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OPTIMUM DEWATERING AND METAL RECOVERY OF METAL PLATING WASTE SLUDGES

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CIVIL AND ENVIRONMENTAL ENGINEERING DEVELOPMENT OFFICE
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Bench scale experimentation was initiated to evaluate the solubilities and sludge characteristics associated with selected heavy metals and their hydroxides for both homogeneous and heterogeneous solutions. Data suggests that in a mixed-metal solution, mixed-metal co-precipitants form and the point of zero charge (PZC) for these precipitants depends upon the specific metal content of the colloidal precipitants. In general the presence of chromium (III) depresses the overall PZC while nickel and cadmium, when major waste components, tend to raise the PZC.

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Aging was found to impact chromium hydroxide dewatering but it is not clear that the theoretical aspects of aging chemistry can be used to predict changes. High molecular weight anionic polymers were effective in conditioning metal sludges with respect to cake formation/filtrate clarity but help dewatering rates very little. Previously developed relationships for inorganic sludges which allowed predictions about sand bed, centrifugation, and vacuum filtration dewatering processes based on gravity thickening data were found to hold for metal sludges. Based on these relationships and the laboratory data gathered here it is concluded that vacuum filtration is the only reasonable process to insure a handleable sludge. If direct reclamation of the metals from the mixed hydroxide slurry is to be attempted centrifugation may be employed.

Based on a literature review and a basic economic evaluation, liquid/liquid extraction was recommended for further study as the metal recovery process of choice.

PREFACE

This report was prepared by the Department of Civil Engineering, University of Missouri, Columbia, Missouri 65201, under Contract No. FO8638-76-C-0223 with the AF Civil Engineering Center/EVW, Tyndall AFB FL (1 May 76 - 15 Apr 77) and the Civil and Environmental Engineering Development Office (CEEDO), Detachment 1, Armament Development and Test Center (ADTC)/ECW, Tyndall AFB FL (15 Apr 77 - 28 Feb 78).

Capt Stephen P. Shelton was program manager for this work. Captain Jay A. Farmwald provided editorial comments during the publication phase.

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

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

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SECTION I

INTRODUCTION

A. General

Metal plating and finishing wastes are important to the United States Air Force from both an environmental and economic standpoint. Included in the waste from plating and finishing processes are variable concentrations of zinc, copper, chromium, cadmium, lead, tin, silver, and nickel. These heavy metals represent a lost resource when discharged as hydroxide sludges to landfills, and, due to their documented toxicity, raise significant questions with respect to the potential for ground water contamination. Concerns such as these have, therefore, prompted the Environmental Protection Agency, as well as state and local regulatory agencies to promulgate specific treatment requirements and discharge limitations for the metal finishing point source category which will impact USAF Air Logistics Center operations.

Metal finishing wastes are of serious environmental concern if discharged to natural waters since these materials may become cumulative poisons when ingested. The removal of metals such as chromium, zinc, cadmium, and others from waste streams has been studied extensively, and several feasible waste treatment schemes are available. For the most part, these metal-removal schemes involve adsorption or ion exchange followed by hydroxide precipitation of the concentrated metal ion wastewater. In all instances, metal removal produces a concentrated metal sludge which requires further treatment prior to ultimate disposal. These relatively small quantities of metal precipitate sludges can create environmental problems which are proportionally greater than their volumes. These slurries are often difficult to handle, resist most dewatering processes, and when finally disposed, may create an environmental hazard.

Once the precipitation step is accomplished several methods of sludge disposal are available (Reference 1). These are:

1. Lagooning the waste sludge. This disposal method would require the least amount of equipment.

2. Baffled settling basin with the overflow going to the sewers. The sludge collected, usually to 2 percent solids, would go to a landfill.

3. Gravity thickening of the waste followed by vacuum filtration. From an equipment cost standpoint, this is probably the most expensive solution to the problem. It should be noted that vacuum filtration without sludge thickening is not considered feasible.

4. Neutralization followed by clarification and centrifugation. It should be pointed out that the light flocs which come from the treatment do not lend themselves well to centrifugation.

5. Direct pressure filtration.

Patterson et al (Reference 2) suggested there might be other methods to remove heavy metals from industrial wastewaters, including evaporation, electrolysis, carbon adsorption, and cementation.

The sludges that are generated from precipitation of plating wastes are generally high in trivalent chromium and may also contain varying amounts of copper, silver, zinc, nickel, cadmium, and occasionally smaller quantities of gold and platinum. These sludges have been found to be among the most difficult residues to dewater, often yielding less than 1 percent solids upon thickening and less than 20 percent solids by filter pressing (Reference 3). Dewatering rates are slow and therefore process yields when using mechanical dewatering devices are low, resulting in high costs per volume of liquid handled.

Environmental problems are often encountered when using some of the previously mentioned waste treatment systems. In lagooning, if the lagoon bottom is not properly lined or watertight, the heavy metals can reach the ground water. Lagooning would also be impractical in regions where the annual evaporation rate was much less than rainfall. In such regions the lagoon surface runoff may contain metal levels that would be detrimental to the receiving stream. A similar problem could exist when disposing of the dried sludge in a landfill. Acidic ground-waters could redissolve the metals resulting in leaching of the metals to groundwater.

In addition to the problem of handling and disposing of these sludges, there is a definite economic value in the sludges in that they contain large quantities of valuable metals which are often in short supply. The value of nickel and chromium lost in plating wastes in the United States has been estimated at 25 to 30 million dollars. There are between 15 and 20 thousand metal finishing facilities in the United States alone. It has been shown that some of the larger commercial metal finishing installations each year discard sludges containing metals valued at $150,000 to $200,000 and often pay in excess of $50,000 for hauling these sludges to disposal sites (Reference 4). The total estimated loss of Ni and Cr alone is 25-30 million dollars annually (Reference 23).

B. Background

The Air Force operates five Air Logistics Centers that maintain metal plating operations. Effluent limitations for one base which houses such a facility are listed in Table 1. There is concern that the discharges from these bases may not comply with the effluent limits, especially with regard to metal discharge requirements. Because of this concern, the Air Force has undertaken a program to review waste treatment practices at their metal finishing facilities.

TABLE 1. EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS:
INDUSTRIAL WASTE TREATMENT PLANT EFFLUENT,
TINKER AFB OK (NPDES PERMIT NO. OK0000809)

EFFLUENT CHARACTERISTIC	DISCHARGE LIMITATIONS (Lb/day)	
	Daily Avg	Daily Max
Flow (MGD)	-	-
COD	312	938
Total Suspended Solids	125	280
Cadmium	.12	.54
Chromium, Total	.62	2.70
Chromium, Hexavalent	.30	.90
Cyanide, A	.03	.14
Copper	.07	.32
Lead	.37	1.66
Nickel	1.25	5.62
Zinc	.62	2.70
phenols	.05	.22
Oil and grease	125	280
Cyanide, Total	.06	.27
pH	Not less than 6.0 standard units nor greater than 9.0 standard units	

There shall be no discharge of floating solids or visible foam in other than trace amounts.
Effective Dates: 7-01-77 through 12-15-79
Monitoring Requirements: Three 24 hour composites per week.

Currently, plating metals are discharged to the base industrial waste treatment plant. These wastes are treated along with a variety of other process wastes, some of which are discharged on a batch basis making treatment difficult. In some of the facilities, wastes from the plating shop are passed through an ion exchange unit in order to recover the process water. In these facilities the ion exchange regenerant is discharged directly to the treatment facility as a slug, complicating the treatment scheme and rendering efficient metal removal impossible.

The Air Force is currently considering modification of their metal-finishing operations in order to reduce the total mass discharged and investigate the feasibility of recovery and reuse of plating metals. This basically would involve segregating the plating waste from other waste streams for separate treatment.

Current plans call for concentration of finishing wastes through ion exchange units, precipitation of metals, dewatering of the precipitant slurry, followed by disposal of the concentrated sludge or recovery/recycling of metals.

C. OBJECTIVES

It is noted that while many methods have been suggested for dewatering/disposal and recovery of plating waste residues, little data exists to show what methods are feasible.

In considering the problems associated with dewatering, it must be determined if these plating waste sludges behave in a fashion similar to those chemical sludges which have been studied previously. If the metal hydroxide sludge properties are in fact similar, these characteristics can be used to predict dewatering efficiencies by a variety of processes, including sand beds, vacuum and pressure filters, and gravity and centrifugal thickening. Also, existing process loading

parameters such as those developed by Novak (Reference 5) and Shaefer (Reference 6) can then be applied for design purposes. If, however, plating wastes are unique in terms of their dewatering characteristics, the special problems which may be encountered with these sludges must be described.

The primary intent of this study then, was to determine the dewatering characteristics of metal hydroxide sludges using laboratory methods as developed by Novak (Reference 5) and make inferences with respect to potential process performance.

As a result of these indirect evaluations a process or processes may be recommended for further study. Studies will be conducted using pure metal hydroxide precipitants to determine some of the variations in sludge character which can be expected as the metal compositions of the waste change.

While the major emphasis is to be on dewatering characteristics a review of potential recovery schemes will also be conducted. Preliminary recommendations based on available technology and economics will be made.

Specific objectives of this study were as follows:

(1) To determine the dewatering characteristics of heavy metal precipitants. The primary characteristics to be determined are the dewatering rate as measured by the sludge specific resistance, the solids concentration in the filter cake, and the coefficient of compressibility of the sludge. These parameters should be sufficient to permit an evaluation of potentially applicable dewatering methods.

(2) To determine the factors which can cause significant variation in sludge properties. These studies will concentrate upon the effects of the pH of precipitation (NaOH as source of hydroxyl ion) and age of the precipitant on sludge properties.

(3) To determine the applicability of polymers for the conditioning of sludges.

(4) Some characterization work was also conducted using existing Air Force sludges or waste streams. These sludges or waste streams may not be entirely representative of future Air Force residues after desirable process modifications are made but provide some data regarding relative metal concentrations and sludge dewatering characteristics. The data for these sludges are included in Appendices A and B.

(5) Perform a literature review of potential recovery options and make a basic economic evaluation.

SECTION II

METHODS AND MATERIALS

A. SAMPLES

The primary source of materials used in this study were pure metal hydroxide sludges prepared in the laboratory. Two other sludges were also characterized: a mixed metal hydroxide sludge that was obtained by precipitation of metals from an ion exchange regenerant solution generated at Tinker AFB, Oklahoma, and a sludge from the waste treatment plant at Hill AFB, Utah. Most of the pure metal hydroxide data was obtained from a chromium (III) hydroxide sludge ($Cr(OH)_3$), but additional data was obtained for nickel (II) and zinc (II) hydroxide slurries.

The chromium sludge was obtained by mixing crystalline chromium (III) nitrate $Cr(NO_3)\cdot 9H_2O$ with water to obtain a solution of chromium (Cr^{+3}) and nitrate (NO_3^-) ions. The chromium hydroxide was then precipitated by adding a concentrated solution of sodium hydroxide during continuous mixing on a magnetic mixer to the pH level desired. Nickel hydroxide and zinc hydroxide sludges were obtained by adding sodium hydroxide to solutions of $NiCl_2$ and $ZnCl_2$. Solutions were generally prepared at 1000 mg/l of total salts prior to precipitation.

The mixed metal hydroxide sludge was obtained by adding the concentrated sodium hydroxide solution to the acid regenerant waste stream. This backwash solution was sent to the University of Missouri in 55-gallon drums. Because of delays in sample collection and transportation, no samples were characterized until at least six weeks after collection.

B. SOLUBILITY STUDIES

Limited solubility studies were conducted to determine if mixtures of metal ions would follow the theoretical solubility versus pH patterns

for the individual metal ions. It was expected that the heterogenous solution would precipitate as complex metal mixtures due to the tendency of these metals to adsorb on the surface of precipitating metal hydroxides.

Soluble metal concentrations were determined by filtering a portion of the precipitated supernatant liquor through a 0.45-micron membrane filter and the metals in the filtered portion determined using atomic adsorption spectrometry.

C. SLUDGE CHARACTERIZATION

1. Parameters

Filtration

The bench scale filtration test was performed using a 9-cm Buchner funnel, No. 40 ashless filter paper, a 100-ml graduated cylinder and a vacuum pump. One hundred ml samples of the sludge were filtered at a vacuum pressure of 15 inches mercury, and the time of filtration was recorded for each 10-ml increment of filtrate accumluated in the graduated cylinder.

Specific Resistance

Specific resistance is a measure of the internal resistance of a sludge cake to the passage of water. The rate of filtration is inversely proportional to the specific resistance as follows:

$$\frac{dv}{dt} \propto \frac{1}{r^n}$$

where dv/dt is the volume of filtrate passing through the sludge per unit time and r is the specific resistance of the sludge. Thus, specific resistance can be used as an index of dewatering rate. As the

specific resistance increases, the time required for filtration also increases.

The specific resistance for each sludge was calculated according to the equation given by Eckenfelder (Reference 7)

$$r = \frac{2bPA^2}{\mu c}$$

where:

r = specific resistance (m/Kg)*

b = slope of t/V versus V plot (sec/m^6)

t = time (sec)

V = filtrate volume (m^3)

P = vacuum pressure (N/m^2)

A = filtration area (m^2)

μ = filtrate viscosity ($N\text{-}sec/m^2$)-assumed to be identical to water at 20^oC

$$c = \frac{1}{\frac{100 - c_i}{c_i} - \frac{100 - c_f}{c_f}} \quad (Kg/m^3)$$

c_i = initial solids concentration (%)

c_f = filter cake solids concentration (%)

c = weight of solids deposited per unit volume of filtrate

*Note: Specific resistance is often expressed in units of sec^2/gm. These units are based upon the use of incorrect units for pressure and filtrate viscosity. To convert to the correct units of meters/Kg, specific resistance as sec^2/gm should be multiplied by 980 (Reference 8).

Except where otherwise stated, the vacuum pressure was maintained at 15 inches of mercury. Prior to each filtration the initial solids concentration was measured for the test, and the cake solids concentration was measured after the sample had been filtered to the extent that a crack formed in the filter cake. Solids were measured as grams dry solids remaining after drying at 103^oC per total grams of sludge.

Compressibility

The coefficient of compressibility of a sludge can be determined, according to Eckenfelder (Reference 7), by the following equation

$$r = r_o P^s$$

where r_o = value of specific resistance at log P = 1

r = specific resistance at pressure P

s = coefficient of compressibility

The values of specific resistance used to calculate the coefficient of compressibility were measured at vacuum pressures of 15 and 10 inches of mercury on identical samples. The coefficient of compressibility was calculated by finding the slope of the line of the plot of natural log specific resistance versus natural log pressure for each sample.

Sludge Thickening Velocity

Sludge interfacial thickening velocities were obtained by measuring the subsidence of the interface with time in 250-ml graduated cylinders. Schaefer (Reference 6) has observed that, for chemical sludges, the thickening velocity is independent of cylinder size. Therefore, small samples could be used to model thickening behavior. The interfacial settling data was plotted against elapsed time, and the slope of the straight line portion of the curve was taken as the settling velocity of the sludge for the initial sludge solids concentrations.

2. Variables:

pH of Precipitation

Pure solutions of Cr (III), Ni(II), and Zn(II) were precipitated at different pH's to determine the effect of precipitation pH on dewatering characteristics.

Age

Sludge samples were prepared as previously discussed at several pH values. These samples were allowed to sit undisturbed in Erlenmeyer flasks in the laboratory at temperatures ranging from 28^{o}C to 31^{o}C for several months. Specific resistance, percent solids, and compressibility were observed at various stages of sludge age.

Polymer Conditioning

Several tests were run using Betz 1120® as a sludge conditioning aid. Betz 1120® is an anionic polymer with a molecular weight of 15 to 20 x 10^{6} with an acrylic acid and sodium acrylite

structure (Reference 9). The polymer solutions were prepared in the laboratory according to the procedure described by O'Brien (Reference 9). To avoid the effect of polymer aging, no polymer solution was used after it was more than one week old. The standard procedure used in this study for adding polymer to the sludge was to place 100 ml of the sludge sample in 500-ml beakers and to mix the samples with a standard Phipps and Bird mixer. After the polymer was added to the sludge sample, the solution was rapid mixed (about 100 rpm) for 30 seconds and then slow mixed (about 30 rpm) for two minutes. The specific resistance at a single pressure, as described earlier, was measured immediately following the slow mix.

D. DEWATERING OPTIONS

Several dewatering options were to be considered for the plating waste residue. These included sand beds, vacuum filters, pressure filters, gravity thickeners, and centrifugation. The acceptability of a sludge for dewatering by any of these methods is determined by several factors. These include:

(1) The solids concentration required for the dewatered sludge.

(2) The purity of the dewatered residue.

(3) The cleanliness of the waste liquid (supernatant, centrate, or filtrate) from the dewatering process.

(4) The ability of the process to perform adequately for the sludge type.

Once a sludge dewatering method is found acceptable, its applicability is determined by cost and operational considerations. Cost and operational requirements are determined largely by the specific sludge dewatering requirements and the volume of sludge to be processed.

The acceptability of each dewatering method can generally be determined from the sludge dewatering characteristics, specific resistance, compressibility, and filter cake solids concentration. The following guidelines may be used to evaluate the acceptability of a process for sludge dewatering.

Sand Beds

To be acceptable for sand-bed dewatering, a sludge must have a coefficient of compressibility greater than 0.7. Sludges with lower coefficients of compressibility will penetrate through a sand bed.

High purity sludges cannot be obtained when using sand beds because some mixing of sand and sludge will occur.

Vacuum Filters

To be acceptable for vacuum filtering, a sludge would ideally have a specific resistance of less than 30×10^{11} m/kg. Vacuum filtering usually provides a moist but handleable cake; however, poor filtrate quality can be a problem.

Pressure Filters

Pressure filters generally perform in the same manner as vacuum filters except that much higher dry solids concentrations can be obtained. Sludges with specific resistance values below 1×10^{13} m/kg and with coefficients of compressibility below 1.0 are generally acceptable for dewatering by pressure filters.

Gravity Thickening

The performance of gravity thickeners can be predicted from measures of the interfacial thickening velocity. Gravity thickeners will not produce a solid capable of being handled but may be useful as a sludge concentration method prior to dewatering by other methods.

Centrifugation

Centrifugation can be used to produce a semi-solid material for either recovery or ultimate disposal. Centrifuged sludges are often of the consistency of wet concrete so they must be handled in vehicles that are leak proof. The centrate from centrifugation processes is seldom clear, and solids removals in the centrate of greater than 95 percent are seldom attainable.

SECTION III

THEORY, RESULTS, AND DISCUSSION

A. SOLUBILITY STUDIES

The metals which are present in plating wastes are known to form insoluble metal hydroxide precipitates over specific pH ranges. Solubility diagrams for the metals used in this study are shown in Figure 1. Chromium attains a minimum solubility at pH 8; zinc and nickel attain a minimum solubility near pH 10. Cadmium requires a pH of approximately 12 to attain minimum solubility. However, Thomas and Thies (Reference 10) have shown that $Cr(OH)_{3(s)}$ may form stable colloid suspensions. Ultimately metal precipitation occurs through coagulation by charge neutralization and is dependent upon the anions in solution and the presence of other metal precipitants. The neturalization of colloidal charge can occur through adsorption of counter ions or by pH adjustment to the point of zero charge (PZC). At pH levels below the PZC, the colloids will be positively charged ($Me\ (OH)^{+}$), and above the PZC they will be negatively charged ($Me\ (OH)_{z}^{-}$). In either instance, a stable colloidal suspension will result. When metals are mixed such as in the case of a bimetal mixture, the PZC tends to be a pH somewhere between the PZC for the two pure metal hydroxides. The PZCs for several pure metal hydroxides were obtained from the literature by Thomas and Thies (Reference 10) and are presented in Table 2.

An example of the effect of varying chromium levels on nickel precipitation can be seen in Figure 2. As the fraction of chromium in solution increases, the pH at which metal precipitation occurs decreases. The reduction in the nickel concentration to below its solubility level as $Ni(OH)_2$ suggests that nickel is being precipitated along with the chromium hydroxide.

Likewise, the presence of chromium will result in zinc insolubilization and precipitation at a pH below that required for pure zinc alone.

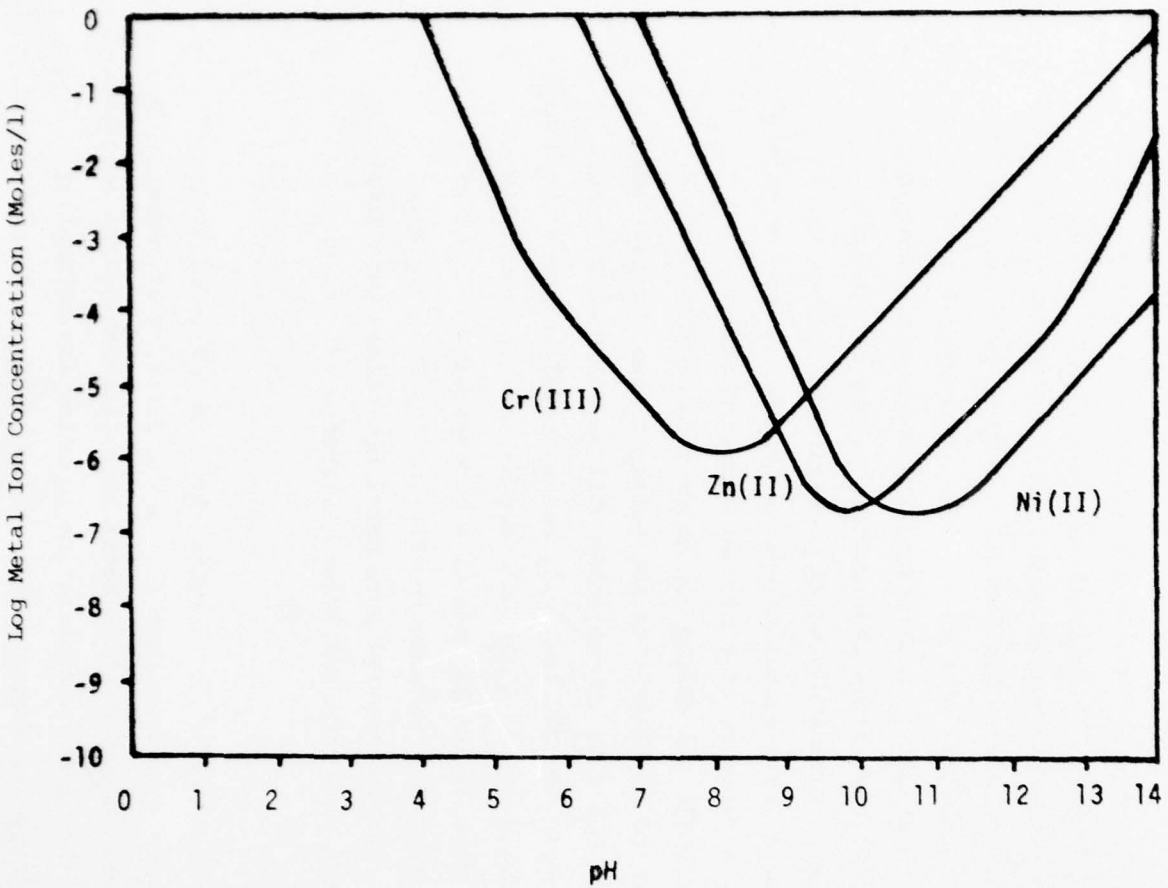


Figure 1. Concentration of Soluble Metal Ion Hydrolysis Products as a Function of pH-after Patterson et al (Reference 2)

TABLE 2. POINT OF ZERO CHARGE FOR METAL HYDROXIDES (From Thomas and Thies (Reference 10))

Metal Hydroxide	PZC (pH)	
$Cr(OH)_3$*	7.0	7.8
$Fe(OH)_3$		8.5
$Zn(OH)_2$		10.3
$Cd(OH)_2$		10.5
$Ni(OH)_2$		11.1

*Two references report different values

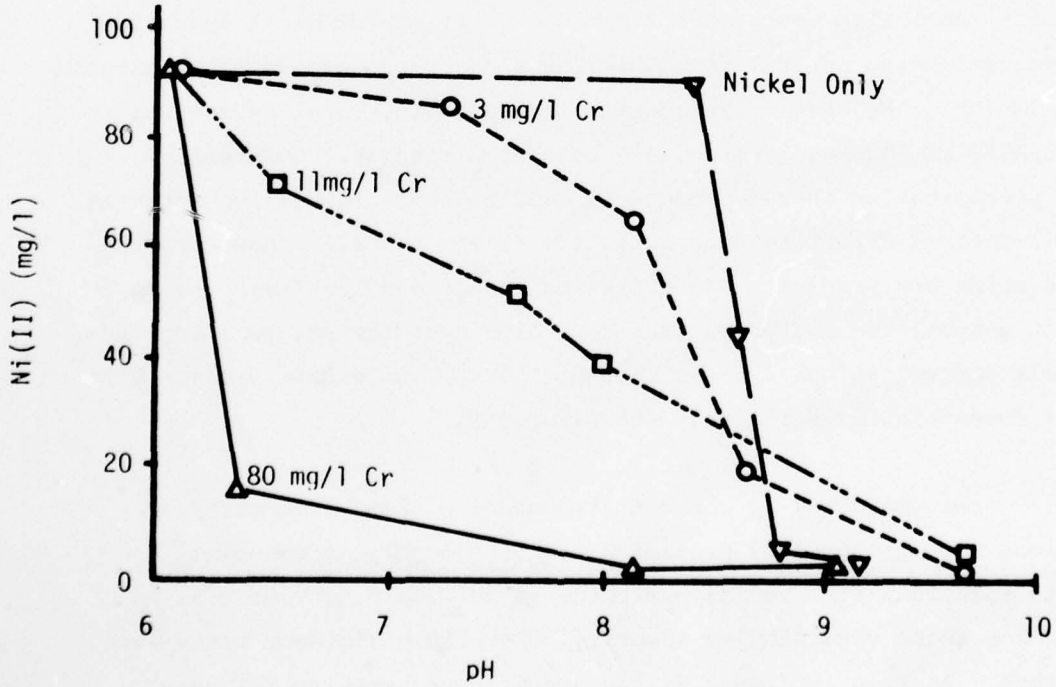


Figure 2. Effect of Chromium on Nickel (II) Concentration in the Supernatant Liquor Following Precipitation and One Hour of Settling

Thomas and Thies (Reference 10) have suggested that the inclusion of cationic impurities in a metal hydroxide floc will result in a shift in the PZC and therefore change the pH range for colloidal precipitation. For solutions of mixed metals, it can be expected that the pH for precipitation will depend upon the major components and their relative compositions. For plating waste residues, the operational pH for metal removal in a treatment facility can be expected to change as the plating operation changes. When nickel and cadmium are major waste components, higher pH levels may be necessary for efficient metal removal. When chromium dominates, lower pH levels may be used.

B. SLUDGE CHARACTERIZATION STUDIES

1. Precipitation pH. It is known that the composition of metal hydroxides will vary with pH. Stumm and Morgan (Reference 11) have discussed the chemistry of iron and aluminum at length. Metal hydroxides generally react with hydroxyl ion to form a variety of metal hydroxide species, including neutral insoluble forms ($Me(OH)_y^o$) and various charged forms ($Me(OH)_x^+$, $Me(OH)_z^-$). In addition, many of the metal hydroxides are capable of forming intermediate polymeric species. Eventually, metal precipitation should produce an aged ordered crystalline material of well-defined structure and properties (Reference 12). However, the metals which are precipitated in plating operations are fresh and may vary in composition and properties depending upon the pH, reaction time, and salt concentration. It was thought that pH would have a major effect on the dewatering properties of the sludges.

For the study of chromium hydroxide sludge, five chromium solutions were prepared by precipitating five identical chromium nitrate solutions with sodium hydroxide at pH 8.0, 8.5, 9.0, 9.5, and 10.0. For these five samples identical specific resistance tests were performed. As seen in Figure 3, the specific resistances of these samples seemed to be affected either directly or indirectly by the pH of the solution. For these five samples, as the pH increased, the specific

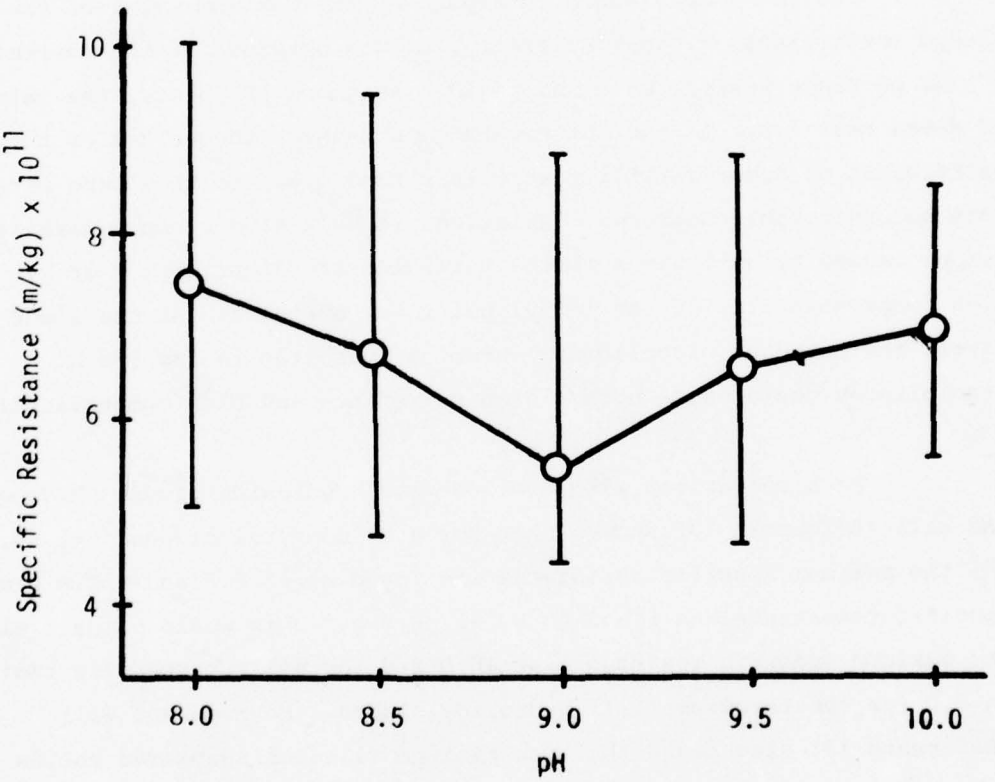


Figure 3. Effect of the pH of Precipitation on Specific Resistance for a Chromium Hydroxide Sludge. Values represent eight replicates at an applied vacuum of 15 inches of mercury

resistance decreased until it reached its minimal value at pH 9.0 and then began to rise again.

The filter cake solids concentration shown in Figure 4 was a maximum at pH 8, was slightly lower over the pH range from 8.5 to 9.5, and then dropped substantially at pH 10.0 The change in cake solids was from 16.8 percent at pH 8 to a low of 12.9 percent at pH 10.0, a decrease of about 2 percent.

For the sample shown in Figure 5, the maximum value of the sludge coefficient of compressibility, s, was obtained at the extremes of the pH range tested, pH 8 and pH 10. At these pH points, the value of s was near 1.0. At the intermediate pH ranges, the values of the coefficient of compressibility were less than 0.6, and they were erratic with no predictable pattern. Variations in bulk sludge compressibility can be caused by variations in the particle size distribution or by high compressibility of the individual floc particles. At the lower pH level, the presence of colloidal chromium hydroxide in the fresh precipitates could cause both a high resistance and high compressibility.

As a comparison with a mixed-metal hydroxide sludge, McVaugh and Wall (Reference 13) showed that for a mixed-metal sludge (Cr, Fe, Pb, Zn) the maximum specific resistance was found at pH 9.8 and the minimum specific resistance was found to be at pH 8.5. This would compare with the maximum specific resistance at 10.0 and the minimum specific resistance at 9.0 for the chromium (III) hydroxide sludge. McVaugh and Wall (Reference 13) also found that the minimum filtrate suspended solids were obtained at a process pH of 9.5, and the maximum suspended solids were obtained at a process pH of 8.5. They found that the maximum cake solids were obtained at process pH 9.2 and the minimum filter cake solids at pH 9.8. Their filter cake solids varied from 24.1 percent to 25.3 percent, whereas the chromium hydroxide sludges in this study were less than this value but did tend to decrease as the pH increased, the same as experienced by McVaugh and Wall (Reference 13).

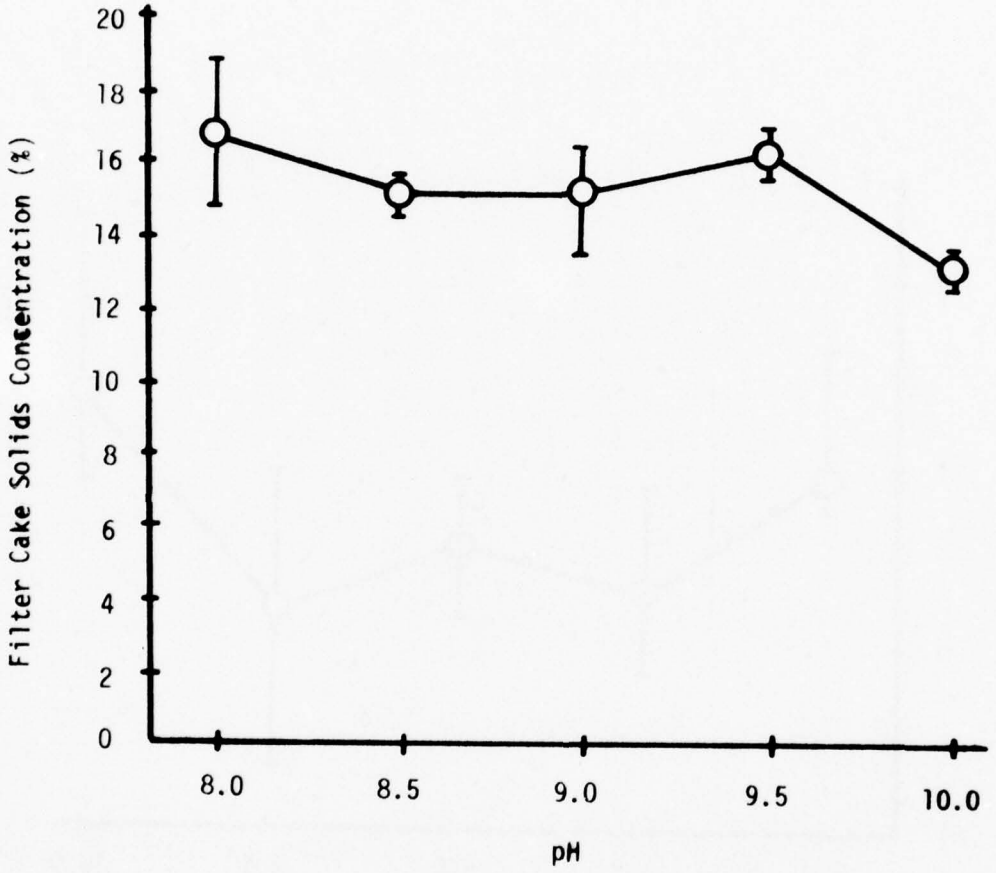


Figure 4. Effect of the pH of Precipitation on Filter Cake Solids Concentration for a Chromium Hydroxide Sludge. Samples represent six replicates at an applied vacuum of 15 inches of mercury

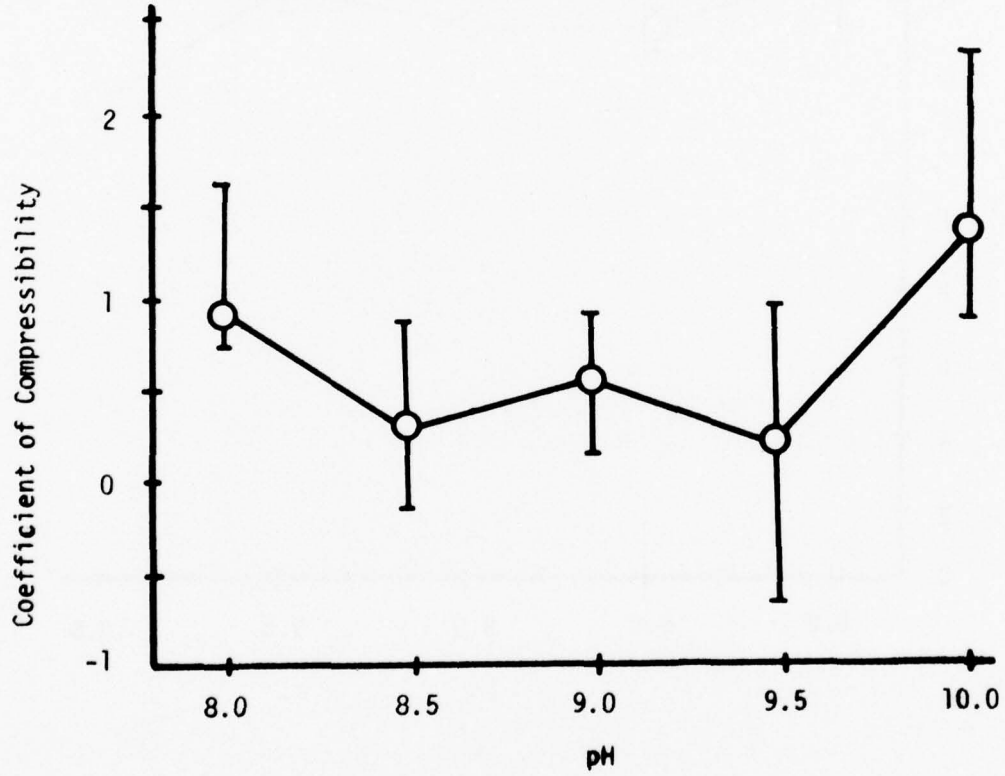


Figure 5. Effect of the pH of Precipitation on the Coefficient of Compressibility for a Chromium Hydroxide Sludge. Samples represent six replicates at an applied vacuum of 15 inches of mercury

The pH tests described herein show that the values of cake solids, specific resistance, compressibility, and intial solids are not totally dependent upon the process pH. Thomas and Theis (Reference 10) have shown that the effectiveness of pH adjustment for coagulation and sedimentation of chromium hydroxide colloids is related to the other cations and anions in the solution. The ionic composition of the solution could also influence the sludges generated in this study. However, it is more likely that the aging effects which are considered in another section of this report had a greater influence on sludge properties. Some of the sludges were generated at temperatures as high as $40^{o}C$, and fresh sludges were characterized over a period of two days. This would permit the aging reactions to occur and alter the sludge properties from other fresh sludges collected at lower temperatures and immediately characterized.

The specific resistance and coefficient of compressibility were also determined for zinc and nickel hydroxides as a function of the precipitation pH. As can be seen in Figure 6 and 7, the nickel hydroxide had a much greater specific resistance value than either the zinc or chromium hydroxide sludges. Sludges which dewater well will generally have specific resistance values below 20×10^{11} m/kg while poorly dewatering sludges generally exceed 100×10^{11} m/kg.

The nickel hydroxide specific resistance was in the range of 300 to 500×10^{11} m/kg as compared to chromium and zinc hydroxides with r values in the range of 4 to 25×10^{11} m/kg. This places nickel among the worst sludges encountered in wastewater treatment and is comparable to some of the septic biological sludges.

All pure metal hydroxide sludges had coefficients of compressibilities which were at a minimum near pH 9 but increased as the pH of precipitation was raised. The coefficient of compressibility is a useful indicator of the effect of pressure on the sludge dewatering rate. A sludge with a high coefficient of compressibility will deform

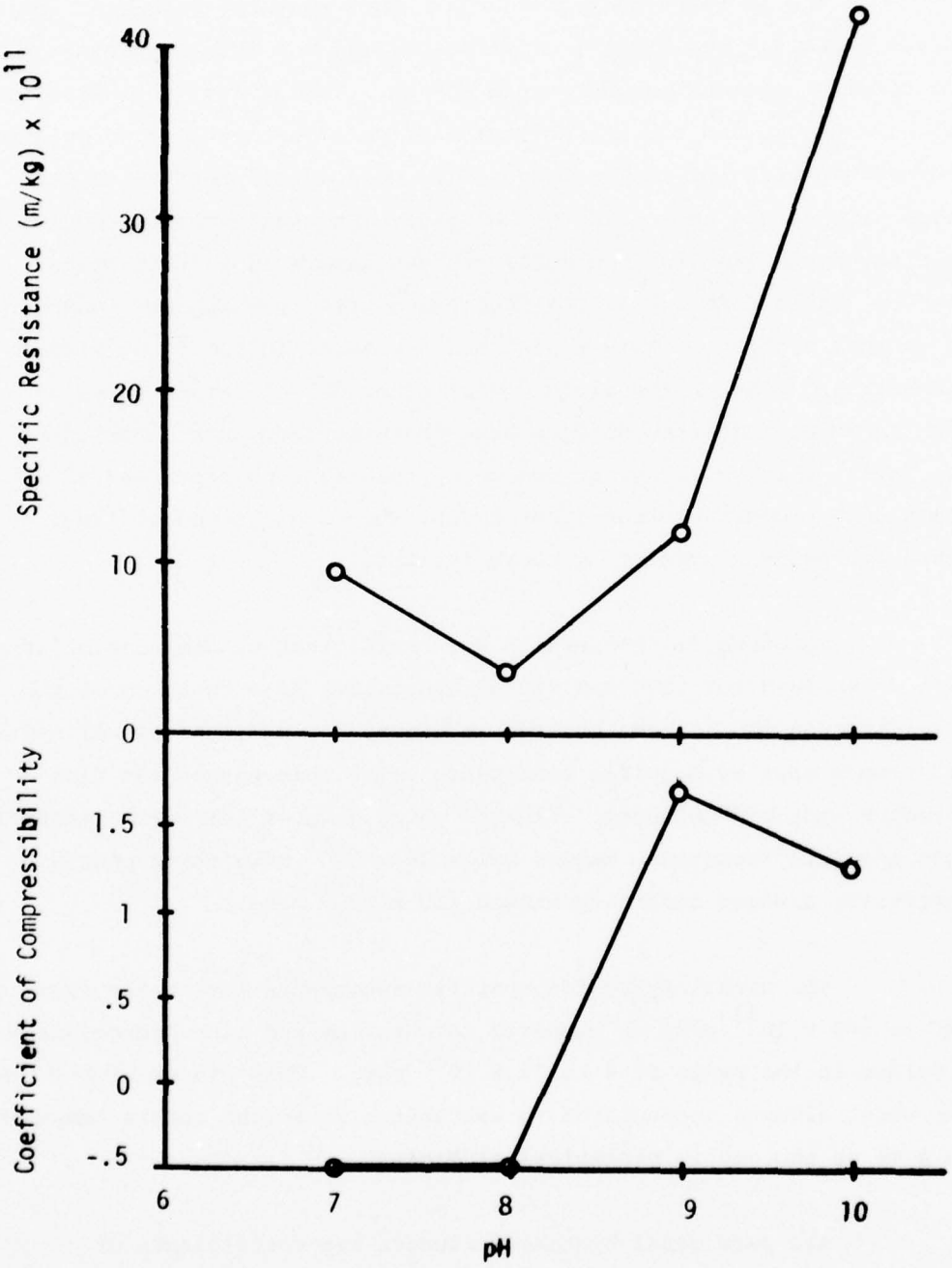


Figure 6. Variation in Specific Resistance and Coefficient of Compressibility with Precipitation pH for a Zinc Hydroxide Sludge. Values represent a single test run

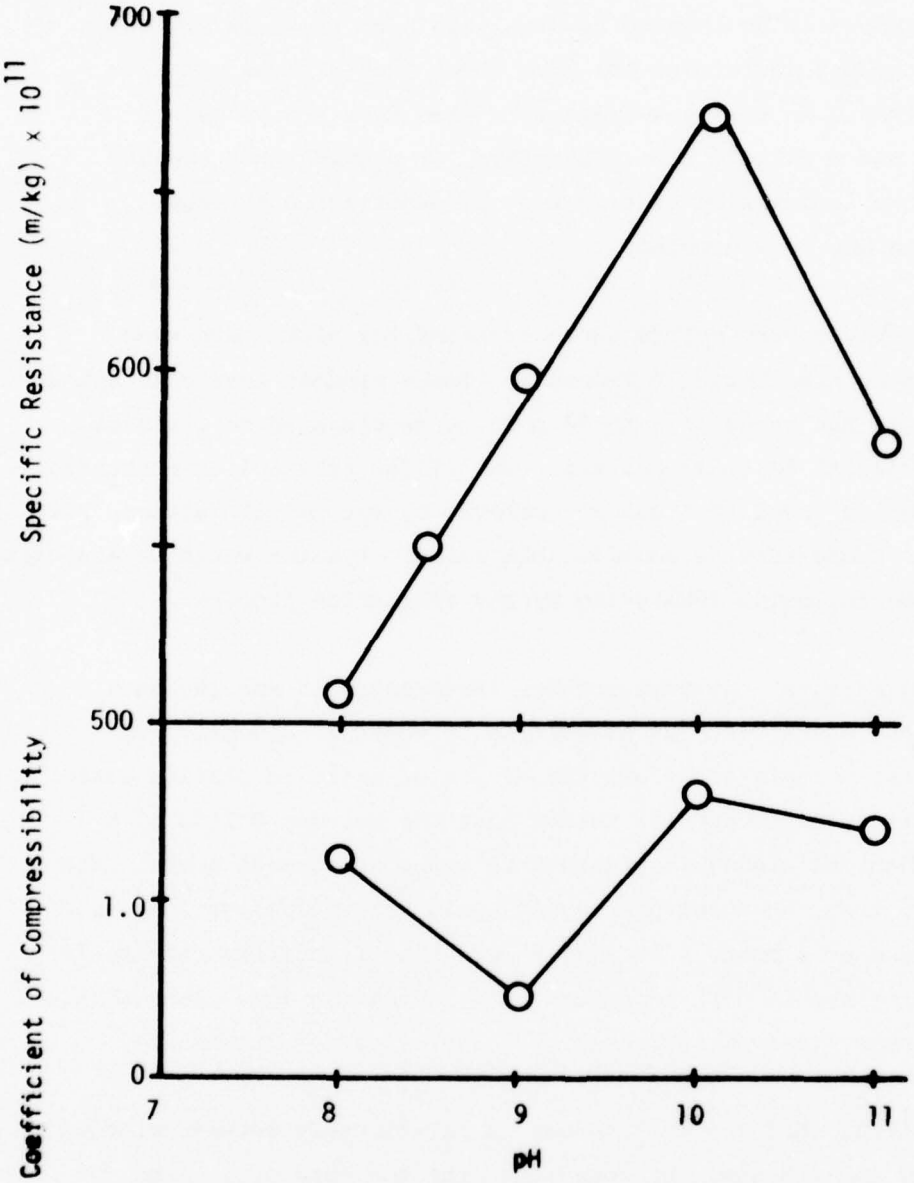


Figure 7. Variation in Specific Resistance and Coefficient of Compressibility with Precipitation pH for a Nickel Hydroxide Sludge. Values represent a single test run.

under pressure and resist dewatering while sludges with s values less than 1 can be expected to respond favorably to high pressure processes. Novak and Montgomery (Reference 14) have shown that sludges with low s values (less than 0.6) will penetrate into sand beds and produce a poor filtrate and a clogged bed. Therefore, it appears that because low s values are common with plating wastes, penetration through filtering media may be a problem.

The filter cake solids concentrations for nickel and zinc hydroxide sludges are listed in Figure 8. These sludges have cake solids concentration in the range of 8 to 14 percent as compared to chromium hydroxide sludges at 12 to 17 percent. The filter cake solids concentration selects the solids level that can be achieved by vacuum filtration. For the pure metal hydroxides, a considerable amount of water would be associated with the sludge following dewatering by any filtration process.

2. Aging Effects. Several authors (References 15 and 16) have shown that aging can affect the properties of chemical sludges. Of special interest to this study was the effect of aging on plating waste sludges. Calkins (Reference 15) showed that the percent solids of a water plant chemical sludge increased with aging of several weeks. His data indicated that the aging phenomenon would take place over a period of several weeks or a month. He also showed that filtration cake solids and specific resistance both increased with increasing age. Some of his specific resistance values increased by a factor of as much as 2.4.

Luttrell (Reference 17) showed a relationship between sludge compactability and its age. He found that the tendency of an iron hydroxide sludge to compact took place over a period of about six weeks. In his work the maximum percent solids in settled sludge was obtained following 39 days of aging. After this period of time the settled solids had increased by 16 percent. Luttrell also showed that his fresh sludges appeared to be more hydrophyllic than the aged sludges.

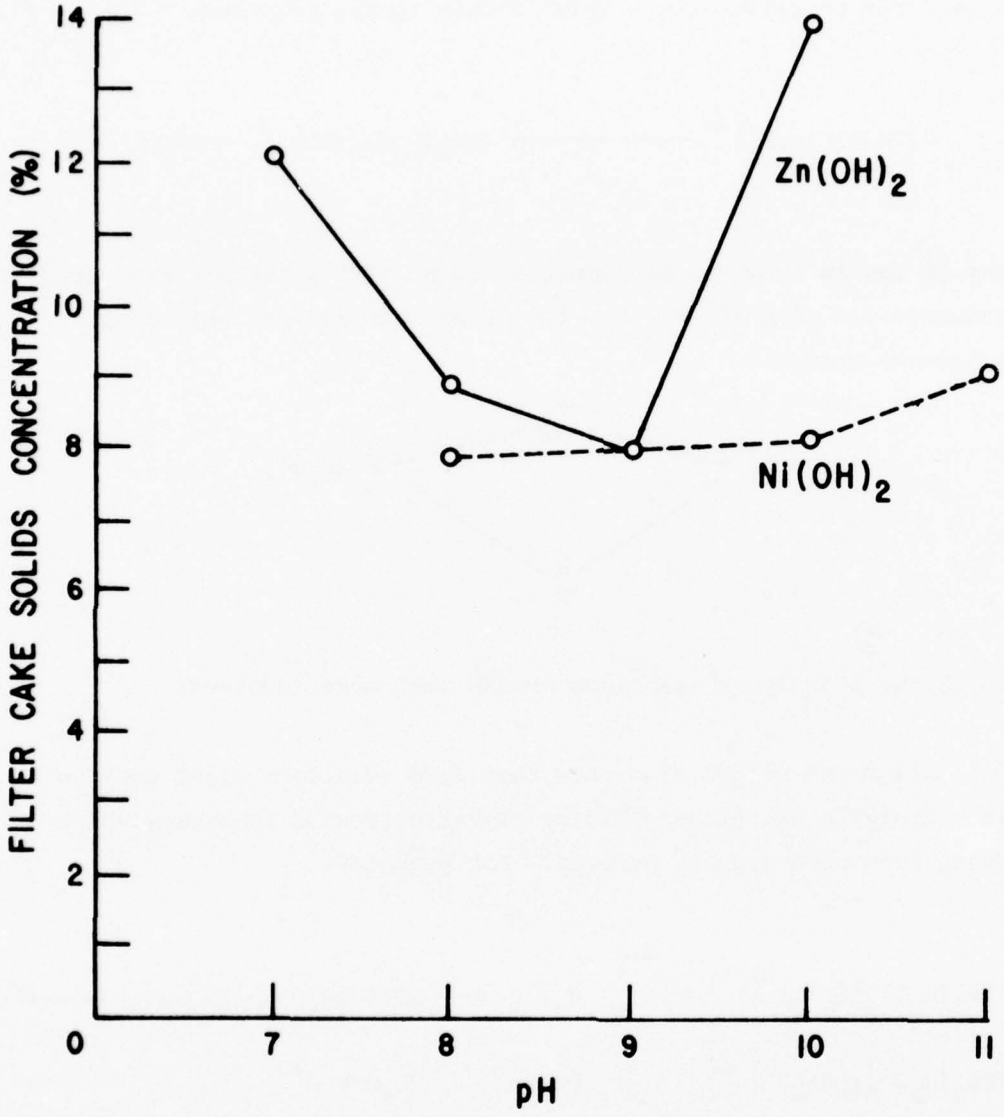
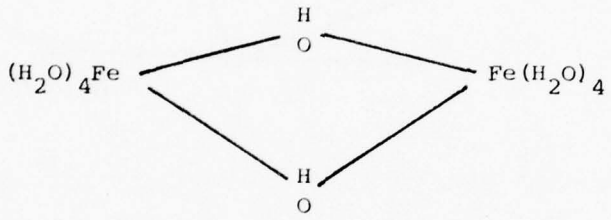


Figure 8. Effect of pH of Precipitation on Filter Cake Solids Concentration for a Zinc and a Nickel Hydroxide Sludge. Values represent a single test run

Stumm and Morgan (Reference 16) show that ferric hydroxo complexes have a tendency to polymerize. This is seen in the reaction:

$$2(Fe(H_2O)(OH))^{++} \longrightarrow (Fe_2(H_2O)_8(OH)_2^{4+} + 2H_2O$$

The dimeric ion is shown to be stable in iron (III) solutions that are more concentrated than 10^{-4}M. The two metal ions are probably bound by two hydroxo bridges:



At high pH the hydrolysis reactions become much more involved.

Stumm and Morgan also show that aged solutions might undergo further hydrolytic reactions yielding higher hydroxide complexes which could then form more hydroxo bridges. For example:

$$(Fe_2(H_2O)_8(OH)_2)^{4+} + (Fe(H_2O)_5(OH))^{2+} \longrightarrow$$

$$(Fe_3(H_2O)_5(OH)_4)^{5+} + 7H_2O + H^+$$

As the charge of the iron (III) species decreases through coordination with hydroxo groups, the repulsion between the ions decreases and the tendency toward polymerization is increased. Eventually, colloidal hydroxo polymers, and ultimately, insoluble hydrous ferric oxide precipitates are formed. In the same article Stumm and Morgan state that it was evident from the observed pH decrease that, during the aging process, the extent of coordination of Fe (III) with OH^-

progressively increases. Also, the aging reactions are more rapid in solutions having higher hydroxide concentrations or at elevated temperatures.

Feitknecht and Schindler (Reference 12) have shown that at low pH the freshly precipitated products are more active (monomeric hydroxide) than the aged products (polymeric hydroxides). They also showed that at high pH, where the metal solution is supersaturated with hydroxide ions, nucleation and nuclear growth are decreased. This results in initial formation of an inactive (aged) form of metal hydroxide. The presence of the high hydroxide concentration seems to aid the aging process in that several intermediate steps are eliminated.

It is seen that the fresh precipitate is amorphous or crystalline with a disordered lattice and an aged precipitate has larger more ordered crystals (Reference 17). Aging appears to be a process of polymer formation of the metal hydroxide which tends to arrange the particles into ordered crystals. This is a dynamic process over the period of aging that is aided by the introduction of supersaturated hydroxide concentrations. The aging process is also accelerated by elevated temperatures (Reference 11). The aging process can be illustrated by the following equation for the aging of chromium:

$$Cr^{+3} + OH^{-} \longrightarrow Cr_x(OH)_y \longrightarrow Cr(OH)_3$$

Increasing age $\longrightarrow$

The middle product in this equation, $Cr_x(OH)_y$, can include both mononuclear complexes, $CrOH^{+2}$, $Cr(OH)_2^{+}$ and $Cr(OH)_4^{-}$, and polynuclear complexes, $Cr_6(OH)_{12}^{+6}$ and $Cr_{12}(OH)_{30}^{+6}$ (Reference 12). These disordered materials may be quite porous when subjected to filtration because they are relatively incompressible.

In the laboratory a series of tests were performed at several pH levels to determine the effect of age on the characteristics of a chromium (III) hydroxide sludge. The effect of sludge age on the cake solids, coefficient of compressibility, and specific resistance of the sludges was observed.

For chromium hydroxide precipitates, the cake solids for 15 inches of mercury vacuum filter pressure varied for the different sludge ages and at the various pH levels, as seen in Figure 9. From this figure it is seen that, although the cake solids generally tended to increase with increasing age, the change in solids was not large.

The specific resistance values at all pH ranges were higher after aging for 24 days than the values for specific resistance at the one-day and eight-day sludge age. However, the specific resistance of the eight-day sludge was not always greater than that of the one-day sludge, as seen in Figure 10. At pH 8.0 and 8.5, the eight-day value for specific resistance was lower than that of the one-day value while at pH 9.0 and 9.5 the eight-day specific resistance was greater than the one-day value. At pH 10.0, the eight-day and one-day specific resistance values were almost identical. After 24 days of aging the sludges assumed nearly constant values for specific resistance and the coefficient of compressibility (Figure 11). It is apparent that the changes due to aging had a marked impact on the sludge properties, but it is not clear that the theoretical aspects of chromium hydroxide aging can be used to predict these changes. It would be expected that at the higher pH levels the large and more ordered crystalline structure would dewater most readily; however, this is obviously not observed from the measured sludge properties. It is probable that surface charges may be important in evaluating chromium hydroxide sludge dewatering properties.

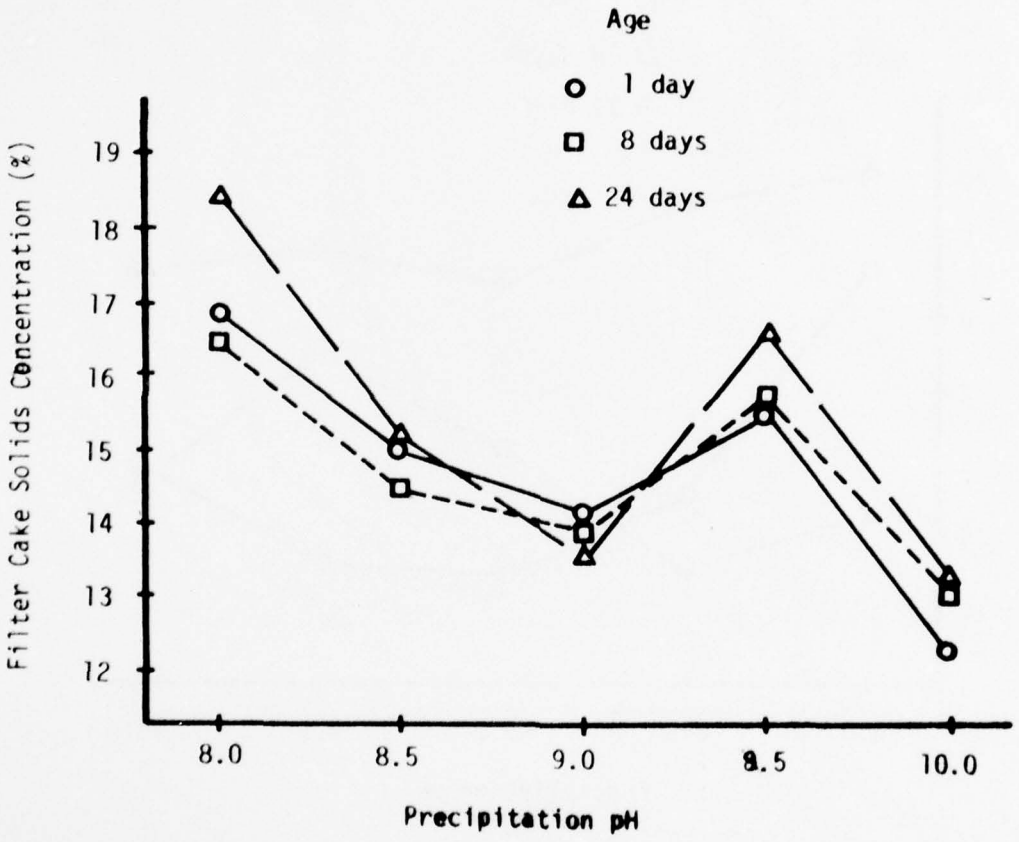


Figure 9. Effect of Aging on the Filter Cake Solids Concentration for a Chromium Hydroxide Sludge

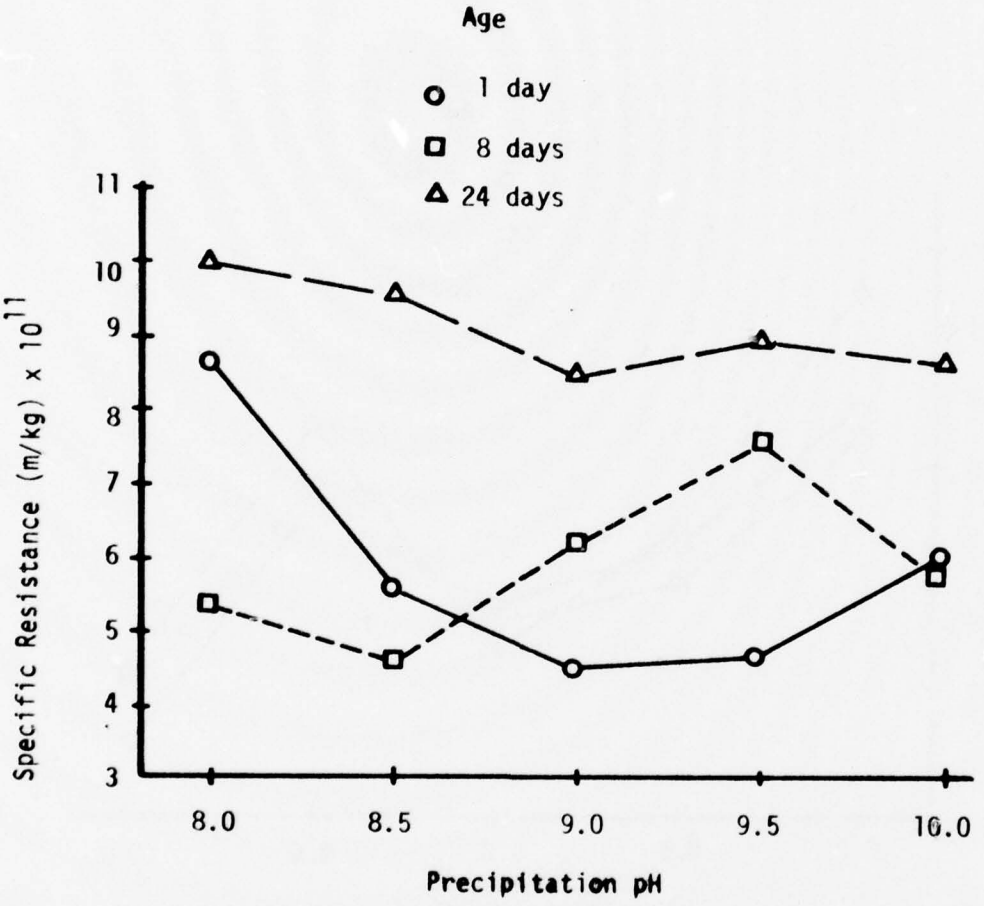


Figure 10. Effect of Aging on the Specific Resistance for a Chromium Hydroxide Sludge

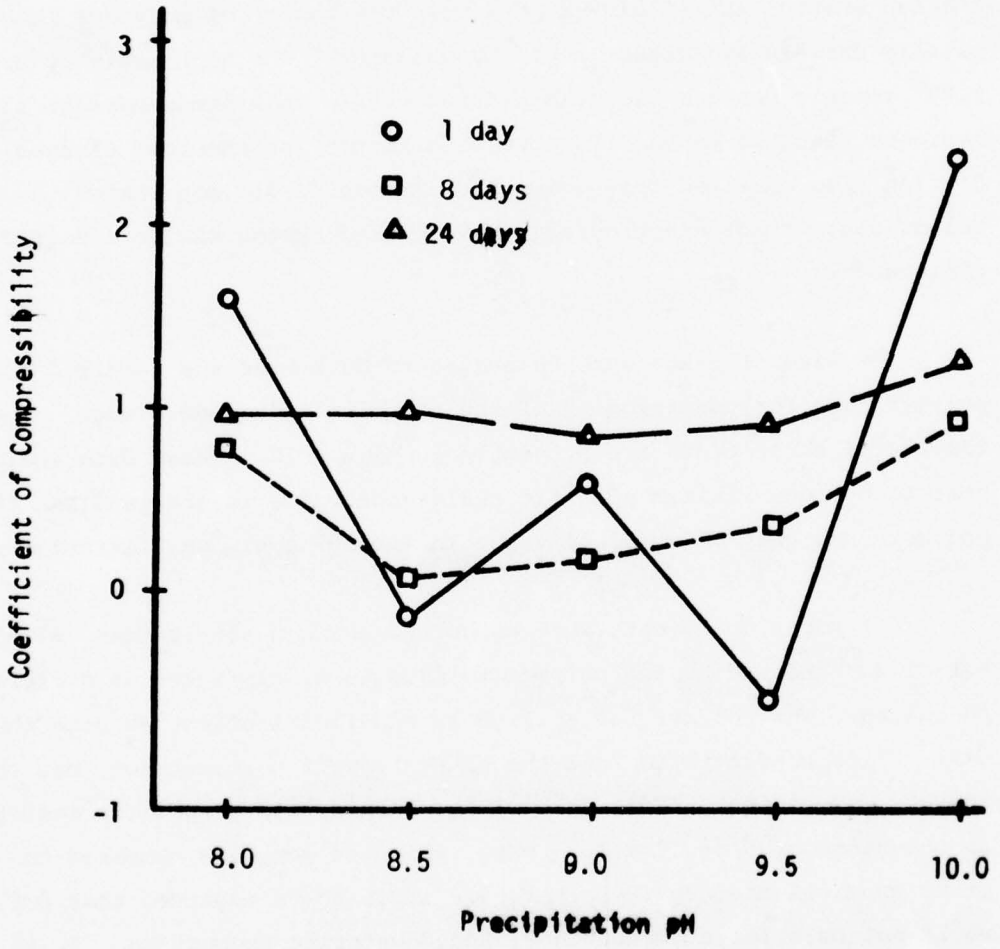


Figure 11. Effect of Aging on the Coefficient of Compressibility for a Chromium Hydroxide Sludge

3. Polymer Effects

Polymers were used to condition chromium hydroxide sludges in order to evaluate effectiveness and the doses required. O'Brien (Reference 9) performed an extensive study to determine the effects of polymer addition on various sludges. In his work polymer effectiveness was found to be dependent upon the pH of the sludge being considered. O'Brien stated that at higher pH levels the choice of polymers is usually between the higher activity anionics. The high activity Betz 1120® anionic polymer was selected for use in this study because it has been found to be an effective conditioner for chemical sludges. O'Brien also observed that polymer conditioning did not change the cake solids concentration appreciably but did reduce the sludge specific resistance.

Several tests were conducted to determine the required polymer dose for conditioning of the chromium hydroxide sludge. The results of these tests are presented in Figure 12. These data indicate that no obvious minimum specific resistance value is obtained and that polymers are only of marginal value in improving sludge filtration rates.

Additional tests were conducted using a single dose, 47 mg/l Betz 1120® and adding the polymer to sludges precipitated at different pH values. The polymer had a slightly beneficial effect on both the cake solids concentration and the sludge specific resistance, but these changes were slight. Since the sludge already has a specific resistance in the range of 5 to 10 x 10^{11} m/kg, which is very low compared to other chemical sludges (Reference 6), it is to be expected that polymers would not have large impact on sludge dewatering properties. It is surprising, however, that a sharply defined minimum resistance is not observed and that polymer overdosing is not apparent.

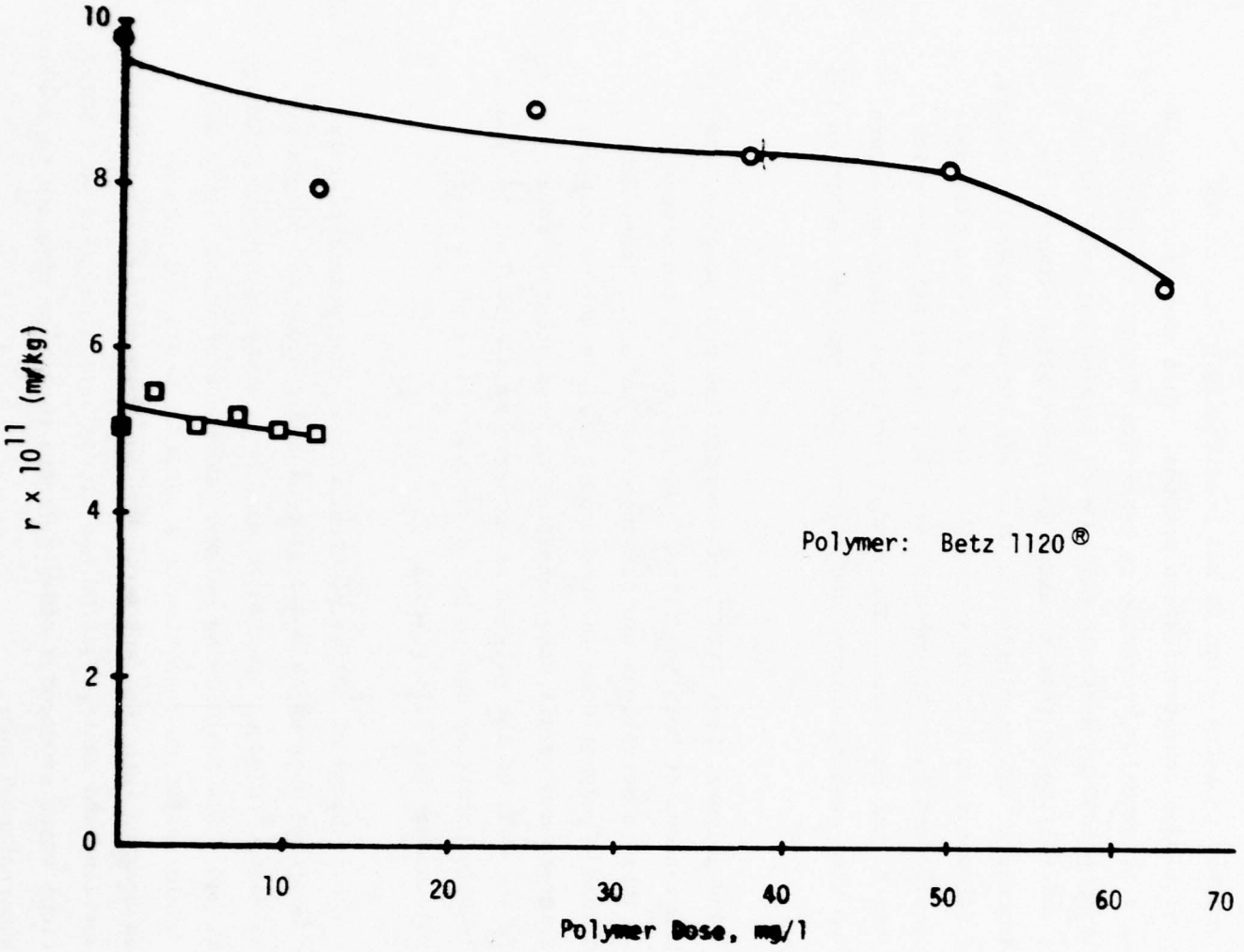


Figure 12. Effect of Polymer on the Specific Resistance of a Chromium Hydroxide Sludge

4. Other Properties

Visual observation of the chromium hydroxide sludge also indicted another property which is not predictable by any of the conventional sludge characterization methods. This characteristic is the tendency of chromium hydroxide to penetrate through the filtering media, either producing a cloudy filtrate or passing entirely through the media and failing to form a cake. The penetration occurred to varying degrees at all precipitation pH levels but was generally random, occurring for one test but not another. A few samples were examined microscopically and found to contain particles in the filtrate which exceeded the filter pore size. The sludge particles appear to deform or break up when passing through the filter media and then reform in the filtrate.

The polymer, Betz 1120®, was added to several samples, and visual observations of both the filter cake and the filtrate were recorded. These observations are presented in Table 3. These data indicated that a polymer dose in excess of 5 mg/l is needed to produce a clear filtrate and permit cake formation to consistently occur. Apparently the role of the polymer is to serve as a coagulant for the metal hydroxide particles and to build stronger flocs which resist penetration through the filter media.

The problems of solids penetration and supernatant clarity were also observed when using model sand beds for study and in gravity thickening tests. Sludges applied to sand beds always penetrated through the media, and a few tests using polymer additions provided little help. Polymers would assist in formation of a cake but would not prevent solids penetration into the sand bed. The supernatant liquor from both gravity settling and centrifugation was cloudy unless polymers were added. The additions which produced a clear filtrate were also adequate to produce a clear supernatant liquor.

TABLE 3. VISUAL OBSERVATIONS OF FILTRATE CLARITY AND FILTER CAKE FORMATION. Cr(III) HYDROXIDE AT A PRECIPITATION pH OF 9.5

Polymer Dose (mg/l) Betz 1120®	Observation
Test 1	
0	Cloudy filtrate - no cake formed
2.5	Cloudy filtrate - little cake formation
5	Partly cloudy filtrate
10	Clear filtrate - excellent cake
20	Clear filtrate - excellent cake
30	Clear filtrate - cake was balled up, indicating polymer overdose
Test 2	
5	Cloudy filtrate - little cake formation
10	Clear filtrate
15	Clear filtrate
20	Clear filtrate

Gravity-thickening tests were conducted for a chromium hydroxide sludge sample, and the results are presented in Figure 13. The calculated flux curve for these data is also presented in this figure. It is apparent from these data that it will be difficult to obtain a gravity-thickened sludge in excess of 2-percent solids.

C. DEWATERING OPTIONS

1. Requirements

In evaluating the process choices for plating waste residues, several requirements were considered necessary for the process to be considered acceptable. These were:

(a) The dewatered solid must be handleable, as defined by Novak (Reference 5). The handleability requirement was thought to be important because the sludge would require handling prior to recovery or ultimate disposal. A handleable sludge is one which does not flow and can be lifted by conventional earth-moving equipment. Such a sludge could be transported and stored without loss of materials due to leakage. In Figure 14, the relationship between the settled solids concentration and the solids concentration achievable by several dewatering processes is shown. Two shear tests were conducted using chromium hydroxide residues to determine if these sludges would also follow the pattern predicted by Figure 14. The sludges, one with a filter cake solids concentration of 10.3 percent solids and another with a filter cake solids of 14.3, were tested for shear strength using a Torvane Shear Tester. The sludges were concentrated by gravity settling for one hour and then vacuum filtered until the discharge had ceased. The shear strength was then measured directly on the sludge in the Buchner funnel. The sludge with 10.3 percent solids had a shear strength of 0.043 ton/ft^2 and the 14.3 percent solids sludge yielded 0.052 ton/ft^2.

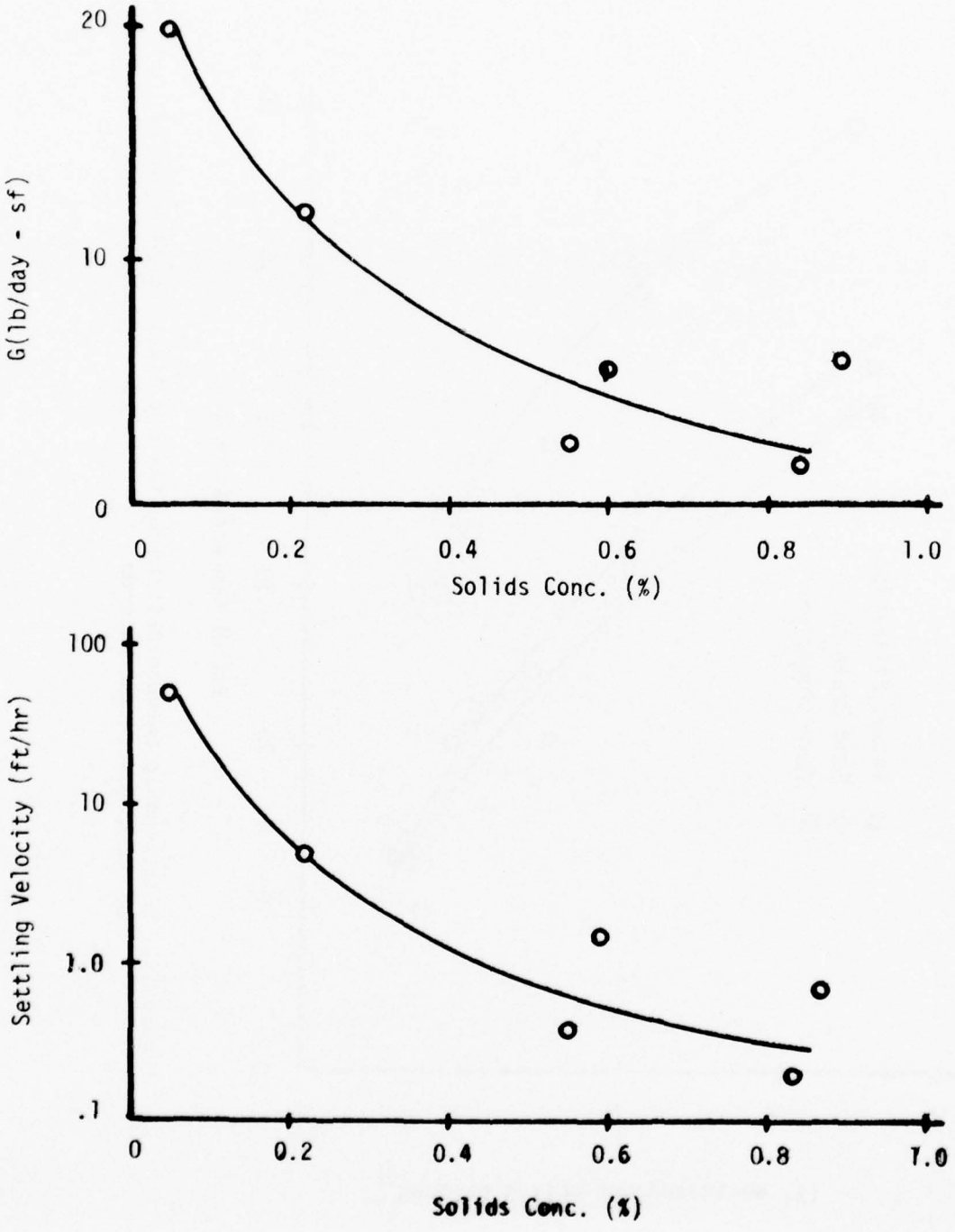


Figure 13. Solids Flux, G, During Thickening and Settling Velocity for a Chromium Hydroxide Sludge

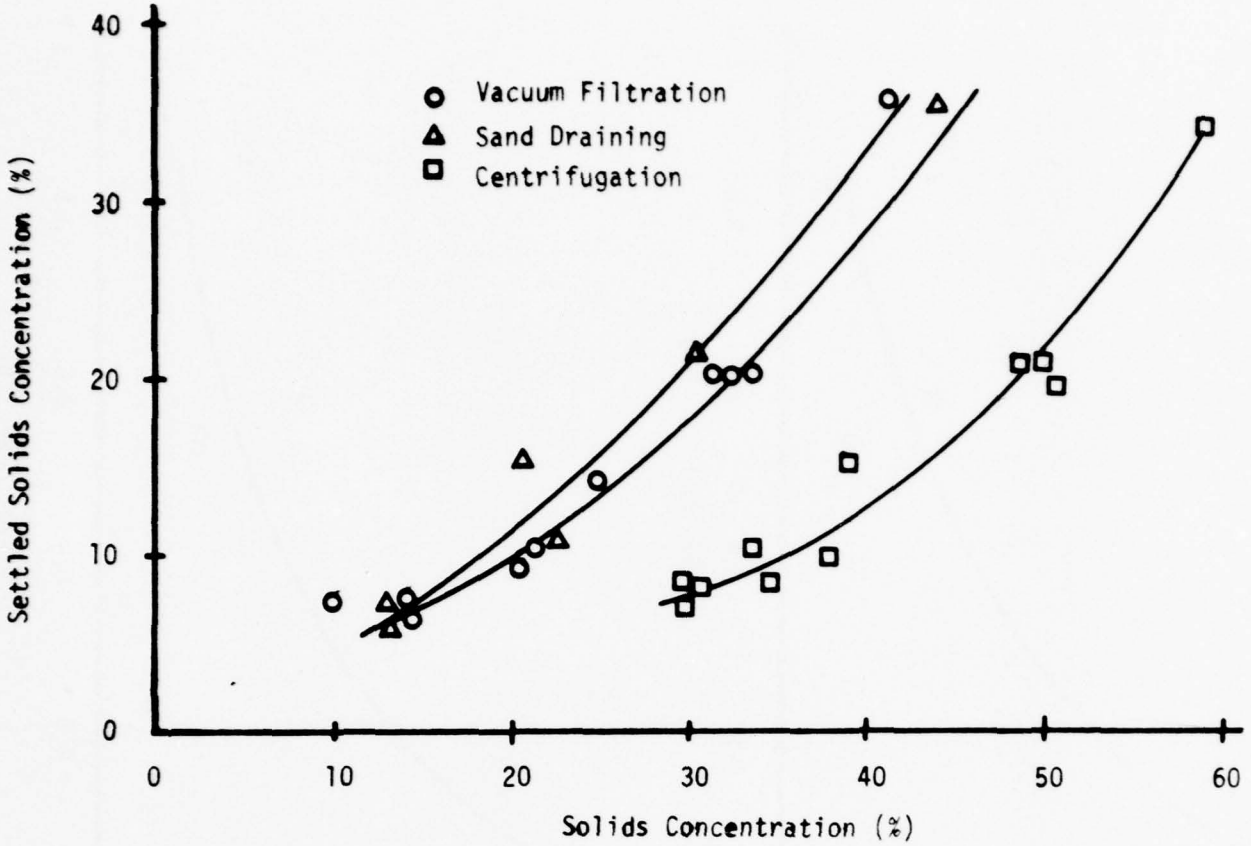


Figure 14. Relationship between Settled Solids and Solids Level Achieved by Other Dewatering Methods

These sludges would be expected to attain a shear strength slightly in excess of 0.04 ton/ft^2, the shear strength necessary for handleability, which indicates that the relationship between settled solids and sludge handleability shown in Figure 14 is probably valid for metal-plating sludges.

(b) The dewatering process should produce a concentrated sludge which is capable of being recovered without extra purification steps.

(c) The process must perform adequately for the sludge to be dewatered. Processes are inadequate if they do not retain or concentrate a high percentage of the waste residue or if they fail to perform under certain conditions. The inability of a sand bed to retain the solids as a cake is an example of such an inadequacy.

2. Evaluation

For the plating waste residues which were tested in this study, it is probable that only vacuum filtration would be acceptable for providing a sludge ammenable to transport and ultimate disposal. Polymer conditioning will also be required to produce a sludge of sufficient floc strength to be retained by filtering media. A high molecular weight anionic polymer with a moderate degree of hydrolysis (15 to 25 percent) was found acceptable for this sludge.

Eckenfelder (Reference 7), Gale (Reference 8), and others have shown that process loading factors for vacuum filters to be used on compressible sludges can be estimated by the formula,

$$Y = \sqrt{\frac{2Pf_c c}{\mu r t_c}}$$

where, Y = filter yield ($Kg/m^2/day$)

P = pressure drop across filter (N/m^2)

f_c = filter form time/filter cycle time

t_c = filter cycle time (days)

μ = filtrate viscosity ($N\ sec/m^2$)

r = specific resistance (m/Kg)

$$c = \frac{1}{\frac{C_i}{100 - C_i} - \frac{C_f}{100 - C_f}} \quad (Kg/m^3)$$

c_f = moisture content after filtration (%)

c_i = initial sludge moisture content (%),

The parameters required to estimate process loading factors can either be derived from operational variables or the specific resistance and filter cake solids data presented earlier.

Pressure filters would be unacceptable because it is unlikely that the strength of the metal plating flocs would be sufficiently strong enough to withstand the pressures encountered in this type of dewatering device. One of the unique properties of chromium hydroxide sludge is the tendency of this material to pass through filtering media which is much finer than the flocs. Although polymers can increase the floc strength to a degree sufficient to retain the floc on a vacuum filter, it is highly unlikely that polymers can increase floc strength for the higher pressure filtering devices.

Centrifuges have found widespread use for sludge concentration because of their small size relative to other processes and because their operation and maintenance are relatively simple. This process will, however, seldom produce a sludge which can be easily handled. Centrifuges are particularly ineffective when used for flocs because these flocs are not easily scrolled, producing a liquor which may contain in excess of 20 percent of incoming process solids. This necessitates complete recirculation of all centrate liquor back through the solids preciptation process.

Even with the drawbacks mentioned above, centrifugation may be useful if the dewatered sludge is to be fed directly into a metal recovery process which is operated in conjunction with the dewatering process. If the sludge does not require transport and handling and the moisture content is not critical, this process can lend itself to automation and is a clean process. Operation of a centrifuge will also require polymer doses in the range of 1 gram of polymer per 200 grams of dry solids in the sludge.

If metal recovery is to be considered, the effect of the polymer conditioning agent and the low moisture content of the sludge (8 to 12 percent) must be considered. If these are not harmful to the recovery process, centrifuges should be considered for sludge concentration.

In laboratory tests with model sand beds, problems were consistently encountered with solids penetration into and through the sand-filtering media. For this reason, sand-bed dewatering is not considered to be applicable to plating waste sludges.

Gravity thickening can be used to concentrate sludges prior to vacuum filtration or centrifugation. Data presented in Figure 13 shows a flux curve for which a settling basin surface area can be calculated once the flow rate and solids concentration in the unit are known (Reference 18). It can be expected that a maximum concentration of 2-percent solids can be obtained by this process.

SECTION IV

METAL RECOVERY

A. ALTERNATIVES

With increasing pressure for metal removal being levied by the regulatory agencies, various methods have been investigated for the treatment of metal-finishing wastewaters. These include electrochemical processes (Reference 19), reverse osmosis (Reference 20), cementation (Reference 21), ion exchange, neturalization-precipitation, and activated carbon (Reference 22). All of these processes are effective in obtaining removal and producing a clean reusable water. Unfortunately, the metals are left behind as a problem. The general method for their disposal is the production of metal sludge which is taken to a landfill for disposal. These metals are, however, becoming more scarce and valuable. Transportation and landfill expenses are rising also. Considering these factors, plus the increasinly stringent regulations concerning landfill usage, the reclamation of the metal waste is now becoming an economical necessity.

Many different methods are being tried for reclaiming this sludge (Reference 24), but common problems are found in all--lack of versatility and inability to handle mixed sludges containing several metals with varying concentrations. Therefore, if the various waste streams in a plating plant can be kept separate, several processes for the recovery of the individual metals exist, with electro-deposition being the most widely used. However, for established facilities where many different metals are being plated, segregation of individual metal sludges may not be practical. A process is needed which can separate several metals at one time. Furthermore, the process must lend itself to automation resulting in reduced labor load. These requirements eliminate multi-technique processes employing combinations of precipitation, distillation, electro-deposition, and others.

Liquid-liquid exchange has all of the above desired requirements. This method has long been used in analytical laboratories for selective separation of metals in multi-component systems with excellent results (Reference 25). It has, however, seen surprisingly limited application in the reclamation of plating wastes. The Bureau of Mines (References 26 and 27) used liquid-liquid exchange to remove Cobalt in the reclaiming of superalloy scrap. This was, however, only one part of a multi-technique procedure. Liquid-liquid exchange also has been evaluated using naphthenic acid in kerosene as the extracting medium (Reference 23). The authors concluded unsatisfactory overall results from this approach. However, naphthenic acid is a non-chelating organic acid and should not be expected to possess sufficient selectivity for different metals in a multicomponent matrix of the type encountered in this situation.

A proposed scheme for the precipitation of metals from electroplating wastes, dewatering of resultant sludges, and recovery of metals by liquid-liquid extraction along with effluent polishing by filtration is shown in Figure 15.

B. ECONOMICS

A tentative economic analysis was made to estimate the value of metals recovered from the rinse water at Tinker AFB, Oklahoma. The concentrations of metals in the rinse water were obtained from a report by The Air Force Weapons Laboratory, Kirtland AFB, New Mexico (Reference 28). They are as follows:

Metal	Concentration (mg/l)
Cr	8.55
Ni	8.7
Cd	0.22
Cu	0.016
Ag	0.36

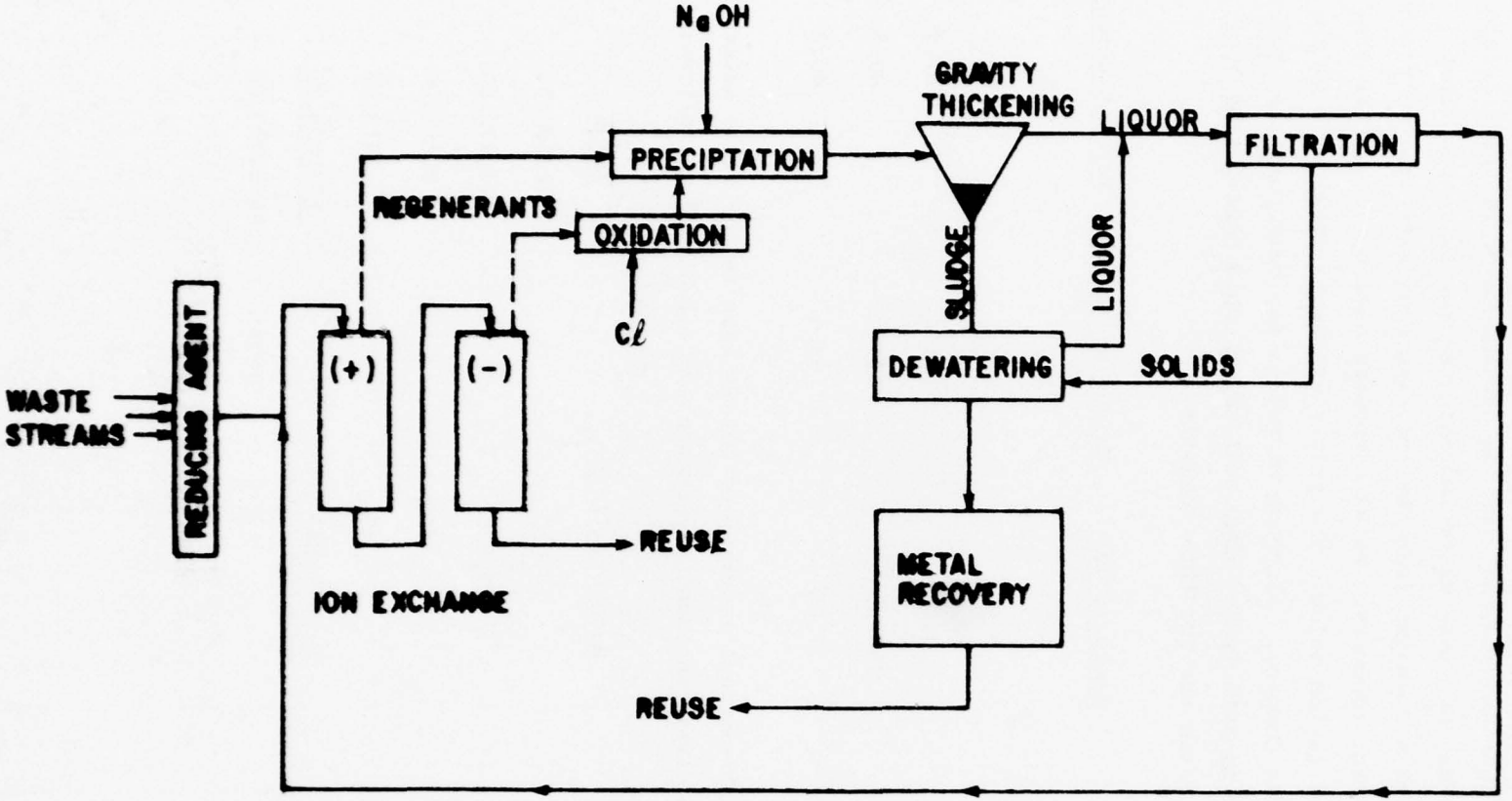


Figure 15. Proposed Metal Recovery and Treatment Process for Air Force Facilities

It was further assumed that the ion exchange process units treated 500,000 gallons/day of rinse water and that the metals concentrated in the regenerant wastewater from the ion exchange units will be further processed for metal recovery. Metal compounds used by Tinker AFB are assumed to be as listed below. The prices used were obtained from the Fisher Scientific Company. Although no prices for bulk purchases could be obtained, it is anticipated that bulk rates could possibly be 50 percent of the rates use for this analysis.

Compound	Costs ($/lb)	Molecular Weight	Percent Weight
CrO_3	4.50	100	52
$NiCl_2 \cdot 6H_2O$	7.00	237.7	24.7
CdO	24.00	128.4	87.5
AgCN	290.00	134	80.5
CuCN	7.00	89.6	40.7

Assuming 100-percent recovery of metals lost in the rinse water (500,00 gallons/day), the monetary return was calculated as follows:

Metal	Recovery (lb/yr)		Value
Cr	13,010		$112,590.00
Ni	13,225		374,770.00
Cd	334		9,161.00
Cu	24		413.00
Ag	547		197,056.00
		TOTAL	$693,990.00

SECTION V

CONCLUSIONS

1. Metal hydroxide sludge characteristics depend upon the pH of precipitation and specific metal content.

2. Metals removal from a plating waste solution does depend upon insolubilization and upon coagulation of the colloidal suspensions.

3. Coagulation depends upon pH adjustment to near the point of zero charge (PZC) for the metal hydroxide colloids.

4. Data from this study suggests that in a mixed-metal solution, mixed-metal co-precipitants form and the PZC for these precipitants depends upon the specific metal content of the colloidal precipitants.

5. Aging impacts chromium hydroxide dewatering but it is not clear that the theoretical aspects of the aging chemistry can be used to predict these changes.

6. High molecular weight anionic polymers can be effectively used to condition plating waste sludges.

7. Vacuum filtration is the most viable dewatering option for metal hydroxide sludges.

8. Centrifugation may be used to dewater metal hydroxide sludges if integrated with a recovery process.

SECTION VI

RECOMMENDATIONS

pH OF PRECIPITATION

The data collected in this study shows that plating waste sludge characteristics will vary considerably depending upon the specific metal constituents and pH of precipitation. It is not possible or desirable to develop a rigorous scheme for plating waste treatment for a plating shop because of the variability in the waste stream. Therefore, it is recommended that all the waste from the cation exchange unit be collected in a holding tank following regeneration, immediately neutralized to pH 6, then samples withdrawn and tested in the laboratory to determine the optimum pH for precipitation. The selection of a precipitation pH should be based upon metals removal and can be monitored by monitoring solution turbidity. It is important that excess pH levels not be provided since metal resolubilization can occur if the pH is above the PZC for the metal co-precipitant. Future investigations should also evaluate the use of other precipitating agents such as $Ca(OH)_2$, Na_2CO_3, CaO, and Na_2S.

CONDITIONING

Anionic polymers will effectively condition either type of sludge and should be considered as a conditioning step for all sludges. At pH 10 or less, sludge doses above 5 mg/l may be needed, and for sludges produced at the higher pH, doses at or near 1 mg/l can be used.

DEWATERING

Vacuum filtration appears to be the most promising process for dewatering the sludges of interest. Further study at the bench scale level should be undertaken to establish process efficiencies and establish design criteria.

RECOVERY

Liquid to liquid extraction is an attractive recovery process which should be evaluated at the bench scale using actual metal hydroxide sludges.

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APPENDIX A

SLUDGE FROM THE ION EXCHANGE REGENERANT WASTE FROM TINKER AFB

INTRODUCTION

The samples used in this portion of the study were obtained by precipitating a mixed metal residue from the regenerant generated by the cation exchange unit at the Oklahoma City Air Logistics Center Electroplating Facility, Tinker AFB, Oklahoma.

Two samples of ion exchange regenerant solution were provided by the Air Force. The volume of the first sample was only about two gallons, an amount insufficient to provide sludge quantities for study. The metal content of this sludge did, however, provide some information about the relative metal content of the regenerant. The metal content, as determined by atomic absorption, was:

Cr(III)	Zn(II)	Cd(II)	Ni(II)
7.0 mg/l	1.1 mg/l	0.23 mg/l	32.0 mg/l

The second sample had been neutralized to greater than pH 7 before shipment. When received, the samples were found to contain a very low concentration of plating metals and many of these were in particulate form. Total metal concentrations for Ni(II) and Cr(III) were approximately 1.2 and 4.5 mg/l, respectively. Other metal concentrations were 0.1 mg/l or less. These metals were constantly precipitating from solution so slightly different concentrations were encountered as the solution was used.

Because the metal content was so low in these samples and since they had been neutralized prior to shipment, it was apparent that these samples were not representative of ion exchange regenerant

solutions. It was also likely that the characteristics of the sludges could be vastly different from other plating waste residues with the same composition because the precipitates from the Air Force regenerant solution consisted of coagulated metal hydroxide particulates of an undetermined age rather than freshly formed metal hydroxide flocs. However, because this material was provided for study as part of the research contract and since some useful information could possibly be obtained, studies of these materials were undertaken.

RESULTS

Precipitation Studies

Because most of the metals in the plating waste regenerant solution were in particulate form, the coagulation/precipitation of the plating wastes could be easily monitored by following the turbidity change with pH. Turbidity was measured in Jackson Turbidity Units using a Hach turbidimeter. The pH was adjusted using sodium hydroxide solutions.

The effect of pH adjustment on the turbidity of the regenerant solution is shown in Figure A-1. From this figure it is evident that no coagulation occurs at a pH below 10, but that between pH 10 and 11 coagulation of the particulate metals occurs. Since nickel (II) attains both its minimum solubility and point of zero charge (PZC) near pH 11.0, it was believed that coagulation of stable metal precipitants could be occurring by the action of $Ni(OH)_2$.

To investigate the role of nickel as a coagulant for stable metal precipitants, studies were conducted in which the concentrations of both dissolved and particulate Ni(II) and Cr(III) concentrations were monitored as the pH was varied to determine if nickel insolubilization accompanies turbidity reduction. The results of this study, shown in Figure A-2, indicate that nickel insolubilization and precipitation occurs between pH 10 and 11 and is accompanied by a decrease in the chromium concentration. Both the dissolved and particulate chromium fractions decrease as the pH increases from 10 to 11, indicating that coagulation of stable metal hydroxides and some co-precipitation or adsorption of dissolved chromium also occurs.

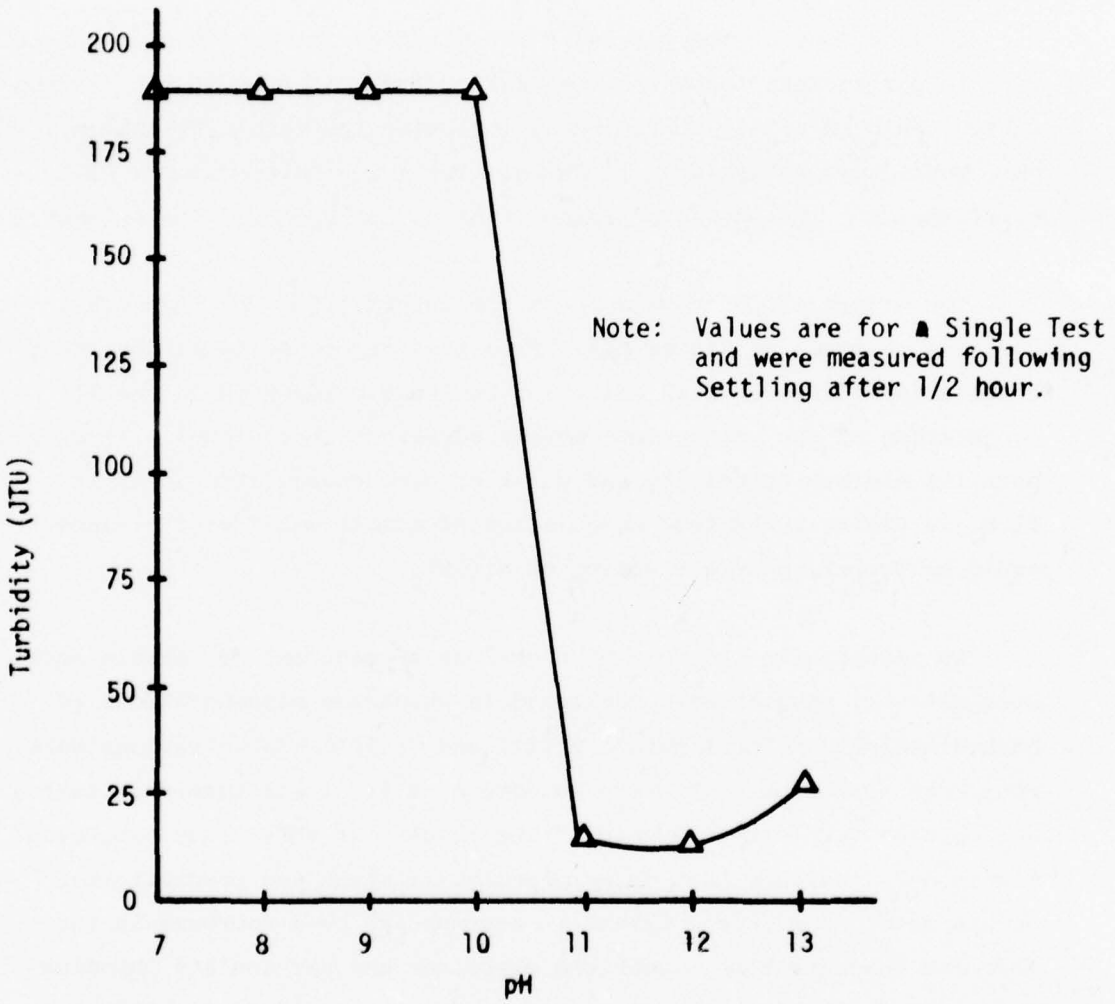


Figure A-1. Variation in Turbidity with pH for the Regenerant Backwash Solution

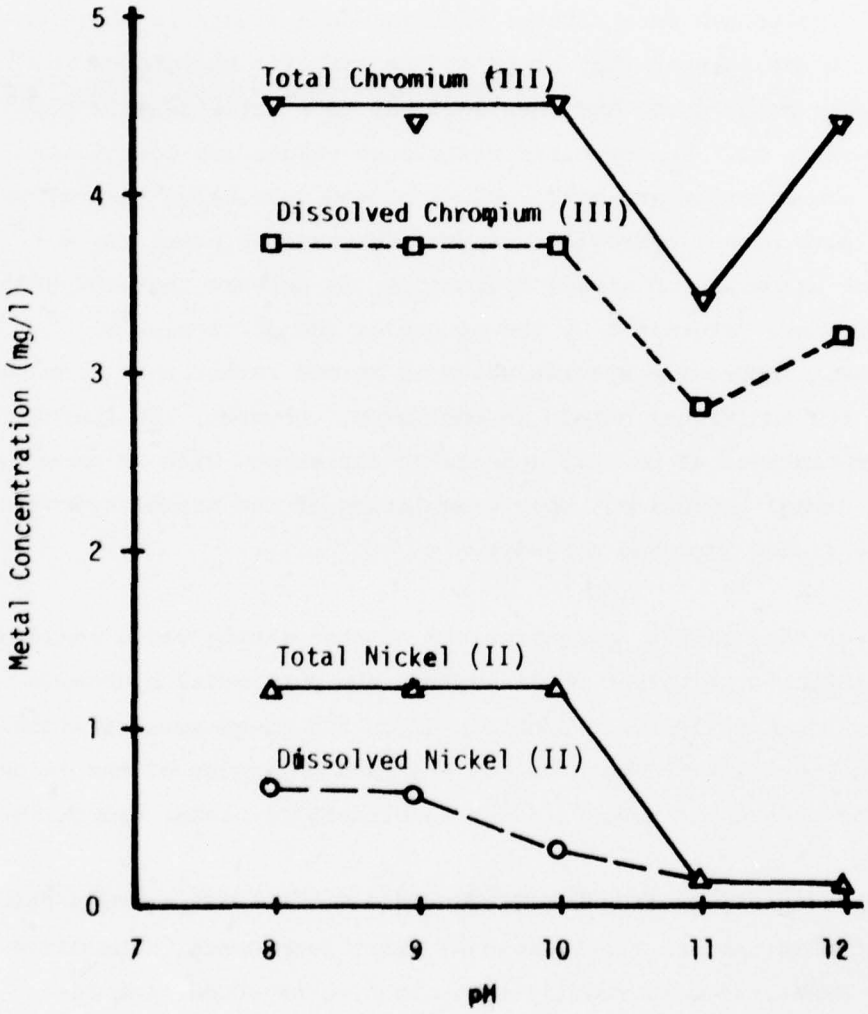


Figure A-2. Variation in Nickel and Chromium Concentrations as a Function of pH for the Regenerant Solution

Sludge Characteristics

Specific Resistance and Filter Cake Solids

Specific resistance data for the plating waste sludge is shown in Figure A-3. It can be seen that at pH 10 the specific resistance is quite low, peaks at pH 10.5, and then declines to a value near 12 x 10^{11} m/kg at pH 10.8 to 11. The specific resistance values are near those observed for the chromium and zinc hydroxides and much below the values obtained for pure nickel hydroxide. Since the waste is primarily a combination of chromium and nickel hydroxides, it appears that the sludge characteristics are determined by the nature of the particular co-precipitant metal hydroxide species which is formed rather than from the character of the individual metals in the waste. However, the increase in specific resistance at pH 10.5 appears to correspond with an increase in suspended nickel hydroxide. Upon coagulation of the nickel hydroxide at pH 11, the sludge improved markedly.

The filter cake solids concentrations of the plating waste residues also do not reflect the values obtained from the pure metal hydroxide precipitates. Cake solids values obtained for the mixed-metal residue are listed in Figure A-4. These values are much in excess of the values for any of the pure metal precipitates and especially nickel hydroxide.

It appears that significant differences exist between mixed-metal sludge characteristics and the individual metal components. The mixed-metal sludge dewatered more readily than might be expected from its component metals and produced a higher cake solids concentration. It appears from precipitation data that the metals in the waste stream do not form individual metal hydroxides but rather form mixed-metal precipitates. The nature of these mixed-metal precipitates may not be predictable from pure metal hydroxide data.

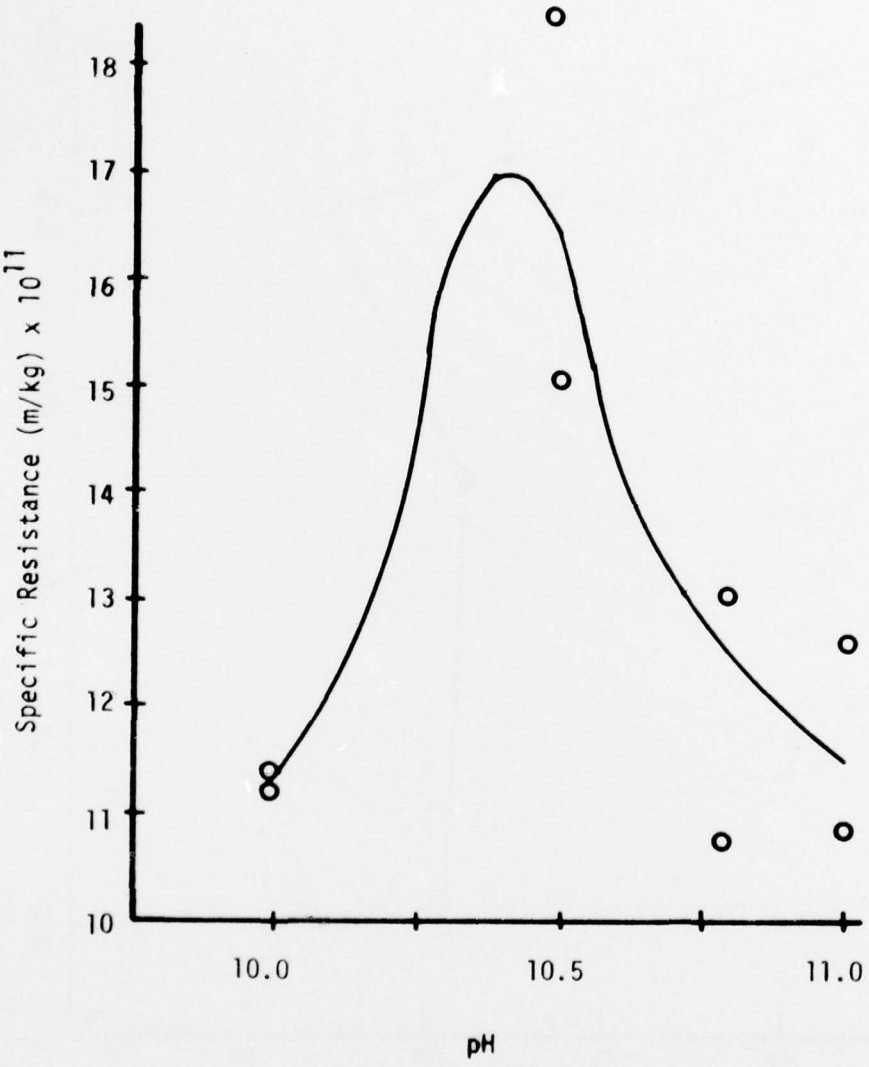


Figure A-3. Effect of Precipitation pH on the Specific Resistance of the Regenerant Sludge

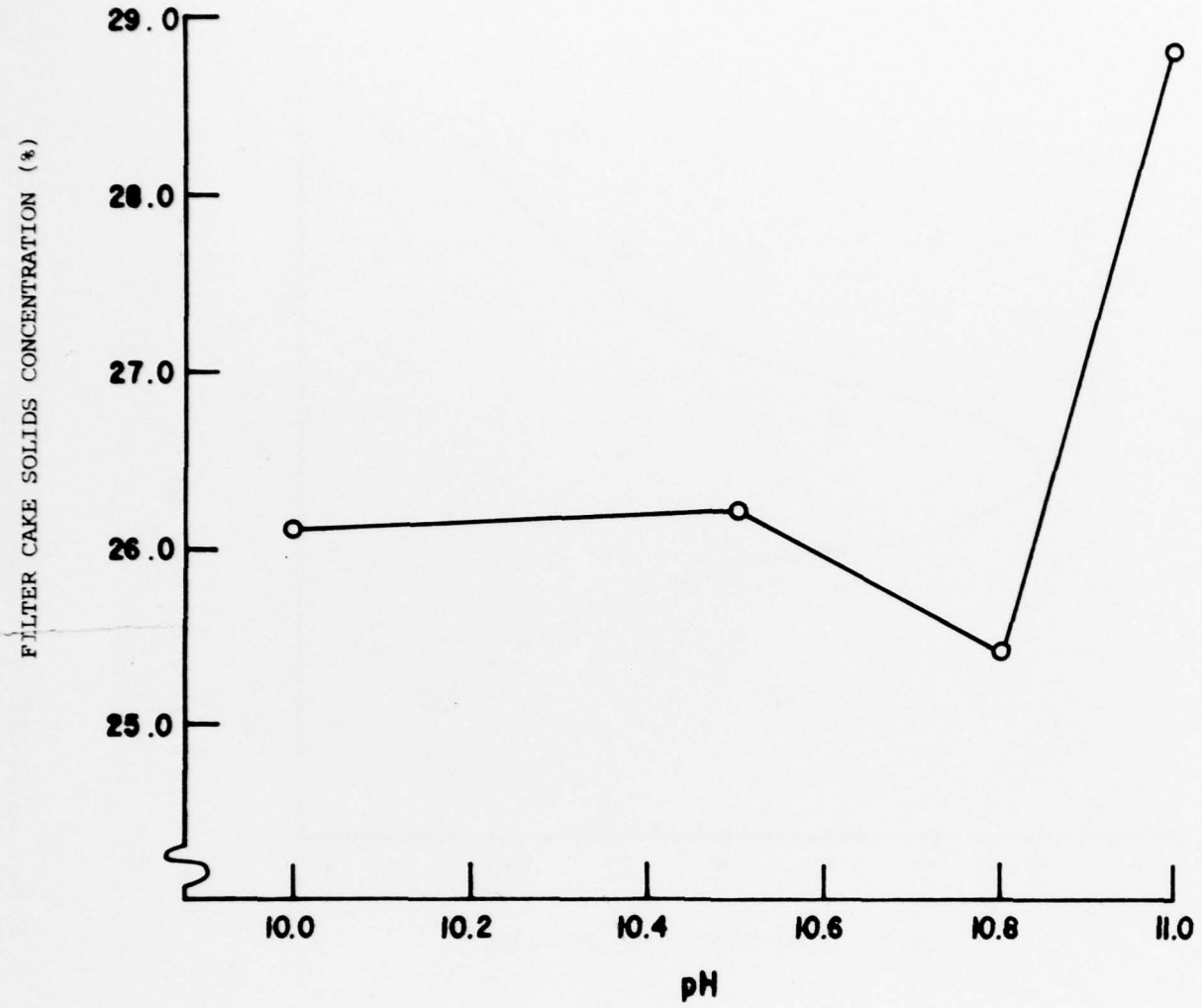


Figure A-4. Effect of Precipitation pH on the Filter Cake Solids Concentration for the Regenerant Sludge

Aging

Several aging tests were also conducted for the regenerant sludge. The easiest method for monitoring aging is to monitor pH. Since much of the aging effect is due to a slow reaction with OH^- ions, a pH decline with age is indicative of aging. The change in pH for the mixed-metal sludge is shown in Figure A-5. It can be seen that over a nine-day period the pH dropped from pH 11 to pH 9.6, indicating a continuing reaction of the metals with OH^- ions. This change in pH was accompanied by a decline in specific resistance, as shown in Figure A-6, from approximately 50×10^{11} m/kg to a value of less than 20×10^{11} m/kg after two days of aging. The filter cake solids concentration was unchanged by aging, as shown in Figure A-7.

Polymer Conditioning

Experiments were conducted to determine the effect of polymeric conditioning agents on the sludge filtering properties. In these studies the time to filter 50 ml was used as an indication of sludge filtering properties. For any specific sludge sample the time to filter can be shown to correlate well with the sludge specific resistance. Since the purpose of this study was to obtain an indication of the ability of polymers to successfully condition the regenerant sludge, it was believed that time to filter measurements would be adequate.

The data shown in Figure A-8 are for the regenerant sludge precipitated at pH 11.0. They indicate that polymers can improve sludge filtering rates to some degree, but the improvement is not substantial. It can be expected that the specific resistance would be reduced to approximately one-half of its original value using the high molecular weight ($10\text{-}15 \times 10^6$) and moderately charged (15 percent) anionic polymer while the cationic polymer of 3×10^6 molecular weight will be less effective. Novak and O'Brien (Reference 9) have observed that polymers generally are less effective as pH levels increase above 7. It is apparent that the success of polymer conditioning will depend upon the pH of precipitation.

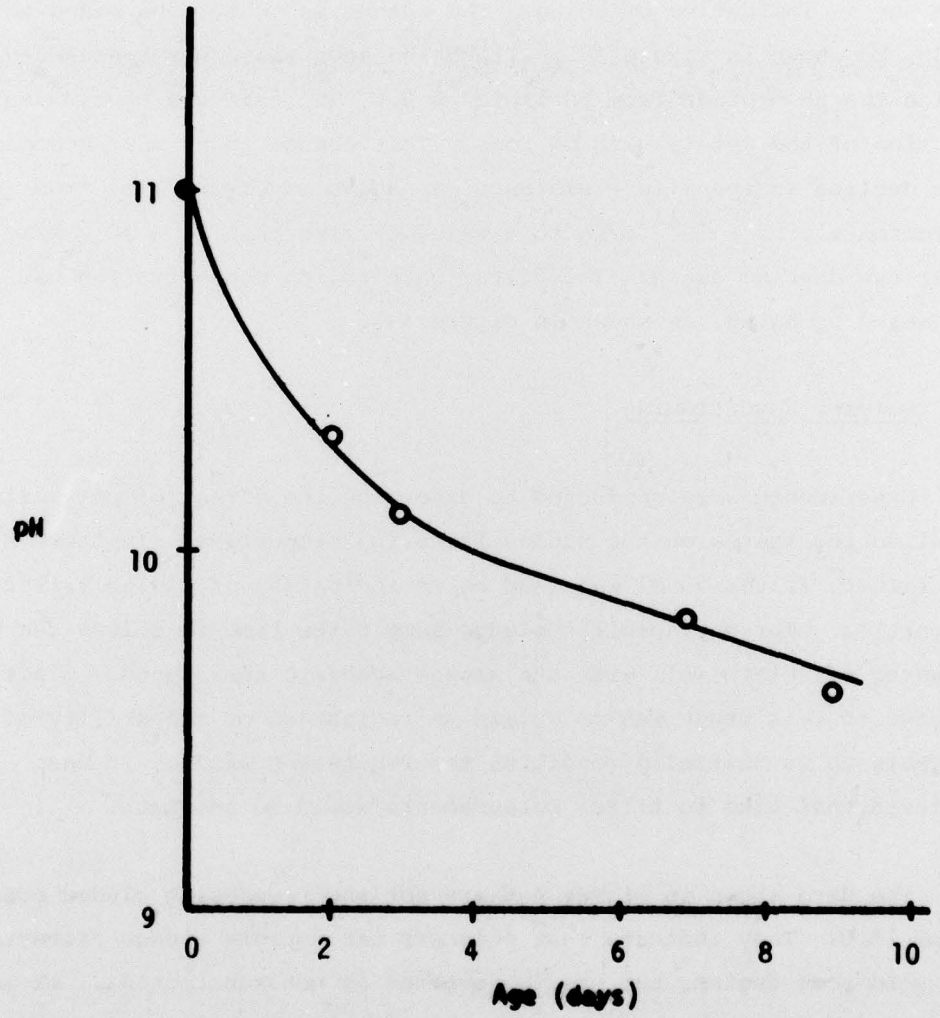


Figure A-5. Effect of Aging on pH of the Regenerant Sludge

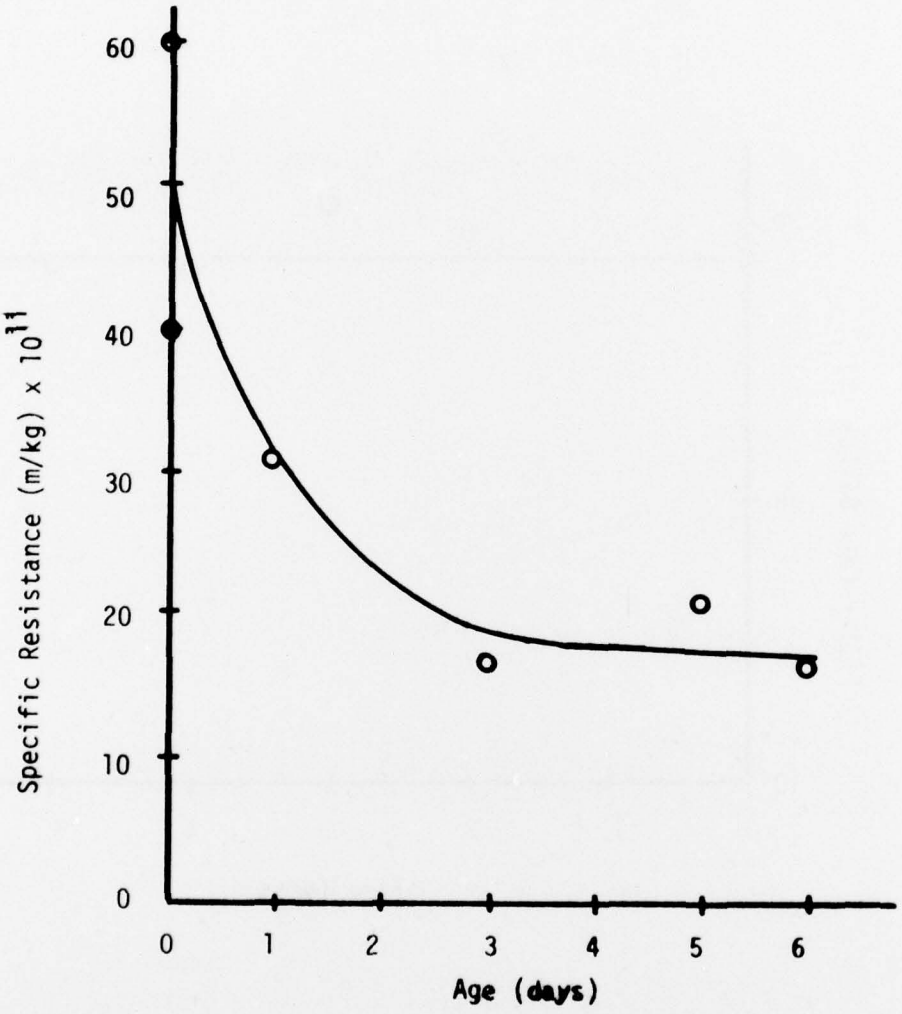


Figure A-6. Effect of Aging on Sludge Specific Resistance

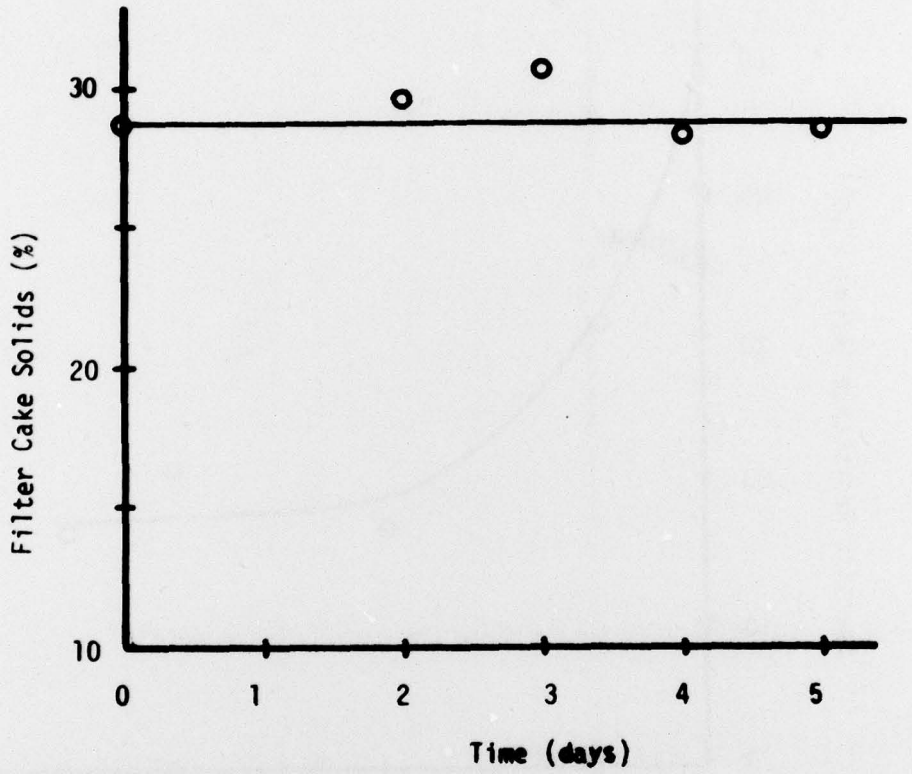


Figure A-7. Effect of Aging on the Filter Cake Solids Concentration of the Regenerant Sludge

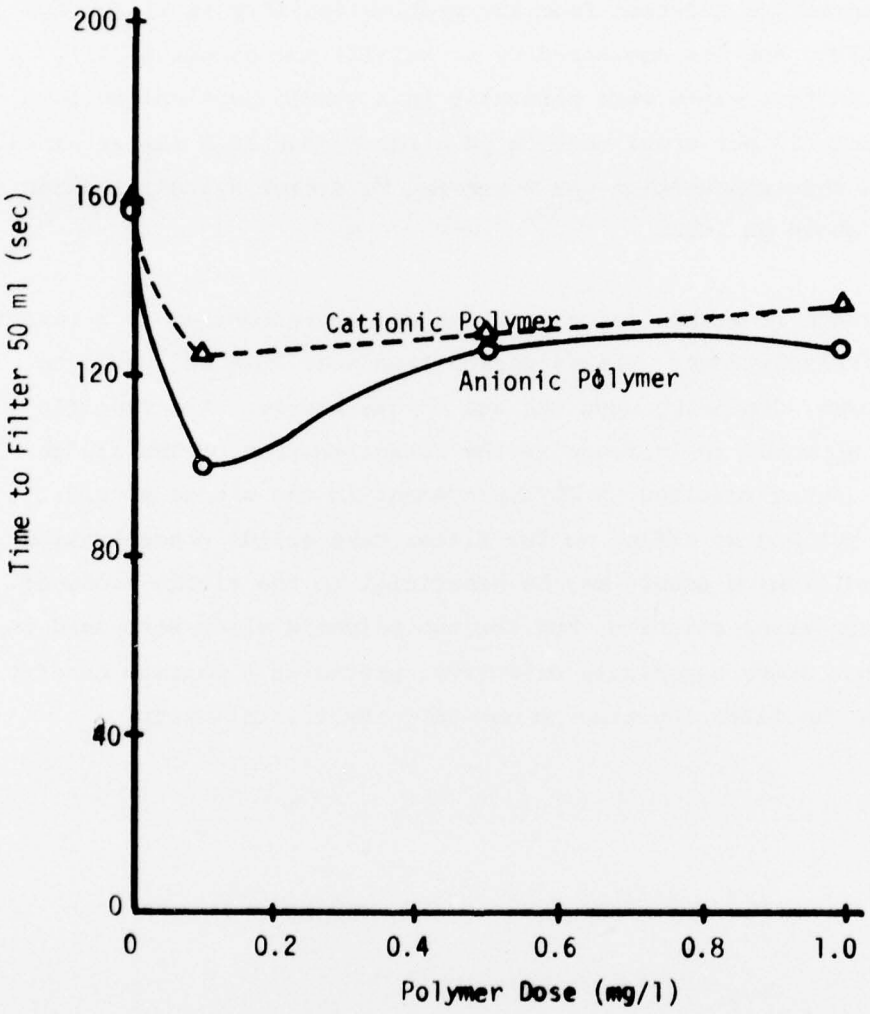


Figure A-8. Effect of High Molecular Weight Polymers on the Dewatering Properties of a Regenerant Sludge

DISCUSSION

The regenerant solution from the plating facility at Tinker AFB was very dilute and was dominated by nickel(II) and chromium(III). The metals in this waste were partially in a stable particulate form. Precipitation did not occur until a pH greater than 10.0 was attained. It appeared that coagulation was occurring by nickel hydroxide which was formed above pH 10.0.

The sludge from this waste solution was characterized by a relatively low specific resistance. Values varied from near 10×10^{11} m/kg to 50×10^{11} m/kg, depending upon the age of the sample. The specific resistance appeared to increase as the nickel content of the sludge increased. Aging resulted in an improvement in the sludge specific resistance but had no effect on the filter cake solids concentration. Polymer conditioning agents may be beneficial to the sludge produced from the regenerant solution, but the two polymers which were used in this study did not prove especially effective, providing a maximum benefit of reducing the filtering time to one-half the initial value.

APPENDIX B

SLUDGE FROM INDUSTRIAL WASTE TREATMENT PLANT AT HILL AFB

All preceding discussion has been concerned with the characterization of an ion exchange regenerant solution which is a byproduct from a treatment scheme for plating wastewater. Preliminary analysis was also performed upon the sludge produced in an existing industrial waste treatment plant which received plating wastes. A qualitative metal analysis by atomic absorption of the Hill Air Force Base sludge is presented in Table B-1. The high iron content results from the addition of ferrous sulfate within the plant for coagulation and chromium (VI) reduction. A large amount of calcium is also present in the sludge and can be attributed to the addition of lime (CaO) for pH adjustment.

Studies were made of the dewatering characteristics of this sludge to determine the nature of the sludge and also to evaluate the use of polymers for sludge conditioning. The specific resistance of the sludge was 28×10^{11} m/kg, indicating that this sludge was similar in character to the plating waste sludge produced from the Tinker AFB ion exchange unit. The filter cake solids concentration gave a similar value to the Tinker sludge, 23.3-percent solids.

The effect of polymer addition on the sludge dewatering rate is shown in Figure B-1. The addition of approximately 15 mg/l Betz 1120® produced the maximum dewatering rate. The specific resistance at that chemical dose was 14.4×10^{11} m/kg. It appears that polymers can be successfully used to condition the Hill AFB sludge.

The addition of large quantities of iron permits precipitation to occur at a nearly constant pH. Data from the mixed-metal system suggests that metals precipitate as a mixed-metal hydroxide rather than as the individual metals. By overwhelming the system with iron, a reasonably constant pH of precipitation can be maintained and treatment problems can be minimized.

TABLE B-1. METAL CONTENT OF HILL AFB SLUDGE

	Results (µg/g of Wet Sludge)
Copper	140
Zinc	160
Lead	225
Cadmium	2280
Iron	12630
Gold	2.1
Magnesium	2420
Calcium	12000
Chromium	8600
Nickel	240

Metal analysis by atomic absorption

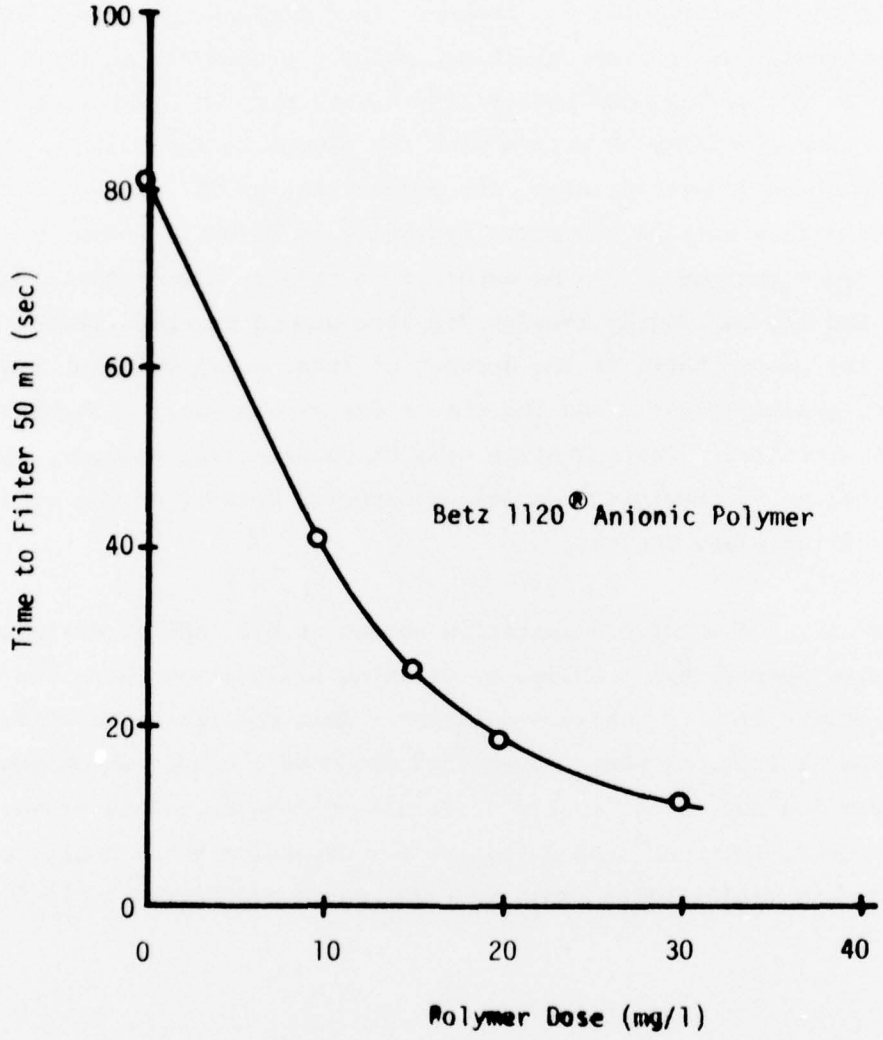


Figure B-1. Effect of a High Molecular Weight Polymer on the Filtering Rate of Hill AFB Plating Waste Sludge

With the addition of iron, however, land disposal problems might be encountered. Since iron can change valence states and thereby increase in solubility, the possibility exists for the production of a much greater mobility of metals when the sludge is landfilled. If the metals exist as co-precipitates, the solubilization of iron will free the other metals until a new metal hydroxide is formed. Under lower pH conditions the metals can be expected to remain soluble for a period of time and may be readily transported into ground waters. If the metals were precipitated in the absence of iron, metal resolubilization should be greatly reduced and the chance for ground water contamination would be minimized. Precipitation will be complicated, however, since the optimal pH of precipitation can be expected to vary as the metal content of the waste varies.

Overall, the metal precipitation scheme at Hill AFB is designed to minimize operational problems by creating a situation where the optimal pH of precipitation is nearly a constant. This results in an efficient metal removal from the waste stream and produces a sludge which should be uniform and not exceptionally difficult to dewater. This scheme does, however, introduce the potential for excessive metal mobility if the sludge is landfilled.

INITIAL DISTRIBUTION

ADTC/CS	1
DDC/TCA	2
HQ AFSC/DL	1
HQ AFSC/SD	1
EPA/ORD	1
USA Chief, R&D/EQ	1
USN Chief, R&D/EQ	1
OEHL/CC	1
Det 1 ADTC/PRT	1
NCEL, Code 25111	1
Naval Ship R&D Ctr	1
Det 1 ADTC/ECC	1
Det 1 ADTC/ECW	10
HQ AFLC/DEE	1
HQ AFLC/DEPV	1
HQ AFLC/SGB	1
HQ AFLC/MANT	1
HQ AFLC/MMRF	1
US Army/CERL	1
Dept of Civil Engrg Univ of S. Carolina	1
Dept of Civil Engrg Univ of Missouri	1
OO-ALC/DEE	1
OO-ALC/MAA	1
SA-ALC/DEE	1
SA-ALC/MAA	1
OC-ALC/Dee	1
OC-ALC/MAA	1
OC-ALC/MAEEE	3
SM-ALC/DEE	1
SM-ALC/MAA	2
WR-ALC/DEE	1
WR-ALC/MAA	1