



UNIVERSITY OF THE
WITWATERSRAND,
JOHANNESBURG

**THE REDUCTION OF CHROME IN UG-2 FLOTATION
CONCENTRATE USING HYDROMETALLURGICAL MEANS**

Prepared by

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Submitted to

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of Master of Science in engineering

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Johannesburg, 2022

MSc Dissertation	The Reduction of Chrome in UG-2 Flotation Concentrate by Hydrometallurgical Means	2022
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DECLARATION

I declare that this dissertation is my own unaided work. It is being submitted to the degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any other degree or examination in any other University.



Abel Monele Mokadze

20th Day of July 2022

ABSTRACT

Flotation concentrates produced from processing UG-2 ore typically contain high Cr_2O_3 grades (>3 wt.%), which are not amenable to conventional PGM smelting processes. The solubility limit of Cr_2O_3 to deport to the silica glass phase is approximately 1.8 wt.% and below. Above this limit, the slag phase reaches saturation limits, which results in the formation of the infamous refractory Cr_2O_3 spinel phases. The overall net effect of high Cr_2O_3 in smelter operations includes, inter alia, increased furnace specific energy consumptions (kWh/t), the reduction of effective furnace capacity and poor PGM recovery. Existing interventions such as modification of slag chemistry by Cr_2O_3 dilution methods, redesign, and modification of existing physical and pyrometallurgical operations have not yielded any sustainable solutions. Thus, in this study, an acid leaching process using sulphuric acid was investigated to reduce Cr_2O_3 in UG-2 flotation concentrates.

In the preliminary leaching experiments, exploratory batch leaching tests were conducted to study the leaching behaviour of Cr in UG-2 concentrate at different parameter levels of sulphuric acid concentration, leaching time and solid-to-liquid ratio. The experimental results showed that Cr extraction proportionally increased with the increase in sulphuric acid concentration and leaching time. On the contrary, Cr extraction increased with a decrease in solid-to-liquid ratio. Using a range of different solid-to-liquid ratios in the preliminary experiments, a 1:26 solid-to-liquid ratio gave a maximum Cr extraction of 87% at 75 %v/v acid concentration, 120°C temperature, 17 mL/min air flowrate and 5 hours leaching time.

Using a fixed solid-to-liquid ratio of 1:3, at a temperature of 85°C, the Design of Experiments (DOE) was employed to establish optimum leaching conditions. From an industrial point of view, a 1:3 solid-to-liquid ratio and a temperature of 85°C were selected in alignment with the % solids that are generally required for minimum engineering design and practical operations, as well as the 85°C temperature for energy conservation. The DOE identified oxygen flowrate and acid concentration as significant process factors for Cr extraction. The interaction of temperature, leaching time and acid concentration was also found to be statistically significant. The response surface methodology (RSM), in conjunction with the central composite rotatable design (CCRD), established 45 v/v% sulphuric acid concentration, 15 mL/min pure oxygen flowrate and 3 hours reaction time as optimum leaching conditions.

Using the optimised leaching conditions, further experiments conducted to test different solid-to-liquid ratios yielded a Cr extraction of 7.6% at 1:2 solid-to-liquid ratio and 36.8% at 1:26 solid-to-liquid ratio. The 36.8% Cr extraction represents 1.33% reduction in Cr_2O_3 content from 3.63 wt.% to 2.3 wt.% in the UG-2 concentrate. The difference between the 87% Cr extraction obtained at 120°C and the 36.8% Cr extraction obtained at 85°C is attributed to the difference in the leaching temperature.

Although the target for the solubility limit of Cr_2O_3 to deport in the silica glass phase was approximately 1.8 wt.% and below, the actual Cr_2O_3 content in the current smelter operations tends to fluctuate between 2 wt.% and 4 wt.%. Therefore, the Cr reduction from 3.63 wt.% to 2.3 wt.% achieved in the current study is considered to be within acceptable limits for PGM smelting processes. Thus, the reduced chrome content to 2.30 wt.% is a significant step towards achieving the 1.8 wt.% target.

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DEDICATION

Dedicated to
my son Tiyani Mokadze, and my late grandmother Shalati Famate.

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List of symbols

Δ	Change of a quantity
E	Energy (J)
G	Gibbs free energy (J)
H	Enthalpy (J)
S	Entropy (J/K)
T	Temperature (K)
p	Pressure (Pa)
A	surface area (m ²)
E_a	Activation energy (J/mol)
M	Molarity, concentration of solution, moles per litre (Mol/L)
E	Potential (V)
E_h	Electrode potential (V)
E°	Standard potential (V)
F	Faraday constant (96 489 A/mol)
pH	Potential of hydrogen
K_r	Rate constant
R	Ideal gas constant (8.314 J/K.mol)
t	Time (s)
T	Absolute temperature (K), temperature (°C)
wt.%	weight percentage
x_i	i^{th} value in a data set
ρ	Density (g/cm ³)
kWh	kilo Watt hour (3.6x10 ⁶ J)
pK_a	negative log of a dissociation constant
ΔG°	Standard conditions Gibbs free energy
ΔH°	Standard conditions enthalpy (J)
ΔS°	Standard conditions entropy (J/K)

Chapter 1

INTRODUCTION

1.1 Introduction

South Africa (SA) is the largest producer of Platinum Group Metals (PGMs) in the world, and it hosts up to 95% of the world's PGM reserves (Kinnaird, 2005; Viljoen, 2016). The PGMs, also known as precious metals, include Platinum (Pt), Palladium (Pd), Rhodium (Rh), Ruthenium (Ru), Iridium (Ir) and Osmium (Os). These are typically formed in association with traces of Gold (Au). The economic value of PGMs is largely derived from their catalytic qualities, corrosion resistance, high melting point, and chemical inertness. Their industrial applications are mostly found in the automobile, jewellery, chemical, and fuel cell industries.

The PGM reserves in SA are geologically located within the three narrow-mineralised horizons of the Bushveld Igneous Complex, the largest known layered igneous intrusion in the world (Merkle et al., 2002; Viljoen, 2016). The three PGM-bearing horizons (ores) include the Merensky reef, Upper Group Two reef (UG-2) and Platereef. These PGM-bearing ores are commonly accessed and extracted via underground and surface mining methods. Their run-of-mine is typically processed via a sequence of established physical techniques, pyrometallurgical and hydrometallurgical processes. The generic process flowsheet currently utilized by the SA platinum industry involves comminution, flotation, smelting, converting, and refining of base metals (BMs) and PGMs (Lamya, 2007; Liddell et al., 1986).

The chemical and mineralogical characteristics of the final flotation concentrates produced from processing Merensky and Platereef ores are similar. Their composition constitutes high quantities of sulphide minerals and low chromite (chrome) contents, which are amenable to traditional PGM smelting methods (Barnes and Newall, 2006; Liddell et al., 1986; Nell, 2004). In contrast, UG-2 concentrates are typically characterised by low sulphide and high chromite (chrome) contents. The general chemical composition of flotation concentrates of Merensky-type, UG-2 and a blend of the two ore concentrate are illustrated in **Table 1.1**. The high chrome grades (>3 wt.%) in UG-2 flotation concentrates, render the material unattractive and difficult

to process using the current PGM smelting methods (Hay and Roy, 2010; Liddell et al., 1986; Shaw et al., 2013).

Table 1.1: Chemical composition of flotation concentrates and their blend (wt.%) (Barnes and Newall, 2006).

Concentrate type	SiO ₂	MgO	Cr ₂ O ₃	Total Fe	Al ₂ O ₃
Merensky	41	18	0.4	18	1.8
UG – 2	49.6	22.3	3.8	13.7	4.4
Merensky:UG-2 blend (30:70)	47	22	2.8	15	3.6

The primary PGM smelting operations in SA use exclusively electric furnaces; viz. rectangular six-in-line submerged-arc furnaces and circular three-electrode furnaces (Jones, 2005; Nell, 2004). In all smelters that use either of the two designs, the main objective of the unit operations is to produce a molten bath through conduction of electrical current in a bed of concentrate material (Nell, 2004). The molten bath is normally comprised of immiscible dense sulphidic matte and light oxidic slag phases. The typical composition of the matte phase is made up of molten prills of base metals, iron, and sulphur that act as PGM collectors, while the slag mainly contains silica and magnesia (Du Preez, 2010; Lamya, 2007; Nell, 2004). The efficiency of PGM furnaces to achieve optimum matte-slag separation is mainly influenced by slag chemistry and furnace operating conditions (Nell, 2004).

Slag chemistry is normally a function of feed composition, i.e., total iron oxide, silica, magnesia, and chrome. Normal operating conditions include slag liquidus temperatures of 1300-1600°C and oxygen and sulphur potentials of $\log(pO_2) = -8$ and $\log(pS_2) = -4$ bars, respectively (Barnes and Newall, 2006; Du Preez, 2010; Nell, 2004). Under these operating conditions, the solubility limit of chrome to deport to the silica glass phase is approximately 1.8 wt.% (Du Preez, 2010). Above this limit, the slag phase reaches saturation limits and results in chromium forming refractory chrome spinel phases (Du Preez, 2010; Eksteen et al., 2011). These phases are typically characterised by the following physical properties, which render their formation undesirable:

- High compound stabilities that are characterised by high melting points.

- High viscosity and density.
- Low solubility in silicic slags and partial solubility in matte.
- High specific heat capacities of between 40 Cal/mole/°C and 55 Cal/mole/°C.

These inherent physical properties normally result in the formation of an intermediate spinel layer interfacing the matte and slag phases. The partially liquid layer, under normal operating conditions, is typically suspended in the molten bath and ultimately deposits on furnace sidewalls and hearth. The technical problems that are commonly associated with the presence of the spinel layer in traditional PGM furnaces include:

- The reduction of effective furnace capacity due to accumulation of the spinels.
- The increase in slag viscosity, thus causing poor slag-matte separation and entrapment of matte prills containing PGMs.
- The increase in slag thermal resistance which in turn increases slag liquidus temperature, refractory wear and power consumption.

Generally, the net negative effects of high chrome contents in PGM smelting operations involve process inefficiencies and high operating costs (OPEX). Various process solutions have been developed and proposed to minimise these negative effects. The solutions include the dilution of UG-2 concentrates, the use of gravity techniques to recover chromite and the modification of pyrometallurgical processes.

The dilution of UG-2 concentrates with the Merensky type of material has been widely used for decades to dilute chrome and other notorious oxides (Jones, 2005). This has been considered as the most reliable processing strategy to modify the slag chemistry for efficient chromium solubility. The UG-2: Merensky dilution ratios typically vary between 70:30 and 90:10. This practice is however, fast becoming non-viable as the remaining resources of Merensky ore are at levels that are too deep for economic extraction. Spiral and hydro-cyclone gravity techniques have also found large application in UG-2 mill-float-mill-float (MF-2) plant configurations to recover and prevent overgrinding of chromite prior to flotation (Maharaj et al., 2011; Wills and Finch, 2015). These technologies are generally inefficient to separate fine chromite and coarse

silicates due to their major differences in specific densities and particle size, i.e., fine chromite phases of density 4.2 are typically recovered with coarse silicates of density 2.7.

The common pyrometallurgical solution that has found significant application in the smelting of enriched-chrome concentrates is furnace technology with high hearth power densities (Eksteen et al., 2011; Nell, 2004). This technology can operate at high liquidus temperature that solubilizes chromium into slag glass (Eksteen et al., 2011; Du Preez, 2010). This is typically accompanied by a hybrid design of furnace plate coolers and graphite waffle coolers on the lower and upper sidewalls of the furnace. Some smelters use this with temperature monitoring systems in the form of fibre-optics to monitor the wear of liners and tap-holes of the furnace (Shaw et al., 2012; Eksteen et al., 2011). However, higher energy inputs and the regular maintenance required remain the major drawbacks of the technology. Other pyrometallurgical solutions that have not found industrial application include metallic alloy smelting that uses an iron-rich alloy as a PGM collector (Jones and Geldenhuys, 2011; Jones et al., 2009; Jones and Kotze, 2004), a selective solidification process that involves the tapping of the spinel layer (Barnes and Newall, 2006), and the modification of smelting conditions by adding reductants.

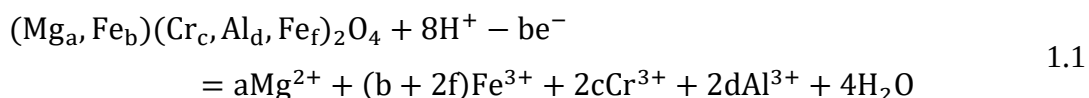
To date, the PGM industry has not explored a hydrometallurgical technology to reduce chrome in UG-2 flotation concentrates. A hydrometallurgical process prior to pyrometallurgical stages has the potential to reduce the chrome content due to the chemical reactivity of chromium in acidic or alkaline environments. Thermodynamically, it is possible to dissolve chromium (Cr) into various soluble species and compounds under oxidising or reducing conditions at low and high pH environments.

The alkaline process route has historically found application in the production of chromium salts from the primary resources of chrome. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) of 50-60 wt.% concentrations under leaching temperatures of 200-320°C, are generally used in the alkaline process in the presence of pure oxygen as an oxidising agent. The main Cr products produced in this process include various compounds of Cr^{6+} (Chen et al., 2014; Zhang et al., 2016). Apart from the health and environmental safety drawbacks associated with the production of Cr^{6+} , the complex operability and operating cost of the process limits its

compatibility in the overall process value chain to produce PGMs. On the contrary, acidic leaching conditions generally produce Cr species which are tolerable to the health and environmental safety requirements. Under acidic and oxidative environments, Cr extracted from chromite is chemically stable as aqueous Cr^{3+} in the Cr-O-H system. This is typically attainable under pH conditions of less than 3.5 and electrode potential range of -0.4 and 1.5 volts (Takeno, 2005). Typical conditions employed to treat primary resources of Cr include 40-85 (v/v%) sulphuric acid concentration and 140-210°C leaching temperatures (Geveci et al., 2002; Jiang et al., 2014; Vardar et al., 1994).

In this study, a hydrometallurgical option was thus investigated to reduce chrome in Sibanye-Stillwater's Eastern Platinum (EPL) UG-2 flotation concentrate to levels compatible with the stability of the slag glass phase. An oxidative acid leaching process was considered in this study. The circular three-electrode furnaces used at Sibanye-Stillwater's smelter can efficiently process furnace feed containing approximately 1.8 wt.% and below of chrome due to their high hearth power densities. EPL flotation concentrates typically contain 3-5 wt.% chrome grade depending on the efficiency of the upstream unit operations. The material used in this investigation contained 3.6 wt.% chrome grade, suggesting that the target of 50% Cr extraction will suffice to reduce chrome to the desirable 1.8 wt.% using a hydrometallurgical leaching process.

Sulphuric acid was selected as the main lixiviant in this investigation due to its strong oxidizing properties, effective solubilization of metals, cost efficiency, environmental safety and ease of use. Pure oxygen was chosen to re-inforce an oxidative environment required to fasten the decomposition rate of the chromite spinel structure. The typical process chemistry for chromite dissolution entails the hydrogen ions reacting with the divalent metals in the tetrahedral site, followed by the dissolution of the trivalent metals in the octahedral site of chromite. Equation 1.1 shows the typical chemical dissolution of chromite under oxidative acid leaching conditions:



Where a, b, c, d and f are coefficients; $a + b = 1$ and $c + d + f = 1$.

This reaction brings the metallic contents of chromite into the bulk solution in similar proportions to their formation in the crystal lattice structure (Biermann and Heinrichs, 1960).

The primary objectives of this study, therefore, include the identification of significant factors that drive the dissolution of Cr from chromite, optimisation of the identified significant factors, and the evaluation of the effect of solid-to-liquid ratio (pulp density) using optimum leaching conditions. The evaluation of pulp density is critical for determining the compatibility of the proposed acid leaching process in the smelter complex. Designing and operating a leaching plant for low pulp densities in the PGM smelter operations may have the following potential drawbacks:

- Increased retention time (backlogs) of material in the smelter. This may negatively impact the flow of material to the downstream hydrometallurgical unit operations (refineries).
- High capital costs and intense engineering design.
- High operating costs emanating from high leaching reagent consumptions.

Process factors investigated in the study include acid concentration, leaching time, leaching temperature and oxygen flowrate. The key benefits associated with the acid leaching unit operation prior to smelting would be improved energy efficiencies and high PGM recoveries due to low viscosity, increased refractory life-span and high furnace utilization as a result of improved furnace availability.

It is expected that under the same sulphate system favourable for Cr dissolution, Ni and Cu base metals will form soluble sulphate salts, which will go into solution where they can be purified en route to the base metal refinery. A proposed process flowsheet indicating the proposed acid leaching and purification circuits for Cr recovery and base metal purification is shown in **Figure 1.1**. This figure indicates how the acid leaching (green box) and purification (marked yellow) circuits can be integrated into the existing process value chain for PGMs and BMs production. The residue from the acid leaching circuit is proposed to be charged into the existing pyrometallurgical unit operations marked in red in **Figure 1.1**. The residue can either

be charged directly in the smelting stage depending on the Cr_2O_3 grade or it can be blended with Merensky type of material. The purified solution enriched in Ni, Cu, and traces of leached PGMs, is proposed to be charged in the first leaching stage of the base metal refinery (grey).

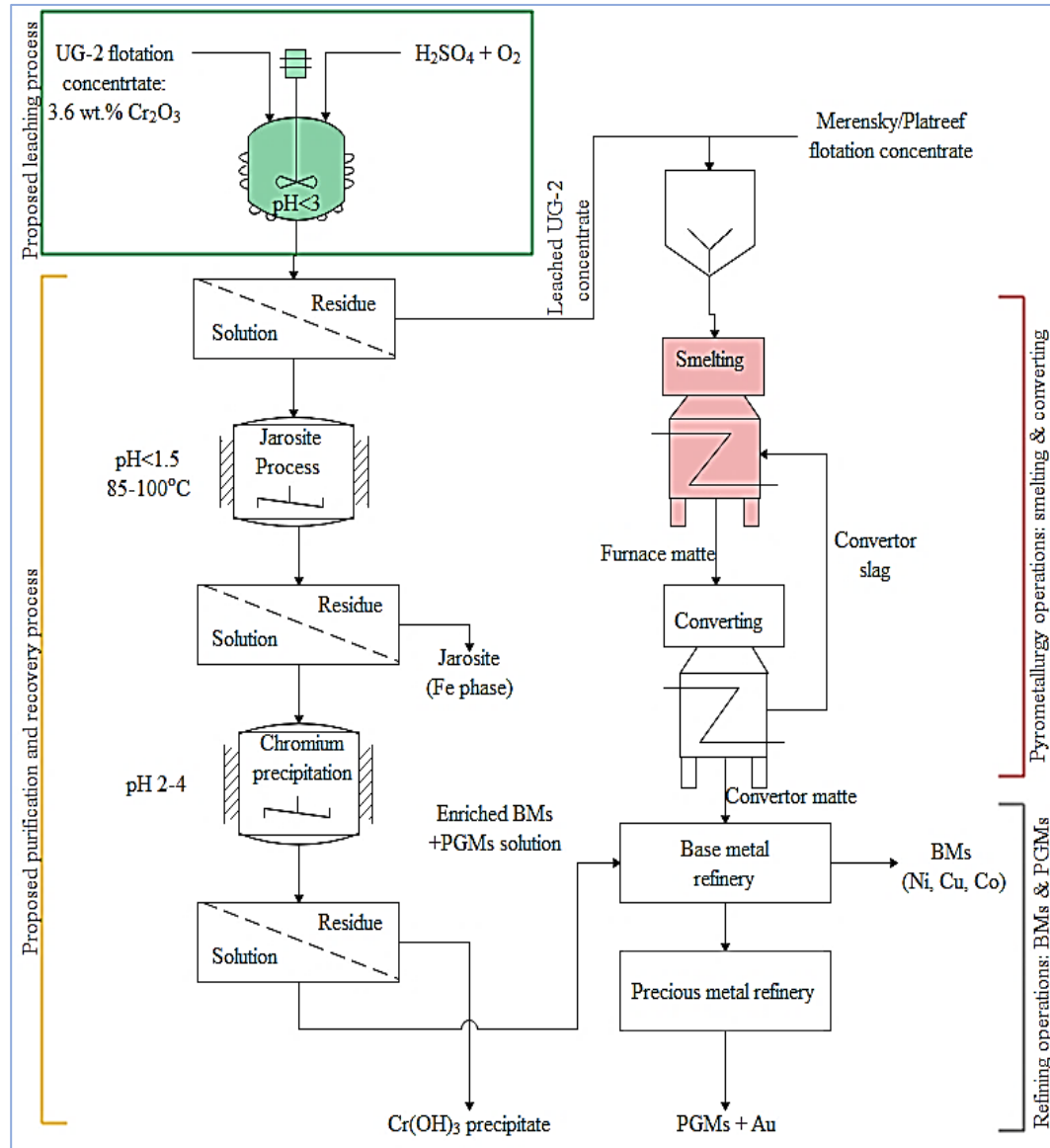


Figure 1.1: Proposed process flowsheet.

1.2 Problem Statement

The conventional PGM furnace technology used at Sibanye-Stillwater smelter complex can competently process smelter feed material comprising Cr_2O_3 grades less than 1.8 wt.%. Above this limit, the solubility of Cr_2O_3 to deport to the slag glass phase is significantly reduced,

resulting in the formation of the unwanted semi-liquid layer containing refractory Cr_2O_3 spinel phases. The overall negative effects of the formation of the refractory spinel phases are low PGM recoveries due to the inefficient process operability and heightened specific energy requirement for smelting, which increases the operating costs.

1.3 Aim

The primary aim of this research project is to investigate the feasibility of the application of a hydrometallurgical leach process to reduce chrome in UG-2 flotation concentrate to < 1.8 wt.% levels that are deportable to the slag glass phase in conventional PGM furnace processes.

1.4 Objectives

The aim of the project will be achieved through the following objectives:

- To develop a sulphuric acid leaching process capable of extracting chromium in UG-2 concentrates.
- To identify significant process factors that influence the dissolution of chromium.
- To determine optimum leaching conditions suitable for chromium extraction.
- To evaluate the effect of the solid-to-liquid ratio on chromium extraction under optimum conditions.

1.5 Research Methodology

The research methodology adopted for this study includes the following: literature survey, statistical design of experiments, batch leaching tests, analysis of test results, conclusions and recommendations.

1.6 Dissertation Structure

Chapter 1 *Introduction*: The introductory chapter provides a brief background and motivation to the research study; problem statement, the primary project aim and objectives.

Chapter 2 *Literature Survey*: This section of the study firstly reviews the geology and mineralogy of PGM-bearing ores in the Bushveld Igneous complex. Secondly, it reviews specific unit operations of the process value chain currently used to beneficiate the PGM ores,

i.e., comminution, flotation, smelting and converting. The last section of the chapter reviews the properties and chemistry of chromium in Cr-O-H system, and it concludes by summarising previous research work done under alkaline and acidic conditions.

Chapter 3 *Materials and Methods*: This chapter presents the classification and composition of the material used in the experiments. This includes particle size distribution, ASEM bulk modal mineralogy and the XRF chemical composition. The experimental methods for conducting experiments include one-factor-at-a-time (OFAT) and statistical design of experiments (DOE). The tested process factors include acid concentration, leaching time, leaching temperature and oxygen flowrate.

Chapters 4 to 6 *Results and Discussions*: Chapter 4 presents results and discussions of preliminary experiments. This is followed by Chapters 5 and 6 that present the identification of significant process factors and optimisation of leaching conditions, respectively.

Chapter 7 *Conclusions and Recommendations*: This chapter discusses conclusions and makes recommendations on various aspects of the study.

All materials referenced in this dissertation are listed under the references section.

Chapter 2

LITERATURE SURVEY

2.1 General Introduction

The first section of this chapter discusses the mineralogical differences between the three narrow-mineralised horizons of the Bushveld Igneous Complex (BIC), which host the largest resources of Platinum Group Metals (PGMs) in the world. These include the Merensky reef, the Upper Group Two reef (UG-2), and the Platreef. The subsequent sections of the chapter describe the current metallurgical unit operations used to beneficiate these PGM-bearing ores, i.e., comminution, flotation, smelting, and converting. Finally, the chapter concludes by highlighting the properties and chemistry of chromium in the Cr-O-H system. The chapter also highlights case studies of previous research work done under alkaline and acidic conditions.

2.2 Bushveld Igneous Complex (BIC)

There are four known layered igneous intrusions in the world that are considered as the primary sources of PGMs and other related value metals. These include the Bushveld Igneous Complex (BIC) in SA, the Great Dyke in Zimbabwe, the Norilsk Complexes in Russia, and the Stillwater Complex in the USA (Cawthorn, 1999; Schouwstra and Kinloch, 2010; Stribny et al., 2000). Among the four, BIC is the world's largest known igneous layered intrusion with an estimated total regional area of 66 000 km² (Cawthorn and Walraven, 1997; Kinnaird, 2005; Penberthy, 1999; Viljoen, 2016; Von Gruenewaldt et al, 1985). The isotope data estimate the formation of BIC to have occurred approximately 2.06 billion years ago (2.06 Ga) (Kinnaird, 2005; Viljoen, 2016; Von Gruenewaldt et al, 1985).

The BIC largely comprises three different types of rock groups. These include the volcanic Rooiberg Group that is dominated by thick Felsic rocks, the Lebowa Granite Suite containing Granophyric facies, and the Rustenburg Layered Suite (RLS) comprising mafic/ultramafic rocks (Cawthorn and Walraven 1998; Kinnaird, 2005; Opoubou-Lando, 2009; Viljoen, 2016). The RLS is the most economically important group as it hosts the largest estimates of resources and reserves of PGMs, Chromium (Cr) and Vanadium (V) in the world. The RLS is mainly exposed in the Western, Eastern and Northern Limbs of the BIC as shown in **Figure 2.1**. The

figure also shows other dominant rock groups and the distribution of the mineralised horizons containing valuable minerals (Cawthorn and Walraven, 1998). The Western and Eastern Limbs are characterised by similar stratigraphy and distinctive lithology that correlates over 320 kilometres (km) from west to east (Kinnaird, 2005; Cawthorn and Walraven, 1998).

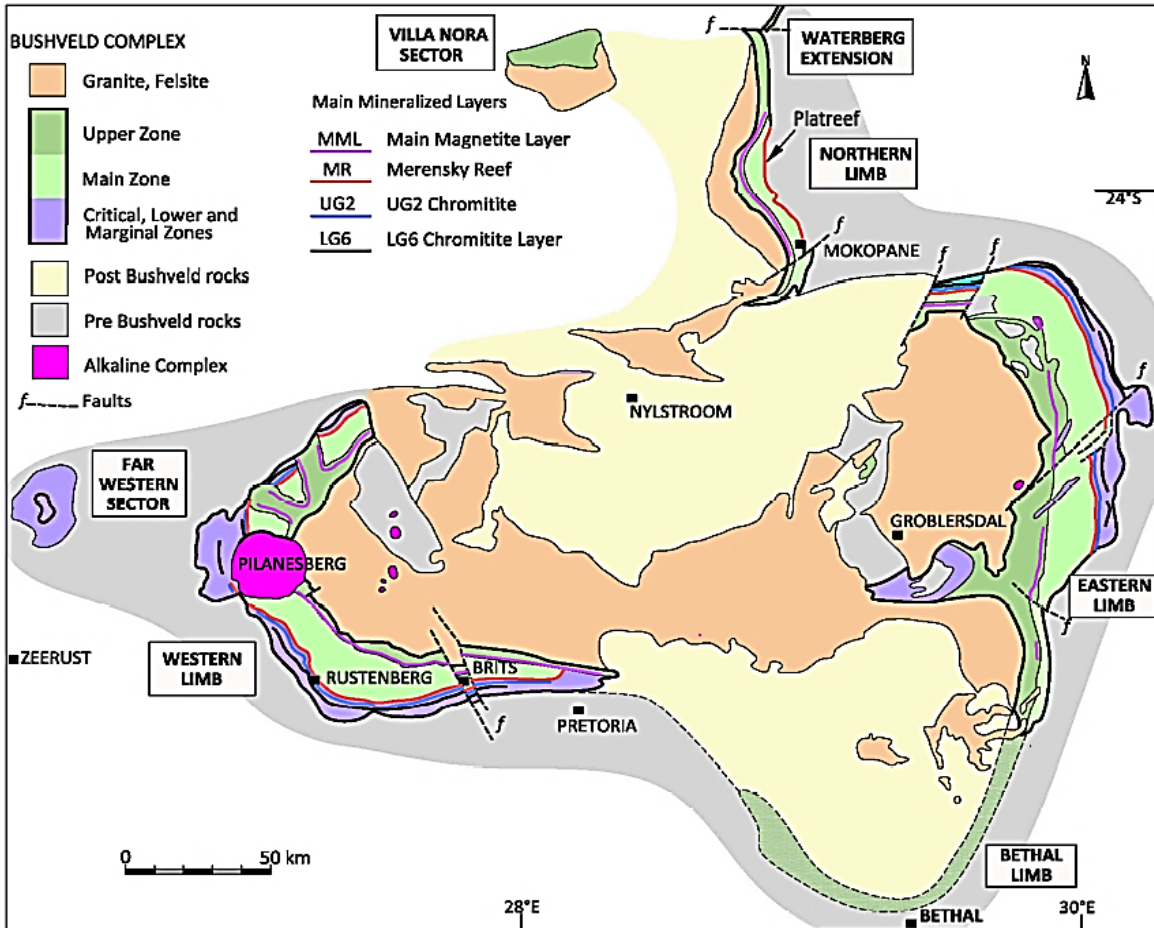


Figure 2.1: Aerial geological map of the Bushveld Igneous Complex illustrating the dominant rocks and distribution of value-bearing mineralised horizons (Cawthorn and Walraven, 1998).

The stratigraphy of RLS in the west and east is subdivided into five well-developed zones that sum up to a total average thickness of 7 km (**Figure 2.2**). The series of zones include Marginal Zone, Lower Zone, Critical Zone (lower and upper), Main Zone, and Upper Zone (Viljoen, 2016). **Figure 2.2** also lists major rock types characterising each zone. The Marginal Zone forms the base of the RLS and it contains norite and feldspathic pyroxenite as the major rock types (Viljoen, 2016). This is typically followed by the Lower Zone, which is mainly comprised of orthopyroxenite, harzburgite and dunite as the major rock phases (Kinnaird, 2005).

Superimposing the Lower Zone is the Critical Zone that contains well-defined mineralised horizons of enriched Cr and PGMs in interlayers of pyroxenite, norite and anorthosite phases (Viljoen, 2016). The lower part of the Critical Zone hosts mainly chromitite reefs that include Lower Groups (LG) 1-6 and Middle Group (MG) 1-3; while the upper part of the Critical Zone hosts the economically important PGM-bearing UG-2 (chromitite) and Merensky reefs. Overlying these economic zones is the Main Zone that comprises gabbro and norites. The Upper Zone forms the top part of RLS with gabbro and olivine-norite as major rock types. This zone hosts the mineralised lower magnetite layers (LML) and the main magnetite layer (MML) (Cawthorn and Walraven 1998; Kinnaird, 2005; Opoubou-Lando, 2009; Viljoen, 2016).

The stratigraphic lithology of the Critical Zone (of RLS) in the Northern Limb does not correlate directly with those characterising the Western and Eastern Limbs. The lowermost part of the stratigraphy is mainly dominated by the ultramafic pyroxenite unit, which is also referred to as the Platreef (Hutchinson and Kinnaird, 2005). This hosts the important PGMs resources, which are associated with the mineralised sulphidic value minerals i.e., pentlandite, chalcopyrite, pyrrhotite, pyrite, etc. North of the limb, the pyroxenite unit is in direct contact and transgresses basement Archean granite and gneiss, while in the south part this occurs on the sediments of the Transvaal Super group (Viljoen, 2016; Cawthorn and Walraven, 1998). The hanging wall to the unit is the Main Zone with the gabbro norite facies. Consistent with the Western and Eastern Limbs, this is overlaid by the Upper Zone. The average thickness of the unit is 2 km, with a large variation of gabbro norite, harzburgite and pyroxenite sequences (Hutchinson and Kinnaird, 2005; Viljoen, 2016).

In totality, the Critical Zone of the RLS is estimated to contain approximately 90 % of the global resources of PGMs; and the chromite resources are estimated to be 75 %. Vanadium resources in the Upper Zone are estimated at approximately 45%. The large resources of PGMs are primarily found and extracted in the planitiferous UG-2, Merensky and Platreef ores (Cawthorn, 1999; Cawthorn and Walraven, 1998).

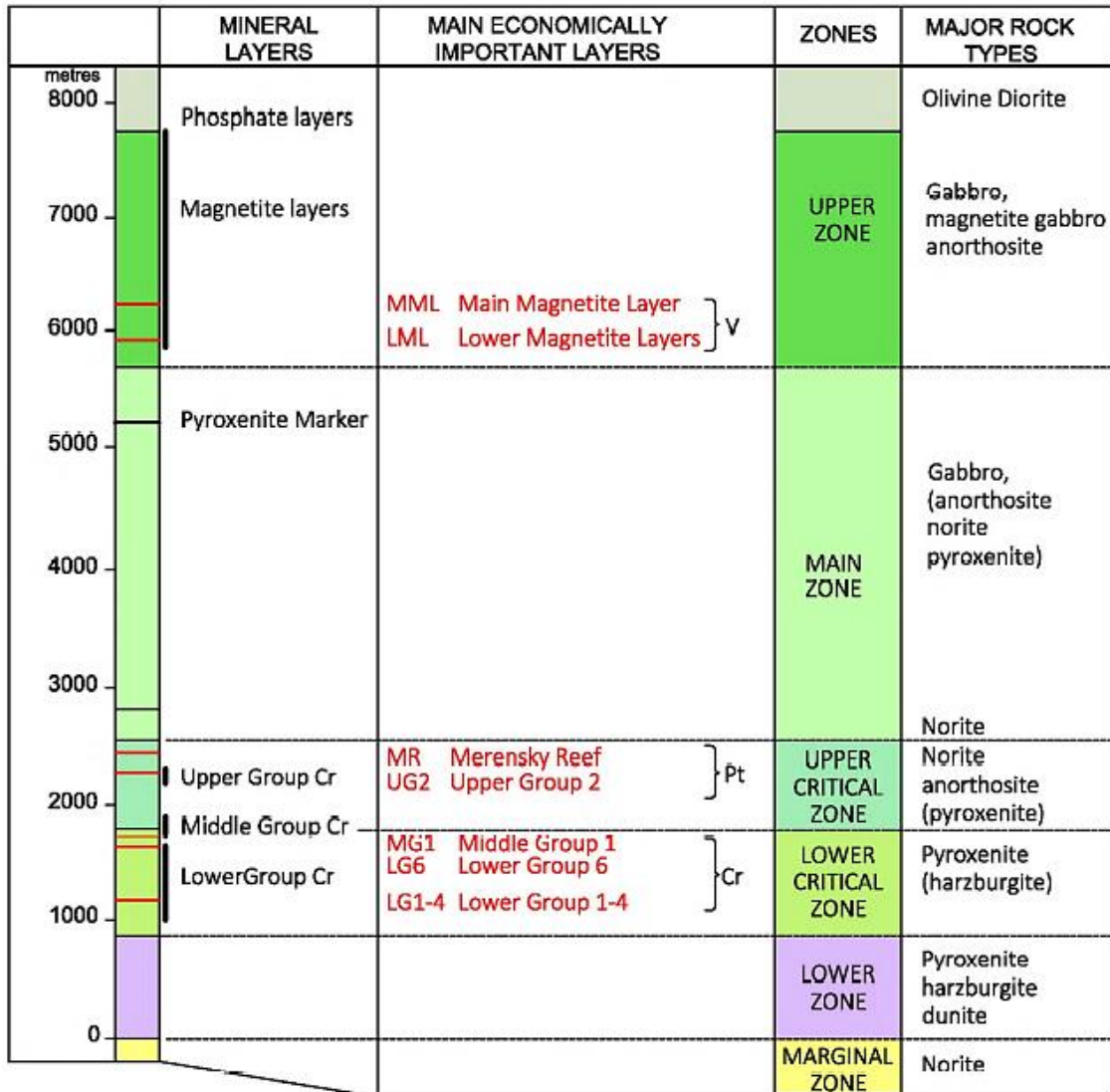


Figure 2.2: Schematic cross-section of the Rustenburg Layered Suites (RLS) with the highlighted major five zones, rock types and mineralised horizons (Viljoen, 2016).

2.2.1 The Merensky Reef

The advent of large-scale platinum production in SA since 1928 has been primarily based on the exploitation of the Merensky reef. Prior to the full exploitation of UG-2 chromitite layer, the Merensky reef was classified as the most important source of PGMs in the world (Cawthorn and Walraven, 1998; Kinloch, 1982; McLaren and De Villiers, 1982). The enriched mineralised reef is located at the top section of the Upper Critical Zone in the Western and Eastern limbs of the BIC. In the west, the average PGM grade is 8-9 g/t, while in the east it is about 7 g/t (Cawthorn and Walraven, 1998; Kinloch, 1982; Viljoen, 2016). These grades typically vary

with the thickness of the reef, in which, the highest grades are found in locations where the reef is thin. The reef is typically characterised by chromitite stringers of 1-2 cm thickness, which occurs in the transgressive pyroxenite layer (Cawthorn and Walraven, 1998; Kinnaird, 2005; Viljoen, 2016). The thin chromitite stringers (2-4 cm) are generally used as indicators to identify parts of the reef that are highly concentrated in PGMs, and they often define the lower and upper limits of mineralisation (Cawthorn and Walraven, 1998; Kinnaird, 2005; Viljoen, 2016). The strike of the Merensky reef is traceable for distances of more than 280 km with inward dip strikes of 8° to 27° in the Western limb and up to 65° in the Eastern limb (Kinnaird, 2005; Viljoen, 2016). The reef thickness varies from 0.1 and 4 m across the stratigraphy of the complex (Kinnaird, 2005; Viljoen, 2016). The lithology forming the hanging and foot walls to the reef vary with the geological locations in the BIC. The pyroxenite and norite/anorthosite commonly form the hanging and foot walls of the reef, respectively (Cawthorn and Walraven, 1998; Kinloch, 1982).

In contrast to UG-2 reef, the total amount of sulphide minerals in the Merensky reef is relatively higher (McLaren and De Villiers, 1982; Penberthy et al., 1999). The main sulphide phases in this reef are identified as pyrrhotite (41 %), pentlandite (37%), chalcopyrite (18%) and pyrite (4%) in most locations. Sphalerite, galena and sulpharsenides are identified in other locations as minor sulphide minerals (Kinnaird, 2005; Merkle and McKenzie, 2002; Penberthy and Merkle 1999; Vermaak, 2006; Viljoen, 2016). These sulphides are generally associated and found in matrix of silicate and chromite as interstitial blebs. The particle size distribution and texture of these sulphide accumulations range from coarse particles (0.5-1 cm) in the pegmatiodal pyroxenite to finely disseminated particles in the hanging wall pyroxenite (Kinnaird, 2005; Merkle and McKenzie, 2002). The platinum group minerals of the reef are mainly associated with sulphide minerals and partly with the silicate gangue minerals (Cawthorn and Walraven, 1998; Merkle and McKenzie, 2002).

The mineralogical assemblage of platinum group minerals of the reef is predominated by PGM-sulphides (60 %), PGM-tellurides (11 %), arsenide and sperrylite ((Pt, Rh)As₂) (6 %) (Penberthy and Merkle, 1999). The sulphide fraction is mainly dominated by Pt-Pd sulphides, i.e. braggite ((Pt,Pd,Ni)S) and cooperite (PtS). In some regions, moncheite ((Pt,Pd,Ni)(Te,Bi,Sb)₂), laurite (Ru) and merenskyite (Pd,Pt,Ni)(Te,Bi,Sb)₂ are formed as part

of the major platinum group minerals (Merkle and McKenzie, 2002; Penberthy and Merkle 1999; Vermaak, 2006). The PGM-alloys and gold-silver phases form the balance fraction of the valuables' distribution. The PGM-alloys, Pt-Fe alloy-dominant, commonly characterises PGM mineralogy in regions where the geological profile of the reef is dominated by potholes (Viljoen, 2016; Kinnaird, 2005). Other phases include Palladian electrum (Au, Ag, Pd, Cu) and gold electrum (Au-Ag) (Merkle and McKenzie, 2002; Penberthy and Merkle 1999; Vermaak, 2006).

In general, the Merensky reef largely comprises rocks ranging from heterogeneous pegmatiodal feldspathic pyroxenite to pure feldspathic pyroxenite (Cawthorn and Walraven, 1998; Kinnaird, 2005; Viljoen, 2016). The orthocumulate rock unit is typically composed of orthopyroxene (70-90 wt.%) as the major mineral phase (Dzvinamurungu et al. 2013; Merkle and McKenzie, 2002; Schouwstra et al. 2000; Vermaak, 2006). The grain size is normally coarse, with a grain texture that ranges from subhedral to euhedral. The second major mineral phase is plagioclase, which inter-cumulates up to 30 wt.% (Penberthy and Merkle, 1999). Other phases such as Clinopyroxene and mica are present as common accessories (McLaren and De Villiers, 1982; Penberthy et al., 1999).

The mineralogical characteristics of Merensky ore are generally considered as ideal for processing using the conventional processing technologies and methods developed over the past nine decades for PGM production in SA. Despite the high mining costs due to its relatively low density, Merensky ore is generally amenable to conventional flotation, smelting and refining unit operations.

2.2.2 The Upper Group Two Reef (UG-2)

The UG-2 chromitite layer is appraised to host a bulk of PGM resources in the BIC (Cawthorn, 2010; Cawthorn 1999; Kinnaird, 2005; Schouwstra et al., 2000). Its geological variations in the Western and Eastern Limbs are similar along the strike of approximately 280 km. The strike of the UG-2 layer is also traceable for distances of more than 280 km, with inward dip strikes of 8° to 27° in the Western limb and up to 65° in the Eastern limb (Kinnaird, 2005; Viljoen, 2016). The average thickness of the UG-2 layer typically varies between 0.5 and 1.5 m, and it is located below the Merensky reef at parallel depths of 15-400 m (Kinnaird, 2005; McLaren and De

Villiers, 1982; Viljoen, 2016). The footwall to the UG-2 layer mainly consists of pegmatoidal feldspathic pyroxenite and rarely anorthosite, while the hanging wall is characterised by feldspathic pyroxenite and harzburgite (Viljoen, 2016). The PGM grades of the layer are estimated to be 6-8 g/t depending on the geological location in the reef. Stratigraphically, these PGM grades are mainly concentrated at the top and bottom seams of the UG-2 layer (Cawthorn, 1999; Kinnaird, 2005; Viljoen, 2016). It is thus common that the mining of the UG-2 layer will include fractions of rocks forming the footwall and hanging wall.

The bulk mineralogy of the UG-2 chromitite layer is predominantly composed of chromite (60-90 wt.%) as the abundant mineral; and the chromium oxide (chrome) content is averaged at 43.5 wt.%. The average ratio of Cr to Fe ranges within 1.26-1.4 (Kinnaird, 2005; Mondal and Mathez, 2007; Viljoen, 2016). Other major minerals which form as interstitial phases include pyroxene (5-25%) and plagioclase (<5%). The base-metal sulphide (BMS) minerals in the UG-2 are present in trace amounts (<0.1%) (Penberthy and Merkle, 1999; Vermaak, 2006). The most abundant valuable sulphide minerals include pentlandite and chalcopyrite, while pyrrhotite, pyrite, arsenopyrite and millerite are present as the important secondary valuable minerals. The particle size of sulphide minerals in the UG-2 is typically measured to be fines of less than 30 microns (μm) (Penberthy et al., 1999). Their presence mainly occurs at the grain boundaries of chromite (87 %) and within chromite and silicate minerals (13 %) (McLaren and De Villiers, 1982; Penberthy et al., 1999).

The platinum group minerals' assemblage in the UG-2 ore is mainly dominated by PGM sulphides and some fraction of PGM non-sulphides, which depend on the extent of the post-magmatic evolution of the reef (Penberthy et al., 1999; Schouwstra et al., 2000; Vermaak, 2006). The common PGM sulphide minerals found in the UG-2, include braggite ((Pt, Pd)S), cooperite (PtS), malanite ((Pt, Rh, Ir)₂CuS₄), laurite ((Ru, Os, Ir)S₂), and occasionally vysotskite (PdS). The PGM non-sulphides fraction varies extensively between PGM alloys (Pt-Fe and Pt₃Fe), tellurides, bismuth tellurides, bismuthinides, PGM-arsenide, sulpharsenides and other rare minerals such as rustenburgite (Pt₃Sn), geversite (PtSb₂), arsenopalladinite (Pd₈(As, Sb)₃), plumbopalladinite (Pd₃Pb₂), potarite (PdHg), and isomertierite (Pd₁₁Sb₂As₂) (Cawthorn 1999; Mondal and Mathez, 2007; Penberthy et al., 1999; Schouwstra et al., 2000; Vermaak, 2006).

The grain size of these PGM phases is generally equivalent at different geological locations of the BIC. Despite the limitations of the analytical techniques that are used to measure grain sizes on polished thin sections, the grain size of PGM-minerals is mostly less than 10 microns (μm) (Penberthy et al., 1999; Vermaak, 2006). A bulk of these minerals is formed as discrete phases and also locked in base metal sulphides and gangue minerals (chromite and silicates) (McLaren and DeVilliers, 1982; Mondal and Mathez, 2007; Penberthy et al., 1999; Vermaak, 2006). The mode of occurrence and association with these phases involve inclusion, solid solutions and formation on grain boundaries (Penberthy et al., 1999).

The UG-2 ore's distinctive mineralogical properties delayed its full exploitation until the 1970s. Its inherent high chromite and low sulphide mineral grades have rendered the ore material not fully amenable to the conventional PGM processing methods, in particular, the smelting processes. The limitations of this unit operation are fully highlighted in Chapter 1.

2.2.3 The Platreef

The Platreef, in the Northern limb of the BIC, is the only economically important horizon of the RLS (Hutchinson and Kinnaird, 2005; Langa et al., 2021). Its thickness is more than that of the UG-2 and Merensky reefs. However, its lateral extension is shorter (Hutchinson and Kinnaird, 2005). The thickness of the Platreef in the northern part reaches a maximum 50 m, while in the southern part the reef varies from 400 m. The Platreef strikes north-south, and its lateral extension is approximately 35 km with a dip of 40-45° to the west (Langa et al., 2021; Kinnaird, 2005; Viljoen, 2016).

The Platreef is a heterogeneous mostly pyroxenitic zone with subordinate amounts of peridotites, norites and anorthosite cycles (Kinnaird, 2005; Viljoen, 2016). The suite has a common occurrence of hornfelsed (baked) country rock xenoliths. Compared to the Merensky and UG chromitite reefs, the Platreef has a typical grade of 4 g/t of PGMs, especially in sections where the footwall is dolomite and varies between 1-2 g/t elsewhere (Kinnaird, 2005; Viljoen, 2016).

Different mineralisation styles are found to exist in the Platreef. The sulphide minerals are disseminated, or net-textured, ranging from a few microns to 2 cm grains of pyrrhotite and

pentlandite with chalcopyrite and minor pyrite (Langa et al., 2021; Viljoen, 2016). The bulk of the sulphide minerals is reported to mostly occur towards the contact boundary with the footwall metasedimentary rocks of the Transvaal Supergroup. The PGMs in this reef mainly occur as PtFe, Pt₃Sn and variable Pd or Pt-tellurides, bismuthides, arsenides, antimonides, bismuthoantimonides and complex bismuthotellurides (Langa et al., 2021; Kinnaird, 2005; Viljoen, 2016).

The mineralogical characteristics of the Platreef are similar to those of the Merensky reef, and as a result, their beneficiation processes are fundamentally similar.

2.3 Extractive Metallurgy

The beneficiation process of the three PGM-bearing ores in SA typically involves a process value chain comprising distinct but interlinked major unit operations. The major key unit operations, in ascending order of application, include:

- i. Comminution (crushing and milling) - size reduction.
- ii. Froth flotation - physical and physiochemical separation of value minerals from gangue.
- iii. Pyrometallurgical operations (smelting and converting) – production of an upgraded Ni-Cu-PGMs matte.
- iv. Base metals refinery (BMR) - extraction and recovery of Ni, Cu and Co; and upgrading of PGMs.
- v. Precious metals refinery (PMR) – production of individual PGMs.

A generic process flowsheet of the distinct interrelated unit operations for PGM concentration and refining is illustrated in **Figure 2.3**. The figure also shows estimates of PGM grades at various stages of the process value chain. A descriptive summary of some of the processing stages is presented in sections 2.3.1-2.3.3.

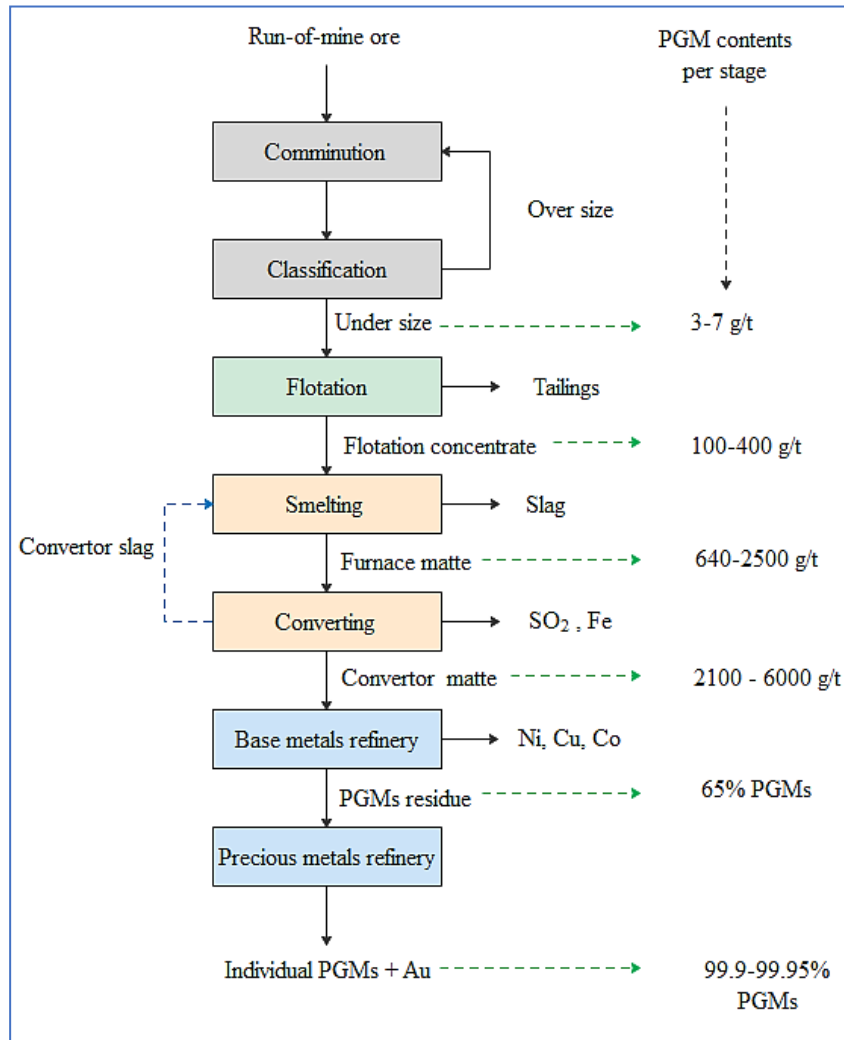


Figure 2.3: Generic process flowsheet of the interrelated unit operations of PGM concentration and refining

2.3.1 Comminution

The comminution stage forms the important first stage in the processing of Merensky, UG-2 and Platreef ores. This stage aims to liberate the platinum group minerals for optimum recovery in the subsequent flotation unit operation (**Figure 2.3**).

The comminution of the three PGM-bearing ores generally involves the crushing and milling circuits. These circuits, together with intermediate screens and hydro-cyclones, are employed to mechanically reduce PGM run-of-mine into size fractions which are manageable as well as to achieve ideal liberation of valuable minerals (Wills and Finch, 2015). Various process equipment and circuit configurations are employed depending on the mineralogical properties

of the ore type and hardness. The crushing circuits involve a configuration of either jaw crushers, gyratory crushers, and/or a series of cone crushers. In other operations, high-pressure roller (HPR) crushers and autogenous/semi-autogenous (AG/SAG) mills are used as part of the primary comminution circuits (Wills and Finch, 2015). The milling circuit commonly involves a conventional tumbling mill with steel balls as grinding medium. Each of the comminution stages is typically enclosed with vibrating screens and/or hydro-cyclones. In other plant set-ups, spiral plants are used to remove and prevent the over milling of dense minerals such as chromite.

The comminution properties of PGM-bearing ores in the BIC are shown in **Table 2.1**. The grindability of the ores is defined in terms of bond work index (BWI) (Powell and Mainza, 2006; Solomon, 2011; Wills and Finch, 2015). The BWI of the UG-2 ore is generally lower compared to the BWI of the Merensky reef and Platreef (Hay and Roy, 2010; Solomon, 2011). This is consistent across various size fractions of the ores. The hardness characteristics of the UG-2 ore are classified as softer and the material is friable compared to the latter ores (Liddell et al., 1986).

Table 2.1: Comminution properties of 3 PGM-bearing ores in the BIC (Powell and Mainza, 2006).

Ore type	BWI at 300 μm (kWh/t)	BWI at 75 μm (kWh/t)
Merensky reef	21	25
UG-2 reef	18	21
Platreef	18-25	23-27

2.3.2 Flotation

Froth flotation is considered as one of the most important minerals processing techniques in the beneficiation of the 3 PGM-bearing ores in SA. The technique is used at the concentrator plants to upgrade the PGMs from run-of-mine via separating valuable minerals from unwanted minerals (gangue). This process follows the comminution stage as shown in **Figure 2.2**.

Wills and Finch (2015) define flotation as “a physico-chemical separation process that utilises the difference in surface properties of the valuable minerals and the unwanted gangue

minerals”. The separation process normally occurs in aqueous media, which involves a three-phase system, i.e., water, air bubbles and solid particles. Flotation is well known as the most selective process, and its selectivity is generally a function of the hydrophobicity and hydrophilicity properties of minerals (Vignes, 2013; Wills and Finch, 2015). Suspended hydrophobic minerals in the pulp phase have the affinity to attach to air bubbles and form a particle-bubble aggregate, which is transported to the froth phase and subsequently recovered at the concentrate launder (Wills and Finch, 2015). This mechanism is mainly attributed to the low wettability degree of hydrophobic particles. In contrast, hydrophilic minerals have a high wettability degree, which results in particles being hydrated and reporting to flotation tailings (Wills and Finch, 2015). The main mechanisms of minerals’ recovery in the flotation processes include

- i. True flotation – hydrophobic minerals selectively adhere onto air bubbles and are transported to the froth phase.
- ii. Mechanical entrainment – fine particles recovered in the flotation water which passes through the froth.
- iii. Physical entrapment in a non-draining froth or sticky froth.

Over the years, the processing route of PGM ores in SA has evolved into a process configuration entailing a mill-float-mill-float circuit (MF2) as shown in **Figure 2.5**. The evolution of the plant circuits has been largely influenced by the increase in mining and processing of UG-2 ores. The MF2 circuit has been widely adopted to improve the overall plant (PGMs) recoveries, which is a function of mineralogical properties of the ores. The operational philosophy of the circuit generally entails milling coarser in the MF₁ circuit to liberate coarse grained value minerals and milling finer in the MF₂ circuit for optimal liberation of fine-grained value minerals. The Merensky and Platreef ores, however, can simply be processed with a circuit configuration that involves a mill-float (MF₁) due to the coarse grain sizes of platinum group minerals in these ores. The milling degree required to achieved optimal liberation of these platinum group minerals is historically estimated to be 55-65% passing 75 µm (Cole and Ferron, 2002; Hay and Roy, 2010; Valenta and Mapheto, 2011).

In contrast, the grain size of platinum group minerals in UG-2 ore are inherently finer compared to the Merensky ore (and by extension Platreef) as shown in **Figure 2.4**. The MF2 configuration has been found to be more suitable for processing UG-2 ore due to the particle size distribution and mineral association of platinum group minerals of the ore (Merkle et al., 2002). The primary milling stage (MF₁) is normally set at a grind of 35-45% passing 75 µm to liberate sulphides associated with PGMs, while the secondary milling stage (MF₂) is set at a grind of 70-80% passing 75 µm to liberate PGMs locked in silicate and chromite gangue minerals (Cole and Ferron, 2002; Hay and Roy, 2010; Valenta and Mapheto, 2011). On some plants, the MF₂ is commonly reported to be the main source of ultrafine chromite which is typically recovered in flotation concentrate via mechanical entrainment. The mining activities, through blasting, are also reported to contribute to the generation of ultrafine chromite (Liddell and McRae, 1986).

Other secondary mechanisms of chromite recovery involve the entrapment of coarse chromite particles in a non-draining froth phase. This is usually caused by a high proportion of naturally floating gangue or ultrafine particles in the processed material. The type of reagent suite and the amount of flotation reagents used can activate the flotation of chromite via true flotation. The net effect of these recovery processes is high chromite content in the smelter feed. This typically influences slag chemistry in a manner which renders the material not amenable to the traditional smelting processes in the SA's platinum industry.

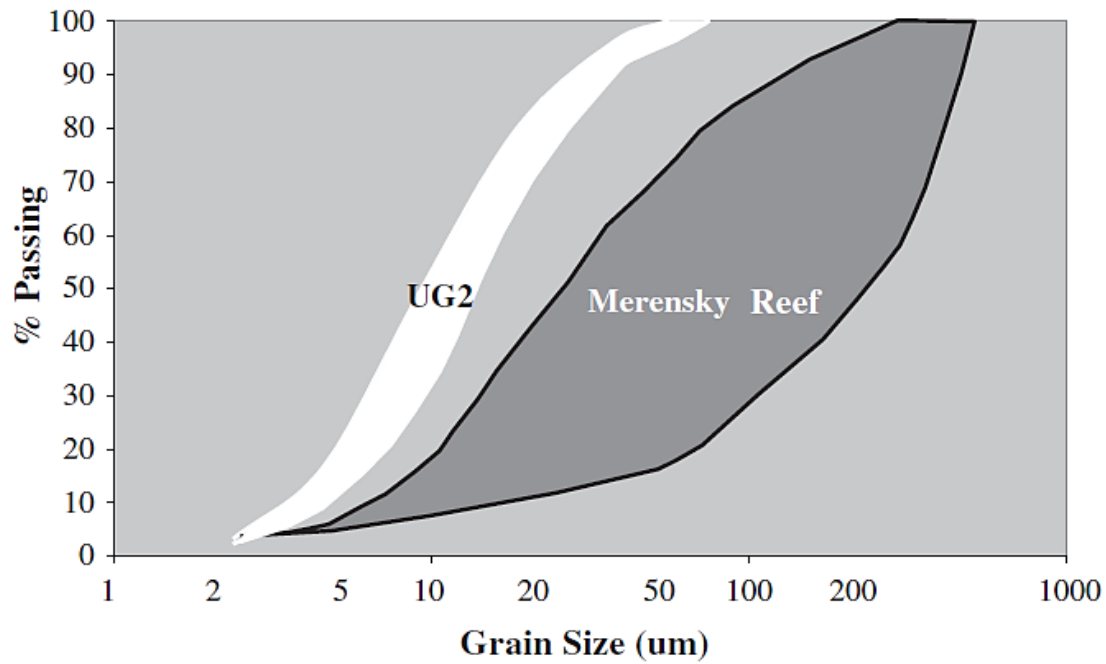


Figure 2.4: Typical grain size of platinum group minerals in UG-2 and Merensky ores (Hay and Roy, 2010).

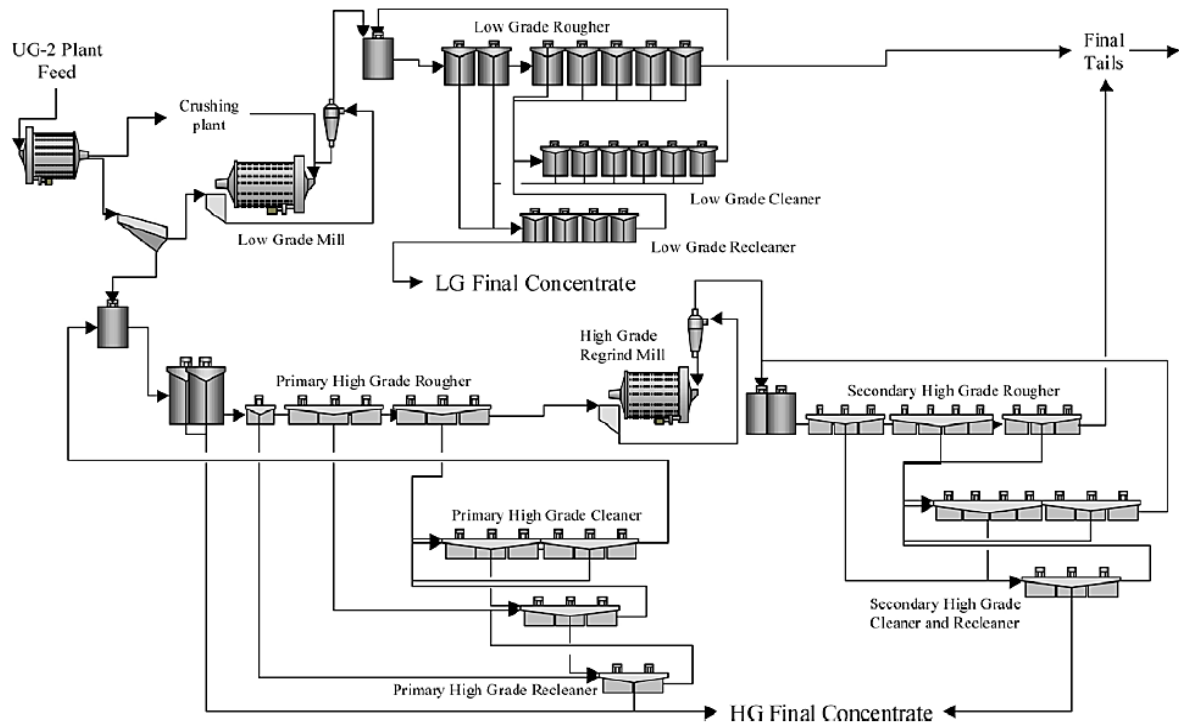


Figure 2.5: Example of MF2 concentrator to beneficiate UG-2 and Merensky ore (Cole and Ferron, 2002).

2.3.3 Pyrometallurgical concentration

The major unit operations which follow the concentration of PGMs via flotation plants are the smelting and converting stages in the smelter complexes. In the smelting unit operation, the base metals (BMs) and PGMs are upgraded into a dense sulphidic furnace matte. Nickel (Ni) and Copper (Cu), as BMs, are upgraded to 10-20 % and 5-15 %, respectively, while the PGMs are upgraded to 650-2600 g/t. The furnace matte is subsequently processed in the converting stage, in which Ni and Cu are upgraded to 45-50 % and 25-35 % respectively in the convertor matte. The PGMs grade in the convertor matte typically varies between 2000 and 6000 g/t (Jones, 2005; Liddell et al., 1986).

2.3.3.1 Smelting of flotation concentrate

The primary PGM smelting processes in SA occur exclusively in electric furnaces; viz. rectangular six-in-line submerged-arc furnaces and circular three-electrode furnaces (Jones, 2005; Lamya, 2007; Shaw et al., 2013). In all smelter complexes that use either of the two designs, the main objective of the unit operation is to form a molten bath comprising immiscible dense sulphidic matte and light oxidic slag phases (Jones, 2005). The slag phase, due to its low relative density of approximately 2.7, characteristically overlies the matte phase of a relative density of approximately 5.2. The matte phase is mainly composed of molten prills of base metals, iron and sulphur that act as PGM collectors, while the slag mainly contains silica and magnesia (Du Preez, 2010; Lamya, 2007).

The smelting technique involves the immersion of furnace electrodes in a bed of furnace feed (concentrate, charge) to form a circuit. Through passing electrical current in the formed circuit, heat is generated by electrical resistance of the charge (slag) (Jones, 2005; Liddell et al., 1986). The electrode depth and the voltage input are generally used to effect temperature control during the smelting processes. The temperature of the slag during smelting varies within 1400-1600 °C, while the matte temperature is reported within 1200-1400 °C (Barnes and Newall, 2009; Eksteen et al., 2011; Liddell et al., 1986; Nell, 2004). The matte and slag temperature differences generally form a temperature gradient which effects the thermal convection and the gravity settling of the matte on the furnace hearth. This is commonly accompanied by the erosion of the furnace liners and refractories (Eksteen et al., 2011; Shaw et al., 2013).

i. Smelting of platinum group minerals

The decomposition of platinum group minerals in the smelting unit operations occurs over a wide range of smelting temperatures. The platinum mineral which starts to decompose is braggite ((Pt, Pd, Ni) S), at the lowest smelting temperature of 600°C. At smelting temperatures of above 1000°C, braggite decomposes into Pt-Pd alloy phases and elemental sulphur (Lamya, 2007; Nell, 2004). The platinum alloys of isoferroplatinum commonly decompose to form alloys of Pt-Pd. The melting points of these alloys are determined by the melting points of the constituted elements, Pt and Fe, which are 1769°C and 1535°C, respectively. These smelting temperatures are noticeably above the practical operating conditions. Other common platinum minerals and their melting points are shown in **Table 2.2**. Many of these minerals are characterised by higher melting points. As a result, lime is added in the furnace feed to lower the high melting points (Biswas and Davenport 1976; Lamya, 2007). The addition of lime also aids in the reduction of melt viscosity for efficient slag-matte separations.

Table 2.2: Common platinum minerals and their melting points.

Platinum groups minerals	Melting temperature (°C)
Sperryrite (PtAs ₂)	1400°C
Cooperrite (PtS)	1175°C
Moncheite (PtTe ₂)	1150°C
Laurite (RuS ₂)	>1000°C
Vysotskite (PdS)	912°C
Merenskyite (PdTe ₂)	740°C
Kotulskite (PdTe)	720°C

ii. Smelting of base metal sulphides

The major base metal sulphide minerals in the flotation concentrates of the PGM bearing ore include pentlandite, pyrrhotite/pyrite, chalcopyrite, etc., as discussed in section 2.1. The melting process of sulphide phases involves a series of solid-state alterations at different smelting temperatures (Biswas and Davenport 1976; Lamya, 2007). At 610 °C, pentlandite becomes unstable and forms solid solutions of heazlewoodite (Ni, Fe)_{3±X}S₂ and monosulphide

($\text{Fe}_{1-x}\text{S} \cdot \text{Ni}_{1-x}\text{S}$). The former melts at 800-900°C to form sulphide liquid and $(\text{Ni}, \text{Fe})\text{S}_2$, while the latter melts at 635°C to form Ni-S compounds and Fe-S at increased temperatures of 912°C. The co-existence of pyrrhotite and chalcopyrite renders the latter to decompose at lower temperatures of 334–450°C. Within this range, chalcopyrite melts are stable over a wide range composition and temperature (Biswas and Davenport 1976; Lamya, 2007).

iii. Smelting of Silicate

Silicate minerals are commonly decomposed into oxidic species, which form a large part of the oxidic slag phase during the smelting of PGM concentrates. These are typically categorised into low and high temperature melting mineral phases. The first mineral phases to decompose are the minor hydrated silicate minerals such as talc, chlorite, serpentine, etc. These minerals are commonly decomposed in the temperature range of 600-900°C through a series of dehydration mechanisms to form silica-rich melts, enstatite and forsterite (Du Preez, 2010; Lamya, 2007). The second type of silicate minerals to decompose are non-hydrated minerals such as pyroxenes, feldspars, and plagioclase in the temperature range of 1000-1500°C (Lamya, 2007). In some smelter operations, it is not uncommon to add calcium oxide (CaO) in the system to reduce these liquidus temperatures (Du Preez, 2010). The pyroxenes typically melt at a temperature of approximately 1250°C through a solid-state transformation to form ferrous wollastonite (Barnes and Newall, 2009; Lamya, 2007; Nell, 2004). Feldspars and plagioclase begin to melt at 1400-1450°C and ends at temperatures of approximately 1480-1520°C. In the presence of diopside, the melting point of plagioclase starts at 1250-1275°C and ceases at approximately 1400°C (Lamya, 2007; Nell, 2004).

2.3.3.2 Converting of furnace matte

The converting unit operation follows the smelting processes as illustrated in **Figure 2.3**. The engineering equipment which finds wide application for this stage is Pierce Smith convertors. Other smelter complexes have also adopted the use of the Ausmelt furnace technology.

In the production of PGMs, the converting process stage is employed to oxidise furnace matte so as to upgrade BMs and PGMs by reducing the iron and sulphur concentrations. The process entails addition of silica, reverts and injection of air as an oxidant. Iron is typically oxidised by oxygen to form iron oxide (FeO), which in turn reacts with silica to form a fayalitic slag (Barnes

and Newall, 2009; Nell, 2004). The sulphur component is oxidised to sulphur dioxide (SO_2), which is recovered as an off-gas to produce sulfuric acid in the acid plant (Eksteen et al., 2011; Shaw et al., 2013). This is common for material of Merensky/Platreef ore as they are rich in sulphidic phases. Fe oxidation reaction is achieved at oxygen potentials of $10^{-8.4}$ and at 1200°C temperature, which is comparable to the general quartz-fayalite-magnetite QFM redox buffer (Du Preez, 2010; Eksteen et al., 2011; Shaw et al., 2013). In this system, Fe forms the most stable oxide and the least stable sulphur compound with respect to base metals. In the work done by Terry (1987), the process of oxidising Ni-Cu-Fe-S mattes by using standard free energies of Ni, Cu and Fe oxides and sulphides are achieved under converting temperatures of 1250 - 1350°C .

In summary, the converter matte is commonly rich in Ni-sulphides, Cu-sulphides, alloys of Ni-Cu, PGMs and a small quantity of unreacted FeS, which settles out of the converter slag due to a higher specific gravity. The converter slag comprises Fe-silicates, dissolved Ni and Cu oxides, and refractory phases such as magnetite. The handling of the final converter matte involves pouring and slow cooling or granulating the matte in water. The slow cooling process of the converter matte allows the crystallization of the metallic Ni-Cu-Fe alloy, which hosts a bulk of PGMs and formation of a nonmagnetic PGM-free Ni-Cu matte phase. The drawbacks of the slow cooling process are the formation of trevorites ($\text{NiO} \cdot \text{Fe}_2\text{O}_3$) and magnetite (Fe_3O_4), which are noticeably insoluble in the leaching stages of the BMR. The granulation of the matte is typically preferred in industry as it does not form the above problematic phases and is more reactive (Steenekamp and Dunn, 1999).

2.4 Properties and the leaching processes of chromium

2.4.1 Chromium

The element chromium (Cr) is the 24th most abundant metal (0.012%) in the earth crust. In nature, it occurs as four stable isotopes, namely, ^{50}Cr , ^{52}Cr , ^{53}Cr and ^{54}Cr . The ^{52}Cr is the most abundant (83.8 %) of these isotopes (Lunk, 2015). Elemental Cr is commonly classified as a transitional metal on the periodic table, with an atomic number 24. It is a member of group 6 of the d-block which includes groups 3-12. Cr is also classified as one of the refractory group

metals which are characterised by melting points that are higher than that of platinum (1772 °C). Its molecular weight is 51.9961 g/mol (Lunk, 2015).

Cr has a wide range of physical properties. In nature, it assumes a body centred cubic (bcc) crustal structure with a unit cell parameter of $a = 291$ pm. Under high temperature conditions, it starts to melt at 1907 °C and boils at 2671 °C. Its density is 7.19 g/cm³, its Mohs hardness is 8.5, and it is also brittle. Chromium's other physical properties include heat of fusion of 210 kJ/mol, heat of evaporation of 347 kJ/mol and molar heat capacity of 23.35 J/mol.K (Lunk, 2015). **Table 2.3** summarises the chemical and physical properties of Cr as well as its abundance in nature (Lunk, 2015).

Table 2.3: Properties of elemental chromium (Cr) and its abundance (Lunk, 2015).

Chromium in the periodic table	Atomic properties	Physical properties	Natural abundance (%) in
Atomic number 24	Electronegativity (Pauling scale) 1.66	Crystal structure	Oceans 6×10^{-8}
Molar mass 51.9961 g mol ⁻¹	Ionization energies (kJ mol ⁻¹)	Body-centered cubic (bcc)	Humans 3×10^{-6}
Group 6; Period 4	1st: 652.9	Cell parameter a : 291 pm	Universe 1.5×10^{-3}
Electron configuration	2nd: 1,590.6	Melting point 1,907 °C	Sun 2×10^{-3}
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$	3rd: 2,987	Boiling point 2,671 °C	Earth's crust 1.4×10^{-2}
	Atomic radius 128 pm	Density 7.19 g cm ⁻³	Meteorites 3×10^{-1}
	Covalent radius 139 ± 5 pm	Heat of fusion	Cr:Mo:W = 100:1:1
		21.0 kJ mol ⁻¹	
		Heat of vaporization	
		347 kJ mol ⁻¹	
		Molar heat capacity	
		23.35 J mol ⁻¹ K ⁻¹	

2.4.2 Chromium aqueous species

The element Cr has an electron configuration of [Ar] 3d⁵ 4s¹. The low energy atomic levels 's' and 'd' are the common cause of Cr's existence in oxidation states of 0-VI in aqueous medium. The most common Cr species in aqueous medium include Cr (II), (III), and (IV). The IV and V oxidation states commonly form as intermediate species in the reduction-oxidation (redox) reactions. These products are disproportionally unstable with respect to Cr (III) and (VI), and they commonly react with alkalis or acids (Beverkog and Puigdomenech, 1997; Lunk, 2015; Vardar, 1994). Thus, in the water systems, the most stable Cr oxidation states are Cr (II) and Cr (III), with the former acting as a strong reducing agent and it is easily oxidised to Cr (III)

under oxidising environments. All aqueous species of Cr (VI) are oxycompounds and they are very strong oxidising agents under low pH conditions, i.e., acidic medium (Jiang et al., 2014; Vardar et al., 1994; Zhao et al., 2014).

In the work done by Beverskog and Puigdomenech (1997), 40 Cr compounds in aqueous systems were identified. These are listed in **Table 2.4**. The table shows a series of possible solid, gas and aqueous species of Cr. The most important and common solid compounds (oxides) include CrO_2 , CrO_3 and Cr_2O_3 , with CrO_2 being the least stable and Cr_2O_3 being the most stable. CrO_2 mainly appears at high temperatures.

Table 2.4: Chromium compounds in aqueous systems (Beverskog and Puigdomenech, 1997).

Condition	Oxidation number	Included	Excluded
crystalline	0	Cr	
solid	I		CrH
crystalline	II		CrO
solid	"	Cr(OH)_2	
"	"		CrH_2
gaseous	"		CrH_2
crystalline	II/III		Cr_3O_4
"	III	Cr_2O_3	
"	"		$\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$
"	"		$\text{Cr}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$
"	"		$\text{Cr}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$
"	"	Cr(OH)_3	
"	"		$\text{Cr(OH)}_3 \cdot n \text{H}_2\text{O}$
"	"		CrOOH
"	III/IV		Cr_2H_7
"	IV	CrO_2	
solid	"		Cr(OH)_4
crystalline	VI	CrO_3	
"	VIII		CrO_4
"	X		CrO_5
dissolved	II	Cr^{2+}	$\text{CrH}_2(\text{aq})$
"	III	Cr^{3+}	CrO_3^{3-}
"	"	CrOH^{2+}	Cr(OH)_6^{3-}
"	"	Cr(OH)_2^+	
"	"	$\text{Cr(OH)}_3(\text{aq})$	
"	"	$\text{Cr(OH)}_4^- (?)$	
"	"		$\text{Cr}_2(\text{OH})_4^{4+}$
"	"		$\text{Cr}_3(\text{OH})_4^{4+}$
"	V		CrO_4^{3-}
"	VI	H_2CrO_4	CrO_4^{4+}
"	"	HCrO_4^-	CrO_2^{2+}
"	"	CrO_4^{2-}	$\text{Cr}_3\text{O}_{10}^{2-}$
"	"	$\text{Cr}_2\text{O}_7^{2-}$	$\text{Cr}_4\text{O}_{13}^{2-}$
Σ		$6 + 10 = 16$	$14 + 10 = 24$

2.4.3 Cr-O-H system

The thermodynamic feasibility of Cr dissolution under a wide range of conditions can be explored using the Pourbaix (Eh-pH) diagram for the Cr-water system shown in **Figure 2.6** (Pourbaix, 1974). The diagram shows equilibrium boundaries of thermodynamically stable regions in which Cr and its other chemical compounds are predominant (Beverkog and Puigdomenech, 1997; Pourbaix, 1974; Takeno, 2005; Vardar et al., 1994). The main Cr compound in the UG-2 flotation concentrate is chromic oxide (Cr_2O_3), which is the major constituent of chromite. In nature, partial substitutions of Cr^{3+} by Fe^{3+} and Al^{3+} occur; however, Cr_2O_3 is commonly used to simplify the construction of Eh-pH diagram for Cr (Takeno, 2005).

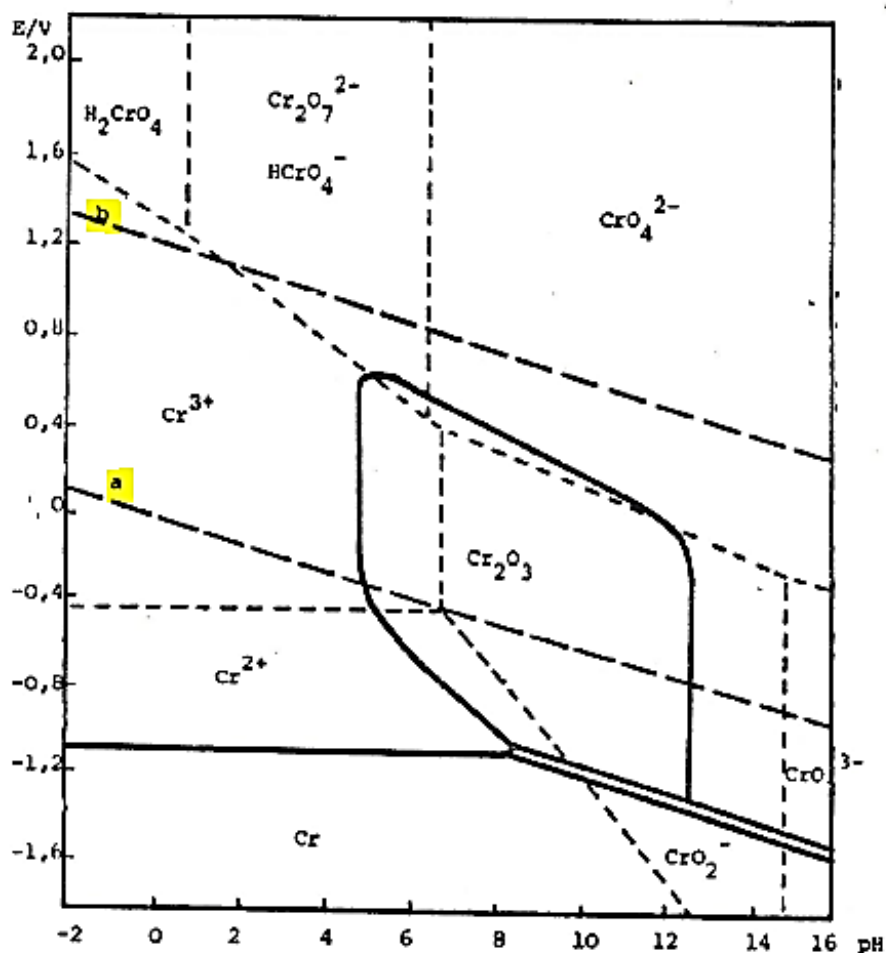


Figure 2.6: Eh-pH diagram of the system Cr-O-H. 298.15K, 105 Pa (Pourbaix, 1974).

The construction of Eh-pH diagrams mainly involves three reactions that result from the possible chemical and electrochemical equilibria in a specific system. The reactions represent vertical, horizontal, and sloping lines on the Eh-pH diagram depending on the reactants and products of the reactions. The three reactions commonly used in the construction of the Eh-pH diagram can be described as follows:

- i. A chemical reaction which involves the reaction of a solid substance, aqueous substance and H_2 ions in water without the exchange of electrons. This reaction is commonly represented by a vertical straight line which is independent of Eh. This is typically expressed by Van't Hoff equation (equation 2.1) in which standard free energy reactions are considered at constant pressures:

$$\ln k = - \frac{\Delta G}{RT} \quad 2.1$$

Where,

ΔG : Standard energy change ($G_{\text{products}} - G_{\text{reactants}}$)

K: Equilibrium constant

T: Temperature (K)

R: Universal gas constant

- ii. A chemical reaction which involves the reaction of a solid substance and an aqueous substance, plus free electrons without the involvement of hydrogen ions. This reaction typically represents horizontal lines that are independent of pH.
- iii. A redox reaction that involves a solid substance, an aqueous substance, free electrons, and hydrogen ions. This reaction is commonly represented by a straight line with a gradient, i.e., dependent on the Eh and pH. For this reaction, voltage and Gibbs free energy change of substances at unit activity under standard conditions is presented in equation 2.2.

$$E^{\circ} = - \frac{\Delta G}{nF} = \frac{2.303RT}{nF} \log k \quad 2.2$$

Where,

E° : standard potential (V)

F: Faraday constant (96500 C/mol e⁻)

n: number of electrons involved in the reaction

For non-standard conditions, Equation 2.2 changes to:

$$E_h = E^o - \frac{2.303RT}{nF} \log Q \quad 2.3$$

Where,

E_h: electropotential for non-standard conditions

Q: the reaction quotient

The Cr Eh-pH diagram illustrates the thermodynamic equilibrium of Cr-water systems under standard conditions of 298.15K and 105 Pa. The equilibrium lines confining the aqueous and solid compounds were constructed with an assumed Cr concentration of 10⁻⁶ mol/L. The diagram comprises thick and dashed boundary lines, which represent the phase boundaries of solids and dissolved species, respectively. The equilibrium potentials of oxygen and hydrogen evolution reactions are denoted by diagonal lines (a) and (b). Below line (a), the evolution reaction of hydrogen occurs when water decomposes; while above line (b) the evolution of oxygen occurs when water decomposes. Between the diagonal lines, water is thermodynamically stable (Beverkog and Puigdomenech, 1997; Vardar et al., 1994). The horizontal line passing through Eh=0 divides the Eh-pH diagram into the upper region, which has oxidizing conditions, and the lower region, which has reducing conditions.

Cr under neutral pH conditions forms chromic oxides and hydroxides on the metal surface. Similar passivating species are formed at slightly alkaline conditions. Under high pH and reducing conditions, Cr is dissolved to form CrO₂⁻ and CrO₃³⁻. Under oxidising conditions (and high pH), Cr mainly dissolves to form CrO₄²⁻. In acidic and reducing conditions, Cr is stable as Cr⁰ and chromous Cr²⁺. These are formed below the (a) line in which the evolution reaction of hydrogen occurs when water is decomposed. Under oxidising conditions (and low pH), between (a) and (b) lines, Cr is stable as Cr³⁺; while above (b) line, Cr is predominately stable as H₂CrO₄, Cr₂O₇²⁻ and HCrO₄⁻ (Beverkog and Puigdomenech, 1997; Pourbaix, 1974; Vardar et al., 1994).

In summary, the Cr Eh-pH diagram thermodynamically confirms the possible dissolution of Cr from chromic oxide (Cr_2O_3) in the UG-2 flotation concentrate material. The Cr in this material, which occurs as Cr^{3+} , is thermodynamically likely to dissolve under oxidizing alkaline and acidic leaching conditions. The alkaline conditions predominately form stable compounds of Cr^{6+} which are hazardous, while acidic conditions form mainly Cr^{3+} and rarely Cr^{6+} , which forms under extremely oxidizing conditions.

2.4.4 Leaching processes

2.4.4.1 Alkaline leaching of chromium

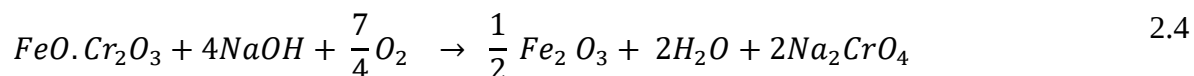
The alkaline leaching process route is widely used to beneficiate chromite ore deposit to produce Cr salts (Chen et al., 2014; Chen et al., 2013; Zhang et al., 2016). In this process, the water insoluble Cr (III) phase is chemically converted to Cr (VI), which is water soluble under oxidative environments. The common lixivants used in this process are sodium hydroxide (NaOH) and potassium hydroxide (KOH) in the presence of oxygen as an oxidising agent.

i. Pressure oxidative leaching of chromite using NaOH

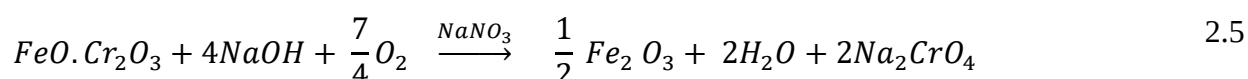
The leaching of chromite using oxidative alkali medium has been investigated by many researchers as an alternative to the traditional roasting methods of producing Cr as chromates from chromite ores. Farrow and Burkin (1975) are some of the earliest researchers to investigate the direct pressure leaching of chromite using sodium hydroxide (NaOH). The conditions employed in their investigation involved leaching temperatures of 190-270 °C under partial pressure of 10 bar, and the obtained results indicated that the decomposition of chromite occurred by oxidising the divalent and trivalent cations in the chromite crystal structure. Leached Cr and Mg species from the chromite surface were removed and replaced by Fe through diffusion mechanisms. This resulted in the formation of a product layer enriched in Fe. The growth of the product layer resulted in a thick Fe-rich layer around chromite, which in turn, served as a rate-limiting factor (Farrow and Burkin, 1975).

In the investigations conducted by Zhang et al. (2016) and Zhang et al. (2010), the leaching efficiency of Cr under alkaline and strong oxidising environments were investigated. Molten sodium hydroxide was used as a leaching medium due to its high chemical activity. The conditions employed by Zhang et al. (2016) included NaOH concentration of 60 wt.%, leaching

temperature of 250 °C, solid to liquid ratio of 4:1 and oxygen partial pressure of 3.2 MPa. These researchers reported that these conditions yielded a Cr extraction of 99 % using the ore size fraction of 40-50 µm. The decomposition mechanism of chromite involved the oxidation of Fe^{2+} to Fe^{3+} and the dissolution of Al^{3+} and Cr^{6+} . Mg^{2+} and Fe^{3+} were inert, thus, left unreacted and resulted in the formation of $MgFe_2O_4$. The results showed a solid product layer formed on mineral surfaces, which limited the diffusion of reactants and products; thus, forming a rate limiting step.



Zhang et al. (2010) introduced sodium nitrate ($NaNO_3$) as a catalyst in their optimisation study to improve mass transfer of oxygen in the production of sodium chromates using molten NaOH and oxygen (**Figure 2.7**). Process factors that were explored included leaching temperature in the range of 300-400 °C, solid to liquid ratio of 1:4 and material size fraction of less than 58 µm. These achieved a Cr extraction of 99.9%. $NaNO_3$ was reported to have served as an oxygen carrier, which reduced the effect of mass transfer on oxygen movement. The mechanism of carrying oxygen using $NaNO_3$ involved the oxidation of $NaNO_3$ to $NaNO_2$ as a reduction product. The latter was then oxidised back to $NaNO_3$. The reaction kinetics data showed that the decomposition process of chromite was internal diffusion controlled at activation energy of 106 kJ/mol. The decompositions of chromite are expressed as follows:



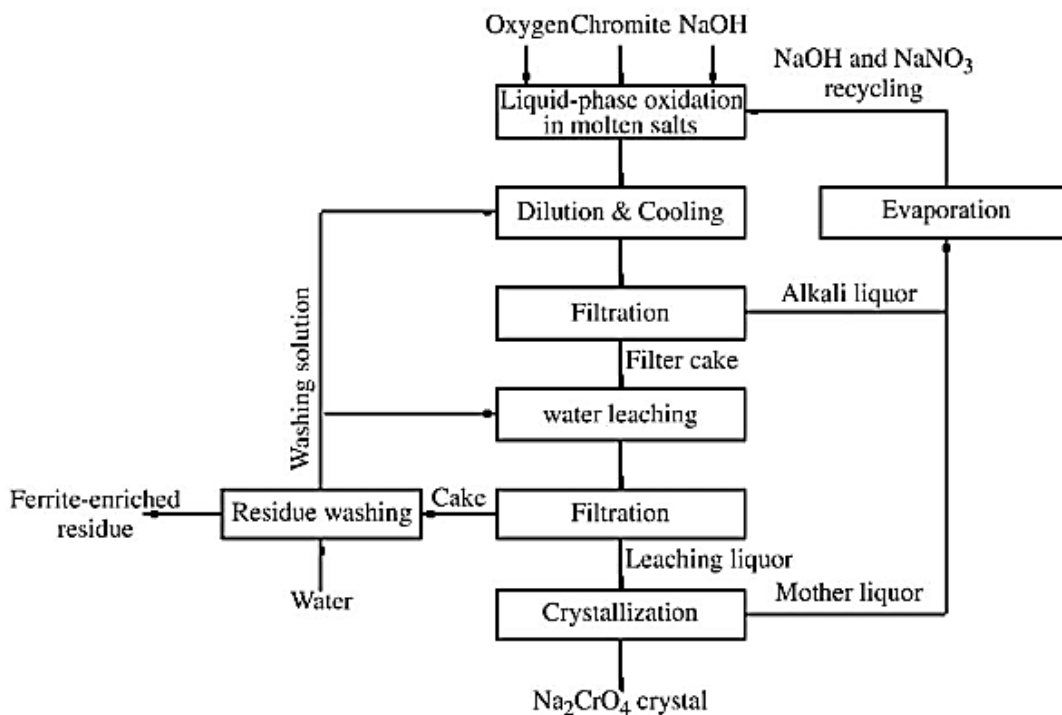


Figure 2.7: Process flowsheet for chromate salt production using NaOH (Zang et al., 2010).

ii. Potassium hydroxide

The leaching process of Cr using Potassium hydroxide is widely documented as a green metallurgical process (Chen et al., 2013; Chen et al., 2014; Xu et al., 2005; Zheng et al., 2006). The process was developed to mitigate the environmental problems that are associated with Cr (VI), which is commonly generated by conventional roasting processes and leaching using NaOH solutions (in residues) (Chen et al., 2013).

Pressure leaching of Cr in a 50 wt.% KOH solution was investigated by Chen et al. (2014), Cheng et al. (2013), Xu et al. (2005) and Zheng et al. (2006); and a Cr extraction of 99% was achieved with a Cr (VI) residue content that satisfied the health, safety, and environmental regulations. This was achieved under leaching temperature of 320 °C and oxygen partial pressure of 2.0 MPa (Chen et al., 2013). The simplified process flowsheet of the technology is shown in **Figure 2.8**. The residue from the leach process was analysed and it contained mainly Fe_2O_3 with a compact structure and no layer of ash was formed. The leaching mechanism was chemically controlled. The Fe_2O_3 contained in residue was observed to depend on the amount of KOH concentration used for the leaching process. This was coupled with the measurements

of residual Cr toxicity levels of the residues. The residues of the experiments conducted at lower KOH concentrations contained Cr (VI) levels that satisfied the environmental standards for Cr disposal. Thus, this process is referred to as an efficient and cleaner chromate salt production process (Chen et al., 2014).

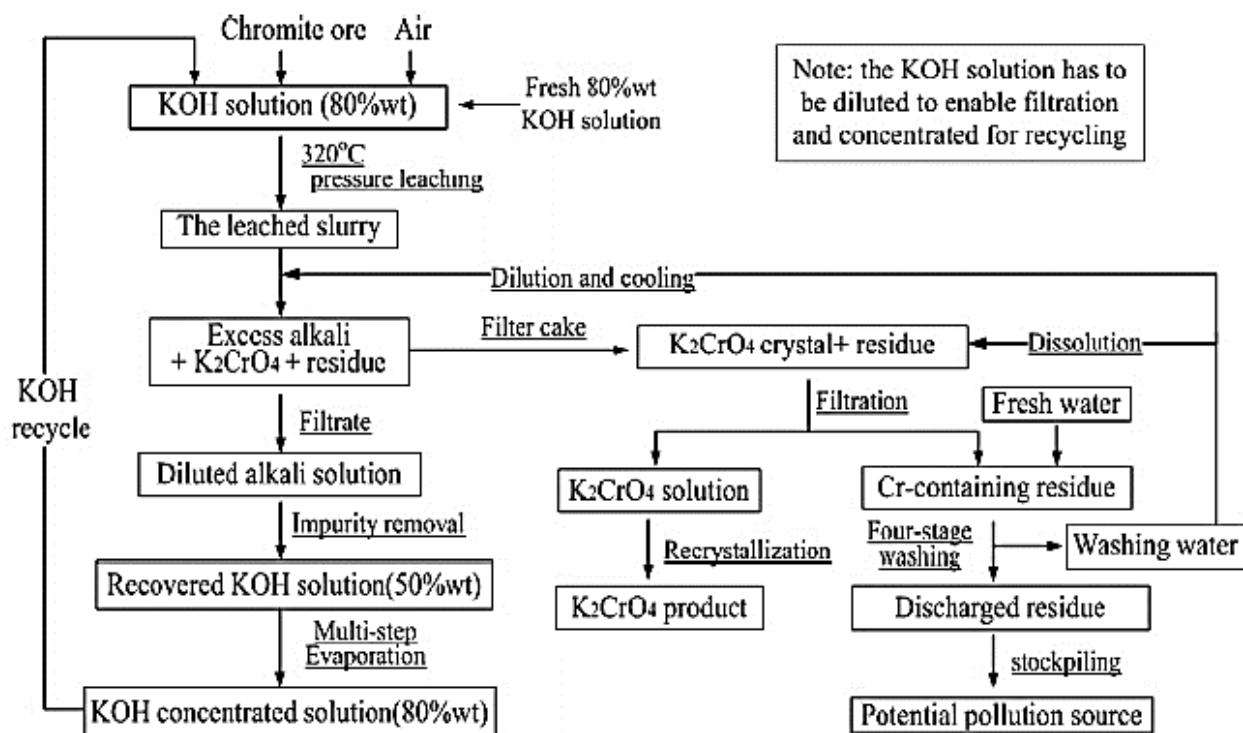
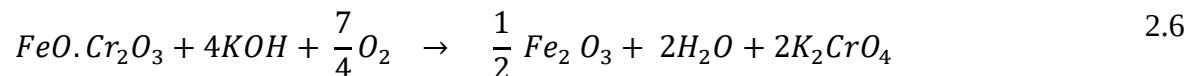


Figure 2.8: Process flowsheet for chromate salt production using KOH (Chen et al., 2013).

The main disadvantage of the alkaline leaching processes as a route to reducing chrome in the UG-2 flotation concentrate is the production of hexavalent Cr (VI), which is detrimental to human health. The substance is toxic and carcinogenic. Other disadvantages of this process route include inefficient operability due to the non-selectiveness and high operating costs caused by high leaching temperatures.

2.4.4.2 Acid leaching of chromite

Lloyd et al. (1948) conducted extensive test work on the production of electrolytic Cr on a pilot plant scale. The leaching of Cr from chromite was performed using 40 wt.% H₂SO₄ and 2.5-3wt.% of chromic acid (HCrO₄). The latter was used as a catalysing agent in the decomposition reaction of chromite. The Cr pressure leach was done under leaching temperature range of 130-160°C at oxygen partial pressures of 2-10 bars. For the electrowinning bath, ammonium sulphate was added in the leach liquor. The process achieved a Cr extraction of 99%. The solid-liquid separation process was done while the solution was still hot and consequently mixed with the ammonium sulphate spent electrolyte of 40 g/L concentration. The temperature of the mixed solution was at 80°C to prevent the formation of alums containing Cr sulphates before filtration. The temperature of the solution was then cooled to 3°C to separate iron and aluminium as ammonium alums. Alums of chromium ammonium (NH₄)₂.SO₄.Cr₂(SO₄)₃.24H₂O were formed by crystallization through heating the solutions to 35°C and then cooling to 15°C.

The chemical and electrochemical extraction of Cr from chromite was investigated by Westby (1957) using an ore sample from the black chromite sands deposit. In this study, 70-80wt.% H₂SO₄ concentration and 150 °C leaching temperature at atmospheric pressure were used in the leaching stage. The filtration stage then followed, in which the undissolved silicious material and species of calcium sulphate were separated from the leach solution. The filtrate containing aqueous sulphates was heated to a temperature range of 170-225°C to form metallic sulphates of Cr₂SO₄ and Fe₂SO₄. This process was followed by a solid-liquid separation stage entailing settling of the metallic sulphates and decantation of the solution. Fe₂SO₄ was then separated from Cr₂SO₄ by adding water and ferrous sulphates to dissolve and filter its solution off. The residue of Cr₂SO₄ was finally dissolved in a mixture of water and anhydrous chromic sulphate. This was subsequently dispatched in a catholyte circuit for electrowinning. At this stage, titanium sulphate (Ti₂(SO₄)₃) was added in the system to reduce Cr₂SO₄ to CrSO₄ as indicated in **Equation 2.7**. As a final step, Cr was electrowon from the Cr (II) sulphate solution. The benefit of introducing titanium was that it saved on electricity by one third.



Sodium bisulphate (NaHSO_4) was used and patented by Morgan et al. (1974) in their study to extract Cr from chromite. The process entailed a pre-treatment step in which the chromite ore was preheated in temperatures of 500 and 1200 °C in an oxidising environment before the leaching step. The benefit of the process was reported to be improved efficiency in digestion. The digestion process was performed in molten sodium bisulphate under temperatures of 180-220 °C. The discharge from the digestion step was treated with small quantities of water to reduce fusion temperature (130-170 °C). The Cr salt product formed during the digestion process was oxidised electrochemically to chromic acid (CrO_3) and this was purified via recrystallisation from the strong aqueous solution.

Amer (1992) investigated the kinetics of pressure leaching of Cr in a circuit comprising a stirred ball mill stage followed by a pressure leaching stage in a stainless-steel autoclave. The milling process was conducted in a H_2SO_4 solution. The overall leaching reaction rate was defined as chemically controlled. The dissolution mechanism of Cr fitted the first order reaction. A leaching temperature of 250 °C, oxygen partial pressure of 5-15 bar, leaching time of 30 minutes and H_2SO_4 concentration of 50 wt.% were experimentally found to favour the optimum dissolution of Cr for material less than 64 μm . The Fe and Al were found to have co-leached with Cr. Fe dissolution as ferrous sulphate was reduced by adding manganese oxide (MnO) as an oxidant, and Al dissolution was minimised by adjusting the temperature and acid concentration. At temperatures of 180 °C, the hydrolysis of $\text{Al}_2(\text{SO}_4)_3$ was favoured while Al dissolution was minimised.

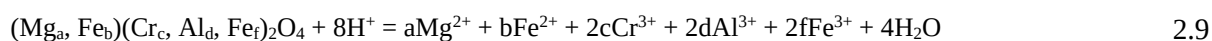
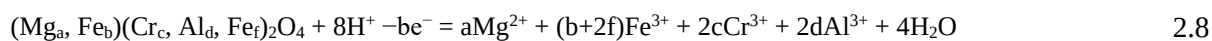
The leaching kinetics of Cr in H_2SO_4 to form violet Cr (III) sulphates at a temperature range of 140-210°C was investigated by Vardar (1993). The experimental data from the investigation suggested the dissolution of Cr was chemically controlled. The process factors explored included leaching temperature, H_2SO_4 concentration and the addition of perchloric acid as a catalyst to improve the dissolution rate of Cr. The addition of perchloric acid increased the Cr dissolution rate while the increase of H_2SO_4 concentration resulted in the formation of insoluble $\text{Cr}_2(\text{SO}_4)_3$ precipitates. Within the leaching temperature range of 140-210 °C and 82 wt.% H_2SO_4 concentration, the activation energy of the Cr dissolution reaction was 77 kJ/mol.

Similar research work done by Vardar (1993) was done by Geveci et al. (2002). The latter investigated the leachability of Turkish chromite concentrate in H_2SO_4 and perchloric acid. Process factors investigated include H_2SO_4 concentration, addition of perchloric acid, temperature, and leaching time. The optimised leaching conditions of 70 wt.% H_2SO_4 , $\frac{1}{2}$ perchloric acid/chromite ratio, 175 °C temperature and leaching time of 2 hours yielded 83 % Cr extraction. These conditions produced stable aqueous species of Cr (III), which are environmentally friendly.

In recent investigations, part 1 and 2, done by Zhao et al. (2014) and Jiang et al. (2014), the leaching behaviour and kinetics of chromite from the BIC was studied in an oxidative H_2SO_4 leaching process. Zhao et al. (2014) in part 1, investigated the leaching behaviour of Cr from a chromite lump and the surface characteristics of the lump thereafter. In other investigations, a milled chromite sample of different size fractions was used to extract Cr followed by studying the leached residues. In all the investigations, silicates and chromite experienced different changes at a leaching temperature of 160 °C. The silicate formed a porous amorphous product layer as magnesium and aluminium were both extracted, while chromite mineral shrank in size as the leaching time progressed. The chromite lump was found to be passivated by silicate leached products, which in turn obstructed the Cr dissolution on the chromite surface. As a result, the separation of the chromite and silicate through crushing was recommended as part of the conclusion.

Jiang et al. (2014) investigated the effect of H_2SO_4 concentration, leaching time, temperature, and an unspecified oxidant on Cr extraction. The dissolution of Cr was reported to increase with increase in temperature until 180 °C. At temperatures exceeding 180 °C, it was found that precipitates of $\text{Cr}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3$, $\text{Al}_2(\text{SO}_4)_3$ and MgSO_4 began to form, which negatively impacted Cr recovery. After a leaching time of 60 minutes at a leaching temperature of 160 °C, 93 % of Cr was extracted. This was with 80 wt.% H_2SO_4 concentration and chromite: oxidant ratio of 1:10, and agitation rate of 1800 rpm.

The process chemistry of chromite decomposition in these studies is presented in **Equations 2.8** and **2.9**. These equations illustrate the interaction of ions and chromite under oxidising and non-oxidising conditions, respectively.



Where a, b, c, d, and f are coefficients; $a + b = 1$ and $c + d + f = 1$.

The chromite dissolution mechanism mainly involves the reaction of the chromite crystal structure with an acid (Amer, 1992; Biermann and Heinrichs, 1960; Bronsted, 1931; Vardar et al., 1994). The hydronium ion reacts with the chromite crystal structure causing the chromite to become oxidized, thus inducing metal dissolution. The process chemistry entails the dissolution of the divalent metals in the tetrahedral site, followed by the dissolution of the trivalent metals in the octahedral site of chromite. This process brings the metallic contents of chromite into the bulk solution in similar proportions to their formation in the crystal structure (Biermann and Heinrichs, 1960). In the presence of an oxidant, the degree of dissolution significantly improves as the oxidation rate of divalent metals in the tetrahedra site increase (Jiang et al., 2014; Vardar et al., 1994; Zhao et al., 2014). The high sulphuric acid concentration was also reported to form water insoluble polynuclear products of anhydrous Cr (III) sulphates.

In literature, three types of $\text{Cr}_2(\text{SO}_4)_3$ chemical species have been found and described. The species are namely anhydrous Cr (III) sulphates $[\text{Cr}_2(\text{SO}_4)_3]$, violet Cr (III) sulphate hydrates $[\text{Cr}(\text{H}_2\text{O})_6](\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, and green Cr (III) sulphate hydrates $[\text{Cr}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}]$.

Different authors have reported that the amount of water molecules in the violet Cr (III) sulphates vary between 12 to 18 moles (Vardar, 1993). The violet Cr (III) sulphates typically change to green Cr (III) sulphate hydrates as temperature is increased. This chemical transition typically occurs when the water molecules are lost from $[\text{Cr}(\text{H}_2\text{O})_6](\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ compound. The green solution begins to form at 100 °C by losing 8-10 moles of water molecules. The water molecules in the violet Cr (III) sulphate hydrates are reported to be 6 moles, i.e., $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ (Vardar, 1993). As the water compounds are released, the solubility of the Cr sulphates species decreases. Anhydrous Cr (III) sulphates ultimately form an end-product by heating up violet Cr (III) sulphates. The latter is typically water insoluble.

Overall, the acid leaching process using sulphuric acid in the foregoing investigations have showed great potential on the extraction of Cr from chromite resources. The material used in these investigations was run-of-mine and Cr_2O_3 concentrates from physical concentrators. These materials were mainly characterised by higher Cr_2O_3 grades of 20-46 wt.%.

The acid leach process was widely reported to have obtained higher Cr extractions of more than 75%. These were achieved with the production of Cr^{3+} species which are not detrimental to the environment.

A limited number of process factors and conditions were found to be critical for the high extraction of Cr. The most explored and reported as influential factors in literature were sulphuric acid concentration, leaching temperature and leaching time. The levels of the influential process factors reported ranged as follows:

- Sulphuric acid concentration: 40-85%
- Leaching temperature: 140-210°C
- Leaching time: 1-5 hours.

Process factors such as solid-to-liquid ratio, oxidant concentration, oxygen partial pressures and agitation rate were not explored extensively. The levels of these factors were generally kept constant in most of the above investigations. The fixed levels of these process factors in literature are indicated below:

- Different investigations fixed solid-to-liquid ratio at 1:4, 1:10 or 1:25
- Agitation rate was fixed at 1000-2000 rpm.
- Air partial pressure at 2-15 bars.

Although the experiments in these investigations were mainly conducted on material enriched in Cr_2O_3 , the fundamental principles and mechanisms of Cr dissolution indicate that it is chemically possible to also extract Cr from material of low Cr_2O_3 grade.

2.4.5 Leaching reagents properties

2.4.5.1 Sulphuric acid

Beside its low cost per unit, availability in the market and the ability to be regenerate; sulphuric acid (H_2SO_4) is mostly preferred in this investigation due to its outstanding properties to protonate as an acid leaching medium. These factors have the potential to render the proposed leaching process economical and efficient. Its other properties include a high boiling point of 337°C and high corrosivity. This requires the engineering equipment for this process to be made of corrosion resistant stainless steel such as the Grade 904L which is a low carbon high alloy austenitic stainless steel.

Sulphuric acid ionization process is typically expressed as follows:

i. High H_2SO_4 concentration



ii. Dilute H_2SO_4 concentration



The Hammet acidity function can be used to quantitatively measure the acidity of a strong acid as employed in this study.

$$h_o = a_{H^+} \left(\frac{f_B}{f_{BH^+}} \right) = [H^+] f_{H^+} \left(\frac{f_B}{f_{BH^+}} \right) \quad 2.12$$

Where,

$[H^+]$ is the protonic concentration,

f_{H^+} is the proton coefficient,

$\left(\frac{f_B}{f_{BH^+}} \right)$ is the ratio of activity coefficient and conjugate acid.

a_{H^+} is the activity of H^+ .

At an acid concentration of 50 wt.%, it was reported that the proton can hydrate as H^+ , $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$ which account for the acidity media.

At 25 °C, the sulphuric acid reaction dissolution is given as:



$$\Delta G^\circ = -12871 \text{ cal/mol}$$

$$\Delta H^\circ = -22844 \text{ cal/mol}$$

$$\Delta S^\circ = -12871 \text{ cal/(mol K)}$$

2.4.5.2 Oxygen

Oxygen is commonly used as an oxidising agent to facilitate chemical reactions that involve reduction-oxidation reactions. Its high electronegativity and/or its high affinity to accept electrons makes it attractive for chemical processes in which high electropotential is required. Depending on the application, oxygen is used as either pure or diluted (air).

In work studies done by several researchers (Jiang et al., 2014; Zhao et al., 2014 and Vardar et al., 1994), pure oxygen was used as an oxidising agent to increase the reduction potentials of the sulphuric acid solution to above 0 V, as high reduction potentials are significant to the dissolution rate of chromite (Geveci et al., 2006; Jiang et al, 2014; Vardar et al., 1994). The oxidising agent, through redox reactions, destabilises the chromite crystal lattice by reducing the ionic radius of Cr (III) and iron (II), which results in the decomposition of the mineral.

2.5 Summary

The Bushveld Igneous Complex in SA is the largest layered igneous intrusion in the world. It is characterised by three PGM -bearing ores; namely, UG-2 reef, Merensky reef, and Platreef.

The Merensky reef and Platreef are similar. They are characterised by high quantities of sulphide minerals and low chrome contents. In contrast, UG-2 resources are characterised by trace amounts of sulphide minerals and large quantities of chrome.

The inherent high chrome grades (>3 wt.%) have fundamentally rendered the smelting of UG-2 concentrates unattractive and difficult to process using the current PGM smelting technologies. The solubility limit of chrome for efficient deportment in silica slag glass is 1.8 wt.%. Above this limit, the slag phase forms refractory chrome spinel phases. The net effect of high chrome includes, inter alia, increased furnace specific energy consumptions (kWh/t), the reduction of effective furnace capacity and poor PGM recovery.

Various interventions ranging from the dilution of UG-2 concentrates with Merensky/Platreef concentrates, redesigning and modifying existing physical and pyrometallurgical operations have been introduced to mitigate the negative effect of chrome. However, these have not yielded any sustainable solutions.

Under high pH and reducing conditions, Cr is predominant as CrO_2^- and CrO_3^{3-} . Under high pH and oxidising conditions, Cr is predominant as CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ and H_2CrO_4 . Alkaline conditions favour the production of hexavalent Cr (VI), which is toxic and carcinogenic to humans. Under acidic and reducing conditions, Cr is stable as Cr^0 and chromous Cr^{2+} . Under acidic and oxidising conditions, Cr is stable as Cr^{3+} . Under acidic and higher oxidising conditions, Cr exists predominantly as H_2CrO_4 , $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- .

Factors reported to be influential in the Cr dissolution process include sulphuric acid concentration (40-85 v/v%), leaching temperature (140-210°C) and leaching time (1-5 hours). Other process factors found to be equally influential, though less explored, include solid-to-liquid ratio, oxygen partial pressures and agitation rate.

Chapter 3

MATERIALS AND METHODS

3.1 Introduction

This chapter gives details of how the experiments were set up and performed, the equipment used, the material preparation as well as the analytical methods used.

3.2 Materials

3.2.1 Material characterisation

A production sample obtained from the final UG-2 flotation concentrate stream was used in this investigation. The sample was supplied by Eastern Platinum concentrator, Sibanye-Stillwater (Pty) Ltd, formerly, Lonmin (Pty) Ltd, South Africa.

The characterisation of the sample was carried out using an automated quantitative scanning electron microscope (A-SEM) and X-ray fluorescence (XRF) spectroscopy.

A single 30 mm diameter cast resin stub was produced for the concentrate sample received. The stub consisted of a 0.5 g sample mixed with 0.2 g of graphite. The cured stub was halved, turned, and recast to present a cross-section of the original cast stub. The recast stub was polished, coated with carbon then scanned. The scanning was carried out using an ASPEX X-ray backscattered Electron Image (XBSE) scanning electron microscope equipped with Bruker energy dispersive X-ray spectrometer (EDS) operated with the Mineral Liberation Analysis (MLA) software suite. The XBSE measurement technique was used to scan a minimum of 20 000 particles equivalent to a maximum of 6 hours scan time. All particles less than 2 μm or with a BSE greyscale of less than 35 (graphite) were electronically excluded from this scan.

The mineral phases in the particles were identified using a best fit technique through the use of MinIdent-Win4 software and the FEI-MLA mineral reference editor. The basis for the identification was spectra and chemical composition obtained from EDS.

The MLA mineral identification software suite was used to extract the scan data and populate the Dataview database. It is important to note that some particle agglomeration is possible

during the manufacturing of the polished stubs and particle intergrowth may be less than reported. Mineral phase identification is done by chemical composition, and it is possible that some mineral phases may not be identified.

3.2.2 Particle size analysis

Table 3.1 and **Figure 3.1** illustrate the mineralogical characteristics of the production sample analysed using the Tyler test sieve technique as well as the ASEM-measured particle size distribution (PSD).

The ASEM software typically stores the particle area in a database. This is commonly compared with the sieve analysis performed by the Betachem (Pty) Ltd Process Mineralogy team using the Tyler test sieves. The comparison is done as a quality control measure as it is well known that ASEM reports the PSD finer than the physical screening data.

The comparison between the equivalent circle PSD data (ASEM) and PSD by physical sieve analysis, using slopes of regression lines through the zero axis, is shown in **Table 3.1**. Slopes of closer to 1 commonly represent a fit between the ASEM measured PSD and the Tyler test sieve PSD. Slopes smaller than 1 typically indicate that the ASEM reported a finer PSD.

Table 3.1: Quality control dashboard.

			PSD slope acceptance			0,8	to	1,2
	Description		PSD	PSD as Cumulative % Passing				
			Slope	150	106	75	53	38
G260	EPL Conc	Lab		100	98	95	91	80
		ASEM		100	100	97	93	85
Slope (regression MLA vs screen PSD)			1,02	% Difference				

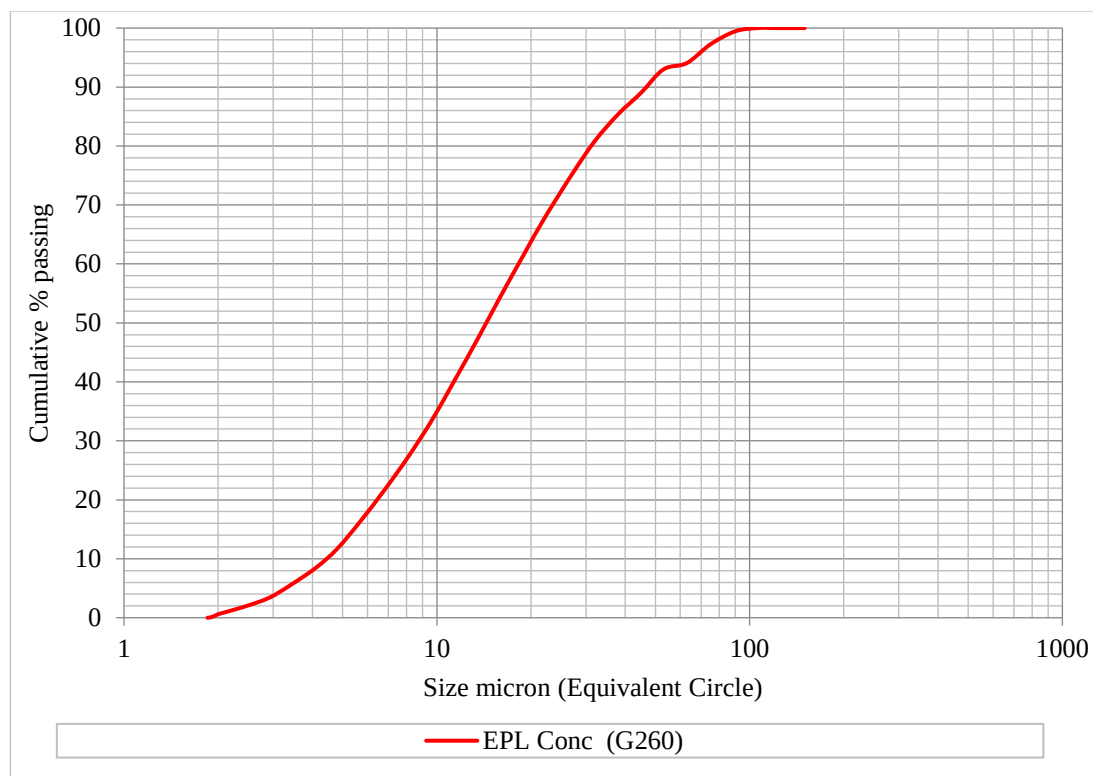


Figure 3.1: Particle size distribution of EPL UG-2 flotation concentrate.

3.2.3 Chemical composition

The chemical composition of this concentrate sample was determined using XRF analytical technique. ARL ADVANT'X series was used as the instrumental model and the method of identification involved the use of UIS-XF-PTA-T003. The chemical composition of this sample is shown in **Table 3.2**. Its analysis was conducted on the -38 μm size fraction as it constituted the bulk of the sample material (85 wt.%) and contained the high Cr_2O_3 content (3.6 wt.%). This size fraction contained 92 wt.% of total Cr_2O_3 in the concentrate.

Table 3.2: Chemical composition of EPL final concentrate (wt.%).

Fe_2O_3	SiO_2	MgO	Cr_2O_3	CaO	Al_2O_3	TiO_2	Na_2O	Mn_3O_4	CuO	ZnO	Co_3O_4	NiO	LOI
13,89	47,13	23,60	3,63	2,19	4,74	0,27	0,13	0,17	0,44	0,02	0,05	0,93	3,46

^a LOI: Loss on ignition

3.2.4 Reagents

All reagents used in this study were of analytical grade and were purchased from Merck-Sigma Aldrich and Afrox (Pty) Ltd, South Africa. Sulphuric acid (98% w/w), deionised water and pure oxygen were used in the experiments.

3.3 Experimental

3.3.1 Equipment and experimental procedure

The key components of the experimental apparatus included a 2000 mL leaching vessel, an overhead stirrer, a gas cylinder for oxygen supply and a thermal recirculating bath for external heating of the leaching vessel. Other components of the experimental set-up are displayed in **Figure 3.2**. A 1500 mL Erlenmeyer flask, filter funnel and a vacuum pump formed the filtration set-up.

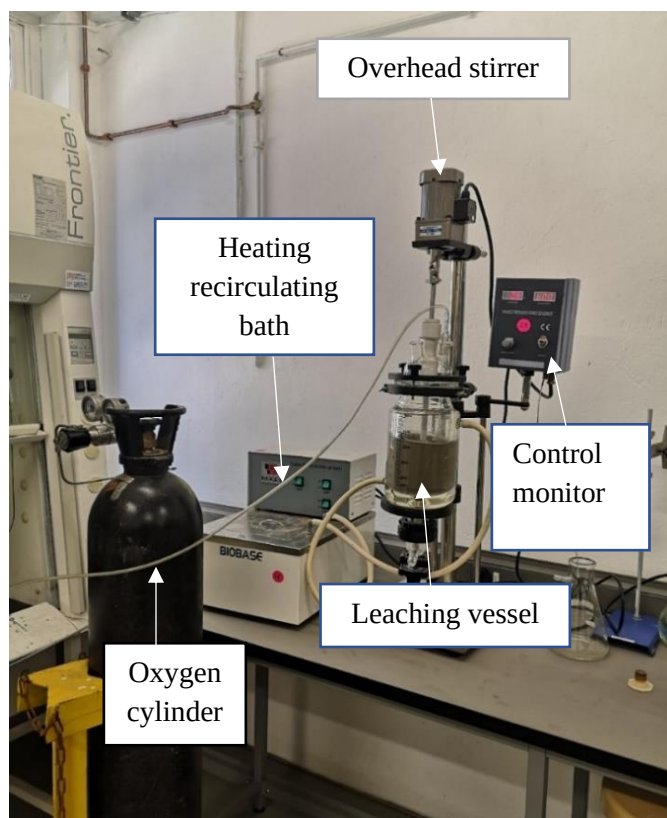


Figure 3.2: Experimental set-up.

The leaching experiments entailed adding 200g of UG-2 concentrate to 600 mL sulphuric acid solution with a set temperature as per test condition. The solid to liquid ratio (1:3) used in the

current study was based on typical industry practice. The agitation mechanism was fixed and operated at 1000 rpm. The completion of each batch leaching test was followed by a filtration step to physically separate the green in colour primary leach liquor from the residue. The residue was subsequently washed off using deionized water to recover any entrapped leach liquor. The washing process was continuously conducted until the filtrate colour from the residue was colourless. Quantitatively, a colourless filtrate for experiments conducted with 45% (v/v) H_2SO_4 concentration was attained with an average of 1400 mL wash water; while experiments conducted with 85% (v/v) H_2SO_4 concentration required an average of 2500 mL wash water. The primary leach liquor and washed liquor were then mixed to make the total leach liquor. The last step involved sampling the total leach liquor to obtain a representative sample for Atomic Absorption Spectroscopy (AAS) analysis.

3.3.2 Design of Experiments

In this investigation, the Design of Experiments (DOE) was used as a statistical tool to develop an experimentation plan for conducting the leaching experiments. The experiments were mainly aimed at identifying process factors that have a significant impact on Cr dissolution. The identified significant factors were then optimised and employed in modelling the optimal leaching conditions.

DOE was preferred in this investigation due to its versatility with enabling a study of the effect of multiple process factors simultaneously. This method aids to achieve precision in determining the effect of process factors and their interactions thereof.

3.3.2.1 Identification of Significant Factors

DOE was used to screen factors which have a strong influence on the leaching behaviour of Cr using a 2^4 full factorial design. The selection of process factors and their levels was based on data from preliminary experiments and literature. The leaching factors were classified as varied and fixed variables. The varied factors included leaching time, temperature, acid concentration and oxygen flowrate, while the solid-to-liquid ratio and agitation rate were fixed. The process factors and their levels are listed in **Table 3.3** and the experimental plan is outlined in **Table 3.4**.

Table 3.3: Process factors and factor levels.

Process factors	Low (-1)	Centre point (0)	High (+1)
Time (hr)	1	3	5
Acid concentration (%)	45	60	75
Temperature (°C)	43	62	85
Oxygen Flow Rate (ML/min)	10	20	30
Solid to liquid ratio (g/mL)	1:3		
Agitation Rate (rpm)	1000		

Table 3.4: Experimental plan for identification of significant factors.

		Control factors			
Standard Run Order	Random Run Order	Temp	Time	Acid Conc	Flowrate
		(°C)	(hrs)	(%)	(mLmin ⁻¹)
		A	B	C	D
1	1	-	-	-	-
2	4	+	-	-	-
3	14	-	+	-	-
4	18	+	+	-	-
5	6	-	-	+	-
6	19	+	-	+	-
7	25	-	+	+	-
8	15	+	+	+	-
9	24	-	-	-	+
10	5	+	-	-	+
11	7	-	+	-	+
12	27	+	+	-	+
13	10	-	-	+	+
14	26	+	-	+	+
15	17	-	+	+	+
16	9	+	+	+	+

i. *Normal probability plot*

The normal probability plot is a statistical method that is used to evaluate the significance of factors. In the assessment of effects from unreplicated factorials, occasionally real and meaningful higher-order interactions occur and therefore it is necessary to allow for selection (Box et al., 1978). Daniel (1959)'s method by which effects are plotted on a normal probability plot often provides an effective way of helping with selection. This is a plot of the actual value of the effect estimates against their cumulative normal probabilities. It has been observed that if the effects occur simply as a result of random variation about a fixed mean, and the changes in levels of the independent variables have no real effect at all on the response, then all the main effects and interactions tend to be distributed about mean zero (normal distribution). The effects, therefore, plot on a normal probability plot as a straight line whereas if significant effects are significant, they will have a non-zero mean and will not lie along the straight line. To test and see whether they do, the main effects are ordered in increasing order and plotted with an appropriate scale. The scale is obtained by employing the generalized **Equation 3.1** (Box et al., 1978):

$$P = (i - 0.5) * \frac{100}{m} \quad 3.1$$

Where, m = total number of effects, P = Probability points, i = Order number

ii. *Pareto chart*

Plotting the effects on a Pareto chart provides an alternative and equally effective way of helping with the selection of significant factors. The Pareto chart is based on an algorithm that produces a statistically based acceptance limit of significance (Tague, 2004; Wilkinson, 2006). The level of significance is represented by horizontal bar graphs. Based on the Pareto principle of the “vital few”, this statistical technique is used for the selection of factors that produce a statistically significant overall effect. The critical value line that cuts across the bar graphs serves to separate the vital from the non-vital effects. The insignificant (non-vital) effects lie to the left side of the critical value line while the significant (vital) effects lie beyond the line to the right side.

3.3.2.2 Optimisation of significant factors

The statistically based optimisation approach called Response Surface Methodology (RSM) was used, in conjunction with the Central Composite Rotatable Design (CCRD) to determine the optimum conditions for leaching Cr from UG-2 concentrates. RSM is a famous technique used to find optimal conditions by using a quadratic polynomial regression model and is applied after diagnostic or screening experiments (Box et al., 1978). The CCRD is an experimental design used to collect data for building a second order quadratic model for the response variable. **Tables 3.5** and **3.6** list suggested process factors, factor levels and the optimisation experimental plan respectively.

Table 3.5: Process factors and their factor levels.

	Factor Levels				
	$-\alpha$	-1	0	+1	$+\alpha$
Oxygen Flow Rate (w/v)	10	15	28	40	45
Time (hours)	2	3	5	7	8
Temperature (°C)	85				
Acid concentration (%)	45				
Solid to liquid ratio (g/mL)	1:3				
Agitation Rate (rpm)	1000				

Table 3.6: Experimental plan for optimisation of significant factors.

		1	2
Standard Order	Random	Oxygen Flowrate	Time
Factorial Points	Order	2^{k-1}	2^{k-1}
1	1	-1	-1
2	6	+1	-1
3	7	-1	+1
4	12	+1	+1
5	3	$-\lambda$	0

6	4	$+\lambda$	0
7	9	0	$-\lambda$
8	10	0	$+\lambda$
9	2	0	0
10	5	0	0
11	8	0	0
12	11	0	0
13	13	0	0

i. *Central Composite Rotatable Design*

The data for fitting the second order response was collected by using the central composite rotatable design (CCRD). The experimental results were analysed statistically by using the analysis of variance (ANOVA) using Fisher's ratio test; standard errors of model coefficient (t-test) and the coefficient of determination (R^2). For the variables under consideration, a second order polynomial regression model was proposed as follows:

$$y = \beta_o + \sum_{i=1}^2 \beta_i x_i + \sum_{i=1}^2 \beta_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^2 \beta_{ij} x_i x_j + \varepsilon \dots \dots \dots 3.2$$

Where,

$\hat{y}$ is the predicted response, β_o is the coefficient for intercept, β_i is the coefficient of linear effect, β_{ii} is the coefficient of quadratic effect, β_{ij} is the coefficient of interaction effect, ε is a term that represents other sources of variability not accounted for by the response function; x_i and x_j are coded predictor variables for the independent factors. The coefficients of the regression model were estimated by fitting the experimental results using Design Expert® 11 software.

ii. *Response Surface Methodology*

The Response Surface Methodology (RSM) was used in this study. The main objective of employing the RSM is to optimise the response surface that is significantly influenced by

various process variables (Tripathy and Murthy, 2012). RSM is based on quadratic programming and is used in conjunction with the Central Composite Design (CCRD) to fit the experimental data and development of the second order regression model.

3.4 Data Analysis

The raw data was obtained as described in the preceding sections of this chapter. The data obtained was used to determine relationships between Cr extraction (the desired response) and the parameters tested. The experimental results and the relationships are discussed in the subsequent chapters of this dissertation. Cr extraction was calculated as a percentage of the Cr in the liquid phase to that in the UG-2 concentrate. Appendix A shows the sample calculations used.

3.5 Summary

Table 3.7 summarises the experimental plan of this research study. The table also includes material used, the process factors for each experimental segment and methodologies for data analysis.

Table 3.7: Summary of experiments conducted in the current study.

	Material	Process factors	Method	Data analysis
Preliminary leaching experiments	EPL UG-2 concentrate	-Time (hr) -Acid concentration (%) -Temperature (°C)	One factor at a time (OFAT)	Graphical
Identification of significant factors	EPL UG-2 concentrate	-Time (hr) -Acid concentration (%) -Temperature (°C) -Oxygen Flow Rate (mL/min)	Design of experiment: 2 ⁴ full factorial design	Graphical
Optimisation of significant factors	EPL UG-2 concentrate	-Oxygen Flow Rate (mL/min) -Time (hrs)	CCRD in conjunction with RSM	Graphical and numerical

Chapter 4

PRELIMINARY EXPERIMENTS

4.1 Introduction

The study presented in this Chapter aimed at investigating parameters which promote chromium (Cr) dissolution in the UG-2 flotation concentrate using an acid leach process. The characterisation of the material properties of the flotation concentrate is presented in the initial part of this chapter. Leaching characteristics of the flotation concentrate were investigated in order to understand the physical and chemical properties of the material as well as the limitations of the Cr extraction process.

Cr has inherent electrochemical properties, which fundamentally render it leachable under oxidative acid leaching conditions. Under these conditions, Cr dissolves to form water soluble Cr (III) (Cr^{3+}) sulphate hydrate species, which are environmentally friendly compared to Cr (VI) (Cr^{6+}) produced in alkali processing routes. It is widely recognized that the presence of Cr^{6+} has a negative impact on the environment and must, therefore, be avoided (Cheng et al., 2014). Most literature available on this topic has focused on chromite ore or chrome (Cr_2O_3) concentrates from physical concentrators. The chemical composition of this material is characterised by high concentrations of Cr_2O_3 (20-46 wt.%). This range is significantly higher than the Cr_2O_3 in the UG-2 flotation concentrate, which is rarely more than 7 wt.%. The difference in the Cr_2O_3 content between the chromite resources and the flotation concentrate used in this investigation necessitated preliminary investigations to establish appropriate process factor levels for Cr extraction from the low Cr_2O_3 material.

With the intention of exploring a hydrometallurgical route for reducing Cr_2O_3 in the UG-2 flotation concentrate, low pH values were adopted as the fundamental principle for Cr leaching conditions. In order to explore the possible influence of factors and to find appropriate lower and upper factor ranges, preliminary experimental tests were conducted according to the procedure that will be described later in this Chapter. The parameters investigated included leaching time, acid concentration and solid-to-liquid ratio. The understanding obtained from

these preliminary experiments was used as a basis for the screening and optimisation investigations that follow in subsequent Chapters.

4.2 Material characteristics

A UG-2 flotation concentrate sample from Eastern Platinum mine (EPL) was used in this preliminary experiments. The sample was received as thickener underflow slurry, which was re-pulped and wet screened to obtain +75 μm , +38 μm and -38 μm size fractions.

4.2.1 Mineralogical composition

The mineralogical composition of the UG-2 flotation concentrate used in this investigation is shown in **Table 4.1**. This sample contains 5.7 wt.% of base metal sulphides as the valuable mineral group. This group includes, among others; chalcopyrite, pentlandite, pyrrhotite and pyrite which are typically associated with the platinum group minerals.

The major gangue minerals in this sample are talc (63.62 wt.%), mica (7.40 wt.%), pyroxene (7.00 wt.%) and chromite (6.20 wt.%). Chromite in this concentrate sample assumes a crystallographic structure represented by a general formula $\text{X.Y}_2\text{O}_4$, where X represents the tetrahedral site of the crystal lattice for divalent cations (Mg^{2+} , Fe^{2+}), Y, the octahedral site for the partitioning of trivalent cations (Cr^{3+} , Fe^{3+} , Al^{3+}), and O, oxygen atoms. This is shown by the ASEM spectra for chromite in **Figure 4.1** and further supported by the elemental deportment data (for chromite) in **Table 4.2** and Appendix B.

The backscattered electron images of different chromite particles found in the sample used in this investigation are shown in **Figure 4.2**.

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Table 4.1: Ungrouped mineral composition of EPL final flotation concentrate.

Mineral Group	Mineral	Density	Formula	Mineral (wt.%)
Base Metal Sulphides	Chalcopyrite	4,20	$\text{CuFe}^{2+}\text{S}_2$	1,48
	Millerite	5,50	NiS	0,11
	Pentlandite	4,80	$\text{Fe}^{2+}_{4.5}\text{Ni}_{4.5}\text{S}_8$	2,37
	Pyrrhotite	4,62	$\text{Fe}^{2+}_{0.95}\text{S}$	0,57
	Pyrite	5,01	Fe^{2+}S_2	1,12
	Laurite	6,99	$(\text{Ru}, \text{Os})\text{S}_2$	0,03
Talc	Talc	2,75	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	63,62
Plagioclase	Anorthite	2,74	$\text{CaAl}_2\text{Si}_2\text{O}_8$	1,46
	Na-Plagioclase	2,69	$\text{Na}_{0.5}\text{Ca}_{0.5}\text{Si}_3\text{AlO}_8$	3,90
K-Feldspar	Orthoclase	2,56	KAlSi_3O_8	0,06
Pyroxene	Augite	3,40	$(\text{Ca}, \text{Na})(\text{Mg}, \text{Fe}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6$	2,93
	Diopside	3,40	$(\text{Ca}, \text{Mg})(\text{Si}_2\text{O}_6)$	3,66
	Ferrosilite	3,95	$\text{Fe}^{2+}\text{MgSi}_2\text{O}_6$	0,04
	Pigeonite	3,38	$(\text{Ca}, \text{Mg}, \text{Fe})(\text{Mg}, \text{Fe})\text{Si}_2\text{O}_6$	0,32
Quartz	Quartz	2,63	(SiO_2)	2,05
Serpentine	Lizardite	2,58	$(\text{Mg}, \text{Fe}^{2+})_3\text{Si}_2\text{O}_5[\text{OH}]_4$	0,58
	Chrysolite	3,36	$(\text{Mg}, \text{Fe})_2\text{SiO}_4$	0,32
Chromite	Chromite	4,80	$(\text{Fe}^{2+}, \text{Mg})(\text{Cr}, \text{Fe}, \text{Al})_2\text{O}_4$	6,20
Mica	Biotite	3,10	$\text{KMg}_{2.5}\text{Fe}^{2+}_{0.5}\text{AlSi}_3\text{O}_{10}(\text{OH})_{1.75}\text{F}_{0.25}$	7,16
	Muscovite	2,83	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_{1.9}\text{F}_{0.1}$	0,28
Carbonates	Calcite	2,71	$\text{Ca}(\text{CO}_3)$	0,15
	Dolomite	2,85	$(\text{Ca}, \text{Mg})(\text{CO}_3)_2$	0,02
Oxides	FeOxide	5,30	Fe_3O_4	1,22
	Rutile	4,25	TiO_2	0,12
Others	Unknown	1,00		0,24
Total				100.01

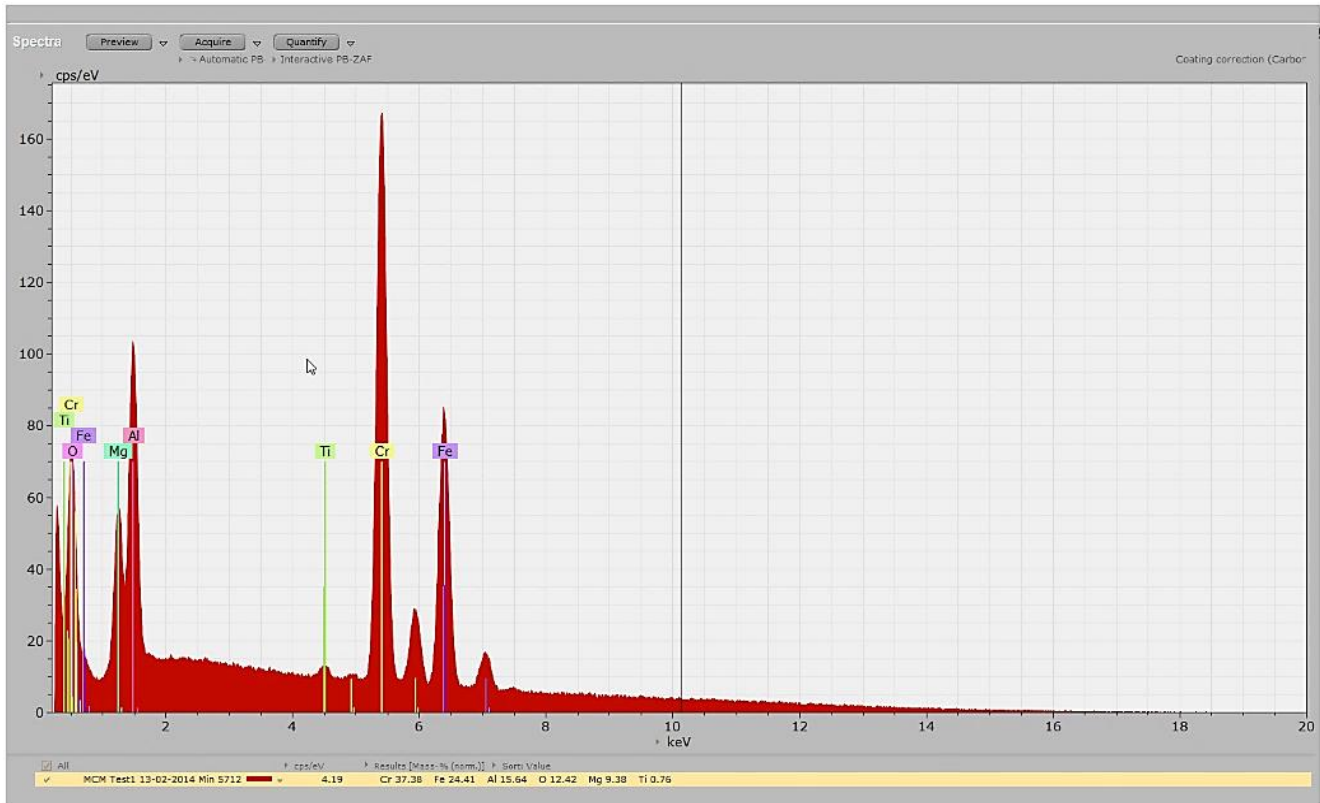


Figure 4.1: Chromite spectra.

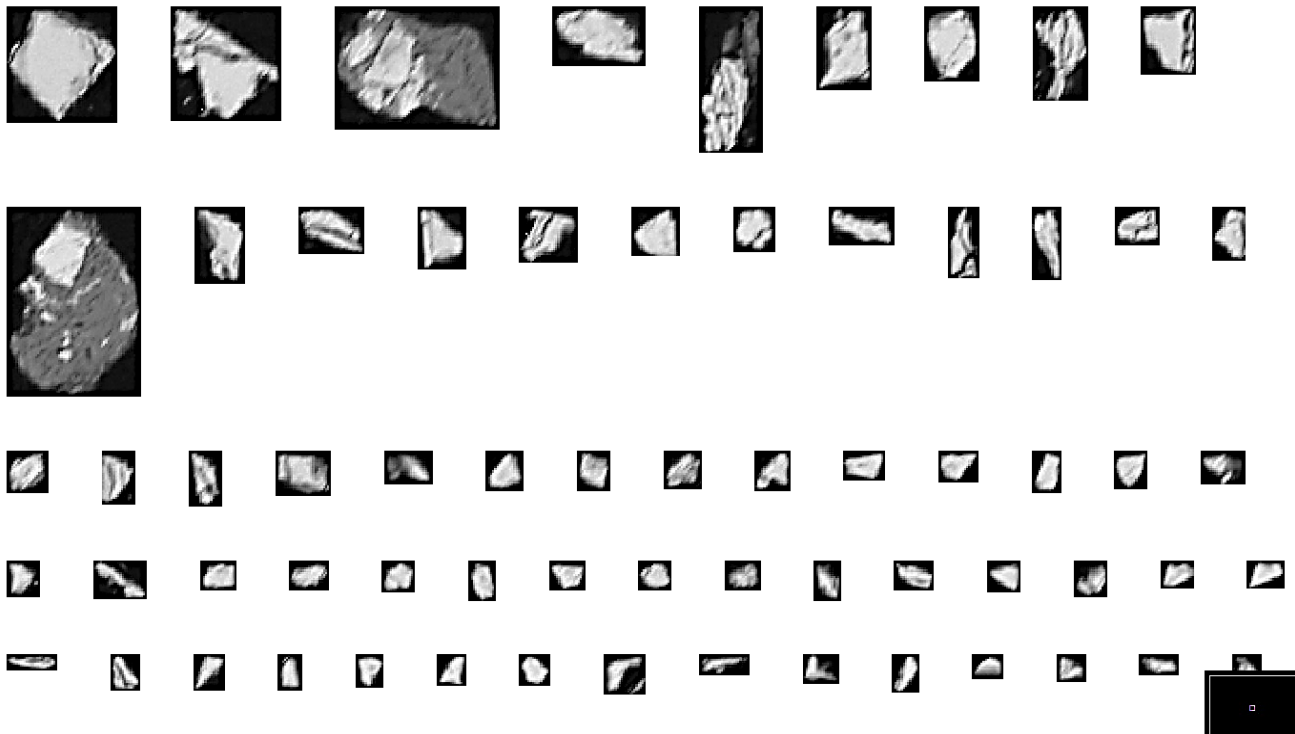


Figure 4.2: ASEM backscattered electron images of chromite.

4.2.2 Elemental deportment and mineral liberation analysis

The ASEM elemental deportment and mineral liberation data of the concentrate sample are shown in **Table 4.2**.

The elemental deportment data shows chromite as the only source of Cr in this UG-2 flotation concentrate. That is, 100 % of Cr in the sample is deported in the chromite mineral as shown in **Table 4.2**.

The bulk of the chromite in this material was well liberated. The MLA definition of liberation for this material was set at more than 80%. This degree of liberation means 80% of the particle surface area is exposed. **Figure 4.3** shows the recovered chromite in the final concentrate classified as fine grained (52%), well sized and liberated (43%), well sized and locked (5%). The fine-grained size fraction was defined as less than 10 µm, while the well-sized particle size fractions were defined as 10-150 µm. The latter includes the well sized and liberated and/or locked. Size fractions greater than 150 µm are defined as coarse grained.

In this sample, chromite was mainly locked with talc. Other mineral phases locked with chromite include the pyroxene group, mica, and other oxides (**Table 4.3**).

Table 4.2: Mineralogy, elemental distribution and liberation analysis of UG-2 concentrate

EPL Concentrate												
Calc. Assay (wt.%)				Mass	Elemental deportment				Liberation data (wt. %)			
Cr	Fe	Mg	Al	Total	Cr	Fe	Mg	Al	Fine grained	Well sized		Coarse grained
2	11,7	14,4	2,5	wt%	%	%	%	%		Lib	Lock	
Sulphides				5,7	0	18	0	0	22%	67%	12%	0%
Talc-Enstatite				63,6	0	47	85	0	20%	76%	4%	0%
Plagioclase				5,4	0	0	0	37	20%	67%	13%	0%
K-Feldspar				0,1	0	0	0	0	50%	33%	17%	0%
Pyroxene				7.0	0	2	5	5	32%	48%	20%	0%
Quartz				2.0	0	0	0	0	6%	63%	31%	0%
Serpentine				0,9	0	1	2	0	20%	64%	16%	0%
Chromite				6,2	100	19	2	20	52%	43%	5%	0%
Mica				7,4	0	6	5	37	18%	66%	15%	0%
Carbonates				0,2	0	0	0	0	23%	49%	29%	0%
Oxides				1,3	0	7	0	0	61%	29%	10%	0%
Others				0,2	0	0	0	0	65%	11%	24%	0%
Total				100	100	100	100	100	22%	0%	78%	0%

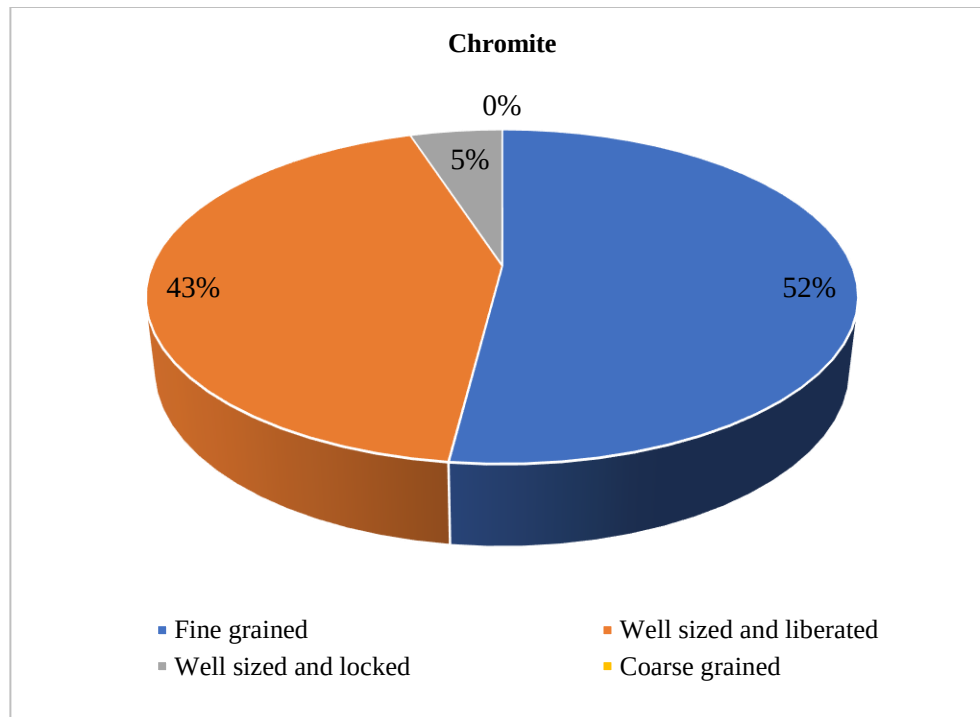


Figure 4.3: Chromite liberation data.

Table 4.3: Minerals locked with chromite and size fractions.

		Total (wt.%)	Fine grained (wt.%)	Assuming: "Well Sized" for recovery by flotation is the range 10 to 150 micron. >80% surface definition of liberation					Coarse grained	Well sized (wt.%)
	Liberated	94	51	29	13	1	0	0	0	43
	Locked	6	1	3	1	2	0	0	0	6
	(μm)	Unfiltered	0-10	10-25	25-50	50-75	75-100	100 -150	+150	10-150
Chromite Locked with....	Sulphides	0,1	0,0	0,1	0,0	0,0	0,0	0,0	0,0	0,1
	Talc	5,0	0,3	2,0	0,4	2,4	0,0	0,0	0,0	4,8
	Plagioclase	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
	K-Feldspar	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
	Pyroxene	0,3	0,1	0,2	0,0	0,0	0,0	0,0	0,0	0,2
	Quartz	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
	Serpentine	0,1	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
	Mica	0,4	0,0	0,2	0,1	0,0	0,0	0,0	0,0	0,3
	Carbonates	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
	Oxides	0,4	0,1	0,3	0,0	0,0	0,0	0,0	0,0	0,3
	Others	0,2	0,1	0,1	0,0	0,0	0,0	0,0	0,0	0,1

4.2.3 Mass distribution by size fraction

The flotation concentrate's mass distribution by size fractions is shown in **Table 4.4** and **Figure 4.4**. The sample was divided into +75 μm , +38 μm and -38 μm size fractions. Of the total sample mass, 78.95% reported to the -38 μm size fraction while the balance, 14.3% and 6.75%, reported to the +38 μm and +75 μm size fractions, respectively.

In summary, the bulk of this concentrate sample is fine grained. The advantage of the fine-grained particle size for the proposed acid leaching process could be higher leaching kinetics due to a large surface area. The downside, however, could be poor physical solid-liquid separation (filtration) rates due to the inefficiency and limitation of filtration equipment to process ultrafine material. Filtration aids to coalesce the ultrafine particles for faster and efficient filtration typically find large application in various mineral processing applications. In order to mitigate the downside of treating and handling this type of fine-grained material, the use of a filtration aid could be a potential intervention measure.

Table 4.4: Mass distribution of EPL flotation concentrate.

EPL Concentrate			
Size (μm)	Mass (g)	Mass %	Cumulative wt. % Passing
+75	221.56	6.75	93.25
+38	469.04	14.3	78.95
-38	2590.29	78.95	-
Total	3280.89	100	-

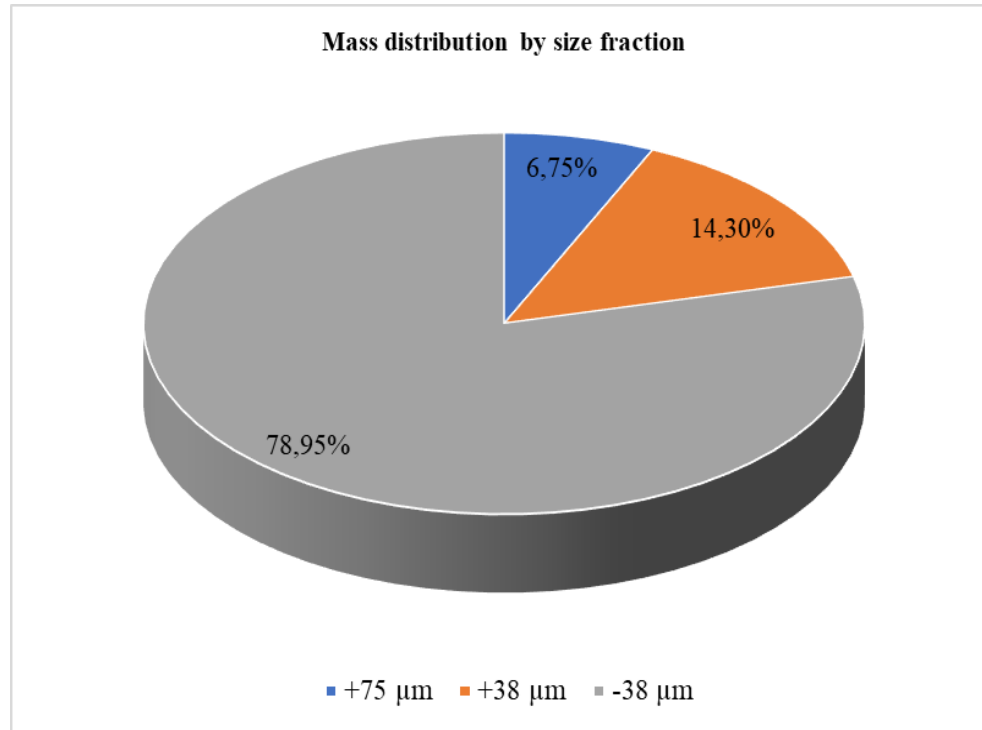


Figure 4.4: Mass distribution of the sample by size fraction

4.2.4 Chemical composition and Cr_2O_3 distribution by size fraction

Table 4.5 lists the chemical composition of the major size fractions characterising EPL's UG-2 flotation concentrate. The -38 μm size fraction, the largest in terms of mass distribution, has a Cr_2O_3 grade of 3.07 wt.%; while +38 and +75 μm size fractions contain grades of 1.48 and 1.81 wt.% Cr_2O_3 respectively.

Table 4.5: Chemical composition of divided size fractions of the EPL flotation concentrate.

Size (μm)	Chemical Composition (wt.%)							
	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Cr_2O_3	NiO
+75 μm	43.45	7.98	14.90	0.13	16.82	4.13	1.81	2.41
+38 μm	50.66	4.73	12.11	0.16	23.52	2.59	1.48	1.11
-38 μm	49.22	4.68	13.40	0.17	24.11	2.26	3.07	0.94

The Cr_2O_3 distribution by size fraction is shown in **Table 4.6** and **Figure 4.5**. Proportionally, the -38 μm size fraction contains the highest Cr_2O_3 content. That is, of the total Cr_2O_3 in EPL's flotation

concentrate, 88% is reported in the fine size fraction. The +38 and +75 μm size fractions host approximately 8% and 4% of the total Cr_2O_3 in the concentrate. Moreover, the +38 and +75 μm size fractions have Cr_2O_3 grades that are equal to or less than the maximum 1.8 wt.% allowed in the smelter feed for efficient solubility in the slag phase. Thus, on a plant scale, these size fractions can bypass the leaching step and report directly to the smelting process.

Table 4.6: Cr_2O_3 distribution by size fraction of the EPL flotation concentrate.

Size (μm)	Mass (g)	Mass (wt. %)	Cr_2O_3 Grade (%)	Cr_2O_3 Distribution by size fraction
+75 μm	221,56	6.75	1.81	4.43
+38 μm	469,04	14.30	1.48	7.67
-38 μm	2590,29	78.95	3.07	87.89
Total	3280,89			100

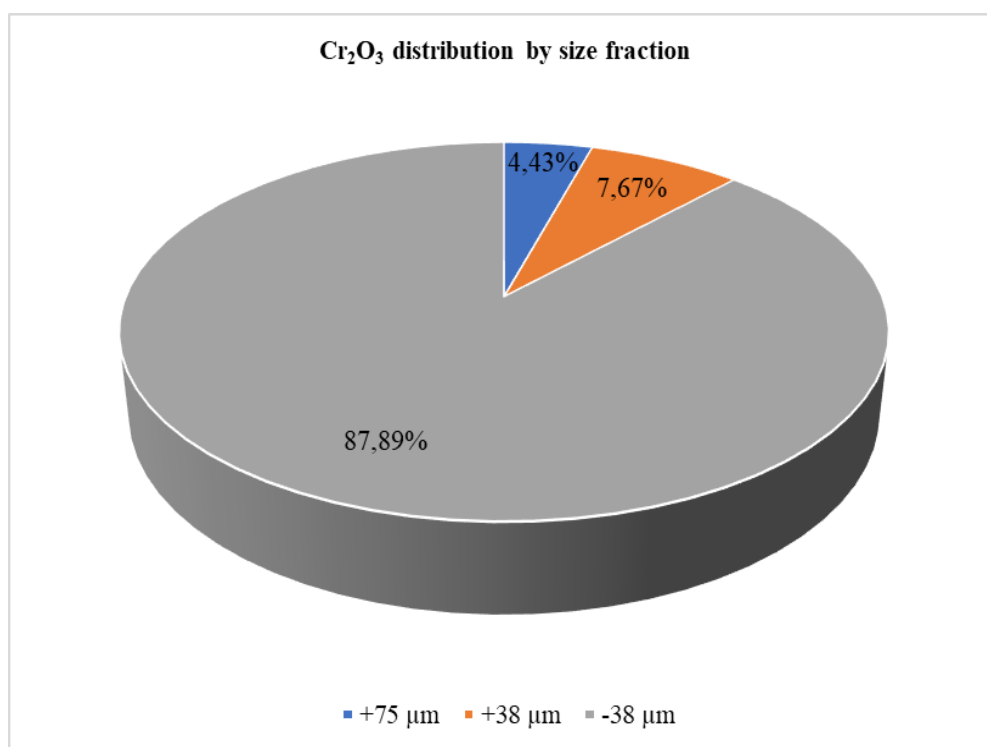


Figure 4.5: Cr_2O_3 Distribution by size fraction.

Based on the chemical composition and Cr_2O_3 distribution in the various particle sizes of this concentrate sample, preliminary experiments were performed on the $-38\ \mu\text{m}$ size fraction. The Cr_2O_3 grade of this size fraction is proportionally higher, and its particle size is relatively finer, which is ideal for faster leaching kinetics and in line with the aim and objectives of the current study. These results were also used to guide sample preparation and handling of sample material used in the screening and optimisation experiments discussed in Chapters 5 and 6.

4.3 Experimental Procedure

Varied and fixed process parameters used in the preliminary experiments are listed in **Table 4.7**. Solid-to-liquid ratio (1:2-1:26), leaching time (1-5 hrs) and acid concentration (45-85 v/v%) were used, while leaching temperature ($120\ ^\circ\text{C}$), agitation rate (500 rpm) and air flowrate (17 mL/min) were kept constant.

The choice of values for variable and fixed leaching conditions was based on literature. For instance, work done by Zhao et al. (2014) and Jiang et al. (2014) showed that chromite dissolves in concentrated sulphuric acid below $200\ ^\circ\text{C}$ in the presence of an oxidant. Cr extraction of plus 80% was obtained when chromite was leached by 70-85 %v/v sulphuric acid and perchloric acid at $175\ ^\circ\text{C}$ (Amer, 1992; Geveci et al., 2002; Vardar, 1994). Work done by Jiang et al. (2014) and Zhao et al (2012) showed that magnesium and aluminium were leached out together from the silicate phase and porous amorphous silica was produced as a product layer, while the spinel phase gradually shrank with increased duration of leaching. Consequently, the extractions from the silicate phase and shrinkage of the spinel phase led to the exposure of Cr, thus enhancing Cr leaching rates. From these works, it seems apparent that the processing of chromite is associated with high acid concentrations and temperatures.

Based on the above literature findings, leaching conditions were formulated to explore factor ranges of solid-to-liquid ratio, leaching time and acid concentration. The fixed leaching temperature of $120\ ^\circ\text{C}$ was however chosen in the current study as it was relatively lower compared to temperatures used in the previous studies. The maximum H_2SO_4 concentration of 85 %v/v was chosen since acid concentrations above this level significantly increase the viscosity of the leach solution, which in turn, reduces mass transfer (Vardar, 1994).

Each experimental run entailed preparing a batch of leaching solution of known concentration and volume. This was dispatched into a 2-litre leaching vessel, which was then placed in a heating oil bath. The oil bath was set to heat the leaching solution to 120 °C. Once the desired leaching temperature was attained, an overhead stirrer was started and run at 500 rpm. This was followed by charging a known mass of the sample into the leaching vessel. The feeding of air into the reaction mixture marked the beginning of the experiment. The leaching conditions used in the preliminary experiments are listed in **Table 4.7**.

Table 4.7: Leaching conditions used in the preliminary experiments.

Varied parameters	Varied conditions
Solid-Liquid ratio (g/mL)	1:2; 1:6; 1:10; 1:14; 1:18; 1:22; 1:26
Leaching time (hrs)	1; 2; 3; 4; 5
H ₂ SO ₄ Conc (%v/v)	45; 55; 65; 75; 85
Fixed parameters	Fixed conditions
Temperature (°C)	120
Agitation rate (rpm)	500
Air-flowrate (mL/min)	17

At the end of each experiment, the pulp was filtered to obtain a filtrate and residue. The residue was adequately washed with deionised water to recover the entrained and adsorbed leached metal species. The wash water and the primary filtrate of known volumes were then mixed, and the total volume was recorded. The mixed solution was thereafter sampled for Atomic Absorption Spectrometry (AAS) analysis. A flow diagram of preliminary experiments and the experimental set-up are presented in **Figures 4.6** and **4.7** respectively.

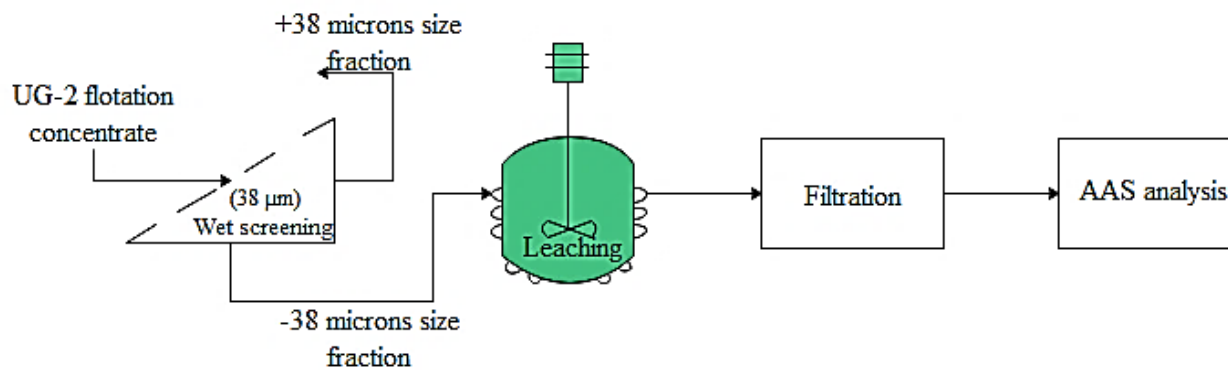


Figure 4.6: The flow diagram of preliminary experiments

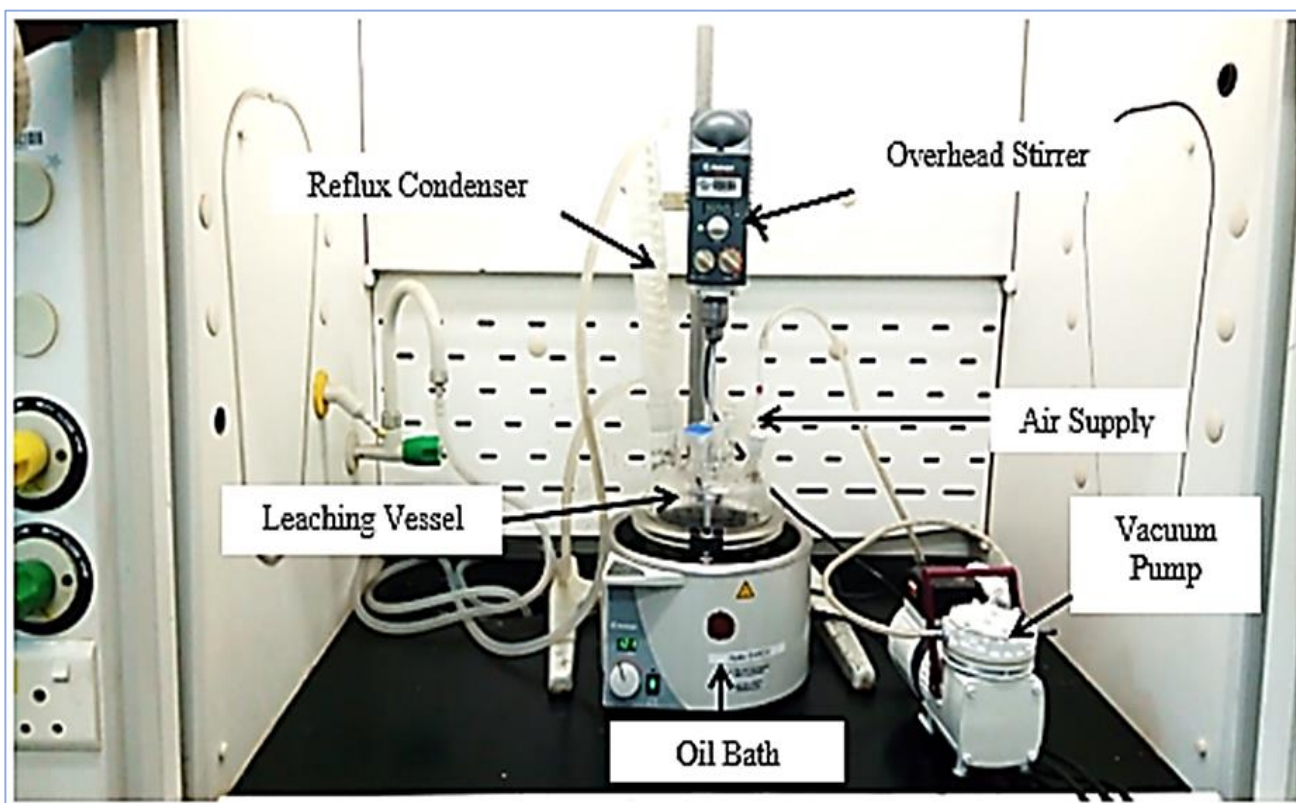


Figure 4.7: Experimental set-up for preliminary tests.

4.4 Results and Discussion

Table 4.8 shows Cr extraction efficiency as a function of solid-to-liquid ratio, acid concentration and leaching time. The factor levels explored for each process factor are shown in **Table 4.7**. The experimental work in this section involved a total of 15 experimental runs.

Table 4.8: Chromium extraction results.

Test No.	S-L ratio	H ₂ SO ₄ Conc. % (v/v)	Time (hr.)	Temperature (°C)	Agitation rate (rpm)	Air flowrate (mL/min)	Cr Extraction (%)
1	1:2	75	3	120	500	17	8.20
2	1:6	75	3	120	500	17	17.58
3	1:10	75	3	120	500	17	23.54
4	1:14	75	3	120	500	17	35.60
5	1:18	75	3	120	500	17	39.57
6	1:22	75	3	120	500	17	46.62
7	1:26	75	3	120	500	17	67.33
8	1:26	45	3	120	500	17	32.53
9	1:26	55	3	120	500	17	43.70
10	1:26	65	3	120	500	17	55.16
11	1:26	85	3	120	500	17	73.74
12	1:26	75	1	120	500	17	61.89
13	1:26	75	2	120	500	17	62.84
14	1:26	75	4	120	500	17	76.37
15	1:26	75	5	120	500	17	87.12

4.4.1 The effect of solid-to-liquid ratio

The effect of solid-to-liquid ratio on Cr extraction is shown in **Figure 4.8**. The ratios explored included 1:2; 1:6; 1:10; 1:14; 1:18; 1:22 and 1:26 at fixed levels of H₂SO₄ concentration (75%v/v), leaching time (3hours), temperature (120 °C), agitation rate (500 rpm) and airflow rate (17 mL/min).

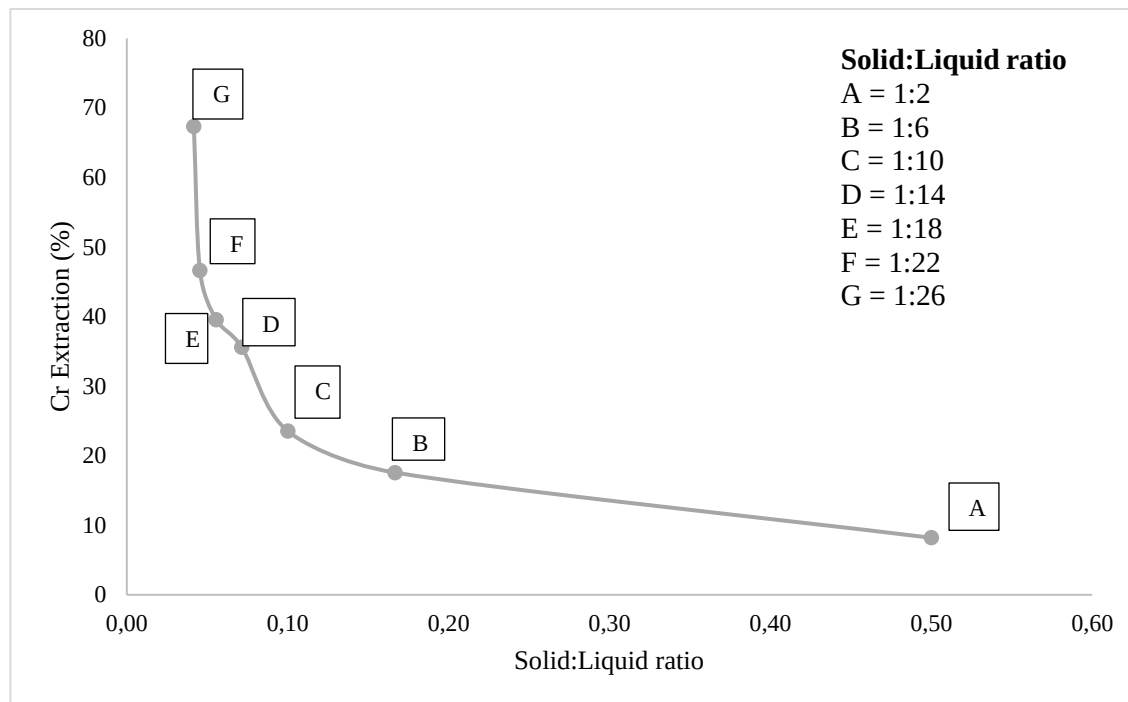


Figure 4.8: Cr extraction as a function of solid-to-liquid ratio.

A low Cr extraction of 8.20% was obtained at the highest solid-to-liquid ratio of 1:2, while 67.33% Cr extraction was obtained at the lowest solid-to-liquid ratio of 1:26 under fixed conditions highlighted above. The data shows an exponential increase in the Cr extraction rate as the solid-to-liquid ratio decreases from 1:2 to 1:26. The increased Cr extraction rate with decreasing solid-to-liquid ratio could be attributed to several factors. A possible decomposition process of the spinel structure $[(\text{Fe}, \text{Mg})\text{O}(\text{Cr}, \text{Fe}, \text{Al})\text{O}_4]$, in which metals in the tetrahedral site (X^{2+}) are dissolved first then followed by the metals in the octahedral site (Y^{3+}), has been suggested by some authors (Biermann and Heinrichs, 1960; Vardar, 1993; Zhao et al., 2014). This mechanism delays the dissolution of Cr, which is further impacted by the co-dissolution of unwanted metals from silicate minerals and other oxides (Jiang et al., 2014; Zhao et al., 2014). The results obtained from the research done by Zhao et al. (2014) showed a possible sequential dissolution mechanism when leaching a chromite lump. Mg, Fe, and Al from silicate phases leached out first, followed by the gradual decomposition of chromite via the dissolution of metals in the tetrahedral and octahedral sites, respectively.

At low solid-to-liquid ratios, the ratio of available liquid reactants to solid particulates in the leaching system is significantly higher. The net effect of this is sufficient availability of reactants to extract Cr in chromite and unwanted leachable metals (Fe, Mg, Al, etc.) contained in chromite and other mineral phases. Inversely, at high solid-to-liquid ratios, the reactant to particulate ratios is relatively lower and the dissolution of unwanted metal species fast consumes the reactants prior to the decomposition of the spinel structure. This suggests that at high solid-to-liquid ratios, the availability of reactants is a rate limiting factor to the extraction of Cr.

The impact of solid-to-liquid ratio on Cr extraction can also be explained in terms of mass transfer and dispersion of solid particles in the leaching system. Low solid-to-liquid ratios typically produce pulp densities of lower slurry viscosities, which promotes easy transfer of reactants to the surface of particles, and the transfer of products from the particle surface to the bulk solution. At high solid-to-liquid ratios, pulp viscosity was proportionally observed to be higher. This could have resulted from the constituent solids, reactant products and the possible presence of a silica gel due to the dissolution of some silicate minerals under acidic leaching conditions.

Another factor worth noting about the UG-2 flotation material used in this investigation is its visually observed electrostatic properties. The particles in the EPL concentrate sample were observed to be highly charged when rubbed against plastic surfaces. This suggested that the concentrate material had the affinity to agglomerate through the formation of temporary electrostatic bonds. The net effect of this is the possible reduction of particle surface areas available for solid-liquid contact and consequent metal extraction. Operating at low solid-to-liquid ratios may have caused a dispersive effect, which may have led to the prevention of particle agglomerations, and thus enhanced mass transfer and reaction efficiencies.

4.4.2 The effect of leaching time

Cr extraction as a function of leaching time is presented in **Figure 4.9**. The time interval investigated in this section was 1-5 hours, at a temperature of 120 °C, H₂SO₄ concentration of 75 % (v/v), a solid-to-liquid ratio of 1:26, an agitation rate of 500 rpm and air flowrate of 17 mL/min.

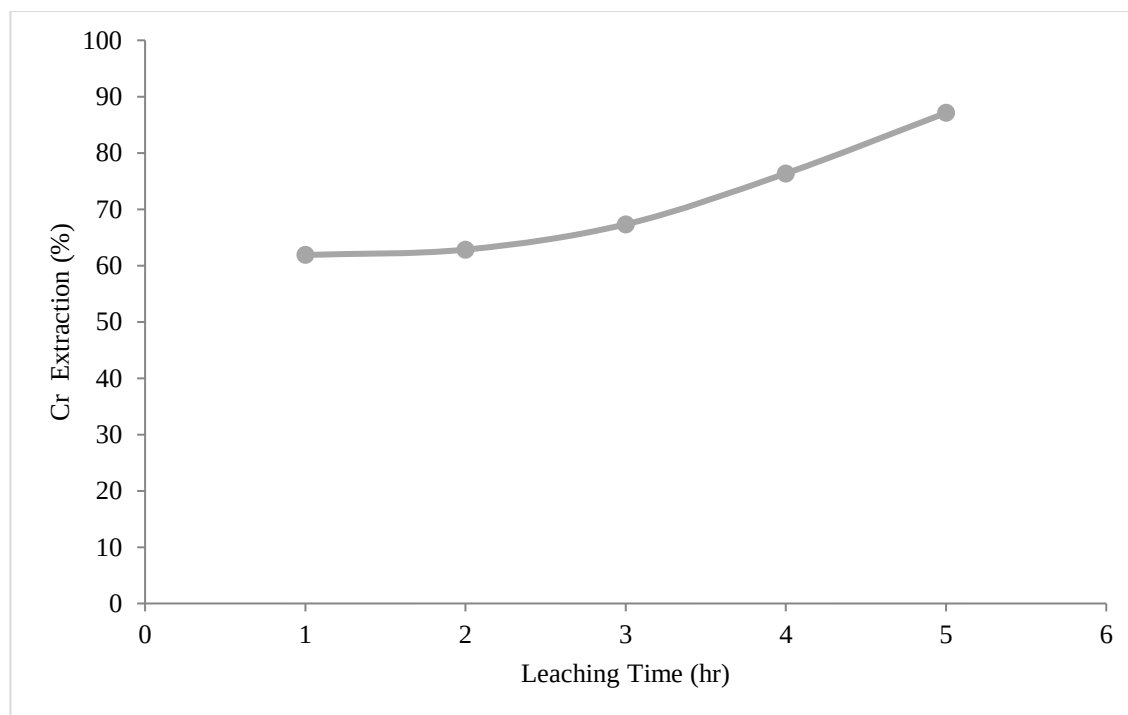


Figure 4.9: Cr extraction as a function of leaching time.

As shown in the figure, Cr extraction proportionally increased with increase in leaching time. From 1 to 3 hours, Cr extraction gradually increased, while significant increments in extraction were observed at 4 and 5 hours. A Cr extraction of 87% was obtained at a leaching time of 5 hours. This was the highest Cr extraction obtained from the preliminary experiments, which suggests that time is also an important process factor for Cr extraction.

The results in this section also provide information about the minimum time required for considerable Cr extraction to reduce Cr_2O_3 to 1.8 wt.% and below in the UG-2 flotation concentrate. The results show that minimum leaching time of 1 hour will suffice to reduce Cr_2O_3 by 60%. i.e., from 3.07 wt.% to 1.23 wt.%.

4.4.3 The effect of sulphuric acid concentration

The effect of acid concentration on Cr extraction was studied by varying H_2SO_4 concentration between 45 and 85 % (v/v). Other leaching process factors were fixed as follows: temperature at 120 °C, 1:26 solid-to-liquid ratio, 3 hours leaching time, 500 rpm and 17 mL/min of air.

Figure 4.10 graphically summarises the effect of H_2SO_4 concentration on Cr extraction. The figure shows a linear increase in Cr extraction with increasing acid concentration. The high Cr extractions of approximately 74% and 67% were obtained at 85 and 75 % (v/v) acid concentrations, respectively. The low Cr extraction of 35% was obtained at 45 % (v/v) acid concentration. This pattern is evident as the increase of acid concentration shifts pH to lower values, which are more ideal for Cr dissolution. As per **Figure 2.6**, Cr is thermodynamically stable as chromic oxide (Cr_2O_3) at neutral pH, which dissolves to form stable aqueous Cr^{3+} species as the pH decreases. Overall, it can be concluded that high H_2SO_4 concentration (low pH) has a positive effect on Cr extraction from the UG-2 flotation material.

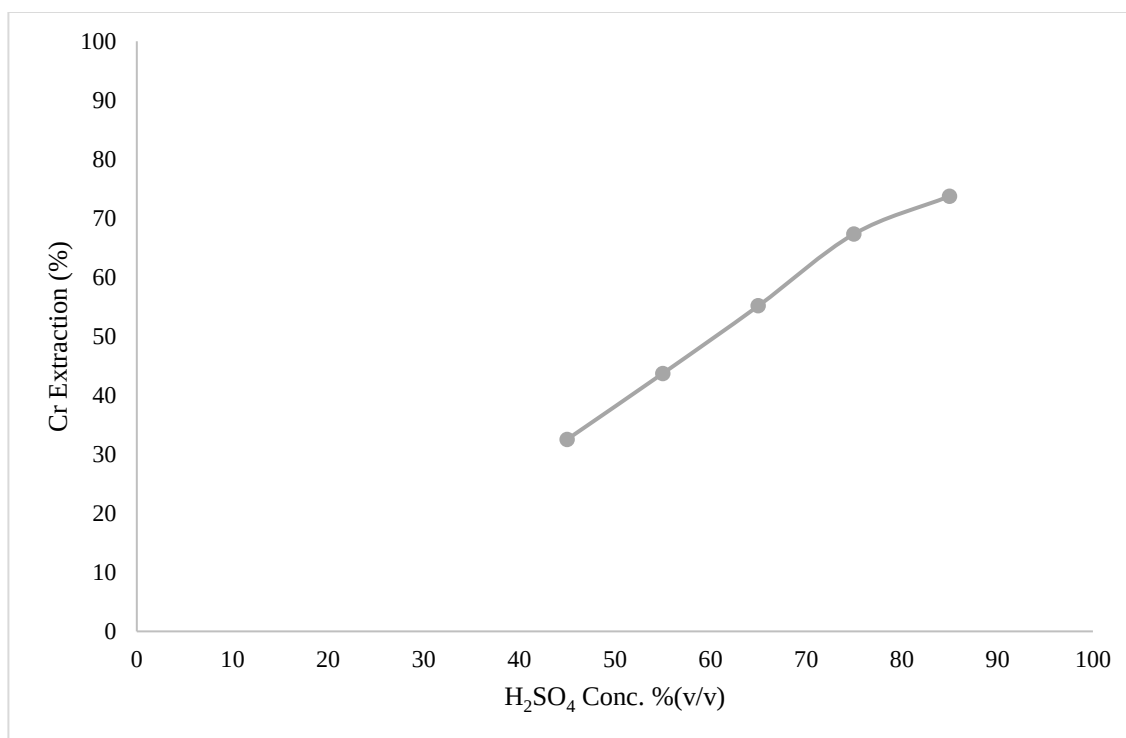


Figure 4.10: Cr extraction as a function of H_2SO_4 concentration.

4.5 Summary and conclusions

The preliminary experiments in this chapter aimed to explore the effect of three selected process factors on Cr extraction from EPL's UG-2 flotation concentrate. The study also aimed to determine appropriate factor levels for possible practical application as well as use in the design

of experiments (DOE) in the subsequent chapters. The process factors investigated included solid-to-liquid ratio, acid concentration and leaching time.

The EPL's flotation concentrate sample was found to be largely fine grained with 79 wt.% of the sample reporting to the -38 μm size fraction. Of the total Cr_2O_3 in the sample, 88 % reported to the -38 μm size fraction. Thus, all preliminary experiments were performed using the -38 μm size fraction.

Overall, the results of preliminary experiments show that all the three selected process factors have a positive effect on the extraction of Cr from the UG-2 flotation concentrate.

Cr extraction increased exponentially with a decreasing solid-to-liquid ratio. This was attributed to the availability of sufficient reactants, high mass transfer rate and a high dispersive net effect at low solid-to-liquid ratios. A solid-to-liquid ratio of 1:26 yielded a Cr extraction of 67% at fixed levels of H_2SO_4 concentration (75%v/v), leaching time (3hours), temperature (120 $^\circ\text{C}$), agitation rate (500 rpm) and airflow rate (17 mL/min). Under the same conditions, a Cr extraction of 8% was obtained at a solid-to-liquid ratio of 1:2.

Leaching time had a positive effect on Cr extraction at fixed 1:26 solid-to-liquid ratio, 75%v/v H_2SO_4 concentration, 120 $^\circ\text{C}$ temperature, 500 rpm agitation rate and 17 mL/min airflow rate. Cr extraction increased with increasing leaching time from 1 to 5 hours. The highest Cr extraction of 87% was obtained at 5 hours. The minimum leaching time of 1 hour was found to be adequate to reduce Cr_2O_3 by 60% from 3.07 wt.% to 1.23 wt.%.

It seems apparent, from these results above, that the processing of chromite is associated with high acid concentrations, high temperatures and low solid-to-liquid ratios.

While solid-to-liquid ratio is evidently one of the most important process factors on Cr extraction, the practicality and economics of operating at low solid-to-liquid ratios limit the commercial application of the leaching process due to high operating costs and high solution volumes that may be required. Thus, for subsequent screening and optimisation of experiments, a solid-to-liquid ratio of 1:3 was elected. To mitigate the effect of fixing the solid-to-liquid ratio at 1:3, the following adjustments are to be employed in subsequent DOE experiments:

- Extend leaching time to 6 hours.
- Use pure oxygen as an oxidising agent. For similar gas flowrates, pure oxygen would produce higher dissolved oxygen (DO) concentrations than air. High DO is required to maintain an oxidative environment for fast Cr solubilisation mechanisms.
- Increase agitation rate to 1000 rpm and use a four-bladed stirrer. A stirrer with four blades orientated at an angle will assist to enhance the dispersion and suspension of particles for maximum contact with the leaching reagents.

High leaching temperatures ($>120\text{ }^{\circ}\text{C}$), which were widely reported in literature to have been suitable for extracting Cr from primary resources of Cr_2O_3 (40-46%) are also considered as a possible limiting factor for scaling up the proposed leaching process to reduce Cr_2O_3 ($<6\%$) in the UG-2 concentrates. The high temperatures have the potential to inadvertently increase the CAPEX and OPEX of the proposed leaching process as special equipment and high energy inputs will be required. Although the scope of the preliminary experiments did not cover the effect of low temperatures on Cr extraction, subsequent experiments will be conducted on the temperature range of below $100\text{ }^{\circ}\text{C}$. This temperature range is selected as low Cr extractions of approximately 50% are aimed for in this study, which are significantly below the targeted Cr extractions of 90% in operations processing the primary resources of Cr_2O_3 . This temperature range is considered economically viable for the proposed leaching process.

Furthermore, a sulphuric acid concentration range of 45-75 % (v/v) is to be employed in subsequent experiments.

The next chapter discusses identification of influential process factors.

Chapter 5

IDENTIFICATION OF INFLUENTIAL FACTORS

5.1 Introduction

Results presented in the previous chapter demonstrated that Cr can be leached from UG-2 material using sulphuric acid leaching. The results established factor ranges that are pertinent to Cr leaching. The current chapter presents identification of process factors which significantly influence the Cr dissolution process. Identification of influential factors is necessary for process optimisation, improved efficiency, higher quality results, greater adaptability and cost control. Once the significant factors of a process are identified, they can then be optimised while the non-significant factors are kept constant at pertinent levels. This study aimed to identify factors which promote Cr dissolution using a statistical design of experiments (DOE) method. The process factors investigated included acid concentration, temperature, leaching time and oxygen flowrate. The significance of each factor and associated interactive effects were evaluated using a two-level factorial design (2^4) and dissolved Cr was taken as the measured response.

5.2 Experimental Plan for Statistical Design of Experiments

In this work, a statistical DOE was used to study the leaching behaviour of Cr from EPL's UG-2 concentrate. At this identification stage, the study looked at the influence of the main factors on the acid leaching of the UG-2 concentrate. The main intention was to identify the key independent variables that affect the response and the interactions among themselves. The major objective was to find the maximum solubilization of Cr using sulphuric acid. The desired response was therefore, Cr extracted into solution. Leaching experiments were carried out at low and high factor levels represented by codified values of -1 and +1 respectively.

5.2.1 Factors and Factor Levels in Experimental Runs

The leachability of Cr from chromite ores under acidic conditions has been extensively investigated (Zhang et al., 2016; Jiang et al., 2014; Zhao et al., 2014; Geveci et al., 2002; Vardar et al., 1994; Amer, 1992). Therefore, the choice of factors and factor levels was based on preliminary runs and literature. This study was designed to determine the influence of some of

these factors in the leaching of Cr using sulphuric acid and quantify them to make sure that the influence is both predictable and measurable. In this work, design factors were categorized as controlled factors and held constant factors. The controlled factors presented in **Table 5.1**, were the factors selected for investigation. The held constant factors such as agitation rate and solid-to-liquid ratio were factors that may have an influence on the response but are of no particular interest in the current study, so they were held constant at 1000 rpm and 1:3 respectively.

Table 5.1: Experimental factors and levels for controlled factors.

Controlled Factors	Low (-1)	Centre point (0)	High (+1)
Leaching temp (°C) [A]	43	62	85
Leaching time (hr) [B]	1	3	5
Acid concentration (%) [C]	45	60	75
Oxygen flow rate (mLmin ⁻¹) [D]	10	20	30
Constant Factors			
Solid-to-Liquid ratio (g/mL)	1:3		
Agitation rate (rpm)	1000		

The use of two levels for each factor at this diagnostic stage allows for simplification of the analysis and provides substantial reduction in the number of runs required.

For brevity and uniform comparison, controlled factors were studied with their codified values of -1 or +1. According to Box and collaborators (1978), the formula for obtaining the levels of controlled variables in coded units is presented as:

$$\text{coded value} = \frac{X - X_0}{0.5(X_2 - X_1)} \quad 5.1$$

Where, Where, X = actual, X₀ = mean, X₁ = lowest, X₂ = highest

5.2.2 Methodology for Data Analysis

5.2.2.1 Normal probability plot of effects

In order to assess effects from unreplicated factorials, it is necessary to allow for selection because occasionally, real and meaningful higher order interactions occur. A method developed by Daniel (1959) through which effects are plotted on a normal probability plot often provides an effective way of helping with selection. If the effects had occurred simply as the result of random variation, then they would plot on a normal probability plot as a straight line and would be distributed about the zero mean (normal distribution). To see whether they do, the main effects are ordered in increasing order and plotted with an appropriate scale. The scale is obtained by employing the generalized equation:

$$P = (i - 0.5) * \frac{100}{m} \quad 5.2$$

Where,

m = total number of effects, P = Probability points, i = Order number.

5.2.2.2 Pareto chart

An alternative and equally effective way of helping with selection of significant factors, known as the Pareto Chart, is suggested by Tague (2004) and Wilkinson (2006). The Pareto chart is based on an algorithm that produces a statistically based acceptance limit of significance represented by horizontal bar graphs. The statistical technique, based on the Pareto principle, is used for selection of the “vital few” factors that produce the significant overall effect. The critical value line that cuts across the bar graphs serves to separate the vital from the non-vital effects. The non-significant effects lie to the left side of the critical value line while those estimated as significant lie beyond the line to the right side.

In order to “average out” the effects of extraneous factors that may have been present, all experiments were randomly run as suggested by Montgomery (1976).

5.3 Results and Discussion

5.3.1 Significant factors

Cr extraction results from experimental runs for the 2^4 full factorial design with codified and actual values are given in **Table 5.2**. The Cr extraction in the leaching of the UG-2 concentrate presented in **Table 5.2** was calculated as a percentage of Cr in leach liquor to that in the unprocessed UG-2 concentrate sample.

Table 5.2: Chromium extraction results for the 2^4 full factorial design.

Standard Run Order	Random Run Order	Control Factors				% Cr Extraction (average)
		A	B	C	D	
1	1	-1	-1	-1	-1	5.2
2	4	+1	-1	-1	-1	7.9
3	14	-1	+1	-1	-1	7.9
4	18	+1	+1	-1	-1	2.9
5	6	-1	-1	+1	-1	3.4
6	19	+1	-1	+1	-1	4.2
7	25	-1	+1	+1	-1	3.6
8	15	+1	+1	+1	-1	4.8
9	24	-1	-1	-1	+1	6.4
10	5	+1	-1	-1	+1	8.2
11	7	-1	+1	-1	+1	8.2
12	27	+1	+1	-1	+1	7.4
13	10	-1	-1	+1	+1	7.0
14	26	+1	-1	+1	+1	5.2
15	17	-1	+1	+1	+1	7.0
16	9	+1	+1	+1	+1	6.3

The actual factor levels coded as values of (-1) and (+) in the table are as follows: A (Temperature): 43°C (-1) and 80°C (+1); B (Leaching time): 2hrs (-1) and 4hrs (+1); C (Acid conc): 45% (-1) and 75% (+1); D (Oxygen flowrate): 10 mLmin⁻¹ (-1) and 30 mLmin⁻¹ (+1).

The experimental data given in **Table 5.2** was used to identify the main and interaction effects presented in **Figures 5.1** and **5.2**. Examination of the individual factors on the normal probability plot in **Figure 5.1** showed that oxygen flowrate (D) and acid concentration (C) were statistically significant.

The significance of these main factors on the normal plot is seen in their distant distribution from the zero mean. The figure also shows the interaction of temperature, leaching time and acid concentration (ABC) to be statistically significant because of their distant distribution from the zero mean as well as not lying on a straight line. The results in the Pareto chart shown in **Figure 5.2** confirmed the findings illustrated by the normal probability plot of effects in **Figure 5.1**. The significance or non-insignificance of an effect on the Pareto chart is distinguished by the critical-value line below which the effect is deemed insignificant. The examination of the Pareto chart shows that effect D (oxygen flowrate), C (acid concentration) and ABC (interaction of temperature, time and acid concentration), are statistically significant factors.

A polynomial model of first order degree was derived to indicate the dependence of the response (Cr extraction) on the significant factors. A simplified expression of the regression model is presented as:

$$\hat{Y} = 5.98 - 0.79X_C + 0.99X_D + 0.74X_{ABC} \quad 5.3$$

Where,

$\hat{Y}$ is Cr extraction; X_C , X_D and X_{ABC} are predictor variables which take on the value of -1 or +1 (low or high). The positive and negative signs in the model indicate that in order to maximize Cr extraction, these factors must be kept at low and high levels respectively.

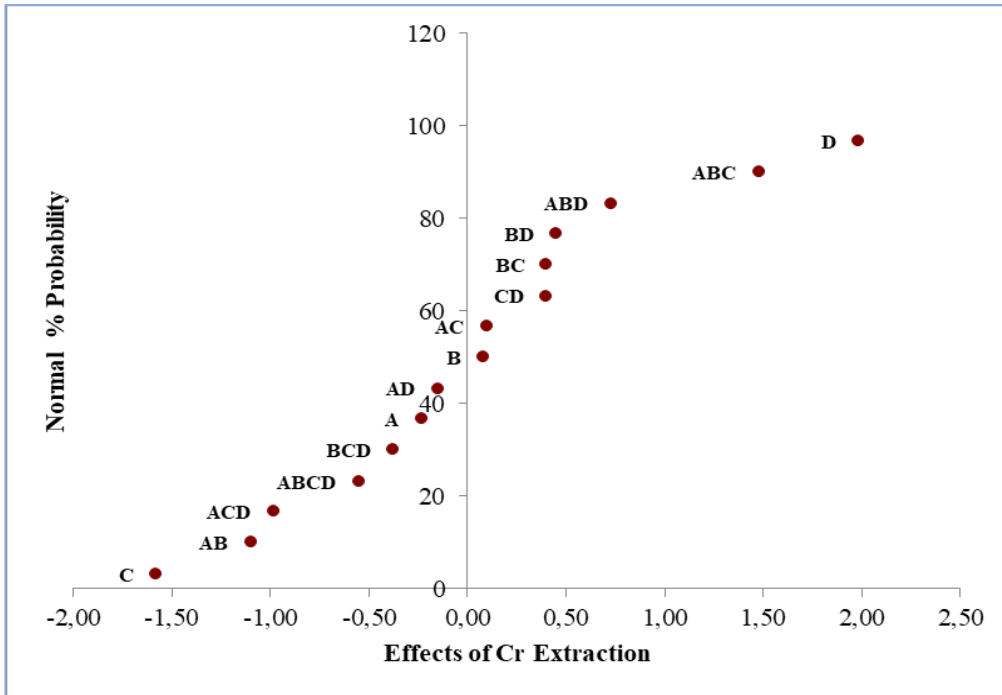


Figure 5.1: Normal probability plot of 2^4 full factorial design of main and interacting factors. A, B, C and D are main factors: A - temperature, B - time, C - acid concentration, D - oxygen flowrate. AB, ACD, ABCD, BCD, AD, AC, BC, CD, BD, ABD and ABC are interacting factors.

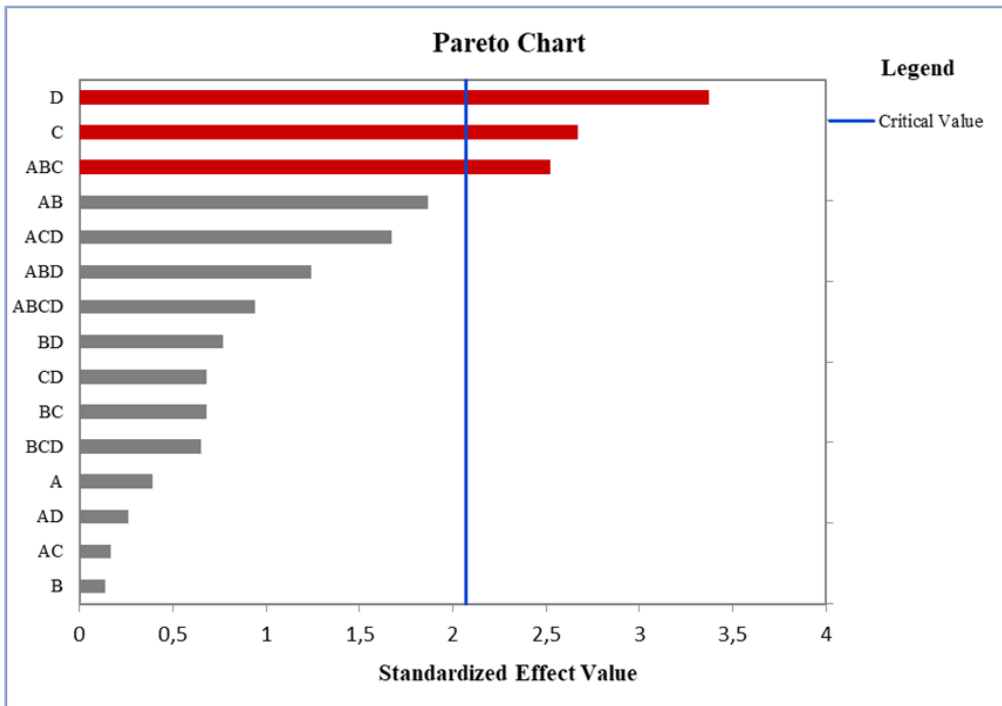


Figure 5.2: Pareto chart of 2^4 full factorial design of main and interacting factors. A, B, C and D are main factors: A - temperature, B - time, C - acid concentration, D - oxygen flowrate. AB, ACD, ABCD, BCD, AD, AC, BC, CD, BD, ABD and ABC are interacting factors.

5.3.2 Influence of process factors on Cr extraction

The interpretation of the influence of factors on the process response may be done in one of two ways: When factor interaction is absent, the variables can be interpreted individually. However, when factor interaction is evident, the variables must be interpreted jointly (Box et al., 1978). In this study, both cases applied. Therefore, all the factors were first interpreted individually and then the interaction factors ABC (leaching temperature, A; leaching time, B; acid concentration, C) variables were interpreted jointly.

5.3.2.1 *The effect of temperature*

The effect of temperature on Cr extraction is shown in **Figure 5.3**. As shown in the figure, higher temperatures had a relatively strong effect on Cr dissolution. An increase in leaching temperature from 25 °C to 43 °C, sharply increased Cr extraction from 2.7 % to 6.1 %. This remained almost constant between 43 and 85 °C with the highest Cr extraction variance of 0.2 %. A further increase in leaching temperature from 85 to 98 °C, steadily increased Cr extraction from 5.9 % to 7.4 %. The similar Cr extractions obtained at temperatures 43-85 °C could be attributed to the insufficient thermal energy required to further drive the chemical reaction forward as explained by Free (2013). Above this range, a pattern in Cr extraction emerged. This is consistent with similar work done by authors like Jiang et al. (2014), Zhao et al. (2014) and Vardar et al. (1994), who achieved definitive Cr extraction patterns at temperatures of 140-210 °C. For practical application, a temperature of 85 °C was chosen as the appropriate level for this study due to the cost implications of operating at high energy intensive temperatures. Therefore, all subsequent experiments were performed at 85 °C.

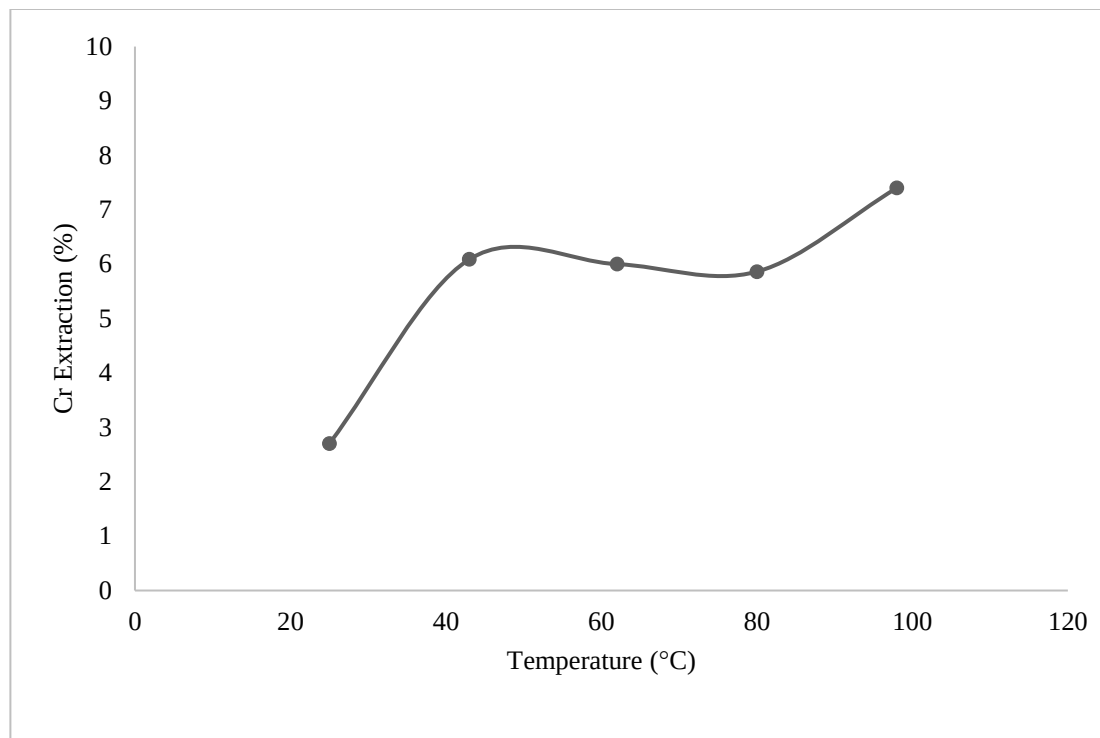


Figure 5.3: Cr extraction as a function of leaching temperature.

5.3.2.2 *The effect of leaching time*

The effect of leaching time is exhibited in **Figure 5.4**. A Cr extraction of 5.5 % was obtained after 1 hour and 6.0 % after 6 hours. The data shows a relatively high Cr extraction rate in the first hour and then plateaus thereafter. The graph shows that Cr dissolution kinetics are very fast within the first hour, suggesting that it was possible to achieve most of the Cr extraction within a shorter leaching time. The results further show that Cr extraction remained constant despite longer leaching times. This trend could be attributed to the high solid-to-liquid (1:3) ratio used in these experiments, which induced high pulp viscosity that negatively affected mass transfer. Another possible explanation could be the formation of a boundary layer comprising precipitated metal sulphates that passivate chromite mineral surfaces as observed in similar studies done by Jiang et al. (2014), Zhao et al. (2014), and Vardar et al. (1994). The other major contributing factor could be that operating at a high solid-to-liquid ratio of 1:3 (**Table 5.1**) could have resulted in a high pulp viscosity, which in turn effectively caused poor diffusion.

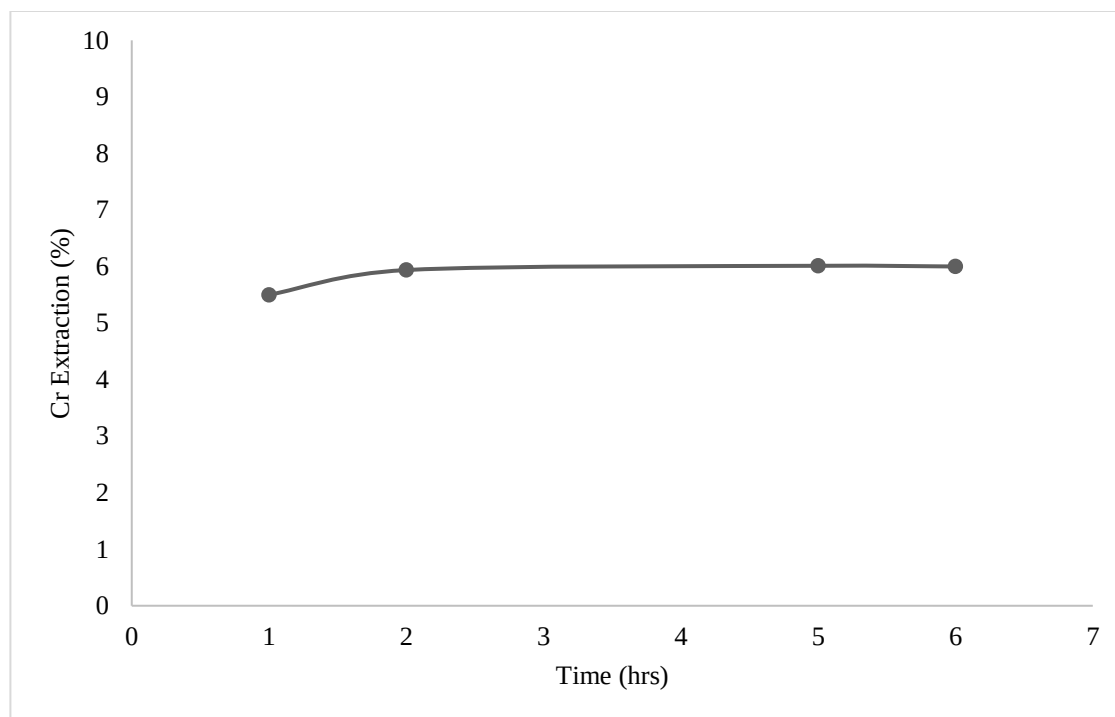


Figure 5.4: Cr extraction as a function of leaching time.

5.3.2.3 The effect of acid concentration

The effect of acid concentration on Cr extraction is illustrated in **Figure 5.5**. The results in the figure show that Cr dissolution increased with increasing acid concentration up to a maximum Cr extraction of 6.8 % at 45 % (v/v) acid concentration. Further increase in acid concentration resulted in a decrease in Cr extraction. This could have resulted from the reactant products and the possible presence of a silica gel due to the dissolution of some silicate minerals under acidic leaching conditions. The negative effect of sulphuric acid on Cr extraction at higher acid concentrations could also be attributed to the precipitation of metal sulphates that form boundary layers on chromite surfaces. These boundary layers are known to form passivation species that limit the diffusion of products and reactants on chromite surfaces (Jiang et al., 2014; Zhao et al., 2014; Vardar et al. 1994). Therefore, 45 % (v/v) acid concentration was adopted as the peak and appropriate level and all subsequent experiments were performed at this level.

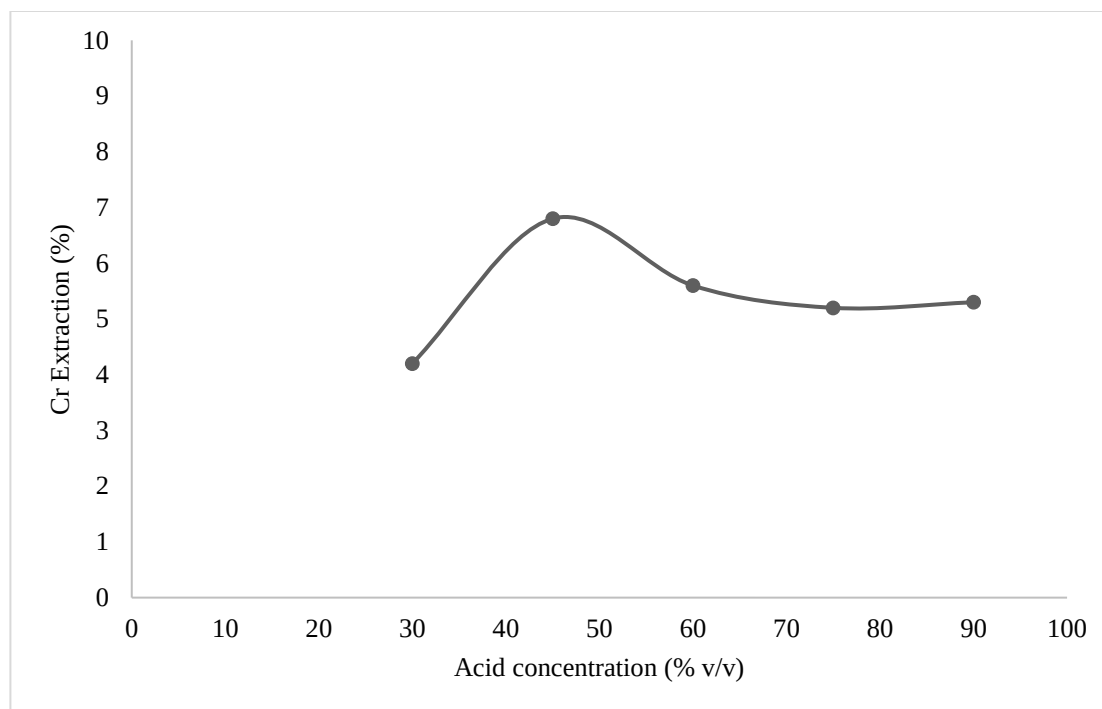


Figure 5.5: Cr extraction as a function of acid concentration.

5.3.2.4 The effect of oxygen flowrate

The effect of pure oxygen flowrate is shown in **Figure 5.6**. The figure illustrates Cr extraction *vis-a-vis* oxygen flowrates from 0 to 40 mL/min. The extraction of Cr proportionally increased with the increase in oxygen flowrate up to a maximum of 6.2 % Cr extraction at 30 mL/min.

Oxygen was employed to induce and sustain an oxidative leaching environment necessary for a two-staged decomposition mechanism for chromite. The sequential decomposition process involves the dissolution of the divalent cations in the tetrahedra site and then followed by the trivalent cations in the octahedra site (Jiang et al., 2014; Zhao et al., 2014; Geveci et al., 2002; Vardar et al., 1994). The tetrahedra site mainly comprises Fe(II), which is dissolved by oxidising it to Fe(III). This is followed by the oxidative leaching of Cr(III) in the octahedra site to Cr(VI). Under the conditions selected, Cr(VI) is thermodynamically not stable and it immediately reduces to form aqueous violet chromium (III) sulphates (Jiang et al., 2014; Zhao et al., 2014; Geveci et al., 2002; Vardar et al., 1994). The conditions selected include an electropotential (Eh) range of 0.2 and 1.18 Volts and a pH range of 1 and 2 (Takeno, 2005). Within this potential range, the redox reactions in both the crystal sites reduce the ionic radius

of the constituent metals which in turn result in the instability of the chromite crystal structure, thus inducing Cr dissolution (**Figure 2.6**).

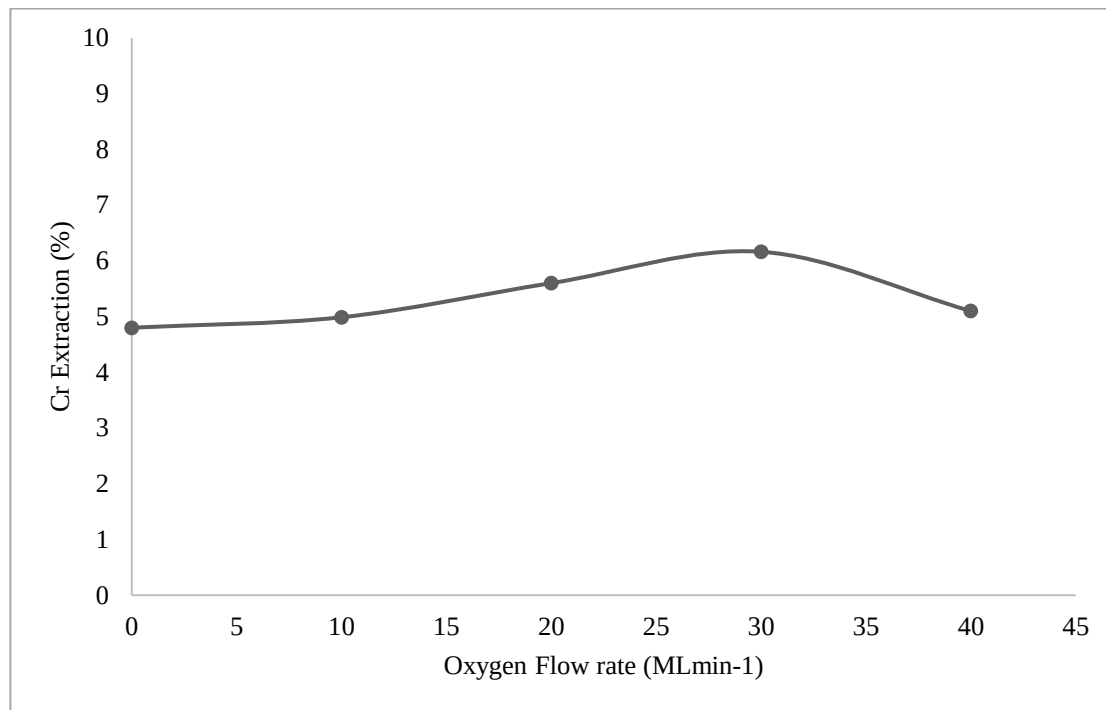


Figure 5.6: Cr dissolution as a function of oxygen flowrate.

5.3.2.5 The effect of interacting factors

The factor interaction effects were normally distributed around zero mean and fell along a straight line on the Normal plot (**Figure 5.1**). On the Pareto chart, all the interacting factors fell below the t-value line except for the ABC interaction (**Figure 5.2**). Some outstanding interactions, though not statistically significant, were AB, AC and BC (**Figure 5.7**). The interaction of variables ABC (temperature, leaching time and acid concentration) was found to be statistically significant. When interpreted jointly, in the ranges studied, the ABC interaction was observed to have a positive influence on the Cr dissolution process (**Figure 5.7**). Analysis of the three variables (ABC), displayed in **Figures 5.3, 5.4** and **5.5**, showed that the negative effect of higher acid concentration (C) was counteracted by the joint effect of leaching temperature (A) and leaching time (B). The negative effect of high acid concentration on Cr extraction is mainly attributed to the precipitation of metal sulphates that form boundary layers on chromite surfaces, i.e. $\text{Fe}_2(\text{SO}_4)_3$, MgSO_4 and $\text{Cr}_2(\text{SO}_4)_3$ (Jiang et al., 2014; Zhao et al., 2014;

Geveci et al., 2002; Vardar et al., 1994). However, at higher leaching temperatures and with long leaching time, there is a possibility that the thin passive boundaries were broken, thus improving diffusion and mass transfer.

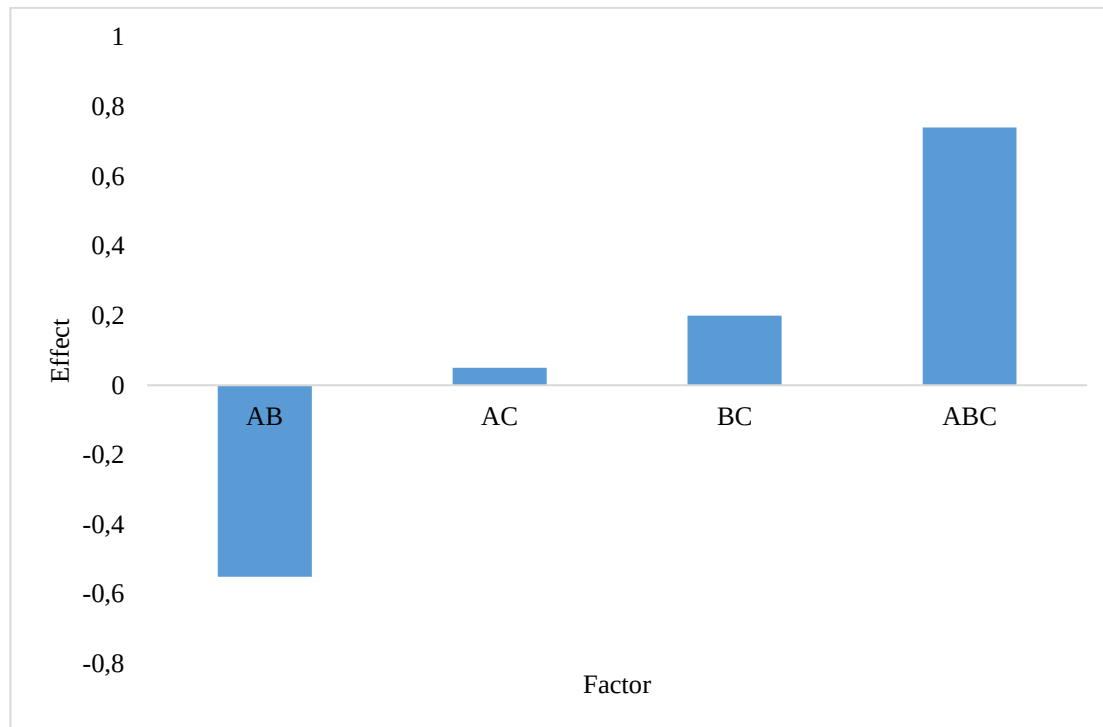


Figure 5.7: Factor interaction effects from the 2^4 full factorial design.

5.4 Summary

The overall purpose of identifying factors that significantly influence a process is for process optimisation, efficiency improvement, higher quality results, greater adaptability and cost control.

Examination of the individual factors using the normal probability plot showed that the oxygen flowrate (D) and acid concentration (C) were statistically significant. The interaction of temperature, leaching time and acid concentration (ABC) was also found to be statistically significant.

An increase in acid concentration was found to have a negative effect on Cr extraction.

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The next chapter discusses optimisation of significant factors.

Chapter 6

OPTIMISATION OF INFLUENTIAL FACTORS

6.1 Introduction

Screening experiments presented in the previous chapter identified factors that have a significant effect on the Cr leaching process. Significant factors of a process can be optimised. The main objective in process optimisation is maximization of yield, minimization of variability and overall process improvement. In this chapter, a statistically based optimisation approach called Response Surface Methodology (RSM) was used in conjunction with the Central Composite Rotatable Design (CCRD) to determine the optimum conditions for leaching Cr from the UG-2 concentrates. RSM is a famous technique used to find optimal conditions by using a quadratic polynomial regression model and is applied after diagnostic or screening experiments (Box et al., 1978). The CCRD is an experimental design used to collect data for building a second order quadratic model for the response variable.

A CCRD consists of 2^k factorial points, coded ± 1 , augmented by $2k$ axial points, coded $\pm \alpha$ (**Table 6.1**) and n_c replicate points at the centre $\{(0,0,0,\dots,0)\}$, where k is the number of factors studied, α is the distance of an axial point from the centre (Khuri and Cornell, 1987). The augmentation of the full factorial design with axial points and centre runs makes the CCRD complete with five factor levels ($-\alpha, -1, 0, +1, +\alpha$). The factor level α denotes an axial point; 1, a factorial point; and 0, a centre point.

Table 6.1: Axial points (Khuri and Cornell, 1987).

1	2	3	...k
$-\alpha$	0	0	0
$+\alpha$	0	0	0
0	$-\alpha$	0	0
0	$+\alpha$	0	0
0	0	$-\alpha$	0
0	0	$+\alpha$	0
0	0	0	$-\alpha$
0	0	0	$+\alpha$

To ensure a constant variance of the predicted response at all points equidistant from the design centre, the number of centre point replications, n_c , for the two factors studied was calculated using the following equation (Khuri and Cornell, 1987).

$$n_c \sim 0.8385 (2^{k/2} + 2)^2 - 2^k - 2k \quad 6.1$$

Where n_c is the number of centre point replications and k is the number of factors studied.

For $k = 2$, $n_c = 5$

The experimental results were analysed statistically using the analysis of variance (ANOVA).

6.2 Experimental Design for the Response Surface Methodology and CCRD

From the screening experiments discussed in Chapter 5, two significant factors, the oxygen flowrate and acid concentration were found to be statistically significant. The interaction of temperature, leaching time and acid concentration was also found to be statistically significant. The oxygen flowrate and leaching time were selected for optimisation. The factors were studied with their codified values $(-\alpha, -1, 0, +1, +\alpha)$. **Table 6.2** shows a relationship between the coded values and actual values for the five levels of each factor.

Table 6.2: Relationship between coded and actual values of variables (Napier-Munn, 2000).

Code	Actual value of a factor
$-\lambda$	$\xi_{\min}$
-1	$(\xi_{\max} + \xi_{\min})/2 - (\xi_{\max} - \xi_{\min})/2\lambda$
0	$(\xi_{\max} + \xi_{\min})/2$
$+1$	$(\xi_{\max} + \xi_{\min})/2 + (\xi_{\max} - \xi_{\min})/2\lambda$
$+\lambda$	$\xi_{\max}$

$\xi_{\min}$ and $\xi_{\max}$ are the minimum and maximum values of the natural variables respectively,

$$\lambda = 2^{(k-q)/4}$$

Where,

λ is the distance of an axial point from the centre

k is the number of factors studied. For this study, $k = 2$ (oxygen flowrate and leaching time)

q is a fraction of the number of factors. For a full factorial design, $q = 0$

$\therefore \lambda = 1.414$

The five levels of each factor shown in actual and coded values calculated using the relationships in **Table 6.2** are shown in **Table 6.3**.

Table 6.3: Experimental layout and runs for the two factor CCRD.

Factor Levels				Standard Run
Coded		Actual		
A (Flowrate)	B (Time)	A Flowrate (mLmin ⁻¹)	B Time (hrs)	
-1	-1	15	3	1
+1	-1	40	3	2
-1	+1	15	7	3
+1	+1	40	7	4
-1.414	0	9.8	5	5
+1.414	0	45.2	5	6
0	-1.414	27.5	2.2	7
0	+1.414	27.5	7.8	8
0	0	27.5	5	9
0	0	27.5	5	10
0	0	27.5	5	11
0	0	27.5	5	12
0	0	27.5	5	13

In **Table 6.3**, the experimental layout and standard runs for the central composite rotatable design are listed. Five centre points were worked out from **Equation 6.1**.

For the two variables under consideration, a second order polynomial regression model was proposed as follows:

$$\hat{y} = \beta_0 + \sum_{i=1}^2 \beta_i x_i + \sum_{i=1}^2 \beta_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^2 \beta_{ij} x_i x_j + \varepsilon \dots \dots \dots 6.2$$

Where,

$\hat{y}$ is the predicted response, β_0 is the coefficient for intercept, β_i is the coefficient of linear effect, β_{ii} is the coefficient of quadratic effect, β_{ij} is the coefficient of interaction effect, ε is a term that represents other sources of variability not accounted for by the response function; x_i and x_j are coded predictor variables for the independent factors. The coefficients of the regression model were estimated by fitting the experimental results using Design Expert® 11 software.

6.3 Results and Discussion

6.3.1 Derivation of the model

The experimental results for the Cr extraction are presented in **Table 6.4**. The coefficients of the regression model were estimated by fitting the experimental (observed) values using Design Expert® 11 software.

Table 6.4: Observed values of Cr extraction.

Standard Run	Factor Levels				% Cr Extraction (Observed)
	Coded		Actual		
	A (Flowrate)	B (Time)	A Flowrate (mLmin ⁻¹)	B Time (hrs)	
1	-1	-1	15	3	6.0
2	+1	-1	40	3	5.6
3	-1	+1	15	7	6.1
4	+1	+1	40	7	6.5
5	-1.414	0	9.8	5	6.0
6	+1.414	0	45.2	5	6.2
7	0	-1.414	27.5	2.2	5.5
8	0	+1.414	27.5	7.8	6.5
9	0	0	27.5	5	6.1
10	0	0	27.5	5	6.2

11	0	0	27.5	5	6.1
12	0	0	27.5	5	6.2
13	0	0	27.5	5	6.1

The re-fitted second order model was derived as:

$$\hat{Y} = 6.13 - 0.13x_1 - 0.098x_2 \dots\dots\dots 6.3$$

Where, x_1 = oxygen flowrate, x_2 = leaching time, within predictor variable limits of:

$$-\lambda \leq x_i \leq +\lambda; i = 1, 2$$

Where x_i are coded predictor variables and $\lambda = 2^{(k-q)1/4} = 1.414$ (for $k = 2$, $q = 0$) is the distance of the axial points from the centre of the CCRD that gives the limits of the valid region under experimentation.

The negative signs in the model indicate that in order to maximize Cr extraction, these factors must be kept at low levels.

For quadratic regression models, the point for which the response is optimised is the point at which the regression partial derivatives $\partial y / \partial x_1$; $\partial y / \partial x_2 \dots \partial y / \partial x_k$, are all equal to zero. This point is called the stationary point. However, since the re-fitted model in **Eq. (6.3)** is linear, the maximum response coincides with the distance of the axial points from the center of the CCRD that gives the limits of the valid region under experimentation. The optimum Cr values were therefore calculated using **Eq. (6.3)**. Using coded values of $x_1 = 1.414$ for optimum oxygen flowrate and $x_2 = 1.414$ for optimum leaching time, the predicted Cr extraction was evaluated as:

$$\hat{Y} = 5.81\%$$

The three-dimensional response surface for the optimised Cr extraction is presented in **Figure 6.1**. An analysis of the response surface shows that it is possible to achieve optimum Cr extraction at a minimal optimum time of 3hours and a minimal optimum oxygen flowrate of 15 mL/min. Further analysis of the response surface also shows that the oxygen flowrate has a

greater impact on Cr extraction than leaching time. This can be seen in the **Figure 6.1** where the oxygen flowrate gradient is much steeper compared to the gradient for leaching time.

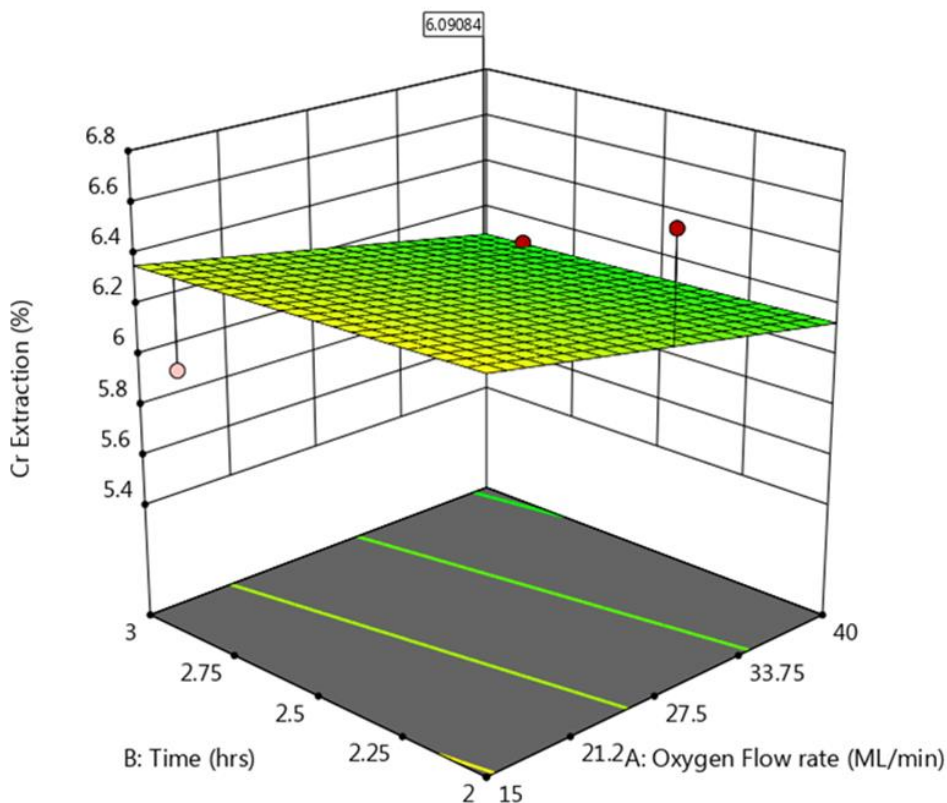


Figure 6.1: 3D response surface for Cr extraction as a function of time and oxygen flowrate.

In order to test the validity of the optimised conditions given by the model, replicated experiments were carried out with parameters suggested by the model. The conditions used in the confirmatory experiments were 15 mL/min for optimum oxygen flowrate and 3 hours for optimum leaching time at 85°C and 45% (v/v) acid concentration.

The Cr extraction, after leaching at a flowrate of 15 mL/min for 3hrs, was found to be 7.0% (**Table 6.5**), which is consistent with the model. With an error margin of 1.2%, the model fits the experimental data quite well, and can therefore be considered to be reasonably valid (Appendix F).

Table 6.5: Cr extraction at optimum leaching conditions.

Parameter	Oxygen Flowrate (mLmin ⁻¹)	Time (hrs)	% Cr Extraction
Model	15	3	5.8
Confirmatory Tests	15	3	7.0

6.3.2 Effect of Parameters

6.3.2.1 The effect of solid-to-liquid ratio

This section discusses the influence of solid-to-liquid ratio (pulp density) on Cr extraction using the optimum leaching conditions established in section 6.3.1 and shown in **Table 6.4**. The motivation for evaluating the effect of solid-to-liquid ratio was mainly influenced by the low Cr extractions obtained at a fixed ratio of 1:3 used in the previous experiments (results in sections 5.3 and 6.3). The 1:3 solid-to-liquid ratio was initially selected because it aligns with the solid content that is generally required for minimum engineering design and practical industrial operations. Economically, this commonly justifies the capital and operational expenditures (CAPEX and OPEX) typical of hydrometallurgical applications. For instance, less reagents (\$/unit) will be required to process suitable throughput (t/hr) with sizeable equipment and ease of handling sizeable volumes of the leach process.

The Cr extraction results obtained from the experiments performed at different solid-to-liquid ratios using optimum leaching conditions are exhibited in **Table 6.6** and **Figure 6.2**. A Cr extraction of 7.6 % was obtained at 1:2 solid-to-liquid ratio and 36.8 % at 1:26 solid-to-liquid ratio. These results were obtained under the fixed leaching conditions of 15 mL/min O₂ flowrate, 3 hours leaching time, 85 °C leaching temperature, 45%(v/v) H₂SO₄ conc and 1000 rpm agitation rate, which are less intensive compared to the conditions used in the preliminary experiments. The data shows an exponential increase in Cr extraction at densities lower than 1:10. The high Cr extraction obtained at the low solid-to-liquid ratios could be attributed to the dispersion effect of mineral particulate due to low slurry viscosities and excess availability of reactants. At high slurry densities, the leach pulp viscosities were high, which negatively impacted mass transfer rates due to the possible formation of high viscous reactant products and silica gel, among others. Noting that Cr was predominantly extracted from the Cr₂O₃ phase,

the 36.8 % Cr extraction, therefore represents a decrease in chrome content from 3.63 % to 2.3 % in the UG-2 concentrate.

Table 6.6: UG-2 concentrates acid leaching conditions.

Tests	O ₂ Flowrate (mLmin ⁻¹)	Time (hrs)	H ₂ SO ₄ Conc. % (v/v)	Temp (°C)	Agitation (rpm)	Solid:Liquid (g/mL)	Cr Extraction (%)
1	15	3	45	85	1000	1:26	36.8
2	15	3	45	85	1000	1:18	25.4
3	15	3	45	85	1000	1:10	14.4
4	15	3	45	85	1000	1:2	7.6

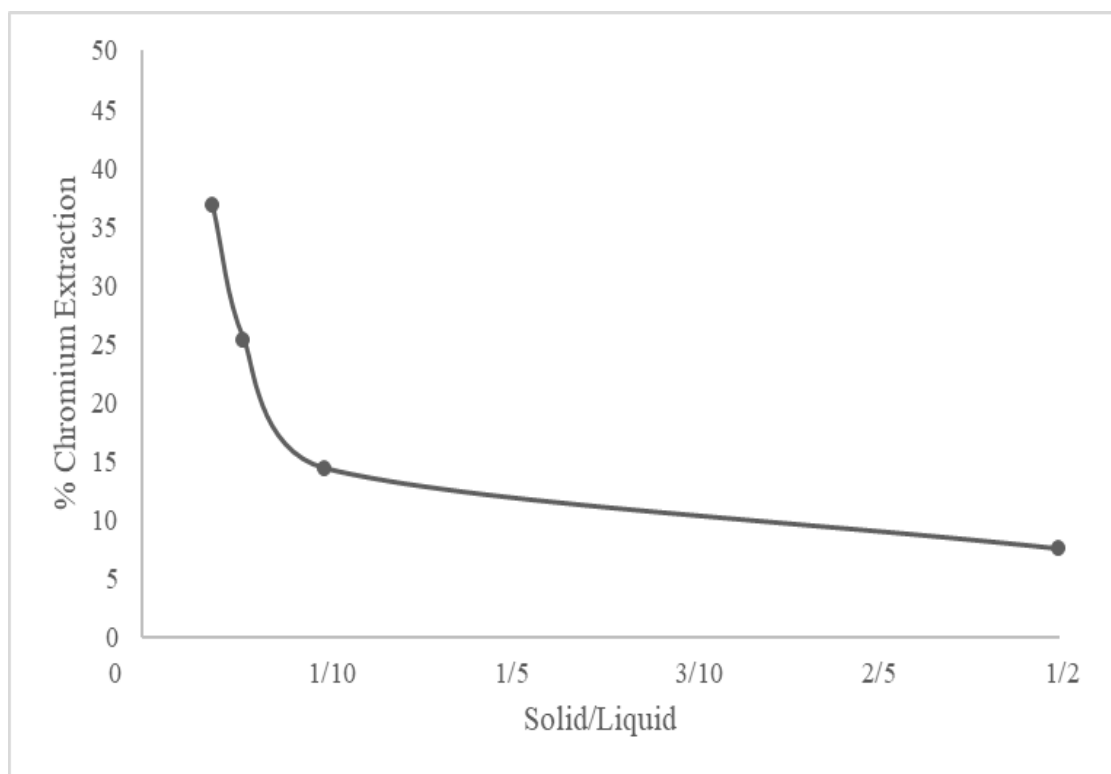


Figure 6.2: Cr extraction as a function of solid-to-liquid ratio.

6.3.2.2 The effect of the acid leach process on base metals and PGMs

The key advantage of the acid leach process is the leaching of deleterious metals such as Cr and iron contained in oxidic gangue minerals. However, the downside of the process is the

partial co-dissolution of base metals (BMs) and platinum group metals (PGMs) contained in value minerals. Maximum nickel and copper extractions of 10.0 and 24.5 %, respectively, were observed, whilst a fraction of partially dissolved PGMs mainly included rhodium (8.0 %) and platinum (9.0 %). The dissolved value metals can be recovered through a process that would involve conventional techniques as a pre-treatment of the leach solution prior to the application of hydrometallurgical processes in the base metal refinery (BMR). The proposed process flowsheet of the hydrometallurgical route for Cr extraction is presented in **Figure 6.3**.

A sequential precipitation method can be employed to purify the leach solution by recovering deleterious metals prior to the first atmospheric leach stage of the BMR. A treatment process that involves the recovery of iron via a jarosite process can precede the precipitation of Cr as Cr hydroxide by adjusting pH to 4-5. This can be followed by charging the solution into the first atmospheric leach stage of the BMR. The purpose of the first atmospheric leach stage of the BMR is to extract nickel from the Ni-Cu-Fe-S Peirce-Smith convertor matte while precipitating copper and PGMs from the spent electrolyte (Schalkwyk et al., 2010; Lamya, 2007). The composition of the spent electrolyte is mainly characterised by copper sulphate, sulphuric acid and dissolved rhodium, ruthenium, and iridium as PGMs (Lamya, 2007). The leach solution from this stage is normally treated in the nickel crystallization unit operation to recover nickel as nickel sulphate, while the residue containing precipitated copper and PGMs is treated in the pressure leaching unit operation (Schalkwyk, 2011). Thus, the solution from the proposed Cr leaching process can be incorporated into the first atmospheric leaching stage of the BMR.

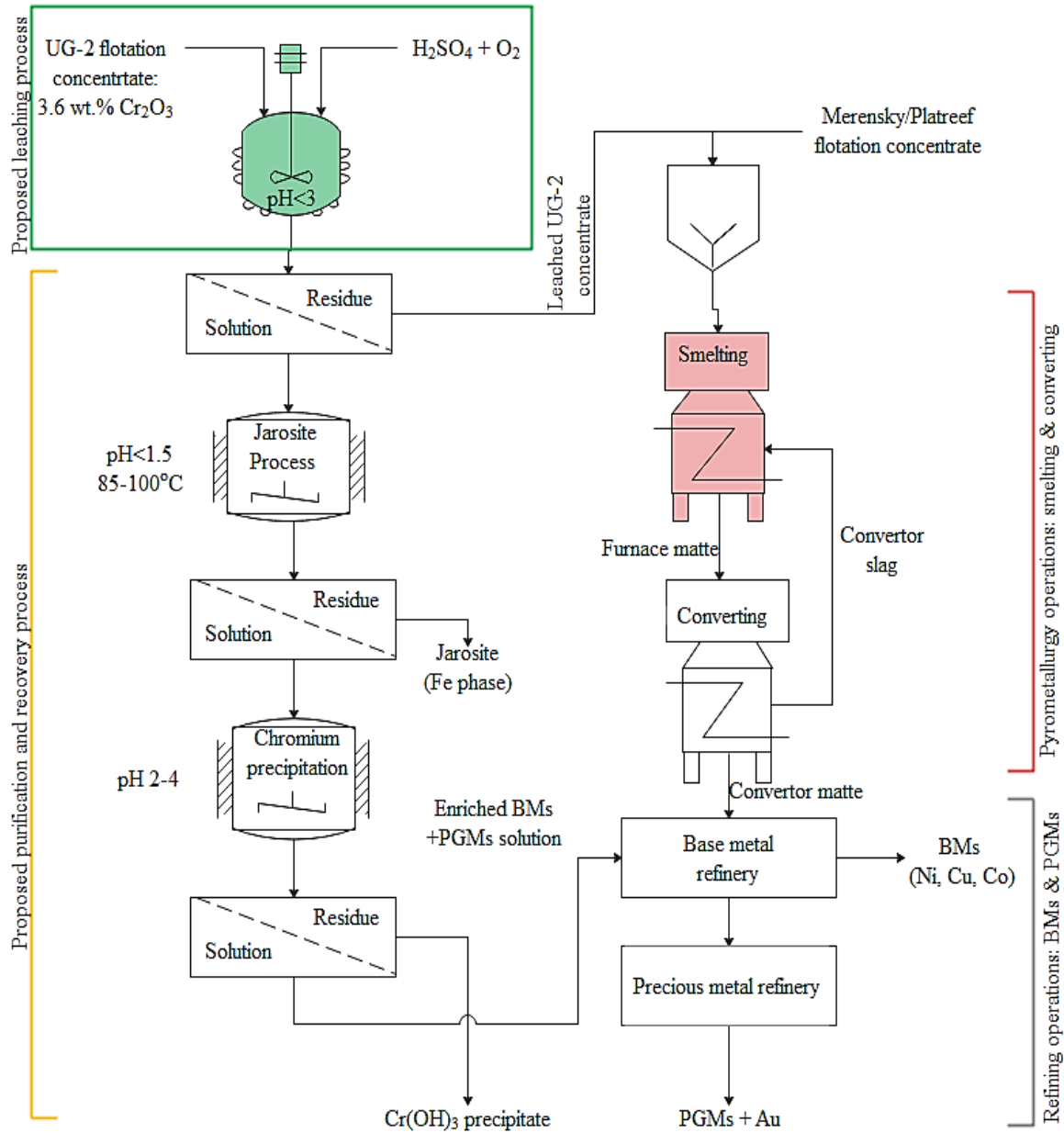


Figure 6.3: Proposed process flowsheet.

6.3.3 Economic implications of chrome reduction in the UG-2 Flotation concentrate

In general, the economic viability and process efficiency of PGMs smelters is mainly influenced by the chemical quality of the flotation concentrates, i.e. chrome content and other refractory oxidic phases. Therefore, the economic viability of the PGMs smelters is a function of operating costs (OPEX), which are typically defined in terms of furnace specific energy consumptions (SEC) in kWh/t, and process efficiency, which is based on the recovery of PGMs.

All these aspects are fundamentally linked to chrome content and the slag chemistry which determines the slag liquidus temperatures and slag viscosities. High liquidus temperatures increase SEC, while high slag viscosities cause poor recovery of PGMs. It is therefore necessary to eliminate or minimize chrome content in flotation concentrates.

The proposed Cr leach process has demonstrated the potential to reduce chrome and other oxidic phases using a less energy intensive approach. The process reduced chrome from 3.6 % to 2.3 % in smelter feed under leaching conditions shown in **Table 6.6**. **Table 6.7** shows the chemical composition of the major phases that are bound to influence slag chemistry after acid leaching. This is a pointer towards a positive influence on SEC and PGMs recovery for the smelters. A reduction on SECs in particular translates into huge savings for the smelters. While this is true, it is also worth noting that the Cr reduction is even more meaningful to junior platinum producers who are penalised by smelters for producing concentrates with high chrome contents that are above contractual obligations. The penalties imposed are typically in orders of millions of Rands for breaching the contractual obligations by a small fraction of % chrome. For the junior platinum producers, it is estimated that the costs associated with the proposed leach process could be offset by the huge savings realised from averting the penalties charged by smelters.

Table 6.7: Chemical composition of smelter feed concentrates after acid leaching.

Cr ₂ O ₃	MgO	Total Fe	SiO ₂
2.3	21.1	9.4	44.3

6.4 Summary

The overall purpose of employing a hydrometallurgical method of extracting Cr from the UG-2 concentrate was to develop and propose an alternative process route that reduces chrome content to low levels that are amenable to conventional PGM smelters. Using an acid leach process, the UG-2 concentrate was initially leached at optimum conditions of 45 % sulphuric acid concentration, a solid-to-liquid ratio of 1:3, the temperature at 85 °C, the oxygen flowrate of 15 mL/min and 3 hours reaction time. Under these conditions, the leaching experiment yielded a Cr extraction efficiency of 7.0 %.

Leaching results from a second experiment performed to investigate the impact of varied solid-to-liquid ratios at optimum leaching conditions gave a Cr extraction of 7.6 % at 1:2 solid-to-liquid ratio and 36.8 % at 1:26 solid-to-liquid ratio. The 36.8 % Cr extraction represents 1.33 % reduction in Cr_2O_3 content from 3.63 % to 2.3 % in the UG-2 concentrate.

This study has shown that 36.8% Cr extraction could be achieved using less energy intensive leaching conditions of up to 85°C temperature while operating at a solid-to-liquid ratio of 1:26.

The possibility that high Cr extractions are attainable within minimum leaching time and at low oxygen flowrates, as observed from the response surface, presents a promising economic feasibility for a less energy intensive leaching process for chrome reduction in UG-2 concentrates.

Low Cr extractions were observed at high slurry densities. This was attributed to the UG-2 material's high affinity to form temporary electrostatic bonds, which reduce the surface area for optimum contact between solid and liquid reactants. Therefore, the amenability of the UG-2 material to leaching could be perceived as a function of its affinity to form temporary electrostatic bonds. Based on this observation, the effect of mechano-activation on the behaviour of the UG-2 concentrate particles could be investigated further with a focus on evaluating the possibility of breaking the electrostatic bonds, which in turn might enhance Cr leaching efficiency.

Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

This section presents the findings and conclusions drawn from the experimental work done to fulfil the aim of the research project.

7.1.1 Introduction

The ability of inorganic acids to leach and collect metallic species from the UG-2 concentrate is based on the metal oxide dissolution mechanism. Therefore, the main objective of this work was to apply this mechanism in order to investigate the possibility of using sulphuric acid in the extraction of Cr from the UG-2 flotation concentrate. The UG-2 concentrate contains chromite (Cr_2O_3) but it is incapable of fully responding to inorganic acids because it is refractory in nature and therefore resistant to acid dissolution. A review of literature suggested a possibility that the chromite could undergo dissolution by adjusting leaching conditions to make it leachable in sulphuric acid.

In order to investigate this possibility, the aims of the study were defined as to:

- Design a sulphuric acid leaching process capable of extracting Cr in UG2 concentrates.
- Identify significant process factors that influence the dissolution of Cr.
- Determine optimum leaching conditions suitable for Cr extraction.
- Evaluate the effect of solid-to-liquid ratio on Cr extraction under optimum conditions.

7.1.2 Preliminary Leaching Tests

The direct leaching of the UG-2 concentrate with sulphuric acid at different parameter levels of solid-to-liquid ratio, leaching time and acid concentration provided a better understanding of the UG-2 concentrate acid leaching process and reaction conditions. The results presented in this study have shown that Cr dissolution in the UG-2 concentrate is a function of the various parameters.

The Cr_2O_3 distribution by size fraction showed that -38 μm size fraction contains the highest Cr_2O_3 content. That is, of the total Cr_2O_3 in EPL final flotation concentrate, 87% reported to the fine size fraction. The +38 and +75 μm size fractions host approximately 8% and 4% of the total Cr_2O_3 in the concentrate. Moreover, the +38 and +75 μm size fractions have Cr_2O_3 grades that are equal to or less than the maximum 1.8 wt.% limit allowed in the final concentrate. Therefore, these size fractions could bypass the proposed leaching circuit.

Batch leaching experiments exploring the effect of solid-to-liquid ratio on Cr extraction, showed there is an inverse correlation between these two functions. Cr extraction showed an exponential increase as the solid-to-liquid ratio decreased from 1:2 to 1:26. This was observed at fixed levels of H_2SO_4 concentration (75%v/v), leaching time (3hrs), temperature (120 °C), agitation rate (500 rpm) and airflow rate (17 mL/min). A high Cr extraction of 67% was obtained at a solid-to-liquid ratio of 1:26, while only 8.2% was obtained 1:2. The increase in Cr extraction with decreasing solid-to-liquid ratio was attributed to a possible sequential dissolution mechanism when leaching chromite. It was assumed that Mg, Fe, and Al in silicate phases leached out first followed by the gradual decomposition of chromite via the dissolution of metals in the tetrahedra and octahedral sites, respectively

H_2SO_4 concentration had a positive effect on Cr extraction. Preliminary leaching results showed Cr extraction increased with the increase in H_2SO_4 concentration, in which, 74% Cr extraction was obtained at 85% (v/v) acid concentration. Lower Cr extractions were observed below 85% (v/v) acid concentration

Experimental results showed that Cr extraction increased with increasing leaching time. A maximum Cr extraction of 87% was achieved after 5 hours of leaching suggesting that leaching time is an important process factor for Cr extraction. This was obtained at a fixed temperature of 120 °C, H_2SO_4 concentration of 75 % (v/v), a solid-to-liquid ratio of 1:26, an agitation rate of 500 rpm and air flowrate of 17 mL/min.

7.1.3 Identification of influential factors

Examination of the individual factors using the normal probability plot showed that oxygen flowrate (D) and acid concentration (C) were statistically significant. The figure also shows

the interaction of temperature, leaching time and acid concentration (ABC) to be statistically significant.

7.1.4 Optimisation Tests

A statistically based optimisation plan was used for optimisation of oxygen flowrate and leaching time at an acid concentration of 45% (v/v), a temperature of 85°C and a solid-to-liquid ratio of 1:3. The choice of the acid concentration, temperature and solid-to-liquid ratio factor levels was guided by preliminary acid leach experiments.

A Central Composed Rotatable Experimental Design (CCRD) was employed in the collection of data to fit to the second order quadratic regression model. Experimental results were analysed, and an appropriate predictive empirical linear model was developed. The linear model representing Cr extraction was expressed as a function of two variables, oxygen flowrate and leaching time.

The effects of individual variables were found to be statistically significant. The results, however, showed that all the model terms and interactions among the investigated variables were statistically insignificant. Cr extraction was found to depend more on oxygen flowrate than on leaching time. This is because a more oxidative environment is required for effective Cr dissolution. This observation indicates that oxygen flowrate is a very important parameter in the acid leaching of UG-2 flotation concentrate.

Within the scope of conditions studied, the optimum conditions established from the statistically based optimisation model at the predicted maximum Cr extraction of 5.81% were found to be a flowrate of 15 mL/min and 3 hrs of leaching time. To verify the optimised results, replicated confirmatory runs were carried out under optimum conditions. The Cr extraction found experimentally was 7.0 %.

Further study to investigate the effect of solid-to-liquid ratio using optimum conditions gave a Cr extraction of 7.6% at 1:2 solid-to-liquid ratio and 36.8% at 1:26 solid-to-liquid ratio. The high Cr extraction obtained at the low solid-to-liquid ratios was attributed to the dispersion effect of mineral particulate at low slurry densities as well as adequate availability of reactants.

At high slurry densities, the UG-2 material was observed to have an affinity to form temporary electrostatic bonds, which reduced the surface area for optimum contact between solids and liquid reactants. As a result, this reduced Cr leaching efficiencies.

Noting that Cr extraction in acid leaching is predominantly from the Cr_2O_3 phase, the 36.8% Cr extraction, therefore, represents a 1.33 wt.% decrease in chrome content from 3.63 wt.% to 2.3 wt.%. Although the target for the solubility limit of chrome to deport in the silica glass phase was approximately 1.8 wt.% and below, the actual Cr_2O_3 content in current smelter operations tends to fluctuate between 2 wt.% and 4 wt.%. Therefore, the Cr reduction from 3.63 wt.% to 2.3 wt.% achieved in the current study is considered to be within acceptable limits for PGM smelting processes. The reduced chrome content to 2.30 wt.% is a significant step towards achieving the 1.8 wt.% target.

7.1.5 Specific Outcomes

- Savings on specific energy consumption
- Savings on improved refractory lifespan
- Savings on cost of production due to improved furnace utilization and recoveries
- Savings realised by junior platinum producers to avert penalties charged by smelters

7.2 Recommendations

With the knowledge gained from the current work, the following recommendations for further investigative studies are proposed:

Economic feasibility

The possibility that high Cr extractions are possible at minimum leaching time and low oxygen flowrates, as observed from the response surface, presents a promising economic feasibility for a less energy intensive UG-2 acid leach process. This study can be extended to investigate economic factors to justify the feasibility of the hydrometallurgical Cr extraction process.

Effect of mechano-activation on the leaching of UG-2 flotation concentrates

In this work, low Cr extractions were observed at high slurry densities. This was attributed to the UG-2 material's high affinity to form temporary electrostatic bonds, which reduce the surface area for optimum contact between solids and liquid reactants. The amenability of the UG-2 material to leaching was perceived as a function of its affinity to form temporary electrostatic bonds. Based on this observation, the effect of mechano-activation on the behaviour of the UG-2 concentrate particles could be investigated further to evaluate the possibility of breaking the electrostatic bonds, which in turn might optimise contact between solids and liquid reactants. A recommended reactor for this investigative study could be a vertically stirred ball mill; shell dimensions, ~15.0 cm x 30.0 cm height; ceramic bead size, ~2.5 mm; the ball mill should have an inlet and outlet for slurry circulation. The vertical ball mill could be fitted with a 4-blade stirrer for efficient suspension of solids and dispersion of injected oxygen as an oxidant.

Zeta Potential

Studies could be extended to investigate the effect of zeta potential on the electrostatic behaviour of the UG-2 particulate material in suspension, and its relation to leaching efficiency.

Concentrated sulphuric acid (98%)

In this study, leaching experiments exploring the effect of acid concentration, were limited to sulphuric acid concentrations of 85% and below. Higher acid concentrations significantly increase pulp viscosity which worsened mass transfer rates. This could be further explored in experiments exploring the effect of mechano-activation. For this, sulphuric acid concentrations of up to 98% are recommended.

Lower solid-to-liquid ratio

This study has shown that 36.8% Cr extraction could be achieved using less energy intensive leaching conditions of up to 85°C temperature while operating at a solid-to-liquid ratio of 1:26. Despite the high Cr recovery, the 1:26 solid-to-liquid ratio is too low in comparison to the 1:3 solid-to-liquid ratio currently obtaining in industry. A practical application of the proposed process in the current study might be a huge challenge to implement due to the high solution

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volumes involved but very little yield in terms of Cr throughput. Further work could be extended to investigate a much higher and more practical solid-to-liquid ratio, while maintaining less energy intensive leaching conditions established in the current study.

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APPENDICES

APPENDIX A

SAMPLE CALCULATIONS

%Cr Extraction

The % Cr extraction during the leaching of UG-2 flotation concentrate was calculated as a percentage of the Cr in the liquid phase to that in the unprocessed UG-2 flotation concentrate.

Example

Chromium Extraction

Basis of calculation:

UG-2 Concentrate weight before leaching	= 200g
% Cr ₂ O ₃ content in concentrate	= 2.9 wt%
Cr ₂ O ₃ molecular weight	= 152 gmol ⁻¹
Cr molecular weight	= 51.996 gmol ⁻¹
Cr moles in Cr ₂ O ₃	= 2

Calculations

Before Leaching:

Cr content in PGM concentrate	$= \frac{5.8 \times 2 \times 52}{152} = \mathbf{3.97\ g}$
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After Leaching:

Leach liquor volume	= 2000 mL (2000*10 ⁻³ Litres)
Cr in leach liquor (ICP-OES analysis)	= 155 ppm (155*10 ⁻³ gpl)
Cr content in 2000mL	$= \frac{2000 \times 155}{1000 \times 1000} = 0.31\text{g}$

∴ % Chromium extraction	$= \frac{0.31 \times 100}{3.97} = \mathbf{7.8\%}$
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APPENDIX B

MATERIALS

Table B1: Mineral groups and elemental deportment by phase minerals.

Mineral Group	Mineral	Elemental deportment by phase minerals					
		Cr	Fe	Al	Mg	Cu	Ni
Sulphides	Chalcopyrite	0,00	3,87	0,00	0,00	100,00	0,00
	Millerite	0,00	0,00	0,00	0,00	0,00	8,00
	Pentlandite	0,00	6,61	0,00	0,00	0,00	92,00
	Pyrrhotite	0,00	3,02	0,00	0,00	0,00	0,00
	Pyrite	0,00	4,46	0,00	0,00	0,00	0,00
	Laurite	0,00	0,02	0,00	0,00	0,00	0,00
Talc Enstatite	Talc Enstatite	0,00	46,99	0,00	85,06	0,00	0,00
Plagioclase	Anorthite	0,00	0,00	11,57	0,00	0,00	0,00
	Na-Plagioclase	0,00	0,00	25,74	0,00	0,00	0,00
K-Feldspar	Orthoclase	0,00	0,00	0,36	0,00	0,00	0,00
Pyroxene	Augite	0,00	1,19	5,31	1,89	0,00	0,00
	Diopside	0,00	0,00	0,00	2,86	0,00	0,00
	Ferrosilite	0,00	0,08	0,00	0,03	0,00	0,00
	Pigeonite	0,00	0,39	0,00	0,33	0,00	0,00
Quartz	Quartz	0,00	0,00	0,00	0,00	0,00	0,00
Serpentine	Lizardite	0,00	0,05	0,00	1,41	0,00	0,00
	Chrysolite	0,00	0,60	0,00	0,78	0,00	0,00
Spinel	Chromite	100,00	19,10	19,68	2,16	0,00	0,00
Mica	Biotite	0,00	6,36	34,79	5,47	0,00	0,00
	Muscovite	0,00	0,00	2,53	0,00	0,00	0,00
Carbonates	Calcite	0,00	0,00	0,00	0,00	0,00	0,00
	Dolomite	0,00	0,00	0,00	0,02	0,00	0,00
Oxides	FeOxide	0,00	7,28	0,00	0,00	0,00	0,00
	Rutile	0,00	0,00	0,00	0,00	0,00	0,00
Others	Unknown	0,00	0,00	0,00	0,00	0,00	0,00
	Low Counts	0,00	0,00	0,00	0,00	0,00	0,00
	No XRay	0,00	0,00	0,00	0,00	0,00	0,00
	Total	100,00	100,00	100,00	100,00	100,00	100,00

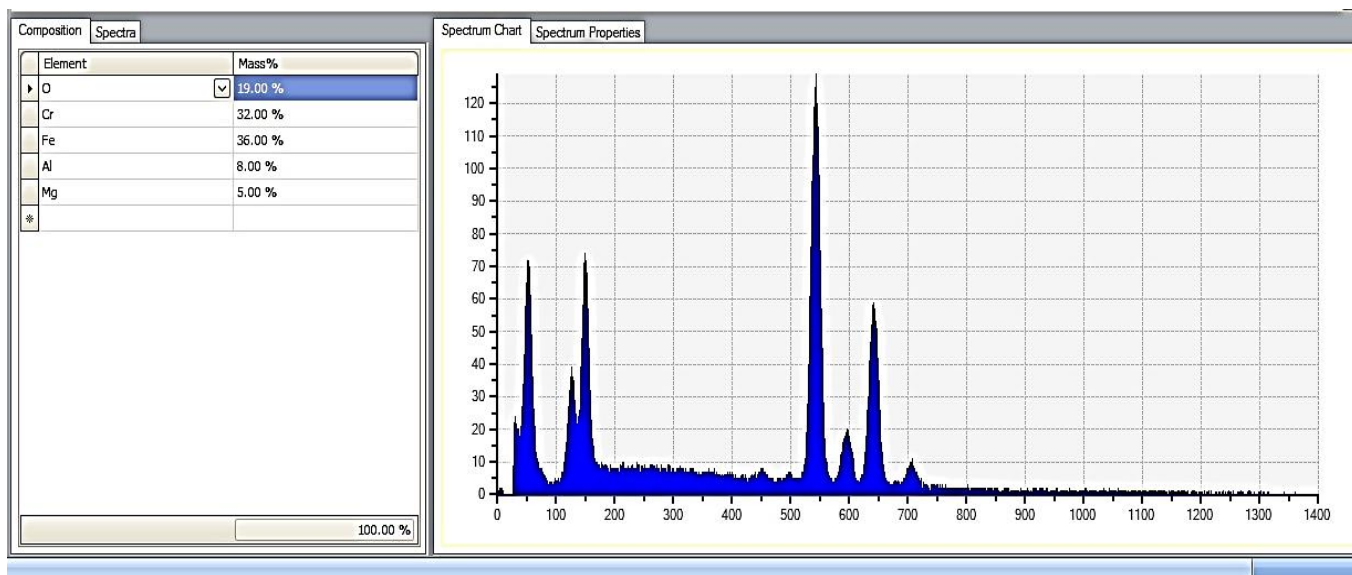


Figure A1: %Distribution of constituent elements in chromite and spectrum properties.

Table B2: ICP OES results of base metals and platinum groups in EPL final flotation concentrate.

Sample Name	Dil. Factor	Rh	Rh	Pd	Pd	Pt	Pt
Sample Name		mg/l	mg/kg	mg/l	mg/kg	mg/l	mg/kg
QC Check (0.5 ppm)	1	0,48		0,48		0,49	
QC Check (2 ppm)	1	2,09		2,02		2,01	
BLANK	1	<0.00		<0.00		<0.00	
AMIS 171A	1000		7,06		36,04		57,28
AMIS 171B	1000		6,95		37,60		59,21
AMIS 171 Average			7,00		36,82		58,24
AMIS 171 Acc.Val.			7,48		36,89		58,28
AMIS151A	1000		0,92		3,06		4,61
AMIS151B	1000		1,10		3,45		4,56
AMIS 151 Average			1,01		3,25		4,58
AMIS 151 Acc.Val.			1,04		3,21		4,71
SARM65A	1000		0,58		1,31		2,43
SARM65B	1000		0,58		1,40		2,32
SARM 65 Average			0,58		1,36		2,37
SARM 65 Acc.Val.			0,52		1,28		2,64
EPL 1A	1000		37,24		120,4		39,55
EPL 1B	1000		36,24		141,0		39,49
EPL 2A	1000		16,80		54,0		30,78
EPL 2B	1000		17,33		55,7		30,91
QC Check (0.5 ppm)	1	0,48		0,48		0,49	
QC Check (2 ppm)	1	2,06		2,03		2,06	

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BMS and 3PGMs							
Sample Name	Co ₃ O ₄	CuO	NiO	Rh	Pd	Pt	3PGE
	(%)	(%)	(%)	(g/t)	(g/t)	(g/t)	(g/t)
EPL +38 microns	0,112	1,745	3,537	37,236	120,38	39,546	197,16
EPL -38 microns	0,047	0,57	1,14	36,24	140,98	39,49	216,71

APPENDIX C

ROAD MAP FOR LIXIVIANT SELECTION

Table C1: Criterion used to select the lixiviant for chromium extraction in EPL flotation concentrate.

Category	Reagents	
Water	H ₂ O	
Acids	H ₂ SO ₄ , HCl, HNO ₃	
Bases	NaOH, KOH, NH ₄ OH	
Aqueous Salt Solutions	Na ₂ CO ₃ , NaCN, NaCl	
Aqueous chlorine and hypochlorite	Cl _(aq) , HClO, NaClO	
Reagents	Advantage	Disadvantage
H ₂ O	Cheap and noncorrosive	Limited to few
H ₂ SO ₄ , HCl, HNO ₃	Decomposes a range of minerals	Unselective, Corrosive, Expensive
NaOH, KOH, NH ₄ OH	High recoveries	Produces Chromium (VI)
Na ₂ CO ₃ , NaCN, NaCl	Suitable for acid-consuming gangue	
Cl _(aq) , HClO, NaClO		Corrosive

APPENDIX D

ROAD MAP FOR LIXIVIAT SELECTION

Table D1: Total mass of concentrate sample and Cr for preliminary experiments.

	Mass of Cr in Sample per experiment						
	Mass of sample (g)	Mass of Cr ₂ O ₃ in sample (g)	Molar mass Cr ₂ O ₃ (g/mol)	Moles Cr ₂ O ₃	Moles Cr	Molar mass Cr (g/mol)	Mass Cr (g)
EXP 01	200	6,51	152	0,04	0,09	52	4,45
EXP 02	150	4,88	152	0,03	0,06	52	3,34
EXP 03	60	1,95	152	0,01	0,03	52	1,34
EXP 04	40	1,3	152	0,01	0,02	52	0,89
Exp 05	40	1,3	152	0,01	0,02	52	0,89
Exp 06	30	0,98	152	0,01	0,01	52	0,67
Exp 07	25	0,81	152	0,01	0,01	52	0,56
Exp 08	20	0,65	152	0	0,01	52	0,45
Exp 09	20	0,65	152	0	0,01	52	0,45
Exp 10	20	0,65	152	0	0,01	52	0,45
Exp 11	20	0,65	152	0	0,01	52	0,45
Exp 12	20	0,65	152	0	0,01	52	0,45
Exp 13	20	0,65	152	0	0,01	52	0,45
Exp 14	20	0,65	152	0	0,01	52	0,45
Exp 15	20	0,65	152	0	0,01	52	0,45
Exp 16	20	0,65	152	0	0,01	52	0,45
Exp 17	20	0,65	152	0	0,01	52	0,45
Total	745	24,25	2583,95	0,16	0,32	884	16,59

Table D2: Total mass of concentrate sample and Cr for identification and optimisation of significant process factors.

	Units	Mass data per experiment	Total mass of 34 experiments
Mass of sample	g	200	6800,00
Mass of Cr_2O_3 in sample	g	6,51	221,34
Molar mass Cr_2O_3	g/mol	152	5167,90
Moles Cr_2O_3		0,04	1,46
Moles Cr		0,09	2,91
Molar mass	g/mol	52	1768,00
Mass Cr	g	4,45	151,45

APPENDIX E

IDENTIFICATION OF INFLUENTIAL FACTORS

Table E1: Factor coding. C = Acid concentration, D = Oxygen flowrate. ABC is an interaction of temperature, time, and acid concentration. Due to this interaction of A; B and C, the effect of factor C (acid concentration) may therefore not be interpreted alone.

Response 1: Cr Extraction							
	Source	Sum of Squares	df	Mean Square	F-value	p-value	
	Model	39.97	8	5.00	3.79	0.0478	significant
	A-Temp	0.2025	1	0.2025	0.1538	0.7066	
	B-Time	0.0225	1	0.0225	0.0171	0.8997	
	C-Acid conc	9.92	1	9.92	7.54	0.0287	
	D-Oxygen Flowrate	15.60	1	15.60	11.85	0.0108	
	AB	4.84	1	4.84	3.68	0.0967	
	AC	0.0400	1	0.0400	0.0304	0.8666	
	BC	0.6400	1	0.6400	0.4860	0.5082	
	ABC	8.70	1	8.70	6.61	0.0370	
	Residual	9.22	7	1.32			
	Cor Total	49.19	15				

Factor coding is **Coded**.
Sum of squares is **Type III - Partial**

The **Model F-value** of 3.79 implies the model is significant. There is only a 4.78% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case C, D, ABC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Table E2: Coefficient in terms of factors.**Coefficients in Terms of Coded Factors**

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	5.98	1	0.2869	5.30	6.65	
A-Temp	-0.1125	1	0.2869	-0.7909	0.5659	1.0000
B-Time	0.0375	1	0.2869	-0.6409	0.7159	1.0000
C-Acid conc	-0.7875	1	0.2869	-1.47	-0.1091	1.0000
D-Oxygen Flowrate	0.9875	1	0.2869	0.3091	1.67	1.0000
AB	-0.5500	1	0.2869	-1.23	0.1284	1.0000
AC	0.0500	1	0.2869	-0.6284	0.7284	1.0000
BC	0.2000	1	0.2869	-0.4784	0.8784	1.0000
ABC	0.7375	1	0.2869	0.0591	1.42	1.0000

The model for this process is:

$$Y = 5.98 - 0.11A + 0.04B - 0.79C + 0.99D - 0.55AB + 0.05AC + 0.02BC + 0.74ABC$$

Dropping the insignificant factors

The modified model is

$$Y = 5.98 - 0.79C + 0.99D + 0.74ABC$$

The interaction A, B and C could be indicative that a linear model is inadequate and a higher third order polynomial model may be required to optimize the process.

APPENDIX F

OPTIMIZATION OF INFLUENTIAL FACTORS

A central composite design (CCD) was used to study the effects of two factors on the extraction of Cr from UG2 concentrate. The factors are:

1. Oxygen flow rate, mL/min.
2. Leaching time, hours.

The CCD experimental layout and runs with observed values for the two factors is given below:

Table F1: CCD experimental layout and runs

	1	2	Cr Extraction (%)
Standard Order	Oxygen Flowrate	Time	
Factorial Points	2^{k-1}	2^{k-1}	
1	15	3	6.0
2	40	3	5.6
3	15	7	6.1
4	40	7	6.5
Axial Points			
5	10	5	6.0
6	45	5	6.2
7	28	2	5.5
8	28	8	6.5
Centre Points			
9	28	5	6.1
10	28	5	6.2
11	28	5	6.1
12	28	5	6.2
13	28	5	6.7

This rotatable design (with $\alpha = 1.414$) has five center points.

Table F2: Central composite design.

Central Composite Design

Each numeric factor is set to 5 levels: plus and minus alpha (axial points), plus and minus 1 (factorial points) and the center point. If categoric factors are added, the central composite design will be duplicated for every combination of the categorical factor levels.

Numeric factors: (2 to 50) ☒ Horizontal ☐ Enter factor ranges in terms of ± 1 levels

Categoric factors: (0 to 10) ☐ Vertical ☒ Enter factor ranges in terms of alphas

	Name	Units	Low	High	-alpha	+alpha
A [Numeric]	Oxygen Flow rate	ML/min	15.1256	39.8744	10	45
B [Numeric]	Time	hrs	2.87868	7.12132	2	8

Type: Blocks:

Points

Non-center points: 8

Center points: 5

alpha = 1.41421 13 Runs

Table F3: Central composite design.

Sequential Model Sum of Squares [Type I] Model Summary Statistics Lack of Fit Tests

Sequential Model Sum of Squares [Type I]

	Source	Sum of Squares	df	Mean Square	F-value	p-value	
	Mean vs Total	488.62	1	488.62			
	Linear vs Mean	0.2219	2	0.1109	1.00	0.4008	Suggested
	2FI vs Linear	0.0000	1	0.0000	0.0000	1.0000	
	Quadratic vs 2FI	0.0977	2	0.0488	0.3392	0.7235	
	Cubic vs Quadratic	0.4481	2	0.2241	2.00	0.2300	Aliased
	Residual	0.5600	5	0.1120			
	Total	489.95	13	37.69			

Select the highest order polynomial where the additional terms are significant and the model is not aliased.

Table F4: Lack of fit tests.

Σ Sequential Model Sum of Squares [Type I] + Model Summary Statistics ✓ Lack of Fit Tests							
Lack of Fit Tests							
Source	Sum of Squares	df	Mean Square	F-value	p-value		
Linear	0.5658	6	0.0943	0.6986	0.6698	Suggested	
2FI	0.5658	5	0.1132	0.8383	0.5841		
Quadratic	0.4681	3	0.1560	1.16	0.4293		
Cubic	0.0200	1	0.0200	0.1481	0.7199	Aliased	
Pure Error	0.5400	4	0.1350				

The selected model should have insignificant lack-of-fit.

Table F5: Model summary statistics.

Σ Sequential Model Sum of Squares [Type I] + Model Summary Statistics ✓ Lack of Fit Tests							
Model Summary Statistics							
Source	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	PRESS		
Linear	0.3325	0.1671	0.0005	-0.4144	1.88	Suggested	
2FI	0.3505	0.1671	-0.1105	-0.9943	2.65		
Quadratic	0.3795	0.2407	-0.3017	-2.1428	4.17		
Cubic	0.3347	0.5782	-0.0123	-0.5996	2.12	Aliased	

Focus on the model maximizing the "Adjusted R²" and the "Predicted R²".

Table F6: Final equation in terms of coded factors.

β Coefficients = Coded Equation = Actual Equation		
Final Equation in Terms of Coded Factors		
Cr Extraction	=	
+6.13		
-0.1341	* A	
-0.0987	* B	

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

The linear model is developed as:

$$Y = 6.13 - 0.13x_1 - 0.098x_2$$

Where,

$$x_1 = \text{oxygen flowrate}, x_2 = \text{leaching time} \quad -\lambda \leq x_i \leq +\lambda; i = 1, 2$$

Within predictor variable limits of:

Where x_i are coded predictor variables and $\lambda = 2^{(k-q)/4} = 1.414$ (for $k = 3$, $q = 0$) is the distance of the axial points from the centre of the CCRD that gives the limits of the valid region under experimentation.

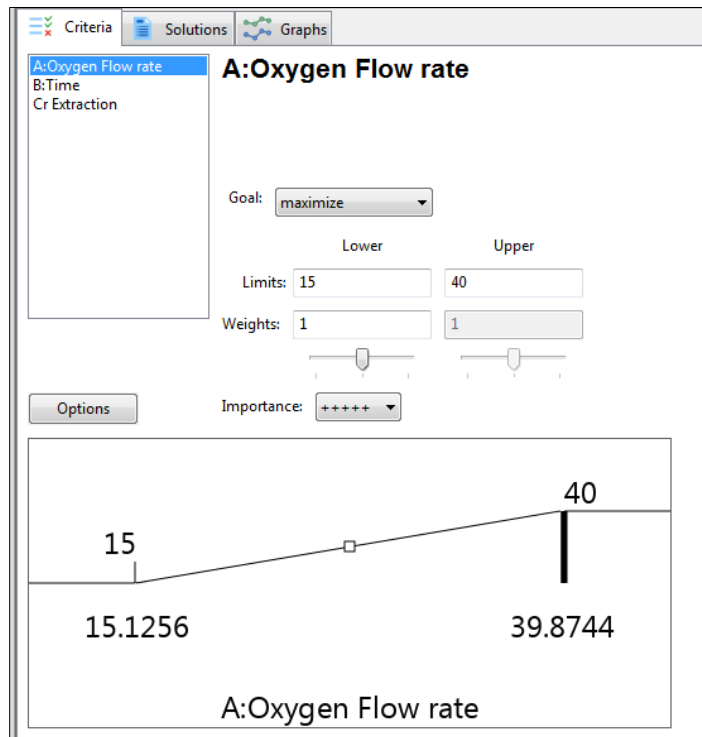
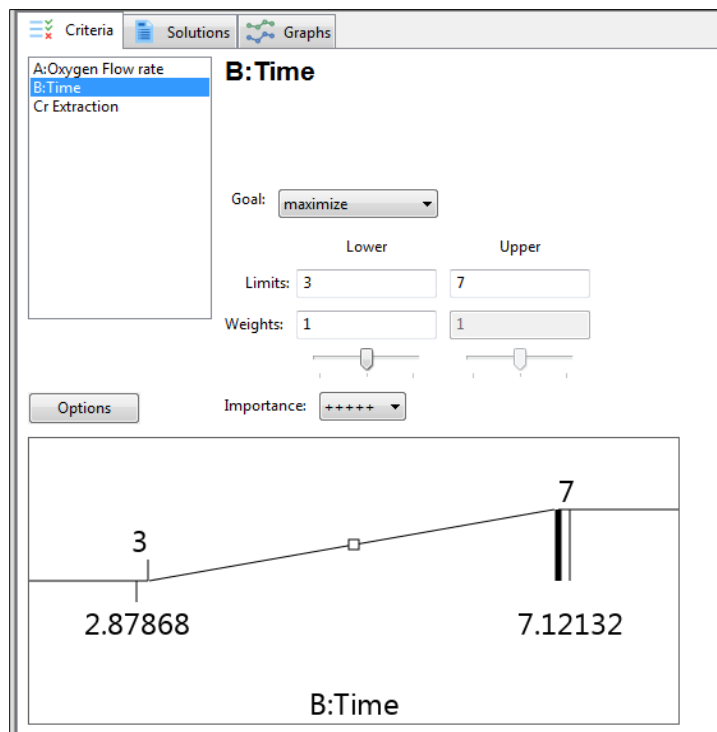
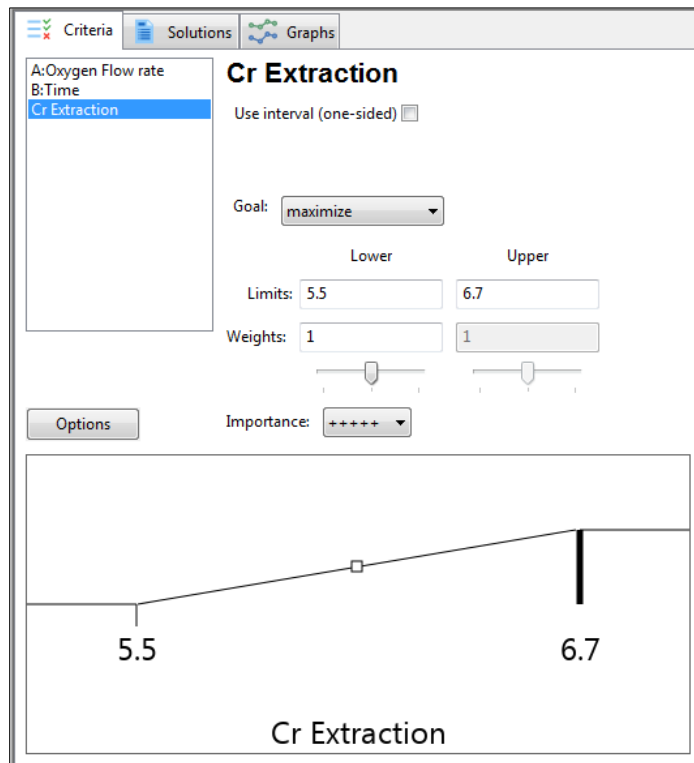
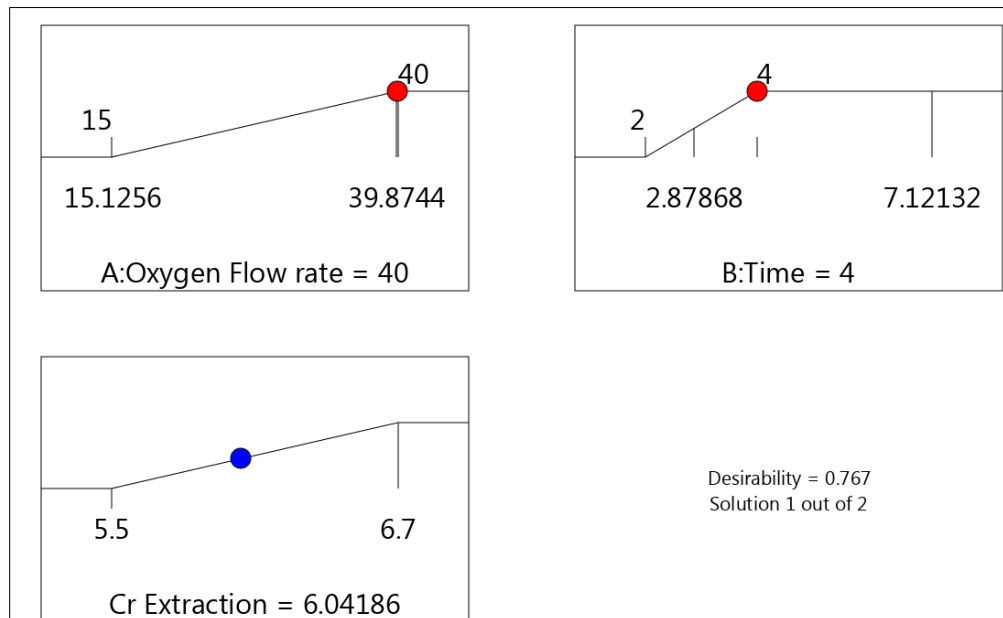
Optimization:**Table F7: Oxygen flowrate.****Table F8: Time.**

Table F9: Cr extraction.**Table F10: Predicted Cr extraction.**

Predicted Cr extraction = 6.04%