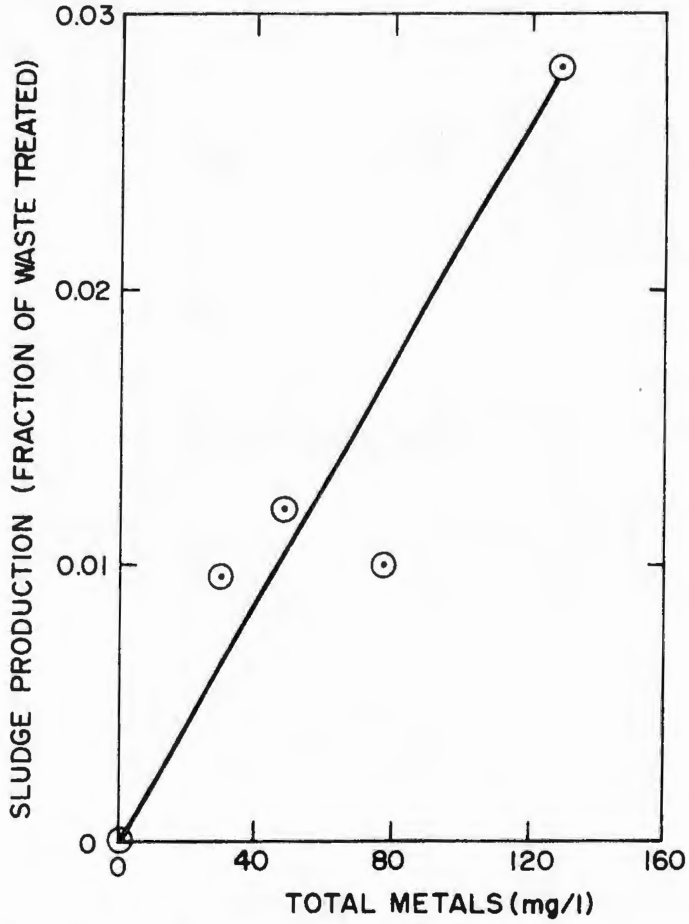

Figure 89. Volume of Sludge Produced (1-Percent Solids) as a Function of Total Metals Treated (Waste Plus Iron).

5. Extraction Testing for Toxicity

Two variations on the standard EP toxicity procedure were used on sludge samples. In one, the concentrated sludge (1-percent solids) was shaken over a 24-hour period, with the pH adjusted with acetic acid. No distilled water was added. In the other procedure, the filter cake from the Buchner Funnel tests was tested, using the standard EP procedure.

Table 14 lists the results for the EP tests performed on the sludges. EPA standards, above which a waste is classified as toxic, are included for reference. The US EPA does not have a nickel standard, although the State of California does, and their value is included for reference. Chromium is seen to have a low extractability for all sludges tested and both methods of testing. Cadmium exceeded the toxic limits in all sludges that contained cadmium. Two of the three wastes containing nickel had extracts that exceeded the California standard. The third had a low nickel content to begin with.

Sludge cakes from Runs 40 and 41 which had been conditioned with varying amounts of lime, were extracted using the EP toxicity test. The effects of

TABLE 14. EP EXTRACT CONCENTRATIONS FOR PILOT PLATE SLUDGES

Run #	EP Test Used (a)	Waste Treated	Cr (mg/1)	Cd (mg/1)	Ni (mg/1)
-	1	EPA Limits for EP Test	5.0	1.0	-
-	1	State of California Extractability Limits	5.0	1.0	20.0
21	2	Synthetic Cr and Cd, Tap Water	<0.1	52	-
24	2	Cr and Ni Plating Baths, Tap Water	<0.1	-	370
32, 33	2	Cr Plating Bath, Med Fe/S, Tap Water	1.5	-	-
34	2	Cr Plating Bath, High Fe/S, Tap Water	0.4	-	-
35, 36, 37	2	Cr Plating Bath, Equal Fe/S, Tap Water	0.9	-	-
39	2	Cr Plating Bath, Low Fe/S, Distilled Water	0.7	-	-
40, 41	1	Cr and Ni Plating Baths, Synthetic Cd	3.2	65	64
46	1	Cr, Cd and NI Plating Baths, Distilled Water	0.9	12.5	4.0

Notes: (a) Test 1: Run with Filtered Sludge
Test 2: Run with Unfiltered Sludge

lime dose on extractability of metals are shown on Figure 90. With increasing

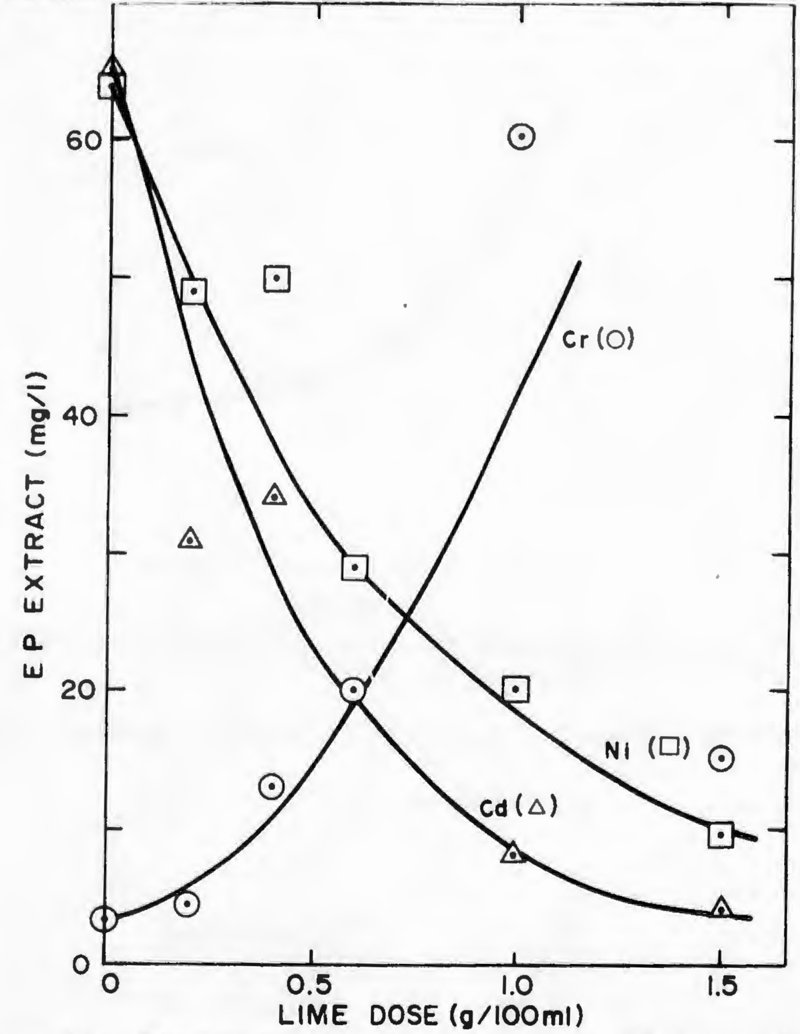

Figure 90. Effects of Lime Conditioning on EP Extraction.

doses of lime, cadmium and nickel extractability decreased with chromium becoming more soluble. No dose of lime resulted in making this waste non toxic under EPA and California regulations.

E. CHROMIUM REDUCTION RATE STUDIES

Batch studies were performed to determine the effect of varying ferrous iron dose and pH on the reduction rate of hexavalent chromium. Figures 91 through 94 show responses to stoichiometric and twice-stoichiometric (16 mg/l excess Fe(II)) doses of ferrous iron. The response of the Auto-Analyzer to a similar step-change in chromium concentration is included for comparison.

The response curves indicate that the reaction is slower at pH 5 and above than at 3 and 4. At pH 3 and 4 (Figure 91) the response curves for stoichiometric doses of iron lie along the Auto-Analyzer step-change curve. This indicates that the reaction time is negligible, compared to the Analyzer response time, but, that with this analysis, no information on the rate of

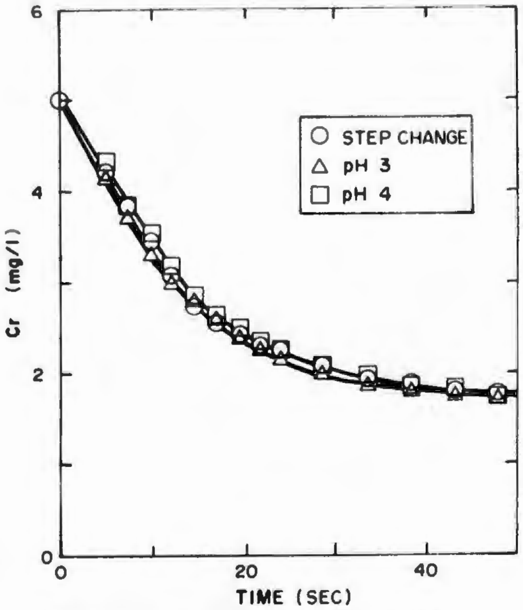

Figure 91. Response Curves for Stoichiometric Ferrous Reduction of Cr(VI) at pH 3 and 4.

reaction could be obtained. At pH 5 (Figure 92), however, the reaction time

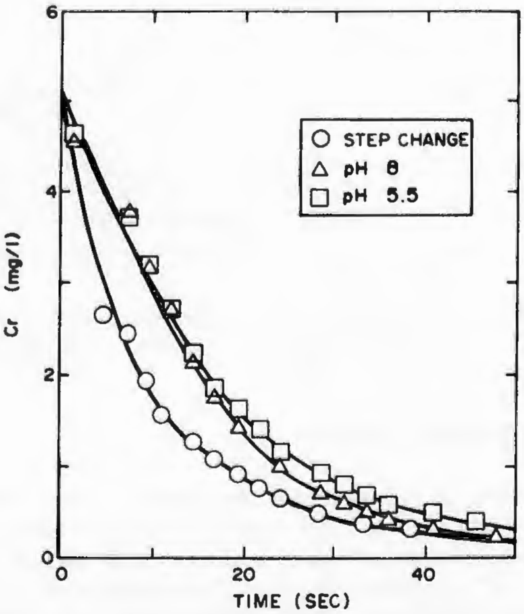

Figure 92. Response Curves for Stoichiometric Ferrous Reduction of Cr(VI) at pH 5.5 and 8.

has about the same order of magnitude as the Analyzer response time, indicating that the reaction is slower at pH 5 and above for stoichiometric iron doses.

The response curves at pH 3 and 4 for excess iron doses of 16 mg/l in Figure 93 are shifted to the right of the Analyzer response curve showing that the reaction has slowed with increased iron dose at these pH values. At pH 5 and above (Figure 94), however, the response is faster than when stoichiometric

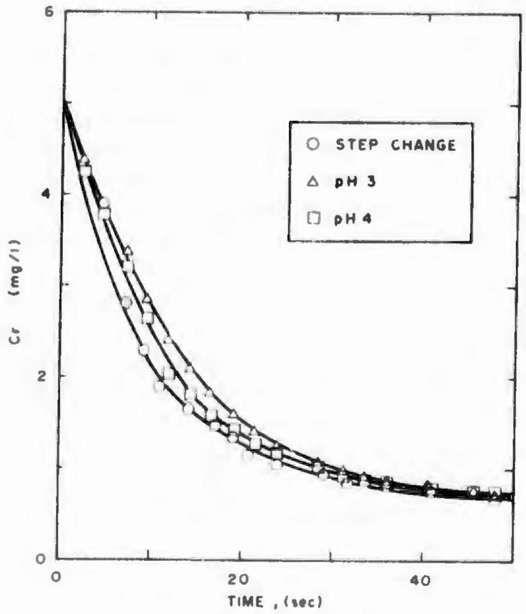

Figure 93. Response Curves for Twice Stoichiometric Ferrous Reduction of Cr(VI) at pH 3 and 4.

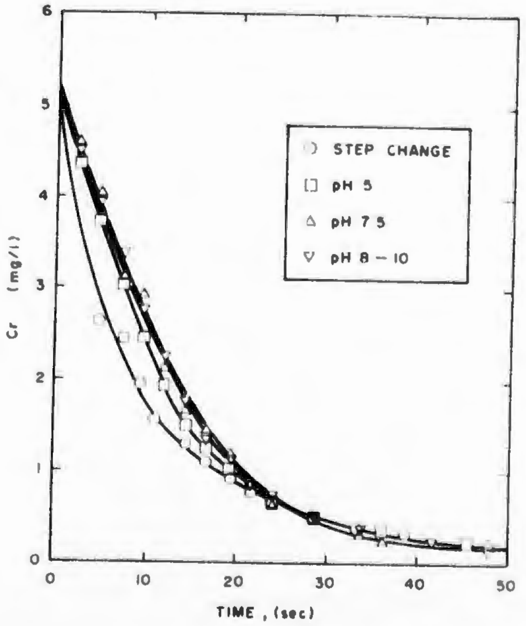

Figure 94. Response Curves for Twice Stoichiometric Ferrous Reduction of Cr(VI) at pH 5 through 10.

iron doses were used, which means that the excess iron may speed up the reaction rate at these pH values. These responses from excess iron doses at higher pH are slightly slower than the responses using the same iron dose at pH 3 and 4.

Although the reaction rate is a few seconds faster at pH 3 and 4, the rate studies show that hexavalent chromium and ferrous iron do not react stoichiometrically at these values. The reaction proceeded from 5.0 mg/l to 1.7 mg/l Cr(VI) when equivalent amounts of iron to chromium were used and from 5.0 mg/l to 0.6 mg/l Cr(VI) when 16 mg/l excess iron was used. At pH 5 and above, however, the reaction was nearly complete at both the iron doses that were tested, proceeding from 5.0 mg/l to less than 0.1 mg/l Cr(VI) in each case.

The figures show that the reaction proceeds more rapidly than Espenson's rate expression predicts (Figure 2). All of the reactions tested were essentially complete within 40 to 60 seconds. (These times are greatly overestimated since the response time of the Auto-Analyzer is included.) The curves derived from Espenson's rate expression indicate reaction times of 5 to 30 minutes for equivalent iron doses and extents of reactions. The difference is thought to be caused by a change in reaction mechanisms due to a shift to CrO_4^{-2} at higher pH. Espenson's reaction assumes that $HCrO_4^-$ is the reacting species.

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

A. CHROMIUM REDUCTION AT ALKALINE PH

Hexavalent chromium is rapidly and stoichiometrically reduced to trivalent chromium and precipitated by the addition of ferrous sulfate at an alkaline pH (7 to 10). The oxidized iron precipitates as ferric hydroxide and aids flocculation of the solids produced in the process. A disadvantage of ferrous sulfate use is the production of excess ferric hydroxide sludge.

Sodium sulfide as a sole reducing agent for hexavalent chromium is not effective at neutral and alkaline pH. In combination with ferrous iron, sulfide is effective, with the ferrous iron acting as a catalyst. The combination is most effective at neutral pH with effectiveness decreasing at higher pH.

In reducing chromium, sulfide was shown to be oxidized to elemental sulfur. Use of sulfide results in significantly less sludge production than when ferrous iron is used as the sole reducing agent. Sulfide precipitates formed rapidly but were finely divided and more difficult to remove than the better flocculated iron sludges. It is advisable to use a combination of ferrous sulfate and sodium sulfide to produce a solid that is easily removed and yet minimize sludge production. Separate control of the addition of these two chemicals is necessary to provide the optimum combination.

B. TREATMENT OF A MIXTURE OF CHROMIUM,CADMIUM,AND NICKEL

Treatment of a mixture of metals is somewhat more effective than individual treatment of metals. Sulfide lowers the solubility of cadmium and nickel. Ferric hydroxide precipitates reduce metal solubilities by incorporation of other metals in an amorphous precipitate and provide surface sites for adsorption.

The presence of cyanide, used in cadmium plating baths, resulted in no removal of nickel and reduced effectiveness in the removal of chromium and cadmium. Increasing the doses of iron and sulfide did not compensate for the adverse effects of cyanide. It is recommended that cyanide-containing wastes be segregated and treated so that the cyanide is destroyed prior to the waste being combined with other wastes for metal removal.

C. DISTILLED AND TAP WATERS

Treatment of wastes prepared in a hard tap water was more difficult to treat than those prepared in distilled water with the following disadvantages: metal solubilities were larger; flocs were smaller and penetrated more deeply into the filter; filter run times were considerably shorter.

D. UNIT PROCESSES

Chromium reduction and metal hydroxide precipitation are virtually instantaneous. Separate reactors are not required for these reactions. In-line mixing is sufficient.

Separate flocculation was found to be unnecessary and somewhat harmful in causing shear stress to the rapidly produced flocculant metal hydroxide precipitate.

A separate clarifier would be required in a prototype treatment plant unless it was designed to treat a waste of consistently low metal content (5 mg/l or less in a hard tap water, 20 mg/l or less in distilled water), or provisions were made for frequent backwashing.

Upflow filtration was effective in removing the high concentration of solids produced by alkaline ferrous and sulfide treatment of a mixed-metal waste. A sand of 0.7 mm effective grain size was found to combine good removal efficiency with high solids storage capacity. A layer of finer sand (0.44 mm effective grain size) was useful in polishing the effluent from the coarser sand, but had little capacity for solids storage. A coarser sand (1.1 mm effective size) was most effective in removing the large flocs formed in the treatment of wastes prepared in distilled water.

The filter was most effective when operating at a loading rate of 3 gallons per minute per square foot. Good removal was accomplished at a loading rate of 5 gallons per minute per square foot, but at the expense of greatly reduced run times.

E. INSTRUMENTATION AND CONTROL

The on-line colorimeter system based on a modification of the cartridge supplied by Alpkem gives accurate and suitably fast analyses of hexavalent chromium levels. With typical electroplating waste streams, reducing the chromium level to within tolerable limits will also result in reducing nickel and cadmium concentrations to analogous low levels and thus the monitoring of only Cr(VI) is sufficient for control purposes. The positioning of the sampling port immediately downstream of the mixing/reaction section and subsequent analysis yields a total dead time of about 33 seconds and a time constant of 13 seconds in the measuring system. This response is fast enough to use as part of an automatic feedback loop to control the addition of ferrous sulfate and sodium sulfide to the process, especially if the process is not subject to rapid changes in Cr(VI) concentration in the incoming waste feed.

The stability of the colorimeter, quantities of reagents used and capacity of the filter in the colorimeter all are compatible with 8-hour runs with no intervention by an operator.

The pH was monitored with no apparent problem with self-cleaning in-line electrodes and the signal from the meter could be used to control the pH of the reaction by addition of NaOH solution.

The use of these two instruments to manually control Cr(VI) levels was proven and it is recommended that future work be done on the development of a control strategy and implementation of suitable hardware to put the pH and Cr(VI) control loops under automatic control.

F. RESIDUALS MANAGEMENT

Significant quantities of liquid sludge are produced in the candidate plating waste treatment process. The amount of sludge produced (per amount of waste treated) is proportional to the concentration of metals in the waste plus chemicals added in treatment. A backwash storage tank would be required and could serve as a sludge thickening tank. Gravity settling and decanting of supernatant should produce a sludge of 1-percent solids content. Mechanical dewatering could produce a sludge cake of 20-percent solids, significantly reducing the volume of sludge to be disposed of.

Provisions would be required for treatment of sludge thickener decant and filtrate water, depending on their quality and specific effluent standards.

The extract obtained when an "EP" toxicity test was performed on the sludge exceeding the standard for cadmium. Chromium concentrations did not exceed concentrations that would classify this waste as toxic. It is anticipated that use of this process to treat wastes containing only chromium and nickel would result in production of a sludge that is not "EP" Toxic.

Lime conditioning of the sludge improved its mechanical dewaterability at the expense of increasing the volume of solids requiring disposal. Conditioned sludge had lower "EP" extract concentrations of cadmium and nickel, although the concentration of chromium was above the toxic limit.

G. CHROMIUM REDUCTION RATE STUDIES

The reaction rate for ferrous reduction of hexavalent chromium is considerably faster at pH values above 3 than that predicted in the literature. Espenson's rate expression was for very acidic pH, where $HCrO_4^-$ is the predominant chromium species. The reaction mechanisms may be different for CrO_4^{-2}, the species that predominates at neutral and alkaline pH.

Smaller doses of ferrous iron are needed for chromium reduction at values of pH 5 and above than at pH 3 and 4. At pH 3 and 4 adding ferrous iron appeared to slow the reaction rate, although improving chromium removal. These data are suspect, however, due to the problems associated with using a measuring device with a relatively slow response time to measure these fast reactions.

At high pH levels (5 to 8), adding excess ferrous iron results in increasing the rate of reaction, but does not affect chromium removal because stoichiometric doses resulted in virtually complete chromium removal.

Since the Auto Analyzer has a response time similar or larger than the reaction being measured, accurate dynamic measurements could not be obtained. Faster measurement, or a way of questioning the reaction, is needed in order to more accurately determine reaction rates.

(The reverse of this page is blank)

REFERENCES

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

2. Watson, M.R., Pollution Control in Metal Finishing, Noyes Data Corp., Park Ridge, NJ, 1973.

3. Nemerow, N.L., Liquid Waste of Industry, Addison-Wesley, 1971.

4. Patterson, J.W., Wastewater Treatment Technology, Ann Arbor Science, 1975.

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

6. Sorg, T.J., "Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics: Part 4," Journal AWWA, 71, 454, 1979.

7. Higgins, T.E., Treatment of Plating Wastewaters by Sulfide Precipitation Coagulation and Upflow Filtration, Report for the U.S. Air Force - SCEEE Summer Faculty Research Program, 40 pp., July, 1980.

8. Higgins, T.E. and TerMaath, S.G., "Treatment of Toxic Metal Wastewaters by Alkaline Ferrous Sulfate and Sodium Sulfide for Chromium Reduction, Precipitation and Coagulation," Proceedings of the 36th Annual Purdue Industrial Waste Conference, West Lafayette, IN, May 12-14, 1981, pp. 462-471.

9. Higgins, T.E, Treatment of Plating Wastewaters by Ferrous Reduction, Sulfide Precipitation, Coagulation and Upflow Filtration, Report No. ERC-R-81014, Engineering Research Center, Arizona State University, 95 pp. May, 1981.

10. Higgins, T.E. and TerMaath, S.G., "Alkaline Ferrous and Sulfide Reduction of Chromium," Proceedings of the 1981 National Conference on Environmental Engineering, sponsored by the American Society of Civil Engineers, in Atlanta, Georgia, July 8-10, 1981, pp. 374-381.

11. Higgins, T.E. and TerMaath, S.G., "Treatment of Heavy Metals Wastewater by Alkaline Ferrous Reduction of Chromium and Sulfide Precipitation," Proceedings of the Third International Conference on Heavy Metals in the Environment, by the Commission of the European Communities and World Health Organization, in Amsterdam, September 15-18, 1981, pp. 88-91.

12. Jenne, E.A., "Controls on Mn, Fe, Co, Ni, Cu, Zn Concentrations in Soils and Water: The Significance of the Hydrous Mn and Fe Oxides," Trace Inorganics in Water, Advances in Chemistry Series, No. 73, ACS, 1964.

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

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

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

16. Stumm, W. and Morgan, J.J., Aquatic Chemistry, Wiley-Interscience, 1981.

17. Kunz, R.G., Hess, T.C. and Yen, A.F., "Kinetic Model for Chromate Reduction in Cooling Tower Blowdown," JWPCF, 52, 2327, 1980.

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

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

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

21. Control and Treatment Technology for the Metal Finishing Industry - Sulfide Precipitation, U.S. EPA Technology Transfer Summary Report, EPA 625/8-80-03, 1980.

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

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

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

25. Smith and Martel, Critical Stability Constants, Vol. 4 Inorganic Complexes, Phenum, 1976.

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

27. Scott, M.C., "Sulfide Process Removes Metals, Produces Disposable Sludge," Industrial Wastes, July-August, 1979.

28. Thomas, M.J. and Theis, T.L., "Effect of Selected Ions on the Removal of Chrome (III) Hydroxide," JWPCF, 48, 2032, 1976.

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

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

31. Hamaan, C.L., and McKinney, R.E., "Upflow Filtration Processes," Journal AWWA, 60, 1023, 1968.

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

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

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

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

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

37. "Extraction Cuts Mercury From Wastewater, Solids," Chemical News, Chemical Manufacture Assoc., Mar, 1973.

38. Survey of Instrumentation for Environmental Monitoring, Lawrence Berkeley Laboratory Rept. LBL-1, 1971-present.

39. Quinby-Hunt, Mary S., "Monitoring Metals in Water," American Laboratory, p. 17, Dec. 1978.

40. Total Chromium in Plating Bath Effluents, Industrial Method No. 371-75WM, Technicon, Tarrytown, NY, July 10, 1981.

41. Larson, P. et al., Introduction to the Pump-Colorimeter Analyzer, Tech. Inf. Series - No. 9, Hach Co., Loveland, Co., March 8, 1979.

42. Hexavalent Chromium Analyzer, Model 40800, Bulletin 40800-2ED, Hach Co., Loveland, Co., 1981.

43. Lachat Chemical, Inc., Quikchem Method No. 800383.ABS for Cr(VI), Mueqon, WI.

44. Alpkem Corp., Clackamas, OK, Personal Communication.

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

46. Gorringe, R., "Water Pollution Control Strategy in Metal Finishing Using On-Line Analysis," 7th Technicon International Conference, New York, NY, Dec. 1976.

47. Saltzman, R. and Bowam W., "Continuous Monitoring of Low Chromium VI Concentration with a Photometric Analyzer System," ISA AID 74418 (95-100), 1974.

48. Ion (Phenanthroline) Method, Industrial Method Ind.-9, Technicon, Tarry town, N.Y., 1968.

49. Lachat Chemicals, Inc., Quikchem Method No. 800582, Fe(II), Mequon, WI.

50. Mracek, W. and Greenberg, L., "Control and Automation of Chromate Waste Reduction Plants," Engineers Society of Western Pennsylvania Proceeding, 1969.

51. Bennett, J., "The Treatment of Effluents From Metal Cleaning and Finishing Processes," Metal Finishing Journ., p. 272, Sept. 1972.

52. Carmen, P.C., "A Study of the Mechanism of Filtration," Journal Soc. Chem. Ind., (Brit.) V. 52, p. 280T (1933), V. 53, p. 159T, p. 301T, 1934.

53. Coakley, P and Jones, B.R.S., "Vacuum Sludge Filtration: 1. Interpretation of Results by the Concept of Specific Resistance," Sewage and Industrial Wastes, V. 28, 963, 1956.

54. Adrian, D.D., Sludge Dewatering and Drying on Sand Beds, U.S. EPA-600/2-78-141, 1978.

55. Metcalf and Eddy, Wastewater Engineering, 2nd Edition, McGraw-Hill, New York, 1979.

56. Baum, Rudy, "California Setting New Hazardous Waste Rules," Chemical and Engineering News, pp. 16-17, Nov. 29, 1982.

57. Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, U.S. Environmental Protection Agency, Office of Water and Waste Management, SW-846, 1980.

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

59. Quality Criteria for Water, USEPA, Office of Water and Hazardous Material, July, 1977.

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

61. Vesilind, P.A., Treatment and Disposal of Wastewater Sludges, Ann Arbor Science Publishers Inc., Ann Arbor, Michigan, 1974.

62. Weast, Robert C., Editor, Handbook of Chemistry and Physics, 62nd Edition, CRC Press Inc., Boca Raton, Florida, 1981.

63. Ligane, James, Analytical Chemistry of Selected Metalic Elements, Rheinhold Publishing Co., 1966.

APPENDIX A

METHODS OF SLUDGE ANALYSIS (References 45 and 57)

A. STEAM TABLE DIGESTION PROCEDURE FOR METALS RECOVERY.

1. Place 20 ml of wet sludge of known solids content in a 250 ml polycarbonate erlenmeyer flask.

2. Add 20 ml of concentrated HNO_3, swirl to mix.

3. Place on steam table for 4 hours, swirling each hour to mix.

4. Cool and filter through a prewashed (0.45 micrometer pore) membrane filter into a 50 ml polypropylene test tube. Wash flask with DI water and add to filter.

5. Bring final volume to 50 ml with DI water.

B. MODIFIED EXTRACTION PROCEDURE FOR METALS RECOVERY (METHOD 1).

1. Filter a representative sludge sample through a filter with Whitmore #4 filter paper.

2. Place the filtered sludge in a tared 250 ml polycarbonate erlenmeyer flask. Weigh sample to 0.01 g. Add 16 times the sample weight of deionized water, and shake to ensure complete mixing.

3. Measure the pH and, if above 5.0, adjust to 5.0 ± 0.2 by adding 0.5 N acetic acid. (Add no more than a total of 4 ml of acid per gram of sample; record volume of acid used.)

4. Place the mixture on a shaker table and agitate sufficiently to prevent stratification and ensure complete mixing.

5. Check the pH and adjust to 5.0 ± 0.2 with 0.5 N acetic acid at 15, 30, or 60-minute intervals, move to the next time interval if adjustments are not more than 0.5 pH units. Continue the adjustment period for 6 hours.

6. After 24 hours, adjust the pH to 5.0 ± 0.2 if necessary (unless maximum acid has been used) and continue the extraction for 4 hours, adjust the pH at 1-hour intervals.

7. At the end of the extraction period, add a volume of deionized water to make the total volume of liquids added to the sample 20 times the sample weight.

   $V = 20w - 16w - A$
   V = volume (ml) of deionized water added at end
   w = wt (grams) of sample
   A = volume (ml) of 0.5 N acetic acid adding during extraction.

8. Filter the sample through a prewashed (0.45-micrometer pore size) membrane filter into a 50 ml polypropylene test tube. Sample is

acidified with 1 drop of concentrated HNO_3.

C. MODIFIED EXTRACTION PROCEDURE FOR METALS RECOVERY (METHOD 2)

1. Place 100 ml of wet sludge of known solids content into a 250 ml polycarbonate erlenmeyer flask. Calculate the weight of solids in the sample and use this as the sample weight.

2. Add no more dilution water, but add 0.5 N acetic acid to adjust pH. (Add no more than 4 ml of acid per gram of solids.)

3. Follow extraction procedure #1.