

RECOVERY OF CHROMIUM FROM F019 WASTE

BY

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ABSTRACT

RECOVERY OF CHROMIUM FROM F019 WASTE

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The United States EPA has defined the waste from aluminum extrusion industries (F019 waste) as hazardous due to chromium concentration above the allowable limit. The industrial process that produces F019 waste involves single stage precipitation of both aluminum and chromium at about 8.5. This project studied a two stage precipitation process to recover chromium hydroxide precipitate at a pH of about 13.5 and aluminum hydroxide at a pH of about 7.0. The optimum pH ranges found from Experiment #1 and #1A were 5.5 - 8.5 for aluminum hydroxide. The range of chromium extended to 13.5 later by Experiment #3. Two separate stages of precipitation gave chromium hydroxide precipitate contaminated with about 10 % of the total aluminum in the first stage and almost pure aluminum hydroxide precipitate in the second stage. The low concentration of chromium in the second-stage precipitate can decrease the cost of disposal, and the chromium in the first-stage precipitate can generate income if a market is found.

Results of the TCLP test on original waste and the total test showed the aluminum precipitates in second stage with low chromium contamination so that it can be disposed in regular landfills (Experiment #2 results). Also, the chromium concentration in the wastewater after two-stage precipitation was found under the safe limit of disposal (i.e. less than 5 mg/l) and 55% of total waste could be recovered from hazardous F019 waste by two-stage precipitation.

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TO MY BROTHER AND SISTER
with whom I shared my childhood &
my world of
emotions

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CHAPTER 1

INTRODUCTION

1.1 Aluminum Industries and Origin of F019 Waste

The Aluminum Extrusion Network (AEN) of the Greater Mahoning Valley, Inc. is an organization whose member companies compete in soft extrusions. In Youngstown, Ohio, several industries extrude different aluminum building materials. Extrusion is often compared to squeezing toothpaste from a tube. An aluminum billet (round ingot) is heated to a proper working temperature and fed into an extrusion press. Under great pressure, the heated metal is forced through a die orifice, which is similar to the cross section of the desired product.

The surface of fabricated "outproducts" is treated by NaOH in first stage and then by an "etchant" such as chromic acid or a combination of chromic and phosphoric acids so that the surface can be finished by anodizing, buffing, etc. The waste water from the surface wash contains chromium, aluminum and other substances that are defined as hazardous by regulatory agencies.

The present treatment of waste water by local aluminum extrusion industries follows these steps:

- 1) Acidification of spent etchant to Ph 2-4 from 6-7.
- 2) Addition of sufficient NaHSO₃ to reduce all

hexavalent chromium to the trivalent state.

- 3) Raising of Ph to 8-8.5 by adding NaOH.
- 4) Addition of CaCl₂ to help form floc, and then filter pressing.

The solid waste gleaned from the filter press is rich with chromium and aluminum concentrations. The U.S. Environmental Protection Agency (EPA) has designated this material as F019 waste. The approximate composition of F019 waste on a dry basis is:

3-15 wt.% Cr, 0.5-10 wt.% Fe, 5-15 wt.% Al, 0.5-2 wt.% Mg, 5-20 wt.% Ca, 0.1-0.5 wt.% Zn, 2-15 wt.% P and 2-5 wt.% S (both as SO₄ and SO₃) (Crnojevich et al., 1990).

The EPA restricts the disposal of solid waste at treatment plants if analysis shows that the waste contains more than the maximum allowable limit of any hazardous substance during the Toxicity Characteristic Leaching Procedure (TCLP) test (Federal Register, 1990). Under current practice, disposal of hazardous F019 waste costs about \$500 per 55 gallon drum (Mettee, personal communication, 1993).

1.2 Goals of the Project

This project's first objective was to define an optimum pH value for the precipitation of chromium and aluminum hydroxides so that both could be recovered separately from process waste water. Another goal was to find a cost-effective disposal method for residue without adversely

affecting the environment. Therefore, any two-stage precipitation process would have to yield minimal hazardous waste. Finally, the project would determine the allowable concentration of chromium in the waste water to ensure that the water could be discharged safely into municipal sewers after two-stage precipitation.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Precipitation of Heavy metals

These factors affect precipitation of heavy metals:

- a) Reactant
- b) Solubility
- c) Temperature
- d) Valence state of metal
- e) Liquid/solid state of waste

The most common and inexpensive method for removing inorganic heavy metals from waste water is chemical precipitation. If the concentrations of heavy metals are sufficiently high to classify the waste stream as hazardous according to regulatory agencies, the best treatment method must be found by considering economic, environmental, and practical aspects. All metals have optimum Ph levels for precipitation that yields an insoluble salt. Heavy metals can be removed from the waste stream after precipitation as sludge residue by physical processes such as filtration, sedimentation, or clarification.

The choice of the reactant greatly affects precipitation. Lime is used commonly for precipitating heavy metal hydroxides because of their insolubility and because lime is inexpensive. The carbonates or sulfides are less soluble than the

hydroxides for certain metals, but are not used commonly for precipitation. In some instances, partial precipitation with lime is followed by a secondary treatment with sulfide.

Precipitation also depends upon the solubility product of the metal that is to be removed. Since temperature affects solubility, it is important in precipitation reactions. The selection of treatment equipment is influenced greatly by these controlling factors (Snoeyink and Jenkins, 1980).

In precipitation, valency of metal is no less important. For example, $\text{Fe}(\text{OH})_2$ is more soluble than $\text{Fe}(\text{OH})_3$. In iron removal processes, it is essential to oxidize all ferrous iron into ferric iron before precipitation. This is also true for chromium since hexavalent chromium, Cr^{6+} , is considerably more soluble than the less hazardous trivalent form. Chromates must be reduced before removal by precipitation (Wentz, 1989).

Waste waters containing ammonia, fluoride, cyanide, or heavy metals form complex ions sometimes. For example, iron may be complexed as the ferrocyanide ion, which is rather soluble, and will remain in solution unless the complex can be broken by chemical treatment.

One final factor in precipitation is the liquid/solid state of the multiphase waste. The waste containing solid particles helps to form floc due to intramolecular forces such as adsorption and electrolytic force between precipitate and solid particles. Chemical reaction with previously

precipitated particles also increases the size of precipitate particles (Wentz, 1989).

The individual factors affecting the chromium recovery experiments of this project are explained in the following sections.

2.1.1 Choice of the Reactant

To raise the pH of the waste water pregnant with heavy metals to form insoluble metal hydroxides, calcium hydroxide (slaked lime), magnesium hydroxide, sodium hydroxide (caustic soda) or sodium carbonate (soda ash) can be used according to economic and practical justification. But the experimental work and the theoretical results of literature review suggest that sodium hydroxide (NaOH) is the most practical reactant. The solubilities of hydroxides are known more precisely than carbonates or sulfides. Since sodium carbonate (Na_2CO_3), and the other two hydroxides generate increased sludge residue, caustic soda (NaOH) is usually best. To adjust to acidic pH, sulfuric acid is the most economical reactant.

2.1.2 Solubility

Reviewing the past extensive experimental work to define the chemical and electrochemical properties of chromium reveals the dual behavior of this metal. In the active state it behaves like an extremely corrodible metal; in the passive state, it behaves as a noble metal (Deltombe et al., 1956). In contact with reducing solutions such as HCl or H₂SO₄, or by cathodic polarization, chromium enters an active state; to reach the passive state requires oxidizing solutions or anodic polarization in solution not containing chloride. A change from one state to the other can be accomplished by modifying the oxidizing-reducing properties of the solutions or by reversing the polarization; even exposure to air is often sufficient for the oxidation, and thereby makes chromium pass from the active state to the passive state (Deltombe et al., 1956).

Chromium and aluminum hydroxides and their respective ranges of solubility is explained by Figures 2-1 through 2-4 (Deltombe et al., 1956). Figures 2-1, 2-2, and 2-3 show electro-chemical potential as a function of pH for oxides of chromium. Figure 2-4 shows the solubility as a function of pH.

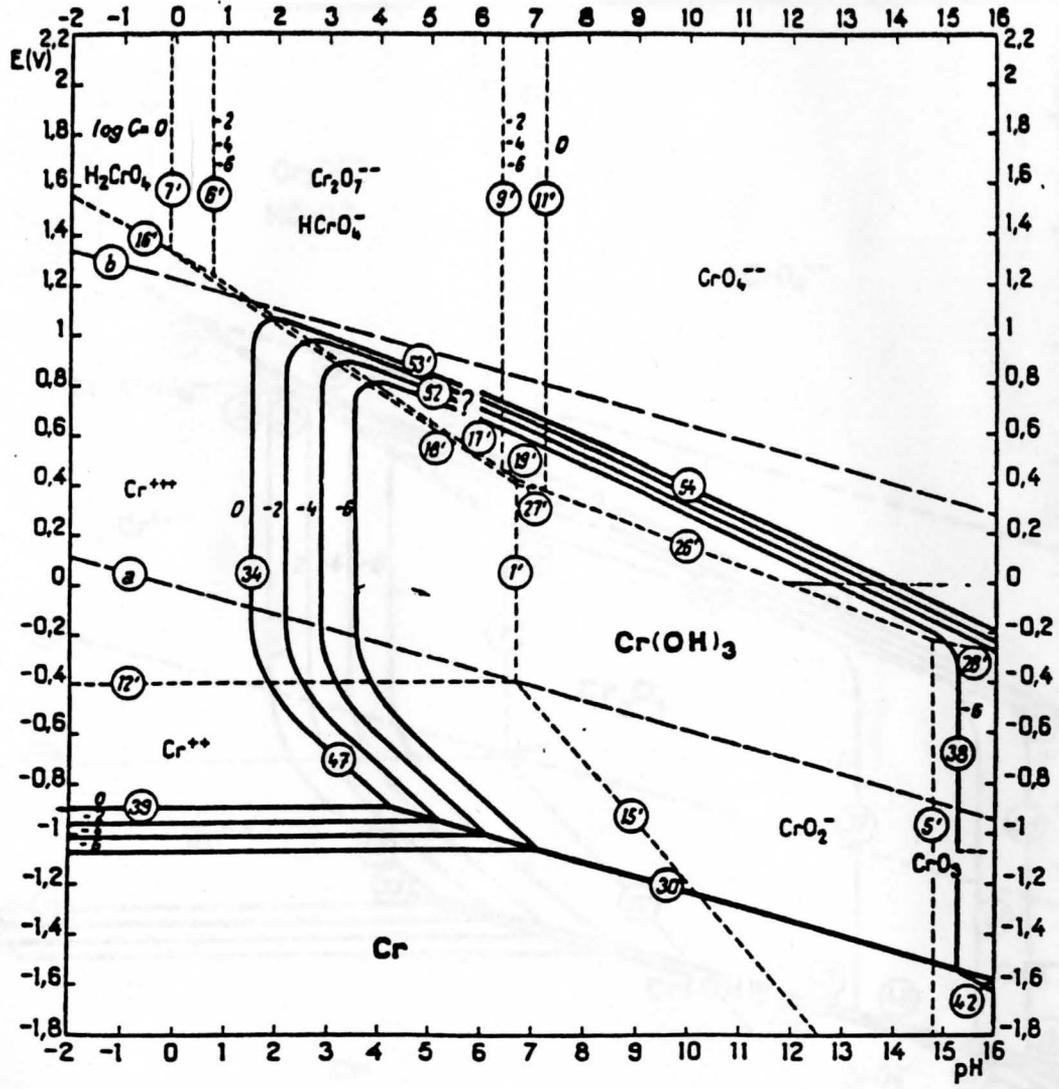


Figure 2-1. Potential-pH Equilibrium Diagram for the System Chromium-Water, at 25°C. In Solutions not containing Chloride. (Figure Established Considering $Cr(OH)_3$) (Deltombe, et al., 1956)

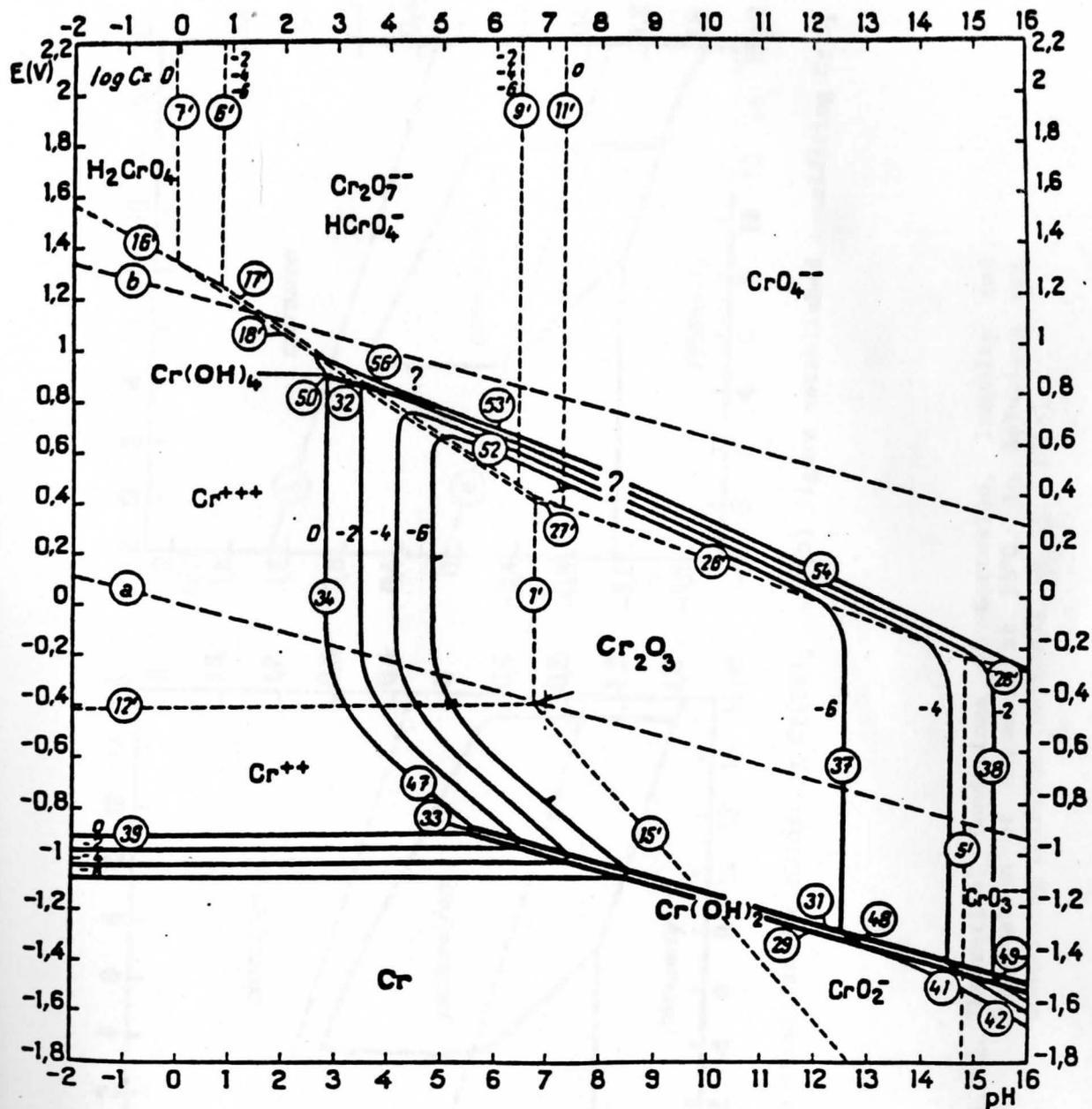
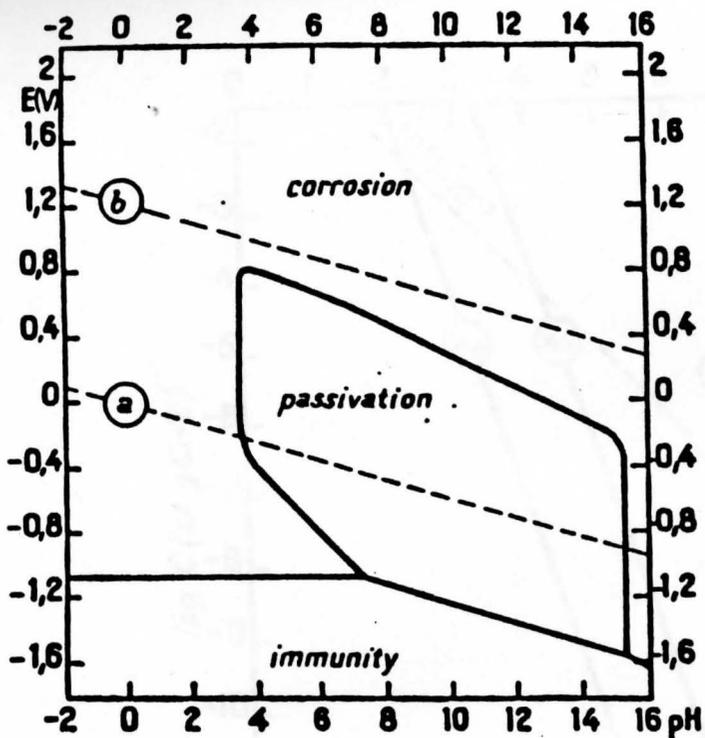
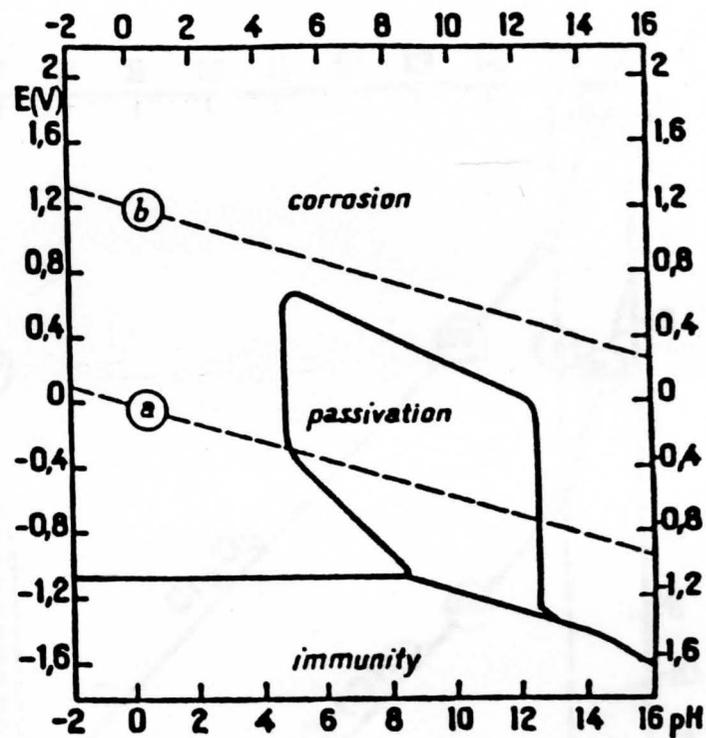


Figure 2-2. Potential-pH Equilibrium Diagram for the System Chromium-Water, at 25°C. In Solutions not containing Chloride. (Figure Established Considering Anhydrous Cr_2O_3) (Deltombe, et al., 1956)



(a) Figure established considering Cr(OH)_3 ,



(b) Figure established considering Cr_2O_3 ,

Figure 2-3. Theoretical Conditions of Corrosion, Immunity and Passivation of Chromium at 25°C. In Solutions not Containing Chloride. (Deltombe, et al., 1956)

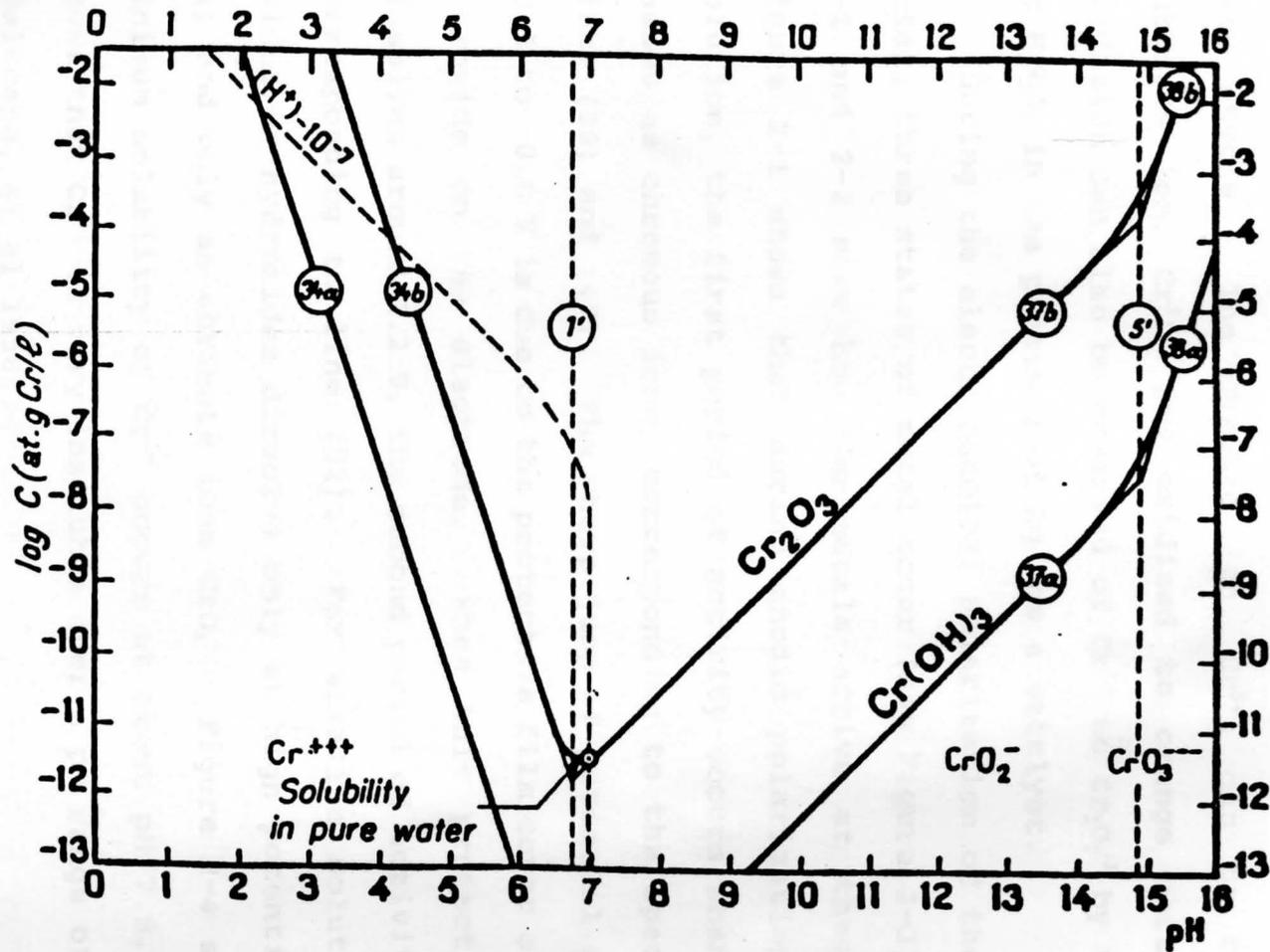


Figure 2-4. Influence of pH on the Solubility of Cr_2O_3 and $Cr(OH)_3$, at 25°C. In Solution not Containing Chloride. (Deltombe, et al., 1956).

The equilibrium diagram reveals that the compounds of trivalent chromium lie in the passivation zone and hence are very stable. The chromic ion, Cr^{3+} , can be reduced to chromous ion, Cr^{2+} , and oxidized to orange chromic acid. Oxidation can also be observed of Cr^{3+} to $\text{Cr}_2\text{O}_7^{2-}$ by the action of $\text{H}_2\text{S}_2\text{O}_8$ in the presence of Ag^+ as a catalyst.

During the electrochemical polarization of the chromium metal, three states of metal occur (see Figure 2-3). Figure 2-1 and 2-2 show how the metals arrive at these states. Figure 2-1 shows that during anodic polarization in acid solution, the first period of activity occurs when chromium passes as chromous ions, corresponding to the space between lines (39) and (47). The sharp jump of potential at about -0.5 to -0.6 V is due to the protective film cover of oxide or hydroxide on the electrode. When this protective cover dissolves around 1.2 V, the second period of activity begins, corresponding to line (52). For alkaline solutions, the oxides or hydroxides dissolve only at high potentials (line 54) and only as chromate ions CrO_4^- . Figure 2-4 shows that minimum solubility of Cr^{3+} occurs at about pH 7.5. It also shows that Cr^{3+} is very insoluble over a pH range of 4-14 (Deltombe, et al 1956).

2.2 TCLP Test Procedure

To determine the mobility of both organic and inorganic analytes in wastes of different forms, the EPA uses

Toxicity Characteristic Leaching Procedure (TCLP). The criteria for classifying waste as hazardous is well defined for liquid, solid, or multiphase waste. The actual procedure is detailed in standard operations (Federal Register, 1990).

In general, any waste is diluted into a standard TCLP solution in defined proportion depending upon the pH of the waste and is stirred thoroughly for 16-20 hours in a standard apparatus. It is then allowed to settle for the same amount of time. The supernatant liquid after settlement is analyzed for hazardous elements, including several heavy metals. If the concentrations of all substances in the analyzed liquid are under the EPA's hazardous limits, landfills can accept the waste. More details of TLCP are described in Chapter 3.

2.3 Integrated Recycling of Chromium-Aluminum F019 Waste

AMAX Metals Recovery, Inc., operates a metals recycling plant near New Orleans, Louisiana, for converting spent petroleum catalysts into four commercial products: molybdenum sulfide, alumina trihydrate, vanadium pentoxide and a nickel-cobalt concentrate. In 1989, they expanded the facility to recycle chromium-aluminum hazardous waste material generated by aluminum finishing operations. The aluminum content of this waste is coprocessed and aluminum is recovered as alumina trihydrate within the existing spent catalyst plant (Crnojevich, et al., 1990).

2.3.1 Recovery Process for the F019 Material

Chromic acid and other chemicals generally are used by the finished aluminum producers for "surface passivation" or a "paint-line preparation". Depending upon individual practice, the composition of these etchant solutions varies greatly, but most solutions contain phosphoric acid, zinc, molybdenum, HF, HNO₃, etc. Nearly all chromium must be removed from the etchant solution to meet stringent EPA regulations before disposal. For this removal, most plants use a process similar to that described in Chapter 1. The precipitated chromium hydroxide is normally recovered by pressure filtration and is classified as F019 hazardous waste. In a few installations, the F019 material is generated in a different manner, where NaHSO₄ is replaced by electrolytic reduction in "Andco" units (Andco units are electrolytic cells with soluble iron anodes for coprecipitation of metal hydroxides.). The chromium waste from the Andco units contains less phosphate and more iron than the previous process (Crnojevich et al., 1990).

U.S. companies annually generate approximately 13,600 metric tons of F019 waste in wet filter cakes that contain 50-75% moisture. The EPA classifies these cakes as hazardous waste. Present regulations mandate immobilization of chromium before disposal at a landfill. The approximate composition of the F019 waste on a dry basis was explained in Chapter 1.

2.3.2 Process used to Recover Chromium Oxide

The following paragraphs describe the present patented recycling process (U.S. Patent No. 4,954,168) AMAX Metal Recovery, Inc. uses for F019 waste. Figure 2-5 shows how AMAX processes etching operation wastes. The waste includes various proportions of Cr, Al, Fe, Ca, Mg and P as well as other elements in minor fractions. No matter what fraction of these elements are present, the waste is treated with sulfuric acid so that aluminum and chromium can be dissolved completely and calcium sulfate and some solid particles can be separated as insoluble residue. Conditions of moderate acidity of pH 1.2-2, and an ambient or moderately elevated temperature of 20-65°C, is achieved. To oxidize the ferrous ion to the ferric state while retaining chromium in its trivalent state, air or other mild oxidant can be used during the dissolution stage (Crnojevich et al., 1990).

The waste pregnant with undissolved solids and dissolved chromium and aluminum is adjusted to 2.0-3.0 pH to precipitate trace elements such as iron and phosphorus as ferric hydroxide or phosphate without the chromium-aluminum interference. The pH adjustment is performed with hydrated lime. The slurry undergoes a solid/liquid separation after the pH adjustment to get a chromium-aluminum solution with

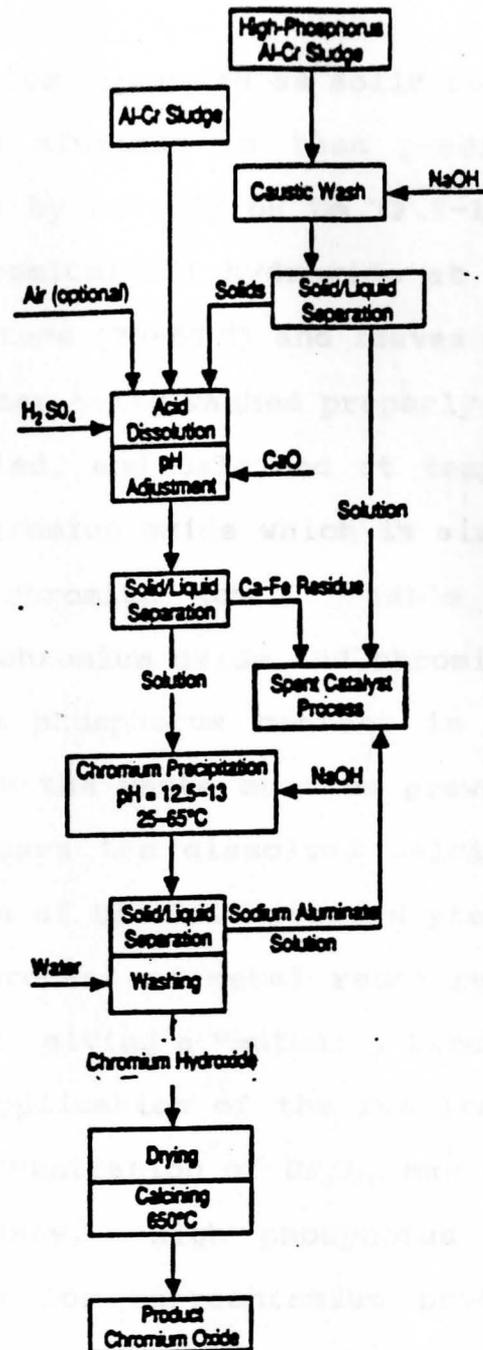


Figure 2-5. Processing Aluminum-Chromium Wastes from Etching Operations. (Crnojevič et al., 1990)

iron and phosphorus separated as solid residue. The solution of chromium and aluminum is then precipitated further to recover chromium by raising pH to 12.5-13.0 with NaOH. The precipitates chromium(III) hydroxide at ambient or slightly elevated temperature (25-65°C) and leaves a separated solution of aluminum. After being washed properly, chromium hydroxide is filtered, dried, and calcined at temperatures of 540 to 705°C to yield chromium oxide which is similar in composition to high-grade chromite ore. Table 2-1 compares the compositions of chromium oxide and chromite ore.

To minimize phosphorus content in the final chromium oxide concentrate the waste must be prewashed with a strong caustic. AMAX uses the dissolved calcium that the solid-liquid separation of the F019 process yields as lime for the spent catalyst process of metal recovery. These processes occur in parallel, giving a "mutually beneficial coprocessing arrangement." Application of the resultant chromium oxide, with its high concentration of Cr_2O_3 , may not be suitable for all industrial uses. High phosphorus concentrations may restrict its use for ferrochromium producers unless it's blended with low phosphorus material. The chromium oxide also may be used in glass industries as a coloring agent, in brick industries that manufacture fire resistant bricks, or as a feed material for producing a chromium chemical of high purity (Crnojevich et al., 1990).

Table 2-1. Comparison of the Compositions of Chromium Oxide Concentrate with a Typical South African Chromite Ore. (Crnojevich et al, 1990.)

Constituent (Wt.%)	Chromium Oxide*	Chromite Ore
Cr ₂ O ₃	50-55	47.0
Iron	4-6	10.0
Aluminum	3-5	12.0
Calcium	4-6	<0.5
Magnesium	1.5-3	7.5
Phosphorus	0.3-0.8	<0.1
Sodium	1-2	NA
Zinc	2-3	NA
Nickel	0.2-0.3	<0.1
Silicon	<0.5	2.5
Carbon	<0.1	NA
Sulfur	0.1-0.3	NA

* Calcined at 650°C.

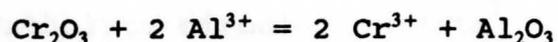
NA- not available.

2.4 Recovery Of Chromium from Chromium Ores

Methods of recovering chromium from its ores include electrowinning, electroplating, and thermal decomposition. This section describes them briefly.

2.4.1 Aluminothermic Process

Aluminothermic process is a form of thermal decomposition. Aluminothermic reduction of chromic oxide to yield chromium at a moderate price was performed successfully by Hans Goldschmidt between 1895 and 1908. His method used the following reaction (Udy, 1956):



The process transpired in a preheated refractory-lined container with a thoroughly mixed Cr_2O_3 charge and metallic aluminum powder. The charge was ignited initially by a starting mix of barium peroxide and aluminum powder, or by powdered magnesium, thereby creating high temperatures. The extremely high temperature created by the reaction of aluminum with chromic oxide produced chromium and aluminum oxide. This method produced chromium with very low carbon and iron content for use in certain nonferrous alloys (Udy, 1956).

2.4.2 Electrowinning Process

The major methods of chromium recovery through electrodeposition are electrowinning of chromium with chromic acid electrolyte, with chromium-alum electrolytes, and the

electroplating process. As this thesis deals in part with aluminum waste, electrowinning from chromium-alum electrolytes and factors affecting the process are pertinent.

Figure 2-6 shows the details of an electrowinning cell and its internal structure, and the flow sheet in Figure 2-7 explains the successive reactions involved. The factors affecting the process are more important than the physical data and the processes themselves. The affecting factors in order of importance are listed below (Udy, 1956):

- a) pH of electrolyte
- b) Catholyte temperature
- c) Catholyte circulation rate
- d) Current density
- e) Cathode preparation
- f) Chromium concentration
- g) Ammonium sulfate concentration
- h) Divalent to trivalent chromium ratio

Figure 2-8 shows the effect of catholyte temperature on current efficiency and the optimum pH. Optimum pH accomplished here depended on the nature and amount of metal deposition, smoothness of operating current, and current efficiency. As the heavy metal impurities increase, the curve of current efficiency travels toward increasing temperature.

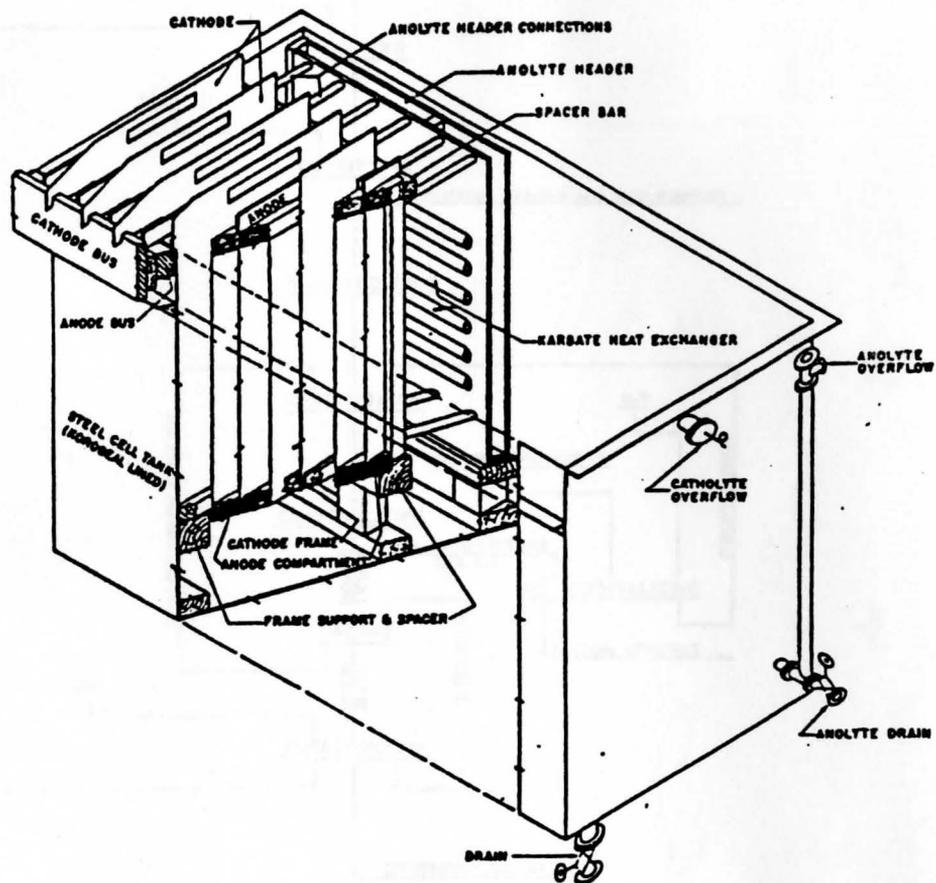


Figure 2-6. Details of Electrowinning Cell (Udy, 1956).

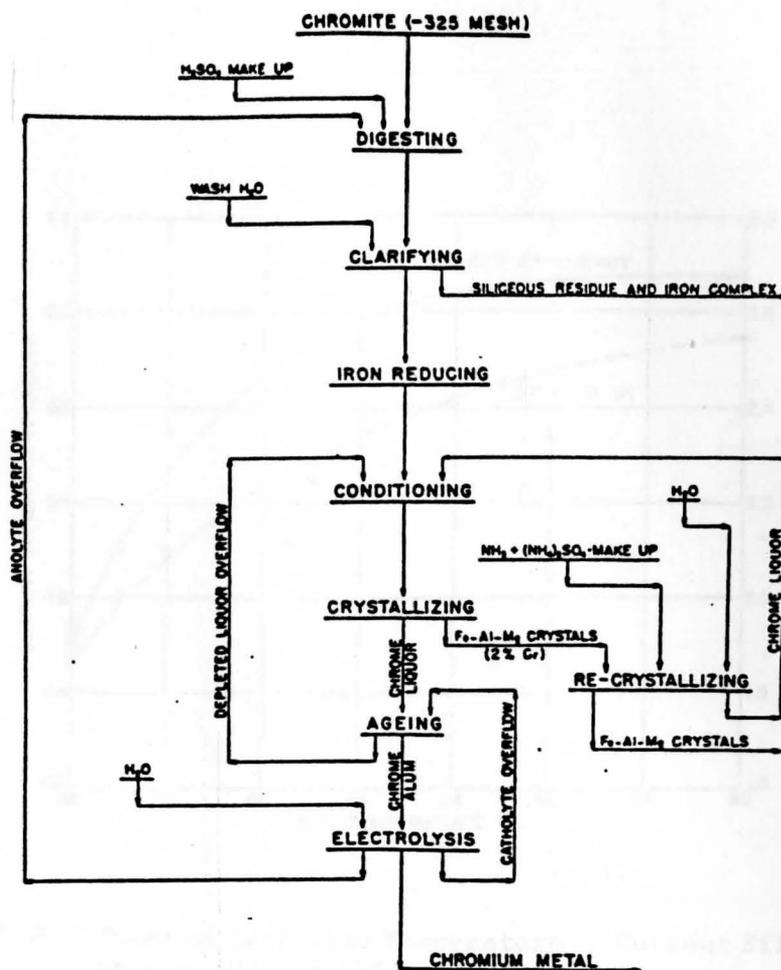


Figure 2-7. Flow-sheet, Production of Electrolytic Chromium from Ore. (Udy, 1956).

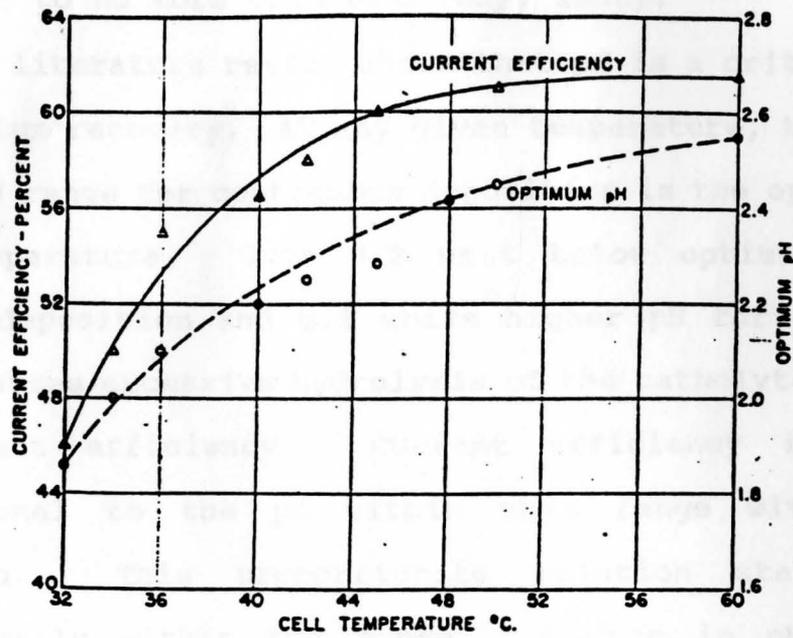


Figure 2-8. Effect of Catholyte Temperature on Current Efficiency and Optimum pH. (Udy, 1956).

According to the results, 20 mg per liter cell feed reached 60% current efficiency at 60°C, only 52-53% at 50°C and insufficient deposit at 40°C or so. As the pH curve flattens at higher temperature, temperature control needs less precision. According to Figure 2-9, a temperature above 60°C is desirable, but in practice, construction materials restrict the limit to no more than 65°C (Udy, 1956).

The literature review shows that pH is a critical factor in chromium recovery. At any given temperature, the midpoint of the pH range for continuous deposition is the optimum pH at that temperature. Just 0.2 unit below optimum pH stops electro deposition and 0.2 units higher pH for a prolonged period causes excessive hydrolysis of the catholyte and a drop in current efficiency. Current efficiency is directly proportional to the pH within this range with only 5% variation. This proportionate relation stabilizes pH automatically within the range. A drop in pH decreases current efficiency, thereby increasing hydrogen formation at the cathode, which increases pH again to its near optimum value. Even if the pH drops to where deposition stops, excessive hydrogen evolution causes pH to rise spontaneously and thereby restarts the process of deposition. In the reverse case of a pH rise, rising current efficiency will decrease hydrogen evolution and concentrate deposition of the metal. The only stabilization failure occurs when pH rises above the upper limit and gives a cumulative rather than

corrective effect. The increased hydrolysis of chromic sulfate with rising pH has limited buffering effect for the catholyte.

It is also worth noting that while efficient removal can be achieved at optimum pH, at pH 2.3 to 2.35 and 60°C the process yields metal with brighter and smoother texture, and with better appearance in general, though it contains more impurities such as sulfur, oxygen, and iron. Impurities in cell feed narrow down the pH range and affect cell design and catholyte circulation. Lead, nickel, or magnesium beyond certain limits decreases current efficiency. Current density also affects the pH factor and thereby the process of deposition. Higher densities deposit the metal uniformly but increase the tendency to form 'trees' after prolonged deposition. The chromium concentration in the catholyte influences the texture and adherence in inverse proportion. Lower concentrations yield a smoother and less adhered deposit.

The final influencing factor is the divalent to trivalent chromium ratio. Current efficiency drops sharply at ratios less than 1.0. A ratio above 1.0 can be maintained easily by protecting the catholyte from excessive aeration (Udy, 1956).

CHAPTER 3

METHODS AND PROCEDURES

This chapter explains the fundamental procedures in the experiments to find optimum pH for precipitation aluminum and chromium, and the details the two major successful experiments.

3.1 Method of Precipitation

Chemical precipitation is the most common and simple method to recover heavy metals, hazardous compounds, or expensive elements from chemical waste. The steps of the laboratory experiments on precipitation follow:

- 1) Acid washing of apparatus and containers.
- 2) Calibration of pH meter.
- 3) Preparation of solutions.
- 4) pH adjustment of samples at wide range of pH.
- 5) Settling of precipitates.
- 6) Analysis of supernatant for concerned metals.
- 7) Graphical or tabular evaluation of results.

Standard practice requires as acid wash of flasks and containers used in experiments to avoid any interference of trace elements that remain from previous use. These items were soaked in 10-20% nitric acid for 10-15 minutes and rinsed

thoroughly with deionized water.

A Fisher Accumet model 810 measured the initial pH and the pH variation after each stage for each solution. Before using the pH meter, it was calibrated by standard buffer solutions; for more acidic ranges, it was calibrated by 4.0 and 7.0 pH buffers; for the alkaline range, it was calibrated by 7.0 and 10.0 pH buffers. For all calibrations, the experimenter adjusted the intercept to the pH 7.0 buffer, and adjusted the slope to the other buffer solution.

After calibrating the pH meter and preparing sample solutions (see section 3.3), known volumes of samples were adjusted to a wide range of pH values so that optimum pH values for the minimum solubility of Al and Cr hydroxides could be determined. To find the concentrations of heavy metals in the supernatant water, the experimenter used Inductively Coupled Plasma Discharge (ICP) analysis. ICP is a convenient approach when concentrations of more than one element at a time are needed from the samples.

3.2 General Procedures for ICP Analysis of Heavy Metals

Heavy metals analysis by Applied Research Laboratories (ARL) Model 3410 includes the following steps:

- 1) Sample feeding to the plasma.
- 2) Dissociation of the sample by plasma.
- 3) Diffraction of light by monochromator grating.
- 4) Collection of signals by photomultiplier.

5) Computer presentation of results.

A cloud of electrons and argon ions held at high temperature is called plasma, and is maintained by applying radio frequency (RF) of several hundred watts. An initial supply of ions and electrons needed to ignite the plasma is generated by the ignitor by applying high voltage to ionize some argon atoms. ARL Model 3410 analyzes samples in solution form. The solution is conditioned to form a fine aerosol that is carried upward to the plasma.

At an operating temperature of 11,000K in plasma, the sample reaches 6000K, which dissociates the sample into free atoms and ions. Dissociated ions and atoms emit light at wavelengths characteristic of the elements present in the analyte. The photomultiplier tube collects the light passing through the exit slit and converts it into count generation, which is represented by computer as a meaningful result (ARL Model 3410 ICP Spectrometer User's Manual). The analytical results can be tabulated and converted into graphs to identify the optimum Ph for precipitation.

3.3 Experiments to Locate Optimum pH for Precipitation

Experiment #1.

Aim: To find the optimum pH for precipitation of Cr and Al hydroxides.

Apparatus: pH meter, stirrer, burets, pipets, buret stand, beakers, flasks, Mettler AE 100 analytical balance, etc.

Chemicals: H_2SO_4 (0.1 M), NaOH (0.2 M), $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, deionized water.

Preparation:

- a) Add 8 grams of NaOH pellets per liter of deionized water to make 0.2 M NaOH .
- b) Take 5.5 ml of concentrated H_2SO_4 per liter of deionized water to make 0.1 M H_2SO_4 .
- c) Take 2.5 grams of $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and 50 grams of $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ per 0.5 liter of deionized water to make synthetic F019 prewaste liquid with Cr:Al ratio of 1:10 by mass.

Procedure:

- a) Wash the apparatus with 10-20% nitric acid, followed by a thorough rinse with deionized water. Calibrate the pH meter by standard buffer solutions. Set two burets in a stand and fill one with 0.1 M H_2SO_4 and the other with 0.2 NaOH . Divide the prepared synthetic F019 waste into 20 aliquots of 25 ml each and place in 200 mL glass beakers.
- b) To make up an adequate workable volume of the samples, dilute the solution by adding

50 mL of prepared 0.1M H_2SO_4 and 0.2M NaOH each for the acidic range, and 50 ml of 0.2M NaOH and DI water each for samples in the alkaline range. The total volume of each sample is approximately 125ml.

- c) Adjust the pH of different samples by adding a measured volume of either acid or base from the burets while continuously stirring the sample on a magnetic stirrer. Adjust samples to pH's ranging from 3.0 to 12.0 in increments of 0.5 pH units.
- d) Settle the precipitate for 24 hours and draw about 25ml of the supernatant liquid from each sample. Analyze the extracted supernatant for Al and Cr by the ICP method and plot the results.

A professional analytical laboratory analyzed the proportion of Cr and Al in the original waste; the synthetic solution for the experiment was based on that analysis. A Cr:Al ratio of 1:10 by mass was used. After experiment #1, the experimenter realized the proportion was incorrect. The actual proportion of Cr:Al found by a second analysis was about 2:1, rather than 1:10. The experiment was repeated with the new Cr:Al ratio and the following changes in procedure.

Two hundred mg/l Cr and 100 mg/l Al (Cr:Al ratio 2:1),

1.0 gram of $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was added to 500 ml of deionized water. The solution was divided into 25 ml aliquots in 100 mL beakers and adjusted for different pHs from 4 to 13 in 1 unit increments. The samples' volumes were maintained by using NaOH pellets and concentrated H_2SO_4 for pH adjustment. The experimenter analyzed the samples for Cr and Al by ICP analysis. Results are shown in chapter 4 as results of experiment 1-A.

3.4 Experiment to Test Recovery and Toxicity of Cr and Al Precipitates

After the optimum pH investigation, an experiment was designed to test the recovery of Cr and Al under different precipitation sequences, and to check the toxicity of the resulting precipitates. Recovery was analyzed by doing total metals analyses on settled precipitate, and toxicity was analyzed using the Toxicity Characteristic Leaching Procedure (TCLP) test.

Experiment #2.

Aim: To compare the results of TCLP tests on sludge from single stage and double stage precipitation.

Apparatus: pH meter, magnetic stirrer, Mettler AE 100 analytical balance, buret, pipets, flasks, vacuum filter etc.

Chemicals: $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, standard buffers, NaOH, H_2SO_4 , original F019 cake, etc.

Preparation:

- a) Make up identical sample solutions 1 and 2 by adding 50 grams of $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and 45 grams of $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ to one liter of deionized water.
- b) Dissolve 100 g of original F019 waste from industry into 1 M H_2SO_4 to make sample solution 3.

Procedure:

- a) Take sample solution 1 and measure the initial pH of the solution. If it is in the acidic range of 2.0-3.0, add 10 g NaHSO_3 to reduce all hexavalent Cr to the trivalent state (Tested for hexavalent chromium by Colorimetric method) (Mettee, personal communication). By adding NaOH pellets, raise pH to 8.5 to mimic the process carried out by the aluminum extruders. Use 0.2 M NaOH to fine tune the adjusted pH and let the precipitate settle for 24 hours. Vacuum filter the precipitate of Cr and Al hydroxides and perform TCLP and total metals tests on the precipitated cake.
- b) Verify that the initial pH of sample

solution 2 is in the range of 2-3; reduce hexavalent Cr to trivalent state by adding 10 g NaHSO₃, and raise the pH to 12.0 by adding NaOH pellets to optimize precipitation of Cr hydroxides. Vacuum filter the precipitate after 24 hours of settlement and perform the TCLP and total metals tests on the resulting cake. Lower the pH of the remaining supernatant solution to 6.5 by adding 1 N H₂SO₄ and settle for 24 hours. Vacuum filter the Al hydroxide precipitate and perform total metal test on the cake.

- c) Follow the same process on sample solution 3 as sample 2 and perform the TCLP and total metals tests on the precipitates. Analyze the liquid remaining after two-stage precipitation for Al and Cr to determine if it is safe for disposal.

3.5 TCLP and Total Metals Analysis

The original TCLP test involves a specific approach and standard operations as described in Federal Register, vol.55, No.126, 1990. A slightly different procedure was used in this study as a TCLP substitute and is described below.

The TCLP procedure involves selecting an extraction fluid

to apply to the solid waste based upon the initial pH, followed by stirring of the mixture for 16-20 hours and analysis of the leachate after 18 hours of settlement. If concentrations of all elements of interest are under the limits defined by the regulatory agency, disposal of the waste by conventional landfilling would be allowed. Instead of using 100 g of solid waste in 2,000 mL of extraction fluid as recommended in TCLP, 25 grams in 500 mL was used in the laboratory equivalent TCLP test. Also, magnetic stirring for 16-20 hours was used instead of a standard stirring apparatus. Details of the procedures used are given below.

3.5.1 TCLP Test

I) Extraction Fluids:

Fluid I : 5.7 ml Glacial Acetic acid + 500 ml deionized water + 64.3 ml of 1 N NaOH (40 gram/L), (pH = 4.93 ± 0.05) all diluted to 1 liter of final volume by adding deionized water.

Fluid II : 5.7 ml Glacial Acetic acid diluted to 1 liter with deionized water (pH 2.68 ± 0.05).

II) Selection of Extraction Fluid:

Take 1.25 gram of solid in a 125 mL beaker, add 25 mL of water, stir for 5 minutes and measure the pH .

If pH < 5.0, use Extraction Fluid I.

If pH > 5.0, add 0.9 mL 1 N HCl, raise the temperature

to 50°C for 10 minutes and cool it. Then:

If pH < 5.0 use Extraction fluid I.

If pH > 5.0, use Extraction fluid II.

(Federal Register, 1990)

III) Procedure:

Take 25 g of solid in 500 mL of extraction fluid and stir it for 18 +.2 hours. Extract the supernatant after 24 hour settlement and test for Al and Cr by ICP method.

3.5.2 Total Cr and Al Analysis

Total Cr and Al were measured also on the precipitate resulting from Experiment #2. The experimenter added 2.5 g of solid waste into 45 mL deionized water and 5 mL of concentrated HNO₃ and thoroughly mixed before ICP analysis.

3.6 Experiment for Mass Balance Analysis

In addition to locating optimum pH and toxicity measurement for Cr and Al hydroxides, one more experiment was performed to track the mass balance of the synthetic and original F019 waste during the recovery process as described below.

Experiment #3

Aim: To perform mass balance analysis of the Cr and Al recovery process.

Apparatus: pH meter, stirrer, beakers, vacuum filters, Mettler AE 100 analytical balance, test tubes, etc.

Chemicals: $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, NaOH, H_2SO_4 , deionized water, F019 waste.

Preparation:

- a) Add 11.25 g $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and 12.50 g of $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in deionized water to make a total volume of 500 ml for sample 1, 2, and 3. This was called "synthetic F019".
- b) Add 50 g of industrial F019 cake in 1 M H_2SO_4 to make total volume of 500 mL for samples 4, 5, and 6. This was called "original F019 waste".

Procedure:

- a) Wash the apparatus and calibrate the pH meter as mentioned in experiment #1. Take 5 mL of each sample and dilute it to 100

mL each by adding 2 mL concentrated H_2SO_4 and deionized water. Use this to analyze for the initial total Al and Cr. Raise pH of sample solutions 1 and 4 to 12.5 by adding NaOH pellets while continuously stirring the samples on a magnetic stirrer. Raise pH of sample solutions 2 and 5 to 13.0 and 3 and 6 to 13.5 in similar way. Settle the precipitates for 24 hours and separate from the liquid by vacuum filtration. Measure the weight of precipitate cakes and the volume of liquid left for each samples. Take 0.5 g of each cake in 3 ml concentrated H_2SO_4 and deionized water to make a total volume of 100 mL each for ICP analysis. Also analyze 5 mL of liquid left after filtration diluted to 100 ml by adding 3 ml concentrated H_2SO_4 and deionized water.

- 2) Drop the pH of liquids left after first-stage precipitation to 6.5-7.0 by adding concentrated H_2SO_4 while stirring continuously. Settle the precipitates for 24 hours and separate the precipitates by vacuum filtration. Measure the weight of each cake and the volume of waste water

after second stage precipitation. Take 0.5 g of each cake for analysis and 5 mL of waste water to analyze for Al and Cr by diluting both of them separately as stated above.

Chapter 4

RESULTS AND DISCUSSION

4.1 Results of Experiment #1

The experimenter prepared a synthetic solution of F019 liquid waste for Experiment #1 by dissolving 2.5 g $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and 50 g $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ into 500 mL deionized water. The Cr:Al ratio by weight of the synthetic sample solution was 1:10. The liquid waste was divided into 25 mL samples and adjusted to different pHs. After 24 hours of settlement of precipitation, the supernatant of each sample was analyzed for Al and Cr by ICP analysis. Table 4-1 shows these results. Figure 4-1 shows a graph for experiment #1.

4.1.1 Interpretation of Results of Experiment #1

In Figure 4-1, pH versus log concentration of metals in mg/l is drawn to present solubility of both metals. The figure shows that at the 5.5-8.5 pH range, aluminum hydroxide is least soluble. From about pH 4.0, aluminum starts to precipitate in acidic media and reaches minimum solubility level at about 5.5. It stays in precipitate form until pH 8-8.5 and returns to solution as the pH becomes alkaline. Similarly, chromium starts to precipitate as hydroxide from about pH 3.5, reaches a minimum solubility

Table 4-1. Final Supernatant Concentrations of Cr and Al from Experiment #1 (Cr:Al of 1:10 in Initial Solution).

Sample	pH	Cr(mg/l)	Al(mg/l)	Log(Cr)	Log(Al)
1	3	112	1465	2.049	3.166
2	3.5	119	1509	2.075	3.179
3	4	22	613	1.34	2.79
4	4.5	1.1	65	0.041	1.81
5	5	0.079	2.9	-1.1	0.46
6	5.5	0.013	<0.075	-1.89	<-1.12
7	6	0.016	<0.075	-1.79	<-1.12
8	6.5	0.005	<0.075	-2.3	<-1.12
9	7	0.007	<0.075	-2.15	<-1.12
10	7.5	0.005	<0.075	-2.3	<-1.12
11	8	0.007	<0.075	-2.15	<-1.12
12	8.5	0.008	0.571	-2.09	-0.24
13	9	0.028	4.4	-1.55	0.64
14	9.5	0.025	13.1	-1.6	1.17
15	10	0.021	45.8	-1.68	1.66
16	10.5	0.02	130	-1.7	2.11
17	11	<.015	390	-1.82	2.59
18	11.5	0.025	807	-1.6	2.91
19	12	0.49	670	-0.31	2.83
20	12.5	2.4	789	0.38	2.9

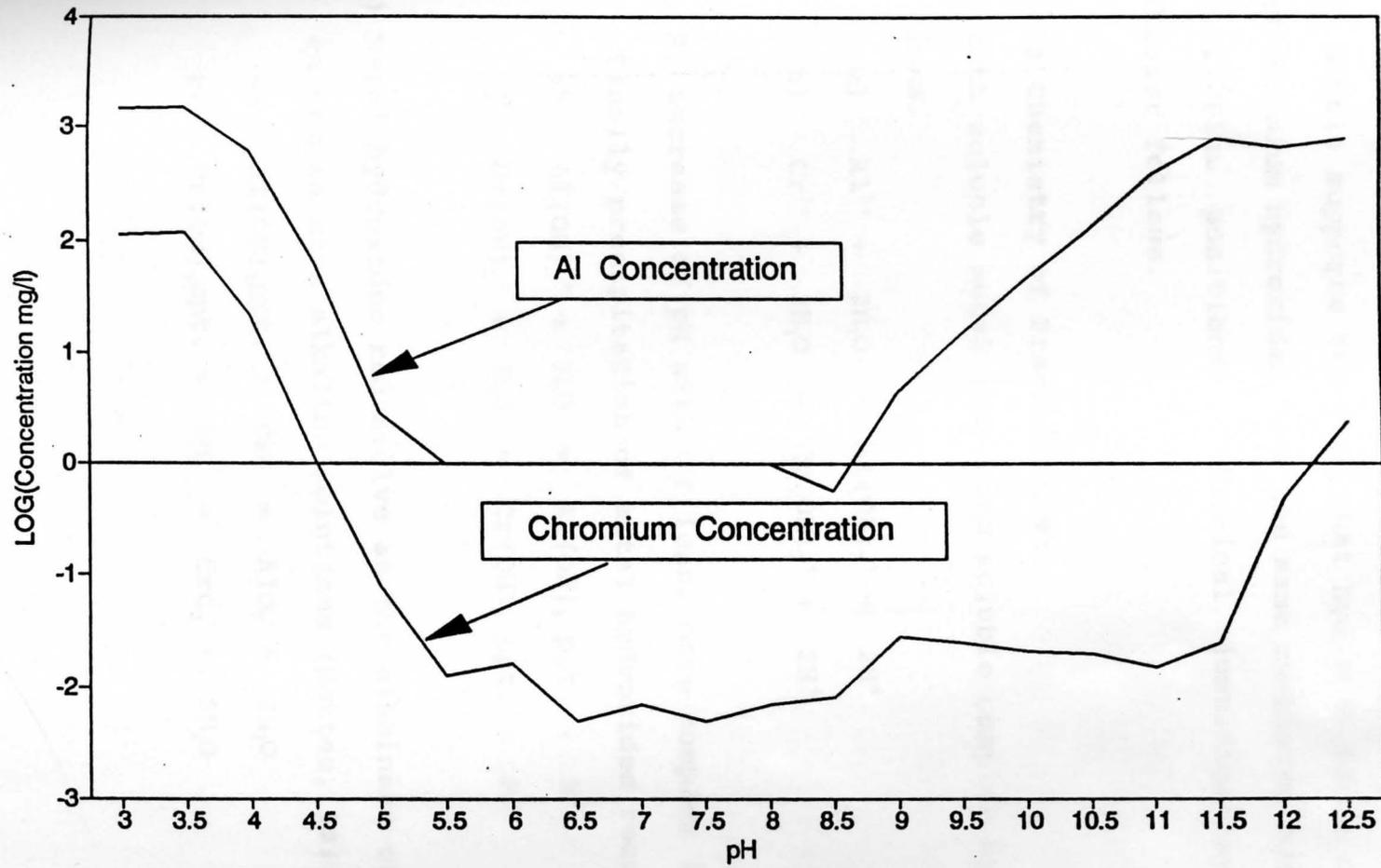
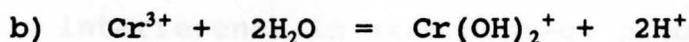


Figure 4-1. Solubility of Aluminum and Chromium Vs pH (Experiment #1).

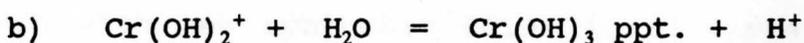
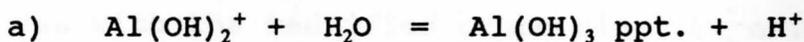
level near 6.0, stays at that level until 11-11.5, and then returns to solution. The noticeably similar behavior of these two metals supports the fact that hydrated forms of aluminum and chromium hydroxides have the same chemistry but different equilibrium positions. Chemical justification of this behavior follows.

4.1.2 Chemistry of Precipitation

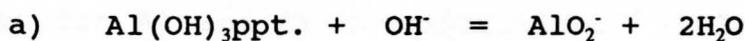
1) Both soluble metal ions form soluble complex hydroxide ions.



2) By increase of pH with OH^- ions, more complex ions and finally precipitation of metal hydroxides results.



3) Metal hydroxides redissolve as the aluminate or chromite anions in more alkaline solutions (Mettee, 1993).



4.1.3 Comments on Results of Experiment #1

The succession of chemical reactions indicate that both soluble metal ions essentially follow the same process of precipitation and dissolution but at different pH ranges. The results also imply that to obtain maximum possible Cr content (with minimum Al contamination) of precipitate, a high pH should be used. Although at a pH higher than 11.5, chromium hydroxide starts to redissolve, chromium hydroxide with a minimum of Al can be recovered at pH 12. The result indicates the best pattern for the process, i.e. to precipitate chromium first at higher pH and then aluminum at lower pH to avoid chromium interference in second stage precipitation.

The proportion of Cr:Al of 1:10 used in Experiment #1 was corrected later to 2:1 in industrial F019 waste after authentic lab analysis. To verify the behavior of metal hydroxides with the rectified proportion, Experiment #1A was performed with new synthetic F019 liquid waste. One g of $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ each were dissolved into 500 mL deionized water and each sample of 25 mL was adjusted to varying pH. Supernatants after 24 hours settlement were analyzed for Al and Cr concentration. Table 4-2 shows the tabulated results and Figure 4-2 plots pH vs concentration in mg/l.

Table 4-2. Final Supernatant Concentrations of Cr and Al from Experiment #1A (Cr:Al of 2:1 in Initial Solution)

Sample	pH	Cr(mg/l)	Al(mg/l)
1	5	0.582	2.475
2	6	0.949	2.447
3	6.5	2.455	2.391
4	7	0.084	0.162
5	7.5	0.274	0.301
6	8	0.326	0.58
7	9	1.394	1.75
8	10	2.838	4.565
9	10.5	2.115	7.408
10	11	1.811	11.449
11	11.5	0.907	24.407
12	12	0.433	45.727
13	12.5	0.501	47.037

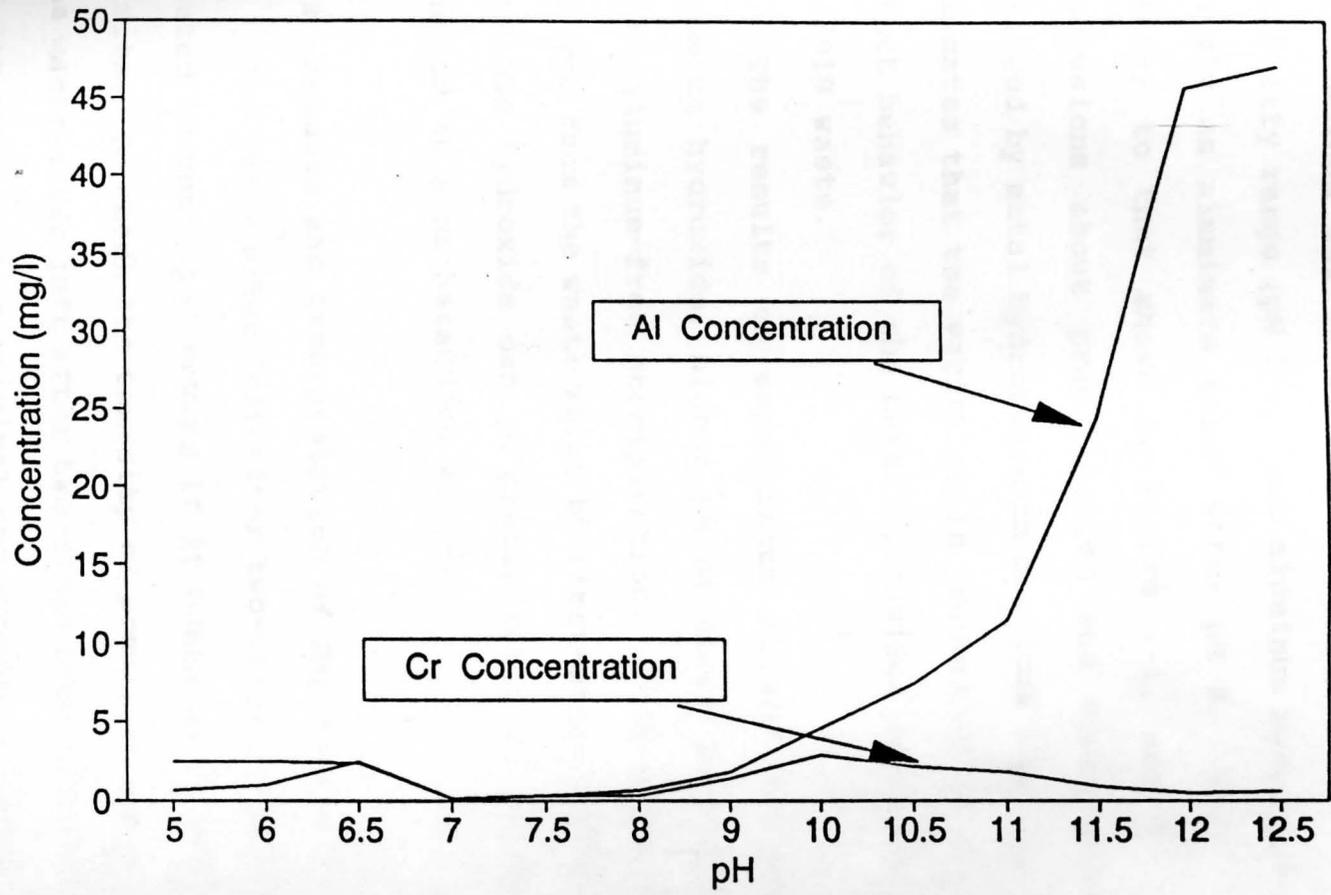


Figure 4-2. Solubility of Aluminum and Chromium Vs pH (Experiment #1A).

4.1.4 Interpretations of Results of Experiment 1A

As shown in the Figure 4-2, metal hydroxides of chromium and aluminum follow about the same curve at its minimum solubility range (pH 7-8), but aluminum hydroxide redissolves sharply as aluminate anion after pH 8. This behavior is similar to that shown in Figure 4-1, and strengthens the conclusions about precipitation and dissolution reactions followed by metal hydroxides in previous experiments. It also indicates that the variation in proportion of metals does not affect behavior of the metal hydroxides in synthetic solution of F019 waste.

The results of experiments #1 and #1A show that for chromium hydroxide, higher pH of about 12.0 is suitable to reach aluminum-free precipitation. Once chromium is nearly removed from the waste water by first-stage precipitation, the aluminum hydroxide can be precipitated at pH around 6-7 and removed as a nonhazardous solid.

4.2 Results and Interpretation of Experiment #2

The waste water left after two-stage precipitation can be routed to municipal sewers if it contains Cr under regulatory limits. To check the toxicity of precipitated solid cakes and the waste water left after two-stage precipitation, Experiment #2 was performed on original and synthetic waste. Section 3.4 describes the details of experiment, and the TCLP and total metal test procedures are

Table 4-3. The Results of TCLP and Total Metal Tests for Experiment #2.

Sample		pH	Cr(mg/l)	Al(mg/l)
TCLP test				
1	Synthetic F019	8.5	64.61	16.049
2	Synthetic F019	12	91.68	16.832
3	Original F019	12	0.769	2.813
Total test (units: mg metal/g wet cake)				
For Cr cake			Cr(mg/g)	Al(mg/g)
1	Synthetic F019	8.5	49.36	25.39
2	Synthetic F019	12	85.81	33.99
3	Original F019	12	17.97	10.74
For Al cake				
1	Synthetic F019	6.5	0.06	49.38
2	Original F019	6.5	0.008	19.64
Wastewater				
			Cr(mg/l)	Al(mg/l)
1	Synthetic F019	8.5	< 0.015	0.423
2	Synthetic F019	12	< 0.015	2.707
3	Original F019	12	0.667	6.915

described in section 3.5.

Table 4-3 describes the results of the TCLP and total metal test performed on synthetic and original F019 cakes. Two synthetic and one original F019 liquid waste samples were prepared as described in section 3.4. The experimenter induced single-stage precipitation on a synthetic sample and two-stage precipitation on a synthetic and an original sample. The TCLP test was done on 25 g of all three filter cakes and the supernatant leachates were analyzed for aluminum and chromium. The total metal test was performed on 2.5 g of each cake dissolved into 50 ml of 1 M HNO₃ and was analyzed for aluminum and chromium. To check the chromium concentration in waste water, all three samples were analyzed by ICP method.

The results of Experiment #2 are as follows:

- a) Chromium concentrations from the TCLP test on synthetic F019 cake were above the allowable limit of 5.0 mg/l in both cases. Conversely, Cr was considerably less than the allowable limit for the TCLP on leachate from original F019 waste cakes. Also, the original waste yielded much less aluminum than the synthetic waste in the TCLP analysis.
- b) Results of the total metal test analysis for aluminum hydroxide cakes (second-stage precipitate) showed very little contamination by chromium for both synthetic and original wastes. About 40% of the aluminum precipitates with chromium in the first stage and 60% precipitates

as pure aluminum hydroxides in second stage for the synthetic waste. In the original waste, about 33% of the aluminum precipitates with chromium in the first stage and 67% precipitates as aluminum hydroxides in the second stage.

- c) Chromium concentration in the waste water after precipitation was under the allowable limit of disposal, i.e. 5 mg/l (Mettee, personal communication, 1993), in all three cases.

From the TCLP test results, a significant difference in concentration of chromium leached from synthetic and original waste is evident. One (or all) of the following could be responsible.

- a) Since the proportion and concentrations of metals in original F019 waste vary for different batches of waste, it is possible that Cr was more concentrated in the synthetic waste solution than in the original waste solution.
- b) As there are many more impurities present in original waste, it is possible that occlusion (due to electrostatic attraction) retained chromium in the solid cake, and thereby avoided leaching it into TCLP supernatant.
- c) Other precipitates besides Cr and Al hydroxides may have formed from the impurities in the original F019 waste.

Total metal test results strongly suggest that the second-stage precipitates of aluminum hydroxide are nonhazardous in both the original and synthetic wastes. The ratio of solid cake mass to liquid volume was identical for the total metal test and the TCLP test. Also, the total Cr fell below the TCLP limits for the second-stage cake. This makes it possible to dispose of a portion of the original F019 waste as nonhazardous waste if two-stage precipitation is used.

Since the synthetic waste was prepared by dissolving 50 g of $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and 45 g of $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ into 1 liter of deionized water, total Cr and Al concentrations were calculated as follows.

Salt	Wt.g	F.W.	A.W.	Metal Wt. mg/l
$\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	50	499.4	52.0	$52/499.4 * 50 = 5206$
$\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	40	474.4	27.0	$27/474.4 * 40 = 2561$

The Cr:Al ratio by weight for synthetic waste was 2:1. This was based on the results of analysis of the three different industrial waste F019 cakes shown in Table 4-4.

Table 4-4. Constituents of F019 Waste (Mettee, personal communication, 1993).

	I	II	III
% water	60.0	71.7	11.2
% solids	40.0	28.3	88.8
Cr(% of solid)	12.8	5.23	7.1
Al(% of solid)	6.62	2.65	1.9

Though the Cr:Al ratio remained constant, the concentration varied with these two cake samples. Therefore, the possibility of less concentrated cake in the TCLP and total metals tests cannot be ignored.

4.3 Results of Experiment #3

After the detailed analysis of recovery and toxicity, the final experiment traced the paths of chromium and aluminum during the process. Experiment #3 analyzed the mass balance. To measure the recovery of chromium at pH higher than 12.0, three samples each of the synthetic and original waste were adjusted to pHs of 12.5, 13.0 and 13.5. Another experiment objective was to obtain the purest chromium hydroxide precipitate (Cr cake) possible in the first stage (i.e. minimum Al content) and the purest aluminum hydroxide

precipitate (Al cake) possible in the second stage (i.e. minimum Cr content). A detailed description of the experiment is in section 3.6.

The experimenter prepared the synthetic waste samples by dissolving 12.50 g of $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and 11.25 g of $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ into 0.5 liter of deionized water. To prepare as original waste sample, the experimenter dissolved 50 g of solid cake from industrial F019 into 0.5 liter of water. Six samples (three synthetic waste and three original waste) were made in these proportions. From four samples, 5 mL was analyzed to measure the initial metal concentrations. Samples of 0.5 g solid cake and 5 mL liquid waste were taken at each stage of two-stage precipitation to test for recovery rates and contamination. For the ICP analysis, the experimenter dissolved all cakes into 100 mL of 1 N HNO_3 , and all 5 mL liquid aliquots were diluted to 100 mL with 1 N HNO_3 . Table 4-5 shows the analytical results of metal concentrations for each case at different pHs.

4.3.1 Interpretation of Results of Experiment #3

Results for the sample solutions indicate the initial total metal concentrations, and results for the supernatants indicate the metal concentrations in the liquid after first-stage precipitation in each case. As all samples had 0.1 liter of diluted volume, to calculate the absolute mass

Table 4-5. Analytical Results and Calculations (Experiment #3).

Stage 1 pH	Sample	Analysis Results		Aliquot Mass		Total Mass	
		Al mg/l	Cr mg/l	Al mg.	Cr mg.	Al mg.	Cr mg.
12.5	Original F019						
	Sample Sol.	100.793	119.465	10.079	11.947	1007.9	1194.7
	Cr cake	21.51	75.064	2.151	7.506	318.1	1110
	Supernatant	86.731	0.111	8.673	0.011	745.9	0.95
	Al cake	99.067	0.025	9.907	0.003	568.1	0.14
	Wastewater	0.854	0.069	0.085	0.007	6.5	0.52
13	Original F019						
	Sample sol.	98.751	114.329	9.875	11.433	987.5	1143.3
	Cr cake	20.415	99.376	2.042	9.938	226.4	1102.1
	Supernatant	93.889	0.173	9.389	0.017	845	1.58
	Al cake	82.661	0.064	8.266	0.006	705.6	0.55
	Wastewater	0.558	0.097	0.056	0.009	4.2	0.73
13.5	Original F019						
	Sample sol.					997	1169
	Cr cake	12.416	101.643	1.242	10.164	136.8	1120.1
	Supernatant	105.673	0.264	10.567	0.026	908.8	2.27
	Al cake	77.594	0.097	7.759	0.009	692.9	0.87
	Wastewater	0.112	0.219	0.011	0.022	0.87	1.71

Table 4-5 Continued

pH	Name	Analysis Results		Aliquot Mass		Total Mass	
		Al mg/l	Cr mg/l	Al mg.	Cr mg.	Al mg.	Cr mg.
12.5	Synthetic F019						
	Sample sol.					607	1324
	Cr cake	45.358	190.171	4.536	19.017	339.27	1422.5
	Supernatant	32.33	0.071	3.233	0.007	284.5	0.62
	Al cake	198.299	0.523	19.829	0.052	273.26	0.72
	Wastewater	1.374	0.097	0.137	0.009	11.4	0.81
13	Synthetic F019						
	Sample sol.	59.778	130.077	5.978	13.008	597.8	1300.8
	Cr cake	40.421	211.113	4.042	21.111	263.7	1377.3
	Supernatant	39.215	0.13	3.926	0.013	352.94	1.17
	Al cake	146.205	0.274	14.621	0.027	302.5	0.57
	Wastewater	1.096	0.112	0.109	0.011	9.31	0.95
13.5	Synthetic F019						
	Sample sol.	61.485	134.734	6.149	13.473	614.9	1347.3
	Cr cake	24.424	176.219	2.442	17.622	182.7	1318.1
	Supernatant	47.659	0.314	4.766	0.031	424.17	2.79
	Al cake	174.86	1.178	17.486	0.118	371.1	2.5
	Wastewater						

in the sample aliquot in mg, each measured concentration was multiplied by 0.1 liter. To calculate the total mass, the aliquot mass was multiplied by the following factors:

a) For the 0.5 g cake samples,

$$\text{Multiplication Factor} = \frac{\text{Total Cake Weight (g)}}{0.5 \text{ (g)}}$$

b) For the 5 mL liquid samples,

$$\text{Multiplication Factor} = \frac{\text{Total Fluid Volume (mL)}}{5.0 \text{ (mL)}}$$

The following are sample calculations for reference.

a) * Mass of metals in 0.5 g sample of Cr cake at pH 12.5 from original waste sample:

$$\text{Al} = 2.151 \text{ mg} \qquad \text{Cr} = 7.506 \text{ mg}$$

$$* \text{ Total cake weight at pH 12.5} = 73.94 \text{ g}$$

$$* \text{ Multiplication Factor} = 73.94 / 0.5 (=147.88)$$

$$* \text{ Total concentration Al} = 318.1 \text{ mg} \quad \text{Cr} = 1110 \text{ mg}$$

b) * Mass of metals in 5 mL of sample solution at pH 12.5 from original waste sample:

$$\text{Al} = 10.079 \text{ mg} \qquad \text{Cr} = 11.947 \text{ mg}$$

$$* \text{ Total volume of sample solution} = 500 \text{ mL}$$

$$* \text{ Multiplication Factor} = 500 / 5 (=100)$$

$$* \text{ Total concentration Al} = 1007.9 \text{ mg} \quad \text{Cr} = 1194.7 \text{ mg}$$

4.3.2 Mass Balance Calculations

According to the law of conservation of mass, the mass of metals must be the same at any stage. If applied to the process of first-stage precipitation, the initial amount of a metal in the sample solution must be equal to the sum of the mass of metal precipitated and the mass remaining in the supernatant. A generalized word statement can be expressed as follows:

$$\begin{array}{l} \text{Mass of metal} \\ \text{In sample solution} \\ \text{(MASS IN)} \end{array} = \begin{array}{l} \text{Mass of metal} \\ \text{In cake + In supernatant} \\ \text{(MASS OUT)} \end{array}$$

Considering the original F019 at pH 12.5, initial metal masses were 1007.9 mg and 1194.7 mg for aluminum and chromium, respectively. The total mass of aluminum in first-stage cake plus supernatant was 1064 mg and chromium was 1110.95 mg. For aluminum, the calculated final mass exceeded the initial mass by about 6-7%. The chromium's final mass was 7% less than its initial mass. Table 4-6 shows the mass balance calculations for the first stage of precipitation in each case. 7-8 % error due to transmission loss and experimental error was acceptable. Therefore, the experimenter assumed that the samples satisfied the law of mass conservation.

4.3.3 Comments and Discussion on the Results of Experiment 3

Table 4-7 that shows that while the chromium recovery

Table 4-6. Mass Balance Results for Experiment #3

Sample	pH	Metal	Mass In mg	Mass Out mg			% Diff.
				Cake	Supernat.	Total	
Original F019	12.5	Al	1007.9	318.1	745.9	1064	5.6
		Cr	1194.7	1110	0.95	1110.95	-7
	13	Al	987.5	226.4	845	1071.4	8.5
		Cr	1143.3	1102.1	1.58	1103.68	-3.5
	13.5	Al	997	136.8	908.8	1045.6	4.9
		Cr	1169	1120.1	2.27	1122.37	-4
Synthetic F019	12.5	Al	607	339.27	284.5	623.77	2.7
		Cr	1324	1422.5	0.62	1423.12	7.4
	13	Al	597.8	263.7	352.94	616.64	3.2
		Cr	1300.8	1377.3	1.17	1378.47	5.9
	13.5	Al	614.9	182.7	424.17	606.87	-1.3
		Cr	1347.3	1318.1	2.79	1320.89	-1.9

Table 4-7. Percentage Metal Recovery Results for Experiment #3

Sample	pH	Cr Reco. %	Al Reco. %
Original F019	12.5	93	31.5
	13	96.4	22.9
	13.5	95.6	13.6
Synthetic F019	12.5	107	55.9
	13	106	44
	13.5	97.8	29.6

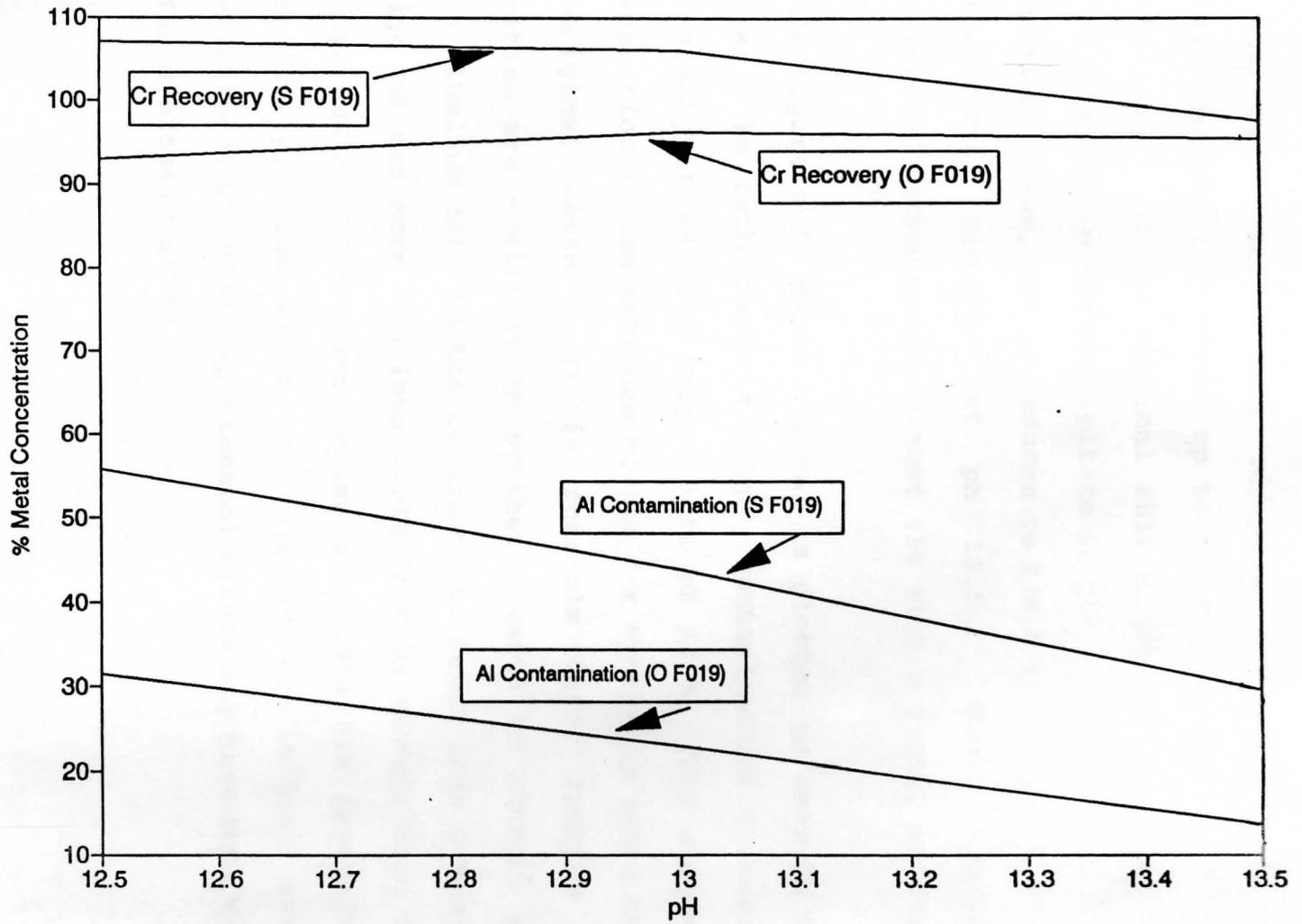


Figure 4-3. Effect of pH on Metal Recovery and Contamination.

in the cake varies only slightly with pH, aluminum contamination can be reduced up to 50% by increasing pH from 12.5 to 13.5. In the original F019 sample at pH 12.5, the mass of aluminum in the precipitate is 318.1 mg, i.e. 31.5% of the total aluminum, but it reduces to 136.8 mg, which is 13.6% of the total aluminum at pH 13.5. Thus, aluminum contamination decreases by almost 45% with a 1 unit increase of pH.

In Figure 4-2, pH vs % metal is plotted to compare the results. In both cases aluminum contamination decreased considerably at pH 13.5 compared to pH 12.5. The aluminum contamination in the cake was higher for synthetic waste than for original waste. It is possible that, because no impurities are available in synthetic waste to attract and retain aluminum ions in the supernatant, fewer ions dissolve at high pH and more aluminum contamination occurs than the original waste. Since recoveries over 100% are impossible theoretically, some error in analysis of initial metal concentrations or other experimental errors may have been made for the synthetic water.

CHAPTER 5

CONCLUSION AND SCOPE OF FURTHER WORK

The goals of this project were to (1) locate the optimum pH for the recovery of chromium from an aluminum extrusion industry waste water, (2) minimize the quantity of hazardous waste produced by two-stage precipitation and (3) keep the concentrations of metals in waste water at nonhazardous levels for final disposal.

The first experiment demonstrated an optimum pH of about 12 for chromium recovery, but the final experiment involving mass balance analysis showed a higher pH of 13.5 to be optimum for chromium recovery with minimum aluminum contamination. If a market can be found for chromium with some aluminum impurities, the recovered chromium at pH 13.5 can provide revenue for aluminum extruders rather than cost them disposal expense. Though the two-stage precipitation would require purchase and installation of additional tank and conveyance pipes, in the industrial setting, costs might be justified when compared to long term disposal expenses.

Following Cr precipitation at pH 13.5, aluminum can be separated as almost pure hydroxides at pH 7.0 and 70-80% of total aluminum can be recovered in the second stage of precipitation. The aluminum hydroxide precipitate separated

from the chromium waste can be disposed of as nonhazardous waste if not utilized in other industries. By separating the precipitation into two stages, disposal costs can be reduced.

Results of experiments #2 and #3 show that the metal concentrations in the waste water after the precipitation process are within the allowable limits. Thus, the waste water can be discharged safely to the municipal treatment plants after metal recovery.

NaOH and H_2SO_4 were used as reactants in the laboratory experiments for the precipitation of metal hydroxides. Alternative reactants should be tested and efficiency and cost compared. If chromium hydroxide with high concentrations of aluminum is found to have no value, it is possible that the impurities can be reduced by adding appropriate polyelectrolytes. When added at a certain stage of precipitation, polyelectrolytes may reduce occlusion and thereby reduce aluminum contamination. Since temperature affects precipitation, further experiments should be performed to find an optimum temperature for chromium recovery. The combination of processes such as precipitation and electrolysis also could be explored.

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