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CR(III) AND ZN(II) REMOVAL ORIGINATING FROM A SYNTHETIC CHROMIUM
PLATING WASTEWATER BY COPRECIPITATION

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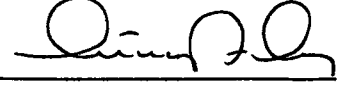
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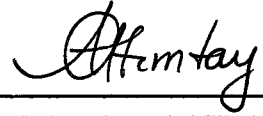
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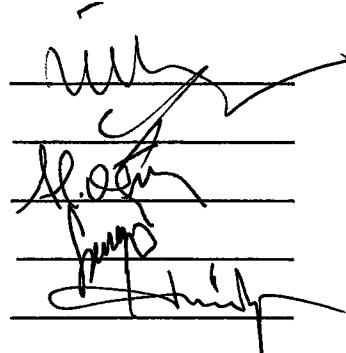
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ABSTRACT

CR(III) AND ZN(II) REMOVAL ORIGINATING FROM A SYNTHETIC CHROMIUM PLATING WASTEWATER BY COPRECIPITATION

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Today, as the discharge limits set for the heavy metals are getting stricter, researches are focused on the evaluation of the additional removal mechanisms to increase the efficiencies of the existing methods. At this point, the supportive effect of these additional removal mechanisms, such as adsorption on preformed flocs, occlusion or coprecipitation during precipitate formation have to be taken into account, where the removals determined by the solubility products through hydroxide precipitation become insufficient to meet the recent standards.

In this study, Cr(III) and Zn(II) originating from a simulated chromium plating wastewater have been removed by coprecipitation through the application of alum, within the framework of the deficiency in terms of evaluating the extent of the supporting effect of coprecipitation in the removal of heavy metals in the application of chemical treatment methods like hydroxide precipitation. Through this objective, in the firsthand, a standard jar test has been applied to Cr(III) and Zn(II) with initial metal concentrations of 100 and 25mg/l respectively to determine the optimum conditions for the coprecipitation of Cr(III) and Zn(II) (alum dose and pH), and for the hydroxide precipitation of Cr(III) and Zn(II) (optimum pH) in the mixed-metal solutions in a comparative approach.

While the optimum conditions determined for the coprecipitation trial are 70mg/l dose of alum and pH of 9.50 with corresponding residual concentrations of 0.044mg/l Cr(III) and 0.038mg/l Zn(II), optimum value obtained for that of hydroxide precipitation trial is pH of 10.80 with the corresponding residual metal concentrations of 0.6mg/l Cr(III) and 0.513mg/l Zn(II). The results have shown that the coprecipitation is effective for both of the metals nearly with an order of magnitude relative to hydroxide precipitation. In the second part of the experimental procedure coprecipitation and hydroxide precipitation trials have been completed in single metal solutions without application of a standard jar test, in order to see the synergistic effects of metals and the difference between single and mixed-metal behavior.

In the coprecipitation trial while the minimum residual Cr(III) concentration has been obtained at the alum dose of 30mg/l and constant pH of 8.70, the minimum value that of Zn(II) of 0.152mg/l have been attained at alum dose of 80mg/l and constant pH of 8.70. In the hydroxide precipitation of Cr(III), minimum residual concentration (3.75mg/l) has been obtained at pH 8.5, while the minimum residual Zn(II) concentration (3.41mg/l) has been attained at pH 10.55. At this point, it is apparent that the coprecipitation is effective also in single metal systems compared to hydroxide precipitation.

On the other hand, while the coprecipitation of Cr(III) alone seems more efficient slightly than that of mixed-metal solution, zinc removal has been enhanced nearly with an order of magnitude by the presence of Cr(III) in the mixed-metal solution. But, it is apparent that the direct precipitation of Cr(III) and Zn(II) in single metal solutions are not efficient in terms of residual metal concentrations and the stability of the flocs (redissolution of the flocs).

Finally, the effects of ligand (sulfate) concentration, aging and initial metal concentration on the removal efficiency of coprecipitation have been investigated for the mixed-metal solutions of Cr(III) and Zn(II) under the conditions near to optimum values determined before. In ligand (sulfate) application, while the maximum residual Cr(III) concentration

(0.083mg/l) has been attained at the sulfate concentration of 1350mg/l, change in the residual Zn(II) concentration has been negligible with the change in sulfate concentration. On the other hand, on aging of the coprecipitated metals, maximum Cr(III) residual concentration of 0.571mg/l and maximum residual concentration of Zn(II) of 1.827mg/l have been obtained at the settling period of 24 hours.

In the end, the effect of the initial metal concentration variation has been searched through the application of four different initial concentrations of 100, 75, 50, 25mg/l and 5, 12.5, 17.5, 25mg/l for Cr(III) and Zn(II) respectively. Minimum residual concentrations of 0.018mg/l Cr(III) and 0.550mg/l Zn(II) have been obtained at the highest initial concentrations (Cr(III)=100, Zn(II)=25mg/l) for both of the metal.

In a general approach, it is apparent that the adverse effects of the ligand (sulfate) concentration, aging and initial metal concentration on the removal efficiency in coprecipitation trial can be compensated to a great extent especially under the conditions near to optimum values (optimum alum dose and optimum pH). This shows also the stability of the coprecipitated flocs against the variations of these parameters.

Keywords: heavy metals, chemical treatment, Cr(III) precipitation, Zn(II) precipitation, coprecipitation, hydroxide precipitation, aluminum sulfate, ligand, sulfate, aging

ÖZ

SENTETİK KROM KAPLAMA ATIKSUYUNDAN KAYNAKLI CR(III) VE ZN(II) METALLERİNİN BİLEŞİK KİMYASAL ÇÖKTÜRME YÖNTEMİ İLE UZAKLAŞTIRILMASI

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Bugün, ağır metaller için uygulanan deşarj limitlerinin giderek katılaşması, arařtırmaları mevcut artım metodlarının verimliliğinin artırılması için ilave mekanizmaların ortaya çıkarılması üzerinde yoğunlařtırmaktadır. Bu noktada, çözünlük çarpımlarına dayalı hidroksit çökeltme yöntemi ile yapılan artımın mevcut standartları sağlamada yetersiz kalmasından dolayı, çökelti oluşumu sırasında sağlanabilecek, yüze toplama, bileşik çöktürme gibi ilave uzaklařtırma mekanizmalarının gözönüne alınması gerekmektedir.

Bileşik çöktürme yönteminin, ağır metallerin uzaklařtırılmasındaki destekleyici rolünün belirlenmesine yönelik çalışmaların eksikliğinden yola çıkılarak, bu çalışmada, sentetik olarak hazırlanmış bir krom kaplama atıksuyundan kaynaklanan Krom (Cr(III)) ve Çinko (Zn(II)), alüminyum sülfat uygulamak suretiyle bileşik çöktürme yöntemiyle uzaklařtırılmıştır. Çalışmada ilk önce, standard bir testle, 100 ve 25mg/lt giriş konsantrasyonlarındaki Cr(III) ve Zn(II)'in bileşik çöktürme ve hidroksit çöktürme için gerekli uygun alüminyum sülfat dozu ve pH mukayeseli olarak test edilmiştir. Bu uygulamanın sonuçlarına göre, bileşik çöktürme için en uygun alum dozu ve pH, 70mg/lt ve 9.50 olarak

belirlenmiş olup, çıkış Cr(III) konsantrasyonu 0.044mg/lt, Zn(II) konsantrasyonu ise 0.038mg/lt olarak tespit edilmiştir. Diğer taraftan, hidroksit çöktürme için en uygun pH, 10.80 olarak belirlenmiş ve bunun sonucu olarak da, Cr(III) çıkış konsantrasyonu 0.6mg/lt, Zn(II) çıkış konsantrasyonu ise 0.513mg/lt olarak tespit edilmiştir. Bu sonuçlar bileşik çöktürmenin hidroksit çöktürmeye nazaran her iki metal için de daha etkili olduğunu göstermektedir. Deneysel işlemlerin ikinci kısmında, bileşik çöktürme ve hidroksit çöktürme yöntemleri her iki metale tek tek uygulanarak, birleşik metal sistemleri ile tek metal sistemleri arıtım verimliliği bakımından karşılaştırılmıştır. Böylece, bileşik çöktürme uygulamasındaki en düşük Cr(III) çıkış konsantrasyonu, 0.034mg/lt, 30mg/lt'lik alum uygulamasında elde edilirken, en düşük Zn(II) çıkış konsantrasyonu, 0.152mg/lt, 80mg/lt'lik alum uygulamasında elde edilmiştir. Diğer taraftan, Cr(III)'un hidroksit çöktürmesi sonucunda elde edilen en düşük çıkış konsantrasyonu, 3.75mg/lt, pH 8.50'da sağlanmış iken, Zn(II) için en düşük çıkış konsantrasyonu, 3.41mg/lt, pH 10.55'de sağlanmıştır. Bu da göstermektedir ki; bileşik çöktürme yöntemi tek metal uygulamalarında da etkindir.

Diğer taraftan, Cr(III)'un tek başına bileşik çöktürmesi, birleşik metal sisteminde elde edilen sonuçtan daha verimli görünürken, Zn(II)'in Cr(III) ile birlikte çöktürülmesi (bileşik), Zn(II) için yaklaşık on kat verimli olmuştur. Fakat, diğer yandan her iki metal için de, tek metal sistemlerinde uygulanan hidroksit çöktürme yöntemi nispeten verimsiz olmuştur.

Son kısımda ise, sülfat konsantrasyonu, çöktürme süresi (yumak olgunlaştırma) ve metal giriş konsantrasyonunun bileşik çöktürme yöntemi üzerindeki etkileri, daha önce belirlenen en uygun koşullara (uygun alum dozu ve pH) yakın koşullarda araştırılmıştır. Sülfat uygulaması sonucunda, en yüksek Cr(III) çıkış konsantrasyonu, 0.083mg/lt, 1350mg/lt'lik sülfat miktarında elde edilirken, Zn(II)'in sülfat konsantrasyonuna bağlı değişimi ihmal edilebilirdir. Diğer taraftan, bileşik olarak çöktürülmüş metallerin olgunlaştırılmasında (yumak olgunlaştırma),

yine en yüksek Cr(III) çıkış konsantrasyonu, 0.571mg/lt, ile en yüksek Zn(II) çıkış konsantrasyonu, 1.827mg/lt, 24 saatlik çöktürme süresinin sonunda elde edilmiştir.

Son olarak, giriş metal konsantrasyonlarının bileşik çöktürme üzerindeki etkilerini araştırmak üzere, Cr(III) için 100, 75, 50 ve 25mg/lt ve Zn(II) için 25, 17.5, 12.5 ve 5mg/lt'lik giriş konsantrasyonları uygulanmıştır. Bunun sonucunda, en düşük Cr(III) çıkış konsantrasyonu, 0.018mg/lt ve en düşük Zn(II) çıkış konsantrasyonu, 0.550mg/lt, her iki metal için de en yüksek giriş konsantrasyonlarında elde edilmiştir.

Genel olarak, bileşik çöktürme uygulamasında arıtım veriminin, özellikle uygun arıtım koşullarında (uygun alüminyum dozu ve pH), sülfat konsantrasyonu, çöktürme süresi (yumak olgunlaştıma) ve metal giriş konsantrasyonu farklılıklarından çok fazla etkilenmediği görülmüştür. Bu da aynı zamanda, bileşik çöktürme yöntemiyle uzaklaştırılmış metallerin değişen koşullara karşı dayanıklılığını göstermektedir.

Anahtar Kelimeler: ağır metaller, kimyasal arıtım, Cr(III) çöktürme, Zn(II) çöktürme, bileşik çöktürme, hidroksit çöktürme, alüminyum, sülfat, yumakların olgunlaştırılması

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CHAPTER 1

INTRODUCTION

1.1 Heavy Metals, Impacts on Environment and Treatment Methods

Increasing industrial waste discharges into water sources have focused attention on heavy metals as pollutants. Main sources of heavy metals are base metal mine drainage, metal finishing industries, electric and electronic industry, tanneries, textile mills, petrochemical industries and other commercial activities. Among these industrial sources, plating industries possess great importance because of their considerable contribution to the industrial wastewater amount with the diversity of the constituents (Chen et al., 1974).

The metals of most immediate concern are; chromium, iron, cobalt, manganese, nickel, copper, zinc, cadmium, mercury and lead. Heavy metals occur largely in neutral minerals as sulfides, oxides, carbonates and silicates. These natural compounds are generally insoluble in water and very slowly broken compounds by weathering. On the other hand, the forms of heavy metals exhibit greater diversity in the wastewaters including soluble, insoluble, inorganic, metal organic, reduced, oxidized, free metal, precipitated, adsorbed and complexed. In such a variety of the forms, treatment type is selected depending on the purpose of either removing the considered metal ions or preventing the harmful effects by converting the metals to safer forms (Maruyama et al., 1975).

Although some of the metals are essential dietary elements, others are cumulative poisons when ingested, and today it is known that metals can be concentrated to toxic levels by bioaccumulation through food chain that may have both acute and chronic impacts on living organisms . But the actual toxicity of heavy metals depends on several factors, such as water hardness, pH, synergistic effects of different metals and etc.

Heavy metals in domestic wastewaters are generally caused by the discharge of industrial waste to the sewer or infiltration of water that has passed through the deposits of metal-bearing minerals. Especially in combined sewer systems, there may be high concentrations of certain metals with an order of 10 to 100 times those normally present in domestic wastewater even in the absence of significant amounts of industrial wastewater discharge (Blakeslee, 1973). And this fact attained in domestic wastewater puts forward another aspect of controlling heavy metals as these metals can interfere with the operating efficiency of treatment plants consisting or being to upgraded to secondary treatment with secondary treatment units and anaerobic digesters (Mytelka et al., 1973).

Achievement of stringent requirements for heavy metal removal is obligatory because of the facts mentioned above. The constraints and the standards are getting stricter day by day with the new national and international requirements and the priorities parallel to the uncontrolled increase of the industrial development. In this respect, although, the typical Environmental Protection Agency's (EPA) limit has been 1 ppm for each metal for the direct discharge to the environment before (Hannah et al., 1977), today it has been pulled down to between 0.5-0.01 ppm. with the last findings and the reassessments. On the other hand, typical discharge limits for receiving body indicated in Water Pollution Control Regulation of Turkey (1995) are 0.5 ppm and 3.0 ppm for chromium and zinc respectively.

There are several methods for the treatment of heavy metals. But, the selection of the most proper method depends on several parameters and your priorities. Mostly, heavy metals are responsive to practical treatment processes which have already been developed for water purification purposes.

Most common methods are physico-chemical processes consisting of precipitation (hydroxide, carbonate or sulfide), coprecipitation, adsorption, ion-exchange, membrane separations (reverse osmosis or electrodialysis), solvent extraction, electrodeposition, cementation and combinations of these.

Among these methods, hydroxide precipitation by lime application is the generally preferred one because of its simplicity and the low cost of the precipitant, particularly where complex chemical compounds are not involved and the recovery of the metals is not considered. On the other hand, the removal efficiencies obtained through the application of the hydroxide precipitation method are observed to be above the expected values predicted according to the solubility product concerns. And this fact is attributed to the additional removal mechanisms occur together with the hydroxide precipitation. At this point, the supportive effect of these additional removal mechanisms, such as adsorption on preformed flocs, occlusion or coprecipitation during precipitate formation have to be taken into account, where the removals determined by the solubility products become insufficient to meet the recent standards. Although the application of adsorption by the addition of coagulants has become widespread in wastewater treatment, coprecipitation is considered to a lesser extent than adsorption. Today, optimization studies for the coprecipitation process are still being carried on in a comparative approach especially with adsorption.

Within this framework, it is easily observed that, while the adsorption of the heavy metal ions on the natural adsorbates or the formed flocs by using alum or ferric sulfate (mostly used coagulants) have been frequently studied in the literature, there is a relative deficiency in terms of the application of coprecipitation, especially by using alum as a coagulant for the removal of heavy metals from wastewaters. On the other hand, some trials of coprecipitation method by using iron salts are insufficient in order to make comparisons between coprecipitation and other removal mechanisms for all kind of heavy metal wastes.

The general criteria in the determination of the proper treatment method is the consideration of cost which should be minimized while the technical objectives are met. In order to achieve the right selection each waste treatment problem must be regarded as a special case demanding a study of the chemistry and the economics involved.

1.2 Scope and Objective

The main objective of the study is to evaluate the difference between the removal efficiencies of coprecipitation and direct precipitation processes while confirming the supportive effect of the coprecipitation through the treatment of Cr^{3+} and Zn^{2+} originating from a simulated chromium plating wastewater. Additionally, the extent of the effects of various parameters, like aging, ligand and initial metal concentrations, and the combined effect of different metals in the mixed-metal solutions on the coprecipitation have been also searched. Because of the deficiency in the literature mentioned above, alum + lime and lime have been used for the provision of coprecipitation and direct precipitation respectively in this study. The main reason of choosing chromium plating wastewater is the wide spreading of chromium plating industry all over the world because of the properties of chromium as a plating element.

In the preparation of the simulated wastewater, zinc and chromium have been used as the main constituents, and sulfate has been selected as the chelating agent which is one of the additives mostly used in plating processes.

Overall aims are:

- Verification of the difference between coprecipitation and direct precipitation processes in terms of the removal of Cr^{3+} and Zn^{2+} in mixed metal solution.
- Determination of the optimum alum dosage and alum/lime ratio for the maximum coprecipitation of Cr^{3+} and Zn^{2+} in mixed metal solution.
- Determination of the optimum alum dosage and alum/lime ratio for the maximum coprecipitation of Cr^{3+} and Zn^{2+} separately in single metal solutions to compare the efficiency of coprecipitation in single metal and mixed metal solutions.
- Determination of the optimum pH for the optimum alum/lime ratio in mixed metal solution.
- Determination of the effects of various ligand concentrations (SO_4) and the initial Cr^{3+} and Zn^{2+} concentrations on the removal efficiency of Cr^{3+} and Zn^{2+} in mixed metal solution.
- Determination of the degree of the expected correlation between coagulation-flocculation process and the aging time in mixed metal solution.

A simulated chromium plating wastewater has been preferred, as the simplicity of a synthetically prepared system could lead better understanding of the mechanisms. Besides, the complex composition of a real plating wastewater may prevent the proper distinguishment of coprecipitation and direct (hydroxide) precipitation.

1.3 Outline of the Study

The experiments below have been performed in order to attain the main objective of the study :

- Evaluation of the optimum alum dosage for the maximum removal of Cr^{3+} and Zn^{2+} at constant pH, in the absence of ligand (SO_4) through the application of alum + lime in mixed metal solution.
- Evaluation of the optimum lime dosage for the optimum hydroxide precipitation, at constant pH (pH adjustment with NaOH) in the absence of ligand, through the application of lime alone in mixed metal solution.
- Evaluation of the optimum alum dosages for the maximum removal of Cr^{3+} and Zn^{2+} at constant pH, in the absence of ligand (SO_4) through the application of alum + lime in single metal solutions.
- Evaluation of the optimum lime dosages for the optimum hydroxide precipitation, at constant pH (pH adjustment with NaOH) in the absence of ligand, through the application of lime alone in single metal solutions.
- Evaluation of the optimum pH for the optimum alum/lime ratio in the absence of ligand (pH adjustment with NaOH) in mixed metal solution.

- Determination of the effects of the different ligand concentrations on the coprecipitation (optimum alum + lime application) of Cr^{3+} and Zn^{2+} , for the same wastewater, at optimum pH .
- Determination of the effects of the different initial metal concentrations on the coprecipitation of Cr^{3+} and Zn^{2+} , for optimum alum + lime dosage at optimum pH, in the absence of ligand in mixed metal solution.
- Determination of the correlation between the aging time and the coagulation-flocculation process in the application of the coprecipitation of Cr^{3+} and Zn^{2+} in mixed metal solution.



CHAPTER 2

LITERATURE REVIEW

In this chapter, an overview on the items which are thought to be within the framework of this study has been accomplished through the literature survey in order to create a baseline for an integrated approach to the subject. And the harmonized background of chemical and aqua-chemical behavior of chromium and zinc, electroplating industry, methods applied for the treatment of chromium plating wastewaters and the differences between direct precipitation, adsorption and coprecipitation in terms of mechanism, removal efficiency and the precipitate structure have been presented in the following sections of this chapter.

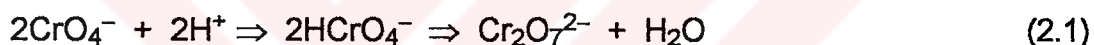
2.1 Aquatic Chemistry of Chromium and Zinc

2.1.1 Chromium Behavior in Aquatic Environment

Chromium exists in aquatic environment in two main oxidation states, chromium(III) and chromium(VI) (or, trivalent and hexavalent chromium respectively) which are characterized by different chemical behavior. Other oxidation states of chromium are rare and unstable in aqueous systems (Imai, 1988).

The oxidation state of chromium has a profound effect on its toxicity and bioavailability. While Cr(VI) is well known for its toxicity for bacteria, plants and animals, Cr(III) is far less toxic.

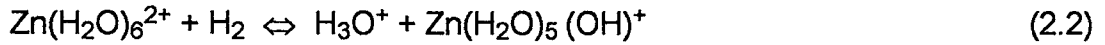
Most natural sources of chromium contain the element in its trivalent condition. In aqueous solutions, Cr(III) undergoes hydrolysis with the formation of hydroxocations including polynuclear chromium species and, chromium(III) speciation in aqueous systems is dominated by these chromium(III) hydrolysis products such as CrOH^{2+} , Cr(OH)_2^+ , $\text{Cr}_2(\text{OH})_4^+$, Cr(OH)_3^0 , $\text{Cr}_4(\text{OH})_6^{6+}$ and $\text{Cr}_6(\text{OH})_{12}^{6+}$. On the other hand, Cr(VI) can form the following anionic forms of CrO_4^{2-} , HCrO_4^- and $\text{Cr}_2\text{P}_2^{-7}$ depending on the concentration of its ions and the acidity of the solution (Nazirmadov et al., 1988). And a mobile equilibrium exists between them like the representation below ;



2.1.2 Zinc Behavior in Aquatic Environment

Although zinc is an essential element, it becomes toxic in high concentrations. Unlike most of the transition metals which are characterized by variable valence, zinc exhibits an oxidation state of +2 only. And in this state, it forms complex cations and anions such as; $\text{Zn(NH}_3)_4^{2+}$ (tetrahedral), Zn(CN)_4^{2-} and ZnCl_4^{2-} (Wood and Holliday, 1977).

In aquatic environment, zinc ions go through hydrolysis like other metal cations, and some of these hydrated cations hydrolyze. The hydrolysis of the zinc ion indicated as $\text{Zn(H}_2\text{O)}_6^{2+}$ can be represented as (Mortimer, 1979);



And as it is seen from the reaction above, through hydrolysis, $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ functions as an acid and donates a proton to H_2O , which acts as a base.

Zinc forms precipitate with hydroxyl ion and this water-insoluble compound acts as an amphoteric hydroxide which can be dissolved in solutions of low pH or high pH.

Abundance ratios of soluble zinc species are dependent on pH and presence of various coexisting materials in the solution. According to the calculated distribution of various soluble zinc species in the presence of sulfate, it was found that Zn^{2+} was a main component under a sulfate concentration of 1.0 gr/m^3 and that ZnSO_4 was a main component over a sulfate concentration of 1.0 kg/m^3 , other zinc species were negligible in all ranges of sulfate concentrations (Chohji et al., 1990).

Distribution of soluble zinc species in accordance with pH and through reactions and equilibrium constants is shown in Table 2.1.

Accordingly, for the total zinc concentration (C_{ZT}), in the absence of any complexing agent, the following equation by Chohji et al. (1990) can be written:

$$C_{\text{ZT}} = [\text{Zn}^{2+}] + [\text{Zn}(\text{OH})^+] + [\text{Zn}(\text{OH})_2] + [\text{Zn}(\text{OH})_3^-] + [\text{Zn}(\text{OH})_4^{2-}] \quad (2.3)$$

Table 2.1 Solution Equilibria and Equilibrium Constants for Zinc
(Crawford et al., 1993)

Solution Equilibria	Constant
$Zn^{2+} (aq) + H_2O \leftrightarrow Zn(OH)^+ (aq) + H^+ (aq)$	$p^* K_1 = 9.25$
$Zn(OH)^+ (aq) + H_2O \leftrightarrow Zn(OH)_2(aq) + H^+ (aq)$	$p^* K_2 = 10.16$
$Zn(OH)_2(aq) + H_2O \leftrightarrow Zn(OH)_3^-(aq) + H^+ (aq)$	$p^* K_3 = 10.96$
$Zn(OH)_3^-(aq) + H_2O \leftrightarrow Zn(OH)_4^{2-} (aq) + H^+(aq)$	$p^* K_4 = 11.70$
$Zn(OH)_2(ppt) + H_2O \leftrightarrow Zn^{2+} (aq) + 2OH^- (aq)$	$p^* K_{s0} = 16.50$

2.2 Electroplating Industry

Large quantities of both metal and plastic parts are electroplated to provide corrosion or wear resistance. Typical plating metals are tin, cadmium, copper, gold, platinum, silver and zinc. In electrolytic finishing industry, chromium is the mostly used metal in surface treatments to prevent corrosion, improve durability of the product and enhance the retention of paints and other final finishes because of the high corrosion resistance of chromium reducing the wear under corrosive conditions.

Chromium plating can be applied on steel beverage cans and as chemical conversion coatings on non-ferrous metals, especially Mg, Al, Zn, and Cd. Chromium plated plastics now are used widely in the automotive industry at the expense of plated die-cast zinc parts (Nriagu, 1988).

In basic process, the parts to be plated are made the cathode and suspended in a solution that contains dissolved salts of the metal to be deposited. And the anode is suspended slab of the metal to be deposited.

Almost all electroplating processes essentially are the same. There are two main types of chromium plating which are known as hard chromium and porous chromium (Avner, 1972). A typical flow chart of chromium plating industry is given in Figure 2.1 (Rudolfs, 1953).

As chromium plating procedures are already changing as a result of some developments, standard characterization of the finishing wastewaters may change also. Especially additions of ferrous, chromium sulfates and other additives made, in order to increase the efficiency and the throwing power of the system, may cause differences in the composition of the chromium plating wastewaters.

The wastes are usually generated in the rinsing step of the plating process after removal from the baths. However, the intermittent dumping of the spent process solution also cause major peaks in concentrations (WHO and UNEP, 1982).

In typical chromium plating systems (both decorative and engineering type), likely contaminants include sulfate, chloride, fluoride, perborate, sulfonate, fluoraborate, phosphates, silicates, sulfide, Cr(III), chromate, nickel (II), zinc (II) and low levels of surface active agents and organic brightening agents (ex: sulfonamide) (Cheremisinoﬀ and Habib, 1972).

Chromium plating wastes are usually colored with floating scum, oil and metal particles containing both suspended and dissolved solids. Generally, chromium is found in a soluble form as CrO_4 salts. The color of the wastes is clear, greenish or reddish according to the type of the process applied and the pH of the system.

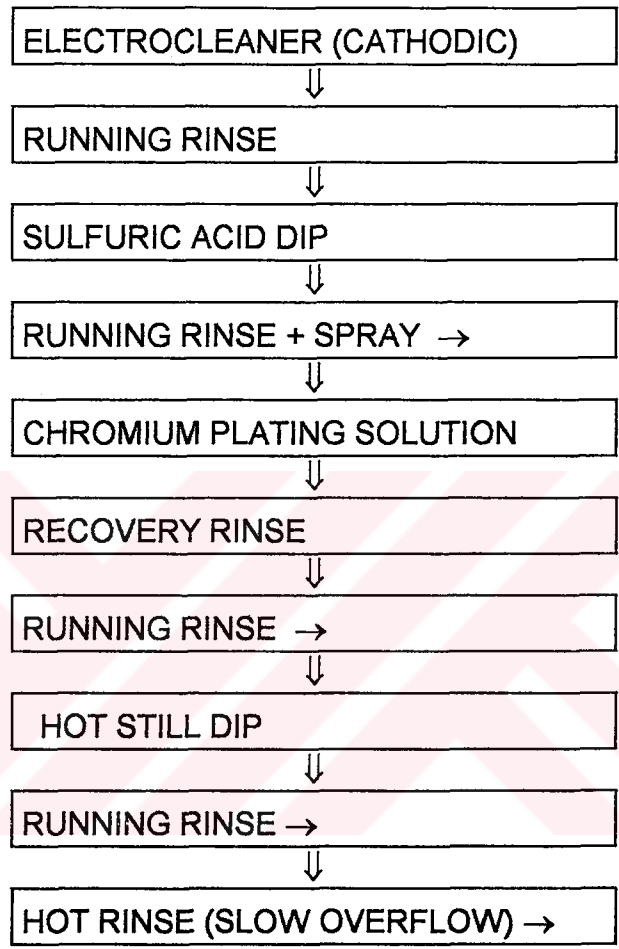


Figure 2.1 Flow Chart of Chromium Plating Process

Water characterization of the samples taken from some small and large electroplating establishments are shown in Table 2.2.

Table 2.2. Characterization of Chromium Plating Wastewaters
(Sanciolo et al., 1992)

Sample	Conductivity (Ω^{-1})	pH	Heavy Metal Concentration (ppm)		
			Cr	Ni	Zn
A	1.39×10^{-3}	2.9	52.0	35.1	0.6
B	1.22×10^{-3}	3.0	79.3	52.9	3.0
C	1.04×10^{-3}	2.9	79.4	24.3	1.0
D	-	2.8	228.0	69.0	0.9

2.3 Handling of Chromium Plating Wastewaters and Types of Treatments

The search for the determination of the efficient, cost-effective options for treatment of chromium plating wastewaters has been intensified in recent years depending on the potential risk arising from the high toxicity of Cr(VI) which is the main component of chromium plating wastewater. Also, better methods of recovery and reuse are concerned while meeting the stringent discharge limits. The following sub-sections review the conventional treatment methods applied for the removal of chromium and zinc in a general approach and the applicability of some other removal mechanisms in the treatment of chromium plating wastewater.

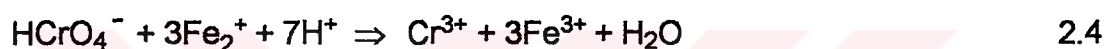
2.3.1 Chromium Removal

2.3.1.1 Hydroxide Precipitation of Chromium

The application of the conventional solid separation methods is the mostly used way in the treatment of chromium plating wastewaters based on the hydroxide precipitation of Cr(III) through the transformation to poorly

soluble compounds after the reduction of highly soluble Cr(VI) compounds to Cr(III) compounds (Zotter and Liesko, 1992). For the reduction of Cr(VI) some reducing agents are used. And then, in a mildly alkaline medium poorly water soluble Cr(III) hydroxides are formed which then can be removed by conventional solid - liquid separation methods (Schlegel, 1963; Parsons, 1965; Eckenfelder, 1989; Patterson, 1985).

In the reduction process, pH of the aqueous environment must be reduced to about 2.0-3.0 with hydrochloric or sulfuric acid, as pH is the controlling parameter for the rate of the reaction. Sulfurdioxide or sodiummetabisulfite are added as the reducing agent. The reduction reaction by ferrous sulfate can be represented as:



On the other hand, the use of NaHSO₃ in a highly acidic medium as the reducing agent for the treatment of the surface finishing wastewaters seems impractical because of the repeated pH adjustments involved. And in some studies, waste iron (II) sulfate instead of N₂HSO₃ appears preferable especially from the viewpoint of economics because of its dual effect as both reducing agent and coagulating agent (Fe(II) is oxidized to Fe(III) compounds). This process requires no pH adjustment but produces more sludge than that of SO₂ or N₂HSO₃. However, it seems more economical than sulfite reduction .

In a general approach, hydroxide precipitation optimization is in line with the minimum solubility of the metal hydroxide. And on account of this, in the treatment techniques based on hydroxide precipitation, metal removal depends heavily on pH. Theoretical precipitation curves for various metals as hydroxides are shown in Figure 2.2 (Feigenbaum, 1977).

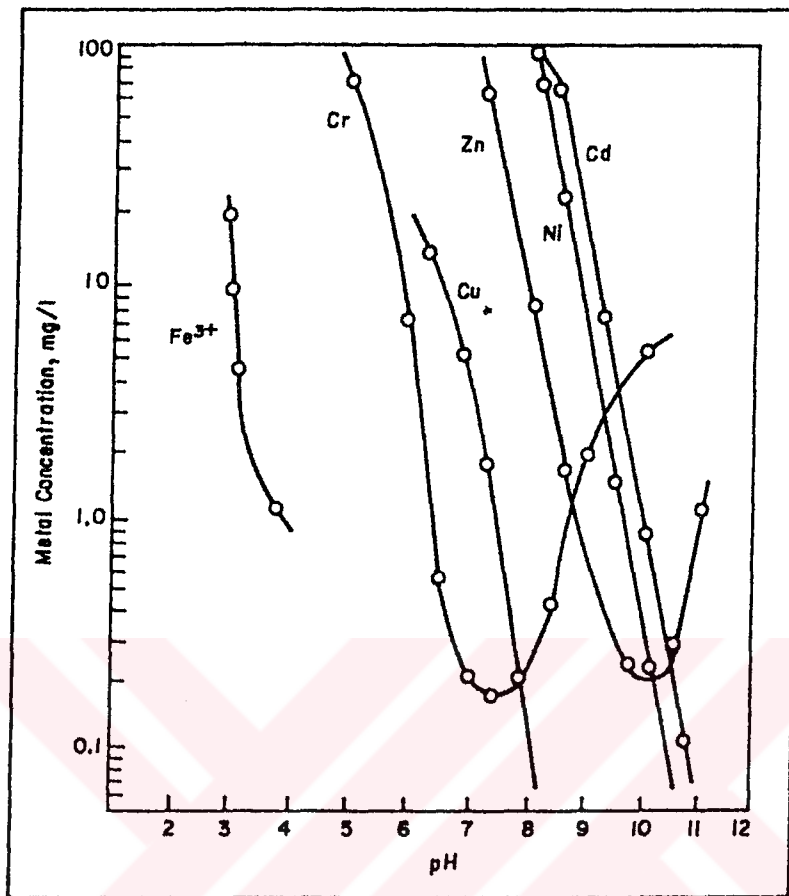


Figure 2.2 Precipitation of Heavy Metals as Hydroxides

Although most of the metal salts will tend to become insoluble in neutral pH range, not all metals will precipitate at the same pH point and to the same extent, e.g. trivalent chromium at pH 7.5, copper at pH 8.0-9.0, zinc at pH 10.0-11.0 and cadmium 11.0-12.0 (US Environmental Protection Agency, 1977). Within this framework, the initial problem in separation may be to decide the optimum pH for most complete precipitation of the metals present in the wastewater where each of them may exhibit great differences in terms of complexation and precipitation.

Other considerations for the provision of the maximum hydroxide precipitation are; choice of precipitant, operating temperature, valence state of the metal and the presence of complexing and chelating agents, especially ammonia, chloride, cyanide, bromide, sulfate having adverse effects on physico-chemical processes (Lanouette, 1977). In order to determine the optimal configuration, bench scale and pilot scale studies including all the factors indicated above should be conducted.

In the precipitation of trivalent chromium, at a pH range of 8.5-9.5, provided by the addition of lime or caustic soda, chromium readily reacts with water to produce insoluble Cr(OH)_3 . And on aging, Cr(OH)_3 transforms gradually into the chromium hydrous oxide, $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, by forming hydroxo-bridges which is amorphous and very insoluble (Imai, 1988). The formation of insoluble chromium hydroxide can be represented as:



Where B_{so} is the hydrolysis constant for chromium.

On the other hand, there is not any accurate data in literature for the solubility product of Cr(OH)_3 and other Cr(III) hydrolysis constants. It is presented in the study of Rai and Sass et al. (1987), that polynuclear species do not become dominant but possibly Cr(OH)_3^0 and Cr(OH)_4^- are the dominant mononuclear species in a pH range of about 2.6 - 14.0. And, the kinetics of precipitation and dissolution are very rapid and that equilibrium is reached in six days or less below pH 2.0. The solubility diagram of Cr(OH)_3 is shown in Figure 2.3 (Imai, 1988).

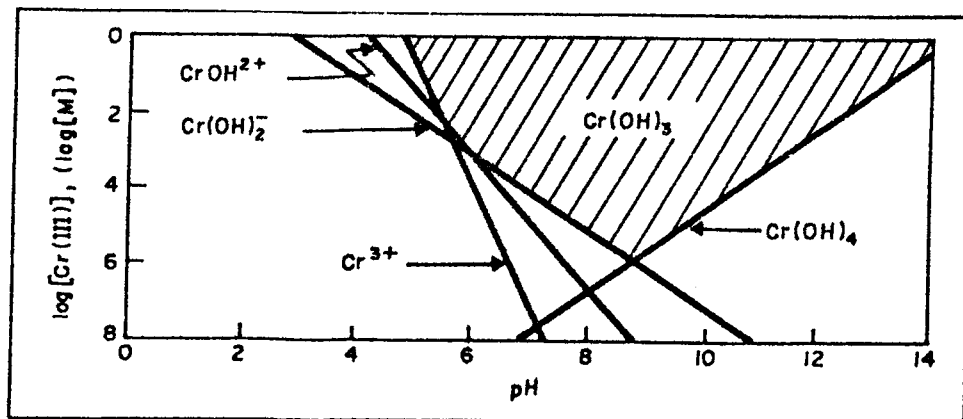


Figure 2.3 Solubility Diagram of $Cr(OH)_3$

2.3.1.2 Other Methods

There are several other methods which are applied for the direct removal of hexavalent chromium without reducing to Cr(III) but these trials have not been optimized yet for widespread applications. Among these methods, especially adsorption on iron hydroxide, aluminum oxide, hair, rice husk, bone powder, bituminous coal, waste biomass, crushed coconut shell and sawdust have been often tried. And in these methods maximum removal of Cr(VI) has been observed at lower pH values.

In another study performed in India (Namasivayam and Ranganathan, 1992), the application of waste Fe(III)/Cr(III) hydroxide as an adsorbent for the removal of the hexavalent chromium from a plating wastewater has given good results. And the maximum removal of Cr(VI) and total chromium has been attained at pH 5.0.

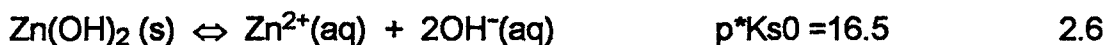
On the other hand, a comprehensive study on the use of removal mechanisms of adsorption, ion-exchange, oxidation-reduction, precipitation and combinations of these has shown that all the mechanisms may work for Cr removal depending on the contaminant concentration, pH, presence of ligands and competing species (Clifford and Sorg, 1986).

2.3.2 Zinc Removal

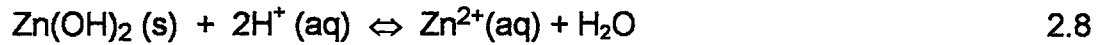
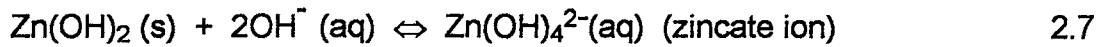
2.3.2.1 Hydroxide Precipitation of Zinc

Hydroxide precipitation by the addition of lime or caustic soda is widely used for the removal of zinc also, the other component of chromium plating wastewater.

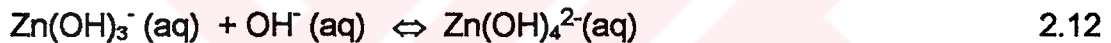
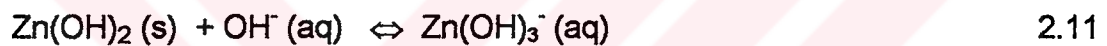
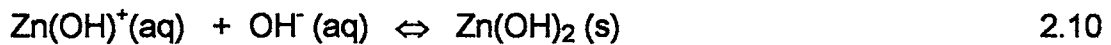
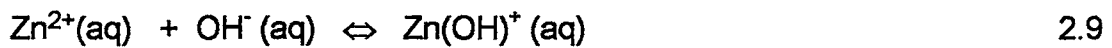
During precipitation, zinc forms a slightly soluble gelatinous hydroxide in the presence of equivalent quantities of the hydroxide ion:



On the other hand, because of its amphoteric nature it may redissolve as the soluble zincate or zinc ion in alkali or acidic solutions respectively (Mortimer, 1979), as shown below:



The following series of equations can be used to describe the distribution of zinc species with gradual increase of the OH^- concentration of a $\text{Zn}^{2+}(\text{aq})$ solution. And these equilibrium relationships can also be represented by a solubility diagram given in Figure 2.4 (Wood and Holliday, 1977).



Although there is a confusion in the literature about the accuracy of the solubility product of Zn(OH)_2 , the optimum pH for the provision of the minimum solubility has been reported between pH 10.50-11.50 (Jenkins et al., 1964). As the required pH adjustment is high, hydroxide precipitation by lime or soda ash is usually not practical and efficient in terms of economics and the amount of sludge produced. In a study performed, while the low lime application has precipitated approximately 85 percent of the zinc, removal of 94 percent of the zinc has been accomplished in the high lime system (Maruyama et al., 1975). And usually, hydroxide precipitation of zinc is needed to be supported by additional treatment methods like activated carbon adsorption, ion exchange etc. to meet the required standards.

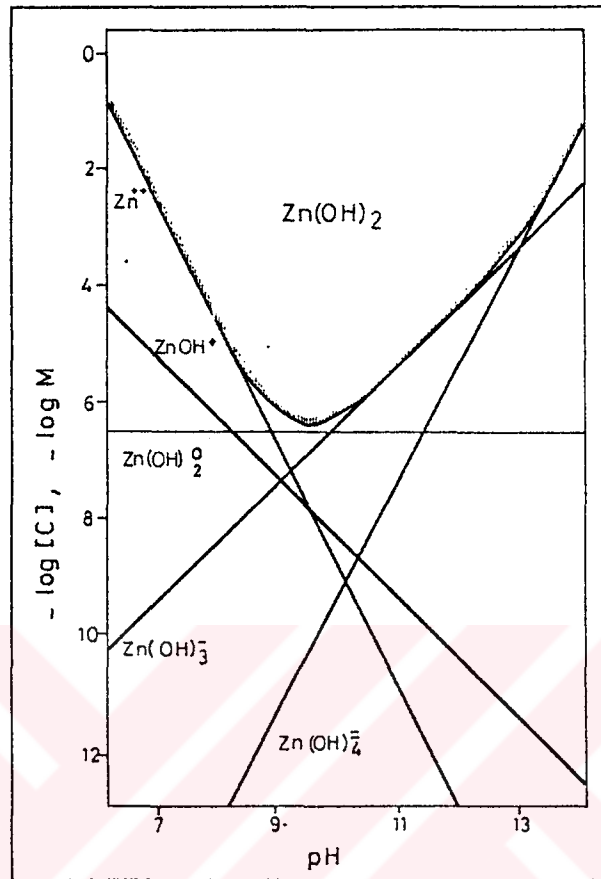


Figure 2.4 Solubility Diagram of Zinc

2.3.2.2 Other Methods

Apart from the hydroxide precipitation of zinc, three types of methods are frequently used in the treatment of zinc: sulfide precipitation, ion-exchange and solvent extraction. Also, new methods have been developed for the elimination of filtration of the precipitate and for large volumes of extremely dilute solutions, such as foam separation methods (Karger et al., 1967; Grieves, 1975; Clarke and Wilson, 1964).

Among these methods, sulfide precipitation using Na_2S or sparingly soluble FeS is the mostly applied method. It has been indicated that the disadvantages mentioned above for the zinc removal by hydroxide precipitation can be compensated to an extent by sulfide precipitation. Sulfide precipitation is efficient even in the presence of chelating or complexing agents where the zinc hydroxide becomes soluble. Besides, sulfide metals are generally less soluble and amphoteric than the corresponding hydroxide and can precipitate over a wider pH range. Finally, sulfide sludge usually has smaller volumes and easier to dewater than hydroxide sludge (Bhattacharyya et al., 1981) .

In another trial performed by Patterson et al., (1977) the removal efficiency of carbonate precipitation of zinc has been searched comparatively with the hydroxide precipitation of zinc. Although the investigation has been initiated through the reported findings that the metal carbonate precipitate is more dense than that of hydroxide, resulting in improved solid separation and decreased sludge volume, and the precipitation occurs at pH values less than that of hydroxide precipitation, the results obtained has indicated that the zinc carbonate system cannot reduce the soluble zinc concentration below that of the hydroxide precipitation system and the filtrate contained higher dissolved solids for the carbonate system than the hydroxide system.

The graphical representation of the extensive study by Maruyama (1975), where the removal of zinc by various treatment methods were reviewed and compared in terms of the zinc removal efficiency, is given in Figure 2.5.

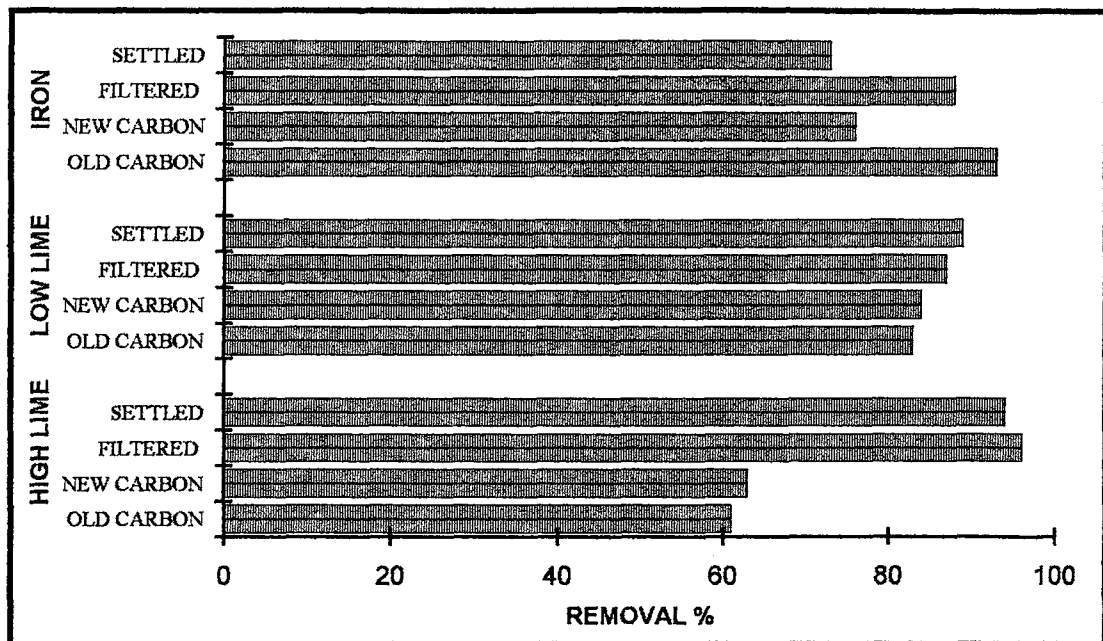


Figure 2.5 Removal of Zinc Under Several Treatment Conditions

2.4 Coagulation - Flocculation

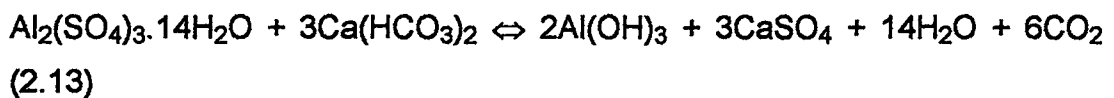
In practice, residual metal concentrations less than those predicted by solubility considerations may be attained by other removal mechanisms ; adsorption, ion-exchange with coagulant hydrous oxides or coprecipitation during precipitate formation. An increase in coagulant dosage would tend to increase removals by these mechanisms.

These chemical precipitation mechanisms based on the addition of a coagulant find an increasingly important role in wastewater treatment techniques and currently used to remove heavy metals from wastewater. In the method including coagulation and flocculation processes, polyvalent hydrolyzable metal ions are used as coagulant. And on dissolution, the metallic coagulant ions hydrolyze to form hydroxymetallic complexes, which polymerize to form the insoluble metal hydroxide. In fact, coagulation

process consists of several removal mechanisms. Among these mechanisms, sorption and coprecipitation are the predominant processes by which most of the metals are retained by metal oxides or hydrous oxides. Sorption is a mechanism by which metals are bound to the surface of an existing solid by adsorption or surface precipitation, whereas coprecipitation is the simultaneous precipitation of a chemical element with other elements including mixed solid formation, adsorption and inclusion. Removal of the ions is attained by enmeshment in and sorption by the voluminous floc of hydroxometallic complexes formed, or by coprecipitation with these metal hydroxides. All of these mechanisms may also occur at the same time.

Principal coagulants used for the provision of the above mechanisms within the coagulation-flocculation process, are aluminum sulfate and iron salts, due to the insolubilities of the precipitates formed $[\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3]$ even at low pH values. And this fact can be seen clearly from the solubility diagram of $\text{Al}(\text{OH})_3$ presented in Figure 2.6 (Reynolds, 1982).

The simplified chemical reaction for the formation the aluminum hydroxide floc is :



In general ferric ions are more insoluble than are aluminum ions, and they can be used over a wider pH range. The best range for alum coagulation is pH 5.5 - 8.0, whereas precipitation of ferric ions is effective over the range pH 4.0 - 12.0. The actual removal efficiency depends on alkalinity, pH and, competing ion and chelant concentrations. In order to determine the optimum pH , the most effective coagulant and the optimum dosage, laboratory jar tests and pilot studies are required.

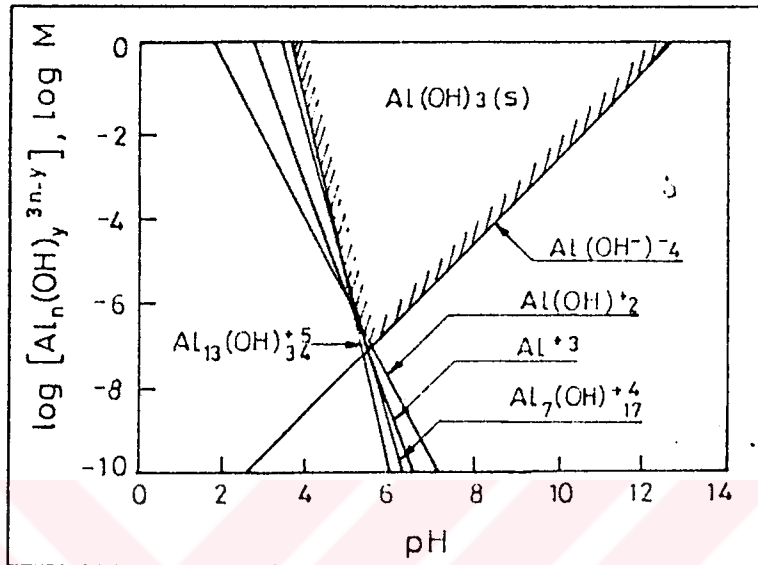


Figure 2.6 Solubility of Aluminum Hydroxide

On the other hand, flocculation conditions must be considered for the accomplishment of optimum removal. The main parameters considered are the mixing conditions and the polymer properties for the optimization of the flocculation. Also, strength of water which is defined as:

$$\text{Strength of water} = \text{Metal Quantity} / \text{Sulfate Content (mass/mass)}$$

is another important factor in determining the optimum mixing condition providing the optimum precipitation. And one of the related findings is that, while the strength of water increases, mixing time for flocculation decreases and mixing speed increases (Huck et al., 1977).

2.4.1 Adsorption of Metal Ions

Adsorption, which can be expressed as the accumulation of matter at an interface without the development of a three dimensional molecular arrangement, is the mostly applied process in coagulation-flocculation applications to enhance the removal efficiency provided by hydroxide precipitation. Oxides of iron, aluminum and silicon have been shown to be strong adsorbents for metal ions and certain metal oxyanions in laboratory studies. On a mass basis, ferrihydrites are among the strongest adsorbents which are insoluble over a wide pH range.

In a general approach, adsorption process where freshly precipitated metal oxyanions are used as adsorbents, consists of precipitation of the coagulant hydroxides, aging of the adsorbent, addition of the metals and pH adjustment. And the patterns following the above order of process through the addition of oxyhydroxide adsorbents (e.g. oxyhydroxides of Fe, Al, Si) , are similar regardless of the identity of the solid.

Although the concentration of adsorbent required for a given metal removal efficiency varies from system to system, the binding strength of metals onto most oxyhydroxides increases in the order with few exceptions (Corey et al., 1981);



The extent of the adsorption is also dependent on the particle surface availability. In other words, the lower limit of the treatment capability in adsorption is generally considered with the initial contaminant concentration and the surface area of the primary floc.

As it is seen from the above order of binding strength, chromium is one of the most insoluble ions, and it has been indicated by Leckie et al., (1981) that 80% of Cr with a molarity of 5×10^{-5} has been adsorbed at pH = 4.5, and in addition, both adsorbed and precipitated Cr may be affecting the sorption of the other ions in some of the systems.

On the other hand, it is reported that the sorption or the precipitation of chromium do not interfere with the removal of the other metal ions. Furthermore, in a study by Schultz et al., (1987), it was indicated that the adsorption of some metals (zinc and cadmium) were significantly enhanced with the presence of chromium in the system, as shown in Figure 2.7, where the adsorption of several metals on ferrihydrite, in the presence and absence of adsorbed Cr is represented.

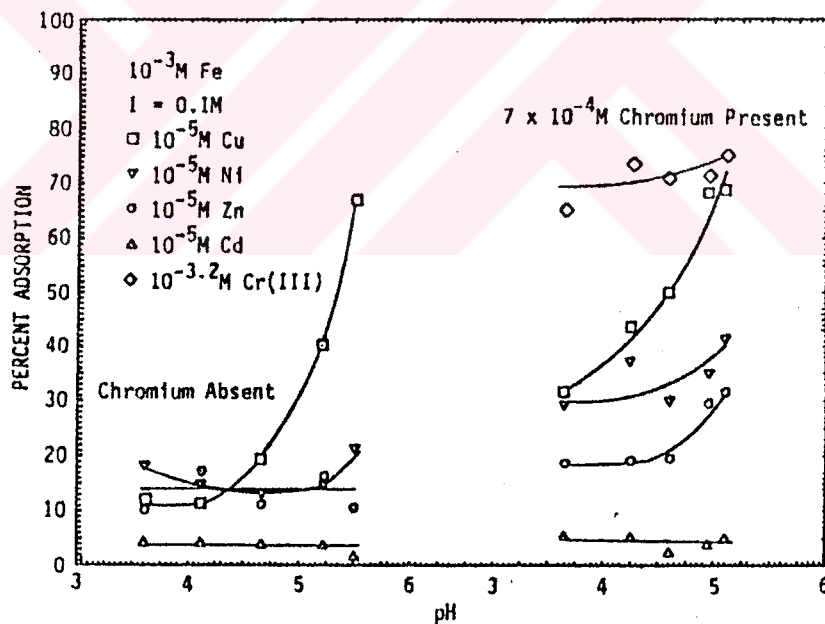


Figure 2.7 Adsorption of Several Metals On Ferrihydrite In the Presence and Absence of the Adsorbed Cr(III)

Also, it has been indicated that the chromium is incorporated into the ferrihydrite matrix, and either enhance the affinity of the ferrihydrite for other metals or is providing strong binding sites itself.

An example of the predicted adsorption removal dependence on area calculated using the James-Healy model for Zn(II) adsorption on amorphous iron(III) oxide is given in Figure 2.8 (Crawford et al., 1993a).

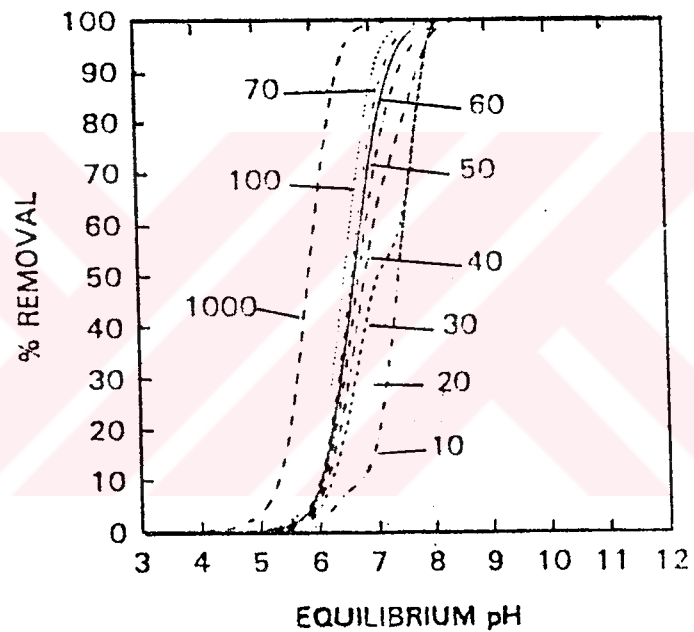


Figure 2.8 Adsorption of Zinc on to Amorphous Iron (III) Oxide as a Function of Specific Surface Area (in m².L⁻¹)

2.4.2 Coprecipitation of Metal Ions

The transition from metal ion adsorption to coprecipitation with other metal ions is of primary importance in a wide variety of contexts, such as material science, environmental engineering (industrial wastewater treatment and recycling of metals), oceanography (scavenging of trace elements), geochemistry (control of groundwater pollution and ore deposition). Especially, the treatment of toxic metals such as As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Se and Zn from fossil-fuel and nuclear-fuel cycle waste streams, geothermal fluids, and electroplating wastes by coprecipitation is under consideration and still being studied for the optimization and the improvement of the mechanism .

In the light of the recent findings and the trials, coprecipitation appears to remove trace metals from solution more efficiently, although it has not been well studied as adsorption. Especially, the removal of toxic metals from waste streams by coprecipitation with iron seems to be a very efficient and economically feasible method.

On the other hand, the extend of coprecipitation depends on the chemical similarity of the ions to the constituent ions of the precipitate and on the solubility of the compound formed between foreign ion and oppositely charged constituent ion. Besides, mode of coprecipitation determines the state of the incorporation of the metal ions in to the coprecipitate.

In an experimental study performed by Francis and Dodge (1990), where the dissolution profile of several metals from the mixed-metal coprecipitate after acid treatment is shown in Figure 2.9, analysis of coprecipitate of several heavy metal ions and goethite showed that, the coprecipitates contained 78% - 80% of the added iron, but the extend of the incorporation of the added toxic metals with goethite differed.

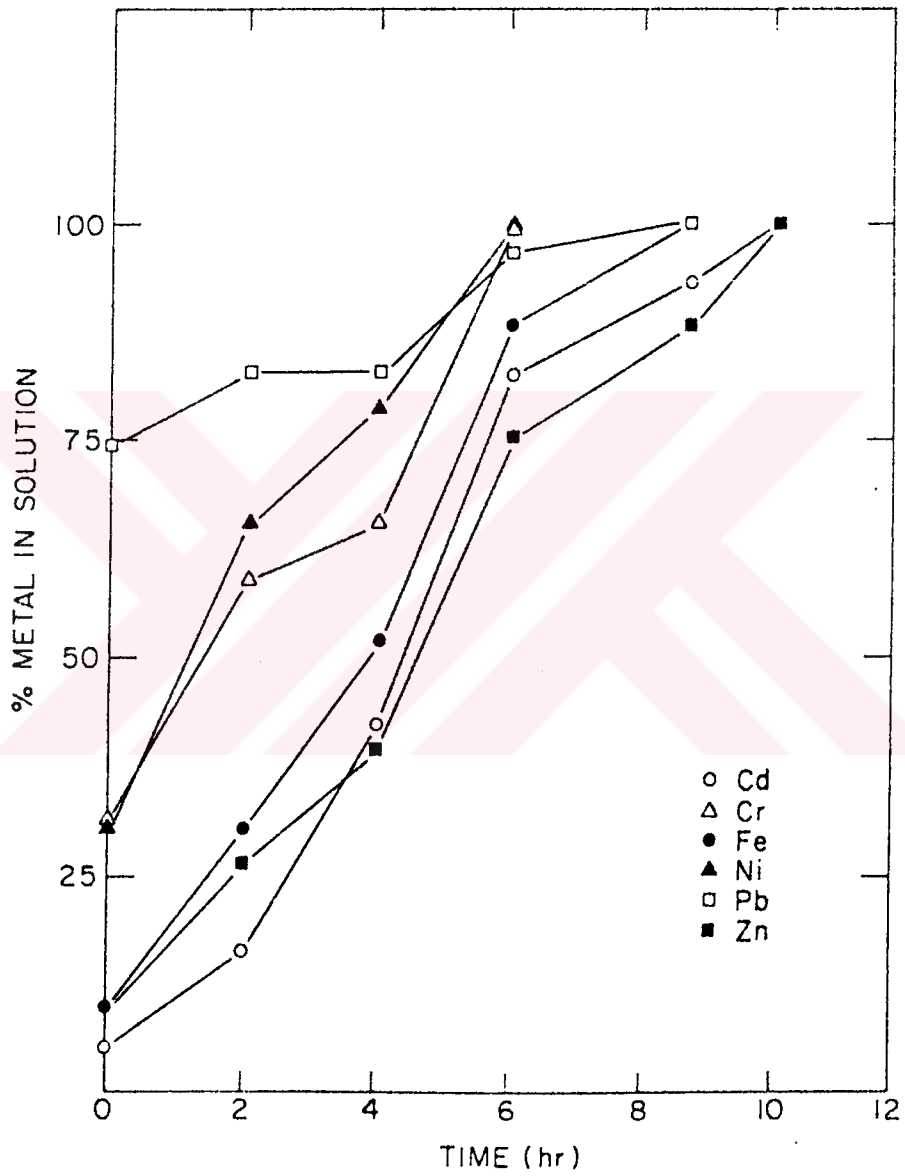


Figure 2.9 Dissolution Profile of Several Metals Coprecipitated with Goethite in 50% HCl

About 69% of added Zn, 67% Cr, 54% Pb and 50% each of Cd and Ni were found in the coprecipitate. Also, different dissolution patterns of the metals indicate the nature of the association of these metals in the coprecipitate. The data has indicated that Cd and Zn are more closely associated with iron than Ni and Cr, whereas, Pb is poorly associated with iron.

McIntire (1963) described three mechanisms within the coprecipitation process as; surface adsorption, occlusion and solid solution formation. In general, it is assumed that the coprecipitation occurs by the formation of a solid solution (the substitution of the trace elements into the lattice site of the precipitate). Sorption of chromium can be given as an example for this determination, that Cr atom substitutes for Fe in the HFO/HCrO coprecipitated lattice, it is therefore present in a local α - (Cr, Fe)OOH environment.

Different local structures of mixed metal hydrous oxides are dependent on their history, i.e., on whether one ion was sorbed on an hydrous oxide previously formed with other metal ion or the two metal ions were coprecipitated. In the study by Charlet and Manceau (1992), coprecipitation phenomenon has shown greater efficiency with respect to the surface precipitation in removing chromium (III) from solution.

Structural interpretations of Cr(III) coprecipitated with, and adsorbed on goethite respectively are shown in Figure 2.10 (Charlet and Manceau, 1992).

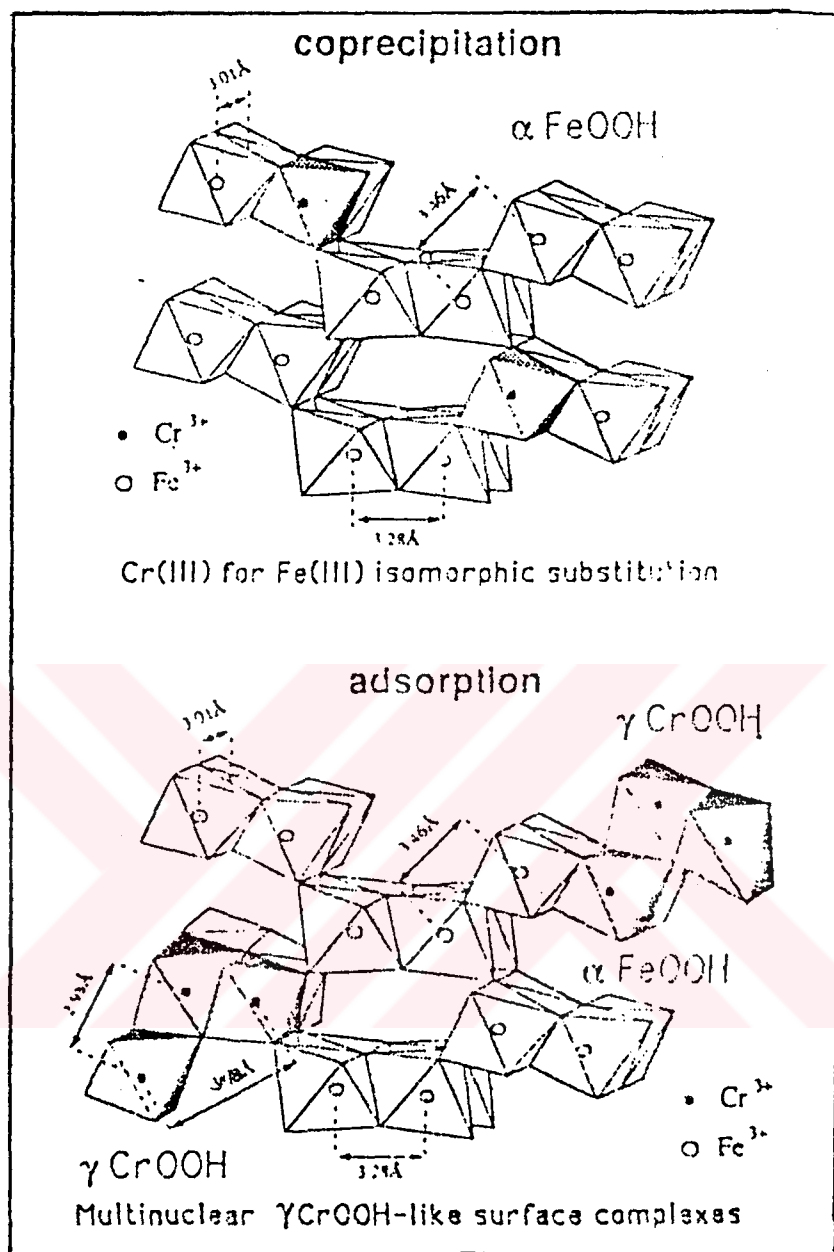


Figure 2.10 Structural Interpretation of Adsorbed and Coprecipitated Cr(III)

2.4.3 Differences Between Adsorption, Coprecipitation and Direct (Hydroxide) Precipitation

Precipitation, adsorption and coprecipitation of heavy metals find an increasingly important role in the removal of these ions from wastewater streams. On the other hand bioavailability and toxicity of trace metals in aquatic environments is strongly related with whether they are adsorbed, coprecipitated or directly precipitated.

The distinction between simple precipitation, coprecipitation and adsorption is not always clear. These processes are illustrated in a general approach in Figure 2.11 (Crawford et al., 1993a).

As indicated before, increasing the pH of a heavy metal ion will eventually result in the formation of an insoluble metal hydroxide precipitate. Simple hydroxide precipitation typically results in a sharp sigmoidal removal profile, and at very high pH levels redissolution of the heavy metal hydroxide may occur.

Adsorption processes occur whenever a solid substrate present and also typically result in a sigmoidal isotherm, but not as steep as that observed for simple hydroxide precipitation. And it is well known that adsorption processes occur at a lower pH than that of simple precipitation.

In the case of coprecipitation, the solid substrate is formed in the presence of the metal ion to be removed from solution. While the enhancement of removal by adsorption or coprecipitation over simple precipitation is well studied, the relationship between coprecipitation and adsorption is not as clear.

Although few studies directly compare all three processes, particularly using a well defined model surface, it is a general belief that coprecipitation will enhance (shift to lower pH) the removal profile to an even greater extend than that of adsorption.

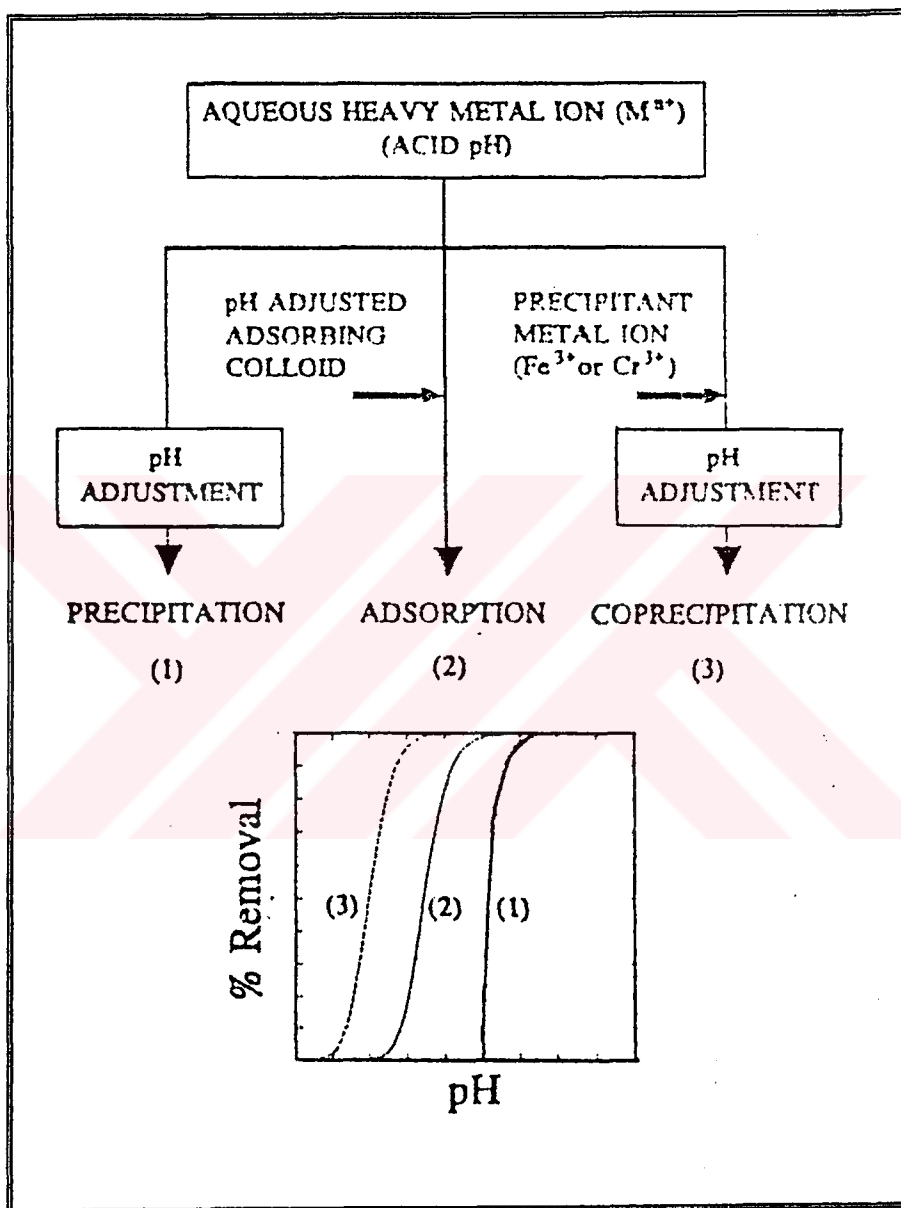


Figure 2.11 Schematic Representation of the Three Processes Responsible for the Removal of Heavy Metal Ions From Solution.

Removal characteristics of precipitation, adsorption and coprecipitation for the removal of Cr(III), and Zn(II) by using amorphous iron(III) oxide are shown in Figure 2.12 and Figure 2.13 respectively (Crawford et al., 1993a).

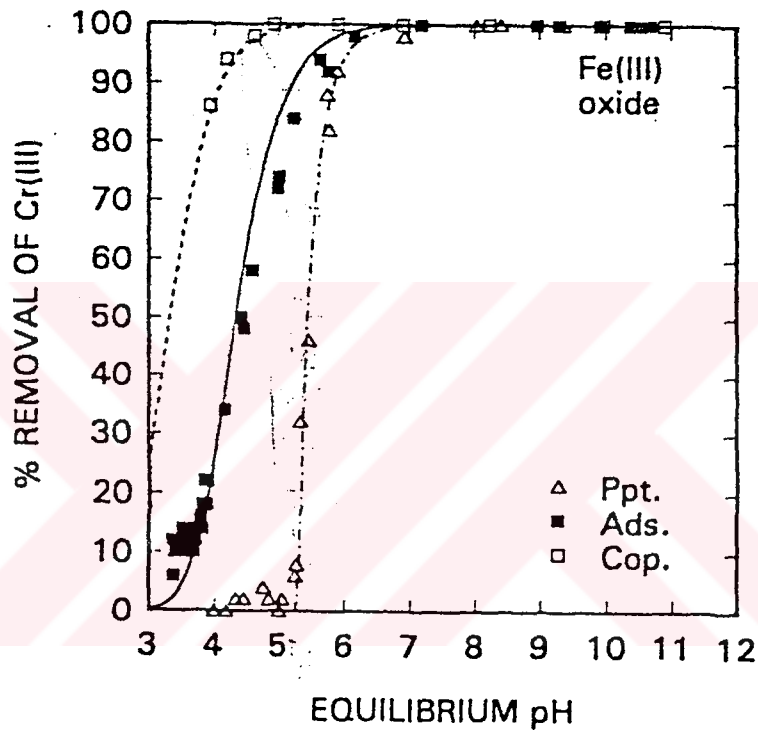


Figure 2.12 Adsorption and Coprecipitation of Cr(III) with Amorphous Iron(III) Oxide Compared to Precipitation of Cr(III) Alone.

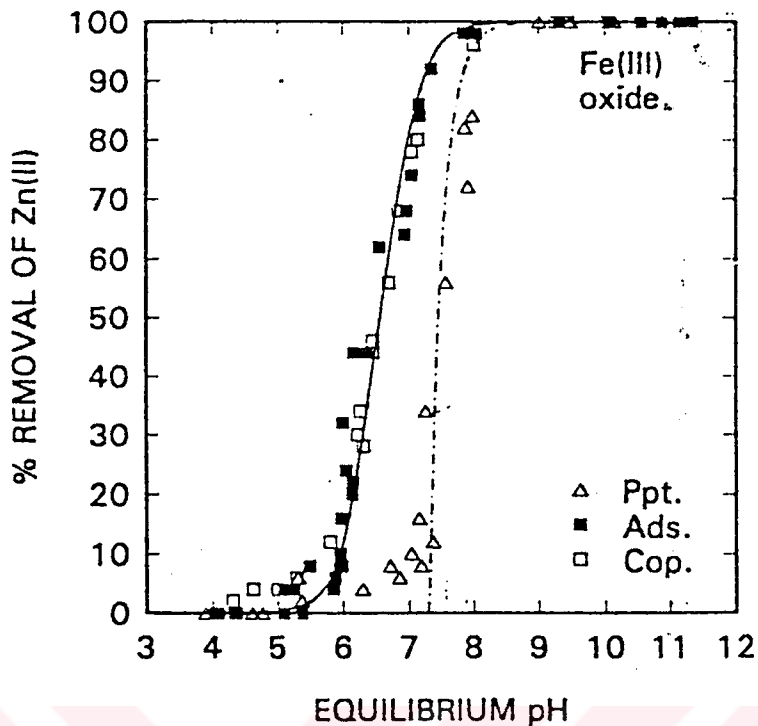


Figure 2.13 Adsorption and Coprecipitation of Zn(II) with Amorphous Iron(III) Oxide Compared to Precipitation of Zn(II) Alone.

According to the above figures, the extend of removal at any given pH, resulting from coprecipitation is greater than the extend of removal resulting from adsorption for Cr(III), and is barely perceptible for Zn(II).

Corey (1981) has argued that the main difference between adsorption and coprecipitation lies in the geometry of the adsorbate surface. But, both adsorption and coprecipitation enhance the removal of metal ions at a given pH, with respect to simple precipitation.

2.4.4 Factors Affecting Coprecipitation Process

In coprecipitation process, actual removal efficiency depends on several factors where simple precipitation and adsorption are also affected, like alkalinity, pH, competing ion and chelant concentrations, initial contaminant concentration, and surface area of primary floc.

Ligands contained in the solution can interfere with coprecipitation process in either of two ways : firstly, by forming complexes between heavy metals and ligands, and secondly, by forming complexes between coagulants and ligands. It is well known that, sulfates interfere with the coprecipitation system. But, the factors affecting the efficiency of coprecipitation or any coagulation process have to be assessed, also in an integrated approach, in order to evaluate the cumulative effects of the factors.

On the other hand, also synergistic effects of different heavy metal ions must be considered, because multiple metal ions complicate the coprecipitation mechanism defined for single metal ion solutions. But the extend of the influence varies with the metals present in the solution. In such a multiple metal ion solution it is important to know whether it is possible for multiple ions to form a mixed hydroxide as an insoluble precipitate. But as coprecipitation is a simultaneous process, especially at low pH values it will not be possible to obtain such a mixed metal precipitate due to the different solubility curves of the metal ions. So it seems probable to obtain both adsorption and coprecipitation in a mixed metal system but usually this factor enhance the removal efficiency of the metal ions with respect to coprecipitation involving only two metals.

The influence of a second or third metal ion on the resulting coprecipitation profiles and particularly on the $\Delta G^{\circ}_{\text{chemical},i}$ (the chemical free energy of the surface) appropriate to a given metal ion and a given substrate surface can be observed from Figure 2.14 (Crawford, et al., 1993b).

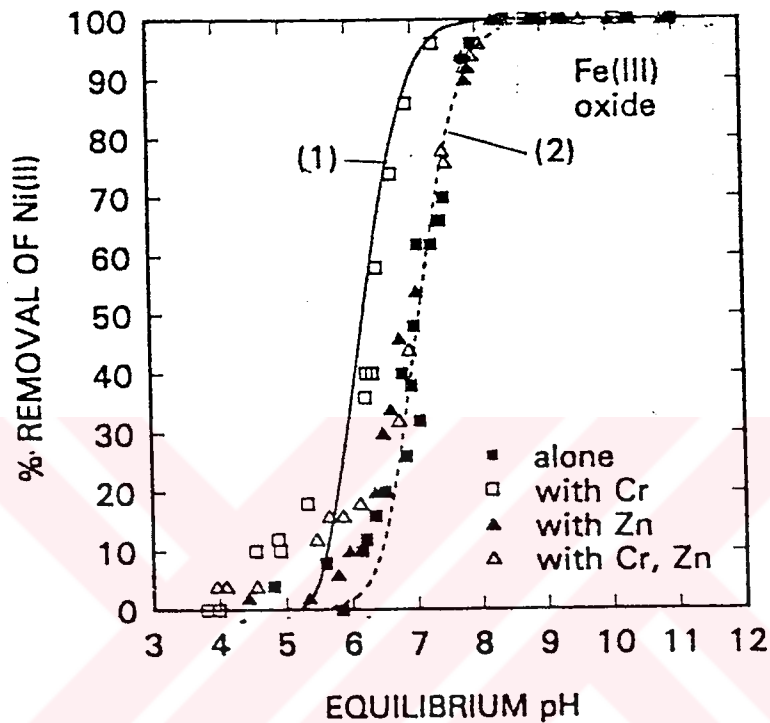


Figure 2.14 Coprecipitation of Ni(II) with Amorphous Iron(III) Oxide alone and with either Cr(III), Zn(II), or both Cr(III) and Zn(II):

- (1) $\Delta G^{\circ}_{\text{chemical},i} = -47 \text{ kJ mol}^{-1}$ amorphous iron (III) oxide surface,
 $\Delta G^{\circ}_{\text{chemical},i} = -52 \text{ kJ mol}^{-1}$ amorphous chromium surface;
- (2) $\Delta G^{\circ}_{\text{chemical},i} = -38 \text{ kJ mol}^{-1}$ amorphous iron (III) oxide surface,
 $\Delta G^{\circ}_{\text{chemical},i} = -43 \text{ kJ mol}^{-1}$ amorphous zinc surface.

CHAPTER 3

MATERIALS AND METHODS

Experimental study has been set on two main bases. In the first part of the experiments, a jar test has been applied to determine the optimum dosages of alum and lime and the optimum pH for coprecipitation and hydroxide precipitation in a comparative approach. In the second part of the experimental study, the extend of the effects of aging time, initial metal and ligand (sulfate) concentration variations, and synergistic effect of multiple metals in the mixed-metal solutions on coprecipitation process have been searched by separate trials. And additionally, also single behavior of the metals [Cr(III) and Zn(II)] have been evaluated in both hydroxide precipitation and coprecipitation trials for the comparison of the mixed-metal and single metal solutions.

3.1 Wastewater

As indicated before, wastewater which has been used through out the experiment has been prepared synthetically as being compatible with the typical concentrations of trivalent chromium, zinc and sulfate present in real chromium plating wastewaters (Sanciolo, et al.,1992; Knill and Chessin, 1986).

3.1.1 Reagents Used

ZnSO₄·7H₂O and Cr(NO₃)₃·9H₂O have been used to make the addition of metal constituents, and Na₂SO₄ has been used for the addition of ligand. Through out the experiments, alum [Al₂(SO₄)₃·18H₂O] has been used as the coagulant to provide chemical precipitation including coprecipitation, and lime Ca(OH)₂ has been used for both adjusting pH and providing hydroxide precipitation.

For the first six sets of experiments, wastewater containing zinc and chromium has been prepared as a stock solution where the zinc and chromium concentrations were 25 and 100 mg/l respectively to provide standardization and compatibility between experiments, as shown in Table 3.1. On the other hand, wastewater has been prepared freshly for the remaining sets of experiments.

Different concentrations of Na₂SO₄ (0.2, 0.6, 2.0, 8.0 and 10.0 gr/l) have been added as an inorganic ligand during the 6th set of experiment for the determination of the effects of ligand on the efficiency of coprecipitation. And for the determination of the effect of initial metal concentration variation, solutions have been prepared freshly with chromium and zinc concentrations of 25, 50, 75, 100 mg/l and 5, 12.5, 19, 25 mg/l respectively. Alum and lime have been prepared as stock solutions of concentrations of 5 g/l and 20 g/l respectively.

Other reagents used during the experiments have been; H₂SO₄ and NaOH for small pH adjustments, nitric acid (HNO₃) for the acidification of the filtered samples prior to analysis by atomic absorption spectrophotometer and pH tablets for the calibration of pH-meter.

3.2 Apparatus Used in the Laboratory

Experimental studies have been accomplished through the application of a standard jar test within the framework of the objectives indicated in the first chapter. And, for hydroxide precipitation and coprecipitation trials, a standard jar test apparatus has been used. The apparatus has been equipped with a six-place stirrer which is operated electrically, and the agitation strength or the mixing rate could be adjusted manually. So, the contents (wastewater and treatment chemicals) in six jars which have been 600 ml cylindrical vessels, could have been stirred simultaneously.

A pH-meter (Hanna Instruments, Model HI 8314 membrane pH-meter) has been used during the pH adjustments. And, the residual metal concentrations have been analyzed by atomic absorption spectrophotometry (A.A.S), which the model is Perkin-Elmer M 1100.

3.3 Experimental Procedure

For the determination of the optimum alum dosage through the first part of the experiments (jar test), synthetic wastewater has been poured into the containers of jar test apparatus. After this, different alum dosages taken from the stock solution have been added at the concentration levels from 5mg/l to 160 mg/l in three different sets of experiment. The solutions have been rapidly mixed for five minutes to provide uniform distribution of the constituents during the coagulation step. While rapid mixing, lime has been added into the containers at the level greater than the stoichiometrically required amount, to provide a constant pH about 8.70. The start of each jar test has been specified by the time the coagulant (alum) and lime have been added. And the test periods have been set as follows;

Table 3.1 Design Matrix & Chemical Composition of Wastewater for Each Set of Experiment

EXPERIMENT SET	REAGENT CONCENTRATION (mg/l)			CONSTITUENT CONCENTRATION (mg/l)			ALUM (mg/l)	LIME (mg/l)	pH
	Cr(NO ₃) ₃ .9H ₂ O	ZnSO ₄ .7H ₂ O	Na ₂ SO ₄	Cr ³⁺	Zn ²⁺	Sulfate			
1	769.23	109.84	-	100	25	-	5-30	200	8.7 ± 0.08
2	769.23	109.84	-	100	25	-	50-110	200	8.7 ± 0.08
3	769.23	109.84	-	100	25	-	115-160	200	8.7 ± 0.08
4	769.23	109.84	-	100	25	-	-	100-350	5.30 ± 10.45
5	769.23	109.84	-	100	25	-	70	-	3.0-11.5 ± 0.08
6	769.23	109.84	0-10000	100	25	0-6760	70	200	8.7 ± 0.08
7	192.31-769.23	21.97-109.84	-	25-100	5-25	-	70	220	9.8 ± 0.14
8	769.23	-	-	100	-	-	10-125	200	8.7 ± 0.08
9	-	109.84	-	-	25	-	10-125	60	8.7 ± 0.08
10	769.23	-	-	100	-	-	-	80-300	4.40 ± 10.80
11	-	109.84	-	-	25	-	-	50-150	4.40 ± 10.80
12*	769.23	109.84	-	100	25	-	70	200	8.7 ± 0.08

* One jar has been prepared on sampling at six different times of settling, 15 min, 30 min, 60 min, 120 min, 240 min, 24 h.

- Rapid Mixing → 5 minutes at 80 rpm.
- Slow Mixing → 45 minutes at 10 rpm.
- Settling Period → 60 minutes

At the end of the sedimentation (settling), all samples have been filtered through 0.45 μm filters, and acidified to pH=2 with HNO_3 to provide the dissolution of the suspended metal coprecipitates and hydroxides before their storage in the refrigerator. Effluent metal concentrations have been measured by an atomic absorption spectrophotometer.

In the determination of the optimum lime dosage for the provision of hydroxide precipitation, the same procedure has been repeated by the addition of different lime dosages in the absence of coagulant (alum), in order to make comparison between coprecipitation and the direct (hydroxide) precipitation.

In the determination of the optimum pH, the procedure has been repeated by the application of different lime dosages together with the optimum alum dosage determined in the first step of the jar test, to provide six different pH values: 3.00, 5.00, 7.00, 8.00, 9.50, and 11.50.

For the second part of the experimental study, in the firsthand, the effect of the aging time on coprecipitation process has been investigated by taking samples from the solution coagulated and flocculated under optimum conditions without ligand (optimum alum dosage and optimum pH) at 15min., 30min., 60min., 120min., 240min., and 24hrs. from the beginning of the settling. After filtration and acidification, samples were analyzed for the residual metal concentrations .

Above trial has been repeated for the same wastewater under the same conditions (optimum alum, optimum pH, and 60min. settling), in the presence of different ligand (Na_2SO_4) concentrations of 0, 200, 600, 6000, 8000 and 10000 mg/l.

The next trial has been the determination of the effect of initial metal concentration variation. For this purpose, synthetic wastewater with different metal concentrations indicated in the previous section have been prepared and the procedure has been repeated under the optimum dosage of alum and constant pH of 9.8 ± 0.14 as indicated in Table 3.1.

In the last part of the experimental study, single metal systems have been searched in both hydroxide precipitation and coprecipitation trials. In the coprecipitation trial, 100 mg/l Cr(III) and 25 mg/l Zn(II) have been coprecipitated separately through the application of different alum dosages of 10, 20, 30, 50, 80 and 125 mg/l, under constant pH = 8.70 ± 0.2 . And, in the hydroxide precipitation trial, again 100 mg/l Cr(III) and 25 mg/l Zn(II) have been directly precipitated separately by the addition of lime with corresponding pHs between 4.40-10.80.

CHAPTER 4

RESULTS AND DISCUSSION

As indicated in the previous section, experimental study has been based on two main parts; the determination of the difference between coprecipitation and hydroxide (direct) precipitation, and the determination of the extent of the effects of ligand and initial metal concentrations, and aging on coprecipitation mechanism.

Through the sections below, the results obtained from the experimental trials have been assessed with respect to the parts mentioned above. And, these assessments contained the comparison of the mechanisms (direct precipitation and coprecipitation) and the behavior of the metals (chromium and zinc) against these mechanisms in terms of the removal efficiencies. Also, the consistency of the results with the theoretical framework and the literature have been searched and the probable facts regarding the deviation from expected trends have been discussed.

On the other hand, the trends of the coprecipitation process in to both single-metal and mixed-metal solutions have been compared in order to see the synergistic effect of different metals.

4.1 Determination of the Difference Between Coprecipitation and Hydroxide (Direct) Precipitation

The first part of the experimental study has been assessed in two different approaches:

- The prediction of the difference between the above-mentioned processes in mixed-metal systems,
- The prediction of the difference between the above-mentioned processes in single-metal systems.

Through the comparison of the results obtained from the two approaches, the differences between the single-metal and the mixed-metal systems in terms of affecting the coprecipitation and the hydroxide precipitation have been cleared out.

4.1.1 Coprecipitation and Direct Precipitation in Mixed-Metal Systems

In the first approach, the application of coprecipitation and the direct precipitation have been completed in the mixed-metal systems where the metal constituents (zinc and chromium) have been present together in the wastewater prepared.

Through the optimum alum and pH determinations for both of the metals in the application of coprecipitation and the hydroxide precipitation under the treatment conditions indicated in Table 3.1, the results of the two trials have been compared in order to clear out the supporting effect of the coprecipitation mechanism in the removal of Cr(III) and Zn(II) from a simulated chromium plating wastewater.

4.1.1.1 Optimum Alum Dosage for the Coprecipitation of Cr(III) and Zn(II)

The removal trends of Cr and Zn by the coprecipitation mechanism have been searched through the steps of a jar test. And, in the first hand, optimum alum dosage has been determined under the constant values of pH (8.7 ± 0.3) and settling period (60 min) which have been assumed to be suitable for the formation of insoluble hydroxo-complexes and precipitates due to the solubility diagrams and the literature review.

As it is seen from Figures 2.3 and 2.4, at the precipitation of Cr(III) and Zn(II) metal ions in the form of metal hydroxides, starts just before the pH 7.0 and reaches optimum between pH 8-10. So, the main reason of fixing pH value between 8.50 and 9.00 is both providing the maximum precipitation and preventing the redissolution of either of the metal hydroxide within the initial phase of a typical removal trend (U-shaped curve) for both of the metals.

The residual metal concentrations obtained from the application of different alum $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$ dosages in the range of 5-160 mg/l are shown in Table 4.1.

Table 4.1 Residual Metal Concentrations of Zn(II) and Cr(III) Versus Aluminum Sulfate at pH=8.7 and 60min Settling Time, Without Ligand where Removal Efficiency (R)= removed metal amount/added aluminum amount.

[Al ₂ (SO ₄) ₃ .18H ₂ O] Added (mg/l)	Soluble Cr(III) (mg/l)	Soluble Zn(II) (mg/l)	R _{Cr} (mg/mg)	R _{Zn} (mg/mg)
5	0.320	0.512	19.936	4.898
10	0.200	0.602	9.800	2.439
15	0.250	0.614	6.650	1.625
20	0.124	0.619	4.990	1.219
25	0.071	0.589	3.997	0.976
30	0.136	0.592	3.328	0.814
50	0.070	0.074	1.998	0.498
70	0.050	0.042	1.428	0.360
80	0.190	0.051	1.247	0.312
90	0.280	0.061	1.108	0.277
100	0.090	0.020	0.999	0.250
110	0.130	0.005	0.908	0.227
115	0.280	0.003	0.867	0.217
120	0.184	0.002	0.832	0.208
125	0.092	0.030	0.799	0.199
130	0.093	0.020	0.768	0.192
140	0.061	0.010	0.714	0.178
160	0.142	0.010	0.624	0.156

i) Chromium(III) Removal Versus Alum Concentration:

In the application of alum+lime, as it is seen from the curve in Figure 4.1, the removal profile or the trend is a typical U-shaped curve with fluctuations which are relatively small with respect to the initial Cr(III) concentration.

In this curve the soluble chromium concentration profile shows a decrease even in the small amounts of alum addition, and the decay of chromium concentration continues with increase in the alum addition until alum concentration has reached 70 mg/l. At this point of alum concentration, soluble Cr(III) has dropped down to 0.05 mg/l which has been the minimum value of the trial. With further increase in the alum dose, Cr(III) concentration has increased due to the formation of soluble hydroxo-complexes and the destabilization of the flocs with negligible fluctuations, especially within the range of the alum addition, 75-120 mg/l. Beyond 125 mg/l of the alum concentration, residual Cr(III) concentration has reached nearly a constant phase.

According to the removal profile of Cr(III), the alum concentration of 70 mg/l seems to be the optimum dose. But the final decision has to be given after the assessment of the removal trend of the zinc obtained from the same set of experiment, as the optimum value will represent the optimum dose of the system but not the metal itself in a mixed-metal solution.

ii) Zinc Removal Versus Alum Concentration:

In order to finalize our assessments regarding the selection of the optimum alum dosage, the removal trend of zinc obtained through the application of alum + lime has been observed.

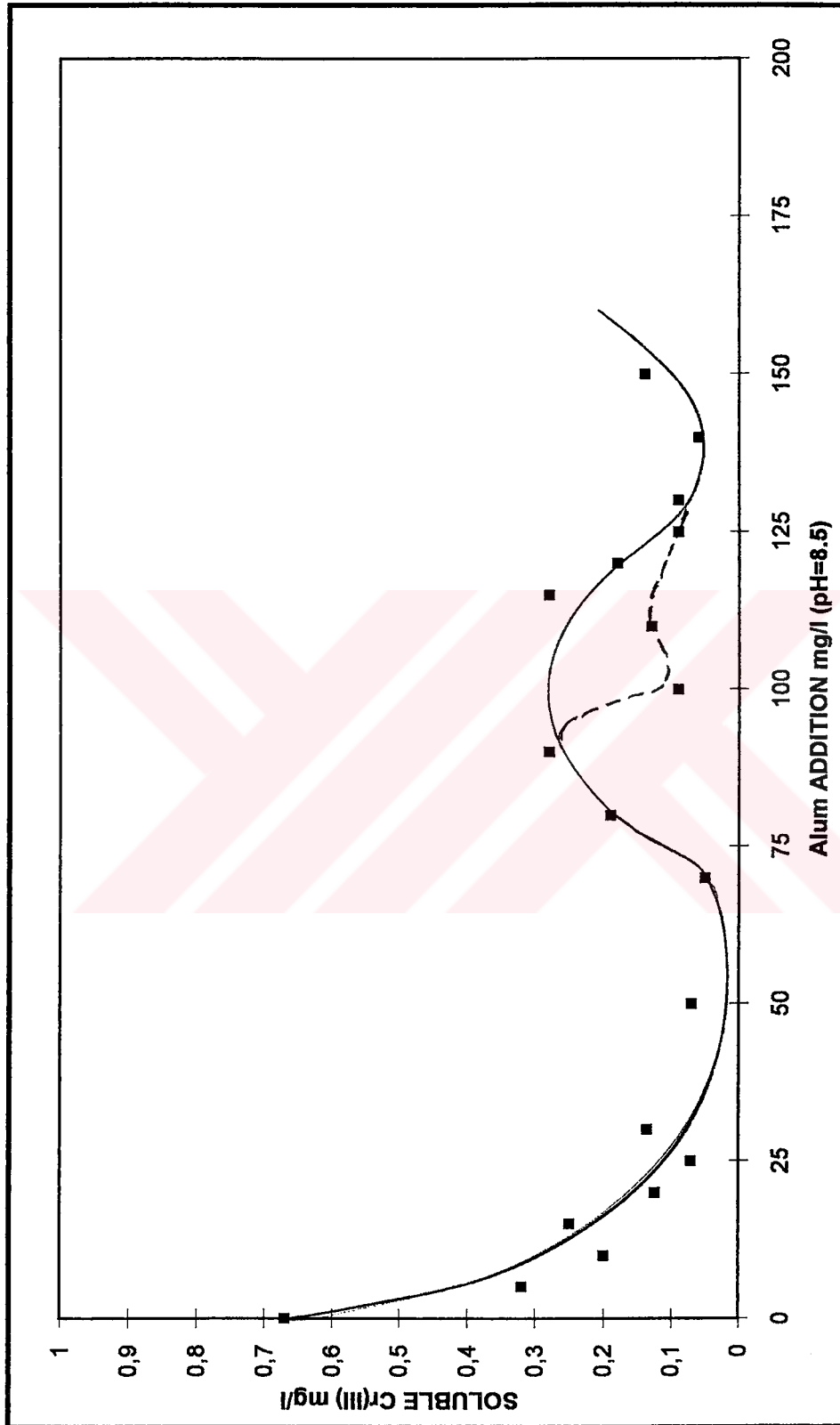


Figure 4.1 Coprecipitation of Chromium as a Function of Alum Concentration at pH 8.70 and Settling Time of 60 min., in Mixed-Metal Solution Without Ligand.

As it is seen from Figure 4.2 that the initial phase of a U-shaped curve has been obtained for the removal of zinc. Initially, up to the alum concentration of 30 mg/l, zinc concentration has not shown considerable variation. But, within the range of 30-70 mg/l alum dosage, a sharp decrease has been observed in zinc concentration. And, with further increase up to 160 mg/l in alum dosage, zinc concentration has become almost constant with small fluctuations. Although the change in alum concentration is too much, zinc removal has not exposed an important variation with respect to the amount of increase in alum concentration. So, it would be reasonable in terms of economics and the amount of sludge produced to accept the beginning of this consistent range as the optimum removal (0.042 mg/l zinc residual) corresponding to the alum dosage of 70 mg/l, although residual zinc has continued dropping gradually to 0.003mg/l on a broad range of alum contribution.

According to the above assessments on the results obtained from the coprecipitation trial, it is seen that the optimum alum dosages predicted for Cr(III) and Zn(II) coincide. So, we can easily say that the optimum alum dosage for the mentioned trial is 70 mg/l.

In this framework it is seen that, although zinc and chromium removals follow the same qualitative pattern, some differences have been observed between the two removal trends. One of the differences exhibited is not to have obtained the redissolution phase of zinc hydroxide as in the case of the chromium due to the formation of soluble metal-hydroxo complexes and the destabilization of the metal flocs. The reason of not being catch the destabilization point for Zn(II) may be the slow occurrence of redissolution even in the thermodynamically favored conditions.

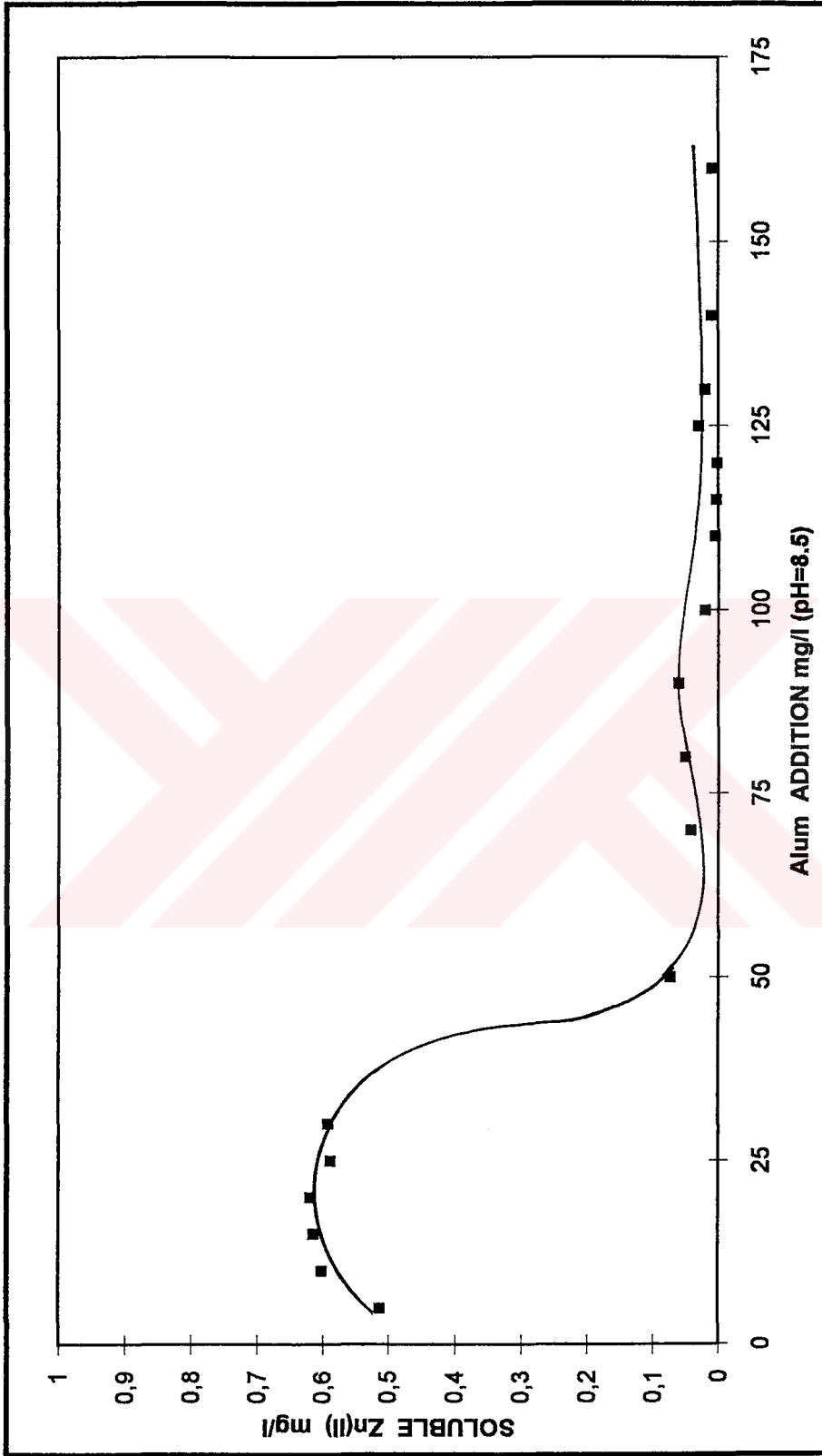


Figure 4.2 Coprecipitation of Zinc as a Function of Alum Concentration at pH 8.70 and Settling Time of 60 min., in Mixed-Metal Solution Without Ligand.

On the other hand, it is easily seen from the figures that the Cr(III) concentration has decreased more efficiently and earlier than the Zn(II) concentration with the increase in alum dose, in spite of the difference between Cr(III) and Zn(II) in the initial concentrations. This situation can be attributed to the fact that, considering the order of precipitation of Cr (III) and Zn(II) as pH of the solution increases, Cr(III) coprecipitates and/or precipitates at a considerably lower pH than Zn(II). And the removal efficiencies of Cr(III) and Zn(II), defined as $R = \text{removed metal amount} / \text{added aluminum}$, at the optimum alum dose, 70 mg/l, are $1.428 \text{ mg} \cdot \text{mg}^{-1}$ and $0.357 \text{ mg} \cdot \text{mg}^{-1}$ respectively, as it is seen from Table 4.1. On the other hand, although the initial concentration of Zn(II) is much smaller than that of Cr(III), residual Zn(II) concentrations (0.614, 0.619, 0.589, 0.590 mg/l) do not meet the standard (0.5 mg/l) set up by Environmental Protection Agency (EPA), especially at the initial alum doses added, while they are well below the Turkish standard (3.0 mg/l).

4.1.1.2 Optimum pH for the Coprecipitation of Cr(III) and Zn(II)

It is well known that, pH is the critical parameter for the achievement of the optimum removal efficiency in the chemical precipitation processes as these processes are strongly pH dependent. So, it is a vital point to determine the optimum pH value providing the optimum coprecipitation in a mixed-metal system, where the optimum pH values differ for each of the metal present.

Within this framework, optimum pH determination has been completed through the application of the optimum alum dose, 70 mg/l, as the second step of the jar test for the coprecipitation trial. The results of the trial where pH has been adjusted within the range of 3-11.50 is shown in Table 4.2.

The removal trends obtained for Cr(III) and Zn(II) and are graphically demonstrated in Figures 4.3 and 4.4 respectively, have been assessed together in order to determine the optimum pH for the mixed-metal solution.

Table 4.2 Residual Metal Concentrations of Zn(II) and Cr(III) Versus pH at optimum alum concentration 70 mg/l and 60 min Settling Time, Without Ligand.

pH	Soluble Cr(III) (mg/l)	Soluble Zn(II) (mg/l)	R _{Cr} (mg/mg)	R _{Zn} (mg/mg)
3.00	80.144	4.039	0.280	0.290
5.00	73.420	3.606	0.380	0.310
7.00	30.540	3.458	0.990	0.310
8.00	1.588	0.936	1.410	0.340
9.50	0.044	0.038	1.430	0.360
11.50	0.039	3.652	1.430	0.310

i) Chromium Removal Versus pH:

As it is seen from the graphical demonstration of the results in Figure 4.3, a sharp decrease in soluble Cr(III) concentration has occurred especially within the pH range of 5.00-8.00. At the point of pH=8.00 soluble Cr(III) concentration has dropped to 1.588 mg/l. And, with further increase in pH up to 11.50, Cr(III) has continued to decrease slightly. Although the difference between the removal of Cr(III) at pH=9.50 and pH=11.50 is quite negligible, the minimum soluble Cr(III) concentration of the trial, 0.039mg/l, has been obtained at pH=11.50.

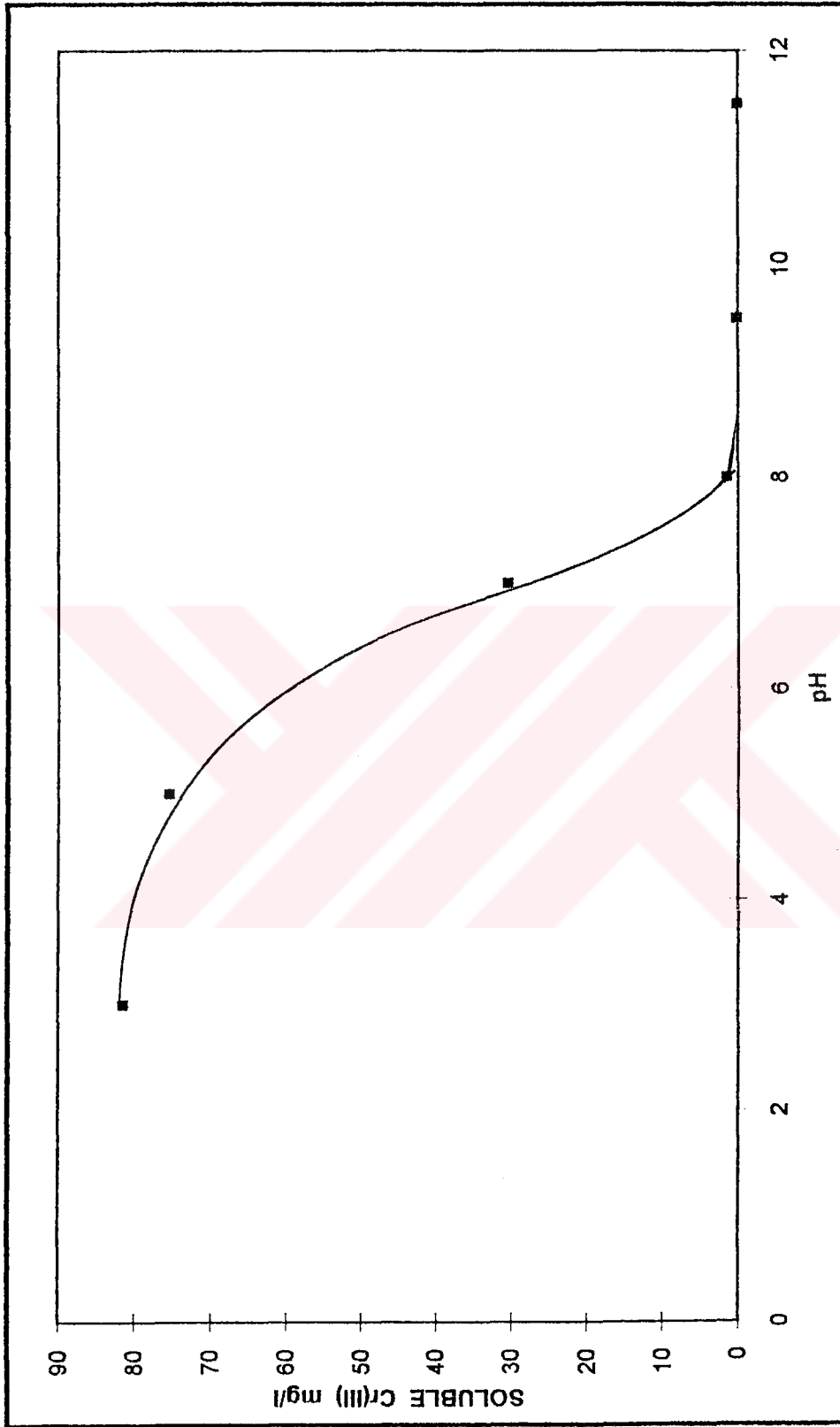


Figure 4.3 Coprecipitation of Chromium as a Function of pH for Optimum Alum Dose, 70 mg/l and Settling Time of 60 min., in Mixed-Metal Solution Without Ligand.

i) Zinc Removal Versus pH:

As it is seen from Figure 4.4, the removal trend of zinc depending on pH variation is a typical U-shaped curve where the decay in the concentration of zinc begins after pH 7.00. Up to pH 7.00 a consistent phase has been observed where the decrease between pH 3.00-7.00 is negligible. The decay in concentration has been observed within the range of 7.00-9.50, and the residual concentration has dropped to 0.038 at pH 9.50. On the other hand, after pH 9.50 redissolution has been occurred depending on the amphoteric characteristic of zinc which may result in the redissolve of the precipitate as the soluble zincate ion. So, the maximum removal efficiency has been obtained at pH 9.50 corresponding to the residual concentration of 0.038 mg/l.

As it is seen from the results obtained for two metals, optimum pHs corresponding to the minimum residual metal concentrations are different for Cr(III) and Zn(II). On the other hand, it is seen from the removal profiles that, although Zn(II) has reached its minimum concentration before than that of Cr(III) as pH increases, the removal trend of Zn(II) exhibits a broader range than that of Cr(III).

In addition, the previous precipitation of Zn(II) as pH increases is inconsistent with both the difference between the solubility products of the two metals (see Figures 2.3 and 2.4) and the order of precipitation of metal ions presented in Table 4.3. But, as the removal of Cr(III) and Zn(II) cannot be adequately described on the basis of equilibrium conditions dependent on solubilities of single compounds, other factors affecting the optimum pH like Al:Cr, OH:Al and Al:Zn ratios, and the competitive action between the ions to occupy sites on the aluminum coordination shell must be considered.

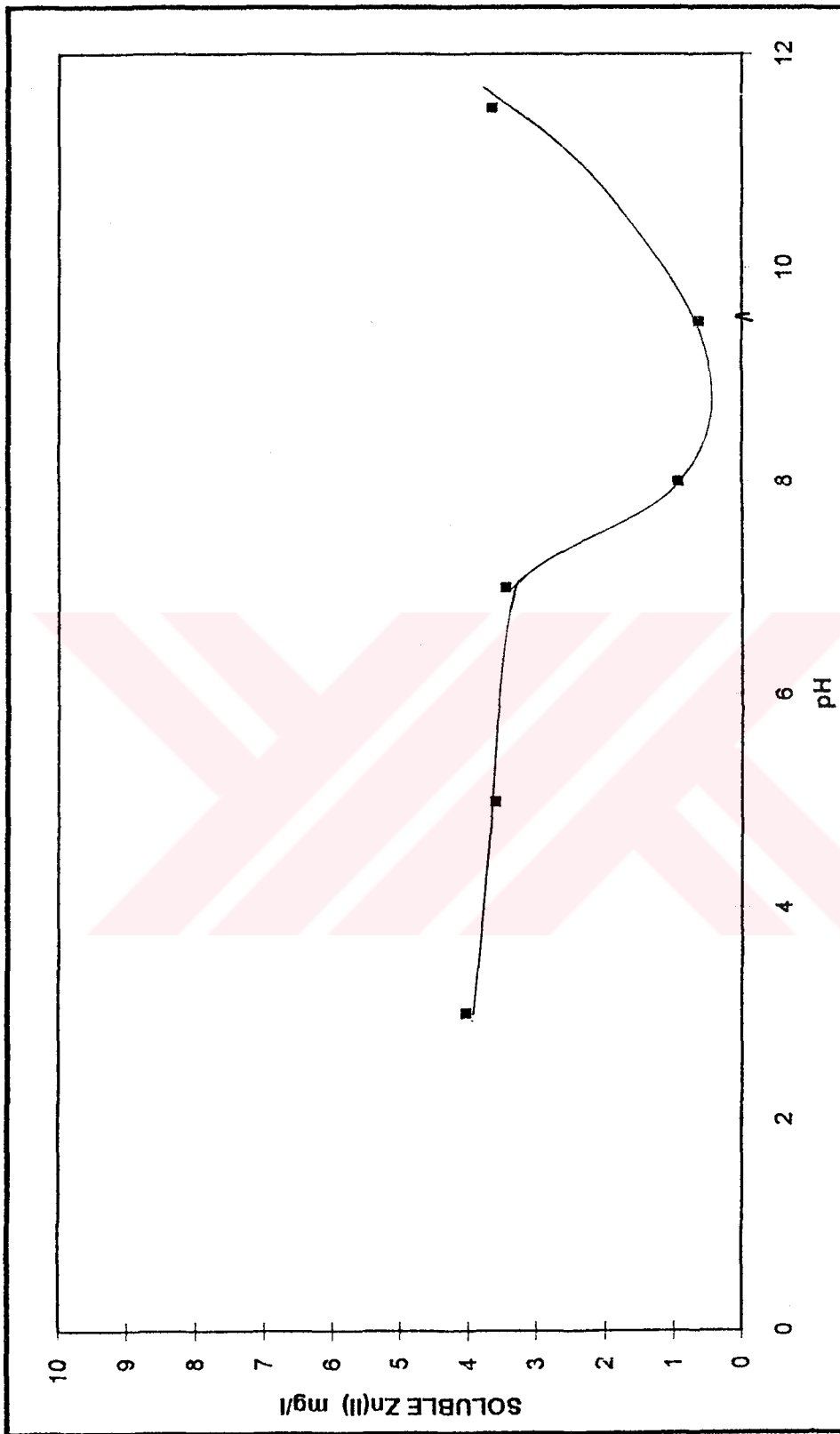


Figure 4.4 Coprecipitation of Zinc as a Function of pH for Optimum Alum Dose, 70 mg/l and Settling Time of 60 min., in Mixed-Metal Solution Without Ligand.

However, combined treatment of trivalent chromium and zinc may yield quite different results which can be inconsistent with the trends of single-metal systems.

On the other hand, although both metals are known with their amphoteric characteristic, while Zn has exhibited redissolution after pH 10.00, Cr has not shown any tendency to redissolve. One of the factors where the above-mentioned point can be attributed to, is the difference between the extends of amphoterism of Cr(III) and Zn(II). And, it is well known that Zn(II) is considerably amphoteric. On the other hand, it might be the effect of coprecipitation mechanism where the coprecipitated metals become more stable against changes in pH than hydroxide precipitates.

In spite of the differences, in a general view the removal trends of the two metals have shown similarity and optimum pHs obtained are near to each other. When the optimum pHs obtained for Cr(III) and Zn(II) have been assessed in order to select a single value which will be the optimum for both of the metals, 9.50 has been accepted as the optimum pH for the mixed-metal system.

Table 4.3 Order of precipitation from dilute solutions as pH is raised
(Dean et al., 1972)

Ion	pH	Ion	pH
Fe ³⁺	2.0	Na ²⁺	6.7
Al ³⁺	4.1	Cd ²⁺	6.7
Cr ³⁺	5.3	Zn ²⁺	7.0
Cu ²⁺	5.3	Hg ²⁺	7.3
Fe ²⁺	5.5	Mn ²⁺	8.5
Pb ²⁺	6.0	Co ²⁺	9.5

4.1.1.3 Optimum Lime Dosage for the Hydroxide (Direct) Precipitation of Cr(III) and Zn(II)

In order to achieve the main objective of the study, to clear out the difference between coprecipitation and hydroxide precipitation in terms of the removal efficiencies, the trial has been completed where Cr(III) and Zn(II) have been directly precipitated through the application of lime in the mixed-metal system.

In this application it could have been possible to determine the optimum lime dosage and the optimum pH simultaneously through only one set of experiment, as being different from a standard jar test. This is because of the impossibility of separating the determination of optimum lime dosage and optimum pH from each other where the application of different dosages of lime has resulted in different pH values. And, it is apparent that, the optimum pH providing the formation of insoluble metal hydroxides represents also the optimum lime dose hydroxides in hydroxide precipitation.

The results obtained from the trial by adjusting pH within the range of 5.30-11.45 through the application of different lime dosages between 100-350 mg/l are shown in Table 4.4.

Table 4.4 Residual Metal Concentrations of Zn(II) and Cr(III) Versus pH at various lime dosages and 60min Settling Time, Without Ligand

Lime (mg/l)	pH	Soluble Cr(III) (mg/l)	Soluble Zn(II) (mg/l)
100	5.30	38.830	7.189
150	7.90	1.034	5.230
200	9.70	0.454	3.226
250	10.20	0.510	0.793
300	10.80	0.600	0.513
350	11.50	0.713	2.652

i) Chromium Removal Versus Lime Concentration:

It is well known that simple hydroxide precipitation typically results in a sharp sigmoidal removal profile. As it is seen from the graphical representation of the results shown in Figure 4.5, the trend has exhibited a profile consistent with the typical case where a sharp decrease over a narrow range between pH 5.30-7.90 has been obtained, and the residual chromium concentration has dropped from 38.80 to 1.034 mg/l. At pH 9.70 the Cr(III) concentration has decreased to 0.454 mg/l which has been the minimum value of the trial. Beyond pH 9.70, the decay in concentration has followed a mild trend in terms of destabilization, and the concentration has begun to increase slightly within the pH range of 9.70-11.50.

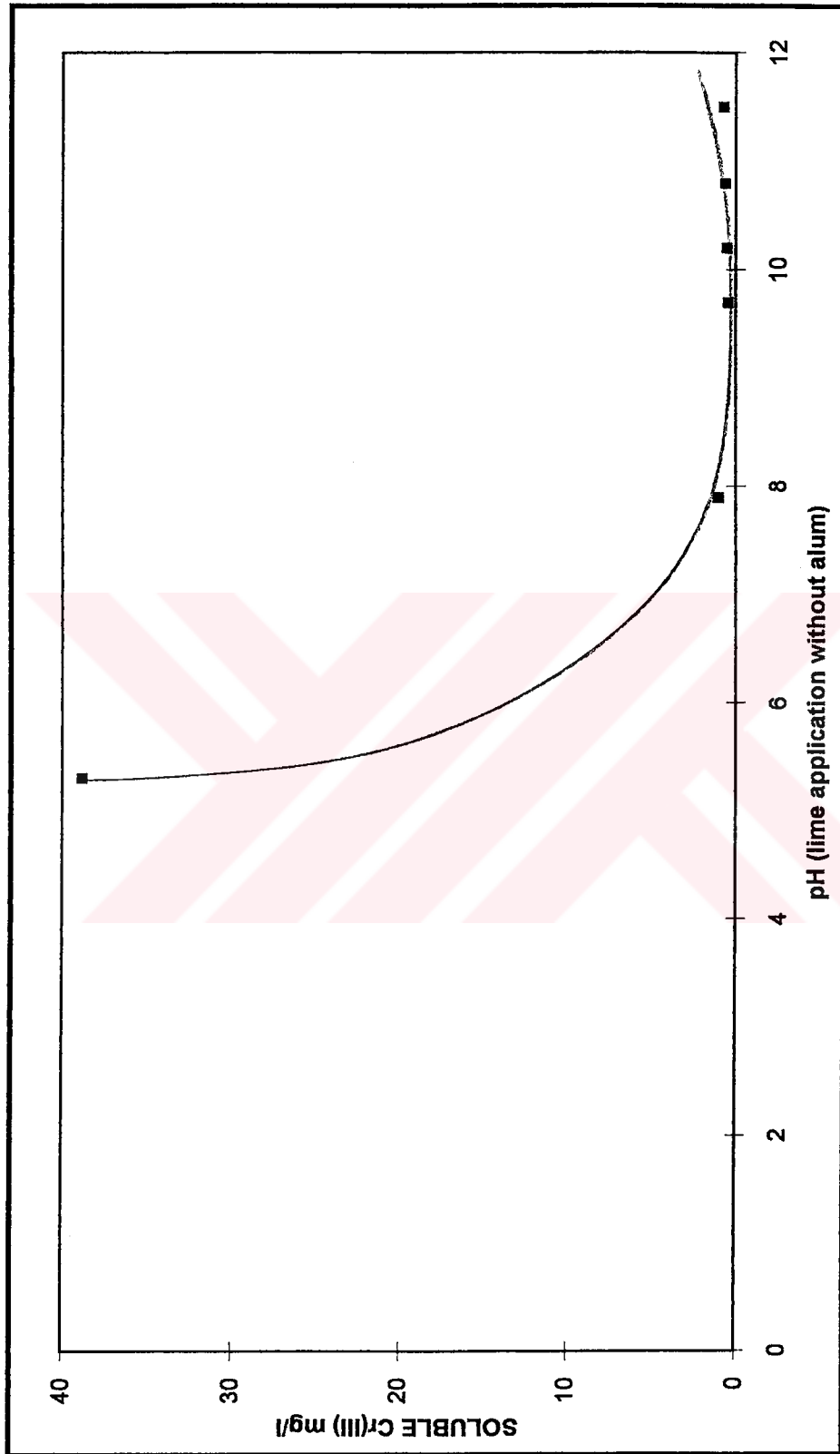


Figure 4.5 Hydroxide Precipitation of Cr as Function of pH for Various Lime Doses and Settling Time of 60min, in Mixed-Metal Solution Without Alum and Ligand. (Initial Cr= 100 mg/l)

ii) Zinc Removal Versus Lime Concentration:

As it is seen from Figure 4.6, although the removal trend is near to the typical one mentioned above, the decay of the Zn(II) concentration has not been sharp all through the application where the maximum decrease has been observed between pHs 9.70-10.20 with corresponding residual concentrations of 3.226mg/l and 0.793mg/l respectively. And at pH 10.80, the concentration has decreased to 0.513 mg/l which is the minimum value of the trial. Beyond the pH 10.80, destabilization has been observed depending on the excess hydroxide in the system.

When we assess the results obtained through the trial based on the provision of hydroxide precipitation by the application of lime, maximum removals of Cr(III) and Zn(II) have been achieved at different lime dosages with corresponding pHs 9.70 and 10.80 respectively. But, as mentioned before, the aim of the search is to find out one pH value which will be the optimum pH and the lime dosage of the mixed-metal system providing the satisfactory insolubility for both of the metals present in the wastewater. So, within this framework, pH 10.80 corresponding to the lime dosage of 300 mg/l seems to be the optimum value, although at pH 10.80 redissolution of Cr(III) has been observed. But it is apparent that the increase in the concentration of Cr(III) due to the dissolution is negligible with respect to the decrease in Zn(II) concentration within the so-called pH range, 9.70-10.80. In addition, the difference in the solubilities of chromium and zinc precipitates is an expected situation depending on the difference between the solubilities of the two metal-hydroxides.

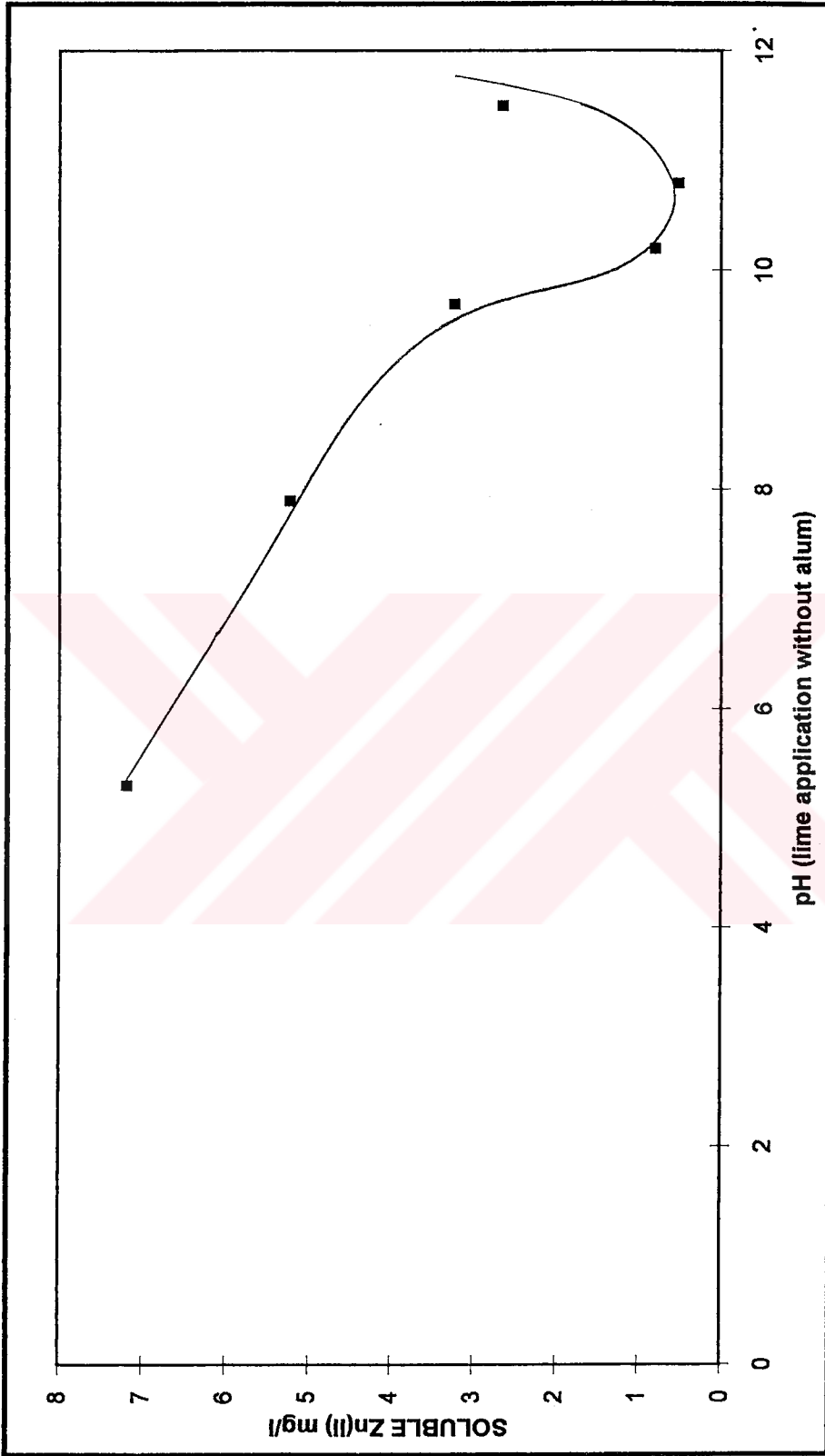


Figure 4.6 Hydroxide Precipitation of Zn as Function of pH for Various Lime Doses and Settling Time of 60min, in Mixed-Metal Solution Without Alum and Ligand. (Initial Zn= 25 mg/l)

On the other hand, although the removal trends are near to each other, Zn(II) profile is not as steep as that of Cr(III). So, from this point of view Cr(III) seems more consistent with the typical sharp sigmoidal profile of hydroxide precipitation. At this point, some probable interactions and mechanisms which may cause such a deviation in the removal trend of Zn(II) have to be considered. In the first hand, we have to take into account the synergistic behavior of the two metals in the mixed-metal system. Depending on the fact that Cr(III) precipitates at a considerably lower pH than Zn(II), it (precipitated Cr(III)) might have acted as a coagulant replacing the function of alum in the system, which draws a picture as if it has been a single-metal system where Cr(III) was the coagulant while Zn(II) was the metal ion to be removed. So, it is possible for zinc to have been adsorbed on or coprecipitated with the previously formed $\text{Cr}(\text{OH})_3$ precipitates while pH increased. Although the experimental accuracy does not allow an accurate distinction to be made on whether Zn(II) has been adsorbed on or coprecipitated with Cr(III), it is well known that coprecipitation can easily occur if the solubility products of the constituent metals are near to each other. On the other hand, this fact can be accepted here only within an order of magnitude because of the difference between the solubility products of chromium and zinc. So it is highly likely that, zinc has been adsorbed on the $\text{Cr}(\text{OH})_3$ precipitates which have been formed before than that of zinc.

The minimum residual concentrations of chromium and zinc obtained at the optimum pH ($\text{Cr}(\text{III})=0.600$ mg/l, $\text{Zn}(\text{II})= 0.5123$ mg/l) do not meet the standards set by EPA (0.5 mg/l). On the other hand, while Cr(III) residual do not meet the Turkish standard (0.5mg/l), Zn(II) residual is well below the limit (3.0 mg/l). In this respect, it is seen that, although the hydroxide precipitation is inexpensive, reliable and the most common method of reducing heavy metal concentrations, it is not sufficient to meet the regulations and the limits getting strict, as the removal efficiency is just constricted with the "solubility product".

4.1.1.4 Comparison of Coprecipitation and Direct Precipitation in Mixed-Metal Systems

After the determination of the optimum conditions (optimum alum dosage and optimum pH) for the provision of the optimum coprecipitation of the metals (chromium and zinc), a trial has been performed with only lime application providing hydroxide (direct) precipitation, in order to see the difference between the coprecipitation and the direct precipitation, in terms of the removal efficiencies of Cr(III) and Zn(II). While the general trends obtained in both of the trials have been compared, especially the optimum conditions providing the optimum removals of Cr(III) and Zn(II) for both of the trials have been focused in order to see the difference between the two mechanisms.

As it is seen from the results indicated above, optimum removals of Cr(III) and Zn(II) corresponding to the residual concentrations of 0.044 mg/l and 0.038 mg/l respectively have been obtained for alum concentration of 70 mg/l at pH 9.50 which are the optimum conditions determined in the coprecipitation trial. On the other hand, the optimum removals of chromium and zinc corresponding to the residual concentrations of 0.600 mg/l and 0.513 mg/l respectively have been obtained at pH 10.80 corresponding to the lime dosage of 300 mg/l in the direct precipitation trial.

Through the evaluation of the results, the improvement of the removal efficiency by the application of the coprecipitation can be easily seen for both of the metals nearly with an order of magnitude. In fact, the occurrence of a mixed hydroxide precipitate is usually difficult in a mixed-metal solution containing more than two metals as being in our case (Al, Cr, Zn) because of different pH values to precipitate depending on different solubility products and the competitive action of the metals to take place on the aluminum coordination shell.

Within this framework, it is very likely that Al(III) and Cr(III) have been coprecipitated while Zn(II) could have been adsorbed on the Al-Cr coprecipitates depending on the solubility concerns and the order of precipitation as pH increases (see Table 4.3)

Although it is difficult to achieve coprecipitation for both of the metals (chromium and zinc) in the same solution, it is seen that the difference between zinc removal efficiencies obtained in coprecipitation and hydroxide precipitation trials is as considerable as that of chromium. In other words, coprecipitation trial has been effective to the same extend for both of the metals (zinc and chromium) although it does not seem possible for chromium and zinc to coprecipitate with aluminum at the same time. This fact brings the idea of the supportive effect of Al-Cr coprecipitates acting as an adsorbent for zinc. And, the precipitate formed may be regarded as a mixed precipitate involving both coprecipitation and adsorption. In this respect, also the possibility, that the incorporation of chromium has enhanced the affinity of the aluminum for other metals (zinc) by providing strong binding sites itself, has to be taken in to the consideration (Schultz et al., 1987) .

4.2 Comparison of Mixed-Metal and Single Metal Systems

Through the sections below, the results obtained from the coprecipitation and hydroxide precipitation trials applied to remove Cr(III) and Zn(II) from single metal systems have been presented and discussed. The main objective of the part is to evaluate the difference between the mixed-metal and single metal systems in terms of the efficiencies of coprecipitation and hydroxide precipitation. Through the evaluation of the difference, the trials accomplished in sections 4.1.1.1 and 4.1.1.3 have been repeated for single metal systems without aiming the determination of the optimum conditions for separate removals of Cr(III) and Zn(II) by

coprecipitation and direct precipitation. In this framework, just a simple repetition of the above-mentioned trials in single metal systems without determining the optimum conditions, have been preferred to an intensive study of a jar test, in order to provide a general picture about the difference.

4.2.1 Coprecipitation of Chromium

In this trial, the coprecipitation of chromium has been performed under the conditions indicated in Table 3.1, for single metal system. And the results obtained are presented in Table 4.5.

Table 4.5 Residual Chromium Concentration Versus Alum at pH 8.70 and 60min Settling Time, Without Ligand

Alum Concentration (mg/l)	Soluble Cr(III) (mg/l)	R _{Cr} (mg/mg)
10.0	0.078	9.992
20.0	0.054	4.997
30.0	0.034	3.332
50.0	0.066	1.998
80.0	0.077	1.249
125.0	0.111	0.799

As it is seen also from the graphical representation of the tabulated results, presented in Figure 4.7, the removal trend of chromium obtained at pH 8.70, is almost constant with negligible fluctuations. And the minimum residual concentration of 0.034 mg/l has been achieved on addition of 30 mg/l of alum. On the other hand, all the residual concentrations obtained are well below the required standards, and the removal efficiencies are very high with respect to the initial chromium concentration, 100mg/l.

According to the removal profile, it is apparent that the coprecipitation of chromium in single metal solution is quite efficient that even at low alum doses residual chromium concentration has decreased considerably. When we compare the trend with the corresponding profile obtained in mixed-metal system, it is seen that, especially at low doses of alum, the removal of chromium obtained in single metal system is greater than that of mixed-metal system nearly with an order of magnitude. And, the minimum residual concentration obtained in single metal system is less than that of mixed-metal system with respective concentrations of 0.034 and 0.050 mg/l. In addition, the minimum residual chromium obtained in single metal system has been achieved at alum dose, 30 mg/l, less than that of mixed-metal system, 50 mg/l.

Within this framework, the supportive effect of the presence of another metal in the system could not have been observed in the coprecipitation of chromium. Moreover, coprecipitation of chromium alone seems more efficient. On the other hand, as the coprecipitation process is directly related with the amount of surface sites available on the coagulant (alum), it is an expected situation that the alum dose required for the maximum removal of chromium is less than that of chromium and zinc.

The lack of influence of zinc on the removal efficiency of chromium is not surprising since Cr(III) precipitates and/or coprecipitates at a considerably low pH than Zn, as mentioned before.

4.2.2 Coprecipitation of Zinc

The coprecipitation of zinc alone have been completed, again through the repetition of the coprecipitation trial accomplished in mixed-metal solution. In this trial, six different alum doses have been applied under the conditions indicated in Table 3.1. The results obtained are presented in Table 4.6.

Table 4.6 Residual Zinc Concentration Versus Alum at pH 8.70 and 60min Settling Time, Without Ligand.

Alum Concentration (mg/l)	Soluble Zn(II) (mg/l)	R _{Zn} (mg/mg)
10.0	2.562	2.244
20.0	0.318	1.234
30.0	0.633	0.812
50.0	0.211	0.495
80.0	0.152	0.310
125.0	0.265	0.198

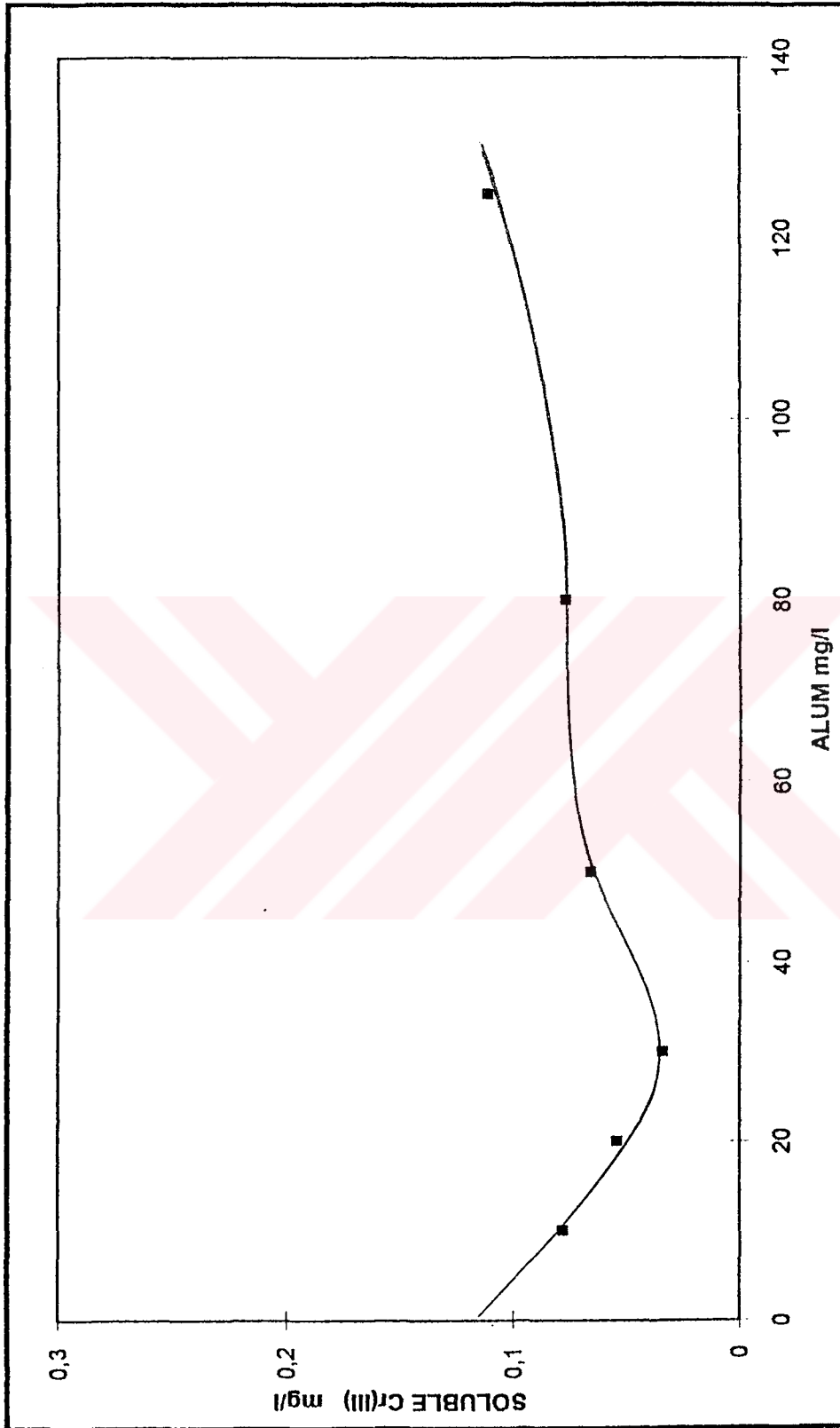


Figure 4.7 Coprecipitation of Chromium as a Function of Alum Concentration at pH 8.70 and Settling Time of 60 min., in Single-Metal Solution Without Ligand.

According to the tabulated results, residual zinc concentration has dropped rapidly from 2.562 to 0.318 mg/l in a narrow range of corresponding alum concentration between 10 and 20 mg/l. And after an increase up to 0.633 mg/l by the alum addition of 30 mg/l, residual concentration has become almost constant within a range of 0.152 and 0.265 mg/l. The minimum zinc concentration of 0.152 mg/l, has been obtained at the alum concentration of 80 mg/l.

Within this framework, when we compare the graphical representation given in Figure 4.8 with Figure 4.2, it is easily seen that the removal of zinc has been enhanced nearly with an order of magnitude by the presence of chromium with respect to the single metal solution. This enhancement is considerable especially at the alum concentration above 30mg/l. While the optimum residual concentration of zinc obtained in the mixed-metal system is 0.042mg/l, the value that of obtained in single metal system is 0.152 mg/l.

The supportive effect of chromium on the removal efficiency of zinc confirms the assumption that the coprecipitated chromium either increases the affinity of alum or forms strong binding sites itself. On the other hand, it is reported that the enhancement by the presence of another metal ion is usually more apparent at low pH values, and in the light of this prediction, it seems quite satisfactory to be able to observe the enhancement at pH value near to optimum (8.70) in this trial. In order to evaluate certain predictions, the comparison has to be carried out at low pH values also.

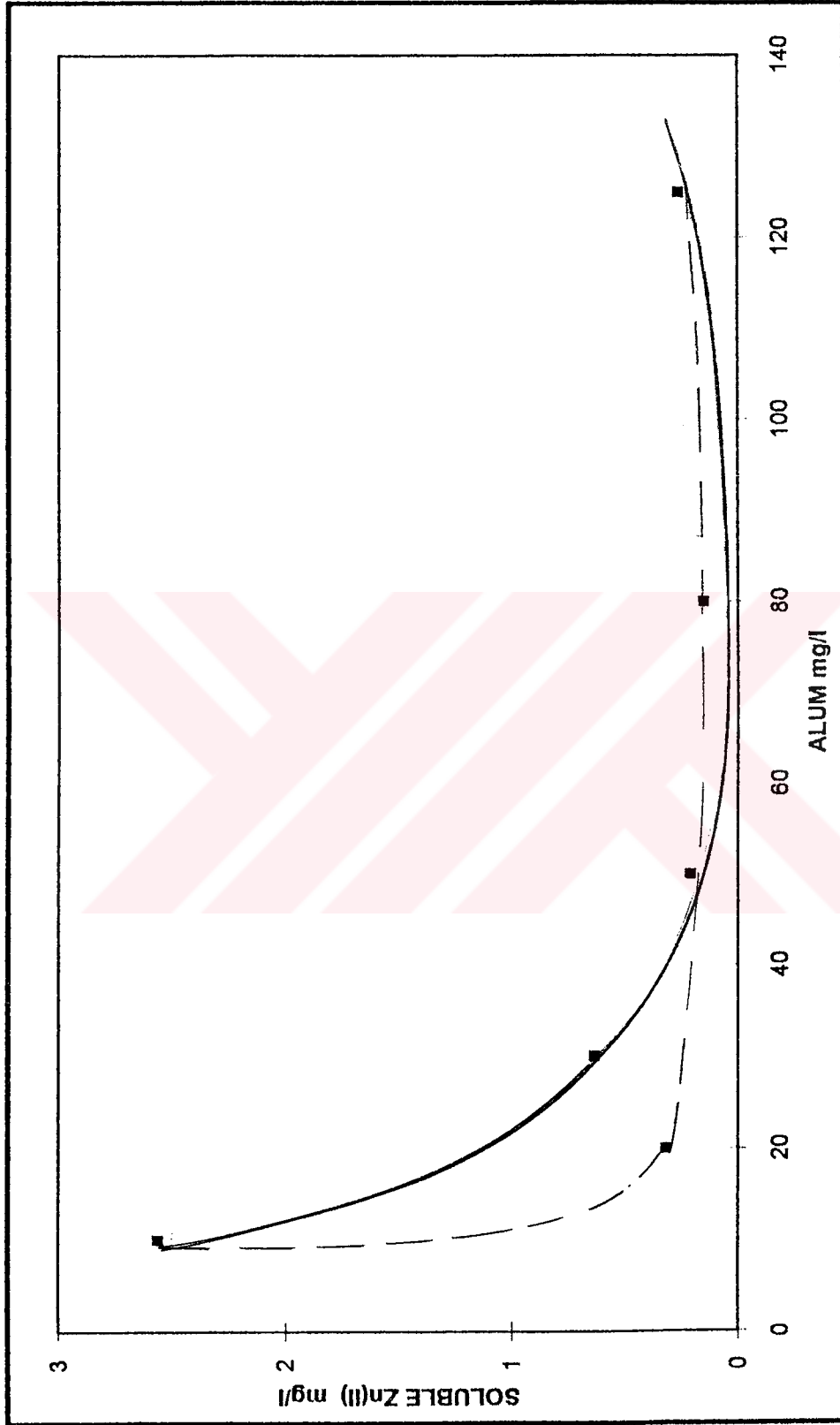


Figure 4.8 Coprecipitation of Zinc as a Function of Alum Concentration at pH 8.70 and Settling Time of 60 min., in Single-Metal Solution Without Ligand .

4.2.3 Direct (Hydroxide) Precipitation of Chromium

The results of the trial which has been performed through the repetition of the application in section 4.1.1.3, for the comparison of the removal efficiencies obtained by direct precipitation in mixed-metal and single metal systems, are tabulated in Table 4.7. In this trial, the same experimental conditions have been applied as in the mixed-metal solution, for the provision of hydroxide precipitation of chromium alone.

Table 4.7 Residual Chromium Concentration Versus pH at Various Lime Dosage and 60 min Settling Time, Without Alum and Ligand.

Lime (mg/l)	pH	Soluble Cr(III) (mg/l)
80.0	4.40	97.21
100.0	6.67	88.50
150.0	8.50	3.75
200.0	9.23	4.88
250.0	10.55	19.20
300.0	10.80	74.40

According to the Table 4.7, it is seen that the removal trend has exhibited a sharp decrease within a quite narrow range of pH variation between 5.70 and 6.67 with corresponding residual Cr concentrations of 88.50 and 3.75 mg/l respectively. On the other hand, a second sharp trend has been observed again within a narrow range of pH variation between 9.23 and 10.80, in terms of the destabilization of the chromium hydroxide precipitates with respective chromium concentrations of 4.88 mg/l and 74.40 mg/l.

These fluctuations has shown, how critical the determination of the optimum pH is, for the provision of the maximum hydroxide precipitation of a metal ion.

As it is seen from Figure 4.9, the profile exhibits a typical U-shaped curve where the fluctuations has occurred within a small range of pH variation. Through the comparison of the trends in mixed-metal (Figure 4.5) and single metal (Figure 4.9) systems, the enhancement of the chromium precipitation in the presence of zinc can be seen easily which contrasts with the situation observed in the coprecipitation of chromium in mixed-metal system discussed above. While the residual concentration has decreased down to 0.454mg/l (minimum value) with a corresponding pH increase up to 9.70 in the mixed-meal system, the value that of attained in the single metal system has been 3.750 mg/l. Furthermore, the difference between the residual concentrations in mixed-metal and single metal systems are considerable, even at low pH values in terms of the supporting effect of multiple metal ions on the hydroxide precipitation of chromium. On the other hand, while the redissolution of chromium hydroxides have occurred in the single metal solution as pH has increased, precipitates that of in mixed-metal solution have exhibited stability in terms of redissolution, where the residual chromium concentration has kept decreasing gradually with pH increase.

All the differences predicted, can be attributed to the possibility of chromium to have been coprecipitated with zinc, where chromium might have acted as a coagulant for zinc in the mixed-metal solution, instead of precipitating as chromium and zinc hydroxides in the same solution. But this fact can only be approved if the similar difference in residual concentrations is attained for zinc also.

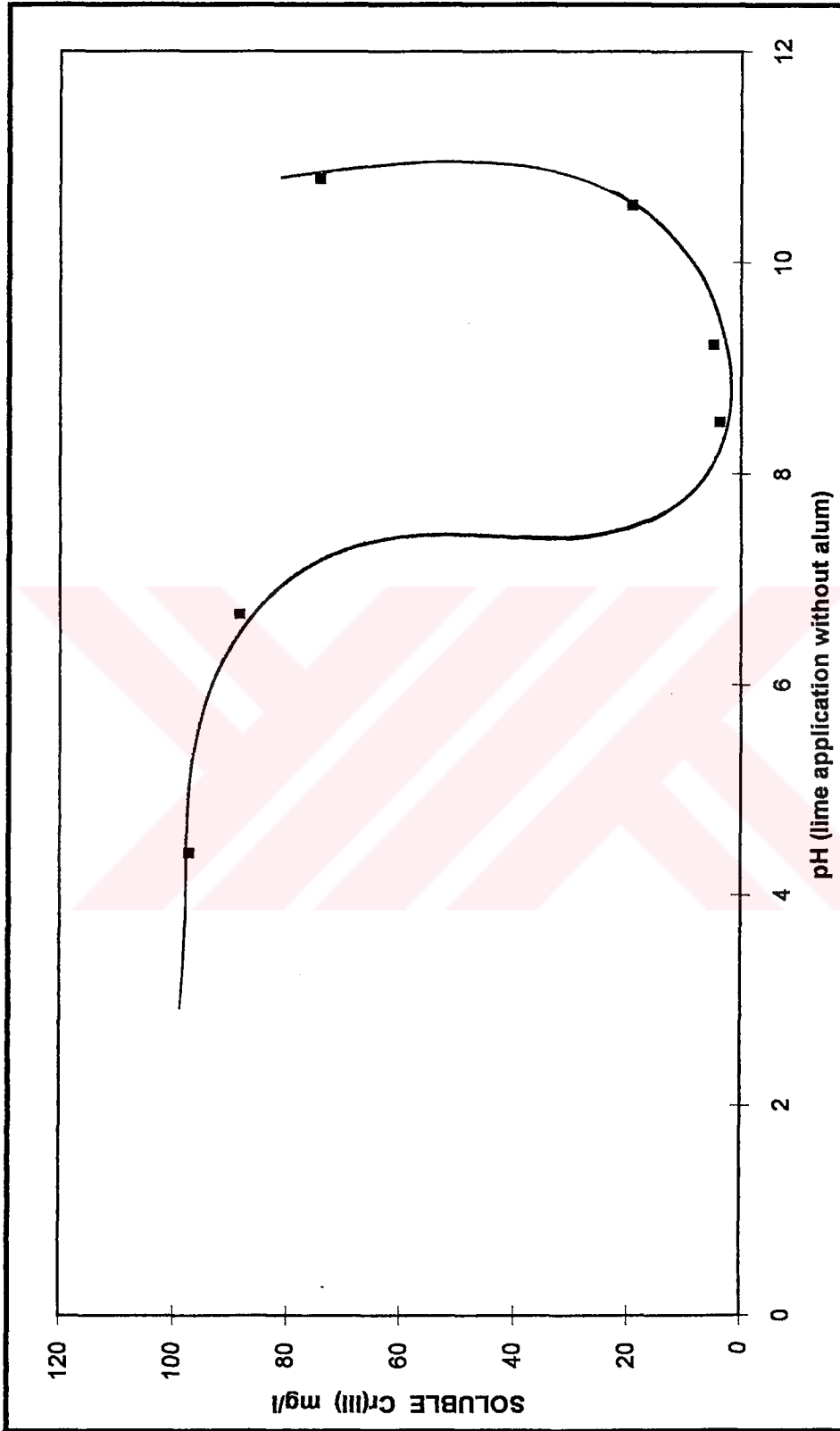


Figure 4.9 Hydroxide Precipitation of Cr as a Function of pH for Various Lime Dosages and Settling Time of 60min, in Single-Metal Solution Without Alum and Ligand.

4.2.4 Direct (Hydroxide) Precipitation of Zinc

The results obtained from the trial where zinc has been directly precipitated by the application of different lime dosages, in the absence of chromium are tabulated in Table 4.8

Table 4.8 Residual Zinc Concentration Versus pH at Various Lime Dosages and 60 min Settling Time, Without Alum and Ligand.

Lime (mg/l)	pH	Soluble Zn(II) (mg/l)
50.0	4.40	20.70
60.0	6.67	18.46
75.0	8.50	12.98
100.0	9.23	12.42
125.0	10.55	3.41
150.0	10.80	5.20

According to the results obtained, it is apparent that the direct precipitation of zinc alone is not an efficient method to decrease the metal concentration as being compatible with the required standards, where the minimum zinc concentration obtained at pH 10.55 is 3.41mg/l. On the other hand, the removal efficiency was quite low on a broad range of pH, between 4.40-9.23. And, the redissolution has been observed at pH 10.80, by which the residual zinc concentration has increased from 3.41 to 5.20 mg/l.

As it is seen from the graphical representation of the tabulated results in Figure 4.10, although the removal of zinc follows a similar trend to that of chromium given in Figure 4.9, the adverse effects of the absence of chromium on the removal efficiency of zinc hydroxide is more prominent than that of chromium.

On the other hand, when we compare the zinc removals obtained in single and mixed-metal solutions, the difference which have to be assessed with the trend obtained for that of chromium strengthens the fact that the coprecipitation of zinc and chromium has likely occurred in the hydroxide precipitation trial of the multiple ions in the mixed-metal system, instead of precipitating as zinc hydroxide.

4.3 Factors Affecting the Coprecipitation In the Mixed-Metal Solutions

Through the sections below, the extend of the effects of some factors on the efficiency of coprecipitation have been discussed according to the results obtained from the trials accomplished through the experimental conditions indicated in Table 3.1. These factors are ligand concentration, sulfate (in this study), aging of the solution and initial metal concentration variation.

4.3.1 Effect of Ligand on the Efficiency of Coprecipitation

It is well known that the presence of an inorganic ligand can adversely effect the precipitation processes by altering the solubilities of the precipitates. Sulfate easily interferes with the precipitation processes

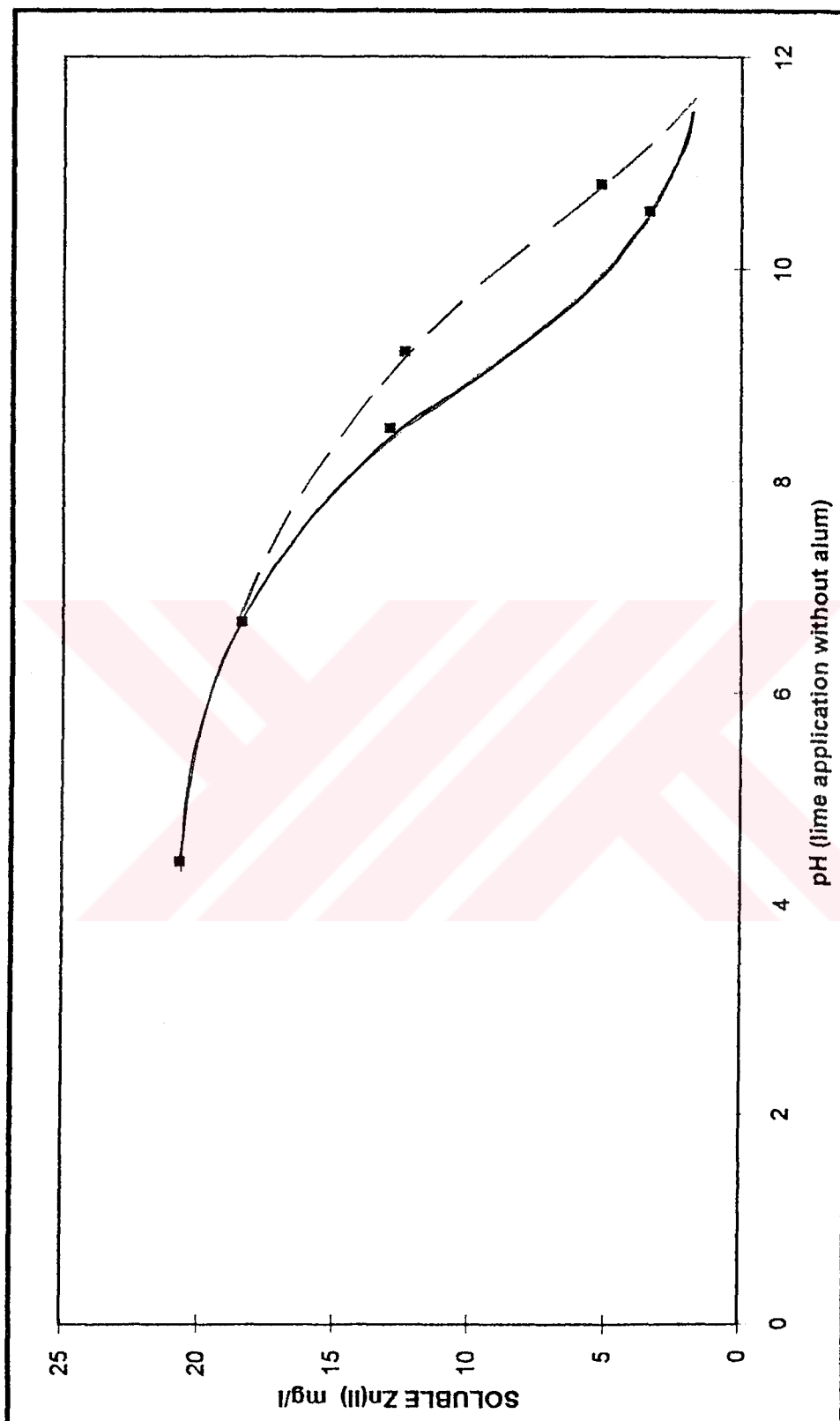


Figure 4.10 Hydroxide Precipitation of Zinc as a Function of pH for Various Lime Doses and Settling Time of 60 min. in Single-Metal Solution Without Alum and Ligand.

through increasing the solubility of the precipitate by forming more soluble compounds with metals in a competitive way with respect to metal hydroxides, and the precipitates become soluble, in turn causing decrease in the removal efficiencies of the metal ions to be removed. Besides, the ionic strength increases with the addition of sulfate, and also this increase rises the solubility of metal hydroxide. Ligands contained in the wastewater can interfere with the coprecipitation process in either two ways;

1. By forming complexes between coagulant and ligands.
2. By forming complexes between metal and ligands.

The results regarding the removals of chromium and zinc versus sulfate concentration obtained from the coprecipitation trial under the experimental conditions indicated in Table 3.1, are presented in Table 4.9. On the other hand, the graphical representations of the results are given in Figures 4.11 and 4.12.

Table 4.9 Residual Metal Concentrations of Zn(II) and Cr(III) Versus Sulfate Concentration at Alum Dosage 70 mg/l, pH 8.70 and 60min Settling Time, For Initial Concentrations of Cr(III)=100mg/l and Zn(II)=25mg/l .

SO₄⁼ Concentration (mg/l)	Soluble Cr(III) (mg/l)	Soluble Zn(II) (mg/l)
0	0.028	0.614
140	0.040	0.592
410	0.069	0.514
1350	0.083	0.571
5410	0.022	0.560
6760	0.067	0.567

i) Chromium Removal Versus Sulfate Concentration :

As it is seen from Figure 4.11, although the removal pattern of chromium versus ligand concentration is not constant and a mild wave has been obtained, this prevents any appreciation of the difference in the removal efficiency depending on the presence of sulfate. In addition, beyond the distinguishment of the effect of ligand, residual concentrations corresponding to all sulfate dosages are well below the required standards. Although there is a decrease in the removal efficiency with the addition of NaSO_4 up to 8g/l, by which the residual concentration of chromium has increased from 0.028mg/l to 0.083mg/l, the difference is negligible to be able to say that the presence of sulfate has interfered with the coprecipitation of chromium because of the order of magnitude of the residual concentrations with respect to the initial concentration of chromium (100mg/l). In the same respect, also the local minima, 0.022mg/l, attained at NaSO_4 concentration of 8 g/l, can not be appreciated as a consequence of the increasing sulfate dosage.

So, it is apparent that for such a high initial concentration of chromium and experimental conditions near to the optimum values, sulfate interference with the coprecipitation of chromium is not considerable.

ii) Zinc Removal Versus Sulfate Concentration :

The experimental results obtained for the zinc removal are not well-simulated with the phenomena considering the dissolution of zinc hydroxide by added sulfate. As it is seen from Figure 4.12, the removal trend of zinc is versus ligand concentration is nearly flat where a considerable change in the removal efficiency with sulfate addition has not been attained.

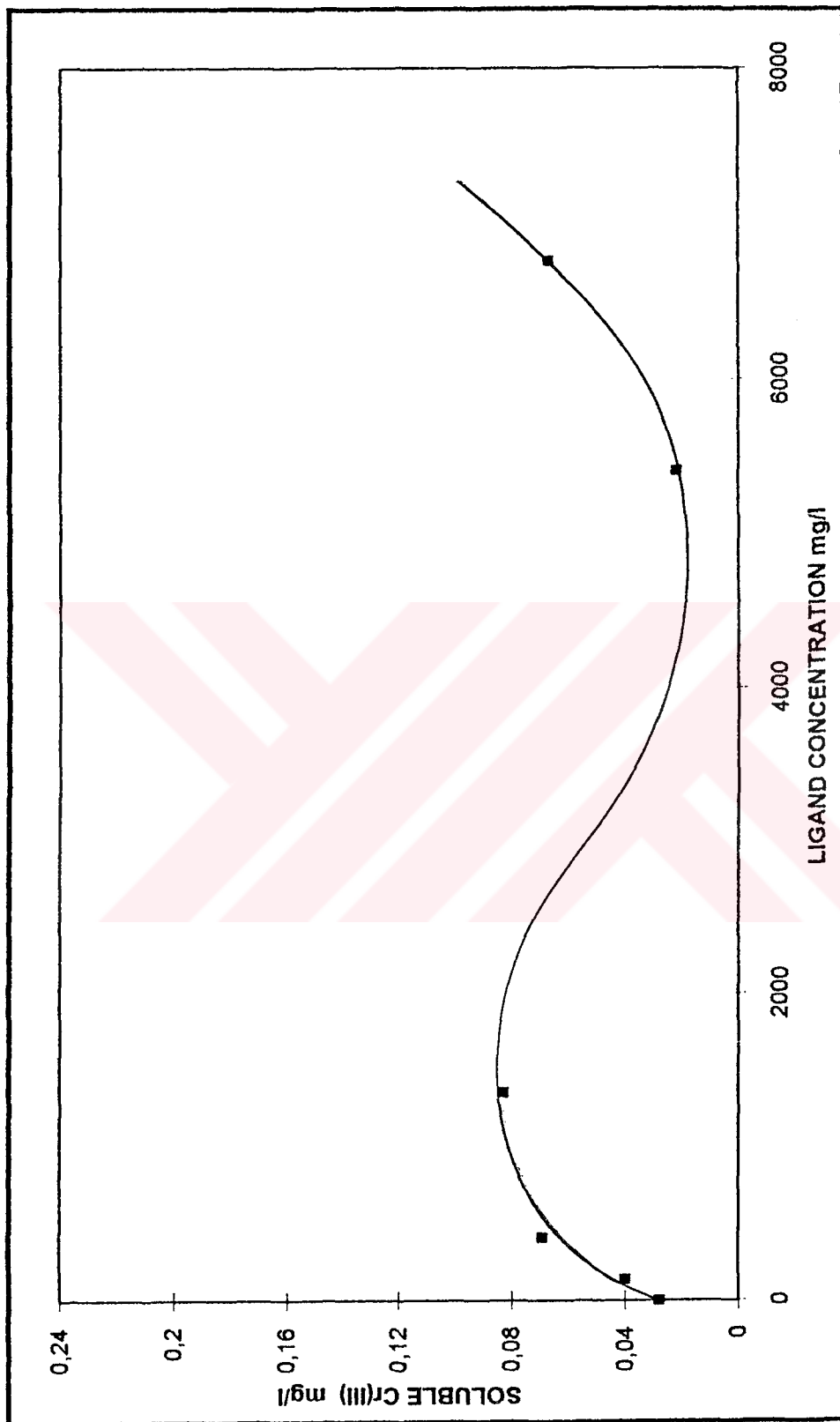


Figure 4.11 Coprecipitation of Chromium as a Function of Ligand (sulfate) Concentration at Alum Dose of 70 mg/l, pH 8.70 and Settling Time of 60min., in Mixed-Metal Solution.

Although, a decrease has been observed in the residual zinc concentration with increase in NaSO₄ dosage up to 2.0 g/l, again these amount of fluctuations are small enough to attribute them to the experimental accuracy. At this point again, it can be concluded that the zinc removal has not been effected by the presence of sulfate in the coprecipitation trial under the experimental conditions near to optimum values, as in the case of chromium.

Through the assessment of the results obtained, although it is an expected behavior that the presence of ligand either decreases the removal efficiency or changes the optimum conditions determined for the ligand-free systems, the extend of the effect depends on several factors like the concentration of the ligand and the metal ions to be removed, the composition of the solution etc.

Within this framework, one of the reasons of not being observe the decay of the removal efficiency with the addition of sulfate for both of the metal ions may be the high initial concentrations of chromium and zinc compared to sulfate concentration which has prevented the formation of soluble metal-sulfate complexes.

On the other hand, it has been reported in the literature that the effect of ligands on the precipitation processes are prominent at lower pH values (Diamadopoulou and Benedek, 1984). Moreover, it is known that the coprecipitated metals are less readily released by changes in the ligand concentrations depending on the three-dimensional structure of the coprecipitates providing the incorporation of the metal into the bulk-particle structure (Fulghum et al., 1988).

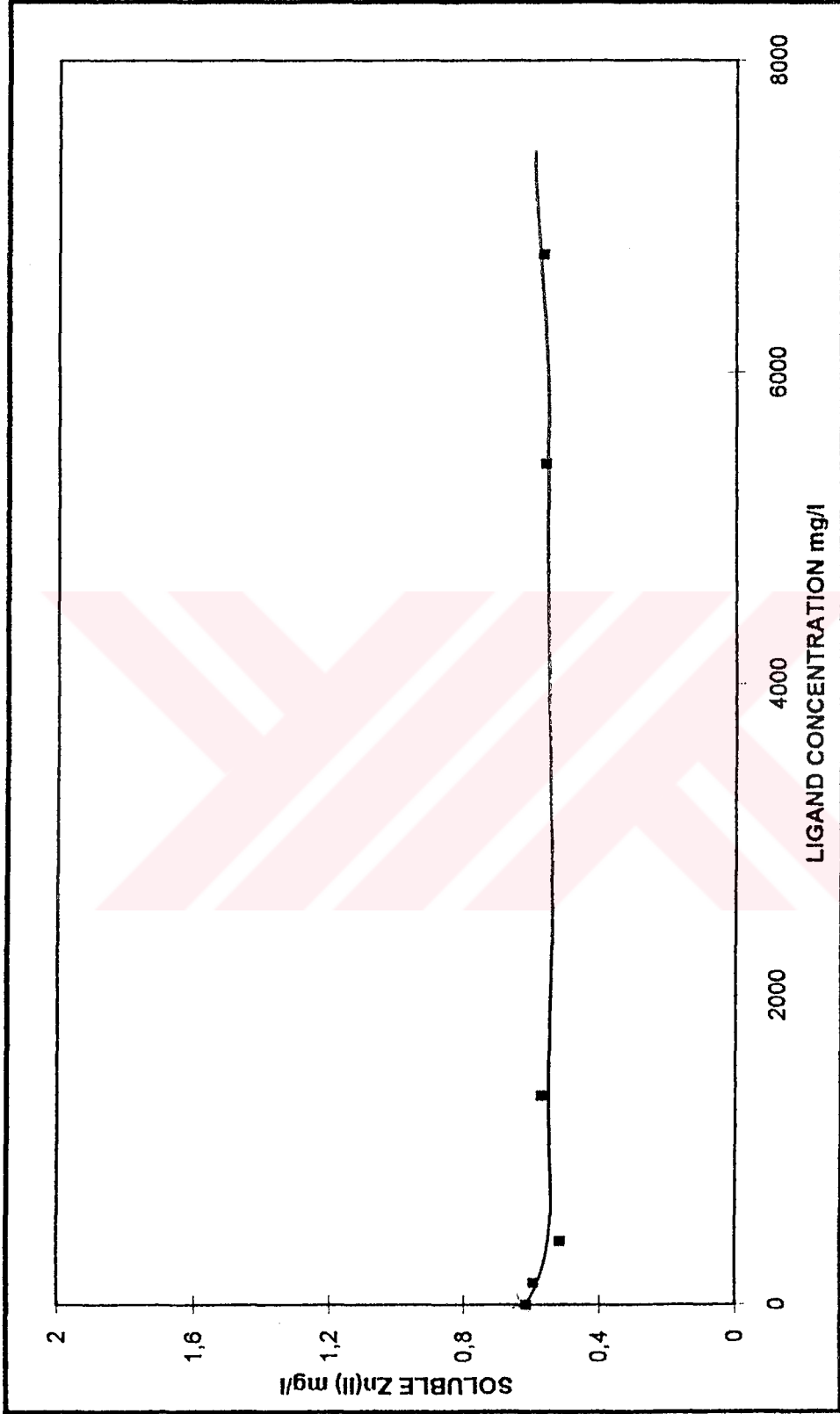


Figure 4.12 Coprecipitation of Zinc as a Function of Ligand (sulfate) Concentration at Alum Dose of 70 mg/l, pH 8.70 and Settling Time of 60min., in Mixed-Metal Solution.

On the other hand, there is also an addition of sulfate from the dissociation of alum and zinc sulfate in the solution. But the amount of sulfate coming from this source is quite negligible compared to the sulfate amount which has been obtained through the addition of NaSO_4 , and as the amount of sulfate coming from the above-mentioned dissociation is constant all through the trial, the fact has not constituted an obstacle for the determination of the ligand effect.

4.3.2 Effect of Aging on the Efficiency of Coprecipitation

For the determination of the effect of the aging on coprecipitation and the investigation of whether an optimal time exists for the maximum removal of chromium and zinc in the coprecipitation trial, samples aged for six different time intervals (15min, 30min, 60min, 120min, 240min, and 24h) have been examined. Other experimental conditions have been kept constant for all of the samples as indicated in Table 3.1 (alum:70mg/l, pH:8.70). The residual concentrations obtained has been tabulated in Table 4.10.

Table 4.10 Residual Metal Concentrations of Zn(II) and Cr(III) Versus Settling Time at Alum Dosage 70 mg/l and pH 8.70.

Settling Time (min)	Soluble Cr(III) (mg/l)	Soluble Zn(II) (mg/l)
15	0.050	0.554
30	0.052	0.618
60	0.052	0.596
120	0.069	0.553
240	0.085	0.721
1440	0.571	1.827

i) Chromium Removal Versus Settling Time:

As it is seen from the graphical representation of the tabulated results in Figure 4.13, chromium removal did not exhibit a significant change with the variation in maturation time within the first two hours. Although there is an increase in the residual metal concentration, this increase is negligible compared to the fluctuation observed after 24h aging (from 0.085mg/l to 0.567mg/l). And, as the actual settlement period for the completion of the coagulation-flocculation process is accepted as 2h, within this period it is apparent that the aging of the coprecipitates or the flocs under the experimental conditions, pH 8.70 and alum 70mg/l, has not made any significant effect on the removal efficiency where the corresponding residual metal concentrations are between 0.050-0.069 mg/l (well below the required standards). After two hours of aging, the redissolution of the chromium has been observed and it has reached a considerable value at the end of 24h of aging where the corresponding chromium concentration has increased to 0.567 mg/l which is above the limit.

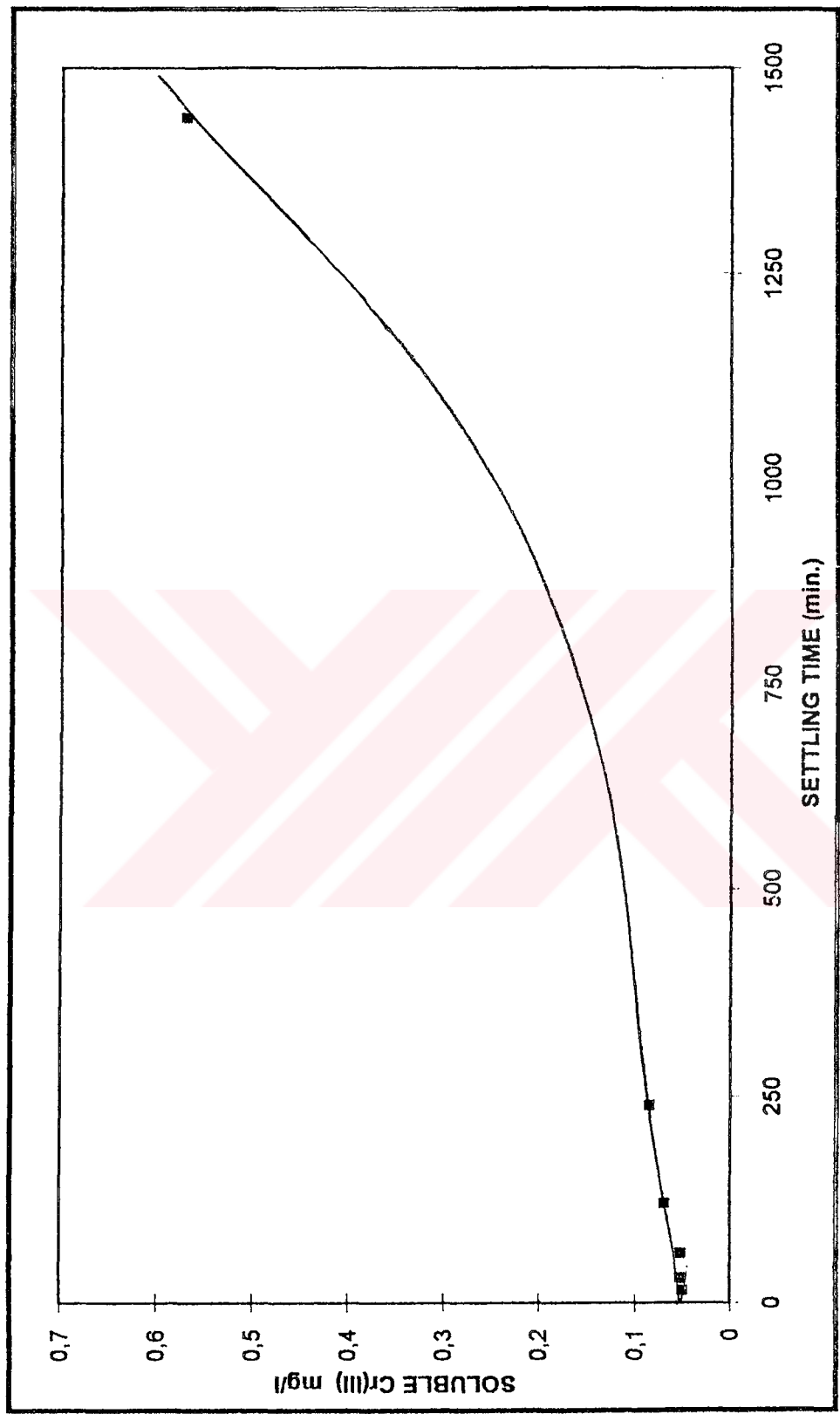


Figure 4.13 Coprecipitation of Chromium as a Function of Settling Time at Alum Dose of 70 mg/l and pH 8.70, in Mixed-Metal Solution Without Ligand .

ii) Zinc Removal Versus Settling Time:

Zinc removal profile as a function of aging time is quite similar to that of chromium. As it is seen from Figure 4.14, mild changes in the zinc concentration have been observed in the first two hours of aging, as in the case of chromium, between 0.554-0.618 mg/l. In addition, a similar fluctuation has been obtained at the end of 24h of aging which has not been as severe as that of chromium, where the corresponding zinc concentration has increased to 1.827. And again, it can be easily said that aging up to two hours has no significant effect on the removal efficiency of zinc either, under the experimental conditions indicated (pH 8.70 and alum 70 mg/l).

As a general acceptance, in conventional coagulation-flocculation process based on hydroxide precipitation or adsorption, the settlement of the precipitates or the flocs is nearly completed and very rapid in the first 30 minute of the sedimentation but the actual settling period is accepted as two hours for the completion of the reactions. On the other hand, the settling rate is getting slow after the first 30 minute and it is nearly negligible after an hour. In our case, it can be easily seen from the graphical representations that the residual concentration change observed within the aging period of two hours is negligible for both of the metals which is not in line with the acceptance mentioned above. The situation shows that the settlement has been nearly completed before the settling time of 15 minute, and this fact may be attributed in the first hand to the difference between the size of the hydroxide precipitates and the coprecipitates, and the simultaneous and the rapid occurrence of coprecipitation compared to direct precipitation, in turn confirming the supportive effect of the coprecipitation also in terms of decreasing the sedimentation period.

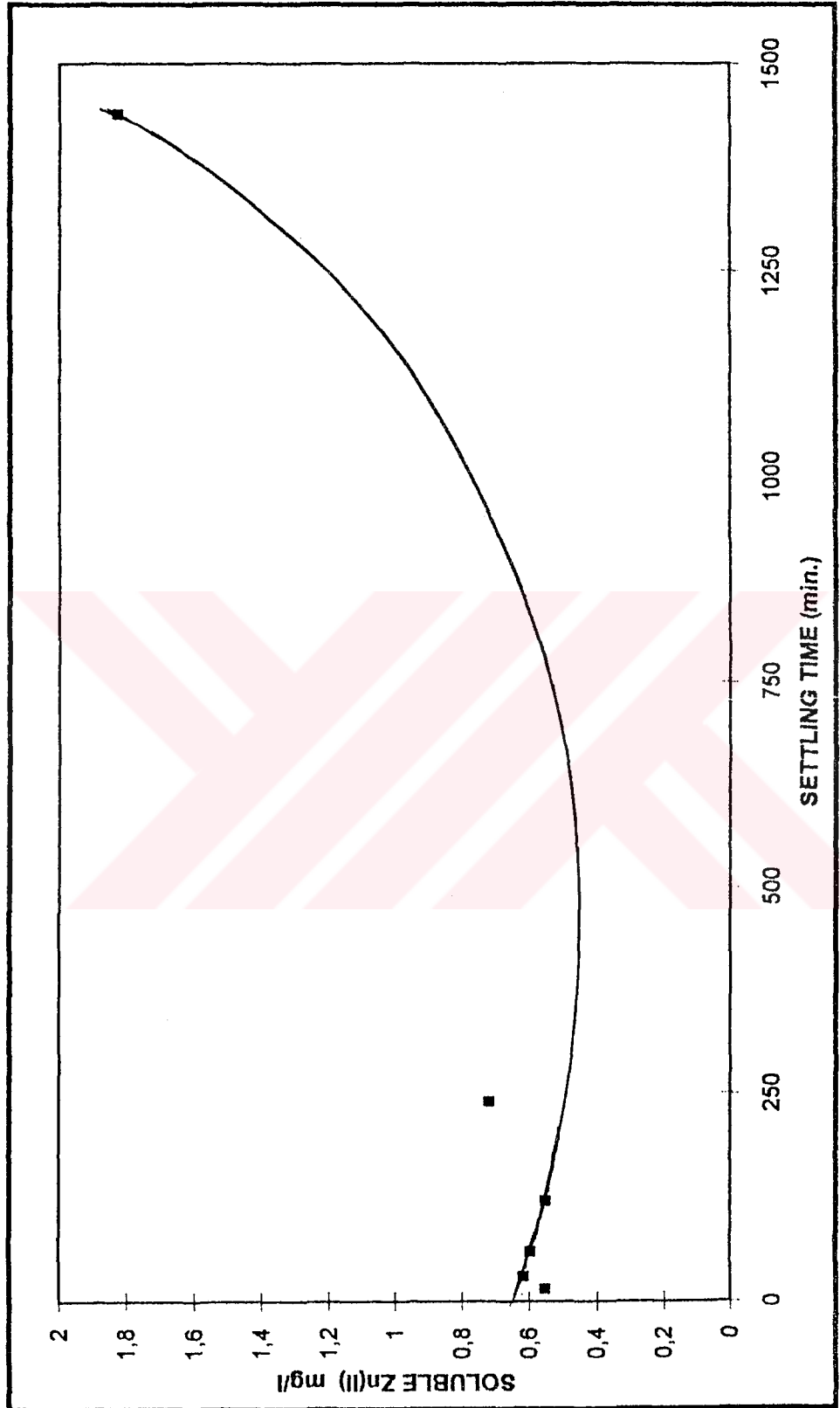


Figure 4.14 Coprecipitation of Zinc as a Function of Settling Time at Alum Dose of 70 mg/l and pH 8.70, in Mixed-Metal Solution Without Ligand .

On the other hand, it is another prediction that the aging, especially in high pH, increases the slowly reversible fraction of the coprecipitates. In other words, aging increases the stability of the coprecipitates (Schultz, et al., 1987). As it is seen from Figure 4.15, this fact is confirmed with another finding, that the structure of the coprecipitates aged turns from vaterite form to calcite form which is thermodynamically preferred (Fulghum, et al., 1988).

The redissolution of the precipitates occurs depending on the increase in the solubility of the precipitate with time. Main reason for this fact may be the change in pH of the solution with time, and this decrease in pH causes an increase in the concentrations of positively charged hydroxometal complexes and free metal ions. In our case this fact could have been observed only at the end of 24 h of aging for both of the metals. On the other hand, it is an expected behavior that the coprecipitates aged redissolve less readily depending on the findings mentioned above. The agreement with this expectation can only be confirmed by comparing the extend of the redissolution of the aged precipitates obtained through hydroxide precipitation or adsorption with that of coprecipitates.

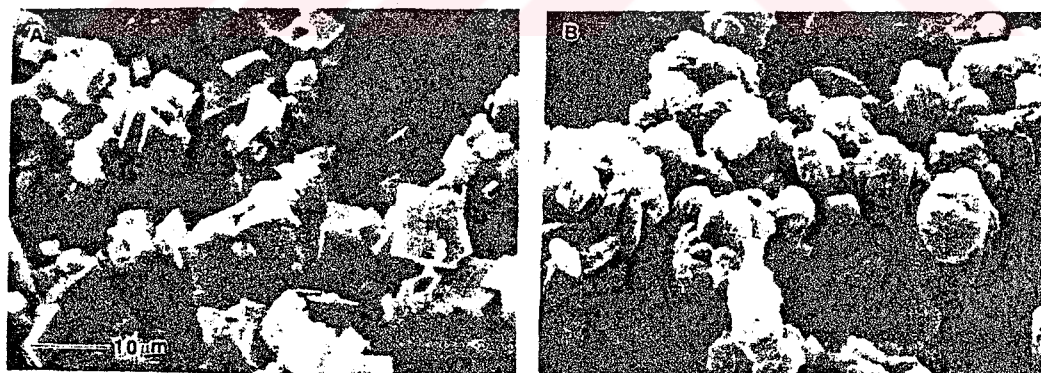


Figure 4.15 Secondary electron micrographs of calcium carbonate with lead, (A) Calcite coprecipitate containing 134 ppm Pb (B) Vaterite coprecipitate containing 124 ppm Pb (Fulghum, et al., 1988).

4.3.3 Effect of Initial Metal Concentration on the Efficiency of Coprecipitation

In general, processes depending on precipitation should yield an essentially constant metal residual (regardless of influent concentration) in accord with the solubility of the metal precipitate. If however, SS removal is not complete then carry-over of precipitated metal will cause metal residual to be more nearly proportional to influent metal concentrations (Maruyama, et al., 1975). On the other hand, initial metal concentrations have to be considered to the extent where the solubility of the metal-coagulant interaction product is exceeded. And, it is known that, up to this mentioned level, percentage removals are higher with increasing initial metal concentrations.

Especially, under the conditions where the only removal mechanism is the precipitation and solid separation, at low ratios of C_0 / C_{sol} where C_0 and C_{sol} are the initial metal and the soluble metal concentrations after precipitation respectively, percent removal rapidly increases with increasing C_0 . On the other hand, at C_0 / C_{sol} of 100 or higher, the percent removals become asymptotic with percent removal of TSS (total suspended solid) and the changes in process variables do not produce obviously significant effects on percent removals. This prediction can be easily seen from the graphical representation given in Figure 4.16 (Hannah et al., 1977).

The tabulated results obtained through the trial performed for the determination of the effect of initial metal concentrations on the efficiency of the coprecipitation of chromium and zinc, and the extent of the deviation from the trend indicated above for hydroxide precipitation are presented in Table 4.11.

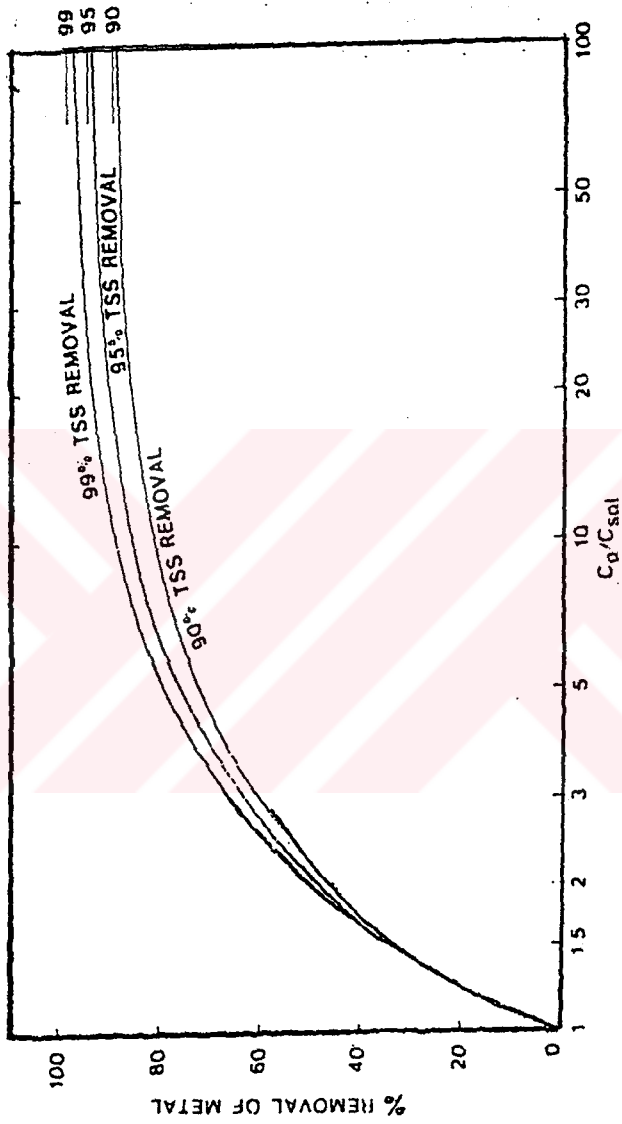


Figure 4.16 Effect of Initial Metal Concentration on Percent Removal By Chemical Purification

Table 4.11 Residual Metal Concentrations of Zn(II) and Cr(III) Versus Initial Metal Concentrations at Alum Dosage 70 mg/l and pH 9.80.

Initial Metal Concentration (mg/l)		Residual Metal Concentration (mg/l)	
Cr(III)	Zn(II)	Cr(III)	Zn(II)
25	5.0	0.052	0.646
50	12.5	0.069	0.641
75	17.5	0.034	0.637
100	25.0	0.018	0.550

i) Chromium Removal Versus Initial Metal Concentration

As it is seen from Figure 4.17, the removal trend obtained through the coprecipitation trials applied to samples having four different initial chromium concentrations (25, 50, 75, 100mg/l) exhibit both descent and ascent within a narrow range, where the respective residual concentrations are between 0.052 and 0.018 mg/l. Although, there is a local maxima in the removal trend, corresponding to the initial Cr(III) concentration of 50 mg/l, the removal profile can be accepted as a descending one with increase in the initial Cr(III) concentration, from 0.052 to 0.018 mg/l.

ii) Zinc Removal Versus Initial Metal Concentration

As it is seen from Figure 4.18, the removal efficiencies obtained are almost constant up to the initial Zn(II) concentration of 100 mg/l, where the residual zinc concentrations are 0.646, 0.641, 0.637 mg/l for the initial Zn(II) concentrations of 25, 50 and 75mg/l, respectively. At the initial concentration of 100 mg/l the residual zinc concentration has dropped to 0.550 mg/l.

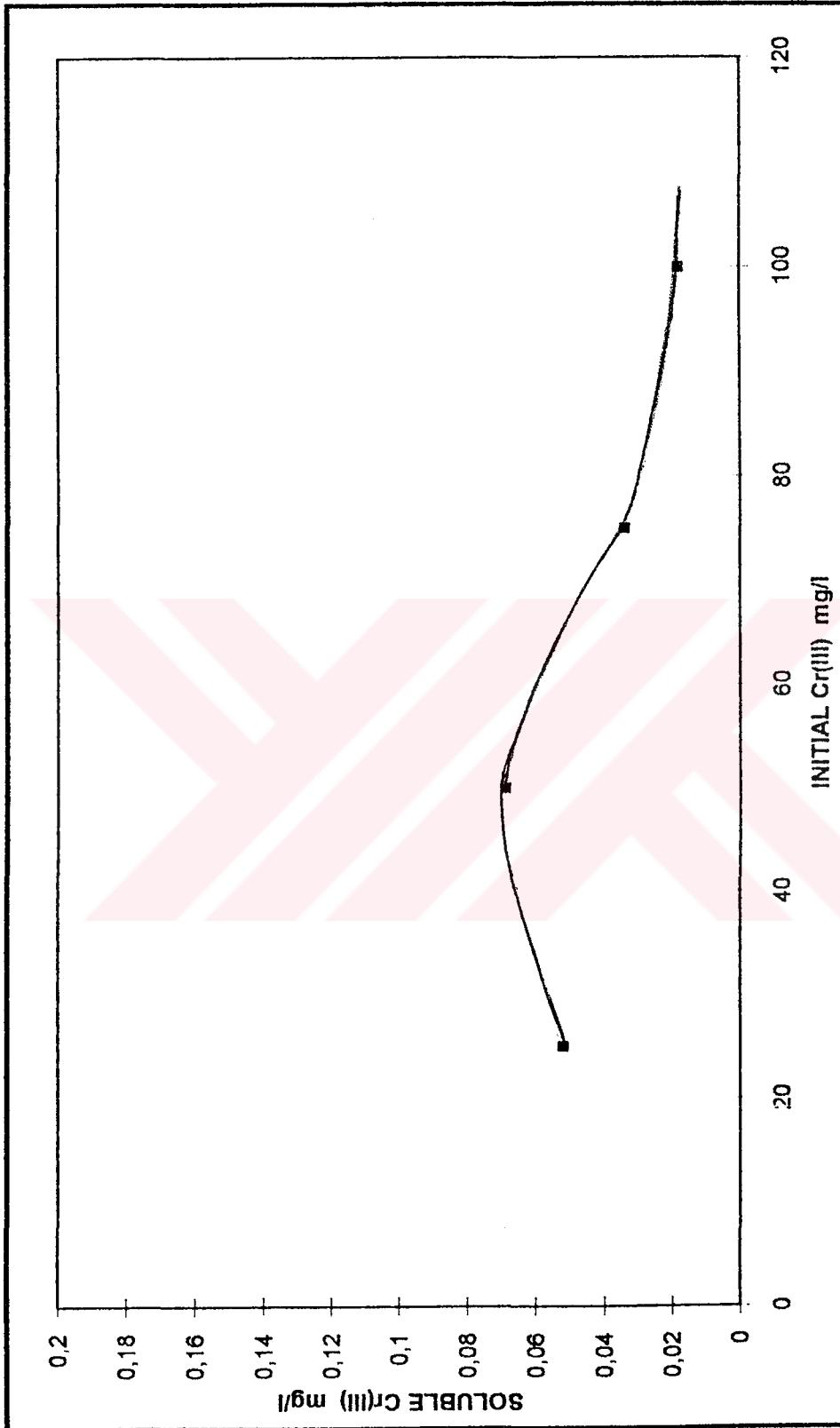


Figure 4.17 Coprecipitation of Chromium as a Function of Initial Chromium Concentration at Alum Dose 70 mg/l, pH 8.70 and Settling Time of 60 min., in Mixed-Metal Solution Without Ligand.

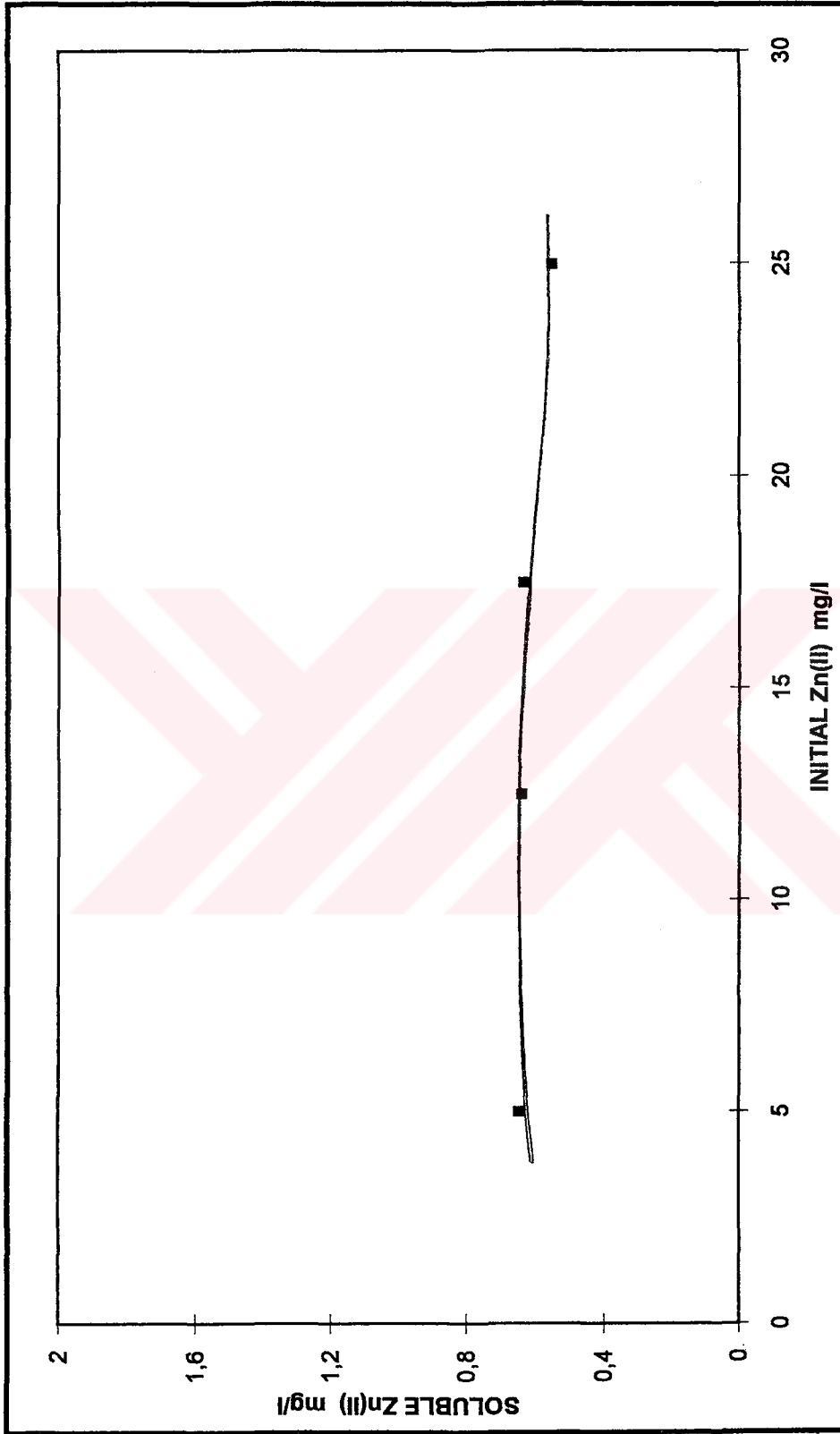


Figure 4.18 Coprecipitation of Zinc as a Function of Initial Zinc Concentration at Alum Dose 70 mg/l, pH 8.70 and Settling Time of 60 min. in Mixed-Metal Solution Without Ligand.

Although a continuous and gradual removal has been obtained with increasing initial concentration, the removal of zinc has exhibited consistency in a narrow range of residual concentration between 0.550-0.646 mg/l, as in the case of chromium.

Within this framework, the removal profiles obtained in Figure 4.17 and 4.18 have shown that the removal efficiency of chromium and zinc seems not to have been affected by the initial metal concentration variation, where the decrease in the residual concentrations for both of the metal ions are negligible with respect to the initial concentration variation. And this situation satisfies the prediction that the initial concentration variation effects the removal efficiency to a level where the metal-coagulant ion product exceeds the solubility product. So, the removal of chromium and zinc following nearly a constant trend can be attributed to the fact that even the minimum initial concentrations [Cr(III):25 mg/l, Zn(II): 5 mg/l] were sufficient to exceed the solubility product of metal-hydroxides providing the hydroxide precipitation. Another aspect of the result is that, the concentration of lime was quite high providing the ion product to be higher than the solubility product. But on the other hand, it is also well known that, the increase of the initial metal concentration enhance the supportive effect of coprecipitation. So the gradual decrease in the residual concentrations of zinc and chromium with increasing initial concentration may be a result of this fact. On the other hand, in spite of narrow ranges of residual concentration variation, the percent removal of chromium is considerably higher than that of zinc.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

This study, regarding the prediction of the effects of coprecipitation process as an additional mechanism on the removal efficiency of chromium and zinc in a simulated chromium plating wastewater, have been completed through the main objective of determining the feasibility of the process. On the other hand, the extent of the effects of some factors on coprecipitation have been investigated. All through the study, it has been taken into the account that the coprecipitation has to be assessed as a mechanism supporting the hydroxide precipitation in chemical treatment rather a treatment process itself.

As a general prediction, it can be said that the trends obtained from the experimental applications have satisfied the expected situations. On the other hand, some deviations have been attributed to new assumptions in line with the existing findings. In the first hand, the experimental results have shown clearly that chromium and zinc removal have been considerably enhanced by coprecipitation mechanism through the application of alum, in both mixed-metal and single-metal solutions in terms of residual metal concentrations and stability of the precipitates against redissolving depending on the amphoteric property of $\text{Cr}(\text{OH})_3$ and $\text{Zn}(\text{OH})_2$ where the results obtained can easily meet both national and international standards set as the discharge limits of Cr(III) and Zn(II).

Also, some trials performed for the determination of the feasibility of coprecipitation in terms of standing out the variation in some parameters like ligand concentration, aging of the coprecipitates and initial metal concentration, have shown that, optimum conditions provided for the coprecipitation (optimum alum dose and optimum pH) have compensated the adverse impacts of these variations. On the other hand, especially in order to be able to assess the exact effect of sulfate (ligand) on the coprecipitation of the chromium and zinc, much additional work is required, particularly application of sulfate under the experimental conditions far from the optimum values, (for example: low alum concentration and pH).

On the other hand, through the comparison of the mixed-metal and single-metal solutions for both of coprecipitation and hydroxide precipitation, it has been seen that while the presence of chromium has an additional support on the removal efficiency of zinc in coprecipitation, the coprecipitation of chromium has not exhibited a remarkable difference in single and mixed-metal solutions. However, the picture is different in hydroxide precipitation that the removal of both of the metal ions have been enhanced in mixed-metal solution over single-metal solution. This supporting effect of mixed-metals attained in hydroxide precipitation strengthens the assumption that Cr(III) and Zn(II) have coprecipitated also, while precipitating as Cr(OH)_3 and Zn(OH)_2 .

As another prediction, although removal trends of both metals were generally near to each other, they have also exhibited differences in both coprecipitation and hydroxide precipitation depending on the difference in solubility products and the order of precipitation.

Optimum conditions obtained in the coprecipitation and the hydroxide precipitation of Cr(III) and Zn(II) with initial concentrations of 100 and 25 mg/l respectively in both mixed-metal and single-metal solution are given at the below table.

Table 5.1 Summary of the Experimental Results

Type of Application	Alum (mg/l)	pH	Cr(final) (mg/l)	Zn(final) (mg/l)	R _{Cr}	R _{Zn}
Coprecipitation in mixed-metal solution	70	9.50	0.044	0.038	1.430	0.360
Hydroxide Precipitation in mixed-metal solution	-	10.80	0.600	0.513	-	-
Coprecipitation in single metal solution	80	8.70	-	0.152	-	0.310
Coprecipitation in single metal solution	30	8.70	0.034	-	3.332	
Hydroxide Precipitation in single metal solution	-	8.50	3.75	-	-	-
Hydroxide Precipitation in single metal solution	-	10.55	-	3.41	-	-

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APPENDIX A

MEASUREMENT OF ABSORPTION BY THE USE ATOMIC ABSORPTION SPECTROPHOTOMETRY

Working conditions for the measurement of the concentrations in Atomic Absorption Spectrophotometry have been summarized in the Table A.1.

Table A.1. INSTRUMENT PARAMETERS

Parameters	Chromium	Zinc
Calibration Mode	Flame	Flame
Flame Stoichiometry	Reducing	Oxidizing
Flame	C ₂ H ₂	C ₂ H ₂
Support	Air	Air
Flame Current	3.0 L/min	2.2 L/min

No chemical interferences causing depression of total absorbances of Cr(III) and Zn(II) have been found in the wastewater solutions studied. In practice, the reading for the standard has been set to zero absorbance whilst a blank solution is aspirated, then the reading for the sample has been given directly in absorbance units. After the absorbance readings of standard solutions and sample, comparisons of these absorbances have been made and sample concentrations have been calculated by the spectrophotometry through the construction of calibration curve.

APPENDIX B

CONSTRUCTION OF THE CALIBRATION CURVES FOR THE CALCULATION OF CR(III) AND ZN(II) CONCENTRATIONS

The calibration curves for Cr(III) and Zn(II) have been prepared by the spectrophotometry all through the measurements. For the construction of these calibration curves, concentrations of standard solutions of Cr(III) and Zn(II) have been fixed throughout the course of measurements to compare it with the blank solution. Typical calibration curves obtained for Cr(III) and Zn(II) are given below.

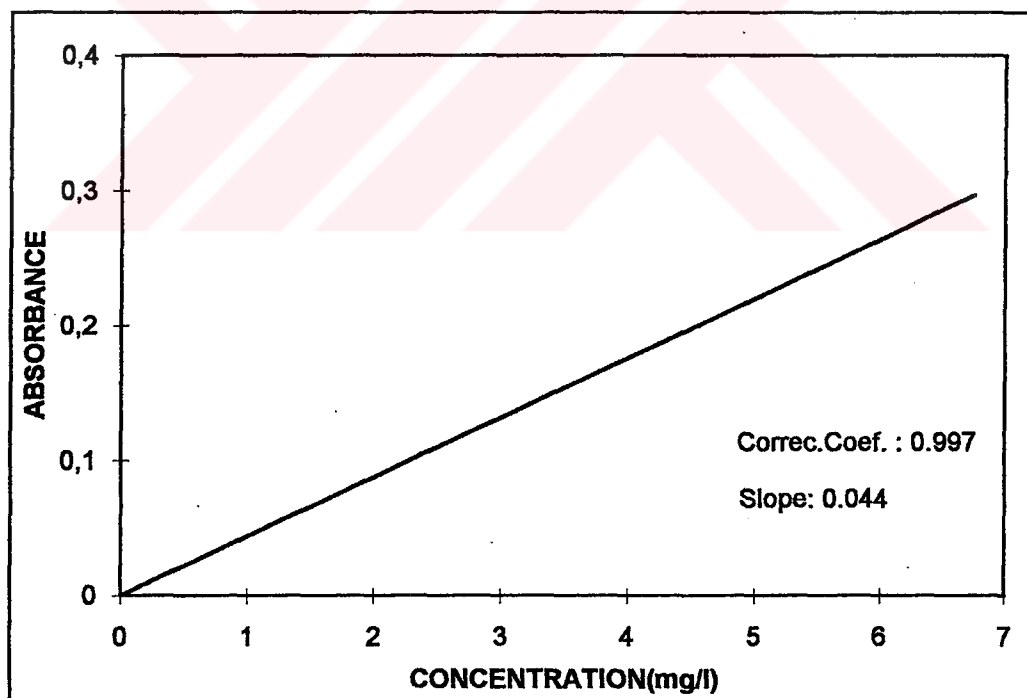


Figure B.1. Calibration Curve of Cr(III) in A.A.S. Measurements

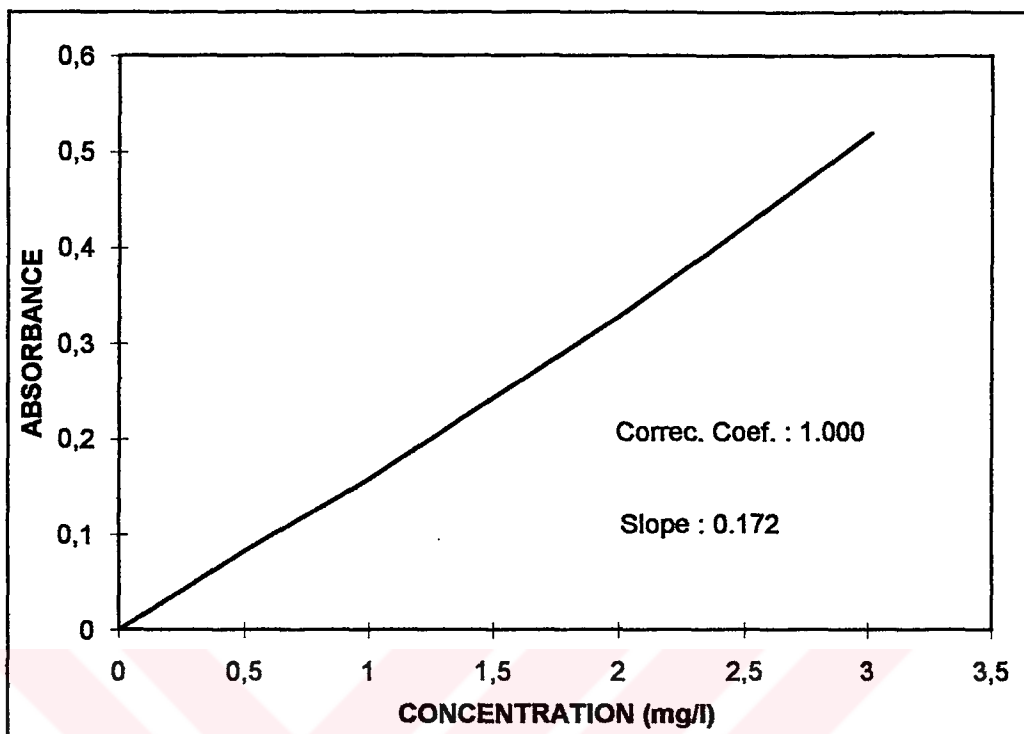


Figure B.1. Calibration Curve of Cr(III) in A.A.S. Measurements