OPTIMIZATION OF CONDITIONS IN SULFURIC ACID LEACHING OF TURKISH CHROMITE CONCENTRATES

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EMRE USTAOĞLU

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Prof. Dr. Canan ÖZGEN
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Tayfur ÖZTÜRK
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Prof. Dr. Ahmet GEVECİ
Supervisor

Examining Committee Members

Prof. Dr. Yavuz TOPKAYA

Prof. Dr. Ahmet GEVECİ

Prof. Dr. İshak KARAKAYA

Prof. Dr. Naci SEVİNÇ

Prof. Dr. Ümit ATALAY

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : Emre USTAOĞLU

Signature :

ABSTRACT

OPTIMIZATION OF CONDITIONS IN SULFURIC ACID LEACHING OF TURKISH CHROMITE CONCENTRATES

Ustaoğlu, Emre

M.S., in Department of Metallurgical and Materials Engineering
Supervisor: Prof. Dr. Ahmet GEVECİ

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In this thesis work, a high grade chromite concentrate obtained from Pınarbaşı, Kayseri region of Turkey was reacted with sulfuric acid solution to determine the optimum conditions of leaching of chromite ores.

Conventional methods for producing chromium are still valid in industry. The main process in production includes soda melting and taking it into solution in the form of chemical compounds such as sodium dichromate. Three and six valence states of chromium have importance in production. Trivalent chromium, chrome ore or chromite have no harmful effects. However, compounds of hexavalent chromium show toxic, irritating and corrosive action to people and environment. In the mentioned conventional method, main products consist of hexavalent chromium compounds. In this study, only trivalent chromium remained in the leach solution and did not change to hexavalent state. Obtained product after leaching was chromium(III) sulfate.

The maximum extraction of chromium in the absence of perchloric acid was 94.1 % under the conditions of 175 °C, 6 hours and 84.6 wt % sulfuric acid. The maximum extraction of chromium in the presence of perchloric acid was 98.7 % under the conditions of 175 °C, 2 hours, 84.6 wt % sulfuric acid and ½ perchloric acid / chromite ratio. The latter one was also the highest recovery value obtained during the experiments. Moreover, in none of the analyzed samples, appreciable amounts of hexavalent chromium was found during analyses.

Keywords: Chromite concentrate, sulfuric acid leaching, trivalent chromium, hexavalent chromium.

ÖZ

TÜRK KROMİT KONSANTRELERİNİN SÜLFÜRİK ASİT İLE LİÇİ İŞLEMİNİN OPTİMİZASYONU

Ustaoğlu, Emre

Yüksek Lisans, Metalurji ve Malzeme Mühendisliği Bölümü
Tez Yöneticisi: Prof. Dr. Ahmet GEVECİ

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Bu tez çalışmasında, ülkemizin Kayseri-Pınarbaşı bölgesinden elde edilen yüksek tenörlü kromit konsantreleri, krom cevherlerinin liçi işlemindeki optimum koşulların araştırılması amacıyla sülfürik asit ile reaksiyona sokulmuştur.

Endüstride, halen konvansiyonel krom üretim metotları geçerliliğini korumaktadır. Üretimdeki temel proses, soda ergitme ve eriyiği sodyum dikromat gibi kimyasal bileşikler halinde çözeltiye alma kademelerini kapsar. Üretim sırasında, üç ve altı değerlikli kromun sahip olduğu önem büyüktür. Üç değerlikli krom, krom cevheri ya da kromit zararlı etkilere sahip değildir. Ancak, altı değerlikli krom insanlara ve çevreye karşı toksik ve korozif etkiler göstermektedir. Bahsedilen konvansiyonel metotta elde edilen temel ürünler ise altı değerlikli krom bileşiklerini içermektedir. Bu çalışmada, sadece üç değerlikli krom liç çözeltisi içerisinde kalmış ve altı değerlikli forma dönüşmemiştir. Liç sonucunda elde edilen ürün krom(III) sülfattır.

Perklorik asitin bulunmadığı ortamda, 175 °C, 6 saat ve ağırlıkça % 84,6 sülfürik asit kullanılan koşullarda elde edilen maksimum krom verimi % 94,1'dir. Perklorik asit kullanımı söz konusu olduğunda ise, 175 °C, 2 saat, ağırlıkça % 84,6 sülfürik asit içeren çözelti kullanılması ve perklorik asit / kromit oranının ½ olarak belirlendiği koşullarda maksimum krom verimi % 98,7 olarak bulunmuştur. Bu değer, aynı zamanda, tüm deneyler boyunca elde edilen en yüksek verim değeridir. Ayrıca, analiz edilen örneklerin hiçbirinde analizler sırasında altı değerlikli kroma rastlanmamıştır.

Anahtar Kelimeler: Kromit konsantresi, sülfürik asit liçi, üç değerlikli krom, altı değerlikli krom.

To My Parents;
Nermin and Zafer Ustaoğlu

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CHAPTER 1

INTRODUCTION

Chromium and chromium chemicals have been playing important roles in our daily lives for years. These are all used for some industrial purposes and they improve some desired features in metal and alloy productions. For instance; chromium gives brightness to our furniture and kitchens, chromium chemicals are used in leather industry and give bright colors to paints for homes, books, clothing etc. Also, chromium steels protect our health.

Nature has been generous in its supply of chromite and although the consumption of chromium in the chemical, refractory, and metallurgical fields is high and increasing rapidly, world reserves of chromite are sufficient for hundreds of years to come.

The mineral chromite is the only commercial source of chromium. Metallic chromium is produced from chromite by pyrometallurgical reduction, using aluminum, silicon, and carbon as reducing agents and by electrolysis. After reduction, purity is around 97-99 %, whereas, after electrolysis product contains approximately 99.8 % chromium.

Besides these techniques, chromite ore or concentrate can be leached with a sulfuric acid solution. In this thesis work, the usefulness of this process was investigated. The ore used in the experiments is from Pınarbaşı-Kayseri region and is already being used by Turkish Kromsan Company in producing chromium chemicals by the classical NaOH fusion or baking and leaching technique.

The aim of this work was to show that from the same ore chromium can be leached with H_2SO_4 (with and without addition of $HClO_4$) with a high recovery of chromium and without hexavalent chromium or minimum of it in solution. The kinetic model of the leaching process was also intended to be determined using experimental results.

CHAPTER 2

LITERATURE REVIEW

2.1. Chromium

Chromium is one of the petrogenic or rock-forming elements of the earth’s crust. Rankama and Sahama [1] place chromium twentieth in order of abundance of the elements in igneous rocks. The atomic number of chromium is 24 and it is one of the transition metals. Its chemical atomic weight is 52.01.

The stable form of chromium has a body centered cubic lattice. The melting point and the density of chromium are 1875 °C and 7.19 g/cm^3, respectively. Impurities, especially oxygen and nitrogen, have a considerable effect on the melting point of chromium.

There are three valance states of chromium, which are +2, +3, and +6. Basic states are +2 and +3, whereas the acidic state is +6. $(CrO_4)^{2-}$ (chromates) and $(Cr_2O_7)^{2-}$ (dichromates) are the examples of the latter one. Being highly acid resistant, chromium is only reacted by hydrofluoric, hydrochloric and sulfuric acids.

2.1.1. Sources of Chromium

Chromium is widely dispersed in natural deposits but is never found in the uncombined state. The mineral chromite is the only commercial source of chromium.

It occurs in a large number of other minerals, which are unimportant as sources of the metal for industrial use.

Chromite has the theoretical composition $FeO.Cr_2O_3$ with a theoretical content of 68 percent Cr_2O_3 and 32 percent FeO by weight. Some specific properties of chromite are stated below according to Sully [2]:

Chromite varies in color from dark brown to jet black and usually occurs in a massive form with a granular structure, although individual crystals are octahedral. Its hardness is 5.5 on Moh's scale. Its density ranges from 4.6 g/cm^3 for high grade ores to 4.0 g/cm^3 for low grade ores. Melting point of chromite varies with its composition in the range 1545 to 1730 °C.

2.1.2. Uses of Chromium Ore

There are three uses of chromium ore commonly; metallurgical, refractory and chemical. These uses will be shortly explained below and compositions of chromite ores used for these purposes are given in Table 2.1 [3].

The metallurgical use results from the addition of chromium to improve the strength, corrosion and oxidation resistance of iron, nickel and other metals. For addition to ferrous alloys, chromium is usually produced as a ferro-chromium alloy containing approximately 70 percent chromium. In order to be suitable for the production of ferro-chromium chrome ore should contain a minimum of 48 percent Cr_2O_3 with sulfur and phosphorus contents each less than 0.1 percent.

Chrome ore is used extensively for refractory purposes. It differs from most other refractories in common use in that it is chemically almost neutral and consequently it resists attack by both acids and bases at high temperatures. For the best quality chromite refractories, it is desirable to have an ore with as low a silicate content as possible and it is desirable to keep this as low as 5 percent if possible. For refractory purposes, an ore is required which has a high total content of Cr_2O_3 and Al_2O_3 with low silica and iron oxide contents.

Table 2.1. Composition of Chromite Ores

Grade	Composition	Ratio Cr:Fe
Metallurgical, high Cr	46 % Cr_2O_3 min.	> 2:1
Chemical, high Fe	40 to 46 % Cr_2O_3	(1.5 to 2) :1
Refractory, high Al	> 20 % Al_2O_3 > 60 % (Al_2O_3+Cr_2O_3)	

The chemical use of chromite is almost entirely for the primary production of sodium dichromate. For this purpose the chromite should contain a minimum of around 45 percent Cr_2O_3. The iron content can be much higher than for metallurgical or refractory use. The largest chemical use of chromite is for tanning and for the production of pigments.

2.1.3. Industrial Use of Chromium Chemicals

Chromium chemicals are essential to the textile industry, oil and gas industries, food and beverage industries, transportation industries, iron and steel industries, aircraft industry, copper industry, electrical industry, pyrotechnical industries and the photographic industries. Here are some industries in which chromium chemicals are mostly used [4]:

2.1.3.1. Modern Chromium Pigments

Chrome Oxide Green: It is known as pure chromic oxide since it consists of more than 97 % Cr_2O_3. It is used for coloring roofing granules, cements, and plasters because of its high reflection of infrared light.

Chrome Yellow: It is known as an excellent paint for wood and metal and has exceptional covering power. It contains over 93 percent $PbCrO_4$.

Zinc Yellow: Zinc yellow is a slightly soluble hydrated basic potassium zinc chromate. It is unequaled as a corrosion-inhibiting primer on aircraft parts fabricated from aluminum or magnesium.

Molybdate Orange: This is a combination of lead chromate with molybdenum salts which cause the color to be redder and more brilliant.

Chrome Green: A mixture of lead chromate with iron blue. It has an excellent covering and hiding power.

2.1.3.2. Chromium Mordants

Chromium mordants are used in dyeing wool. For textile printing, both trivalent and hexavalent compounds are used. The latter are used when an oxidizing action is required to develop the color.

2.1.3.3. Chrome Tanning

The basic chromic sulfates used for chrome tanning are produced from sodium dichromate. Virtually all shoe upper leather, also most glove and garment leather, practically all leathers made from cattle hide, and most of the leathers made from calf, goat, kid, and sheep skins are now chrome tanned.

2.1.3.4. Fungicidal Applications

The fact that chromates combine with soluble metal salts enables resistance to fungi and termite attack. In addition to this, toxic metal salts are fixed onto the fiber. Cleanliness of the wood and suitability for carpentering and painting are the other results. Moreover, it is ideal for window frames, doorways and porches.

2.1.3.5. Insolubilizing Processes

Many uses for chromium chemicals depend on their ability to insolubilize organic substances such as glue, gelatin, casein, and lignin. Chromium compounds compounded with lignin are used for conditioning soil, treating paper and cloth and solidifying road surfaces whereas glue and casein-coated papers with chromium compounds are used where waterproofed, greaseproofed and oil repellent are needed. For hardening photographic films, developing blueprints and coating of blueprint paper, potassium dichromate is used.

2.1.3.6. Corrosion Prevention

Some corrosion prevention applications are as follows; chromium plating, anodizing aluminum, treatment of zinc and magnesium, dips for iron, steel, brass and tin, chromate inhibitors for brines and recirculating water systems, and a multitude of combinations in the oil and gas industries.

2.1.3.7. Organic Oxidations

Chromium chemicals are also used for synthetic dyes, saccharin, benzoic acid, antraquinone, hydroquinone, camphor, synthetic fibers, bleaching and purification of chemicals.

2.1.3.8. Other Chemical Uses

Some of other uses of the chemicals are for analytical reagent, inorganic oxidations, electrochemical oxidations, electrical batteries, slushing compounds and phosphate coatings [3].

Also, in metallurgical field, stainless steels have considerable importance and this stainless quality is provided with a protective surface film formed by chromium. In mild atmospheres, about 12 wt % chromium is required for protection. This amount increases with increasing destructive potential of the environment.

2.2. Toxicity of Chromium

Chromium is generally an abundant element in the earth's crust and occurs in oxidation states ranging from Cr^{2+} to Cr^{6+}, but only the trivalent and hexavalent forms are of biologic significance.

Trivalent chromium is the most common form found in nature, and chromium in biologic materials is probably always trivalent. There is no evidence that trivalent chromium is converted to hexavalent forms in biologic systems. However, hexavalent chromium readily crosses cell membranes and is reduced intracellularly to trivalent chromium.

The absorption, distribution and elimination of chromium in the body tissues has been studied recently in animals and to a limited extent in human by many researchers. The reaction of chromium compounds with proteins has been extensively studied in the low pH range. It is found in these studies that hexavalent chromium remains soluble at the body pH but trivalent chromium is relatively insoluble at normal body pH. This means that while the trivalent compounds are not harmful to body tissues, hexavalent compounds make some undesirable effects on the system. It is also considered that metallic chromium and chromite are harmless and have no harmful effects on body as in trivalent compounds.

According to Fairhall [5]; the toxic action of chromium is confined to the hexavalent compounds of chromium. In contrast to the trivalent compounds, hexavalent compounds exert an extremely irritative, corrosive, and, under some circumstances, toxic actions on the body tissues.

U.S.A. Commitee on biologic effects of atmospheric pollutants [6] explained in their report that investigators agree on those points:

1. People who work with hexavalent chromium can develop cutaneous and nasal mucous-membrane ulcers, whereas exposure to trivalent chromium does not produce these effects.

2. People who work with hexavalent chromium compounds can develop contact dermatisis from these agents, and they react to patch and intracutaneous tests with nonirritant concentrations of potassium dichromate.

3. Hexavalent chromium in tissue is reduced to the trivalent form.

4. Hexavalent chromium has greater diffusibility and solubility in tissue than trivalent chromium.

5. Hexavalent chromium can readily penetrate membranes.

6. Trivalent chromium can readily bind with some proteins to form complexes.

The most common effects of chromium compounds on industrial workers are those which result from direct contact of the skin with the chromates or with chromic acid. These skin reactions cause chrome ulcers and chrome dermatisis.

Ulceration and perforation of the nasal septum are the results of inhalation of chromate dust or chromic acid mist. Cancer of the respiratory tract is another result of these hexavalent compounds. Calcium chromate, chromium trioxide, lead chromate, strontium chromate, and zinc chromate are known as the hexavalent chromium compounds and these are human carcinogens. An increase in incidence of lung cancer has been observed among workers in industries that produce chromate and manufacture pigments containing chromate. An increased rate of lung cancer has also been reported among producers and consumers of pigment containing chromate. One study of chromium-nickel alloy foundry workers showed a statistically significant increase in lung cancers.

Also, some allergic reactions may be present in certain susceptible people. The allergic reactions manifest themselves chiefly as a dermatisis, although occasionally bronchial spasm and asthma occur.

Ulcers of the eyelids and irritation and ulceration of the conjunctiva and of the cornea may occur as a result of contact with chromic acid and its salts.

Intense irritation of the gastrointestinal tract may be a result of oral ingestion of hexavalent chromium compounds. This may cause some severe problems like epigastric pain, nausea and vomiting.

To prevent these effects of the hexavalent compounds, great care must be taken for environmental controls, personal protection, and medical procedures.

2.3. Production Methods of Chromium

A simplified flow chart for the production of metallic chromium and chromium compounds from chromite is shown in Figure 2.1.

2.3.1. Production of Ferrochrome

The initial chromium-containing raw material for smelting of ferrochrome is chromite ore. Solid carbon-containing materials are used as reducing agents. Formation of metal phase (high-carbon ferrochrome) occurs as a result of reduction of iron and chromium oxides. In the first stage of this complicated process, the reduction of iron occurs at relatively low temperatures. At higher temperatures, reactions of the interaction of chromic oxide with carbon are activated. When chromium oxide is reduced with carbon, the reactions considered will always produce high-carbon ferrochrome alloys, rather than low or even medium carbon grades. High carbon ferrochrome is smelted in closed ore reducing electric furnaces [3].

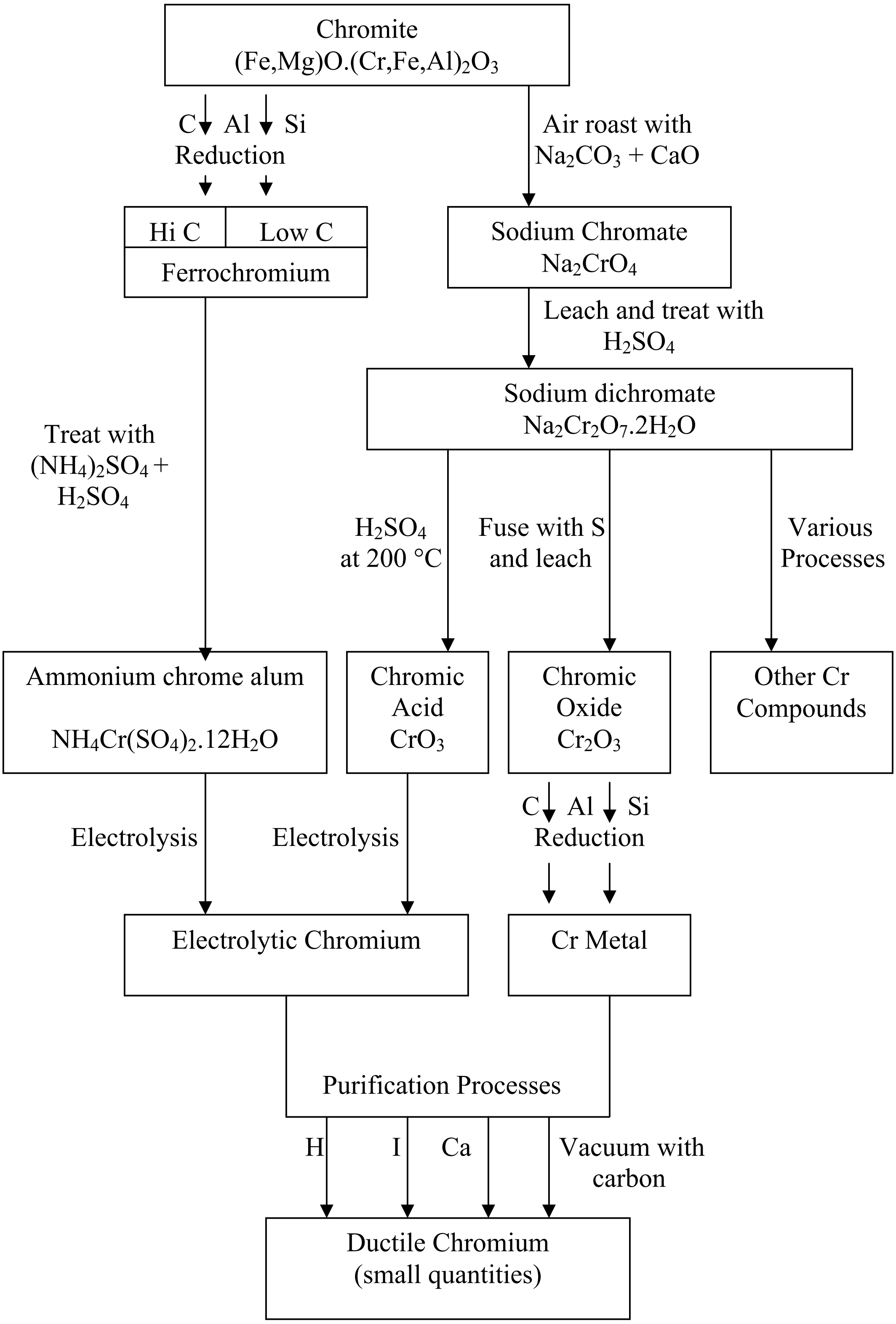

Figure 2.1. Simplified flow chart for the production of metallic chromium and chromium compounds from chromite.

2.3.2. Commercially Pure Chromium

As Sully [2] indicated, commercial chromium metal may be reduced by aluminum. The theoretical quantities required to satisfy the reaction;

$$Cr_2O_3 + 2Al = 2Cr + Al_2O_3 \tag{1}$$

are mixed and ignited with barium peroxide and magnesium powder in a refractory lined vessel. This reaction is exothermic and therefore self-sustaining. The composition of aluminothermic chromium can be adjusted within limits to suit the use which is to be made of the metal. 97-99 % purity chromium metal is obtained. If aluminum is to be present in the alloys to be made from the chromium, the content of this element can be allowed to rise. But if necessary, it can be held down to a limit of 0.1 or 0.15 percent maximum aluminum. Aluminum, iron and silicon are the main impurities in the product and the product also contains carbon, sulfur and nitrogen.

Commercial chromium metal may also be produced by reduction with silicon and carbon in two different processes. Silicon reduction is made in an electric arc furnace:

$$2Cr_2O_3 + 3Si \rightarrow 4Cr + 3SiO_2 \tag{2}$$

In this process aluminum content is lower and silicon content is higher than in aluminothermic reduction.

Carbon reduction at low pressure in a refractory container may also be possible as shown:

$$Cr_2O_3 + 3C \rightarrow 2Cr + 3CO \tag{3}$$

In this process, impurity elements are silicon, iron, carbon, nitrogen, and oxygen.

2.3.3. Electrowinning of Chromium: Chrome Alum Electrolysis

The Union Carbide Corporation's Metals Division Plant at Marietta, Ohio is an example of a typical chrome-alum plant [3]. In this process, high-carbon ferrochromium is leached with a hot solution of reduced anolyte plus chrome alum mother liquor and makeup sulfuric acid. The slurry is then cooled to 80 °C by the addition of cold mother liquor from the ferrous ammonium sulfate circuit, and the undissolved solids, mostly silica, are separated by filtration. The chromium in the filtrate is then converted to the nonalum form by several hours' conditioning treatment at elevated temperature. This is shown in Figure 2.2.

There are two types of ammonium chrome alum, $NH_4Cr(SO_4)_2.12H_2O$, violet and green modification. The green complex is more stable above 50 °C, whereas at room temperature, it changes slowly to the violet form with a change in pH. At higher temperatures, a variety of green nonalum ions such as $[Cr(H_2O)_5\text{-}SO4]^+$, $[Cr(H_2O)_5(OH)]^{2+}$, and $[(SO_4)\text{-}(H_2O)_4Cr\text{-}O\text{-}Cr(H_2O)_5]^{2+}$ form, whereas the violet hexaquo ion $[Cr(H_2O)_6]^{3+}$ predominates in cool, dilute solutions of moderate acidity. The latter permits crystallization of the desired ammonium chromium alum.

After the green, "non-alum" forms, their revision to the hexaquo form on cooling is sufficiently slow that on chilling to 5 °C, a crude ferrous ammonium sulfate can be crystallized, removing nearly all the iron from the system. This crude iron salt is treated with makeup ammonium sulfate, heated again to retain the chromium impurities in the green noncrystallizable form, and then cooled to separate the bulk of the iron as a technical ferrous ammonium sulfate which is sold to fertilizer and other purposes. The mother liquor from this crystallization is returned to the filtration step.

The mother liquor from the crude ferrous sulfate crystallization contains nearly all the chromium. It is clarified and aged with agitation at 30 °C for a considerable period to reverse the reactions of the conditioning step. Hydrolysis reactions are being reversed; therefore, the pH increases. Also, sulfate ions are released from complexes and the chromium is converted largely to the hexaquo ion, $[Cr(H_2O)_6]^{3+}$. Ammonium chrome alum precipitates as a fine crystal slurry. It is filtered and washed and the filtrate sent to the leach circuit; the chrome alum is dissolved in hot water, and the solution is used as cell feed.

A diaphragm-type cell prevents the sulfuric acid and chromic acid formed at the anode from mixing with the catholyte and oxidizing the divalent chromium. Electrolyte is continuously fed to the cells to maintain the proper chromium concentration. The catholyte pH of each cell is controlled by adjusting the amount that flows through the diaphragms into the anolyte compartments. Control of the pH between narrow limits governs the successful electro-deposition of chromium as well as the preservation of divalent chromium at the cathode.

The analyses of the solutions in the electrolytic circuit and cell operating data are shown in Tables 2.2 and 2.3, respectively. 45 % current efficiency shown in Table 2.3 includes low efficiencies that always prevail during the startup of a reconditioned cell. The 2.1-2.4 pH range used in the plant also results in a somewhat lower current efficiency but provides a safe operating latitude.

At the end of the 72-h cycle, the cathodes are removed from the cells, washed in hot water, and the brittle deposit (3-6 mm thick) is stripped by a series of air hammers. The metal is then crushed by rolls to 50 mm size and again washed in hot water. The metal contains about 0.034 % hydrogen and, after drying, is dehydrogenated by heating to at least 400 °C in stainless steel cans. The product composition is shown in Table 2.4. As shown in this table, 99.8 % chromium is produced.

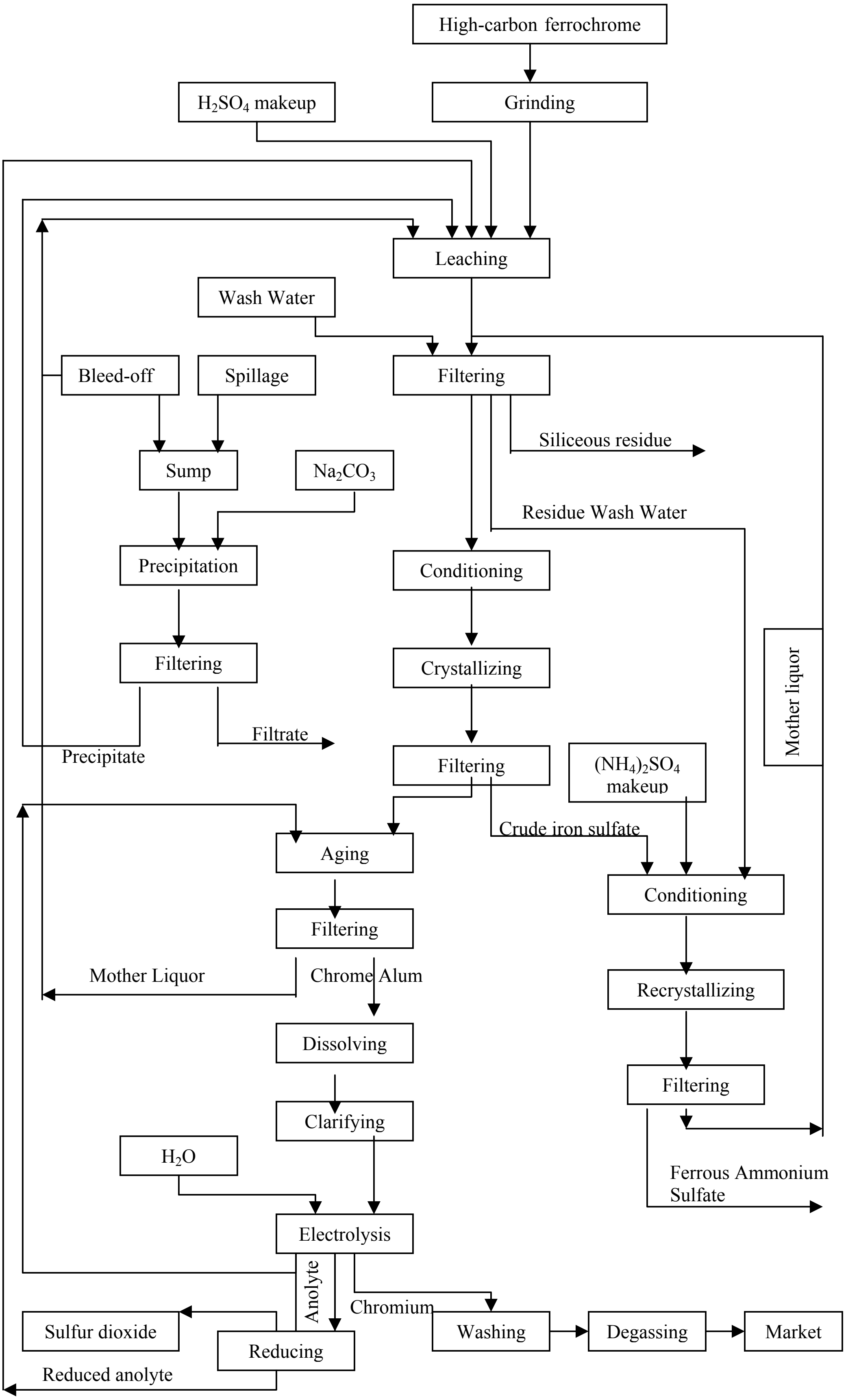

Figure 2.2. Flow sheet for production of electrolytic chromium by the chrome alum process, Marietta Plant, Union Carbide Corporation, Marietta, Ohio [3].

Table 2.2. Typical Analyses of Solutions in Electrolysis of Chrome Alum, g/l

	Total Cr	Cr^{6+}	Cr^{3+}	Cr^{2+}	Fe	NH_3	H_2SO_4
Cell Feed	130	0	130	0	0.2	43	3
Circulating Mixture	65	0	63	2	0.1	68	1
Catholyte	24	0	11.5	12.5	0.035	84	-
Anolyte	15	13	2	0	0.023	24	280

Table 2.3. Operating Data for Electrowinning of Chromium from Chrome Alum

Cathode current density, A/m^2	753
Cell potential, V	4.2
Current efficiency, %	45
Electrical consumption, MJ/kg	67
pH of catholyte	2.1-2.4
Catholyte temperature, °C	53 ± 1
Deposition time, h	72
Cathode material	Type 316 stainless steel
Anode material, wt %	1-99 Ag-Pb

Table 2.4. A Typical Product Composition

Chromium	99.8 %
Iron	0.14 %
Carbon	0.01 %
Sulfur	0.025 %
Copper	0.01 %
Lead	0.002 %
Oxygen	0.50 %
Hydrogen	0.004 %
Nitrogen	0.01 %
Silicon	0
Phosphorus	0
Manganese	0
Aluminum	0

2.3.4. Autoclave Leaching

Amer [7] leached Ras-Shait chromite deposits from Eastern Desert, Egypt, with sulfuric acid using a ball mill type autoclave. Chemical analysis of the chromite deposit showed that deposit contained 54.20 weight % Cr_2O_3 in it. Also, an X-ray diffraction study showed that the chromite deposit contained ($FeCr_2O_4$) and $(Fe,Al,Cr)_2O_3$ in its structure.

After the chromite ore was ground in a ball mill and sieved for different size fractions, leaching experiments with a 5 g sample of chromite ore were done, then the effect of the following factors given in Table 2.5 upon leaching of chromite, were studied.

Table 2.5. Experimental Variables

Temperature	180-250 °C
Sulfuric acid concentration	7-10 M
Grain size of chromite	64-250 μm
Solid / liquid weight ratio	0.5-1.5
Duration of leaching	15-120 min.

At the end of the study, it was found that the best condition for leaching of this chromite deposits with sulfuric acid in autoclave was at a temperature of 250 °C, for a duration of 30 minutes, using 50 wt % sulfuric acid and chromite with a grain size less than 64 μm.

2.3.5. Sulfuric Acid Leaching of Chromite

Vardar[8] and Ayhan[9] studied sulfuric acid leaching of chromite concentrates at University of Witwatersrand and METU, respectively.

Vardar leached the South African chromite with sulfuric acid and small amounts of perchloric acid. The chromite ore sample used was the UG-2 layer ore from the Bushveld complex. Found composition after the chemical analysis is given in Table 2.6.

Table 2.6. Chemical Analysis of the UG-2 Chromite Ore

	Cr_2O_3	FeO	Al_2O_3	MgO	Fe_2O_3	TiO_2	SiO_2	CaO
Weight %	41.58	20.55	15.98	8.96	7.49	0.94	0.6	0.2

The chemical formula of the ore was calculated by using the number of moles of cations per 32 moles of oxygen [10]:

$$(Mg^{2+}_{3.70}\ Fe^{2+}_{4.30})\ [Cr^{3+}_{9.10}\ Al^{3+}_{5.22}\ Fe^{3+}_{1.29}\ Ti^{4+}_{0.19}\ Fe^{2+}_{0.19}]\ O^{2-}_{32} \qquad (4)$$

where round and square brackets represent tetrahedral and octahedral sites, respectively.

All the experiments were done in a leaching vessel at atmospheric pressure. The reaction between chromite and sulfuric acid was studied at temperatures between 140 – 210 °C. The leaching duration varying from 2 to 6 hours, the sulfuric acid concentration from 60 to 90 weight percent and a perchloric acid addition up to a ratio of 1:2, chromite:perchloric acid in mass, were studied. A solid – liquid ratio of 1:25 and particle size of –90 +75 μm was kept constant in all experiments.

The total extraction of chromium by the reaction of chromite with sulfuric acid was considered as the sum of soluble plus insoluble chromium sulfates. Atomic absorption spectrometer (AAS) was used for analysis of the solutions and for solid residues, scanning electron microscope, with an energy dispersive analysis of x-rays (EDAX) attachment was used.

After the experiments, it was found that the rate of extraction of chromium increased by the increase of sulfuric acid concentration up to an optimum value. 77 weight percent sulfuric acid in the absence of perchloric acid and 82 weight percent in the presence of perchloric acid were found to be optimum concentrations.

It was also found that perchloric acid increased the extraction rate by its contribution to the decomposition of chromite. Moreover, the optimum perchloric acid addition was found to be as perchloric acid : chromite ratio of ½.

The results were given as follows:

1. When only sulfuric acid was used the highest extraction rate of chromium was 63 percent at 210 °C, 77 weight percent sulfuric acid for a leaching duration of 6 hours.

2. When perchloric acid was used to improve the rate of reaction, the complete extraction of chromium was obtained at 210 °C, 82 weight percent of sulfuric acid, ½ perchloric acid to solid ratio for a leaching duration of 6 hours.

It was also stated that no appreciable hexavalent chromium was obtained.

When only sulfuric acid was added, chromite ore decomposed by the effect of acidity and temperature in a fast reaction. Metallic ions and oxygen ions diffused from the chromite/liquid phase boundary to the bulk liquid in their same valency level as they occurred in the ore. Metallic ions and sulfate ions diffused to the sulfate/liquid phase boundary and reacted to produce chromium, iron, magnesium and aluminum sulfates.

It was impossible to find that the reaction between UG-2 chromite ore and sulfuric acid both in the absence and presence of perchloric acid was neither chemically controlled nor diffusion controlled.

Ayhan also leached a sample of chromite concentrate from Pınarbaşı region with sulfuric acid and perchloric acid. Composition of the concentrate is given in Table 2.7.

Table 2.7. Chemical Analysis of Chromite Concentrate from Dedeman Company, Pınarbaşı District, Kayseri, Turkey

	Cr_2O_3	Fe_2O_3	Al_2O_3	MgO	CaO	SiO_2	Other Oxides
Weight %	49.6	14.9	10.8	15.9	0.1	2.7	2.4

From chemical analysis, the chemical formula of this chromite ore concentrate was calculated to be approximately;

$$(Mg^{2+}_{6.53}\ Fe^{2+}_{1.47})\ [Cr^{3+}_{10.88}\ Al^{3+}_{3.49}\ Fe^{3+}_{1.63}]\ O^{2-}_{32}\ . \qquad (5)$$

All the experiments were done in a leaching balloon at atmospheric pressure. The reaction between chromite and sulfuric acid was studied at temperatures between 140 – 210 °C. The leaching duration varying from 2 to 6 hours, the sulfuric acid concentration from 70 to 90 volume percent and a perchloric acid addition up to a ratio of 1:2, chromite:perchloric acid in weight, were studied. A solid – liquid ratio of 1:25 and particle size of –38 μm was kept constant in all experiments.

X-ray diffraction analysis of the concentrate showed that Turkish chromite consisted of mainly a high magnesia containing chromite, $(MgFe)(CrAl)_2O_4$, $Fe(CrAl)_2O_4$ and possibly of some $MgO.Al_2O_3.SiO_2$. After experiments, chemical methods were used for the analysis.

It was found that the rate of extraction of chromium increased by the increase of sulfuric acid concentration up to an optimum value. 70 volume percent sulfuric acid in the absence and in the presence of perchloric acid is the optimum value for sulfuric acid concentration.

After perchloric acid addition it was seen that perchloric acid addition increased the reaction rate and optimum value for perchloric acid : chromite ratio was found to be ½.

Ayhan concluded the following results after her experiments:

1. In the absence of perchloric acid, the maximum chromium extraction was about 58 % under the conditions of 175 °C, 70 vol % H_2SO_4 and 2 h.
2. In the presence of perchloric acid, the maximum chromium extraction was about 83 % under the conditions of 175 °C, 70 vol % H_2SO_4, 2h and ½ perchloric acid : chromite ratio.

2.4. Production of Chromium Chemicals

Main chromium chemicals produced are chromates and dichromates. Salts of chromic acid (H_2CrO_4) are called monochromates or simply chromates. Dichromates are the salts of dichromic acid ($H_2Cr_2O_7$). Production methods of some chromium chemicals are given below according to Lyakishev and Gasik [11].

2.4.1. Production of Sodium-Chromates

The method for the production involves sintering of chromite-soda charges and leaching of the sinters. The main interaction reactions is described briefly below, occuring in the system “chromite-soda-filler-furnace atmosphere” during the stage of charge sintering.

$$(Mg,Fe^{2+})O.(Cr,Al,Fe^{3+})_2O_3+Na_2CO_3+O_2 \rightarrow Na_2CrO_4+MgO+Fe_2O_3+Al_2O_3+CO_2 \quad (6)$$

In the course of hydrochemical processing of the chromate sinter, the most important objective is to extract as much sodium chromate into the solution as possible. Leaching of the sinter is done with water.

These produced sodium chromates can be converted to dichromates. This process is known as “pickling”. In pickling with sulfuric acid, the monochromate solution is treated with H_2SO_4. In this case, the formation of dichromate is described by the reaction;

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O \quad (7)$$

2.4.2. Production of Potassium Dichromate

Potassium dichromate ($K_2Cr_2O_7$) can be obtained by several alternative procedures. In terms of its physical chemistry, the most similar process is the soda-based. With this method, sintering of potassium chromate is done with potash K_2CO_3, and carbonic acid is used to pickle the solution of potassium chromate. With this technology, one can carry out the process with regeneration of the potash.

2.4.3. Production of Chromic Anhydride

Production process of the chromic anhydride (CrO_3) is based on the reaction of sodium chromate (60-65 % CrO_3) mixed with sulfuric acid (92-93% H_2SO_4):

$$Na_2Cr_2O_7 + 2H_2SO_4 = 2CrO_3 + 2NaHSO_4 + H_2O. \quad (8)$$

A melt of $Na_2Cr_2O_7$ and H_2SO_4 is first heated slowly. After sulfuric acid addition to the melt, temperature is increased slightly above 200 °C.

2.4.4. Production of Chromic Hydroxide and Chromic Oxide

Sodium dichromate is used as the initial product for the production of the hydroxides. In the process, chromium passes into a solution of chromic chloride from dichromate. After that, chromic hydroxide is precipitated with an excess amount of ammonia.

Chromic oxide with very low carbon and sulfur contents is needed for smelting metallic chromium by aluminum-silicothermal methods in the metallurgical field. To provide the carbon removal as far as possible, chromic oxide is subjected to oxidizing roasting at 600-700 °C in electric rotary kilns. The carbon oxidation process may be accelerated by adding NH_4NO_3 as an oxidizer. Production methods of chromic oxide can be put in order according to the type of chemical reagents used:

1. Sodium (potassium) dichromates + solid (liquid) reducing agents (carbon, sulfur)
2. Sodium (potassium) dichromates + gaseous reducing agents (hydrogen,CO)
3. Chromic hydroxide + heat treatment
4. Ammonium dichromate + ammonium chloride (sulfate) + calcinations

5. Sodium dichromate + ammonia + calcinations (700 °C) + hydrolysis of sodium chromates
6. Alkaline solution of sodium chromate + sulfuric acid + calcinations of the chromates produced
7. Alkali-free chromate solution + sulfur gas, forming chromates at pH=9.2
8. Alkaline solution of monochromate + Na_2CO_3 (or NaOH), lowering the pH to 5.3 according to the reaction + calcinations of $CrO_3.H_2O$

2.4.5. Production of Lead-Molybdate Chrome Pigment

This product is used in the paint and varnish industry for production of paints and enamels, as well as in the printing industry. The production of the pigment is based on the interaction of sodium chromate, lead nitrate, sodium sulfate and ammonium molybdate.

2.4.6. Production of Chromium Tanning Agents

These agents are gained by dissolving hydrated chromates in sulfuric acid as in the following reaction:

$$Cr_2O_3.CrO_3 + 4H_2SO_4 = 2Cr(OH)SO_4 + 3CrO_3 + 2H_2O. \qquad (9)$$

The hexavalent chromium in the solution is reduced by formalin (CH_2O). After reduction of hexavalent chromium, the solution goes into the driers of the “fluidized” bed type.

2.4.7. Production of Aluminochromophosphate Binder

Production of the binder is done by dissolving aluminum hydroxide and chromic anhydride in phosphoric acid, followed by formalin reduction of chromium. Finally, monosubstituted phosphates are gained with the formula:

$$3Al(H_2PO_4)_3.Cr(H_2PO_4)_3. \qquad (10)$$

The monochromophosphate binder is produced as a liquid, viscous, dark-green solution.

2.4.8. Production of Chromium Carbonyl

The first known method for synthesizing chromium carbonyl is done by Zhob as in the following process. Firstly, an ether solution is prepared. Then to 200 ml of this solution, 500 ml of anhydrous benzene (C_6H_6) is added to dissolve magnesium halogenides, plus 5 g of $CrCl_3$. The contents are constantly shaken in the reactor, and CO is added. The products of the isothermal reaction in this reactor are hydrolyzed with acetic acid (CH_3COOH) or 6-normal H_2SO_4, followed by neutralization with sodium bicarbonate. As a result, a yellow amorphous sediment [$(C_6H_5)_4CrBr$] insoluble in alcohol and ether, but soluble in chloroform, is precipitated. After separation of the sediment and during the distillation from the ether solution, white crystals of $Cr(CO)_6$ formed on the cold walls. Later, several researchers carried out modified experiments on synthesis of $Cr(CO)_6$ based on Zhob's idea.

2.4.9. Chromium Chemicals Production in Turkey

Kromsan is the only plant in Turkey, which produces chromium chemicals. It is located 20 kilometers from Mersin, near Kazanlı. The main goal for the construction of this plant was to produce chromium chemicals for leather manufacturing industry. Those chemicals are used mainly for tanning purposes in leather manufacture. Kromsan is important in that, it is one of the few plants all around the world producing chromium chemicals.

Chromite, soda-ash and filling material (waste sludge, ferro-chrome stack dust and limestone) are the raw materials for the process. The overall process consists of raw materials preparation facilities, chromate plant, dichromate plant, sodium sulfide plant, and basic chrome sulfate plant.

Firstly, chromium is converted to monochromate (Figure 2.3.), then the process converts sodium monochromate into sodium dichromate using sulfuric acid (Figure 2.4.). This sodium dichromate is produced H_2O-free and contains minimum 99 % $Na_2Cr_2O_7$. Purification and granulation are done by physical means. Sodium sulfide is produced as a by-product in the plant. Sodium sulfate comes from sodium dichromate unit and it is reacted with coke to give sodium sulfide (Figure 2.5.). This product is used in leather treatment, pharmaceutical industry, textile industry and dye production [9].

Tankrom SB, Tankrom AB, Tankrom OB, Tankrom OBM, Tankrom FS, and Tankrom F24 are the final products of Kromsan, which are basic chrome sulfates. These are all used in leather industry and produced from sodium dichromate (Figure 2.6 and Figure 2.7) [12].

Reduction of sodium dichromate (6+) to three-valance chrome takes place by the reaction with sulfuric acid and glucose. This type of reduction can be called as organic reduction. Reductive organic compounds can be melas, sugar, wood cellulose as well as glucose. The basic chrome sulfate formed at the end can be formulated as $Cr(OH)SO_4.nH_2O$ and it has dark green color. Also, the sodium sulfate content increases the stability of basic chrome sulfates.

Tankrom SB is produced by the reaction;

$$8Na_2Cr_2O_7 + 24H_2SO_4 + C_{12}H_{22}O_{11}(2C_6H_{12}O_6) \rightarrow 16Cr(OH)SO_4 + 8Na_2SO_4 + 12CO_2 + 27H_2O.(28H_2O) \quad (11)$$

This reaction is based on the reduction of Cr^{6+} to Cr^{3+}.

Tankrom AB is produced by the reaction;

$$Na_2Cr_2O_7 + 3SO_2 + H_2O \rightarrow 2Cr(OH)SO_4 + Na_2SO_4 \quad (12)$$

Basicity is the determining parameter for basic chrome sulfates since it is related with the bonds formed between chromium and protein molecules in leather.

Chromic acid is also produced (less than 99.6 % purity) in a small amount due to the necessity of the process. It contains minimum 99.7 % CrO_3 and also used in many areas such as metal coating, wood protection and organic chemicals.

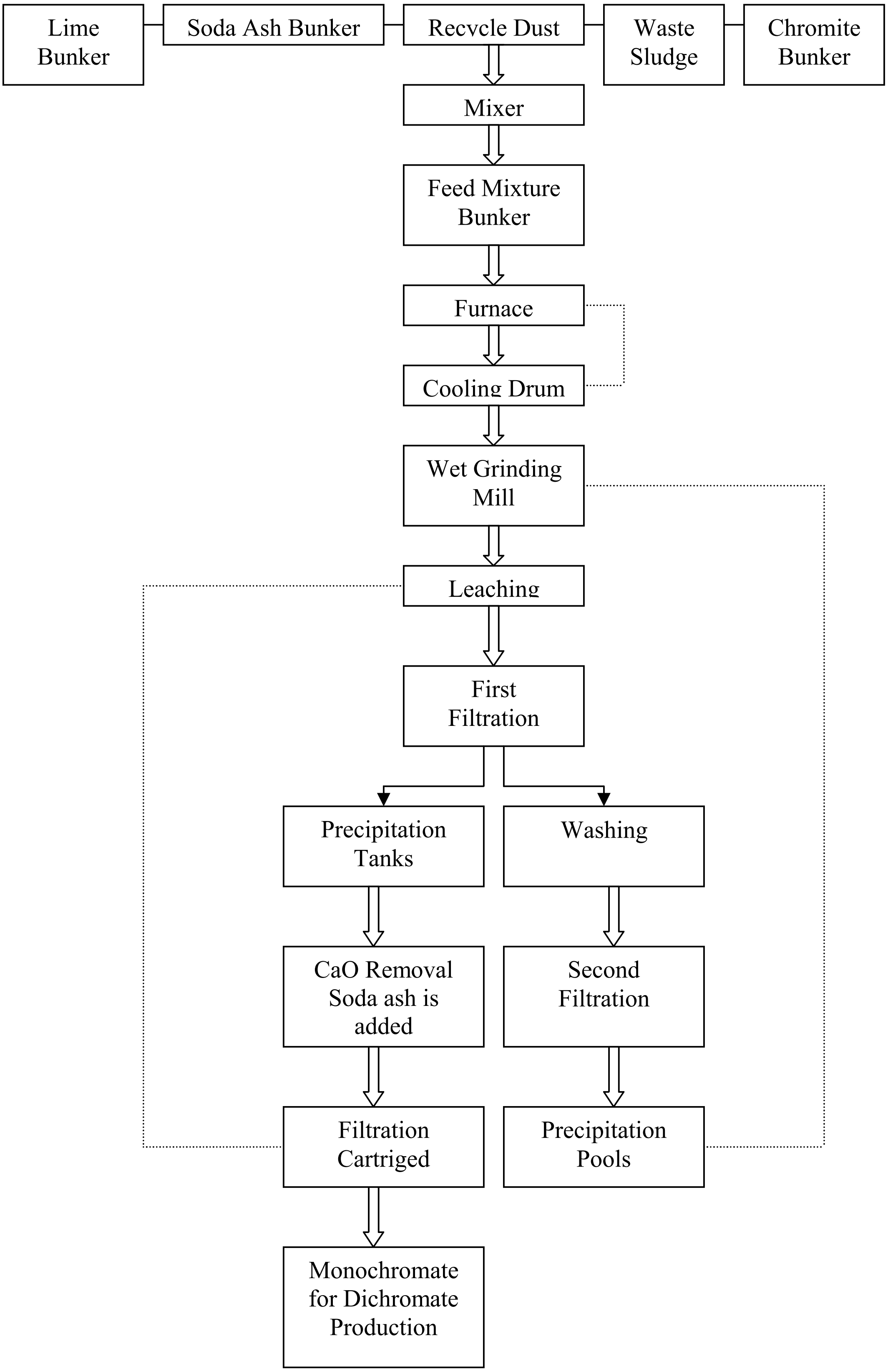

Figure 2.3. Sodium Monochromate Production Flowsheet[9]

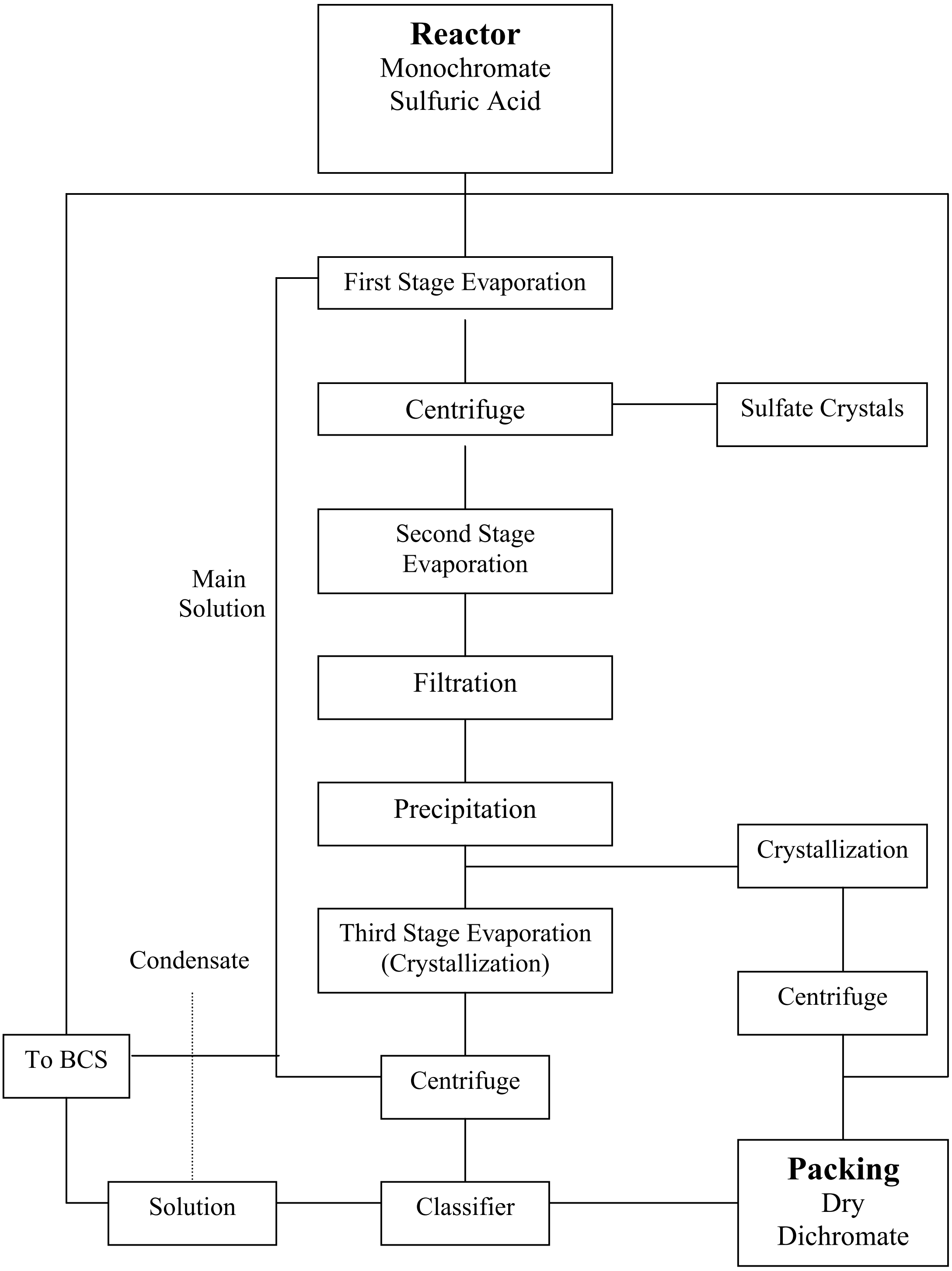

Figure 2.4. Sodium Dichromate Production Flowsheet[9]

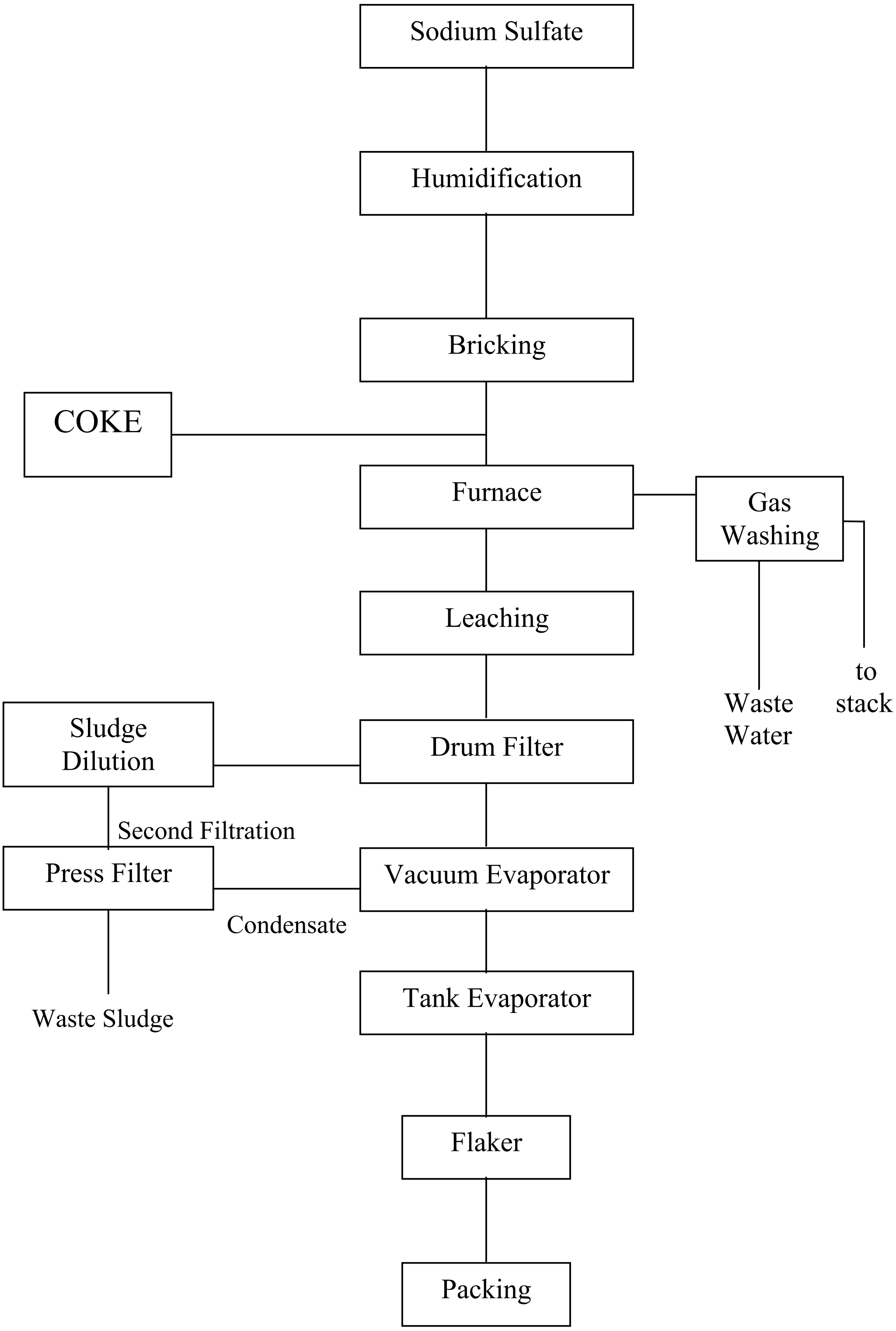

Figure 2.5. Sodium Sulfide Production Flowsheet[9]

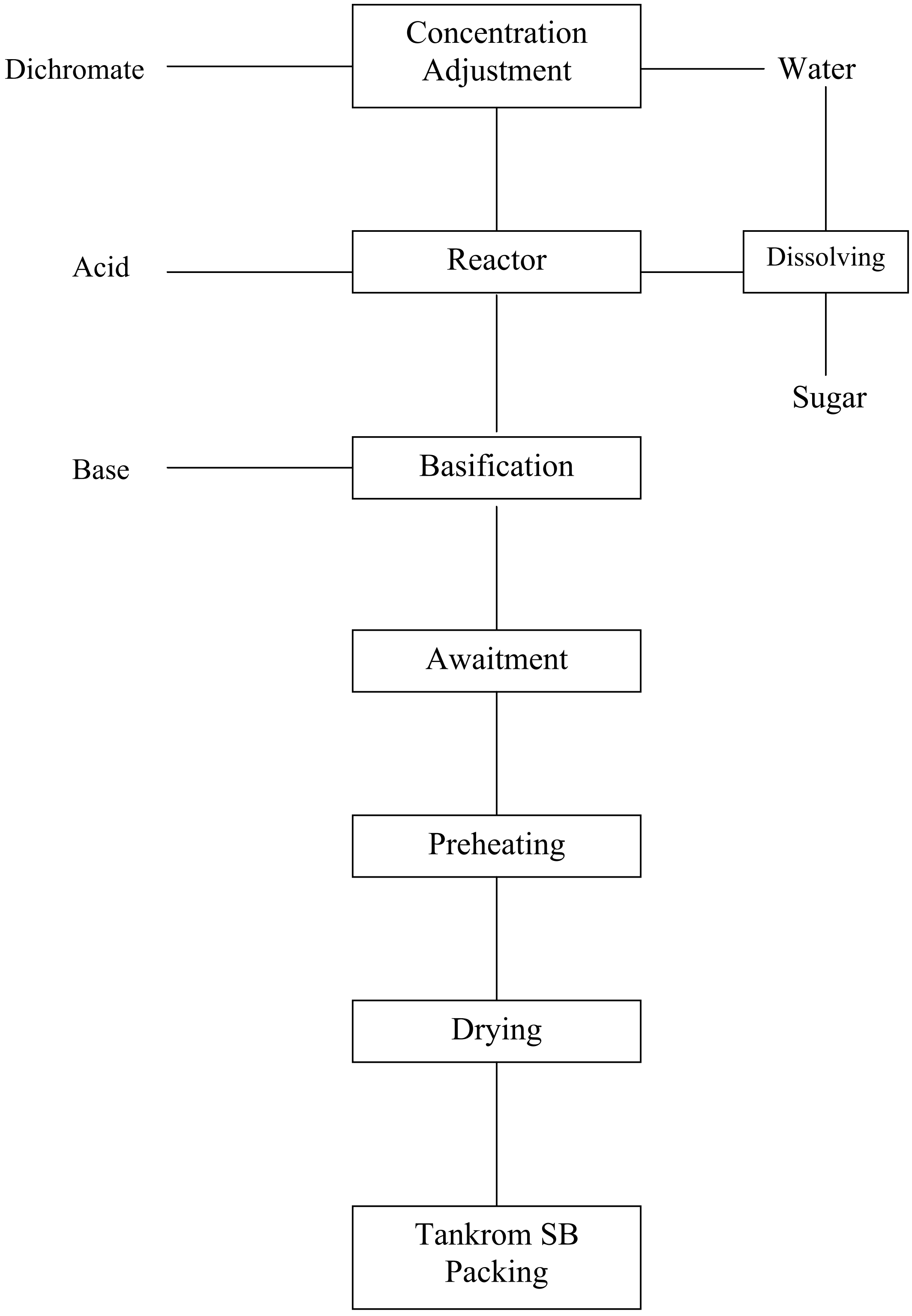

Figure 2.6. Tankrom SB Production Flowsheet[9]

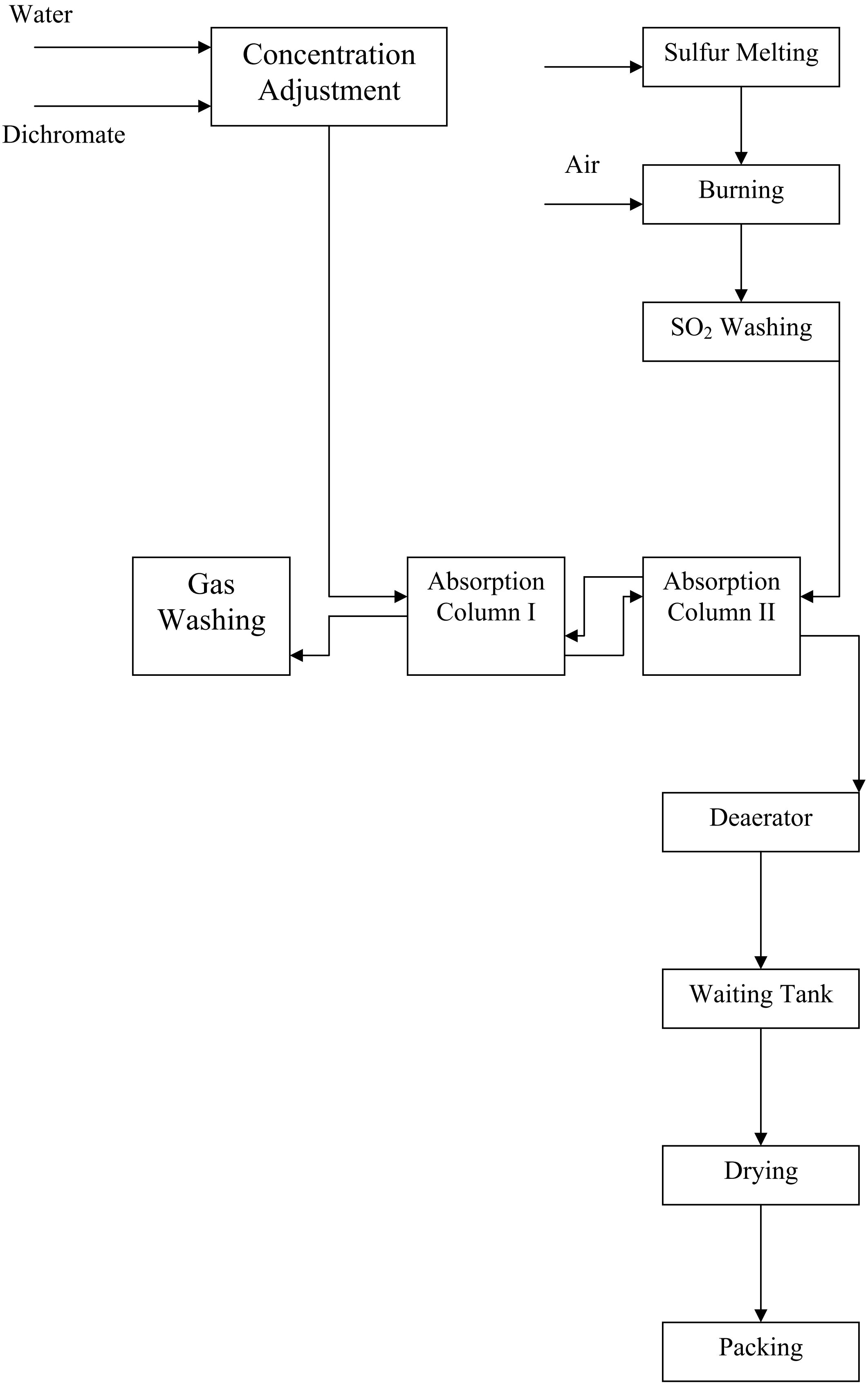

Figure 2.7. Tankrom AB Production Flowsheet[9]

2.5. Hydrometallurgy

2.5.1. General Information

Hydrometallurgy is a field of chemical technology concerned with the production of metals from their ores and secondary sources. The extraction and recovery of metals from their ores by processes in which aqueous solutions play a predominant role is known as hydrometallurgy. Two different processes are involved in hydrometallurgy:

1. Putting the metal values in the ore into solution via the operation known as leaching,

2. Recovering the metal values from solution, usually after a suitable solution purification or concentration step, or both.

Habashi [13], Gupta and Mukherjee [14] indicate the advantages and disadvantages of the hydrometallurgical processes as follows.

Advantages are;

- Metals can be acquired directly in a pure form from the leach solution.

- Hydrometallurgical processes are carried out at relatively low, often ambient temperatures and therefore overall consumption of energy is very low.

- Labor components of leaching are handled much cheaper and easier than pyrometallurgical products such as molten mattes, slags and metals.

- In hydrometallurgical plants, solutions and slurries are transferred easily in closed pipeline systems.

- Hydrometallurgy offers high chemical specifity and flexibility.

- Hydrometallurgical routes can effectively process complex ores and concentrates in which a variety of recoverable metals are present.

- Hydrometallurgy can be used to treat low-grade ores.

- Hydrometallurgical plants usually do not pollute the atmosphere. This factor is important due to the anti air pollution laws.

- A hydrometallurgical process may start on a small scale and expand as required.

Disadvantages are;

- Hydrometallurgical processes lead to significant amounts of liquid and solid wastes that may cause serious disposal problems.

- Engineering of hydrometallurgical plants are complex and it requires the full understanding of processing requirements.

- It requires sophisticated control schemes to maintain satisfactory operation.

- There is no economic gain during processing of reasonably high-grade resource.

2.5.2. Leaching

According to Habashi [13], the first prerequisite of any hydrometallurgical process is leaching or dissolution that is the term applied to the process of extracting a soluble constituent from a solid by means of a solvent. There are two purposes of leaching in extractive metallurgy:

1. Opening of ores, concentrates, or metallurgical products to recover the metal values.
2. Leaching easily soluble constituents (usually gangue minerals) in an ore or a concentrate in order to have it in a more concentrated form.

2.5.2.1. Acid Leaching

As Habashi [13] indicated, the most important leaching medium in hydrometallurgical extraction processes is the acids. Sulfuric, nitric, and hydrochloric acids are used extensively as leaching agents that can be used either alone or in combination with each other, with or without the presence of suitable oxidizing agents, they can dissolve most resources of metals and materials. Among these acids, sulfuric acid is the most important leaching agent. Besides being cheap, sulfuric acid has only minor corrosion problems encountered with its use, and is effective in opening most ores. Moreover, it can be used concentrated, dilute, or sometimes mixed with hydrofluoric acid.

There are two acid leaching agents according to their nature of reactions with other substances; nonoxidizing acids and oxidizing acids. Sulfuric acid can be used in both conditions. Nonoxidizing reactions can be seen when dilute sulfuric acid reacts with metal oxides and certain type of metal sulphides;

$$MO + H_2SO_4 \rightarrow MSO_4 + H_2O \qquad (13)$$

Oxidizing reactions appear when hot and concentrated sulfuric acid is used. Oxidizing agent is supplied by the decomposition reaction;

$$H_2SO_4 \rightarrow H_2O + SO_3 \quad (14)$$

$$SO_3 \rightarrow SO_2 + \frac{1}{2} O_2 \quad (15)$$

Acid leaching processes can be carried out either at atmospheric pressure and temperatures below the boiling points of acids or at elevated pressures and temperatures above their boiling points. However, when high temperature and high pressure leaching of acids is considered, autoclave leaching must be used in order to provide these temperature and pressure conditions.

2.5.2.2. Alkali Leaching

Alkali leaching process is commonly used for ore bodies consisting of a large proportion of acid consuming substances such as calcia and magnesia. There are no serious corrosion problems occurred with alkalies. This leaching process requires high reagent concentration, elevated temperatures and pressures to reach acceptable reaction rates. Sodium hydroxide, ammonium hydroxide and sodium carbonate are the most important alkali reagents.

2.5.2.3. Reactions of Oxides not Involving Oxidation or Reduction in Leaching of Oxides

According to Burkin [15], in many cases metals can be leached from their oxides without a change of valency by dissolution in aqueous acid or alkali, the conditions necessary being controlled by their solubility products. It is stated in his work that, the first step in the leaching of a solid must be wetting of the surface, a process in which interaction between atoms at the solid surface and water molecules takes place, resulting in the formation of M-OH groups. This is referred to as hydroxylation of the surface.

Comparison of the rates at which different metal oxides dissolve in $HClO_4$, HCl, HNO_3 and H_2SO_4 did not show any consistent order in the leaching efficiency of the acids. It is explained that some correlation studies have been made in a number of systems but no explanation was found for the effects of changes in the concentration of acids on the rates of leaching of different oxides. The diffusivity and mobility values control the rate of mass transport to and from the reacting surface and in consequence the model is applicable only when the leaching rate is not controlled by forced diffusion.

2.5.2.4. Reactions of Oxides Involving Oxidation

The industrially important minerals of some metals contain iron also, and frequently other metals as impurities. These include chromite, ilmenite, and wolframite. These are very stable, unreactive substances and, except in the case of wolframite, require very severe conditions in order to decompose them before recovering their metal values. In general attack by alkali is preferred, in order to reject the iron as early in the process as possible, and very concentrated solutions of alkali at high temperatures, or fusion conditions are used. Oxidation is also necessary in order to oxidise the Fe^{2+} and so destroy the crystal lattice. In the case of chromite oxidation of Cr^{3+} is necessary also, to form soluble chromate.

For the production of chromium chemicals the mineral chromite is fused with alkali and oxidised with oxygen to form chromate, which is treated further. More recently attention has been given to the possible advantages of treating ferrochrome instead of the mineral, because it is more reactive. Since the alloy is produced by reducing chromite with carbon and is not porous this increase in reactivity is presumably due to the difference in behaviour of an oxide and a metal containing the same elements. Wood and Black [16] state in their study that, freshly precipitated $Cr(OH)_3$ dissolves to some extent in fairly concentrated solutions of alkali on standing for a month or two, forming the alkali metal chromite, $MCrO_2$; in air this oxidises to the chromate. Ipatiev and Tronev [17] indicated that, Cr_2O_3 dissolves fairly readily in 2.5 M NaOH solution at 210 °C under an air pressure of about 1 MPa. Treatment of this oxide or of chromite mineral under such conditions was suggested as an alternative to roasting for the production of chromate by Ipatiev and Platonova [18] and reactions of this type were claimed in patents. The rate of reaction of chromite mineral was said to be slow and use of chromium oxide or ferrochrome was preferred.

2.6. Aqueous Stability Diagrams

Aqueous stability diagrams are used to help for the interpretation of the chemical mechanism and thermodynamics of many hydrometallurgical systems. Most reactions can be written in such a way as to show that the extent to which they can occur depends on the pH of the solution and on the oxidation potential. This makes a possible way to draw graphics for thermodynamical expressions in corrosion field.

According to Pourbaix [19], two kinds of reactions can be considered when calculating a potential – pH equilibrium diagram:

1. Chemical reactions in which only neutral molecules and positively or negatively charged ions take part, with the exclusion of electrons:

The standard free energy change of a reaction if the pressures are fixed at unity is given by the equation:

$$\ln k = - (\Delta G) / (RT) \qquad (16)$$

where, ΔG is the standard free energy change, k is the equilibrium constant, T is the temperature and R is the gas constant.

2. Electrochemical reactions as being a reaction involving, besides molecules and ions, negative electrons arising from a metal or other substance by metallic conduction. The relation between voltage and free energy change corresponding to a reaction under standard conditions, with all substances at unit activity is given in the following equation:

$$E^0 = (\Delta G) / (nF) = 2.303\ RT \log k / (nF) \qquad (17)$$

where, E^0 is the standard potential (V), F is the Faraday constant, n is the number of electrons involved in the reaction and R is the gas constant.

In nonstandard conditions the equation becomes,

$$E_h = E^0 - [(2.303\ RT\ \log Q) / (nf)] \tag{18}$$

where E_h is the potential at nonstandard state (V) and Q is the reaction quotient.

For T = 298.15 K, the value for the factor 2.303 RT/F is 0.0592; the equation becomes,

$$E_h = E^0 - [(0.0592\ \log Q) / n] \tag{19}$$

which is known as the Nernst Equation.

In the case of electrochemical reactions written in the form:

$$aA + cH_2O + ne^- = bB + mH^+ \tag{20}$$

in which A is the oxidized form and B the reduced form of the element in question, the condition for equilibrium will be of the form,

$$E_h = E^0 + (0.0592\ m\ pH / n) + (0.0592\ \log (A^a / B^b) / n). \tag{21}$$

2.6.1. Cr – H_2O System

Potential – pH equilibrium diagrams have been established for chromium – water system by Pourbaix for 25 °C, diagram is given in Figure 2.8.

As Pourbaix indicates, the equilibrium lines between the dissolved and solid species in the diagram can be calculated assuming metal ion concentration of 10^{-6} mol liter^{-1}. Thick solid lines represent the phase boundaries of the solid phases while

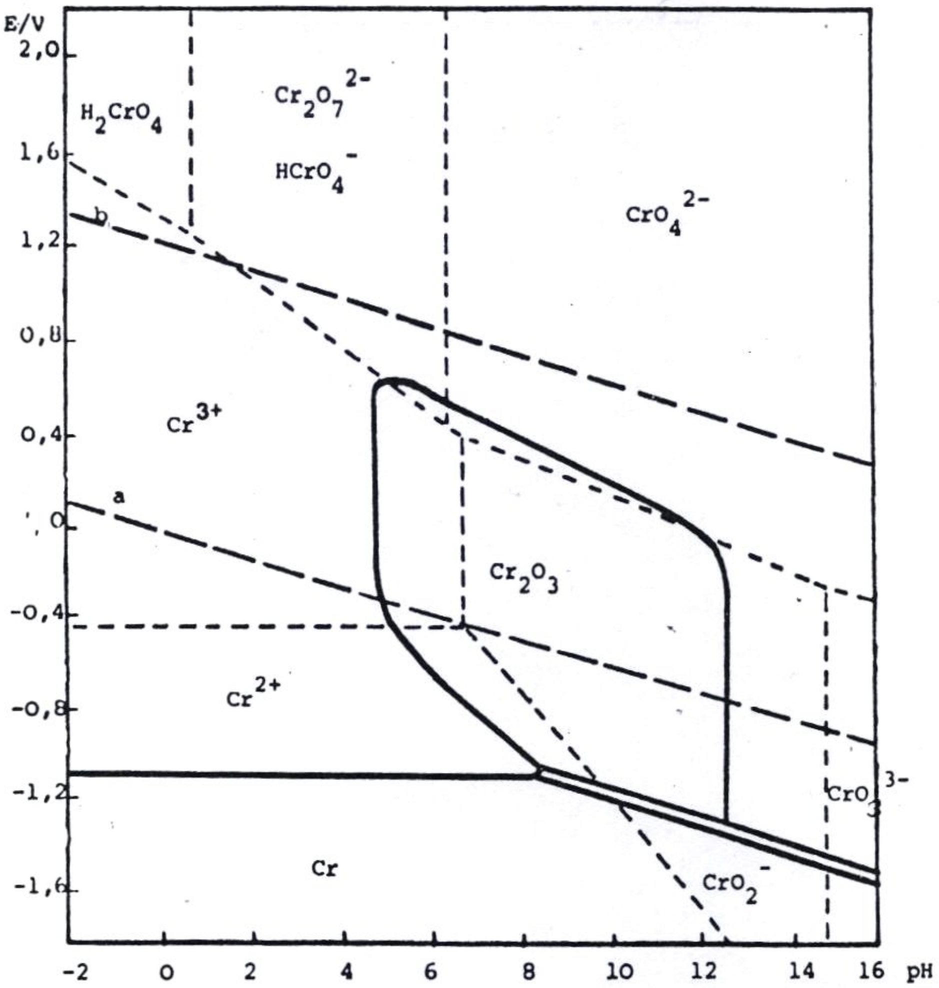

Figure 2.8. Potential – pH equilibrium diagram for the system Cr-H_2O, at 25 °C. Figure established considering anhydrous Cr_2O_3.

broken lines express the equilibria between dissolved species. Diagonal lines “a” and “b” in the diagrams represent the equilibrium potentials of hydrogen and oxygen evolution reactions. Between the lines water is stable, below the line “a” water decomposes with evolution of hydrogen, and above the line “b” water decomposes with evolution of oxygen. In the presence of acid solutions chromium tends to decompose the water with the evolution of hydrogen, dissolving as chromous ions Cr^{2+}.

Potential – pH electrochemical equilibrium diagrams, such as those given in Figure 2.8. represent the conditions under which the reaction considered for their establishment are theoretically possible or impossible, from the thermodynamic point of view.

2.7. Kinetics of Hydrometallurgical Systems

As Burkin [15] expressed, the chemical conditions selected for carrying out a step in a hydrometallurgical process provide an adequate driving force for the reaction or change required, and kinetic considerations then become of particular importance since thermodynamic requirements have been satisfied.

Reactions in solution follows sequences of steps of which one is the slowest and rate controlling step. These steps are basically;

1. Diffusion of reactants towards each other.
2. Reaction of reactants at the surface.
3. Diffusion of products away from each other.

Diffusion and surface reaction can be separated from each other by looking at the effect of stirring and temperature on the rate of the reaction. In many hydrometallurgical studies the activation energy for a chemically controlled reaction is higher than the activation energy of a reaction which is diffusion controlled. Leaching of chromite ore and ores of similar structure resulted in a activation energy of 60-80 kJ/mol according to Farrow and Burkin [20].

The change in the rate of chemically controlled heterogeneous reaction with temperature depends upon several factors. These are the activation energy in the adsorbed layer, which determines the rate at which the adsorbed molecules or ions react, the heat of adsorption of reactants and the heat of adsorption of the products. If the reactants have a large heat of adsorption, as the temperature rises the quantity present at the surface will decrease rapidly, which tends to slow the reaction. If the products are soluble but tend to block a large proportion of the solid surface by adsorption, increasing the temperature will expose more surface if the heat of adsorption is large, thus tending to speed up the reaction.

By maintaining constant high stirring speed the effect of stirring as a variable in the reaction can be minimized. Diffusion may be eliminated as slow step by increased agitation speed. The increase in agitation will remove the products faster from the surface and possibly will prevent the accumulation of reacted material on the surface of the particle, but the diffusion of reactants from the solid structure can still remain as the slowest step. Therefore it is of no assurance that the elimination of stirring as a variable also eliminates diffusion as rate controlling step.

It has been pointed out by Wadsworth [21] that in a system where the surface of a solid reactant advances or recedes during the course of the reaction, the change affects the kinetics. So also does the progressive formation of a solid reaction product around the reacting particles. Mathematical equations were obtained for a number of models based on such behaviour and used to describe the shapes of the rate curves obtained when chalcopyrite was leached under various conditions. Such equations are now widely employed. However when determining the chemical conditions to be used, and in particular when developing a new process, the chemical behaviour of the system is of paramount importance.

2.7.1. Shrinking Core Models of Spherical Homogeneous Grains of Ore

Shrinking core models have been established to explain the reaction behaviour of spherical particles in a solid-liquid reaction. In most hydrometallurgical systems little error is encountered in considering the coefficient of diffusion as constant. Under constant conditions of agitation, the thickness of the diffusion zone remains constant and a steady-state condition is attained in which the amount of material entering the zone balances that leaving the zone.

Two kinds of reactions are considered relating to this study:

1. The particle reacts with the surrounding liquid without formation of a porous diffusion layer with inhibition of soluble reactants transport only in a liquid diffusion layer of a thickness y (constant), around the particle finally disappearing as in the burning of pure carbon (Figure 2.9.). The mathematical expression of such a process can be represented as:

$$1 - (1 - \alpha_1)^{1/3} = k_1 t \qquad (22)$$

where,

α_1 : reacted fraction of the sphere in chemical reaction rate control
k_1 : rate constant (time $^{-1}$)
t : time.

Equation (22) is developed assuming the rate is a surface reaction at a receding interface. It is tested by plotting the left side of equation against t, which should result in a straight line having a slope k_1 with units of reciprocal time. The model assumes that the solid is reacting with the fluid and is shrinking without a formation of an ash layer as the reaction proceeds. Transport of reactants towards each other and away from each other is assumed to be fast. The activation energy for such a reaction is relatively high compared to the second model in which diffusion control is the rate limiting step.

2. The particle reacts with the surrounding liquid with inhibition of transport in a porous diffusion layer of a thickness y_p growing during leaching which is illustrated in Figure 2.10. The mathematical presentation can be given as:

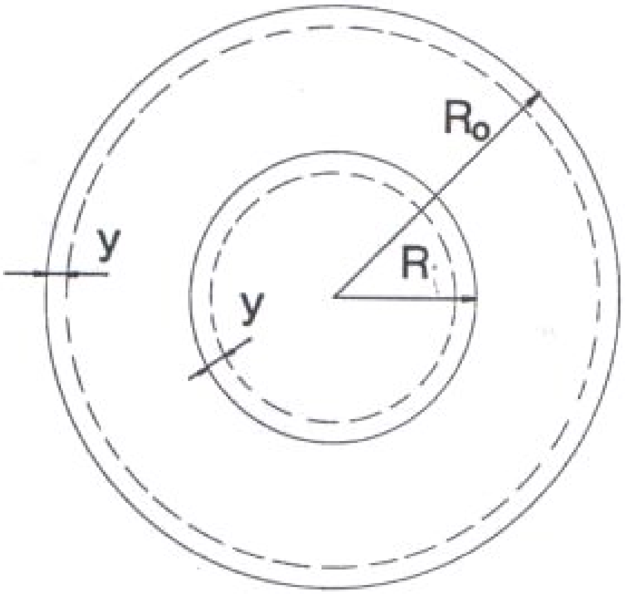

Figure 2.9. Presentation of a shrinking core model when chemical control is the rate limiting step (with inhibition of soluble reactants transport only in a liquid diffusion layer of a thickness y = constant).

R_0 : Radius of unreacted particle
R : Radius of particle during leaching.

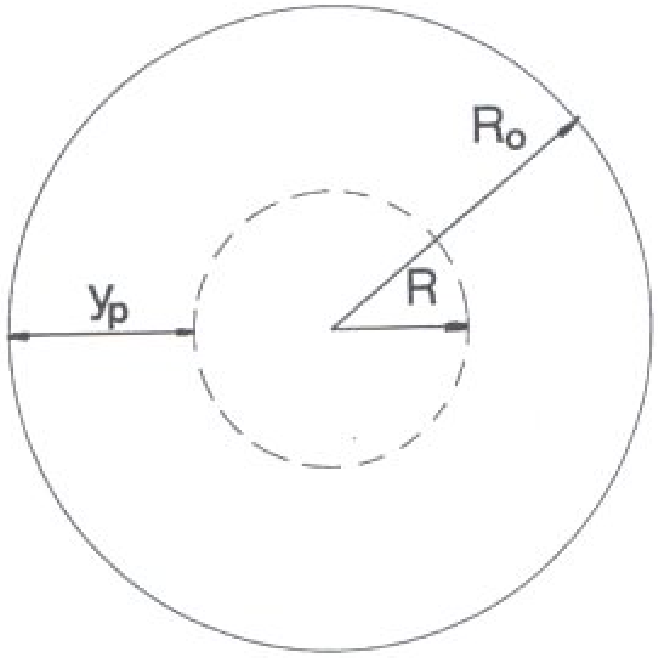

Figure 2.10. Presentation of a shrinking core model when diffusion is the rate limiting step (with inhibition of transport in a porous diffusion layer of a thickness y_p growing during leaching).

R_0 : Radius of unreacted particle
R : Radius of particle during leaching.

$$1 - (2\,\alpha_2 / 3) - (1 - \alpha_2)^{2/3} = k_2\,t \qquad (23)$$

where, α_2 is the reacted fraction of the sphere in diffusion rate control and k_2 is the rate constant.

The model in Equation (23) assumes a porous diffusion layer surrounding the particle growing during leaching which is limiting the rate of reaction. If a reaction is diffusion controlled, by plotting the left side of the equation against t should result in a straight line having a slope k_2 with units of reciprocal time. The mathematical derivation of both shrinking core models is given in Appendix A.

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1. Starting Materials

Raw materials used for the experiments were chromite concentrate, sulfuric acid and perchloric acid. Perchloric acid was used in small amounts with the purpose of increasing the rate of reaction.

The starting materials and their specific characteristics are given below:

3.1.1. Chromite Concentrate

The chromite concentrate used in the experiments was obtained from Pınarbaşı district, Kayseri, Turkey. The dry sieve analysis of this concentrate is given in Table 3.1. A ground chromium concentrate with a particle size of – 400 mesh (-38 μm) was chosen to be used in the experiments. Dry grinding of the concentrate was done with a laboratory disc mill in Metallurgical and Materials Engineering Department, Middle East Technical University.

XRF analysis of the ore concentrate was done in MTA, Ankara. This is given in Table 3.2. It can be seen that this chromite concentrate contained much iron oxide and did not contain much MgO in it.

Table 3.1. Dry Sieve Analysis of the Chromite Ore Concentrate

Particle Size μ (microns)	**Weight Percent**
315	24.32
212	23.21
150	20.88
100	16.08
75	7.94
53	4.95
45	1.1
38	0.67
-38	0.85
SUM	100

Table 3.2. XRF Analysis of Chromite Ore Concentrate From Pınarbaşı District, Kayseri, Turkey.

Component	**Weight Percent**
Cr_2O_3	47.8
$Fe_2O_3{}^*$	31.50
Al_2O_3	9.70
MgO	6.30
SiO_2	3.30
TiO_2	1.0
CaO	0.2
K_2O	<0.1
CuO	<0.1

*Total Fe calculated as Fe_2O_3.

X-ray diffraction analysis of the concentrate is given in Figure 3.1. It shows that Turkish chromite consisted of mainly a high iron oxide containing chromite, $(Mg,Fe)(Cr,Al)_2O_4$, $Fe_{2.30}Si_{0.70}O_3$ and may be some $MgFeAlO_4$.

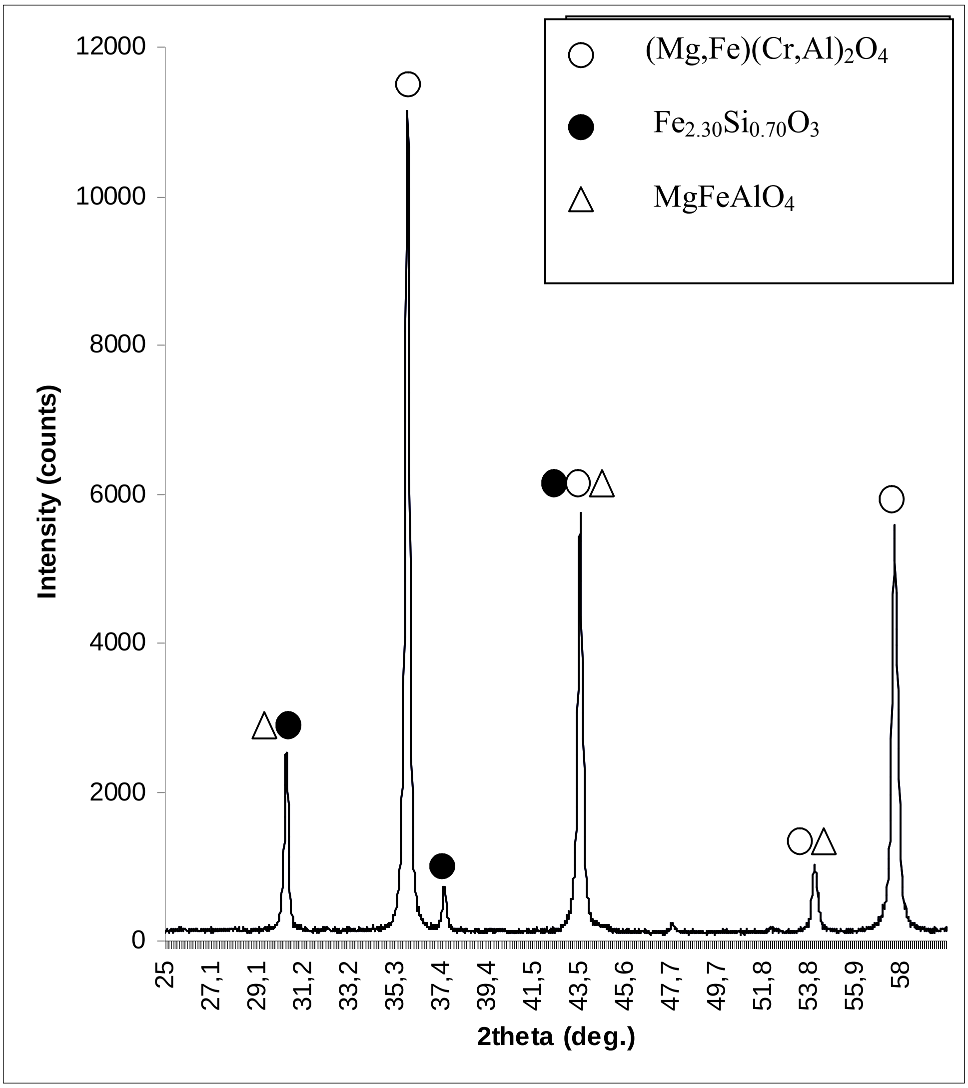

Figure 3.1. X-Ray Diffraction Analysis of Chromite Concentrate from Pınarbaşı District, Kayseri, Turkey.

From XRF analysis, the chemical formula of this chromite ore concentrate was calculated to be approximately;

$$(Mg_{2.31}^{2+}\ Fe_{5.69}^{2+})\ [\ Cr_{11.1}^{3+}\ Al_{3.34}^{3+}\ Fe_{1.05}^{3+}\ Ti_{0.26}^{4+}\ Fe_{0.26}^{2+}\ ]\ O_{32}^{2-} \tag{24}$$

where the parentheses and the brackets show tetrahedral and octahedral sites, respectively. The method of this calculation is given in Appendix B.

3.1.2. Sulfuric Acid

Sulfuric acid, oily liquid, is known as colorless if it is pure. Its density is about twice that of water.

Liler [22] indicates that, the most outstanding property of sulfuric acid/water mixtures as reaction media is their protonating ability related to their acidity function. The ionization of sulfuric acid is given as follows:

1. For concentrated sulfuric acid;

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^- \tag{25}$$

2. For more dilute sulfuric acid;

$$HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-} \tag{26}$$

In this thesis work concentrated sulfuric acid was used during experiments.

3.1.2.1. Physical Properties of Concentrated Sulfuric Acid

Physical properties of concentrated sulfuric acid, which are given by Meyer [23], are given in Table 3.3.

Table 3.3. Physical Properties of Concentrated Sulfuric Acid

Concentration of H_2SO_4 in Water	98.33 wt.%
Specific Gravity	1.84
Freezing Point	10 °C
Boiling Point	338 °C
Solubility in Water	Infinitely Soluble

Dilute sulfuric acid shows all the general properties of an acid. Moreover, aqueous solutions corrode metals, neutralize bases and react with metallic oxides and carbonates.

The characteristics of concentrated sulfuric acid are:

1. Concentrated sulfuric acid dissolves in water. This evolves heat, about – 20 kcal/mole. “ – “ sign indicates that reaction is exothermic. To dissolve concentrated sulfuric acid in water, the most important thing to consider is how the addition is done. This addition must be done slowly to avoid self-ignition of some materials although sulfuric acid is nonflammable.

2. The affinity of concentrated sulfuric acid for water is very high. This causes absorption of constituent water vapor from atmosphere. Therefore, concentrated sulfuric acid dehydrates (removes the elements of water), hydrated compounds and concentrated perchloric acid, $HClO_4$.

$$2HClO_4 \rightarrow Cl_2O_7 + H_2O \qquad \text{Violent Explosion} \qquad (27)$$

This unstable dichlorine heptoxide, Cl_2O_7, immediately decomposes into oxygen and chlorine by the presence of explosive force.

3. One or more hazardous products are formed after the reaction between the concentrated sulfuric acid and a number of substances, i.e. NaBr, NaI, NaCN, NaSCN, $NaClO_3$, HI.

Example:

$$2NaBr + 2H_2SO_4 \rightarrow Br_2 + SO_2 + Na_2SO_4 + 2H_2O \qquad (28)$$

Reaction runs relatively smoothly, but SO_2 and Br_2 are toxic.

Moreover, concentrated sulfuric acid decomposes salts of acids, which possess lower boiling points. After mixing salts and sulfuric acid, the mixture is heated and the more volatile product is distilled. Hydrochloric acid, hydrofluoric acid and nitric acid are the example of this preparation. As a result, sulfuric acid, which is very chemically reactive, takes place in many double-replacement reactions so that chemical substances, which may be very hazardous, are produced.

Example:

$$2NaF + H_2SO_4 \rightarrow Na_2SO_4 + 2HF \qquad (29)$$

4. Sulfuric acid may also react as a strong oxidizing agent. Concentrated sulfuric acid even reacts with carbon.

Example:

$$C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O \qquad (30)$$

After the reaction, SO_2 is formed. Being a toxic gas, sulfur dioxide is a hazardous product.

Sulfuric acid, which is used in all experiments, was a product of Merck (95-97 wt %) with a density of 1.84 g/cc.

3.1.3. Perchloric Acid

Perchloric acid was used to improve the reaction rates in the experiments. It is stable at high temperatures and has a high oxidation potential.

The ionization of perchloric acid in aqueous solution is as follows:

$$HClO_4 + H_2O \rightarrow H_3O^+ + ClO_4^- \qquad (31)$$

The most useful properties of perchloric acid are its stability at high temperatures and its high oxidative potential. A perchloric acid solution of 65 weight percent is stable up to 200 °C. The decomposition of perchloric acid is given as:

$$4HClO_4 \rightarrow 2Cl_2 + 7O_2 + 2H_2O \qquad (32)$$

3.1.3.1. Physical Properties of Concentrated Perchloric Acid

Physical properties of this strongest simple acid, which are given by Meyer [23], are given in Table 3.4.

Because of the explosive reaction given in reaction (32), store areas of perchloric acid must be far away from a source of heat. It is also known as an oxidizing agent and this oxidation is hazardous. Moreover, perchloric acid contacts with cellulosic materials and common organic compounds, both of which give explosive decompositions.

Table 3.4. Physical Properties of Concentrated Perchloric Acid

Concentration of $HClO_4$ in Water	72.4 wt. %
Specific Gravity	1.70
Freezing Point	-18 °C
Boiling Point	203 °C
Solubility in Water	Very Soluble

Perchloric acid, which was used in all experiments, was a product of Merck (60 wt %) with a density of 1.53 g/cc.

3.2. Leaching Equipment

Leaching equipment consisted of a Jenway Model 1000 hot plate & stirrer, 250 ml glass balloon, a temperature probe and a condenser. Also, some sand was used on the hot plate as a surrounding material for the glass balloon to prevent the heat loss from the system.

Since the hot filtration method was used during experimental procedure, “gooch crucible” was used as the filter.

The experimental set-up used for leaching is shown in Figure 3.2.

3.3. Outline of the Experimental Procedure

After the set-up was ready, the calculated amount of sulfuric acid, deionized water and if it would be present, perchloric acid were mixed in the balloon. A condenser was used during the experiments to prevent evaporation losses from the leach solution. Magnetic stirring was used to have homogeneity in the solution, to prevent particle agglomeration and for better solid/liquid contact. After the temperature of the solution was increased to the desired value, chromite was added into the balloon. Then, after the defined duration for the experiment elapsed, the hot plate and the temperature probe were switched off and the reaction balloon was immediately taken for the filtration. Leach liquor was filtered by a “gooch crucible” of number 4. At the end of the filtration, the leach residue was washed with water and a wash water was collected. General flowsheet of the experimental procedure is given in Figure 3.3.

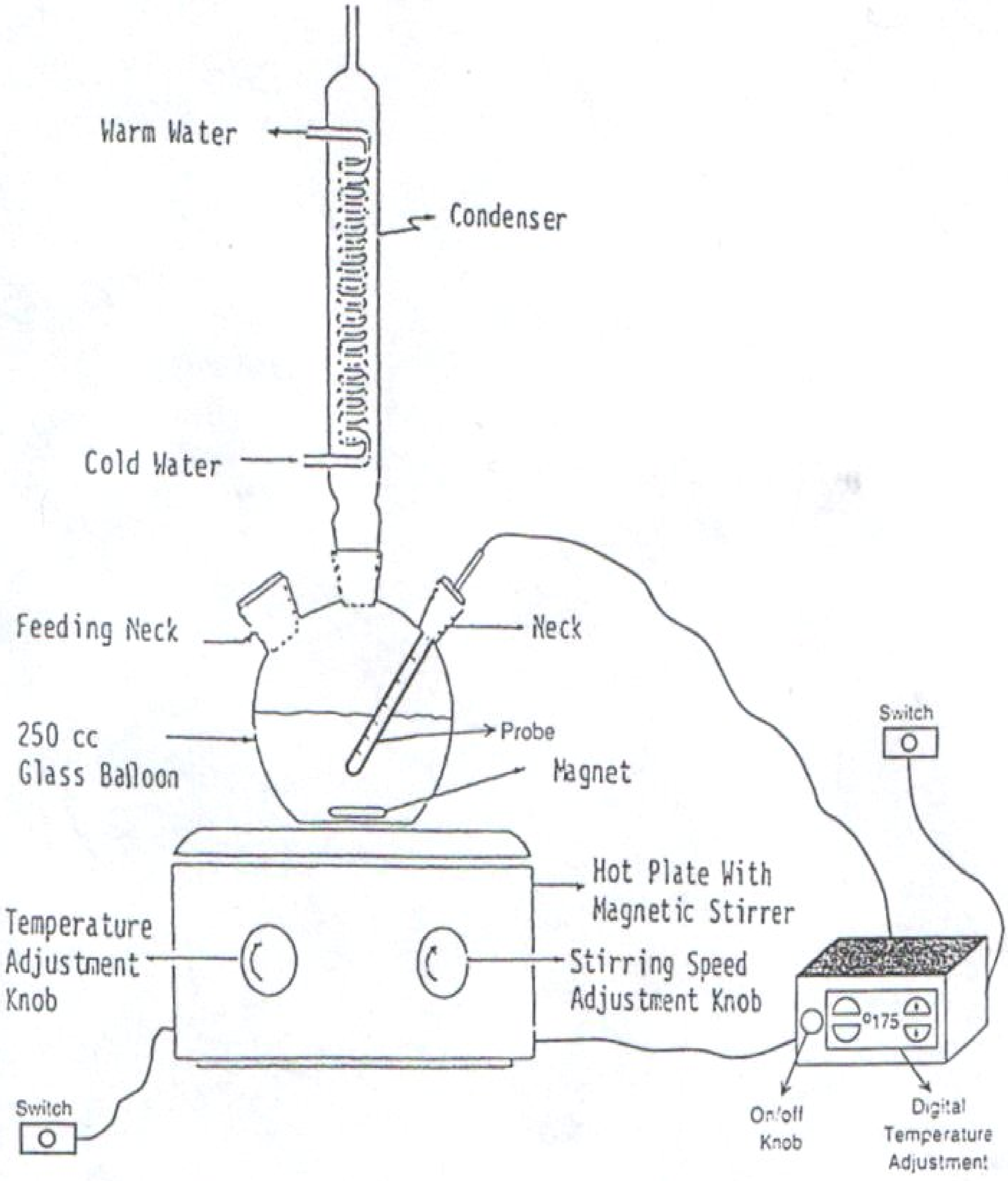

Figure 3.2. Experimental Set-up of Leaching

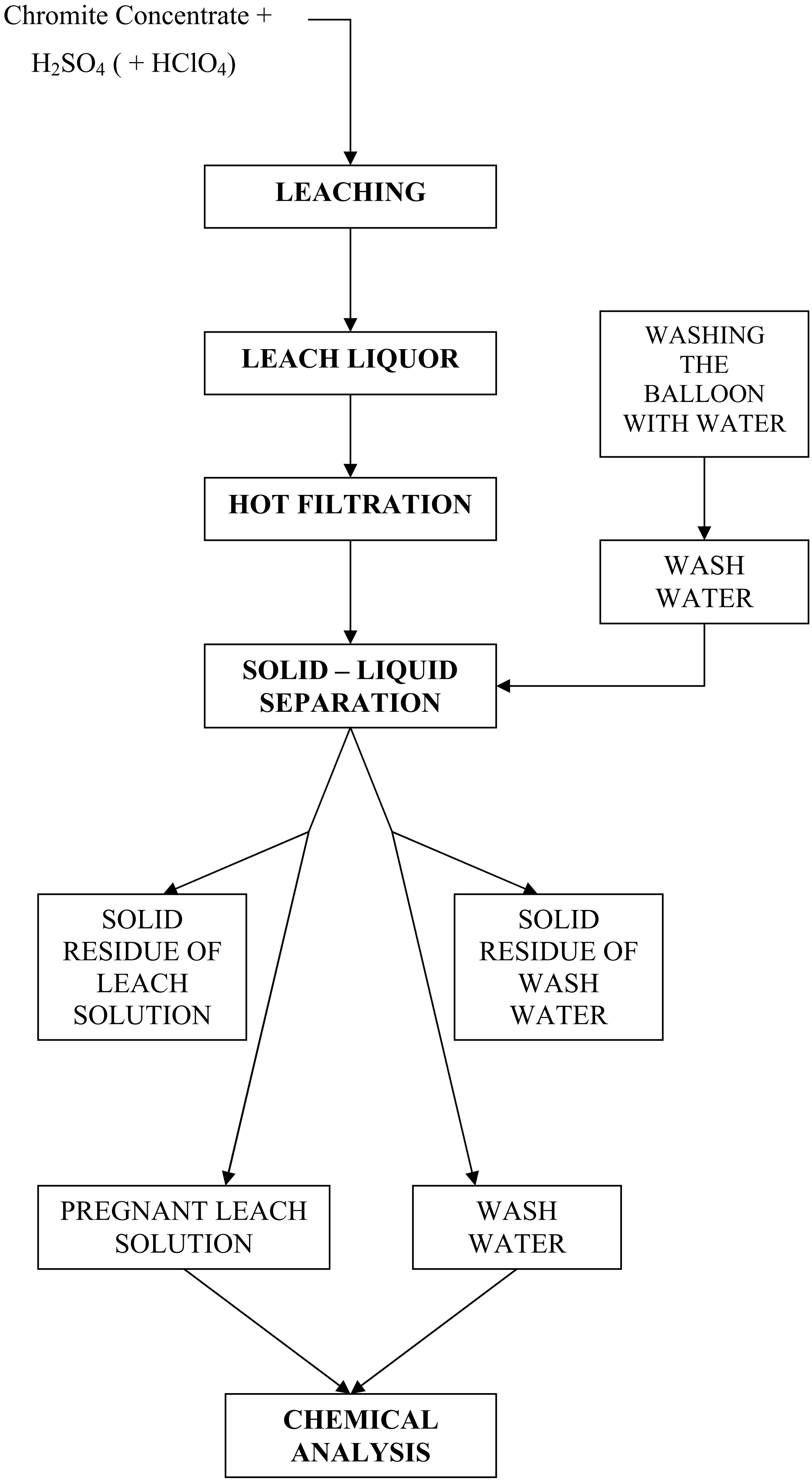

Figure 3.3. General Flowsheet of the Experimental Procedure

3.4. Experimental Variables

The reaction between chromite and sulfuric acid was studied using the following variables in the given ranges:

Table 3.5. Experimental Variables

Variable	**Range**
Temperature (°C)	140 – 175 – 210
H_2SO_4 Concentration (wt %)	73.4 - 81.1 - 84.6 - 89.3 - 95.2
Duration (h)	2 – 3 – 4 – 5 – 6
$HClO_4$/chromite ratio (vol/wt)	0 - ½ - ¼

Experiments were done using the combinations of the parameters given above. The optimum leaching conditions were tried to be found.

In all of the experiments, the amount of chromite concentrate leached was kept constant as 5 g and solid/liquid weight to volume ratio was also taken constant as 1/25 (wt/vol). This low solid content was necessary to allow sufficient contact between the reactants and to prevent the possible rate limiting effect of chemical potential of chromium at a high ratio. Moreover, grain size of chromite concentrate was chosen as – 38 μm to exclude size effect. Stirring was needed to prevent the accumulation of reacted compounds at the reaction site and it was also kept constant.

After the experimental set-up was constructed, 19 experiments were done. Calculations of volumes of water, sulfuric acid and perchloric acid additions are given in Appendix C.

3.5. Chemical Analyses

All leach liquors and wash waters were analysed for total chromium quantitatively and the selected ones were checked for hexavalent chromium by a qualitative method. Total Cr is the sum of Cr^{6+} and Cr^{3+} values.

Total chromium analyses and hexavalent chromium analyses were done at the Chemistry Laboratory of Metallurgical and Materials Engineering Department in the Middle East Technical University.

CHAPTER 4

RESULTS AND DISCUSSION

In this study, at the end of each experiment, two liquid solutions were obtained and analyzed for chromium. These liquids were leach solution and wash water. The former was obtained after hot filtration of the pregnant leach liquor via a gooch crucible and the latter was obtained after washing the balloon and the leach residue with deionized water at the end of the experiment. Wash water was necessary to gain the residuals remained in the experimental glass balloon.

Chromium leach recovery was calculated using the sum of chromium in the leach solution and wash water. The results of the experiments are given in Table 4.1. Recovery calculations are given in Appendix D.

4.1. Leaching of Chromite in Sulfuric Acid

The reaction between a simple chromite and sulfuric acid is given by Gupta and Mukherjee [14] as follows:

$$Cr_2O_3.FeO + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + FeSO_4 + 4H_2O \qquad (33)$$

Table 4.1. Results of the Experiments

Exp. No.	Temperature (°C)	Duration (h)	H_2SO_4 Concentration (wt %)	$HClO_4$/Chromite Ratio (vol/wt)	Recovery (%)
1	175	2	84.6	0	81.1
2	175	4	84.6	0	90.5
3	175	6	84.6	0	94.1
4	210	2	84.6	0	79.2
5	140	2	84.6	0	58.0
6	175	4	95.2	0	52.6
7*	175	4	73.4	0	-
8	140	4	73.4	0	51.2
9	175	4	89.3	0	67.5
10	175	4	84.6	1 / 4	55.7
11	175	4	84.6	1 / 2	74.4
12	175	6	84.6	1 / 2	61.8
13	175	2	84.6	1 / 2	98.7
14	175	3	84.6	0	87.9
15	175	5	84.6	0	92.9
16	175	3	84.6	1 / 2	72.5
17	175	5	84.6	1 / 2	68.4
18	175	2	84.6	1 / 4	73.0
19	175	4	81.1	0	73.3

* Experiment could not be done since the temperature of the leach solution could not be increased to 175 °C with this H_2SO_4 composition.

However, since the structure of chromite spinel is more complex than given by this equation, the amount of water molecules and the valency level of aqueous sulfates cannot be known with sufficient accuracy to calculate the stoichiometric amount of sulfuric acid necessary for this reaction. Therefore, the sulfuric acid concentration in the starting leach solutions was chosen to resemble some typical ones encountered in literature.

It was observed during the experiments that, at the beginning of the experiment, sulfuric acid solution was colorless. After chromite was added at experimental temperature, the color changed to black and when the experiment was finalized, the obtained leach solution was green in color which is the color of trivalent chromium and solid residue. The color of the leach solution became dark green when the chromium content increased.

4.1.1. Effect of Sulfuric Acid Addition

The maximum chromium extraction in the absence of perchloric acid was 94.1 % which was obtained in experiment 3 at 175 °C, 84.6 wt % sulfuric acid and 6 hours.

According to Habashi [13], the rate of leaching increases with increasing concentration of the leaching agent. However, in this work, this statement was valid only for the condition where the concentration was increased from 81.1 % to 84.6 %. At higher sulfuric acid concentrations, the recovery of chromium decreased which was most probably a result of the decrease in reactivity of sulfuric acid at higher acid concentrations. It can be seen in Figure 4.1 that increasing the acid concentration from 84.6 % to 95.2 % (by weight), while the temperature and the duration are constant at 175 °C and 4 hours, respectively decreased the chromium recovery from 90.5 % to about 52.6 %, by weight.

Also, it was seen in experiment 7 that, leaching could not be done at 73.4 wt % sulfuric acid for 175 °C because the temperature could not be increased to this value.

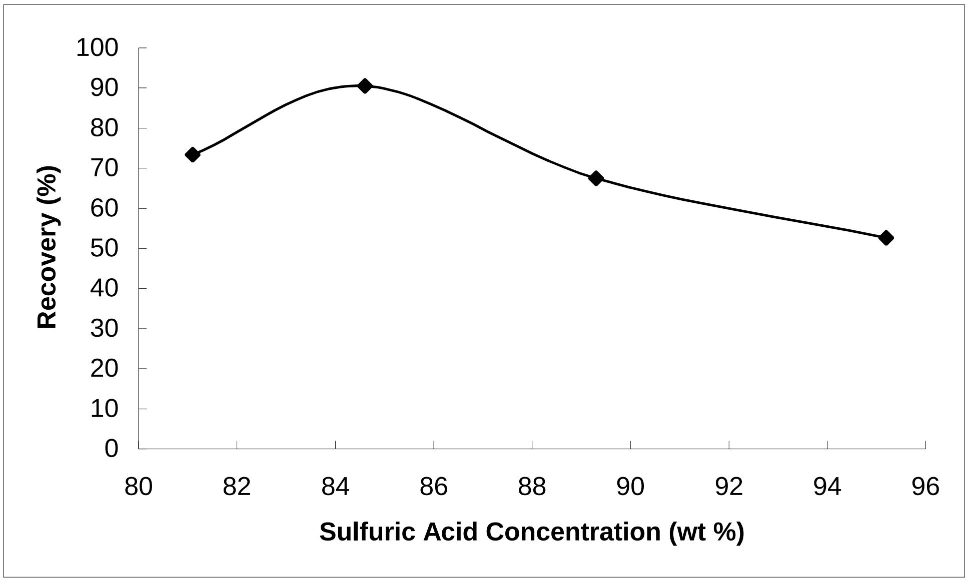

Figure 4.1. Recovery of Chromium as a Function of Sulfuric Acid Concentration (4 h, 175 °C and no perchloric acid addition).

4.1.2. Effect of Temperature

The recovery values for chromium as a function of temperature for 2 hours leaching duration and 84.6 weight percent of sulfuric acid (without addition of perchloric acid) can be seen from Figure 4.2. The extraction of chromium increased from 58.0 % to 81.1 % as the temperature increased from 140 to 175 °C. As the temperature increased, the rate of reaction increased therefore the extraction of chromium increased. However, when the temperature increased from 175 to 210 °C, the extraction of chromium decreased slightly to 79.2 %.

To explain this case, the solid residues of experiments for 175 and 210 °C were analyzed by SEM (Scanning Electron Microscope). Obtained SEM diagrams (Figure 4.3 and 4.4) demonstrated some peaks which include chromium in them. Keeping other conditions constant, the intensity of the main peak including chromium increased with increasing the temperature from 175 °C to 210 °C. Because of these reasons, the mentioned slight decreasing of recoveries was most probably due to increase in precipitation of chromium as some compounds.

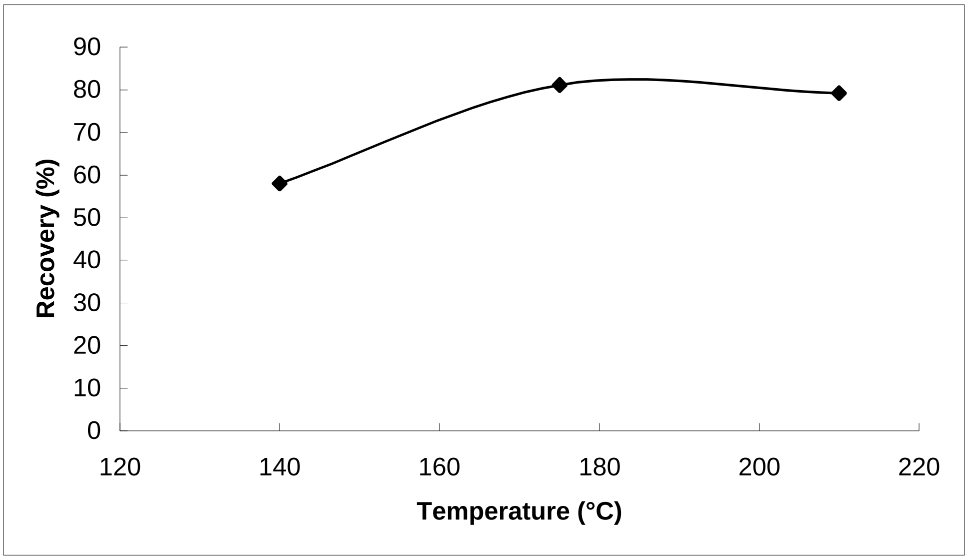

Figure 4.2. Recovery of Chromium as a Function of Temperature (2 h, 84.6 wt % of sulfuric acid and no perchloric acid addition).

4.1.3. Effect of Duration

It can be seen from experiments 1, 2 and 3 that, extraction of chromium increases with increasing durration while other conditions are kept constant. This enhancement can be seen from Figure 4.5. The conditions in the given chart are 175 °C as the temperature, 84.6 wt % sulfuric acid as the concentration and no perchloric acid addition to solution.

When experiments 1, 2 and 3 are compared, the highest chromium recovery can be seen for 6 hours of duration which has the value of 94.1 %. But in the following experiments, a period of 4 hours was chosen as the duration value since the recovery values of the experiments 2 and 3 were close to each other. Therefore, it was easier to finalize the experiment at a shorter time.

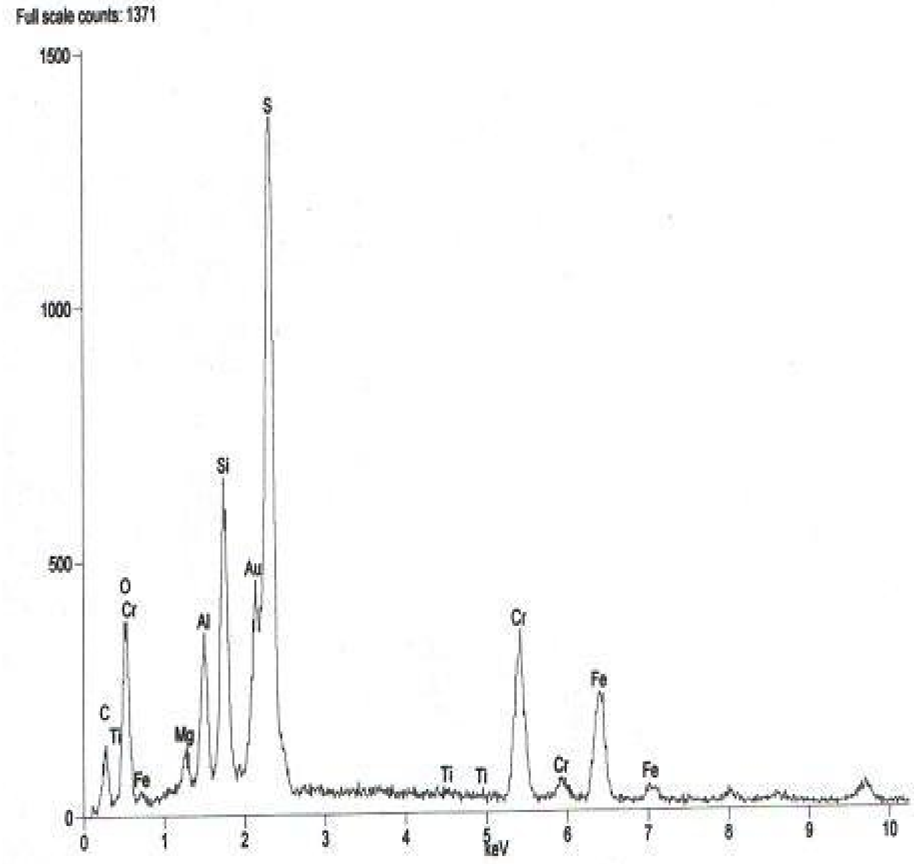

Figure 4.3. SEM (Scanning Electron Microscope) Diagram of the Solid Residue of Experiment 1 (under the conditions of 175 °C, 2 hours, 84.6 wt % sulfuric acid without addition of perchloric acid).

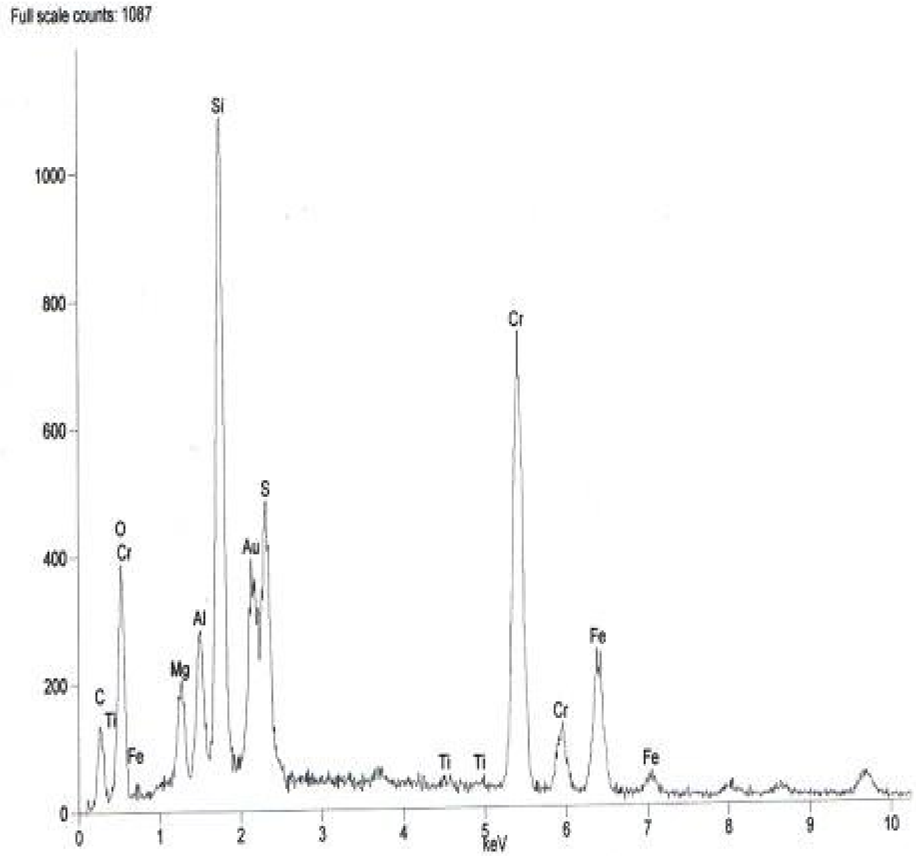

Figure 4.4. SEM (Scanning Electron Microscope) Diagram of the Solid Residue of Experiment 4 (under the conditions of 210 °C, 2 hours, 84.6 wt % sulfuric acid without addition of perchloric acid).

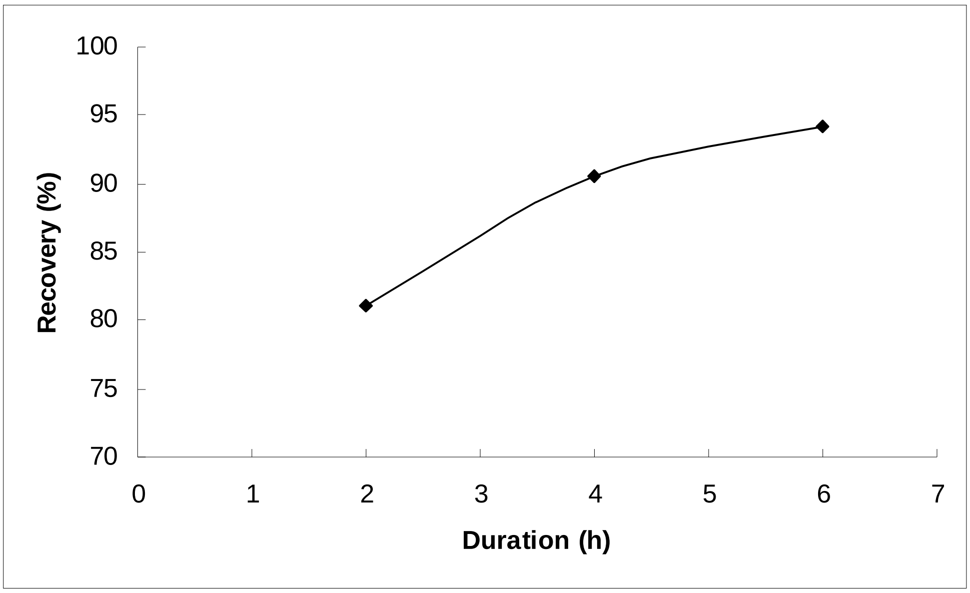

Figure 4.5. Recovery of Chromium as a Function of Duration (175 °C, 84.6 wt % sulfuric acid and no perchloric acid addition).

4.2. Leaching of Chromite in Sulfuric Acid with the Addition of Perchloric Acid

Perchloric acid has a high oxidation potential in acidic media. Because of this reason, an oxidation effect of perchloric acid can be expected. According to Vardar [8], perchloric acid cannot react with chromium to give a compound like $CrCl_6$ for the reason of the stability of perchloric acid at high temperatures (200 °C). Perchloric acid increases the rate and extent of extraction. This is most probably due to the high oxidative potential of perchloric acid, which increases the decomposition of chromite. But this statement was only true for 2 hours of a duration in our experiments.

Vardar indicates that, the increase in the decomposition may be explained with the oxidation of some chromium(III) in chromite concentrate to higher valency levels. It is believed that the oxidized chromium ions immediately react with sulfate ions and are reduced back to their trivalent state forming chromium(III) sulfates. The amount of oxidized chromium(III) to higher degree of valency cannot be concluded from the present data. More intensive investigation is needed in this field of study to explain the reaction behavior of perchloric acid with chromite in sulfuric acid solution.

It was observed during the experiments that, when perchloric acid was added to sulfuric acid solution, the colorless solution became light yellow in color. After the chromite concentrate was added to the balloon the color changed to black and after certain time elapsed, the color was dark green, which was the color of chromium(III) sulfate.

4.2.1. Effect of Perchloric Acid Addition

After the chemical analysis it was seen that the highest extraction of chromium was 98.7 % under the conditions of 175 °C, 2 hours, 84.6 wt % of sulfuric acid and ½ perchloric acid:chromite ratio which was the result of Experiment 13. This value was the highest value among all the experiments.

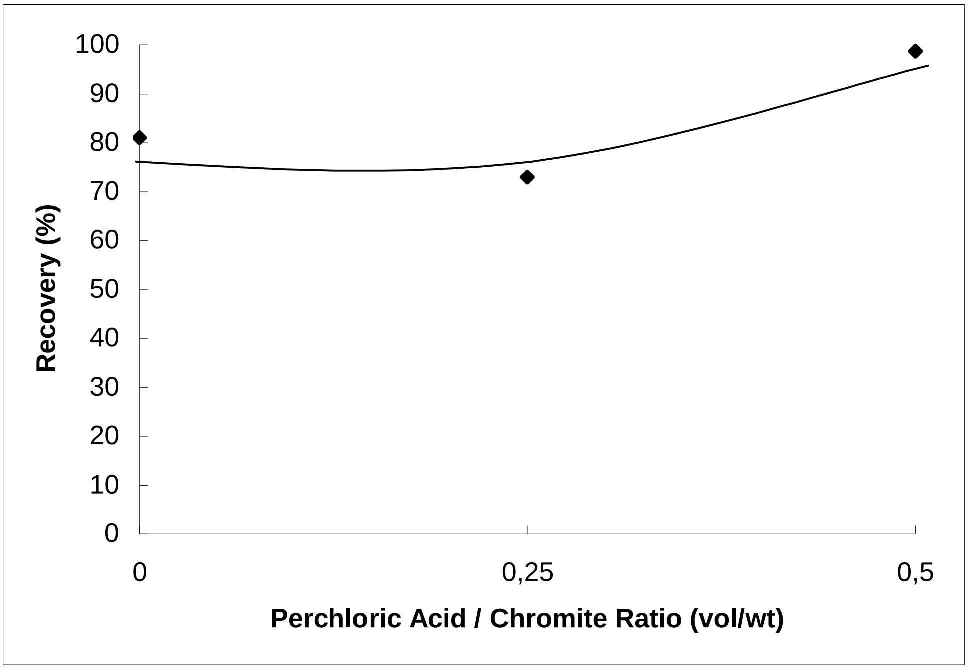

Figure 4.6. Recovery of Chromium as a Function of Perchloric Acid / Chromite Ratio (175 °C, 2 h and 84.6 wt % sulfuric acid).

Figure 4.6 demonstrates the extraction of chromium as function of perchloric acid / chromite ratio for 2 hours of leaching duration, 175 °C and 84.6 wt % sulfuric acid. The recovery values of chromium increased about 81.1 % to 98.7 % when the perchloric acid / chromite ratio was increased from 0.0 to 0.5. This is most probably due to the fact that perchloric acid increased the decomposition of the chromite.

4.2.2. Effect of Leaching Duration

As can be seen from Figure 4.7, extraction of chromium decreased from 98.7 % to 61.8 % as duration increased from 2 hours to 6 hours at 175 °C, 84.6 wt % sulfuric acid and ½ perchloric acid / chromite ratio. To explain this decrease, X-ray diffraction analyses of the leach residues of experiments 11 and 12 were done and some chromium containing compounds were observed. This means that, lower recoveries found at longer durations are due to the precipitation of chromium by time in the addition of perchloric acid.

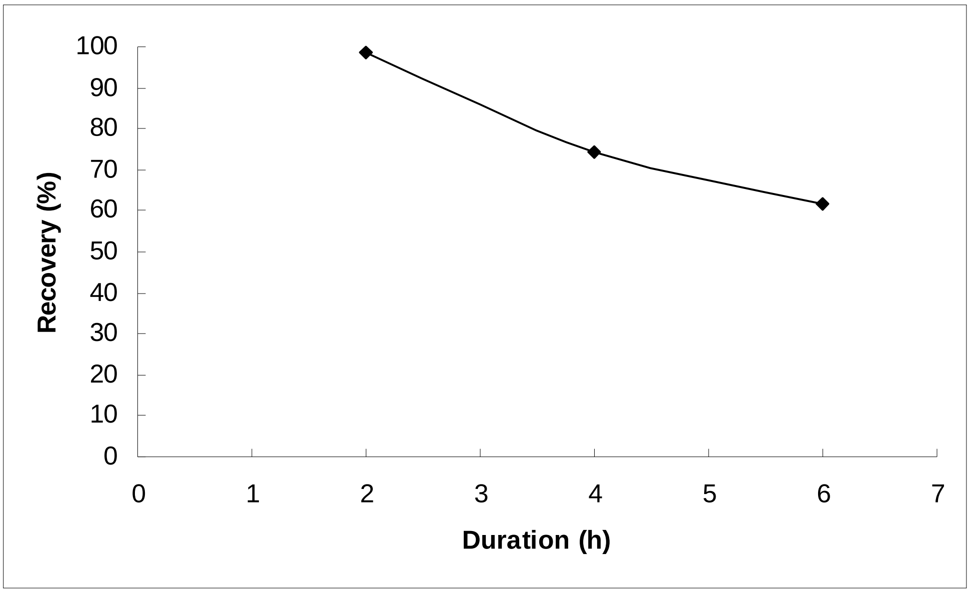

Figure 4.7. Recovery of Chromium as a Function of Duration (175 °C, 84.6 wt % sulfuric acid and ½ perchloric acid/chromite ratio).

4.3. Hexavalent Chromium Analyses

Four samples were chosen for qualitative chemical analysis. If hexavalent chromium were found in the samples, quantitative analysis would be done. Samples of experiments 1, 2 and 3 were chosen to see the change of Cr^{6+} amount with duration on a chart if hexavalent chromium was present in the solutions. Also, experiment 13 was chosen since it had the highest extraction value. But in none of the solutions, there was hexavalent chromium or if there was present in them, the amounts were so low to detect by chemical analyses.

These results are important and indicate the success of the method since there was no hexavalent chromium in the pregnant leach solutions. The toxic and corrosive effects of the hexavalent chromium compounds were mentioned in the previous chapters.

4.4. Mechanism of the Reaction

4.4.1. The Shrinking Core Model – Chemical Reaction Rate Control

The shrinking core models which are derived in Appendix A are established to differentiate between surface reaction control and diffusion control as the rate limiting step. The plot of "$1 - (1 - \alpha_1)^{1/3}$" against time should result in a straight line having a slope k if the reaction is chemically controlled.

Figure 4.8 shows that, the data given for and after the 2 h period of time may be suitable with the model, where α_1 is the reacted fraction at 175 °C, 84.6 wt % sulfuric acid and no perchloric acid addition. But it is not possible to decide the complete suitability of the data with the model. Figure 4.9 shows the plot of "$1 - (1 - \alpha_1)^{1/3}$" against time at 175 °C, 84.6 wt % sulfuric acid and ½ perchloric acid/chromite ratio. In the presence of perchloric acid, model does not fit data and this model is not a possible mechanism for the leaching conditions in the presence of perchloric acid.

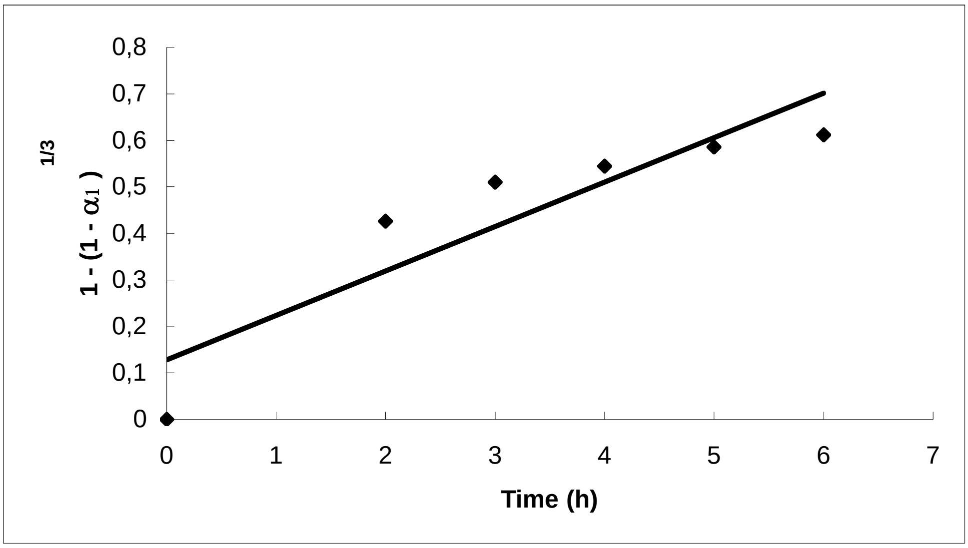

Figure 4.8. Plot of 1 – (1 - α_1)$^{1/3}$ versus time. Reacted fraction α for the experiment at 175 °C, 84.6 wt % sulfuric acid and no perchloric acid addition.

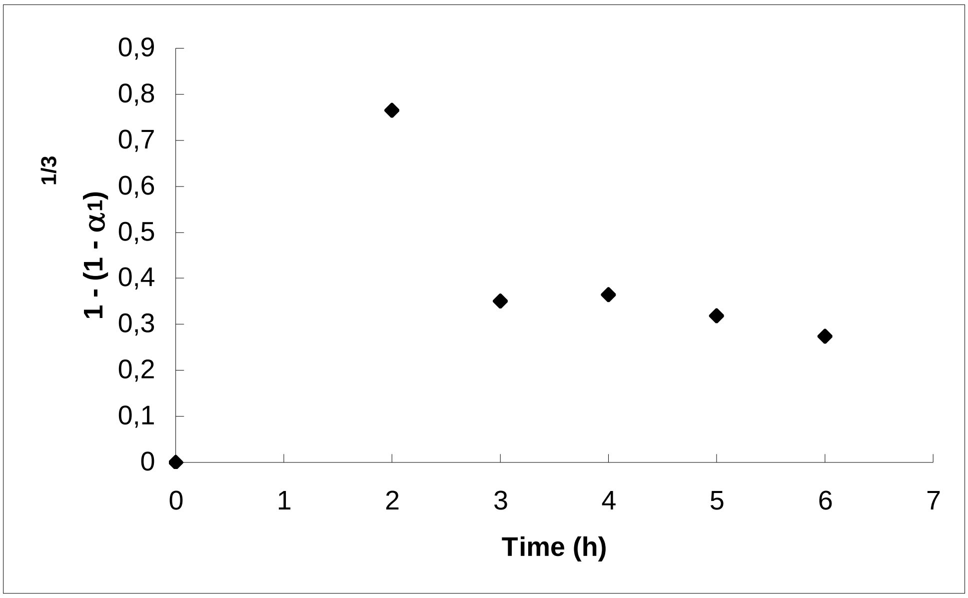

Figure 4.9. Plot of 1 – (1 - α_1)$^{1/3}$ versus time. Reacted fraction α for the experiment at 175 °C, 84.6 wt % sulfuric acid and ½ perchloric acid/chromite ratio.

4.4.2. The Shrinking Core Model – Rate Control by Diffusion

This model is developed assuming the examined reaction is diffusion controlled, if the plot of "$1 - 2/3\alpha_2 - (1 - \alpha_2)^{2/3}$" versus time should result in a straight line. α_2 is the reacted fraction for the diffusion rate control mechanism.

Figures 4.10 shows the plot of "$1 - 2/3\alpha_2 - (1 - \alpha_2)^{2/3}$" versus time at 175 °C, 84.6 wt% sulfuric acid and no perchloric acid addition. From this graph it is seen that the data given for and after the 2 h period of time may be suitable with the model, identical to the previous one. It is again not possible to decide the model definitely.

Figure 4.11 shows the plot of "$1 - 2/3\alpha_2 - (1 - \alpha_2)^{2/3}$" versus time at 175 °C, 84.6 wt % sulfuric acid and ½ perchloric acid/chromite ratio. In the presence of perchloric acid, model does not fit data and this model is not a possible mechanism for the leaching conditions in the presence of perchloric acid.

To select the models definitely in the absence of perchloric acid, future study should be done and this future study might be making more experiments with different temperature values keeping the other conditions constant. From the slopes of the charts for the different temperature values, *k* values can be calculated and ln k vs. 1/T diagrams can be drawn. From the slopes of these diagrams activation energy values can be calculated. These activation energy values may help for determining the right model for the leaching mechanisms.

Calculations made for reacted fraction (α) values for both models are given in Table 4.2.

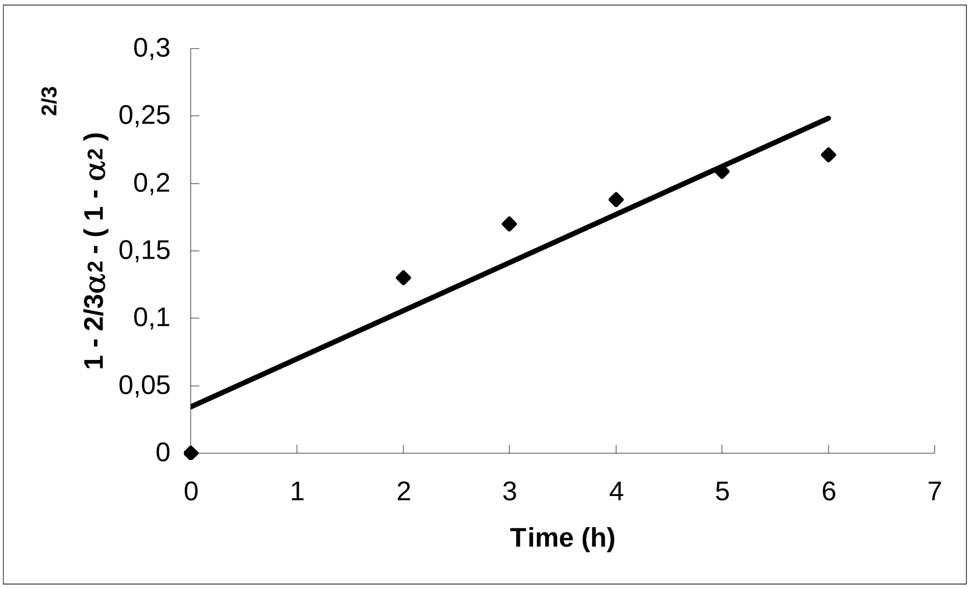

Figure 4.10. Plot of 1 – $2/3\alpha_2$ – $(1 - \alpha_2)^{2/3}$ versus time. Reacted fraction α for the experiment at 175 °C, 84.6 wt % sulfuric acid and no perchloric acid addition.

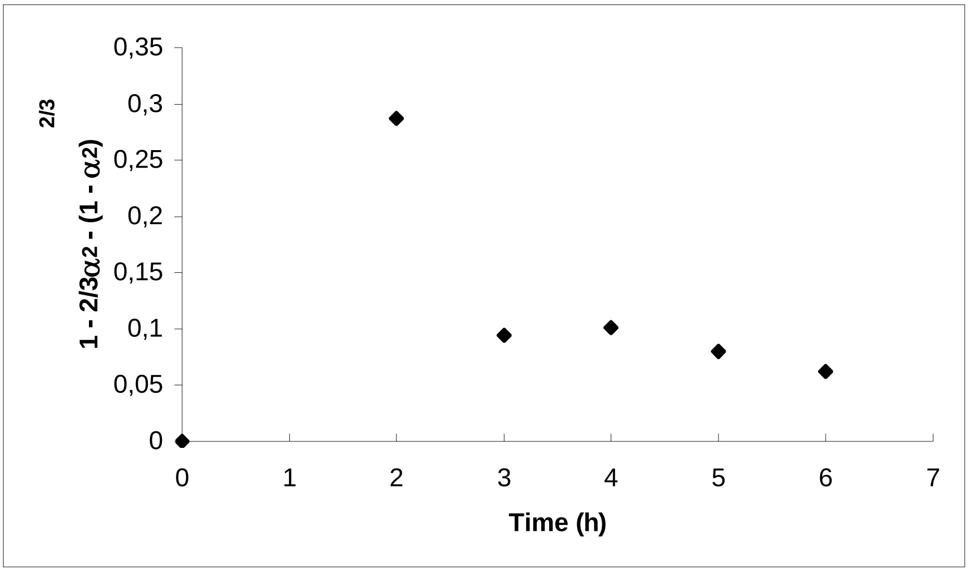

Figure 4.11. Plot of 1 – $2/3\alpha_2$ – $(1 - \alpha_2)^{2/3}$ versus time. Reacted fraction α for the experiment at 175 °C, 84.6 wt % sulfuric acid and ½ perchloric acid/chromite ratio.

Table 4.2. Calculated Values for the Shrinking Core Models

Time (h)	**Reacted Fraction, α**	**$1 - (1 - \alpha_1)^{1/3}$**	**$1 - 2/3\alpha_2 - (1 - \alpha_2)^{2/3}$**
2	0.811	0.426	0.130
2	0.987*	0.765	0.287
3	0.909	0.510	0.170
3	0.725*	0.350	0.094
4	0.905	0.544	0.188
4	0.744*	0.365	0.101
5	0.929	0.586	0.209
5	0.684*	0.319	0.080
6	0.941	0.611	0.221
6	0.618*	0.274	0.062

* Experiments done with the addition of perchloric acid.

CHAPTER 5

CONCLUSIONS

In this thesis work, the recovery and hexavalent chromium content of chromium from Pınarbaşı chromium concentrate were investigated by sulfuric acid leaching.

XRF analysis of the concentrate showed that the concentrate was mainly a high iron oxide containing chromite. XRF analysis of the concentrate determined that there was 47.8 % Cr_2O_3, 31.5 % Fe_2O_3, 9.7 % Al_2O_3, 6.3 % MgO, 3.3 % SiO_2, 1 % TiO_2 and 0.2 % CaO. The chemical formula of the chromite ore concentrate was calculated to be;

$$(Mg_{2.31}^{2+}\ Fe_{5.69}^{2+})\ [\ Cr_{11.1}^{3+}\ Al_{3.34}^{3+}\ Fe_{1.05}^{3+}\ Ti_{0.26}^{4+}\ Fe_{0.26}^{2+}\ ]\ O_{32}^{2-}\ .$$

In all experiments, 5 grams of chromite was taken for the reactions. Stirring rate, solid/liquid weight ratio (1/25) and grain size (- 38 μm) were kept constant. The reaction between chromite and sulfuric acid was studied using the following variables in the given ranges:

Temperature	: 140 – 175 – 210 °C
Duration	: 2 – 3 – 4 – 5 – 6 hours
$HClO_4$ / chromite ratio (vol/wt)	: 0 - ¼ - ½
H_2SO_4 concentration (weight %)	: 73.4 - 81.1 - 84.6 - 89.3 - 95.2.

The optimum conditions for the leaching were found as:

- The maximum chromium extraction in the absence of perchloric acid was 94.1 % under the conditions of 175 °C, 6 hours and 84.6 wt % sulfuric acid.

- The maximum chromium extraction was 98.7 % under the conditions of 175 °C, 2 hours, 84.6 wt % sulfuric acid and ½ perchloric acid / chromite ratio.

Ayhan found the maximum chromium extraction in the absence of perchloric acid as 58 % under the conditions of 175 °C, 70 vol % H_2SO_4 and 2 h. Also, in her study, in the presence of perchloric acid, the maximum chromium extraction was about 83 % under the conditions of 175 °C, 70 vol % H_2SO_4, 2h and ½ perchloric acid / chromite ratio. These two values are both lower than the ones found in this thesis study. These big differences are most probably due to the filtration conditions. Ayhan used cooling and dilution before filtering in her study. However, in this study hot filtration method was used via a “gooch crucible”. Lower recoveries found by Ayhan were most probably due to the precipitation of the chromium during cooling and dilution.

Perchloric acid increased the chromium recovery rate to its maximum value for a period of 2 hours as the leaching duration. It increased the decomposition of chromite by the effects of acidity and temperature for a short time as the duration parameter.

Although the highest extraction of chromium was not very high in sulfuric acid solution without perchloric acid addition as those obtained by conventional methods, it may still be considered for use. The reasons for this consideration are, easy finding of the raw materials and their cheapness. Besides these, small amounts of perchloric acid, also for short periods, was sufficient to increase the recovery of chromium. And the most important factor was that; no appreciable hexavalent chromium was produced during experiments. This is the biggest advantage of this method compared to the conventional methods.

Kinetic model of the leaching was also investigated in this study. However, two known models did not fit the data found after the experiments completely. Therefore, the rate limiting step could not be definitely determined by simply looking at these two different models and further study should be done.

Due to the complexity of the structure of the chromite spinel and limited knowledge about the precipitation of chromium(III) sulfates, this method may not seem to be practical nowadays. Future work may include a more fundamental research of the reason for precipitation of chromium(III) sulfates. A more detailed description of the overall process requires considerably more knowledge of the precipitated acid insoluble chromium(III) sulfates.

Future study should be done after this thesis study to take chromium chemicals from pregnant leach solution with a high recovery.

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APPENDIX A

MATHEMATICAL DERIVATIONS OF SHRINKING CORE MODELS

1. Shrinking Core Model When Chemical Control is the Rate Limiting Step

Burkin [15] gives the derivation of the model as follows. According to the derivation, the particles are assumed to be spherical but the final equation is applicable to particles of any isometric shape. The total number of moles in an unreacted sphere, *n*, is given by;

$$n = 4\pi r^3 / 3V \qquad (1)$$

where V is the molar volume equal to M/ρ where M is the molar mass and ρ is the density of the solid. The rate of reaction at the surface of the sphere of radius r can be written

$$- dn/dt = 4\pi r^2 ck' \qquad (2)$$

where k' being the rate constant for the first-order reaction with a reactant having concentration c in the solution. Differentiating (1) with respect to time and equating to (2) gives the linear rate;

$$- dr/dt = Vck' \qquad (3)$$

Vk' being the linear rate constant k_1. If c is the concentration of the reacting solute in moles cm^{-3} the linear rate of decrease in r is given in cm s^{-1}. If c remains constant, equation (3) represents the constant velocity of movement of the reaction interface, which is the definition of linear kinetics.

If the initial radius of the reacting particle is r_o and α is the fraction of it which has reacted then;

$$\alpha = 1 - (r^3 / r_o^3). \tag{4}$$

Differentiation with respect to time gives;

$$d\alpha/dt = - 3 (r^2 / r_o^3) (dr / dt) \tag{5}$$

and combining (3), (4) and (5) gives;

$$d\alpha/dt = (3ck_1 / r_o) (1-\alpha)^{2/3}. \tag{6}$$

For the condition $\alpha = 0$ when $t = 0$, (6) may be integrated assuming c is constant giving;

$$1 - (1 - \alpha)^{1/3} = kt \tag{7}$$

where $k = ck_1/r_o$ ($time^{-1}$). Plotting the left hand side of the last equation against t should give a straight line of slope k, k having units 1/t.

2. Shrinking Core Model When Diffusion is the Rate Limiting Step

According to Burkin [15], there are many cases where a mineral particle contains several metals, only one of which is dissolved during a leaching process. This can lead to the formation of a porous solid reaction product surrounding each particle of unreacted mineral. The special case in which the diameter of the composite particle remains equal to the original diameter r_o of the particle before reaction commenced has been considered. The shrinking core, of radius r, continues to react at a rate controlled by the rates of diffusion of reactants to the unreacted core, through the reaction products.

If the particle is spherical the rate of reaction can be written;

$$- (dn/dt) = (4\pi r^2/\sigma)\ D\ (dc/dr) \tag{8}$$

where n is the number of moles of unreacted mineral in the core and σ is the stoichiometry factor, the number of moles of the diffusing species required to liberate one mole of the metal to be leached from the core. Integration of this equation between limits r and r_o, assuming steady state conditions, gives;

$$- (dn/dt) = (4\pi D c r r_o) / [\sigma(r_o - r)] \tag{9}$$

where the concentration of reactant at the interface is small compared with c. Combining (1) and (8) gives the equation;

$$- (dr/dt) = (V D c r_o) / [\sigma r(r_o - r)] \tag{10}$$

for the rate of movement of the boundary between the core and reaction products in terms of the radius of the unreacted core. Combining (10) with (4) and (5) gives the rate of reaction in terms of the fraction already reacted, α,

$$(d\alpha/dt) = [(3VDc) / (\sigma r_o^2)]\ [(1 - \alpha)^{1/3} / (1 - (1 - \alpha)^{1/3})]. \tag{11}$$

Integration for the boundary condition $\alpha = 0$ when $t = 0$ gives;

$$1 - [(2/3)\alpha] - (1 - \alpha)^{2/3} = (2VDct) / (\sigma r_o^2). \tag{12}$$

APPENDIX B

CALCULATION OF STOICHIOMETRIC CHEMICAL FORMULA OF PINARBAŞI CHROMITE CONCENTRATE

Mass of elements and compounds (g/mole):

Al = 26.982
Cr = 51.996
Fe = 55.847
Mg = 24.305
Si = 28.086
O = 15.999

Al_2O_3 = 101.961
Cr_2O_3 = 151.990
Fe_2O_3 = 159.692
MgO = 40.304
SiO_2 = 60.084

The chemical formula of this chromite was calculated according to the work done in South Africa by Soykan [10]. An example calculation to find the atom fraction of Cr is given below:

Mass % of Cr^{3+} Ion in Oxide = (47.8 * 2 * 51.996) / 151.990 = 32.7

Mass % of Cr^{3+} Ion/Mole Wt. Cr^{3+} Ion = 32.7 / 51.996 = 0.629

Atom Fraction, N_{Cr} = 0.629 / 3.63 = 0.173

The atomic fractions of the ions in the oxide are given in the following table:

Oxide	**Mass % of Oxide**	**Ion**	**Ion Mass % in Oxide**	**Ion Mass / Mole Wt. Ion**	**Atom Fraction, N_f**
Cr_2O_3	47.80	Cr^{3+}	32.70	0.629	0.173
Fe_2O_3	31.50	Fe^{3+}	22.03	0.395	0.109
Al_2O_3	9.70	Al^{3+}	5.13	0.19	0.052
MgO	5.30	Mg^{2+}	3.20	0.132	0.036
TiO_2	1.00	Ti^{4+}	0.60	0.013	0.004
	The Sum of Ions Mass % in Oxide = 63.66				
	O^{2-} (= 100 – 65.202) = 36.34			2.27	0.63
	Total		100	3.63	

That each spinel unit cell is comprised of 8 AB_2O_4 units, which has 32 oxygen atoms present. Therefore, the number of cations per 32 oxygen ions must be calculated.

Since normal spinels have 8 divalent cations in the tetrahedral sites and 16 trivalent cations in octahedral sites, the results must be normalized to 24 cations. Also, ulvospinel structure should be considered since there is some TiO_2 in the concentrate.

$N_O / 32 = 0.63 / 32 = 0.01954$

N_f / 0.01954		(N_f / 0.01954) * 24 / Total
Cr	8.85	11.1
Fe	5.58	7.00
Al	2.66	3.34
Mg	1.84	2.31
Ti	0.21	0.26
Total	19.14	24

$Mg^{2+} = 2.31$ $Cr^{3+} = 11.1$ $Al^{3+} = 3.34$ $Ti^{4+} = 0.26$

In tetrahedral sites : $Fe^{2+} = 8 – 2.31 = 5.69$

In octahedral sites : $Fe^{2+} = 0.26$

$Fe^{3+} = 7.00 – 5.69 – 0.26$

$= 1.05.$

According to this calculation, the stoichiometric formula of the spinel was found as shown below:

$(Mg_{2.31}^{2+} Fe_{5.69}^{2+}) [Cr_{11.1}^{3+} Al_{3.34}^{3+} Fe_{1.05}^{3+} Ti_{0.26}^{4+} Fe_{0.26}^{2+}] O_{32}^{2-}$.

The parentheses and the brackets show tetrahedral and octahedral sites, respectively.

APPENDIX C

CALCULATIONS OF CHEMICAL ADDITIONS

Chromite amount and solid/liquid ratio was taken as constant:

Chromite concentrate = 5 grams

Solid/liquid ratio = Mass/volume ratio
Solid (gram) / liquid (cm^3) ratio = 1 / 25

So, liquid = 5 * 25 = 125 cm^3

95 – 97 wt % $H_2SO_4 \Rightarrow (95 + 97) / 2 = 96$ wt % H_2SO_4 (taken)

$H_2SO_4 \Rightarrow 1\ cm^3 = 1.84$ g , $H_2O \Rightarrow 1\ cm^3 = 1$ g

1. If ($HClO_4$ volume / chromite weight) ratio is taken 0:
$HClO_4$ / chromite = $HClO_4 / 5 = 0 \quad \Rightarrow \quad HClO_4 = 0$ ml.
125 cm^3 liquid = 0 cm^3 $HClO_4$ + x cm^3 H_2SO_4
125 cm^3 H_2SO_4

- 95.2 % H_2SO_4 preparation:

  90 cm^3 H_2SO_4 + 10 cm^3 H_2O
  90 / 0.96 = 93.75 cm^3 H_2SO_4

$93.75 - 90 = 3.75$ cm^3 H_2O

93.75 cm^3 H_2SO_4 + 6.25 (= $10 - 3.75$) cm^3 H_2O

$125 * 93.75 / 100 =$ <u>117.19 cm^3 H_2SO_4</u>

$125 - 117.19 =$ <u>7.81 cm^3 H_2O</u>

$117.19 * 4 / 100 = 4.69$ cm^3 H_2O in acid

$117.19 - 4.69 = 112.5$ cm^3 H_2SO_4

$112.5 * 1.84 = 207$ g H_2SO_4

$7.81 + 4.69 = 12.5$ g H_2O

$207 * 100 / 217.5 =$ <u>95.2 wt % H_2SO_4</u>

- 89.3 % H_2SO_4 preparation:

82 cm^3 H_2SO_4 + 18 cm^3 H_2O

$82 / 0.96 = 85.42$ cm^3 H_2SO_4

$85.42 - 82 = 3.42$ cm^3 H_2O

85.42 cm^3 H_2SO_4 + 14.58 (= $18 - 3.42$) cm^3 H_2O

$125 * 85.42 / 100 =$ <u>106.775 cm^3 H_2SO_4</u>

$125 * 14.58 / 100 =$ <u>18.225 cm^3 H_2O</u>

$106.78 * 4 / 100 = 4.27$ cm^3 H_2O in acid

$106.78 - 4.27 =102.51$ cm^3 H_2SO_4

$102.51 * 1.84 = 188.61$ g H_2SO_4

$18.23 + 4.27 = 22.5$ g H_2O

$100 * 188.61 / 211.11 =$ <u>89.3 wt % H_2SO_4</u>

- 84.6 % H_2SO_4 preparation:

75 cm^3 H_2SO_4 + 25 cm^3 H_2O

$75 / 0.96 = 78.125$ cm^3 H_2SO_4

$78.125 - 75 = 3.125$ cm^3 H_2O

78.125 cm^3 H_2SO_4 + 21.875 (= $25 - 3.125$) cm^3 H_2O

$125 * 78.125 / 100 =$ <u>97.656 cm^3 H_2SO_4</u>

$125 * 21.875 / 100 =$ <u>27.344 cm^3 H_2O</u>

$97.66 * 4 / 100 = 3.91$ cm^3 H_2O in acid

$97.66 – 3.91 = 93.75$ cm^3 H_2SO_4

$93.75 * 1.84 = 172.5$ g H_2SO_4

$27.34 + 3.91 = 31.3$ g H_2O

$172.5 * 100 / 203.8 =$ $\underline{84.6\text{ wt }\%}$

- 81.1 % H_2SO_4 preparation:

70 cm^3 H_2SO_4 + 30 cm^3 H_2O

$70 / 0.96 = 72.92$ cm^3 H_2SO_4

$72.92 – 70 = 2.92$ cm^3 H_2O

72.92 cm^3 H_2SO_4 + 27.08 (= 30 – 2.92) cm^3 H_2O

$125 * 72.92 / 100 =$ $\underline{91.15\text{ cm}^3\ H_2SO_4}$

$125 – 91.15 =$ $\underline{33.85\text{ cm}^3\ H_2O}$

$91.2 * 4 / 100 = 3.65$ cm^3 H_2O in acid

$91.2 – 3.65 = 87.55$ cm^3 H_2SO_4

$87.55 * 1.84 = 161.1$ g H_2SO_4

$33.9 + 3.65 = 37.55$ g H_2O

$161.1 * 100 / 198.65 =$ $\underline{81.1\text{ wt }\%\ H_2SO_4}$

- 73.4 % H_2SO_4 preparation:

60 cm^3 H_2SO_4 + 40 cm^3 H_2O

$60 / 0.96 = 62.5$ cm^3 H_2SO_4

$62.5 – 60 = 2.5$ cm^3 H_2O

62.5 cm^3 H_2SO_4 + 37.5 (= 40 – 2.5) cm^3 H_2O

$125 * 62.5 / 100 =$ $\underline{78.125\text{ cm}^3\ H_2SO_4}$

$125 * 37.5 / 100 =$ $\underline{46.875\text{ cm}^3\ H_2O}$

$78.13 * 4 / 100 = 3.13$ cm^3 H_2O in acid

$78.13 – 3.13 = 75$ cm^3 H_2SO_4

$75 * 1.84 = 138$ g H_2SO_4

$46.88 + 3.13 = 50$ g H_2O

138 * 100 / 188 = <u>73.4 wt % H_2SO_4</u>

2. If ($HClO_4$ / chromite) ratio is taken ¼:

$HClO_4$ / chromite = $HClO_4$ / 5 = ¼ ⇒ $HClO_4$ = 1.25 ml = 1.25 cm^3
125 cm^3 liquid = 1.25 cm^3 $HClO_4$ + x cm^3 H_2SO_4
123.75 cm^3 H_2SO_4

- 95.2 % H_2SO_4 preparation:

90 cm^3 H_2SO_4 + 10 cm^3 H_2O
90 / 0.96 = 93.75 cm^3 H_2SO_4
93.75 – 90 = 3.75 cm^3 H_2O
93.75 cm^3 H_2SO_4 + 6.25 (= 10 – 3.75) cm^3 H_2O
123.75 * 93.75 / 100 = <u>116.02 cm^3 H_2SO_4</u>
123.75 * 6.25 / 100 = <u>7.73 cm^3 H_2O</u>
95.2 wt % H_2SO_4

- 84.6 % H_2SO_4 preparation:

75 cm^3 H_2SO_4 + 25 cm^3 H_2O
75 / 0.96 = 78.125 cm^3 H_2SO_4
78.125 – 75 = 3.125 cm^3 H_2O
78.125 cm^3 H_2SO_4 + 21.875 (= 25 – 3.125) cm^3 H_2O
123.75 * 78.125 / 100 = <u>96.68 cm^3 H_2SO_4</u>
123.75 * 21.875 / 100 = <u>27.07 cm^3 H_2O</u>
84.6 wt % H_2SO_4

- 73.4 % H_2SO_4 preparation:

60 cm^3 H_2SO_4 + 40 cm^3 H_2O
60 / 0.96 = 62.5 cm^3 H_2SO_4
62.5 – 60 = 2.5 cm^3 H_2O

62.5 cm^3 H_2SO_4 + 37.5 (= 40 – 2.5) cm^3 H_2O

123.75 * 62.5 / 100 = $\underline{77.34\ cm^3\ H_2SO_4}$

123.75 * 37.5 / 100 = $\underline{46.41\ cm^3\ H_2O}$

73.4 wt % H_2SO_4

3. If ($HClO_4$ / chromite) ratio is taken ½:

$HClO_4$ / chromite = $HClO_4$ / 5 = ½ ⇒ $HClO_4$ = 2.5 ml = 2.5 cm^3

125 cm^3 liquid = 2.5 cm^3 $HClO_4$ + x cm^3 H_2SO_4

122.5 cm^3 H_2SO_4

- 90 % H_2SO_4 preparation:

90 cm^3 H_2SO_4 + 10 cm^3 H_2O

90 / 0.96 = 93.75 cm^3 H_2SO_4

93.75 – 90 = 3.75 cm^3 H_2O

93.75 cm^3 H_2SO_4 + 6.25 (= 10 – 3.75) cm^3 H_2O

122.5 * 93.75 / 100 = $\underline{114.84\ cm^3\ H_2SO_4}$

122.5 * 6.25 / 100 = $\underline{7.66\ cm^3\ H_2O}$

- 75 % H_2SO_4 preparation:

75 cm^3 H_2SO_4 + 25 cm^3 H_2O

75 / 0.96 = 78.125 cm^3 H_2SO_4

78.125 – 75 = 3.125 cm^3 H_2O

78.125 cm^3 H_2SO_4 + 21.875 (= 25 – 3.125) cm^3 H_2O

122.5 * 78.125 / 100 = $\underline{95.7\ cm^3\ H_2SO_4}$

122.5 * 21.875 / 100 = $\underline{26.8\ cm^3\ H_2O}$

- 60 % H_2SO_4 preparation:

60 cm^3 H_2SO_4 + 40 cm^3 H_2O

60 / 0.96 = 62.5 cm^3 H_2SO_4

$62.5 - 60 = 2.5$ cm^3 H_2O

62.5 cm^3 H_2SO_4 + 37.5 (= $40 - 2.5$) cm^3 H_2O

$122.5 * 62.5 / 100 = \underline{76.56 \text{ cm}^3\ H_2SO_4}$

$122.5 * 37.5 / 100 = \underline{45.94 \text{ cm}^3\ H_2O}$

After calculations, $HClO_4$ and H_2SO_4 volumes were found as given below:

($HClO_4$ / chromite) ratio vol / wt	**$HClO_4$ cm^3**	**H_2SO_4 wt %**	**H_2SO_4 cm^3**	**H_2O cm^3**
0	0	95.2	117.19	7.81
0	0	89.3	106.775	18.225
0	0	84.6	97.66	27.34
0	0	81.1	91.15	33.85
0	0	73.4	78.125	46.825
1 / 4	1.25	95.2	116.02	7.73
1 / 4	1.25	84.6	96.68	27.07
1 / 4	1.25	73.4	77.34	46.41
1 / 2	2.5	95.2	114.84	7.66
1 / 2	2.5	84.6	95.7	26.8
1 / 2	2.5	73.4	76.56	45.94

APPENDIX D

CALCULATION OF RECOVERY % OF CHROMIUM

In all experiments 5 g chromite was used. 47.8 % Cr_2O_3 was present in the ore concentrate according to the XRF analysis.

The example of recovery calculation of Experiment 13 is given below:

Cr = 51.996 g/mole $\qquad$ Cr_2O_3 = 151.990 g/mole

Weight of Cr_2O_3 in 5 g chromite = (5 * 47.8) / 100 = 2.39 g Cr_2O_3

Weight of Cr in 5 g chromite = (2.39 * 51.996 * 2) / 151.990 = 1.635 g Cr.

After the chemical analysis done following the experiment, 1.4415 g Cr/100 ml in the leach solution and 0.071 g Cr/100 ml in the wash water were found. Since 105 ml leach solution was obtained and 140 ml wash water was used after the experiment:

Weight of Cr in the leach solution = (1.4415 * 105) / 100 = 1.5136 g Cr

Weight of Cr in the wash water = (0.071 * 140) / 100 = 0.0994 g Cr.

Recovery of chromium was calculated using the values found above:

Cr % in the leach solution = (1.5136 * 100) / 1.635 = 92.57

Cr % in the wash water = (0.0994 * 100) / 1.635 = 6.08

Total Chromium Recovery = (Cr % in the leach solution) + (Cr % in the wash water)

Total Chromium Recovery = 92.57 + 6.08
= 98.65 %.

APPENDIX E

CHEMICAL ANALYSES OF CHROMIUM

TOTAL CHROMIUM ANALYSIS

10 mililiters of liquid specimens were taken from the solutions and oxidized in the sulfuric acid (1/1 diluted) medium by perchloric acid (sufficient amount to oxidize the trivalent chromium in the solutions) on the hot plate. With the effect of the perchloric acid, chromium in the liquid solution was oxidized to chromate with +6 value. After oxidation of chromium, it was titrated by mohr salt (ammonium iron(II) sulfate, cryst extra pure) with the barium diphenylamine sulfanat ($C_{24}H_{20}BaN_2O_6S_2$) indicator in the sulfuric acid medium. When the solution reduced again to its trivalent state the color of the solution changed. The volume consumption value of the mohr salt, which causes the change in the color, was observed on the pipette. Amounts of chromium were calculated from this volume consumption values. Specimens from all leach solutions and wash waters were analyzed with this method.

Cr_2O_3 % in the 100 ml = [(Mol weight * Volume Consumption * Factor of Mohr Salt) / (10000 * Weight)] * 100

QUALITATIVE ANALYSIS METHOD FOR HEXAVALENT CHROMIUM

Hexavalent chromium was analyzed by a qualitative method. Certain amount of samples were taken from the leach solutions. Since our samples were so acidic ($pH < 1$), their pH value was increased to 1.3 – 1.5 interval by mixing with 20 %

NaOH by the help of pH meter because chromium is only seen in this interval. 1.5 ml of 0.5 % diphenylcarbazide was added to the samples to see the change in the color. If the color is purple-violet, it means that Cr^{6+} exists in the sample. Otherwise, no appreciable hexavalent chromium exists.

After these analyses, hexavalent chromium could not be seen in our samples. Therefore, there was no need for quantitative analysis.

TRIVALENT CHROMIUM CALCULATION

Trivalent chromium (Cr^{3+}) can be calculated by the subtraction of hexavalent chromium values from total chromium values. However, since hexavalent chromium could not be seen in our leach solutions, total chromium values can be taken as trivalent chromium.