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Ozone treatment of chromium waste materials

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ABSTRACT

Ozonation, or advanced oxidation processes (utilising ozone decomposition products as oxidants) are widely used in industrial waste water and drinking water treatment plants. In these applications the use of ozone is based on ozone and its decomposition by-products being strong oxidants. A case study revealed that several waterworks in South Africa successfully utilise ozone as a pre-oxidant for the treatment of raw waters.

South Africa holds more than three quarters of the world's viable chromium ore (chromite) reserves. Subsequently the Cr-related industry-within is considerable in size and a major producer of large volumes of waste materials. Chromium also occurs commonly in other industrial waste materials (e.g. fly ash and clinkers originating from coal combustion) and is a natural occurring element in natural sediments, since chromium is the 21st most abundant element in the earth's crust with an average concentration of approximately 100 ppm. Considering the abundance of natural and anthropogenic Cr-containing materials in South Africa the possibility exists that some of these materials might be suspended in raw water entering water treatment facilities.

In this dissertation, the possible oxidation of non-Cr(VI) Cr-containing materials suspended in water during ozonation, is presented within the context of water treatment applications (Chapter 4). The results indicate that *in situ* formation of hazardous Cr(VI) is possible during aqueous ozonation. pH had a significant influence, since the decomposition products of aqueous O_3, i.e. hydroxyl radicals that form at higher pH levels, were found to be predominantly responsible for Cr(VI) formation. Increased ozonation contact time, water temperature and solid loading also resulted in elevated Cr(VI) concentrations being formed. Occasionally these values exceeded the drinking water standard 50 ppb Cr(VI). The results therefore indicate the importance of removing suspended particulates from water prior to ozonation. Additionally, pH-control could be used to mitigate the possible formation of Cr(VI) during ozonation.

In Chapter 5, exploratory work is presented on the possibility of utilising Cr(VI) formation via ozonation as a means of recovering chromium from Cr-containing waste materials. Such a study is of particular interest within the local context, considering the large volumes of waste produced by the Cr-related industry in South Africa. This exploratory work is based on the fact that unlike Cr(0) and Cr(III), most Cr(VI) compounds are relatively soluble in water. Cr(VI) is a carcinogen if inhaled, however the probability of negative health effects are substantially reduced if it occurs in solution. Thus a hydrometallurgical route of recovering Cr-units via Cr(VI) generation represents the safest route with regard to Cr(VI) exposure. Such a hydrometallurgical route could also addresses the limitations of the physical separation methods currently applied, which fails to recover fine Cr-containing solids. The degree of Cr_2O_3-liberation achieved in this exploratory work was relatively low. However, the Cr_2O_3-liberation achieved for the ferrochromium slag (15%) indicated some promise, considering the limitations of this exploratory work. Several steps can be considered in future studies, which would in all likelihood improve the Cr_2O_3-liberation further.

Keywords: Chrome, Oxidation, Ozone, Ferrochromium slag

OPSOMMING

Osonering, of ander gevorderde oksidasieprosesse (die aanwending van ontbindingsprodukte van osoon as oksidante) word algemeen gebruik in industriële afval- en drinkwater behandelingsaanlegte. In hierdie toepassings word die gebruik van osoon gebasseer op die vermoë van osoon en die ontbindingsprodukte daarvan om op te tree as sterk oksidante. `n Gevallestudie het aangetoon dat daar verskeie watersuiweringsaanlegte in Suid Afrika is waar osoon suksesvol gebruik word as ‘n pre-oksidant in die behandeling van rouwater.

Suid Afrika besit meer as driekwart van die wêreld se ontginbare chroomerts (chromiet) reserwes en het die grootste Cr-verwante industrië ter wêreld. Hierdie Cr-verwante industrieë produseer groot hoeveelhede afvalstowwe. Chroom kom ook algemeen in ander industriële afvalstowwe voor (bv. vliegas en klinkers afkomstig van steenkool verbranding). Dit is ook ‘n element wat aangetref word in natuurlike sedimente, aangesien chroom die 21ste algemeenste element in die aardkors is, met ‘n gemiddelde konsentrasie van 100 dpm. Indien die algemene voorkoms van natuurlike en antropogeniese Cr-bevattende stowwe in Suid Afrika in ag geneem word, bestaan daar die moontlikheid dat van hierdie stowwe gesuspendeer kan wees in die rouwater wat deur watersuiweringsaanlegte ingeneem word.

Die moontlike oksidasie van nie-Cr(VI) Cr-bevattende stowwe, gesuspendeer in water gedurende osonering, is in hierdie verhandeling binne die konteks van waterbehandelingstoepassings ondersoek (Hoofstuk 4). Die resultate toon aan dat *in situ* vorming van Cr(VI) moontlik is gedurende osonering van water. pH het ‘n groot invloed gehad, aangesien gevind is dat die ontbindignsprodukte van O_3 in water, naamlik die hidroksielradikale wat gevorm word by hoë pH vlakke, hoofsaaklik verantwoordelik was vir Cr(VI) vorming. Verlengde osoneringskontaktyd, asook verhoogde watertemperatuur en soliede belading het ook tot hoër Cr(VI) konsentrasies gelei. Soms het hierdie waardes die 50 dpb Cr(VI) drinkwaterstandaard oorskry. Die resultate het aangetoon dat dit belangrik is om gesuspendeerde partikels uit water te verwyder voor osonering toegepas word.

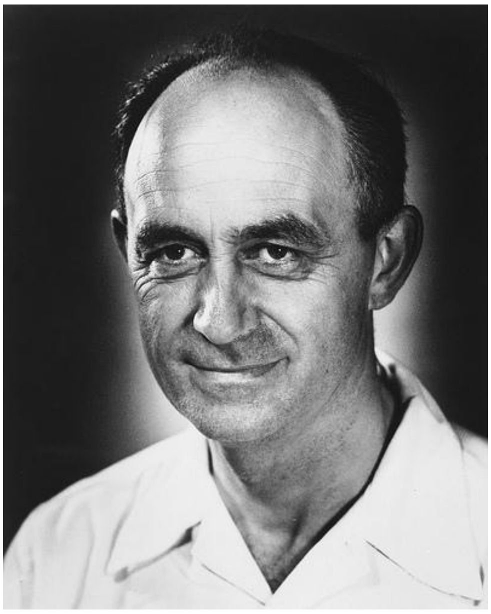
Bykomend, kan pH-beheer gebruik word om die moontlike vorming van Cr(VI) gedurend osonering te verminder.

Hoofstuk 5 toon die resultate van ‘n loodsstudie vir die moontlike herwinning van chroom uit Cr-bevattende afvalstowwe deur Cr(VI)-vorming gedurende osonering. Hierdie loodsondersoek is van besondere belang binne die Suid Afrikaanse konteks, as gevolg van die groot hoeveelhede afvalstowwe wat die plaaslike Cr-verwante industrieë produseer. Die konsep van hierdie studie is gebasseer op die feit dat Cr(0) en Cr(III), anders as die meeste Cr(VI) verbindings, betreklik onoplosbaar is in water. Dit is ook algemeen bekend dat Cr(VI) karsinogenies is indien dit ingeasem word, maar dat die moontlikheid van negatiewe gesondheidsimpakte drasties verminder indien dit in ‘n oplossing voorkom. ‘n Hidrometallurgiese metode om Cr-eenhede deur Cr(VI)-vorming te herwin, verteenwoordig dus die veiligste roete ten opsigte van Cr(VI) blootstelling. Hierdie hidrometallurgiese metode kan ook moontlik die tekortkominge van huidige toegepasde fisiese skeidingsmetodes aanspreek, wat nie daarin slaag om fyn Cr-bevattende soliede material te herwin nie. Die mate waartoe Cr_2O_3 vrystelling behaal is in hierdie ondersoek was egter betreklik laag. Die Cr_2O_3 vrystelling wat behaal is uit die ferrochroomslak was belowend, indien die beperktheid van die loodstudie in ag geneem word. Verskeie stappe kan oorweeg word in toekomstige studies om die Cr_2O_3 vrystelling verder te verbeter.

Sleutelwoord: Chroom, Oksidasie, Osoon, Ferrochroom slak

There are two possible outcomes: if the result confirms the hypothesis, then you’ve made a discovery. If the result is contrary to the hypothesis, then you’ve made a discovery.

Enrico Fermi



CHAPTER 1

MOTIVATION AND OBJECTIVES

In this chapter...

A brief overview of the project motivation (Par. 1.1) and objectives are discussed (Par. 1.2).

1.1 Project Motivation

1.1.1 Water availability in South Africa

Water is possibly the most important resource on earth, since life on earth depends on it and would cease to exist in its absence. It is also a basic human right as stated in the South African Bill of Rights, “everyone has the right to have access to sufficient water” (Constitution,of South Africa, Act No. 108 of 1996, Section 27(1) (b)). However, it is of concern that the availability of water suitable for human consumption is a scarce and diminishing resource in South Africa. South Africa is considered to be a semi-arid country with a mean annual precipitation of 487 mm per year compared to the world average of 860 mm per year. A strong seasonal distribution of rainfall exists resulting in 65% of the country receiving less than 500 mm of rain annually and 21% receiving less than 200 mm per year (Kidd, 1997).

An increase in water demand for domestic, industrial and agricultural consumption can be expected in the near future, which will place additional stress on water resources and the environment (Barrow, 2006). It is foreseen that eventually the availability of water at an acceptable drinking standard could even lead to restrictions being imposed on population growth (Carrim, 2006). Fresh water is therefore set to play a pivotal role in the future socio-economic development of South Africa.

Increased anthropogenic activities have led to eutrophication, increased salinity, acid mine drainage, the presence of radioactive materials and faecal pollution of water resources (Davies & Day, 1998). It is therefore becoming increasingly important to critically evaluate water purification methods, especially within the South African context. In this study, the use of the ozonation process is evaluated.

1.1.2 Ozonation for water purification

Ozonation is used extensively in Europe and North America for water purification (Geldenhuys *et al.*, 2000). The use of ozone or ozone in conjunction with other compounds and catalysts (e.g. advanced oxidation processes) to treat industrial waste waters and effluents is well documented (Nawrocki & Kasprzyk–Hordern, 2010; Coca *et al.*, 2007; Selcuk, 2005; Gogate & Pandit, 2004; Beltrán, 2003). While ozonation is not widely used in the South African water treatment sector, its popularity is gaining momentum. A case study revealed that there are several waterworks in South Africa where O_3 is used successfully as a pre-oxidant for the treatment of raw waters (Rajagopaul *et al.*, 2008). Ozonation or advanced oxidation processes (AOP) have proven to be efficient technologies for enhanced coagulation, flocculation, oxidising organic compounds, as well as combating taste and odour problems in order to produce drinking water (Rajagopaul *et al.*, 2008; Beltrán, 2003).

Although ozonation has many advantages, there are also some disadvantages associated with its use. It is an energy intensive process option and its use can lead the potential formation of harmful disinfection by-products (Rajagopaul *et al.*, 2008; Legube *et al.*, 2004; Beltrán, 2003). The use of O_3 in water treatment is based on ozone and its decomposition by-products, i.e. hydroxyl radicals, being strong oxidants (Audenaert *et al.*, 2010; Lovato *et al.*, 2009; Beltrán, 2003; Sotelo *et al.*, 1987).

The potential for the formation of Cr(VI), a known carcinogen (Stern, 2010; Proctor *et al.*, 2002; Kim *et al.*, 2002; IARC, 1997), by aqueous O_3 has received limited research attention. Rodman *et al.* (2006) investigated the conversion of Cr(III) propionate to Cr(VI) by the advanced oxidation process, as a means of pre-treatment in an analytical technique. As far as the author could assess, an investigation of the possible formation of Cr(VI) via aqueous O_3 oxidation of non-Cr(VI) containing materials, with relevance to water treatment, has not yet been conducted. Such a study is of particular interest within the local context, considering South Africa's considerable chromium ore reserves and the associated industries.

South Africa holds more than three quarters of the world's viable chromium ore (chromite) reserves (Murthy *et al.*, 2011; Cramer *et al.*, 2004) and produced approximately 40% of the world's ferrochrome in 2009 (ICDA, 2010; Beukes *et al.*, 2010). Upper Group 2 chromite (UG2) is also processed in South Africa to produce platinum group metals (PGMs) (Beukes *et al.*, 2010; Cramer *et al.*, 2004; Cawthorn, 1999), with SA producing an estimated 80% of annual global PGMs (Xiao & Laplante, 2004; Cawthorn, 1999). Cr(VI) chemicals are also produced in South Africa (Lanxess, 2011). All these industries produce Cr-containing wastes, albeit wastes containing mostly Cr(III). Coal combustion industries in South Africa (e.g. coal fired power stations, coal to liquid fuel production, boilers) produce fly ash and clinker containing chromium, due to chromium occurring with the trace minerals in coal (Nel *et al.*, 2011; Wagner & Hlatshwayo, 2005).

Considering the abundance of Cr-containing waste in South Africa and the possibility that some of this waste might be very fine and airborne (e.g. combustion off–gas particles), it is not unlikely that some Cr-containing materials might be suspended in raw water, which may enter water treatment facilities. Chromium also occurs in natural sediments, since chromium is the 21st most abundant element in the earth's crust with an average concentration of approximately 100 ppm (Emsley, 2003). It was therefore decided to investigate the possible formation of Cr(VI) during water purification by ozonation.

1.1.3 Ozonation for the recovery of Cr from waste materials

As previously mentioned, South Africa dominates the international Cr-related industry, due to its considerable ore resources. Beukes *et al.* (2010) estimated that approximately 5.3 million tons of slag (waste material) is produced annually by the local ferrochrome industry. Approximately the same amount of Cr-containing waste materials is also produced by the local chromite and platinum industries. In addition smaller, but substantial volumes of Cr-containing waste is produced by the local Cr(VI) chemical industry. Most of the afore-mentioned wastes contain 3.5 to 12% Cr that is currently not recovered. This is mainly due to the limitations of the extraction techniques applied (Erdem *et al.*, 2005; Riekkola–Vanhanen, 1999).

The formation of Cr(VI) is usually avoided due to its carcinogenic impacts (Stern, 2010; Proctor *et al.*, 2002; Kim *et al.*, 2002; IARC, 1997; Yassi & Nieboer, 1988). However, unlike Cr(III), most Cr(VI) species are expected to be relatively soluble in water (Rai *et al.*, 1989). Thus, if the Cr(III) in the Cr-containing wastes could be converted to Cr(VI), it could facilitate the recovery of waste Cr-units. For such a hypothetical recovery process a hydrometallurgical (waterborne) method would be preferred. A published “weight of scientific evidence review” have clearly indicated that waterborne Cr(VI) is much less of a risk than airborne Cr(VI) at similar concentrations (Proctor *et al.*, 2002). Therefore, in addition to the investigation into the possible formation of Cr(VI) during water purification by ozonation (Par 1.1.2), the potential for the application of ozonation in the recovery of valuable Cr-units from waste materials was investigated.

1.2 Project objectives

The specific objectives of the study were to:

i. Compile a thorough literature survey detailing:
   a. The importance of water resources in South Africa,
   b. The importance of the chromium industry in South Africa,
   c. Processes utilised by this industry,
   d. The characteristics of the local chromium waste materials.

ii. Investigate the possible formation of Cr(VI) through oxidation of non-Cr(VI) Cr-containing materials suspended in water during ozonation. This reaction system was investigated as a function of pH, O_3 concentration, solid material loading, contact time, water temperature and other process variables.

iii. Determine the impact of the above-mentioned results on water purification processes and to indicate how associated negative aspects could be mitigated, or preferably eliminated.

iv. Investigate the use of ozonation as a possible means of liberating valuable chromium units from waste materials. This reaction system was investigated as a function of pH and other process variables.

v. Make recommendations with regards to the suitability of the use of ozonation in chromium recovery from waste materials.

vi. Make recommendations with regards to future research which should be undertaken.

He who learns but does not think, is lost!
He who thinks but does not learn is in great danger.

Confucius

CHAPTER 2

LITERATURE SURVEY

In this chapter...

An overview of the relevant literature is provided. An introduction to chromium is given in terms of the historical perspective, general chemistry, natural occurrence and the uses thereof (Par 2.1). A closer look into the importance of the chromium industry in South Africa is presented in Par 2.2, while the core processes for the ferro-chrome industry is discussed in Par 2.3. Waste materials generated by the afore-mentioned industrial processes are discussed in Par 2.4. The possible carcinogenicity and toxicity of chromium is briefly reviewed in Par 2.5. The aqueous chemistry of chromium is discussed in Par 2.6, while ozone chemistry and generation is considered in Par 2.7. Some conclusions drawn from the literature is presented in Par 2.8.

2.1 Introduction on chromium

2.1.1 Historical perspective

Johann Gottlob Lehmann, a professor of chemistry and director of the imperial museum in St. Petersburg, discovered the first chromium containing compound crocoite (lead chromate) in 1761 at the Beryozovskoye deposit (Beresof gold mine) in the Ural Mountains (Roza, 2008). In 1797 the French chemist Nicolas-Louis Vauquelin succeeded in producing chromium oxide (Cr_2O_3) by mixing crocoites with hydrochloric acid. He also isolated metallic chromium the following year (Roza, 2008). Vauquelin named the new mineral chrome, after the Greek word chroma meaning colour (Emsley, 2003). He was also able to detect traces of chromium in precious gemstones, such as ruby and emeralds (Roza, 2008). In 1798 both Klaproth and Tobias Lowitz successfully isolated the metal from chromite ore samples from the northern Urals and in the following year Tassaert isolated chromium in a sample from the chrome iron ore deposits at Gassin, France (Nriagu, 1988a). Since then chromite ($FeO{\cdot}Cr_2O_3$ or $MgO{\cdot}Cr_2O_3$), which is of the “spinel” crystal type, has remained the only commercial source of chromium (Riekkola-Vanhanen, 1999).

After its discovery, commercial production of chromium remained technologically unfeasible for several decades. The first successful attempt was made in 1821 by Pierre Berthier, who produced metallic chromium by reducing the oxides of the metal with carbon. He found that when chromium was mixed with iron, the new metal could resist corrosion, however, it was too brittle to be of any use (Roza, 2008). During the next fifty years, other scientists experimented with combinations of iron, chromium and other metals. In 1872 Woods and Clark filed a patent for a weather-resistant iron alloy that was 30 to 35% chromium and 2% tungsten. This alloy was one step closer to the discovery of stainless steel (Roza, 2008). French chemist Henri Moissan heated ore that contained chromium and iron in an electric furnace with coke (carbon) in 1893. The result was an alloy he called ferrochromium. This metal contained up to 70% chromium and small amounts of carbon that helped to make the metal stronger. Since then many scientists experimented with various concentrations of carbon, iron and chromium until stainless steel as we know it today, was developed (Roza, 2008).

2.1.2 Natural occurrence

Chromium is the 21st most abundant element in the earth's crust, with average concentration of 100 $\mu g \cdot g^{-1}$ (Emsley, 2003; Nriagu, 1988b). It ranks 4th among the 29 biological important transition metals (Nriagu, 1988b). Chromium ore occurs exclusively in ultramafic igneous rocks and mostly as a chromium spinel (chromite, see Figure 2.1) which is a complex mineral containing magnesium, iron, aluminium and chromium in varying proportions depending upon the deposit. As molten magma cools, chromite concentrates to form ore deposits by gravity separation (Nriagu, 1988b).

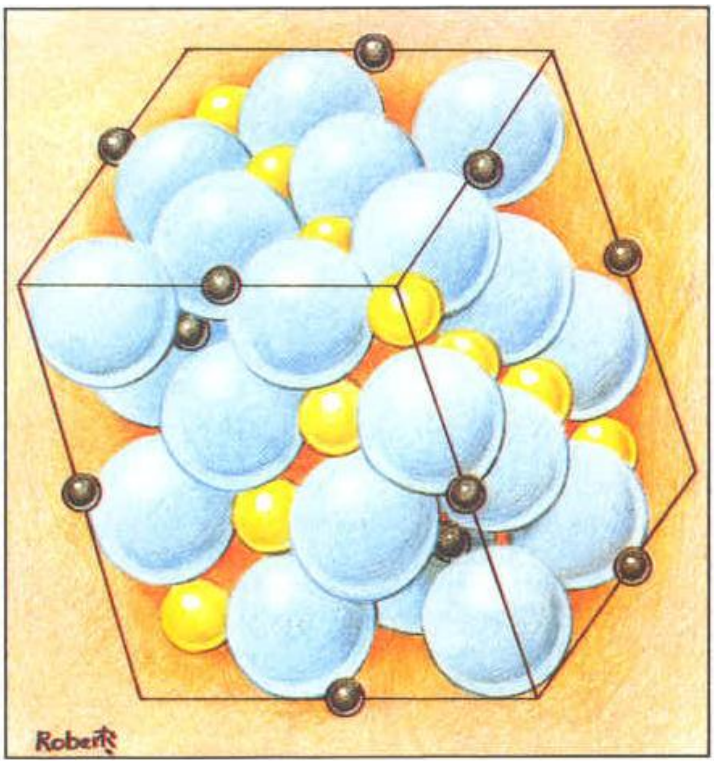


Figure 2.1: Perspective view of the structure of chromite. The white spheres are oxygen, the yellow spheres chromium and the small black spheres iron (Mintek Bulletin, 1990)

Most of the major chromium deposits known occur in three principal geological settings (Nriagu, 1988b):

(1) Stratiform-type deposits, such as the Bushveld Igneous Complex of South Africa, the Great Dyke in Zimbabwe and the Kemi intrusion of Finland. These deposits account for over 90% of the identified chrome ore resources.

(2) Podiform-type or Alpine-type deposits generally associated with island-arcs and the major tectonic belts, such as the Tethyan mountain chains and Ural Mountains. These deposits account for 10% of the world's chromium ore resources.

(3) Lateritic deposits, which are generally derived from the weathering of chromium bearing peridotites. Few of these deposits have been exploited profitably.

Mining of chromite deposits is carried out both by open-pit and by underground mining. The most intensive mining occurs in the Bushveld Igneous Complex in South Africa. According to the United States Geological Survey (USGS), world resources of chromite exceed $11x10^{12}$ kg and are sufficient to meet world demand for many centuries to come. South Africa and Zimbabwe hold about 80% to 90% of the world's chromite reserves (Murthy *et al.*, 2011; Riekkola-Vanhanen, 1999).

2.1.3 General chemistry of chromium

Chromium metal appears as a grey-white, hard, lustrous, brittle, but highly polishable substance of cubic crystalline structure. It is chemically not stable in atmospheric conditions, but becomes passive to form a thin oxide layer with another elements such as nickel or iron. Due to this phenomenon chromium is extremely resistant to ordinary corrosive agents which accounts for its extensive use as an electroplated protective coating. The afore-mentioned passive oxide layer has a spinel structure which is very dense, and prevents the diffusion of oxygen into the underlying material which causes corrosion.

Chromium is a member of the d-block transition metal of Group VIB (or Group 6) in the Periodic Table. Chromium has an electronic configuration of $[Ar]4s^1 3d^5$. Due to the diverse energy levels of spin configurations, chromium exhibits a wide range of possible oxidation states from -4 to +6. The different oxidation states are important in determining which chromium compounds are found in specific environment. Oxidation states -2, -1, 0 and +1 primarily occur in synthetic organic-chromium compounds (Motzer, 2005; Cotten & Wilkinson, 1988). Cr(0) is rarely found in the natural environment in its pure metallic form. In aqueous solutions only the +2, +3 and +6 states are of importance, with Cr(III) being the most stable and Cr(VI) being the most oxidising (Jacobs & Testa, 2005). The +4 and +5 states may occur as intermediates of limited stability in chemical reactions involving Cr(III)/Cr(VI) interconversions (Cotten & Wilkinson, 1988). Chromium has unique magnetic properties. It is the only elemental solid which has antiferromagnetic (no-attraction to magnetic field) ordering at room temperature, while above 38 °C, it transforms into a paramagnetic (attracted to a magnetic field) state (Fawcett, 1988).

Chromium, unlike metals such as iron and nickel, does not suffer from hydrogen embrittlement, however, it does suffer from nitrogen embrittlement. Nitrogen from air reacts with the chromium and forms brittle nitrides at the high temperatures necessary to work the metal (National Research Council (U.S.), 1970).

The metal dissolves fairly readily in non-oxidising mineral acids, for example, hydrochloric acid and sulphuric acids, but not in cold aqua regia or nitric acid (Cotten & Wilkinson, 1988). The standard electrode potentials of the most important chromium oxidation states are:

$$Cr^{2+}(aq) + 2e^{-} = Cr(s) \quad E^{0} = –0.91\ V \qquad (2.1)$$

$$Cr^{3+}(aq) + 3e^{-} = Cr(s) \quad E^{0} = –0.74\ V \qquad (2.2)$$

$$Cr_2O_7^{2-}(aq) + 14H^{+} + 6e^{-} = 2Cr^{3+}(aq) + 7H_2O \quad E^{0} = 1.33\ V \quad pH = 0 \qquad (2.3)$$

$$CrO_4^{2-}(aq) + 4H_2O + 3e^{-} = Cr(OH)_3(s) + 5OH^{-} \quad E^{0} = –0.13\ V \quad pH = 14 \qquad (2.4)$$

2.1.4 Consumption and uses

Chromium is an extremely versatile element and finds a wide variety of uses in modern industrial society, with different applications calling for diverse forms of chromium, such as chromite, ferrochromium, chromium metal, chromite refractory bricks, chromite foundry sands, chromic acid and other chromium compounds. These applications are distributed among three principal industrial end uses: metallurgical, chemical and refractory (Nriagu, 1988b). In 2009, 19 million tonnes of chromite was mined globally (ICDA, 2010). Of this approximately 95% was smelted into ferrochromium (ICDA, 2010). Ferrochromium is subsequently mainly used in the production of stainless steel, steel and other alloys. Less than 2% of the world's production of chromite was used in 2009 for chromium chemicals (ICDA, 2010). The most important chromium containing chemical product is sodium dichromate. From this, a variety of other chemical products are made. It is also used in leather tanning, pigments, catalysts, wood preservatives, plastics, ceramics and metal finishing such as chromium plating (Nriagu, 1988b). Production of chromite for refractory use and foundry sands was about 3% of world production of chromite for 2009. Refractory chromite is used in sectors of ferrous and non-ferrous metallurgy, in cement kilns and in the glass industry (ICDA, 2010).

2.2 Chromium in South Africa

2.2.1 Chromite ore reserves and production

The German explorer Karl Mauch first noted the occurrence of chromium in South Africa in 1865 (Mintek, 1994). He marked an outcrop of chromite in the Rustenburg district. One of the first attempts to exploit the deposits was made in 1917 when a farmer in the Lydenburg district, sent 200 tons of chromite ore to the British Munitions Board. However, the ore was turned down because of the ratio of chromium to iron which was too low. Chromium mining in South Africa started in earnest only in 1921, and by the start of the Second World War, production had reached 180 000 ton per year ($t \cdot y^{-1}$) (Mintek, 1994). Until 1963, the majority of chromite mined in South Africa (approximately 93%) was exported without further beneficiation (South Africa. Natural Resources Development Council., 1964).

It is generally accepted that South Africa holds between 68% (Howat, 1994) to 75% (Cramer *et al.*, 2004) of the world's viable chromite ore reserves. Chromite resources in South Africa are located in a single geological structure known as the Bushveld Igneous Complex (BIC) (Howat, 1994). The BIC is further divided into limbs as a result of the different forms of chromite mined and the geographical separation between the individual deposits. Figure 2.2 shows the limbs of the BIC and the location of ferrochromium smelters in South Africa (adapted from Johnson Matthey, 2008).

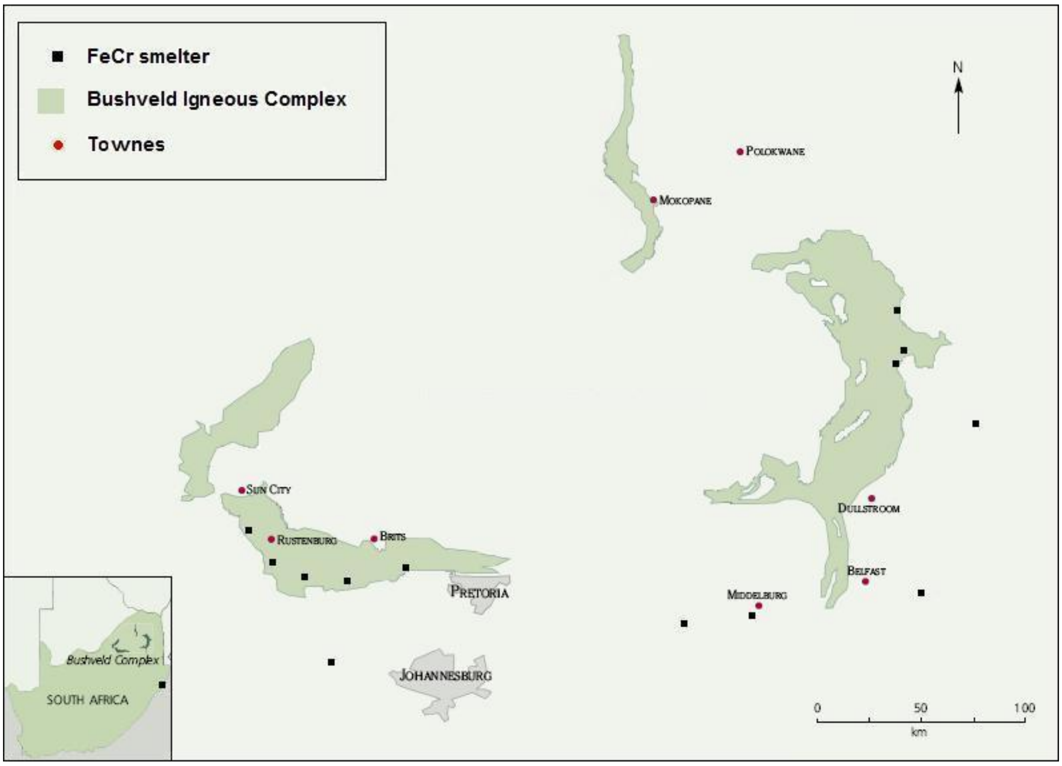


Figure 2.2: A graphical representation of the Bushveld Complex and FeCr smelters of the Merensky reef (adapted from Johnson Matthey, 2008)

The four major areas in which the chromite ore is mined in SA are in the eastern chromite belt, the western chromite belt, the Zeerust district, and the area south of Potgietersrus. The chromite ore in the BIC is mainly in the form of seams in the maffic rock, due to differentiation of separate upwelling of intrusion pyroxinite, anortosite and norite (South Africa. Natural Resources Development Council., 1964). The seams can be seen as partitioned layers in the Merensky (platinum) reef (Xiao & Laplante, 2004; Cramer *et al.*, 2004).

The deposits in the Zeerust and Potgietersrus areas, where resources are limited, have chromium:iron (Cr:Fe) ratios of 2 to 2.9 (Howat, 1994). The major deposits in the western and eastern BIC, with vast deposits, have Cr:Fe ratios of 1.5 to 1.6 (Howat, 1994). The annual production of chromite in South Africa was approximately 6.2 million tons for 2009 (ICDA, 2010).

Three main zones of the chromite seams, namely the lower group (LG), the middle group (MG) and the upper group (UG), are prevalent in the western part of the BIC. The lower group can have up to 17 layers, the middle group 10 and the upper group

5 (South Africa. Natural Resources Development Council., 1964). The economically interesting seams are the LG6 (lower group 6), the MG1/2 (middle group 1 and 2) seams and the UG2 seam (upper group 2). The latter is not only of interest as a source of chromite but as a primary source of platinum group metals (PGMs) (Cramer *et al.*, 2004; Soykan *et al.*, 1991). South Africa produces an estimated 80% of annual global PGMs (Xiao & Laplante, 2004; Cawthorn, 1999).

The local ferrochrome industry also receives significant volumes of UG2 chromite process residue from PGM industry. UG2 chromite ores usually have Cr:Fe ratios of 1.3 to 1.4 (Beukes *et al.*, 2010; Cramer *et al.*, 2004; Soykan *et al.*, 1991). Significant, but smaller, chromite resources are also found in countries such as Zimbabwe and the former USSR states. Those deposits have Cr:Fe ratios of 2.6 to 3.5 and 2.8 to 3.0, respectively (Howat, 1994).

Figure 2.3 indicates the production figures of chromite and high carbon ferrochrome for 2009 (ICDA, 2010), which emphasise South Africa's international dominance of this market. Global distribution of the major chromite ore, ferrochrome and stainless steel producers is shown in Figure 2.4 (Papp, 1994).

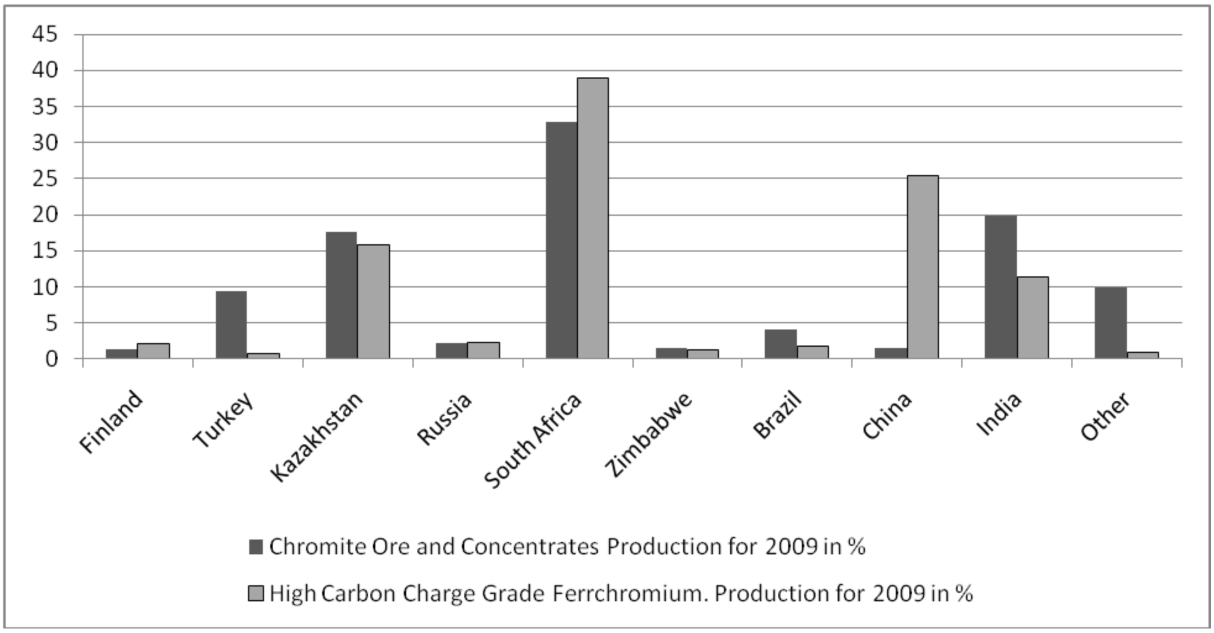


Figure 2.3: Percentage production of ore and ferrochromium for 2009 (ICDA, 2010)

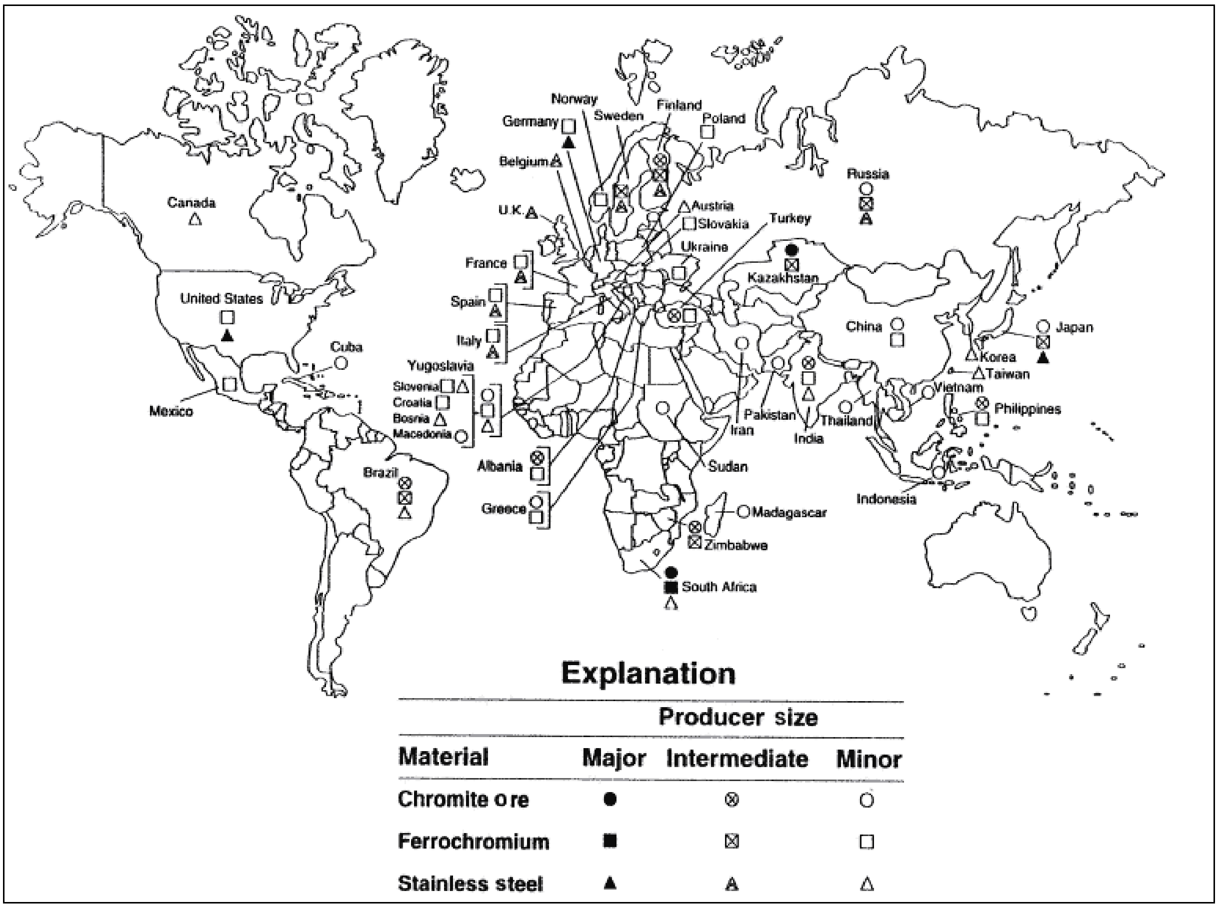


Figure 2.4: World geographic location and size of chromite ore, ferrochromium and stainless steel productions (Papp, 1994)

2.2.2 Ferrochrome and stainless steel production

In 1970 South Africa converted less than 10% of its chromite production into ferrochromium. During 1995 more than 80% of the ore was converted (Wood, 1996). According to the 2009 production statistics of the International Chromium Development Association (Figure 2.3), South Africa produced approximately 39% of the world's charge chrome (ICDA, 2010). Today South Africa is the world's leading producer of both chromite and ferrochromium (ICDA, 2010). There are at least 14 separate ferrochrome production facilities in South Africa as shown in Figure 2.2 (Jones, 2011), with a combined production capacity of 4.34 million tons per year. Table 2.1 gives a summary of the production capacities of these facilities.

Table 2.1: Ferrochromium production in South Africa (Jones, 2011)

Plant	**Locality**	**Production capacity (kilo ton per year)**
ASA Metals	Dilokong (Burgersfort)	125
Assmang Chrome	Machadodorp	300
Hernic Ferrochrome	Brits	260
International Ferro-Metals	Rustenburg-Brits	267
Middelburg Ferrochrome	Middelburg	285
Mogale Alloys	Krugersdorp	130
Samancor Ferrometals	Emalahleni (Witbank)	550
Tata (Steel) Ferrrochrome	Richardsbay	135
Tubatse Ferrochrome	Steelpoort	360
Xstrata Lydenburg	Lydenburg	400
Xstrata-SA Chrome	Boshoek	240
Xstrata-Merafe Lion	Steelpoort	364
Xstrata Rustenburg	Rustenburg	430
Xstrata Wonderkop	Rustenburg-Brits	545
TOTAL		4 340

Stainless steel production in South Africa began in the 1960's, with RMB alloys and SX Stainless with a capacity of 20 $kt \cdot y^{-1}$. In 1980 Middelburg Steel and Alloys already had a capacity of 120 $kt \cdot y^{-1}$. Columbus Stainless Steel is currently producing 600 $kt \cdot y^{-1}$ stainless steel products (Wood, 1996).

Considering South Africa's considerable chromite ore resources and its dominance of world ferrochromium production, it is however lagging behind in terms of stainless steel production. Increased local stainless steel production would enhance the value chain of transforming mineral resources into valuable products and strengthen the economy.

2.2.3 Cr(VI) chemicals production

Cr(VI) chemicals are also produced in South Africa (Lanxess, 2011). This industry fulfils a niche market and is a relatively low volume, higher value industry. Lanxess has chrome production sites in Rustenburg, Merebank and Newcastle.

2.3 Core process

2.3.1 Chromite mining and beneficiation

Although chromite is one of the hardest known minerals, South African chromite is relatively friable and easily breaks down to the size of the chromite crystal (Gu & Wills, 1988). Due to this friability, it is common to only recover 10-15% lumpy ore (particle size of 6 to 150 mm) and 8-12% chip/pebble ores (particle size 6 to 25 mm) during the mining and beneficiation processes employed by South African chromite mines (Glastonbury *et al.*, 2010). The remainder of the ore (73-82%) falls within the <6 mm fraction, which would typically be milled or crushed to <1 mm and upgraded to a >45% Cr_2O_3 content. This upgraded <1 mm ore is generally termed metallurgical grade ore (Neizel, 2010).

South African run-of-mine chromite ores have to undergo at least rudimentary beneficiation. Several methods are employed of which the choice of method depends on the type of product desired. Simple screening operations may be adequate in some cases, but complex heavy-medium, magnetic, flotation and gravity separation methods may be necessary in other cases (Gu & Wills, 1988).

Heavy medium separation is the most economic method for treating coarse (10-100 mm) particles, while finer particles are often treated by jigs, spirals and shaking tables, with spiral concentration currently being preferred. Recovery of chrome via these processes can be up to 80-85%, but there are still limitations on the improvement of the Cr_2O_3 grade. Improvements of 1-4% have been achieved, hence increasing the Cr_2O_3 grade from about 40 to 44% (Gu & Wills, 1988).

All chromites are paramagnetic at room temperature depending on the Fe^{2+} content (Fawcett, 1988). It has been speculated that the distribution of magnetic ions is not uniform in the crystal structure and therefore, ferromagnetism is created in the more concentrated sections. In a low magnetic field (about 0.1 T) chromite can be separated from ferromagnetic minerals as a non-magnetic product (Gu & Wills, 1988).

Although flotation is not a major method of beneficiation for chromite ores, fatty acids, such as oleic acid, have been used where this method has been adopted. One of the major difficulties with flotation is the wide variation in surface properties of chromites from different locations (Gu & Wills, 1988).

2.3.2 Ferrochromium production

Ferrochrome is produced pyrometallurgically by carbothermic reduction of chromite (Riekkola-Vanhanen, 1999). The main reactions are:

$$Cr_2O_3 + 3C \rightarrow 2Cr + 3CO \qquad (2.5)$$

$$FeO + C \rightarrow Fe + CO \qquad (2.6)$$

A generalised process flow diagram, adapted by Beukes *et al.* (2010) from Riekkola-Vanhanen (1999), is shown in Figure 2.5, which indicates the most common combinations of process steps utilised by the South African ferrochrome producers. This process flow diagram does not cover every possible process combination; it is however adequate for the discussions in this study.

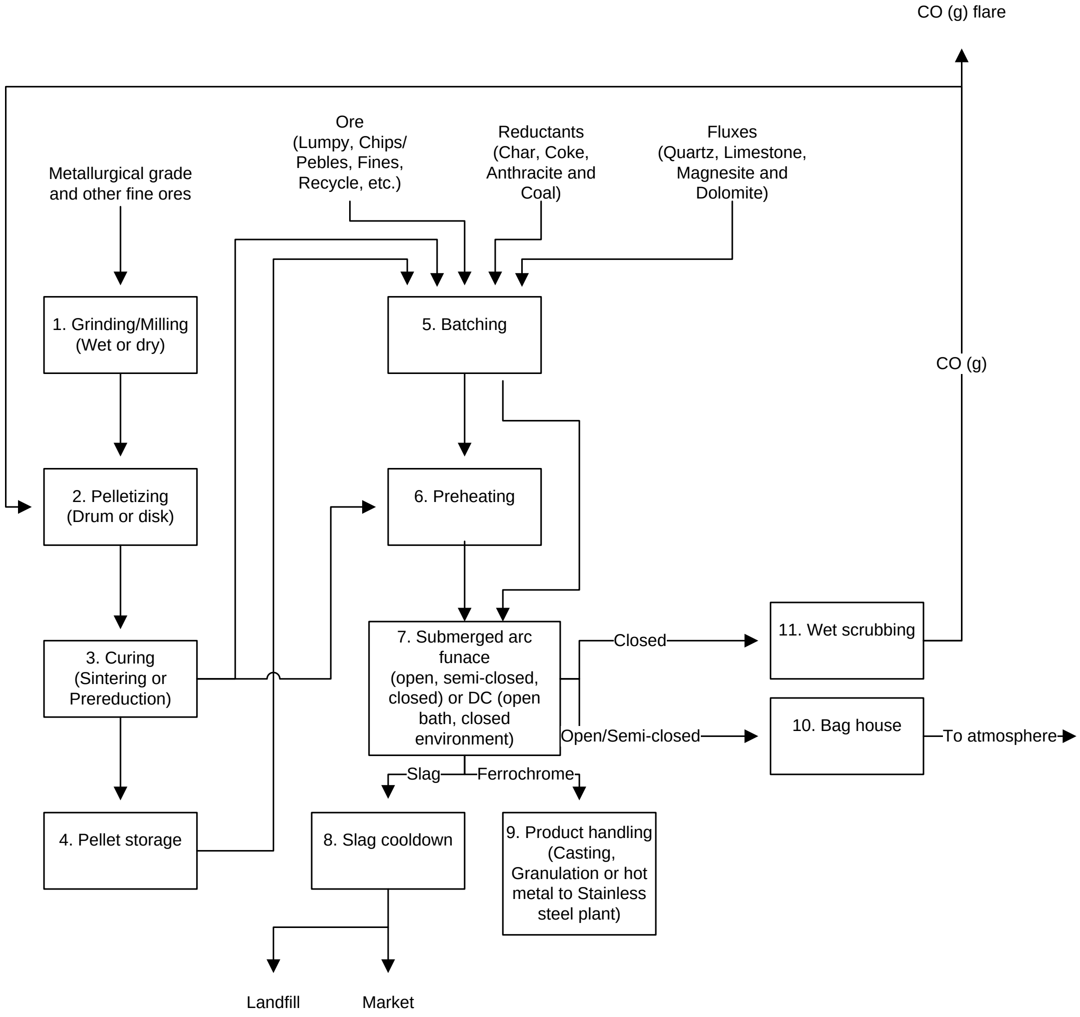


Figure 2.5: Generalised flow diagram adapted by Beukes *et al.* (2010) from Riekkola-Vanhanen (1999), indicating the most common combination of process steps utilised during ferrochrome production in South Africa

In general, four relatively well defined process combinations are utilised by the South African ferrochrome producers (Beukes *et al.*, 2010; Neizel, 2010):

i. Conventional semi-closed furnace operation with bag filter off-gas treatment. This is the oldest technology applied in South Africa, and still accounts for a substantial fraction of overall production (Gediga & Russ, 2007) With reference to the process flow diagram indicated in Figure 2.5, the process steps followed are 5, 7, 8, 9 and 10. In this type of operation, coarse (lumpy and chips/pebble ores) and fine ores can be smelted without an agglomeration process undertaken to increase the size of fine ores. Although it has been mentioned (Riekkola-Vanhanen, 1999) that fine ores cannot be fed directly into a submerged ferrochrome arc furnace without causing dangerous blow-outs or bed turnovers, a substantial amount of fine ores are in fact fed into some SA semi-closed furnaces. Some semi-closed furnaces do consume pelletised feed, in which case process steps 1-4 would also be included. Most of the South Africa semi-closed furnaces are operated on an acid slag, with a basicity factor (BF) smaller than 1. This BF can be defined by equation 2.7

$$BF = \frac{\%CaO + \%MgO}{\%SiO_2} \tag{2.7}$$

Some semi-closed furnaces might operate on BF>1, but these are less common and such operations are sometimes only temporarily undertaken to compensate for refractory linings being in poor condition, or if enhanced sulphur removing capacity by the slag is required.

ii. Closed furnace operation, usually utilises oxidative sintered pelletised feed (Outotec, 2011). This has been the technology most commonly employed in South Africa, with the majority of green and brown field expansions during the last decade making use of this process. Procedure steps usually include steps 1, 2, 3, 4, 5, 7, 8, 9 and 11, with or without 6. In all green field ferrochrome developments the pelletising and sintering (steps 2 and 3) sections were combined with closed furnaces. However, pelletising and sintering sections have also been constructed at plants where the pelletised feed is utilised by conventional semi-closed furnaces. These furnaces are usually operated on an acid slag (BF<1).

iii. Closed furnace operation with pre-reduced pelletised feed (Naiker, 2007; Botha, 2003). The process steps include steps 1, 2, 3, 4, 5, 7, 8, 9, 11. The pelletised feed differs substantially from the oxidative sintered type due to the fact that the pellets are pre-reduced and mostly fed hot, directly after pre-reduction, into the furnaces. The furnaces are closed and operate on a basic slag (BF>1). At present, two SA ferrochrome smelter plants use this process.

iv. DC arc furnace operation (Curr, 2009; Denton *et al.*, 2004). For this type of operation, the feed can consist exclusively of fine material. Currently three furnaces are in routine commercial operation for ferrochrome production in South Africa and typically utilise a basic slag regime. Process steps include 5, 7 (with a DC, instead of a submerged arc furnace), 8, 9 and 11.

2.3.3 Chromium chemicals production

During the production of Cr(VI) chemical, chromite ore is purposefully oxidised to Cr(VI) via the alkaline roasting process (Antony *et al.*, 2001). This is in contrast to the ferrochromium industry, where the production of low concentration Cr(VI) containing waste materials are an unintended by-product.

2.4 Chromium containing wastes in South Africa

The mining of chromite ore for ferrochrome, PGMs and refractory materials results in the generation of waste materials containing unrecovered chromite. The volumes of these waste materials are substantial, although no reliable estimate currently exists (probably millions of tons per year). Chromite is relatively inert (Gu & Wills, 1988) and the chromium in these waste exist almost exclusively as Cr(III).

According to Beukes *et al.* (2010), the main waste products of the ferrochromium industry are slag, as well as bag filter dusts and scrubber sludge. Of these, bag filter dust is the most hazardous, since it contains some Cr(VI) and is a fine dry material that is subject to wind dispersion if not contained properly.

Scrubber sludge is also a fine material, but since it originates from closed furnaces (Beukes *et al.*, 2010) it does not contain as much Cr(VI), nor is it subject to wind dispersion. By volume, slag is the most significant waste material produced by the ferrochromium industry. Beukes *et al.* (2010) estimated that approximately 5.3 million tons of slag was produced in South Africa in 2007 alone.

The Cr(VI) chemicals industry in South Africa fulfil a niche market and is not as volume driven industry. Waste quantities are therefore much less than that of the chromite ore and ferrochromium industry. However, the waste generated by this industry contains some Cr(VI) and has to be handled in an appropriate way. Certain plants associated with Cr(VI) chemicals production have been forced to close down in South Africa, due to occupational health reasons.

Chromium is found as trace minerals occurring in coal. Thus, all the coal combustion industries in South Africa (e.g. coal fired power stations, coal to liquid fuel production, boilers) also produce fly ash and clinker containing chromium (Nel *et al.*, 2011; Wagner & Hlatshwayo, 2005).

2.5 Carcinogenicity and toxicity of chromium

Only trivalent, Cr(III), and hexavalent chromium, Cr(VI), are important oxidation states in natural environments, because of the instability of the other oxidation states. Divalent chromium, Cr(II), is fairly unstable and is rapidly oxidised to Cr(III). Metallic chromium, Cr(0), is also oxidised to Cr(III) unless it is made passive by superficial oxidation (Beukes, 1999).

According to Yassi & Nieboer (1988), Lehmann (1932) was the first to suggest that there is a link between occupational exposure to chromates and increased risk of lung cancer. Extensive reviews on the carcinogenicity of chromium have been published by goverment bodies, international organisations, academic institutions and individuals. However only the hexavalent form of chromium, Cr(VI), is considered to be carcinogenic. The trivalent form, Cr(III), is considered significantly less toxic, presenting only non-carcinogenic adverse effects (Stern, 2010; Proctor *et al.*, 2002; Kim *et al.*, 2002; IARC, 1997; Yassi & Nieboer, 1988). In fact, Cr(III) is an important trace element in a balanced nutritional intake and is sometimes specifically included as a dietary supplement (Hininger *et al.*, 2007).

Due to the toxicity and carcinogenicity of Cr(VI), regulatory agencies have establised drinking water standards of 50 ppb for chromium (WHO, 2008; DWA, 1996). These standards are based in part on the presumed capability of human gastric juices to rapidly reduce Cr(VI) to non-toxic Cr(III). Pharmacokinetic studies suggest that the human gastrointestinal tract has the capacity to reduce Cr(VI) following ingestion of up to 1 liter of water containing 10 $mg \cdot \ell^{-1}$ (Finley *et al.*, 1997).

Thus considering the difference in toxicity of Cr(III) and Cr(VI), it is essential to determine the oxidation state of chromium if one wants to assess its potential health effects. The importance of processes responsible for the conversion of Cr(III) to Cr(VI), and vice versa, also becomes apparent.

2.6 Aqueous chemistry of chromium

2.6.1 Speciation

Chromium(III) forms strong complexes with hydroxides and chromium(III) hydroxo complexes are therefore expected to be the dominant species of Cr(III) in natural waters (Rai *et al.*, 1987). Rai *et al.* (1987) studied the hydroxo complexes, through the solubility of $Cr(OH)_3$ and reported that the dominant species are $Cr(OH)^{2+}$ at pH values from 3.8 to 6.3 (and possibly in the pH range from 2 to 6.3 (Sass & Rai, 1987)), $Cr(OH)_3$ at pH values from 6.3 to 11.5 and $Cr(OH)_4^-$ at pH values above 11.5. Mohan & Pittman (2006) showed that at the expected low chromium concentrations in the environment, polynuclear species, such as $Cr_2(OH)_2^{4+}$ and $Cr_3(OH)_4^{5+}$, do not contribute significantly to total soluble chromium. Amongst the ligands (OH^-, SO_4^{2-}, NO_3^- and CO_3^{2-}) evaluated at concentrations commonly found in the environmental samples, only OH^- was found to significantly complex Cr(III) (Saleh *et al.*, 1989).

The Eh–pH diagram (Pourbaix diagram) shown in Figure 2.6 provides a generalised depiction of the dominant aqueous species and redox stabilities of chromium (Mohan & Pittman, 2006). However it is valid only for conditions of chemical equilibrium.

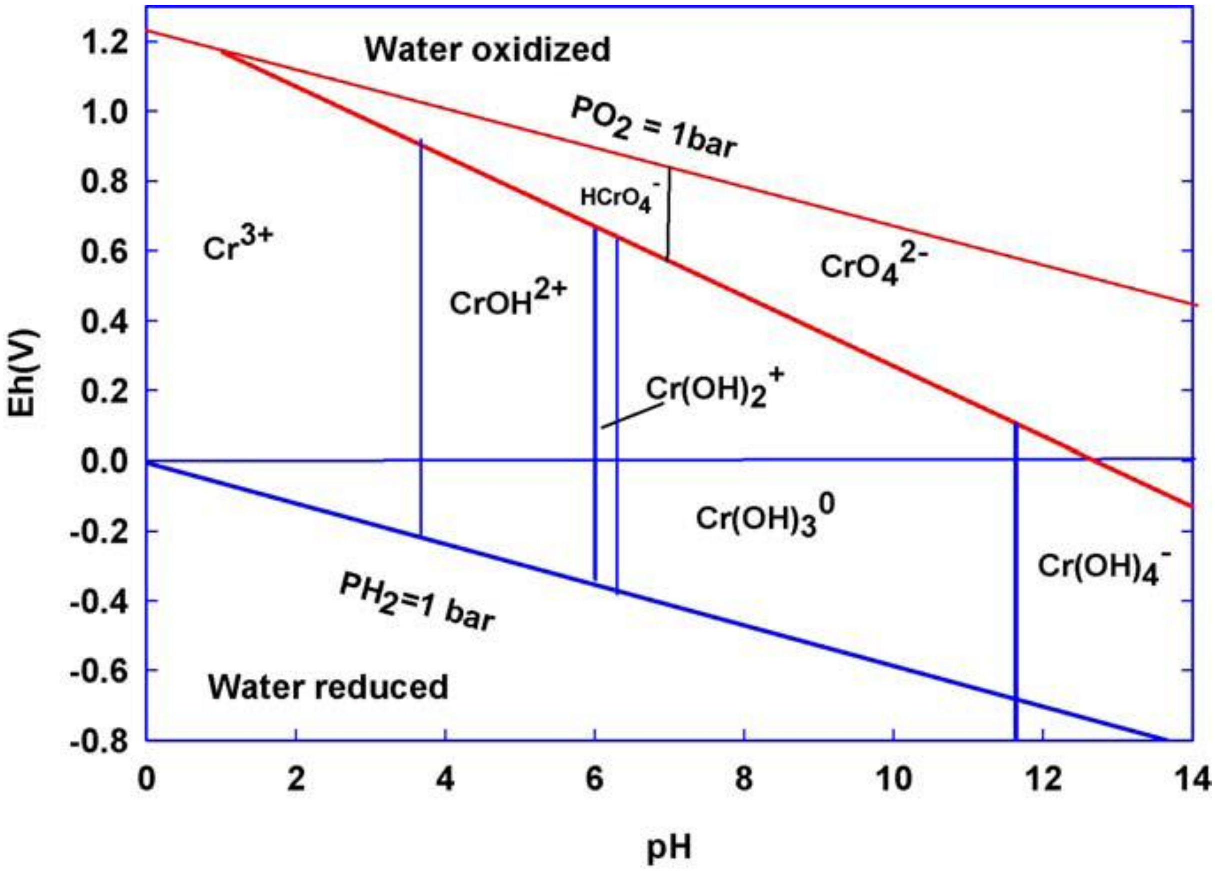


Figure 2.6: Eh−pH diagram for chromium where the grey depicts in solution and white the solid state (Mohan & Pittman, 2006)

The hydrolysis of Cr(VI) produces neutral and anionic species including $HCrO_4^-$ and CrO_4^{2-}. Cr(VI) also forms other species, such as $HCr_2O_7^-$ and $Cr_2O_7^{2-}$, however their formation in significant amounts requires Cr(VI) concentrations greater than 10^{-2} mol.dm^{-3} (Baes & Mesmer, 1976). At low pH and high chromium concentrations, $Cr_2O_7^{2-}$ predominates while at a pH greater than 6.5, Cr(IV) exists in the form of CrO_4^{2-} (Mohan & Pittman, 2006).

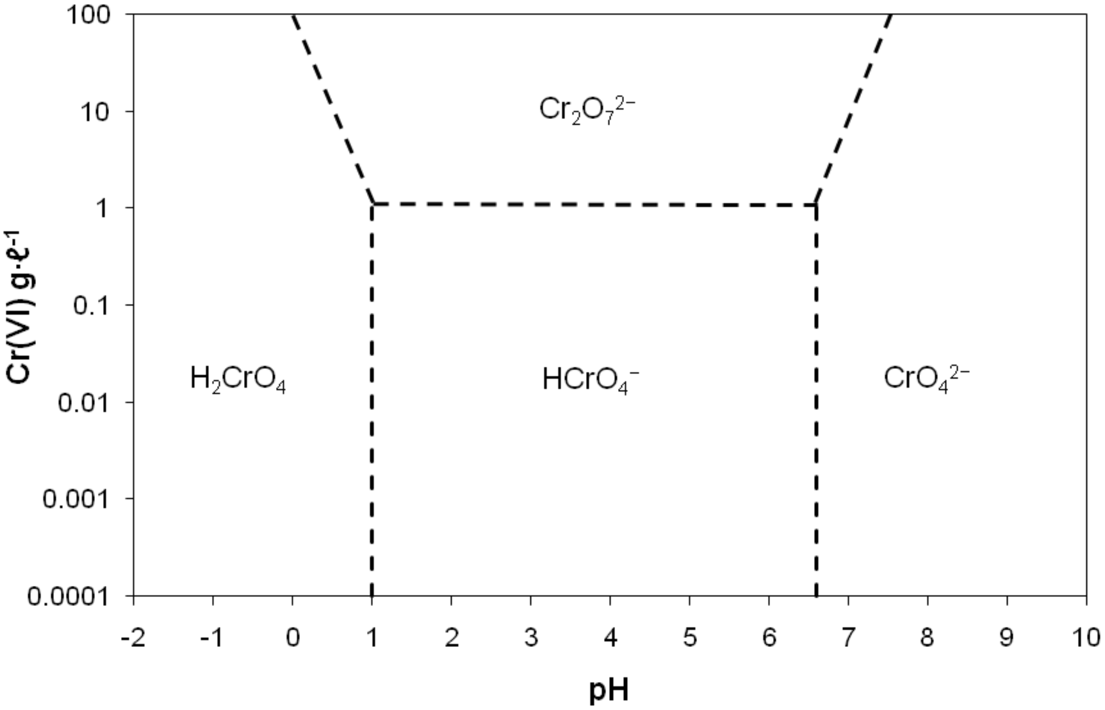


Figure 2.7: Relative *distribution of Cr(VI) species in water as a function of pH and Cr(VI) concentration* (Dionex, 1998)

Cr(VI) exists primarily as salts of chromic acid (H_2CrO_4), hydrogen chromate ion ($HCrO_4^-$) and chromate ion (CrO_4^{2-}), depending on the pH. H_2CrO_4 predominates at pHs below 1.0, $HCrO_4^-$ at pHs 1.0 − 6.0 and CrO_4^{2-} at pHs above 6.0 (Figure 2.7) (Dionex, 1998). Cr(VI) is strongly oxidizing, as shown by its stability only under high redox potentials (see Figure 2.6) and it reacts rapidly with numerous reducing agents.

2.6.2 Precipitation/Dissolution

The total aqueous chromium concentration in equilibrium with $Cr(OH)_3$(s) exhibits amphoteric behaviour in nature where it can behave both as an acid and as a base. Cr(III) is a Lewis acid and forms insoluble $Cr(OH)_3$ (Weng *et al.*, 1994; Bartlett, 1991). Rai *et al.* (1987) investigated the solubility of $Cr(OH)_3$. This was done by leaving mixtures for up to 134 days to reach equilibrium. Chromium concentration first decreased with increasing pH and then, at pH > 11, started increasing again (Figure 2.8). The solubility of $Cr(OH)_3$ also kept chromium concentrations below the drinking water limit of 50 ppb for total chromium (WHO, 2008; DWA, 1996) between pH of 6 and 11 . This pH range value is in correlation with the pH of most natural waters, thus Cr^{3+} will be immobilized in the water systems by precipitating as stable chromium(III)hydroxide (Beukes, 1999).

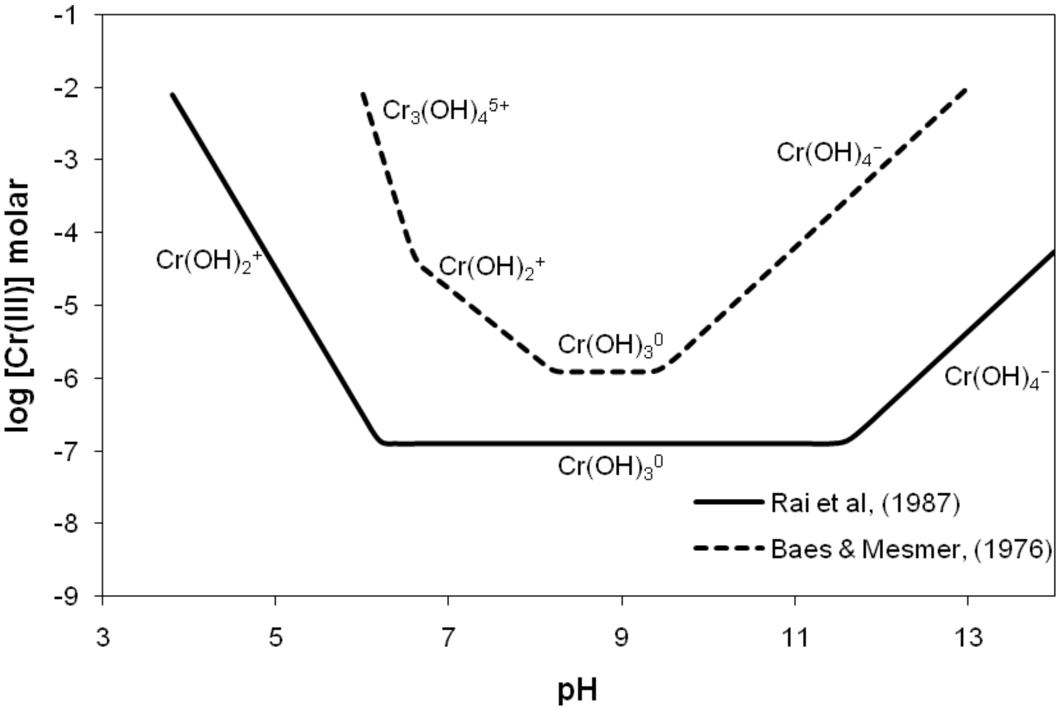


Figure 2.8: Aqueous solubilities of $Cr(OH)_3$ as a function of pH (Saleh *et al.*, 1989)

Figure 2.8 also shows that some soluble species of Cr(III), e.g. $Cr(OH)_4^-$ and $Cr_3(OH)_4^{5+}$, can exist if the Cr(III) concentration is high enough.

Unlike Cr(III) most Cr(VI) solids, except insoluble compound such as $BaCrO_4$, are expected to be relatively soluble under environmental conditions (Rai *et al.*, 1989).

2.6.3 Adsorption/Desorption

Under acidic to slightly alkaline conditions, in the absence of solubility−controlling solids, Cr(VI) aqueous concentrations will primarily be controlled by adsorption/desorption reactions. Mineral solids that have exposed inorganic hydroxyl groups on their surfaces will adsorb Cr(VI) (Rai *et al.*, 1989). As a result of protonation of the surface hydroxyl site and aqueous speciation of Cr(VI), adsorption increase on all of these solids, with decreasing pH.

Of all possible adsorbents (aluminium oxide, iron oxide, kaolinite and montmorillonite), iron oxides exhibit the strongest adsorptivity for CrO_4^{2-} (Rai *et al.*, 1989). An excess of phosphate in the equilibrating solution totally prevents adsorption of Cr(VI) by soils (Bartlett & Kimble, 1976). Cr(VI) adsorption can be described as a surface complexation reaction involving Cr(VI) species, such as $HCrO_4^-$ and CrO_4^{2-} and surface hydroxyl sites.

$$\text{Surface}-OH + H^+ + CrO_4^{2-} \rightleftharpoons \text{Surface}-OH_2^+-CrO_4^{2-} \qquad (2.8)$$

2.6.4 Cr(VI) compounds

Cr(VI) forms a variety of oxygen compounds, of which most have their origin out of Cr(VI)−oxide. These compounds include oxi−halogen compounds and chromyl compounds (CrO_2F_2), chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), trichromate ($Cr_3O_{10}^{2-}$), tetrachromate ($Cr_4O_{13}^{2-}$) and basic chromates. All of these compounds are strong oxidising agents, which show great differences in reactivity (Trotman-Dickenson, 1973). The main Cr(VI) complexes at neutral pH and concentration below 1 $g \cdot \ell^{-1}$ (Figure 2.7) in water exists as $HCrO_4^-$ and CrO_4^{2-} (Dionex, 1998; Palmer & Wittbrodt, 1991).

2.6.5 Cr(VI) reduction

2.6.5.1 Cr(VI) reduction by inorganic compounds

Numerous inorganic compounds can reduce Cr(VI). However, probably the most important to consider is the ferrous ion, i.e. Fe(II). The capacity of Fe(II) to reduce Cr(VI) is well known (Table 2.2). The ferrous ion is considered a natural occurring reducing agent of Cr(VI). Eary & Rai, (1989) proved that residual amounts of ferrous ion in weathering minerals such as hematite and biotite can act as reductants of Cr(VI) (Hug *et al.*, 1997). Fe(II) is also the most commonly used reducing agent for Cr(VI) in industrial applications in South Africa (Beukes *et al.*, 2012).

Table 2.2: Literature on the reduction of Cr(VI) by Fe(II) and Fe(III) (adapted from Beukes, 1999)

Reductant	pH−range	Reference
Aqua−iron(II) and tris−(1,10−phenanthroline)−iron(II)	~1.3 − ~1.9	Espenson & King, 1963
Iron(III) perchlorate reduced under N_2 atmosphere with amalgamated zinc	~1.0 − ~2.0	Espenson, 1970
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	7.1 – 9.1	Schroeder & Lee, 1975
$Fe(OH)_3$	7.0	James & Bartlett, 1983c
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	2.0 − ~12.0	Eary & Rai, 1988
Ferrous ions derived from Hematite and Biotite	3.0 − 12.0	Eary & Rai, 1989
$FeSO_4 \cdot 7H_2O$ in rainwater and hardwater	3.75 − 7.9	Saleh *et al.*, 1989
$Fe_2O_3 \cdot H_2O$, Fe_2O_3 and α-FeOOH	4.0 – 10.0	Rai *et al.*, 1989
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	4.5 – 11.0	Jacobs, 1992
$FeSO_4 \cdot 7H_2O$	2.5 – 11.0	Lin & Vesilind, 1995
$FeCl_2$	6.0 – 8.0	Fendorf & Li, 1996
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	2.0 – 7.2	Buerge & Hug, 1997
$FeSO_4 \cdot 7H_2O$	2.5 – 8.0	Sedlak & Chan, 1997

2.6.5.2 Cr(VI) reduction by organic compounds

It is well-known that most organic compounds can reduce Cr(VI) (Banks *et al.*, 2006; Wittbrodt & Palmer, 1995). Natural occurring organic reductants of Cr(VI), such as citric acid increased the ability of Cr(VI) to be removed by the soils (James & Bartlett, 1983a).

2.6.6 Cr(III) oxidation

2.6.6.1 Possible aqueous oxidation of Cr(III) by dissolved oxygen

Aqueous oxidation of Cr(III) by dissolved oxygen has been identified as a reaction that is most likely to occur in natural water systems such as oceans and lakes. Several attempts in studying this reaction have been carried out. However, the oxidation of Cr(III) by dissolved oxygen has been reported to be very slow.

Schroeder & Lee, (1975) observed that only 2−3% of a 2.3 x 10^{-6} mol·dm^{-3} Cr(III) solution, made up from natural lake water, had been oxidised to Cr(VI) by dissolved oxygen after 14 days. They also stated that the rate of this reaction is slow enough to warrant the participation of Cr(III) in other reactions before appreciable oxidation occurs.

Van der Weijden & Reith (1982), on the other hand, were unable to observe any Cr(VI) formation at room temperature even at extended exposure time of 42 days and higher temperatures. Eary & Rai (1987) also reported no oxidation of 1.9 x 10^{-5} mol·dm^{-3} Cr(III) solutions that had been saturated with dissolved oxygen at 27°C after as long as 24 days.

Saleh *et al.* (1989) observed that direct oxidation of Cr(III) in aqueous solutions at natural pH levels of 4–9 with dissolved oxygen could occur, but with exposure times of 128 days needed for the oxidation to take place and with half−lives ranging from 2 to 9 years.

Three likely reactions dissolved oxygen could have with Cr(III) compounds that have been identified are listed below:

$$4CrOH^{2+} + 3O_2 + 6H_2O \rightleftharpoons 4HCrO_4^{-} + 12H^{+} \qquad \text{(Acidic conditions)}$$

$$4Cr(OH)_3 + 3O_2 + \ \rightleftharpoons 4CrO_4^{2-} + 2H_2O + 8H^{+}$$

$$4Cr(OH)_4^{-} + 3O_2 + \ \rightleftharpoons 4CrO_4^{2-} + 6H_2O + 4H^{+} \qquad \text{(Akaline conditions)}$$

2.6.6.2 Oxidation by manganese oxides

Manganese oxides are considered as the only naturally occurring oxidant of Cr(III), particularly in soil environments (Eary & Rai, 1987). Schroeder & Lee (1975) reported that a significant fraction of Cr(III) in natural lake water had been converted to Cr(VI) when they had added an unspecified form of MnO_2(s).

The oxidation of Cr(III) by manganese oxides is controlled by the surface characteristics of the oxides and the availability of the Cr(III) to the surface. Buildup of Mn(II), attracted by the negative charge on the oxide surface, leads to slower oxidation of Cr(III) since the adsorption of reduced Mn(II) results in a positively charged oxide surface that repels ionic Cr(III) (Bartlett, 1991).

Oxidation by different types of manganeses oxides have been studied. These include pyrolusite (β−MnO_2) (Saleh *et al.*, 1989; Eary & Rai, 1987), birnessite (δ−MnO_2) (Nico & Zasoski, 2000; Fendorf & Zasoski, 1992), buserite ($Na_4Mn_{14}O_{27}\cdot 9H_2O$) (Silvester *et al.*, 1995), manganite (γ−MnOOH) (Johnson & Xyla, 1991), hausmanite ($Mn^{2+}Mn^{3+}{}_2O_4$), todorokite and lithiophorite (Kim *et al.*, 2002)

The equations for these complexes are shown below:

$$Cr(OH)^{2+} + 1.5(\beta{-}MnO_2)(s) \rightleftharpoons HCrO_4^- + 1.5Mn^{2+} \qquad (pH\ 3.0 – 4.7)$$

$$Cr(OH)^{2+} + 3(\beta{-}MnO_2)(s) + 3H_2O \rightleftharpoons HCrO_4^- + 3MnOOH(s) + 3H^+ \qquad (pH > 4.7)$$

$$Cr^{3+} + 1.5(\delta{-}MnO_2)(s) + H_2O \rightleftharpoons HCrO_4^- + 1.5Mn^{2+} + H^+ \qquad (pH\ 4.7 - 5.5)$$

$$Cr(OH)^{2+} + 3(\gamma{-}MnOOH)(s) \rightleftharpoons HCrO_4^- + 3Mn^{2+} + 3OH^- \qquad (pH > 4.7)$$

2.6.6.3 Cr(III) oxidation by the advanced oxidation process

Rodman *et al.* (2006) investigated the conversion of Cr(III) propionate to Cr(VI) by the advanced oxidation process (AOP), utilising hydrogen peroxide (H_2O_2), ozone (O_3) and ultraviolet (UV) irradiation, as a means of pre−treatment for an analytical technique. During this investigation the pH was varied from 0.2 to 10.0. At pH > 4, the conversion of Cr(III) propionate to chromate/dichromate was found to be > 90%. At pH < 4, no Cr(VI) was detected in the AOP-treated samples. During the AOP strong oxidising hydroxyl radicals ($OH^\bullet$) are generated (Beltrán, 2003). In addition to the formation of hydroxyl radicals from the UV irradiation of H_2O_2/O_3, these reactions yield several other reactive species such as hydroperoxyl or peroxyl radicals.

Rao *et al.*, (2002) studied the oxidation kinetics of Cr(III) with hydrogen peroxide in alkaline solutions and found that the overall stoichiometry of the reaction between Cr(III) and hydrogen peroxide was 2:3. The rate of oxidation decreases as the concentration of hydrogen peroxide was increased, due to the release of H^+ that lowers the pH – lower pH results in slower kinetics as discussed in the previous paragraph. Equation 2.9 shows that Cr(III) to Cr(VI) conversion makes the solution more acidic (Rodman *et al.*, 2006).

$$2Cr^{3+} + 3H_2O_2 + H_2O \rightleftharpoons Cr_2O_7^{2-} + 8H^+ \qquad (2.9)$$

Adams *et al.*, (1968) studied the reduction of Cr(VI) by hydrogen peroxide in acidic conditions and proposed equation 2.10, which explains why Cr(VI) wasn’t detected at pH < 4 by Rodman *et al.* (2006).

$$2HCrO_4^- + 3H_2O_2 + 8H^+ \rightleftharpoons 2Cr^{3+} + 3O_2 + 8H_2O \qquad (2.10)$$

2.7 Ozone

2.7.1 Characteristics of ozone

Ozone is made up of three oxygen molecules. It is a colourless gas at room temperature and has a characteristic pungent odour, readily detectable by most people at concentrations as low as 0.01 ppm. It is often occurs at elevated levels in the troposphere after electrical storms and around electrical discharges (Airmet, 2011).

Ozone occurs naturally in the stratosphere (the layer occurring above the troposphere) and it prevents damaging ultraviolet light from reaching the earth’s surface. It is a toxic compound and may be harmful to respiratory systems of animals, but without ozone in the upper atmosphere, life on earth would cease to exist (Beltrán, 2003).

Ozone has a half-life in the atmosphere of 12 hours and is more stable in air than in water. In aqueous solutions, ozone is relatively unstable, having a half-life of only minutes, depending upon the solution pH, temperature and the presence of ozone scavengers. If not consumed in a reaction ozone will decay into its original form of O_2 (Hassan & Hawkyard, 2002; Beltrán, 2003; Sotelo *et al.*, 1987 ;Gurol & Singer, 1982).

2.7.2 General chemistry of ozone

Ozone is a naturally occurring allotrope of oxygen. The reaction of ozone production is indicated in Equation 2.11 and 2.12.

$$O_2 + \text{Energy} \rightarrow O^{\bullet} + O^{\bullet} \qquad (2.11)$$

$$O^{\bullet} + O_2 \rightarrow O_3 \qquad (2.12)$$

Two general accepted deterministic models for ozone decomposition in “pure water” have been developed in the early 1980s, both based on the first model of Weiss in 1935. The model of Staehelin, Hoigné and Bühler, known as the SHB model, was experimentally developed for acidic to neutral pH, while Tomiyasu, Fukutomi and Gordon (TFG) developed their model at high pH values. The initiation decomposition reactions (Equation 2.10, 2.11 and 2.12) are shown below (Beltrán, 2003).

$$O_3 + 2H^+ + 2e^- \rightarrow H_2O + O_2 + \text{energy (Acidic conditions)} \qquad (2.13)$$

$$O_3 + H_2O + e^- \rightarrow 2OH^- + O_2 \text{ (Neutral conditions)} \qquad (2.14)$$

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \text{ (Akaline conditions)} \qquad (2.15)$$

The thermodynamic free energy (Gibbs energy) of these reaction are very high ($\Delta G \approx -400$ kJ·mol^{-1} for equation 2.13), hence ozone is a strong oxidant (Lide, 2005; Glaze, 1987). During decomposition, the single highly reactive oxygen atom combines with materials present and oxidses them. However, once ozone diffuses into solution, it decomposes spontaneously into $OH^{\bullet}$ radicals, which is one of the strongest oxidants in water. Therefore, in water, ozone can decompose in two ways, either by direct oxidation to oxygen or by decompostion via hydroxyl radicals (Rosenfeldt *et al.*, 2006; Glaze, 1987). Decomposition can be initiated by hydroxide ions, formate ions, or a variety of other species. A single initiation step can cause the decompostion of hundreds of molecules of ozone before the chain is terminated (Beltrán, 2003).

In Table 2.3 the standard reduction potential of some strong oxidants are given (Rodman *et al.*, 2006). The standard reduction potential of hydroxyl radicals ($OH^{\bullet}$) is much higher than that of three well known oxidants; ozone, hydrogen peroxide, or chlorine. There are also reactions yielding several other reactive species such as hydroperoxyl or peroxyl radicals (Rodman *et al.*, 2006). In general, the activation of ozone produces several radicals, all of which help oxidise compounds.

Table 2.3: Comparison of standard reduction potentials of different oxidants used in water treatment (Rodman *et al.*, 2006; Beltrán, 2003)

Oxidizing Agent	Chemical formula	Standard potential (V)
Hydroxyl radical	$OH^{\bullet}$	2.80
Ozone	O_3	2.07
Hydroperoxide radical	$HO_2^{\bullet}$	1.70
Hydrogen peroxide	H_2O_2	1.78
Chlorine	Cl_2	1.35

The way ozone reacts in water is dependent on a number of variables. The process of direct oxidation of ozone occurs rather slowly but the concentration of aqueous ozone is relatively high. Conditions of low pH favour the direct oxidation reactions involving ozone and oxidation occurs predominantly through ozone. Conditions that favour the auto-decomposition of ozone, include high pH, exposure to UV, addition of hydrogen peroxide, presence of inorganic radicals and high concentrations of hydroxide ions (Beltrán, 2003).

2.7.3 Ozone generation

Ozone can be produced naturally, by means of the sun's ultraviolet rays or during electrical storms. Anthropogenic produced ozone is generated as required and used immediately after production, due to its instability and relative short half-life (Par 2.7.1). Anthropogenic production of ozone can be done by

- Ultraviolet (UV) ozone generation
- Electrolytic generation
- Radiochemical generation
- Corona discharge (CD) generation

The most commonly used generation is UV or CD methods. Both technologies have advantages and disadvantages. However, CD is generally accepted as the preferred technology for potable water treatment. UV ozone generation offers initial economic benefits in non-potable water treatment, such as the spa industry (Rajagopaul *et al.*, 2008). Because the corona discharge method has a more constant ozone production rate and a higher ozone stability factor than UV, it was determined to be the best suited for this study.

2.7.4 Mass transfer of ozone into water

Rajagopaul *et al.* (2008) state, that because ozone is only slightly soluble in water at the partial pressure at which it is generated and applied, contacting ozone with water involves bringing bubbles of ozone-containing oxygen or air into contact with water. This mass transfer of ozone from the gaseous bubbles occurs across the gas/liquid interface into the water and depends on a number of factors which are themselves affected by design and operation of the systems. These factors include:

- the miscibility with water and ozone demand of substances to be ozonated
- concentration of ozone in the gas
- method and contact times
- bubble size,
- pressure and temperature
- presence of interfering substances

In designing an ozone contacting system, there should be maximum solubility of ozone into the water, with minimum off-gas production (Rajagopaul *et al.*, 2008). The quantity of ozone dissolved will depend on the temperature of the water (see Table 2.4) and the pressure at which the gas is applied (Degrémont, 2007). Ozone is more soluble in water than oxygen but less soluble than chlorine.

Table 2.4: Theoretical ozone residuals indicate that solubility of ozone increases with an increase in concentration and a decrease in water temperature treatment at 1 atm (Morrison, 2009)

Ozone concentration (%w/w)	Ozone solubility (mg·ℓ$^{-1}$)					
	at 5°C	at 10°C	at 15°C	at 20°C	at 25°C	at 30°C
0.001	0.007	0.007	0.006	0.005	0.004	0.003
0.1	0.74	0.65	0.55	0.42	0.35	0.27
1	7.39	6.50	5.60	4.29	3.53	2.70
1.5	11.09	9.75	8.40	6.43	5.29	4.04
3	22.18	19.50	16.79	12.86	10.58	8.09

2.7.5 The uses of ozone into water

Ozonation is used extensively in drinking water treatment plants (Audenaert *et al.*, 2010; Beltrán, 2003; Camel & Bermond, 1998). While O_3 is not yet widely used in the South African water treatment sector, its popularity for this use is gaining momentum. A case study revealed that there are several waterworks in South Africa where O_3 is used successfully as a pre-oxidant for the treatment of raw waters (Rajagopaul et al., 2008).

In South Africa, Midvaal Water company in Stilfontein has been using ozone since the late 1980s to treat 320 Mℓ·day^{-1} of raw water. The plant has a capacity to produce 24 kg·h^{-1} of ozone. Pre-ozonation is used at Midvaal in order to reduce problems associated with high concentrations of iron and manganese, as well as reducing taste and odour causing compounds (Rajagopaul *et al.*, 2008). Wiggings Waterworks in Cato Manor has the capacity to produce 90 kg·h^{-1} of ozone for 350 Mℓ·day^{-1} of raw water. The primary reason for using pre-ozonation is for the oxidation of iron and manganese, reduction of trihalomethane precursors and taste and odour compounds (Rajagopaul *et al.*, 2008). These are but two of the larger water treatment plants in South Africa that utilise ozone for potable water treatment.

The use of ozone or ozone in conjunctions with other compounds and catalysts (e.g. advance oxidation processes) to treat industrial waste waters and effluents is well documented (Nawrocki & Kasprzyk-Hordern, 2010; Coca *et al.*, 2007; Selcuk, 2005; Gogate & Pandit, 2004; Beltrán, 2003).

2.8 Conclusions

An investigation into the formation of Cr(VI) via aqueous O_3 oxidation of non-Cr(VI) containing materials, with relevance to water treatment, has not yet been conducted. Such a study is of particular interest within the local context, considering South Africa's considerable chromium ore reserves, the associated industries and the wastes generated by these industries.

The literature also revealed that very little work has been done on the possible use of ozonation as a process to recover valuable Cr-units from waste materials.

Knowledge is of no value unless you put it into practice.

Anton Chekhov

CHAPTER 3

EXPERIMENTAL

In this chapter...

The reagents and case study materials used are described (Par 3.1). There after the apparatus, experimental methods employed and analytical procedures used are discussed (Par 3.2 and 3.3).

3.1 Reagents

3.1.1 General chemicals

All chemicals used were analytical grade (AR) reagents, obtained from the different suppliers and used without any further purification. Standard Cr(VI) solutions were prepared from a 1 000 $mg \cdot \ell^{-1}$ aqueous chromate analytical solution (Spectrascan, distributed by Teknolab AB, Sweden) and used for the calibration and verification of the analytical techniques employed. 250 $mol \cdot dm^{-1}$ ammonium sulphate and 100 $mol \cdot dm^{-1}$ ammonium hydroxide was combined for the preparation of the eluent and 2 $mol \cdot dm^{-1}$ s–diphenyl carbazide (FLUKA) were used during Cr(VI) determination. Sodium peroxide (Merck), sodium carbonate (Merck) and nitric acid (Merck) was used for the chemical analyse of the Cr–containing materials. Solutions of sodium hydroxide (Merck) and perchloric acid (Merck) were used to adjust the pH of aqueous solutions. Ultra–pure water (resistivity, 18.2 $M\Omega \cdot cm^{-1}$), produced by a Milli–Q water purification system, was used for all procedures requiring water. Afrox compressed medical grade oxygen (99.5% minimum O_2, with remainder consisting of N_2, Ar, CO_2, CO and H_2O) was used as feed gas for the generation of ozone.

3.1.2 Samples

The Cr–containing samples (slag and UG2) used in this investigation were received from a South African ferrochromium producer. The slag originated from one of the smelters operated by this ferrochromium producer, while the UG2 ore was used as a feed material to this smelter. These sample materials therefore are representative of actual materials used and generated in the industry. This enhanced the practical relevance of this study.

3.2 Apparatus and measurement methods

3.2.1 Sample preparation

Since the above–mentioned Cr–containing case study materials, i.e. UG2 ore and ferrochrome slag, were relatively coarse, the materials were pulverized. This facilitated the suspension of these solids in the aqueous medium via agitation. A Siebtechnik pulveriser, commonly used to pulverise solid samples (Figure 3.1a) prior to chemical analysis, was used to conduct all pulverising. All parts of the pulveriser, which made contact with the actual sample material, were made of tungsten carbide (Figure 3.1b). This prevented possible iron contamination of the pulverised samples. It is well–known that metallic iron particles can reduce Cr(VI) to Cr(III) (Par. 2.6.5.1). The slag and UG2 were dried at 40ºC for 1 day and then cooled in airtight containers to avoid possible water absorption and then pulverized to a diameter of ~0.5 mm. Pulverising time was kept as short as possible (20 s for the slag and 25 s for the UG2 ore) to reduce the possible formation of Cr(VI) during pulverisation (Glastonbury, et al., 2010; Beukes & Guest, 2001). The samples was stored in these containers and only removed prior to pulverising experiments.

Figure 3.1a: Siebtechnik pulverizer

Figure 3.1b: Tungsten carbide bowl

3.2.2 pH measurements

The pH of all solutions was measured using a Hanna Instrument (HI) 2211 pH/ORP meter, fitted with a HI 1131B pH electrode and a HI 7662 temperature probe. This pH meter was calibrated daily prior to use with standard Merck buffer solutions (pH 4.0, 7.0 and 10.1).

3.2.3 Particle size analyses

A Malvern Mastersizer 2000 (Figure 3.2) was used to determine the particle size distribution of the pulverised samples (Etxebarria *et al.*, 2005). A diluted suspension of pulverised Cr–containing material was ultra–sonicated for 1 min prior to the particle size measurement, in order to disperse the individual particles and to prevent the use of a chemical dispersant.

Figure 3.2: Malvern laser particle size analyser “Mastersizer 2000”

3.2.4 Scanning electron microscope (SEM)

This instrument is a type of electron microscope that visualise images of sample by scanning it with a high–energy beam of electrons in a raster scan pattern as showed in Figure 3.3. This permits the observation of materials in macro and submicron ranges, due to the very narrow electron beam, the SEM has a large depth of field yielding a characteristic three–dimensional appearance useful for understanding the surface structure of samples. The SEM can produce very high–resolution images of a sample surface (topography) revealing details less than 1 nm in size (0.001 microns) (Rack, 2011).

When SEM is used in conjunction with energy dispersive X–ray spectroscopy (EDS) the analyst can perform elemental analysis or surface chemical characterization on microscopic sections of a sample. EDS analyses X–rays are emitted by the sample in response to being bombarded with charged particles. X–rays are generated as a result of the ejection of an inner level electron (low energy) from the sample, by an energetic electron from an electron column. The ejected electron is replaced by an electron from a higher energy shell. The difference in energy is released, as it moves from a high energy shell to a low energy shell, in the form of X–rays. Each element has its own unique atomic structure with many energy levels and therefore many potential vacancy–filling mechanisms. From this it follows that each element will emit a different pattern of X–rays (Dunlap & Adaskaveg, 2011).

Scanning electron microscopy with energy dispersive spectrometry (SEM–EDS) was used to detect potential surface chemical compositional changes that occurred as a result of ozonation of the Cr–containing materials. A Zeiss MA 15 SEM incorporating a Bruker AXS XFlash® 5010 Detector x–ray EDS system operating with a 20 kV electron beam and a working distance of 17.4 mm was used.

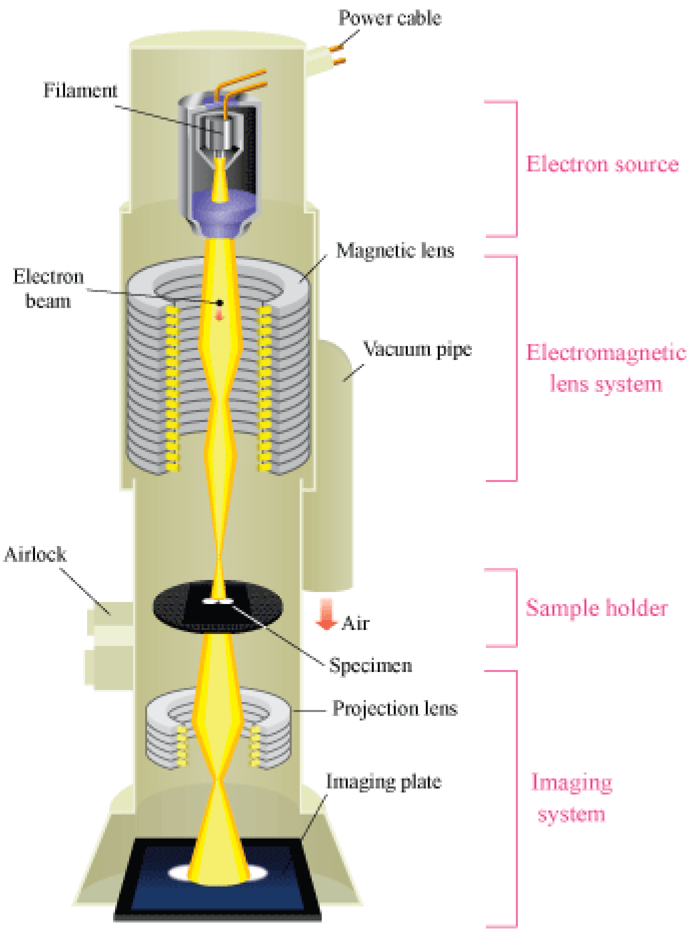


Figure 3.3: Schematic representation of a SEM

3.2.5 Chemical analyses

Inductively coupled plasma optical emission spectrometry (ICP–OES), is an analytical technique that is used for the detection of trace metals. The ICP–OES is composed of two parts: the inductively coupled plasma (ICP) and the optical emission spectrometer (OES). The ICP produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample (PerkinElmer, 2004).

A peristaltic pump delivers an aqueous sample into a nebuliser where it is atomized and introduced directly inside the plasma flame. The sample immediately collides with the electrons and other charged ions in the plasma and is broken down into charged ions. The various molecules break up into their respective atoms which then lose electrons and recombine repeatedly in the plasma, giving off the characteristic wavelengths of the elements involved (PerkinElmer, 2004).

Transfer lenses are used to focus the emitted light on a diffraction grating where it is separated into its component radiation in the optical spectrometer. The light intensity is then measured with a photomultiplier tube at the specific wavelength for each element line involved. The intensity of each line is then compared to previous measured intensities of known concentrations of the element and its concentration is then computed by extrapolation along the calibration line (PerkinElmer, 2004).

A Spectro Ciros Vision ICP–OES was also used to characterize the chemical composition of the Cr–containing materials used in this case study. This method is applicable to all types of chrome containing materials within this study. The sample solution was obtained by fusing the sample with 2 g of sodium peroxide and 0.5 g sodium carbonate in a zirconium crucible until a complete melt was achieved. The mixture was then cooled to room temperature and leached by transferring the mixture to a 500 mℓ beaker with 80 mℓ Milli–Q water and 30 mℓ nitric acid. The solution was then diluted in a 200 mℓ volumetric flask that was brought to volume by Milli–Q water. Finally the solution was analysed by using the ICP–OES.

3.2.6 Ozone generation

Ozone in the laboratory was prepared with a Sanders C100 100 $\text{mg}\cdot\text{h}^{-1}$ certizon ozone generator (Figure 3.4). This is a corona discharge type of ozone generator. They are typically cost–effective and do not require an oxygen source other than the ambient air to produce ozone concentrations of 3 – 6%. Fluctuations in ambient air, due to weather or other environmental conditions, cause variability in ozone production. However, they also produce nitrogen oxides (NOx) as a by–product. NOx can further be oxidised to nitric acid, especially in a moist atmosphere. By using medical grade oxygen as a feed gas increased ozone production was achieved, while the NOx and nitric acid formation was prevented (Hahn, 1997). This ozone generator also has the ability to increase or decrease it resistance, which influence the production of ozone.

Figure 3.4: Sanders ozoniser, model Certizon C100

A constant flow of 210 mℓ·min^{-1} O_2 through the ozone generator was maintained during all experiments, including blank experiments. An Agilent Flow Tracker Series 1000 was used to verify the O_2 flow. The maximum gas concentration of O_3 that could be achieved with this instrument was 0.0072 mg·mℓ$^{-1}$ (approximately 90.1 mg·h^{-1}) at the above–mentioned flow rate. The gaseous O_3 concentration was determined with UV–visible spectrophotometry (Par. 3.3.7). This gaseous O_3 concentration was maintained during all experiments, except when explicitly indicated otherwise.

3.2.7 UV/visible spectra

The gaseous O_3 concentration was determined with UV–visible spectrophotometry as described by McElroy *et al.* (1997) on a Cary 50 Conc UV–visible spectrophotometer from Varian. The preparation and decomposition of ozone as function of time was done in a 1 cm^3 quartz optical cell. The analytical wavelength of 255 nm was chosen for O_3 (Rademeyer, 2006). The concentration for O_3 is dependent on the flow of the oxygen gas feed.

3.2.8 Cr(VI) analysis

The Cr(VI) concentration of aliquots (see Par. 3.4 for details) were determined with a Dionex ICS 3000 (Figure 3.5). All preparation was done according to the Dionex application update144 (Dionex, 2003) and the procedure published by Thomas *et al.* (2002). 250 mol·dm^{-1} ammonium sulphate was used as an eluent and 2 mol·dm^{-1} s–diphenyl carbazide (DPC) solution for post column coloration. The DPC was stored in an amber bottle, in order to minimise the possible photochemical reaction within the bottle. The flow rates of the eluent and colorant were 1.0 mℓ·min^{-1} and 2.0 mℓ·min^{-1} respectively. With this technique, a quantification limit of 0.06 ppb could be achieved (Thomas *et al.*, 2002). Results were expressed by indicating the mean Cr(VI) concentration obtained under specific conditions, as well as the standard deviation resulting from the repetitions for a particular monovariance experiment.

Figure 3.5: Dionex Ion Chromatography System (ICS) 3000

3.3 Experimental setup

A predetermined mass of the pulverised Cr–containing material was suspended for a selected ozonation contact time in 100 mℓ pH adjusted water in a 250 mℓ sealed glass beaker, with a bubble diffuser through which the O_3 rich O_2 gas was fed. A magnetic stirrer (18 mm x 2.5 mm dimensions, rotating at 750 rpm) was used to keep the particles in suspension. A circulation pump fed water from a temperature controlled water bath to a water jacket in which the reaction vessel (glass beaker) was housed. This simple experimental setup allowed monovariance investigation of parameters (e.g. pH, temperature, contact time, etc.). After each specific experiment was completed the gas supply was stopped, the beaker removed from the experimental setup and the water was filtered off by milli–pore filtering (0.45 µm). The aliquot was then analysed for Cr(VI) (Par. 3.3.8) as soon as possible after filtering. All monovariance reaction conditions investigated were repeated a minimum of three times, to ensure repeatability. Blank experiments in which all the reaction conditions were kept identical (including solid loading and O_2 flow), except that the O_3 generator was switched off, were also conducted. These blank experimental results were indicated with the word “blank” in all relevant figures in chapter 4 and 5.

3.4 Managing statistical data

When a small number of observations are made, the value of the standard deviation *s* does not by itself give a measure of how close the sample mean $\overline{x}$ might be to the true mean. In order to make sure that a few outliers did not influence statistical calculated values, such as means and standard deviations, the Q–test was performed (Equation 3.1).

$$Q = \frac{|x_q - x_n|}{w} \qquad (3.1)$$

The absolute value of the difference between the questionable value (x_q) and its nearest value (x_n) is divided by the difference between the largest value and smallest value (w) of the entire data set to give the estimated Q–value (Mendham *et al.*, 2000). This Q–value is then compared to a critical value Q_{crit} found in Table 3.1. If the

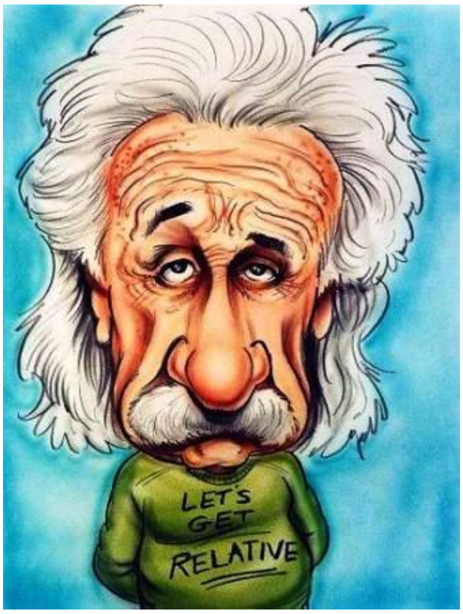
Q–value calculated is larger than the Q_{crit}, then the value is rejected as an outlier. Less than 10% of all data points were eliminated in this.

Table 3.1: Critical values of Q_{crit} *(P=0.05.)* (Mendham *et al.*, 2000)

Sample Size	Critical value
3	0.972
4	0.831
5	0.717
6	0.621
7	0.570
8	0.524
9	0.492

We can't solve problems by using the same kind of thinking
we used when we created them.

Albert Einstein



CHAPTER 4

RESULTS: Cr(VI) formation during ozonation of Cr–containing materials in aqueous suspension – implications for water treatment

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In this chapter...

The chemical compositions of the Cr–containing case study materials utilised in this study are indicated in Par. 4.1 and the possible oxidation of non–Cr(VI) Cr–containing materials are explored as a function of important process parameters, such as pH (Par. 4.2), contact time (Par. 4.3), temperature (Par. 4.4), solid loading (Par. 4.5) and ozone concentration (Par. 4.6). The possible mechanism of chromium liberation from the case study materials are also discussed (Par. 4.7). Since ozone decomposition plays an important role during ozonation, limited O_3 *decomposition data is also presented (Par. 4.8). Finally, some conclusions are drawn from the results (Par. 4.9).*

4.1 Case study material characterisation

Since it is expected that materials will react differently to ozonation, the case study materials (Par. 3.3.2) utilised in this study were physically and chemically characterised. The characteristics investigated included surface and surface chemical analysis (Par. 3.3.4), chemical composition (Par. 3.3.5) and particle size distribution after pulverising (Par. 3.3.3). The “as received” case study materials were too coarse to suspend in water with agitation, thus the materials were pulverised (Par. 3.3.1).

4.1.1 SEM–EDS characterisation

SEM micrographs (Par. 3.3.4) of the pulverised slag and UG2 ore are presented in Figure 4.1 and 4.2, respectively. It is evident from Figure 4.1 that the slag consisted of larger and smaller particles. The distributions of elements within the particles were also not homogeneous. This can be observed by the small white fragments in the area numbered 1 on Figure 4.1. The composition of these fragments were approximately 90% iron and 10% chromium, while most of the slag was made up of a fusion of magnesium oxide (MgO), aluminium oxide (Al_2O_3), silicon oxide (SiO_2) and calcium oxide (CaO). Some unreacted chromium ore particles were also present within the slag as observed in the area numbered 2 on Figure 4.1.

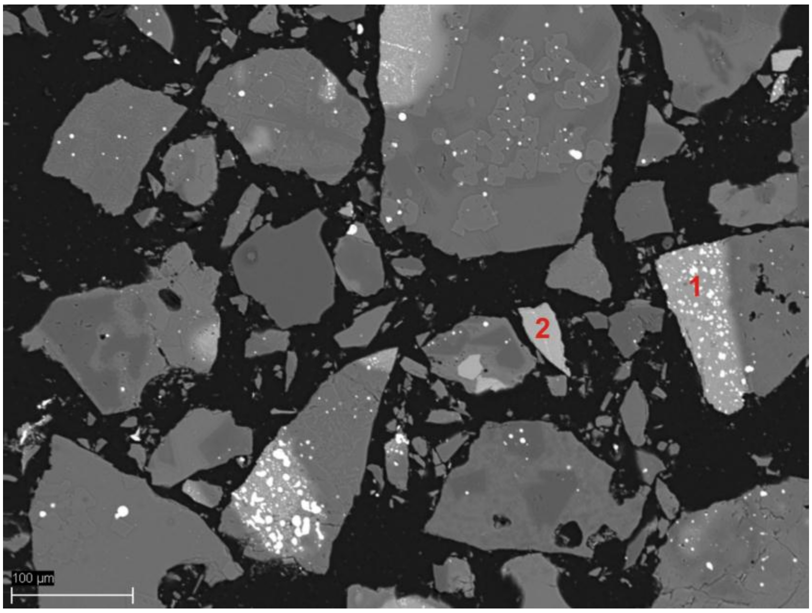


Figure 4.1: SEM micrographs of a polished section of the ferrochromium slag at 300 times magnification

The pulverised UG2 ore (Figure 4.2) was found to be more homogenous, in particle size and chemical distribution, than the slag. The size distribution of the particles seemed to be narrower (close together) than that of the pulverised slag, but this would be confirmed later with particle size analysis (Par. 4.1.3). The UG2 consisted of two types of particles, i.e. ore particles containing approximately 41% Cr_2O_3 (Figure 4.2, Area 1) and gauge materials (Figure 4.2, Area 2).

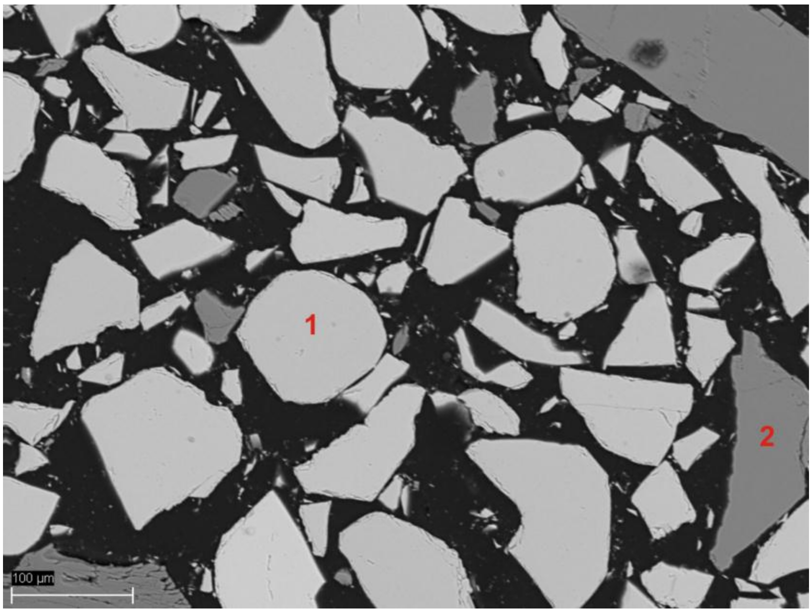


Figure 4.2: SEM micrographs of polished section of the UG2 ore at 300 times magnification

SEM–EDS surface chemical analysis (Par. 3.3.4) of the polished sections of the two case study materials are presented in Table 4.1. These analyses must not be confused with total chemical composition of the material, since surface chemical analysis only provide information on the chemical composition of the outer surface (100 µm) of the particles (Lide, 2005).

Table 4.1: SEM–EDS surface chemical elemental analysis (wt%) of the two case study materials

	Cr	**Fe**	**Al**	**Si**	**O**	**Mg**	**Other**
Slag	6.258	3.062	10.54	8.464	30.59	8.486	32.60
UG2	18.24	15.06	4.770	2.561	25.41	4.929	29.03

4.1.2 Chemical characterisation

The total chemical analysis (ICP–OES, Par. 3.3.5) of the slag and UG2 ore are presented in Table 4.2. The slag contained much less chromium than the UG2 ore, but this was expected since the slag is a by–product from the ferrochrome production process. The composition of this particular ferrochromium slag is not necessarily representative of all ferrochromium slags produced in industry, since different compositions can be expected for different ferrochrome production processes

(Beukes *et al.*, 2010). The chemical composition of the UG2 ore was very similar to that reported in literature (Cramer *et al.*, 2004; Riekkola–Vanhanen, 1999; Curr *et al.*, 1998).

Table 4.2: Chemical composition (%) of the ferrochrome slag and UG2 chromite ore used as case study

	Cr_2O_3	FeO	SiO_2	Al_2O_3	CaO	MgO	Other
Slag	11.44	6.030	26.40	25.61	7.690	17.70	5.130
UG2	40.90	26.48	3.780	15.92	0.300	10.58	2.040

4.1.3 Particle size distribution

The mean particle size (Par. 3.3.3) distribution of the pulverised slag and UG2 samples are shown in Figure 4.3.

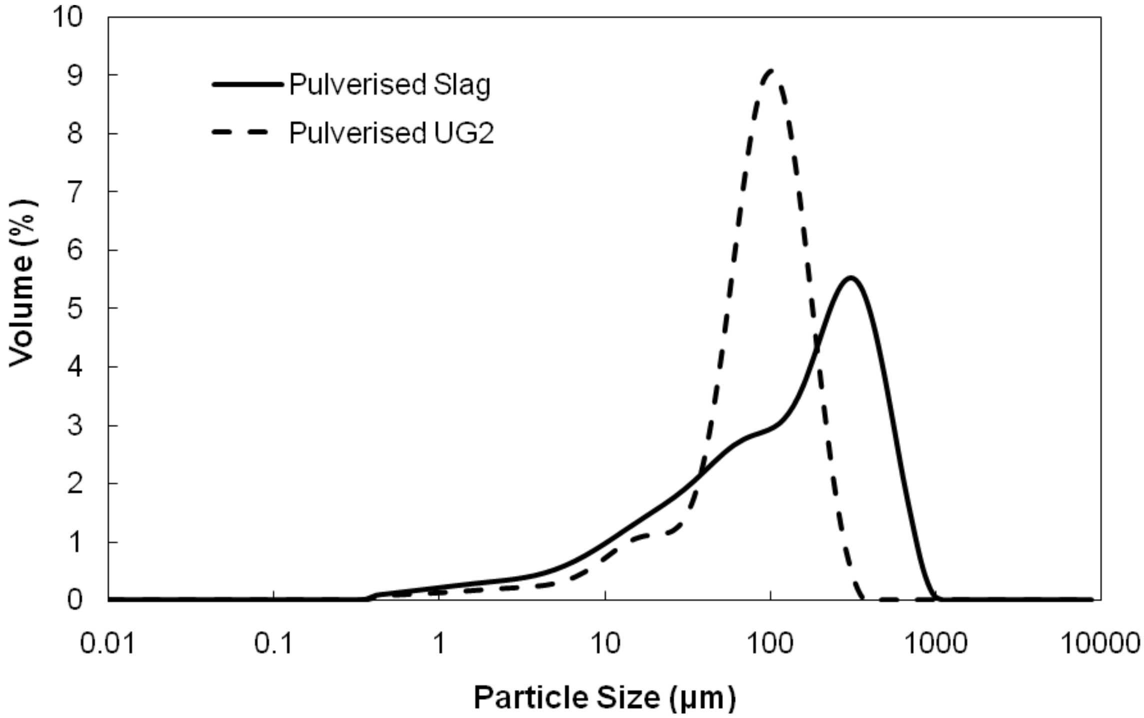


Figure 4.3: Mean particle–size distribution of the Cr–containing materials on a logarithmic scale

As speculated earlier (Par. 4.1.1), it is clear from Figure 4.3 that the pulverised UG2 ore had a narrower size distribution than the pulverised slag. Both materials still contained relatively large particles, which might settle out during agitation. However, it was decided not to pulverise the materials further to prevent the possible generation of Cr(VI) (Par. 3.3.1).

The d_{10}, d_{50} and d_{90} particle size distribution of these materials after pulverising (Par. 3.3.1) are listed in Table 4.3. The d_{90} is defined as the equivalent particle size for which 90% of the particles are finer, with definitions of d_{50} and d_{10} derived similarly.

Table 4.3: The d_{10}, d_{50} and d_{90} of the particle size distribution of the pulverised samples

	d10 (μm)	**d50 (μm)**	**d90 (μm)**
Slag	12.85	154.5	499.3
UG2	21.57	95.04	190.9

4.2 Effect of pH on Cr(VI) generation

In order to determine the effect of pH on the oxidisation of the Cr–containing samples during the ozonation treatment (Par. 1.2), 100 mg of Cr–containing material was suspended in 100 mℓ water, of which the pH was pre–adjusted (Par. 3.4). The pre–adjusted pH was varied between pH 2 and 12, while all other parameters were kept constant. A contact time of 6 min was selected, which is similar to contact times applied in operational ozonation plants (Rajagopaul *et al.*, 2008). The results of the pH–dependence study are shown in Figure 4.4.

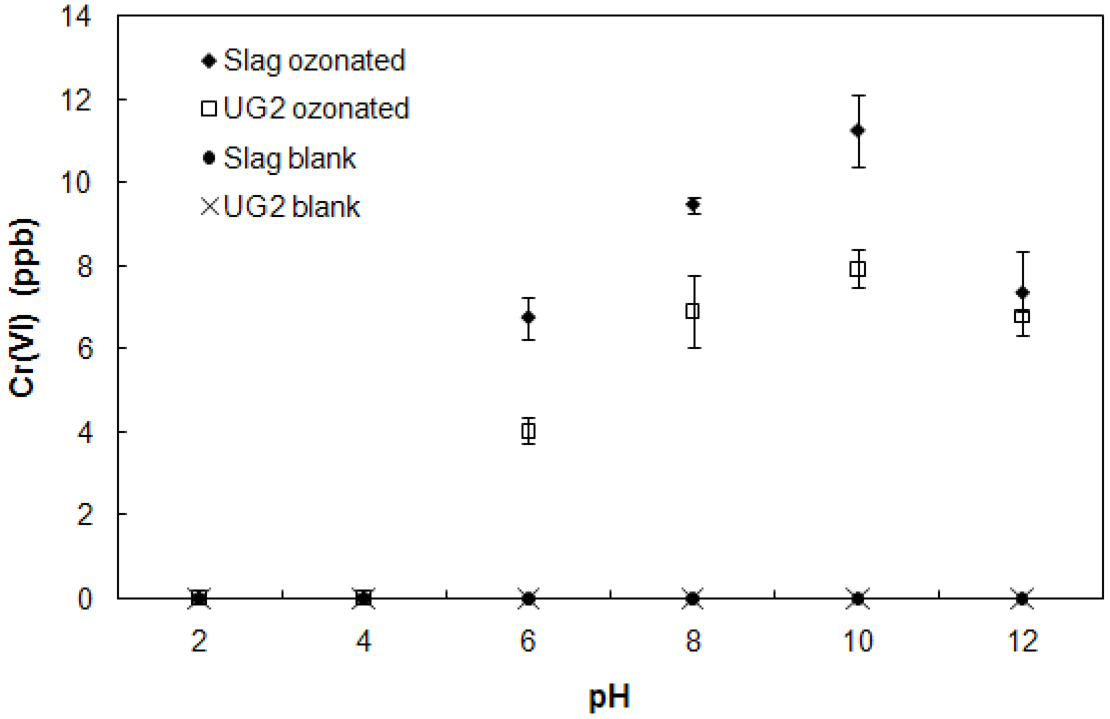


Figure 4.4: Cr(VI) formation during ozonation, as a function of pH. Solid loading = 100 mg Cr–containing material per 100 mℓ water; O_3 in O_2 gas = 0.0072 mg·mℓ$^{-1}$; ozonation contact time = 6 min; T = 20 ± 0.5°C

From these results it is evident that Cr(VI) can be formed during aqueous ozonation of Cr–containing materials. According to literature, dissolved oxygen by itself cannot cause any measurable oxidation of Cr(III) to Cr(VI), even over prolonged periods (Par. 2.6.6.1). Blank experimental results (all experimental conditions the same, but O_3 generator switched off) indicated in Figure 4.4 confirmed that no Cr(VI) was formed by O_2, thus the Cr(VI) formed during ozonation was not merely liberated from the case study materials but was generated in situ. Virtually no Cr(VI) formation were detected at pH 2 – 4. From pH 6, Cr(VI) formation was observed and the Cr(VI) concentration increased with an increase in pH, reaching a maximum Cr(VI) concentration measured at approximately pH 10. Although this study was not aimed at establishing the chemical reaction mechanism of the Cr–containing material oxidation, possible reasons for the observations can be postulated. At low pH values aqueous O_3 decomposition is relatively slow (Lovato *et al.*, 2009; Beltrán, 2003; Sotelo *et al.*, 1987), hence chromium oxidation is mostly dependant on the ability of dissolved O_3 to serve as an oxidant. Gurol & Singer (1982) specifically reported that the rate of ozone decomposition was slow and relatively insensitive to pH below pH 4. However, at higher pH levels, aqueous O_3 decomposition accelerates, which results in the formation of higher concentrations of hydroxyl radicals ($OH^{\bullet}$) (Lovato *et al.*, 2009; Beltrán, 2003). These radicals have a standard reduction potential of 2.8 V compared to the standard reduction potential of 2.07 V for dissolved O_3 (Table 2.3 in Par. 2.7.2), hence the increased Cr(VI) formation at higher pH. Since aqueous O_3 is constantly replenished during ozonation the formation of hydroxyl radicals at higher pH levels are not diminished by O_3 decomposition.

The difference in characteristics of different Cr–containing material will influence their susceptibility to oxidation during aqueous ozonation. In this particular study, higher Cr(VI) levels were measured for the ferrochrome slag compared to the UG2 ore (Figure 4.4), in spite of the ore having a higher total chromium content (Tables 4.1 and 4.2). It is well–known that chromite ore is relatively chemically inert due to its spinel crystal structure (Gu & Wills, 1988), hence it was more resistant to the actions of ozonation.

The concentrations of Cr(VI) formed in water during this pH investigation was well below the 50 ppb drinking water standard (Par. 2.5). However, it would be misleading to correlate these bench–top experimental results directly to practical ozonation plant operations, since many parameters are likely to differ (e.g. solid loading, contact time, pH, O_3 generator efficiency, agitation, etc.). It is, however, apparent from the results presented here that Cr(VI) could be formed via ozonation if Cr–containing materials are suspended in water.

4.3 Effect of ozonation contact time

Rajagopaul *et al.* (2008) reported that the contact time during ozonation in operational plants are in the order of 3 – 6 minutes. However, contact time could be longer, depending on the objective of the treatment and the compounds present in the water (Selcuk, 2005; Beltrán, 2003). In order to establish the effect of ozonation contact time on Cr(VI) formation; ozonation was performed at different contact times (6, 12, 24 and 48 minutes) at two pH values, i.e. pH 7, which represents a neutral water system and pH 10 where the highest Cr(VI) concentrations were measured (Figure 4.4). The results obtained are presented in Figure 4.5 and indicate an almost linear increase in Cr(VI) concentrations with an increase in treatment time for the experimental conditions investigated.

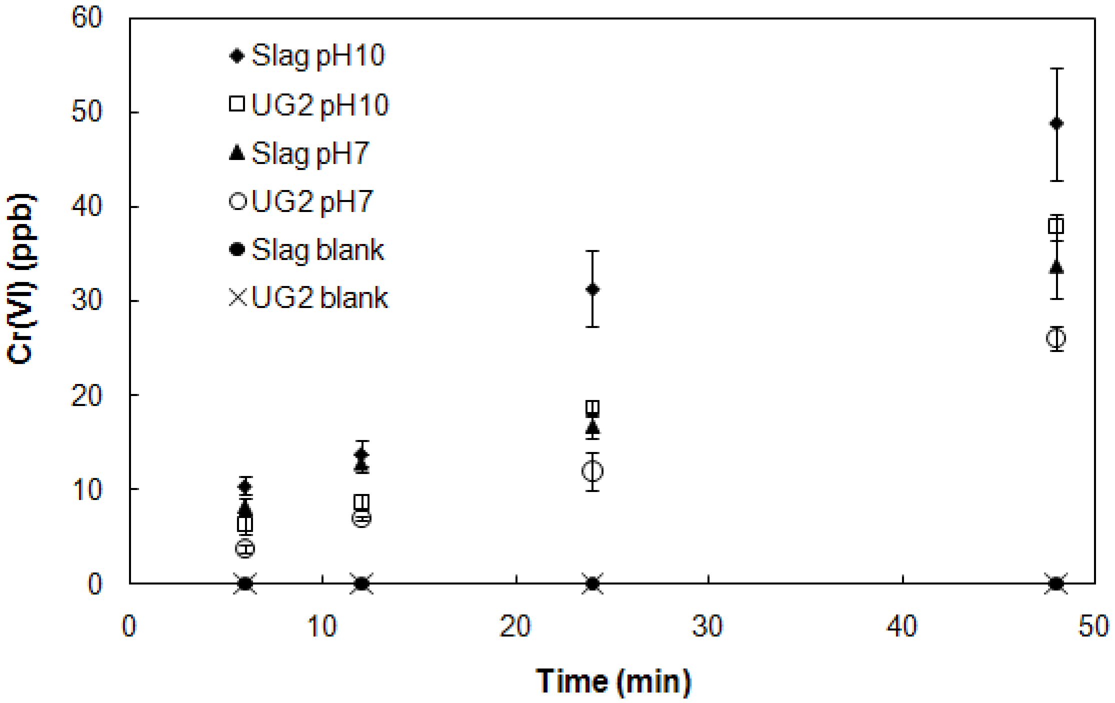


Figure 4.5: Cr(VI) formation during ozonation, as a function of contact time. Solid loading = 100 mg Cr–containing material per 100 mℓ water; O_3 in O_2 gas = 0.0072 mg·mℓ$^{-1}$; pH = 7 and 10; T = 20 ± 0.5°C

The results in Figure 4.5 also show that under severe ozonation conditions, such as extended ozonation contact time, Cr(VI) levels above the drinking water standard of 50 ppb (Par. 2.5) could be formed.

4.4 Temperature effect

It is unlikely that ozonation will be applied at extremely high or extremely low water temperatures. Hence, the effect of water temperature was investigated at 10, 20, 30 and 40°C. This temperature range is representative of ambient and maybe slightly heated water, which might be applicable to some industrial waste waters (e.g. combustion off–gas venturi scrubber water). The results are presented in Figure 4.6.

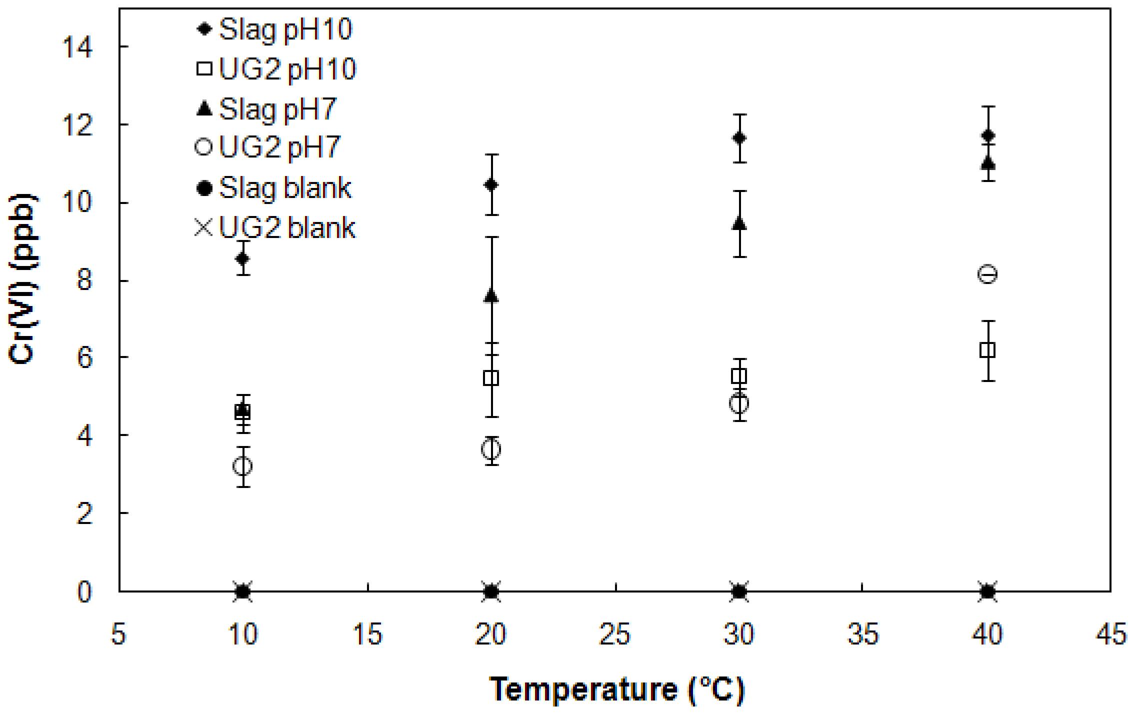


Figure 4.6: Cr(VI) formation during ozonation, as a function water temperature. Solid loading = 100 mg Cr–containing material per 100 mℓ; O_3 in O_2 gas = 0.0072 mg·mℓ$^{-1}$; ozonation contact time = 6 min; pH = 7 and 10

It is evident form Figure 4.6 that increased water temperatures cause increases in Cr(VI) formation. Aqueous O_3 decomposition studies have indicated that higher temperatures lead to increased rates of ozone decomposition (Table 2.4 in Par. 2.7.4), hence higher concentrations of the more aggressive oxidation radicals ($OH^\bullet$), as discussed earlier.

4.5 Effect of solid loading

As could be expected, higher solid loading of Cr–containing materials lead to higher Cr(VI) concentrations (Figure 4.7). These results represent relatively high solid loadings, which is unlikely to be achieved in water treatment applications. However, these high solid loadings were utilised to establish a trend for the formation of Cr(VI). It is also important to note that Cr(VI) levels above drinking water standards (Par. 2.5) were formed under these extreme conditions, i.e. very high solid loading in this particular instance.

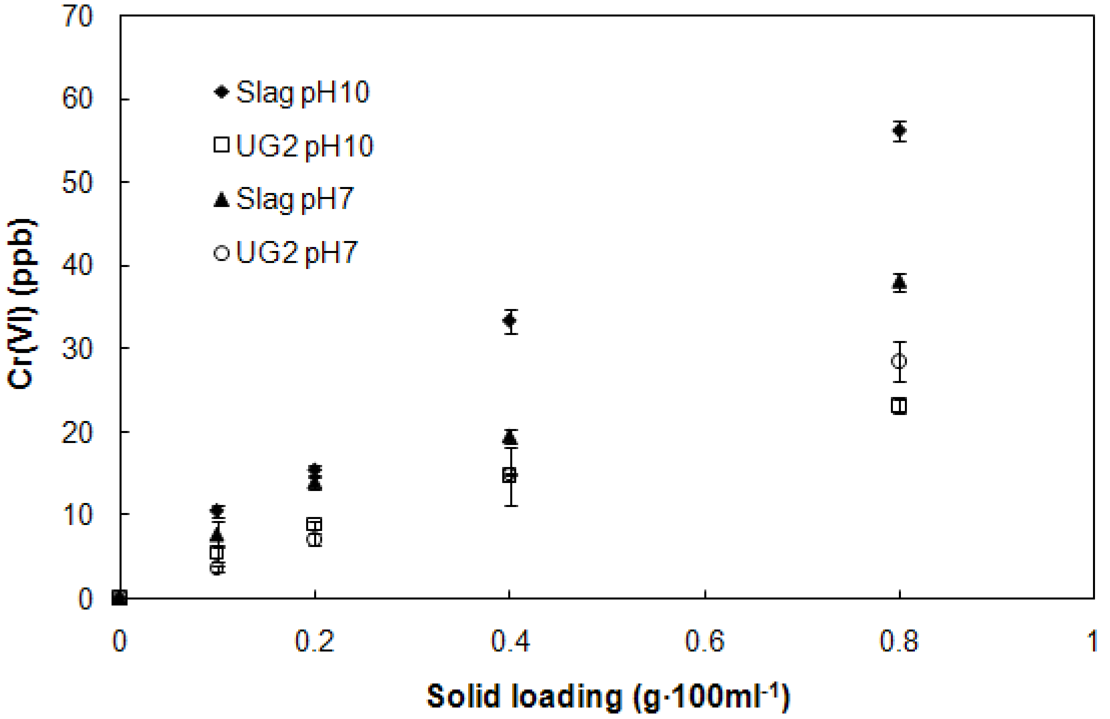


Figure 4.7: Cr(VI) formation during ozonation, as a function of Cr–containing material loading. O_3 in O_2 gas = 0.0072 mg·mℓ$^{-1}$; ozonation contact time = 6 min; pH = 7 and 10; T = 20 ± 0.5°C

4.6 Effect of gaseous O_3 concentrations

The maximum O_3 concentration in the O_2 gas stream was limited by the ability of the O_3 generator utilised in this study. All the results presented in the previous sections were conducted with the maximum setting of the O_3 generator utilised, i.e. achieving 0.0072 mg·mℓ$^{-1}$. In order to assess the effect of O_3 gaseous concentration on the formation of Cr(VI) during aqueous ozonation, two lower settings of the O_3 generator were used. These results are shown in Figure 4.8, which indicate that lower gas O_3 concentrations resulted in lower Cr(VI) formation.

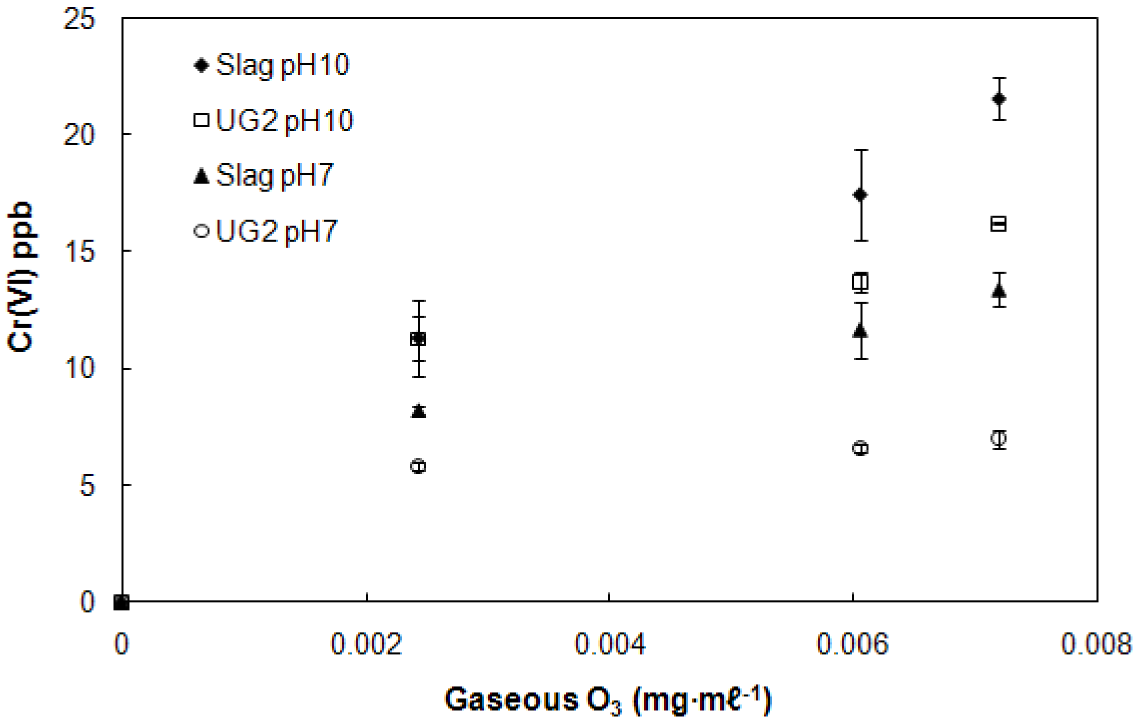


Figure 4.8: Cr(VI) formation during ozonation, as a function of gaseous O_3 concentration. Solid loading = 100 mg Cr–containing material per 100 mℓ; ozonation contact time = 6 min; pH = 7 and 10; T = 20 ± 0.5°C

In actual water treatment applications the gaseous O_3 concentrations could be much higher than the range tested experimentally, e.g. 1.5 mg·ℓ^{-1} for the pre–ozonation and 0.5 – 2.5 mg·ℓ^{-1} for the intermediate treatment as reported by Rajagopaul *et al.* (2008). Although these concentrations were not tested in this investigation, it can be assumed that these higher O_3 concentrations could results in the formation of higher Cr(VI) concentrations. Obviously there would be a limitation on the maximum achievable solubility of O_3 as determined by Henry's Law (Connell, 2005):

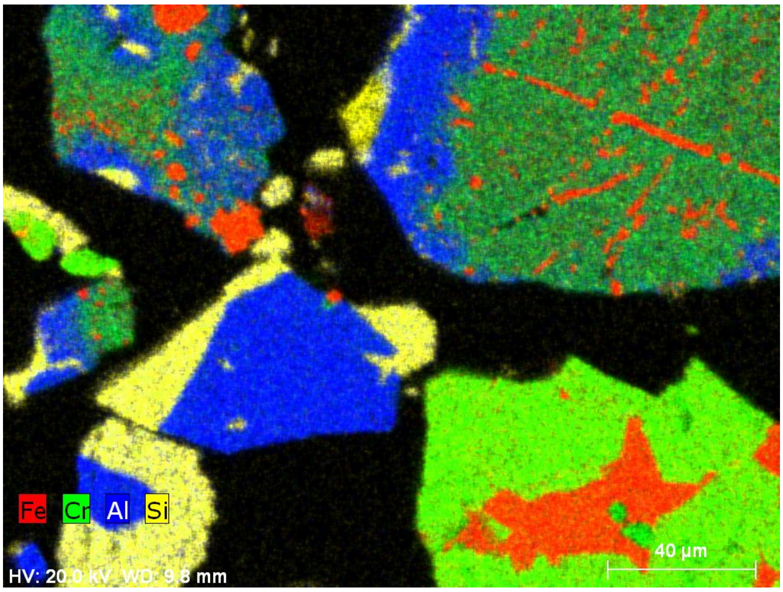
$$H = P/C_w \tag{4.1}$$

P = Partial pressure of the gas in air

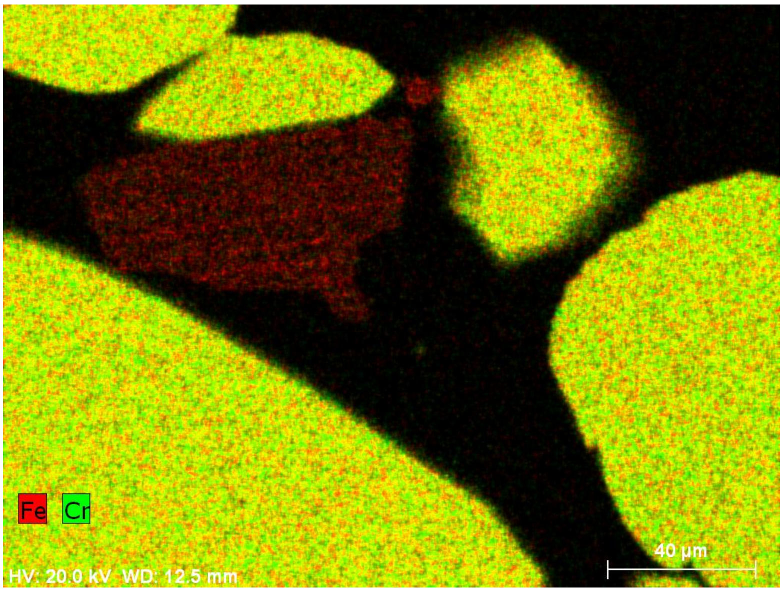
C_w = Concentration in water

4.7 Mechanism of Cr–liberation

In order to obtain insight into the actual liberation mechanism of chromium from the solid Cr–containing materials during ozonation, SEM elemental maps were generated for the ozonated Cr–containing materials investigated (Par. 3.3.4) and are presented in Figure 4.9.



4.9a



4.9b

Figure 4.9: SEM elemental maps (colour representing elements, as indicated on images) of ozonated ferrochrome slag (4.9a) and UG2 particles (4.9b). Solid loading = 100 mg Cr–containing material per 100 mℓ; O_3 in O_2 gas = 0.0072 mg·mℓ$^{-1}$; ozonation contact time = 6 min; pH = 10; T = 20 ± 0.5°C.

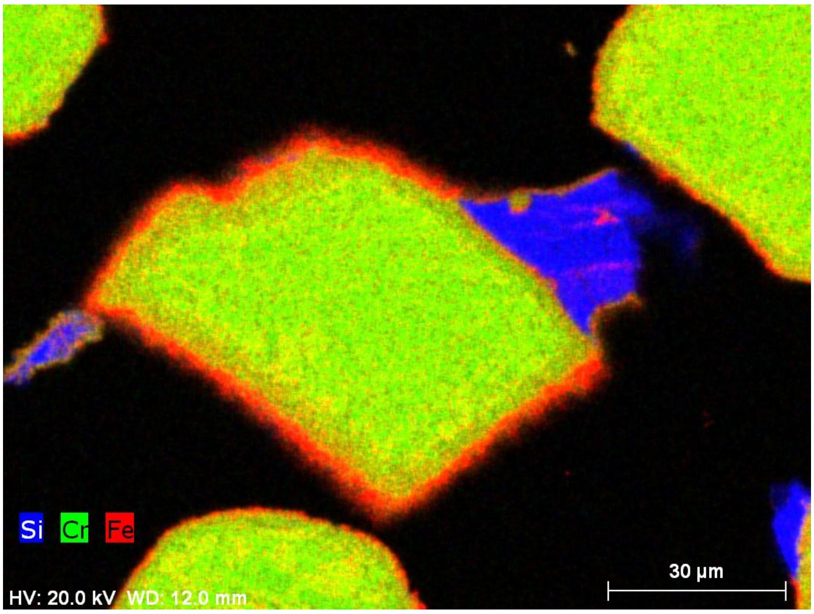


Figure 4.10: Figure indicating chromite ore particles treated in a different manner (not discussed in this dissertation), resulting in iron enrichment on the surface (indicated by red layer on outside of particles)

Figure 4.9a and 4.9b indicate ozonated slag and UG2 ore particles, respectively. It is clear from the colour distributions (colour representing different elements, as indicated on the images) of the two materials utilised, that the slag is much more heterogeneous than the UG2 with regard to elemental distribution. This was expected, since the slag is a re–crystallised waste product, while the UG2 ore is more homogeneous. However, in neither of these two ozonated materials can any form of enrichment of a specific element be observed on the surface (outside) of the particles.

For comparative purposes Figure 4.10 was included, which indicates chromite ore particles that were treated in a different manner (unpublished results). This treatment resulted in the enrichment of iron on the surface of the particles. The lack of enrichment of any elements on the surface of the ozonated slag and UG2 ore particles therefore indicate that ozonation did not selectively extract chromium or any other element. It is therefore most likely that the particle surfaces were eroded due to the strong oxidising conditions, which resulted in the release and subsequent oxidation of chromium. Other elements present in the case study materials were therefore also likely to be liberated, however they were not quantified since it was beyond the scope of the investigation.

4.8 O_3 formation and decomposition

The decomposition of ozone in aqueous solutions is well documented in literature (Par. 2.7.2). Therefore it was not the objective of this study to investigate the formation and decomposition of O_3. However, a limited number of experiments were conducted to observe the formation and decomposition of O_3 in order to obtain an understanding of these processes. Two typical UV/vis–absorbance spectrums obtained illustrating the decomposition of ozone at a pH 2 and 12 are presented in Figures 4.10 and 4.11, respectively. The absorption maximum was at 260 nm.

In Figure 4.12 the time dependency of the decomposition of O_3 at the two pH values are shown. In plots such as these the UV/vis–absorption maxima is directly related to the concentration of dissolved O_3 according to the Beer–Lambert Law. As can be seen the initial dissolved O_3 concentration is much lower at pH 12, due to the relatively fast decomposition at this high pH that had already reduced the dissolved O_3 concentration before the UV/visible measurement started.

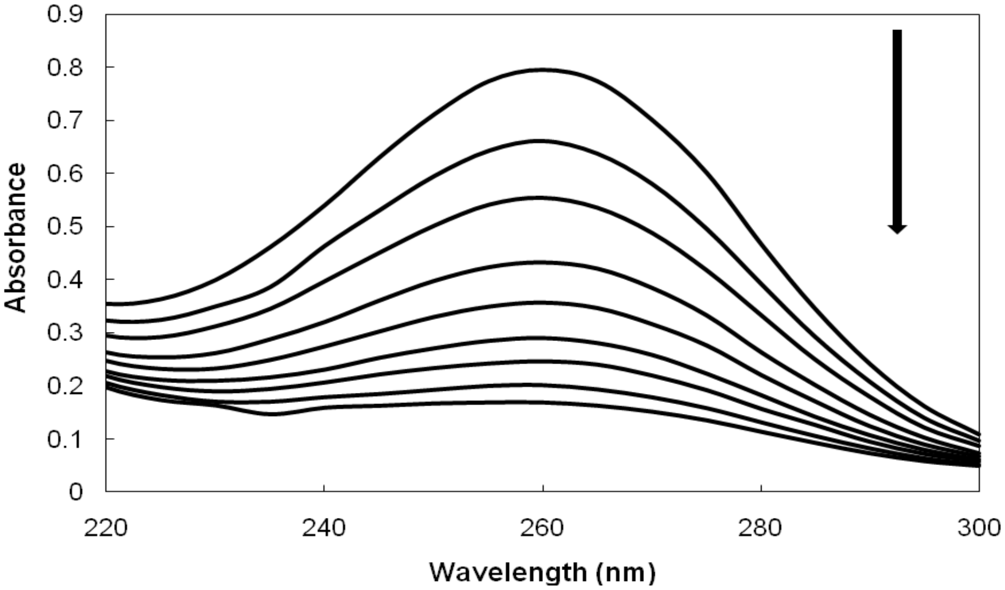


Figure 4.10: UV–absorbance spectrum of decomposition of ozone in water as a function of time pH = 2.0; Δt = 5 minutes; O_2 gas flow = 80.3 mℓ·min^{-1}; T = 20 ± 0.5°C

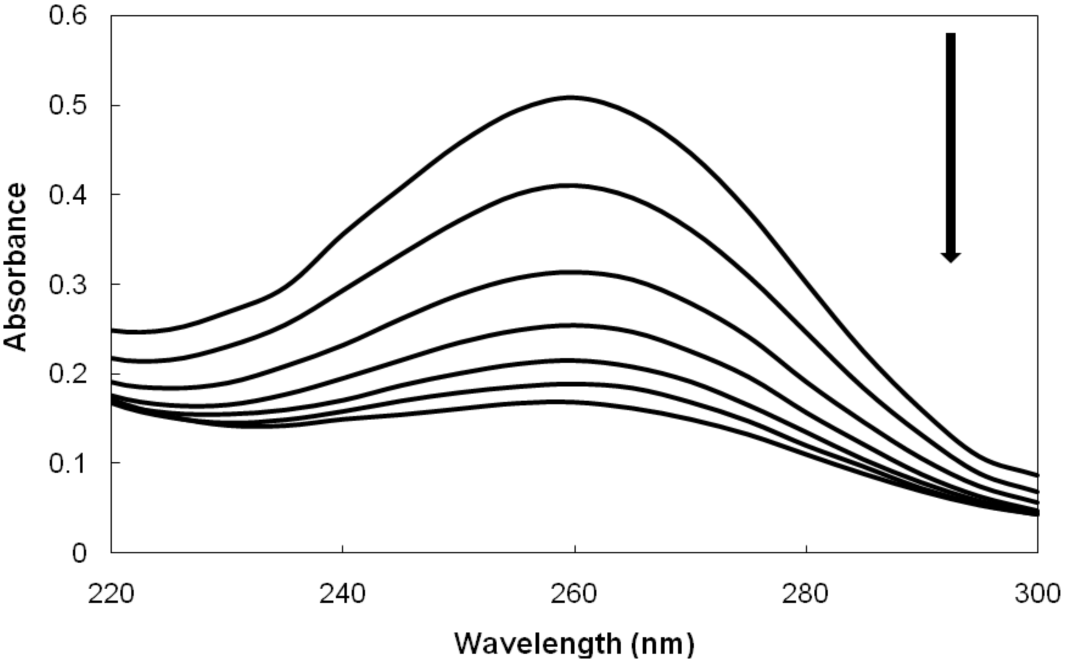


Figure 4.11: UV–absorbance spectrum of decomposition of ozone in water as a function of time pH = 12.0; Δt = 5 minutes; O_2 gas flow = 80.3 mℓ·min^{-1}; T = 20 ± 0.5°C

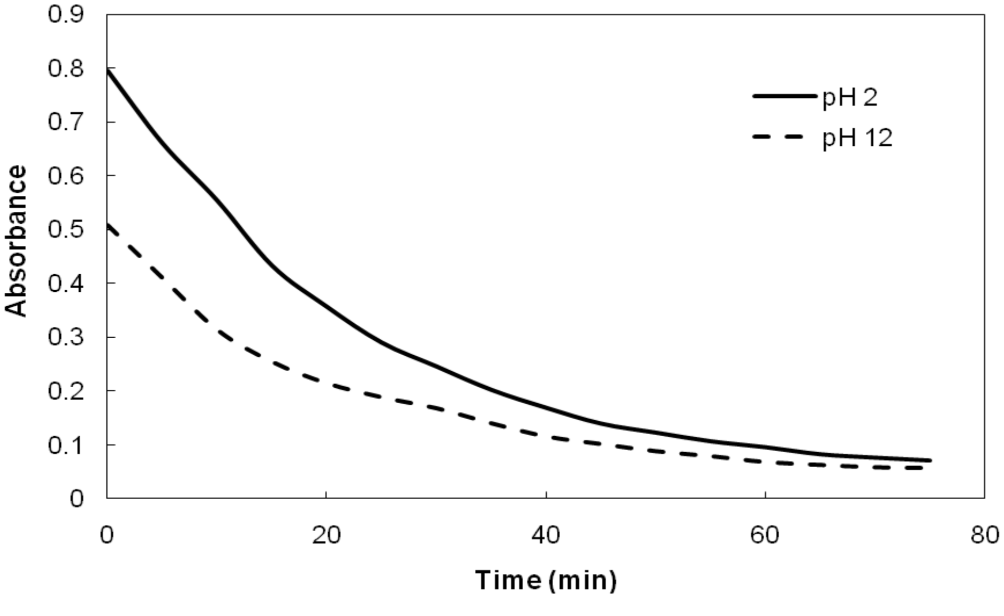


Figure 4.12: Comparing UV/vis–absorbance spectrum of pH 2 and pH 12 decomposition of ozone in water as a function of time O_2 gas flow = 80.3 mℓ·min^{-1}; T = 20 ± 0.5°C; λ = 260 nm

In order to establish the time dependance for the formation of O_3, ozone was bubbled throught a 100 mℓ buffered solution, while the UV/vis–absorbance was monitored.

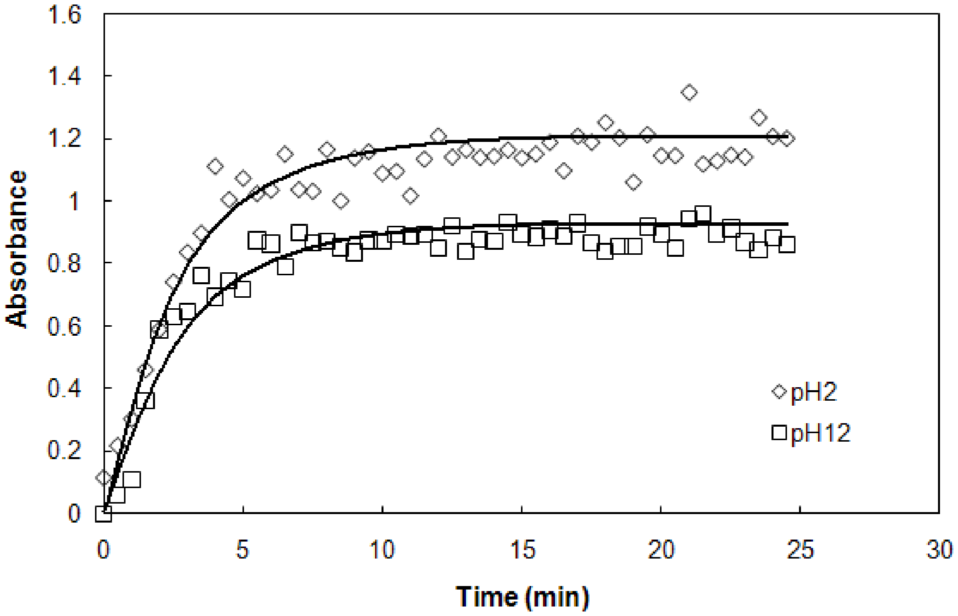


Figure 4.13: UV/vis–absorbance spectrum of ozone in as a function of time pH = 2 & 12; Δt = 30 seconds; I = 0.1 M; O_2 gas flow = 80.3 mℓ·min^{-1}; T = 20 ± 0.5°C; λ = 260 nm

From Figure 4.13 it is clear that the ozone concentration stabilised after approximately 8 min. Most of the previous experiments were conducted at 6 min contact time, which implies that the maximum dissolved O_3 concentration was not reached during those experiments. The results also indicate that the ozone concentration is much lower at a pHof 12 than a pH of 2. The reason for this is that ozone decomposes much faster at higher pH values than at lower pH values (Par. 2.7.2). The direct ozone-water reaction and the hydroxide ion initiation step is the main cause for ozone decomposition.

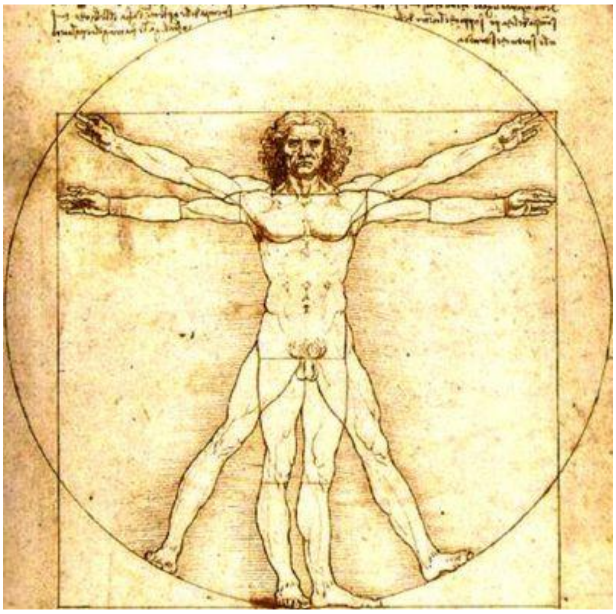
4.9 Conclusions

The experimental conditions employed in this study cannot be related directly to ozonation of drinking or waste water treatment plants, since parameters e.g. solid loading, ozone concentrations, mixing efficiencies are likely to be different. Cr(VI) concentrations measured within the experimental ozonation conditions can therefore not be used as guide to predict possible Cr(VI) formation. However, the results clearly indicate that Cr(VI) can be formed *in situ* during ozonation of water with non–Cr(VI) Cr–containing materials present in suspension. pH seems to be the most important parameter influencing the formation of Cr(VI), with higher pH levels favouring Cr(VI) formation. This can be attributed to the increased rate of aqueous O_3 decomposition occurring at pH > 4, resulting in higher concentrations of $OH^{\bullet}$ radicals that are stronger oxidants than aqueous O_3. Other parameters, such as contact time, water temperature, solid loading, ozone concentration and the characteristics of the Cr–containing material also have an influence on Cr(VI) formation.

The results indicate the importance of removing suspended particulates from water prior to applying ozonation. Although dissolved Cr(III) oxidation was not specifically investigated in this study, it can be assumed that dissolved Cr(III) would be readily oxidised compared to the relatively inert chromite ore utilised as one of the Cr–containing materials utilised in this case study. Although most Cr(III) compounds are precipitated out of solution at pH levels relevant to drinking and waste water treatment plants, some Cr(III) species are soluble (Bartlett, 1991).

Study the science of art. Study the art of science. Develop your senses especially, learn how to see. Realise that everything connects to everything else.

Leonardo da Vinci



CHAPTER 5

RESULTS: Liberation of chromium from waste materials – implications for industrial recovery of chromium

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In this chapter...

The oxidation of Cr–containing materials, with a focus on industrial Cr recovery (Par. 5.1) is explored. The importance of pH on Cr–liberation is discussed in Par. 5.3. Conclusions are drawn from the results and future studies are considered, which would improve Cr_2O_3–liberation further (Par. 5.5).

5.1 Introductory remarks

In Chapter 4 the possible generation of Cr(VI) relevant to the water treatment sector was investigated. Cr(VI) formation is usually avoided due to its health impacts (Par. 2.5). However, in this chapter preliminary work done to explore if Cr(VI) formation via ozonation could serve as a means of recovering chromium from Cr–containing materials is presented. The motivation behind this exploratory work is based on the fact that unlike Cr(0) and Cr(III), most Cr(VI) solids are relatively soluble in water (Par. 2.6.2). Thus by oxidizing the insoluble chromium to Cr(VI) the chromium in the Cr–containing materials can be recovered by means of leaching. It is well known that Cr(VI) is a carcinogen if inhaled, however the probability of negative health effects are substantially reduced if Cr(VI) is in solution (Proctor *et al.*, 2002). A hydrometallurgical route of recovering Cr–units via Cr(VI) generation (as investigated in this chapter) represents the safest route, with respect to Cr(VI) exposure. Such a hydrometallurgical route could also address the limitations of the physical separation methods currently applied, which fails to recover very fine Cr–containing solids (Erdem *et al.*, 2005; Mashanyare & Guest, 1997).

5.2 Case study material characterisation

The Cr–containing materials utilised in this chapter are the same materials characterised in Par. 4.1.

5.3 Effect of pH on Cr–liberation

In Chapter 4 it was proven that Cr(VI) could be formed during ozonation of Cr–containing materials suspended in water. In order to test the feasibility of utilising ozonation as an industrial process, the solid loading (solid material/volume water) during ozonation was increased to 5 g / 100 mℓ water. This was done, to replicate the anticipated concentrations relevant to industrial recovery processes. Additionally, Cr–liberation from the solid materials is discussed. This is indicative of the extraction of the Cr–units from the solid material. Cr–liberation is expressed as Cr_2O_3–liberation, which is calculated as follows:

$$\%\mathrm{Cr_2O_3} - \text{liberation} = \frac{\left(\mathrm{Cr_2O_3}\text{in original sample} \; - \; \mathrm{Cr_2O_3}\text{after ozonation}\right)}{\left(\mathrm{Cr_2O_3}\text{in original sample}\right)}$$

The term Cr_2O_3–liberation was chosen, since the Cr–content of feed materials for the ferrochromium industry is mostly expressed in terms of Cr_2O_3 content. The Cr_2O_3 content of the materials were determined with ICP–OES (Par. 3.3.5).

The effect of pH on Cr_2O_3–liberation during ozonation of the ferrochromium slag is indicated in Figure 5.1, while Cr_2O_3–liberation during ozonation of the UG2 ore is presented in Figure 5.2. Contact time was selected as 6 hours, which was chosen based on the results in Chapter 4 which found that longer contact times resulted in higher Cr(VI) concentrations, i.e. better Cr_2O_3–liberation.

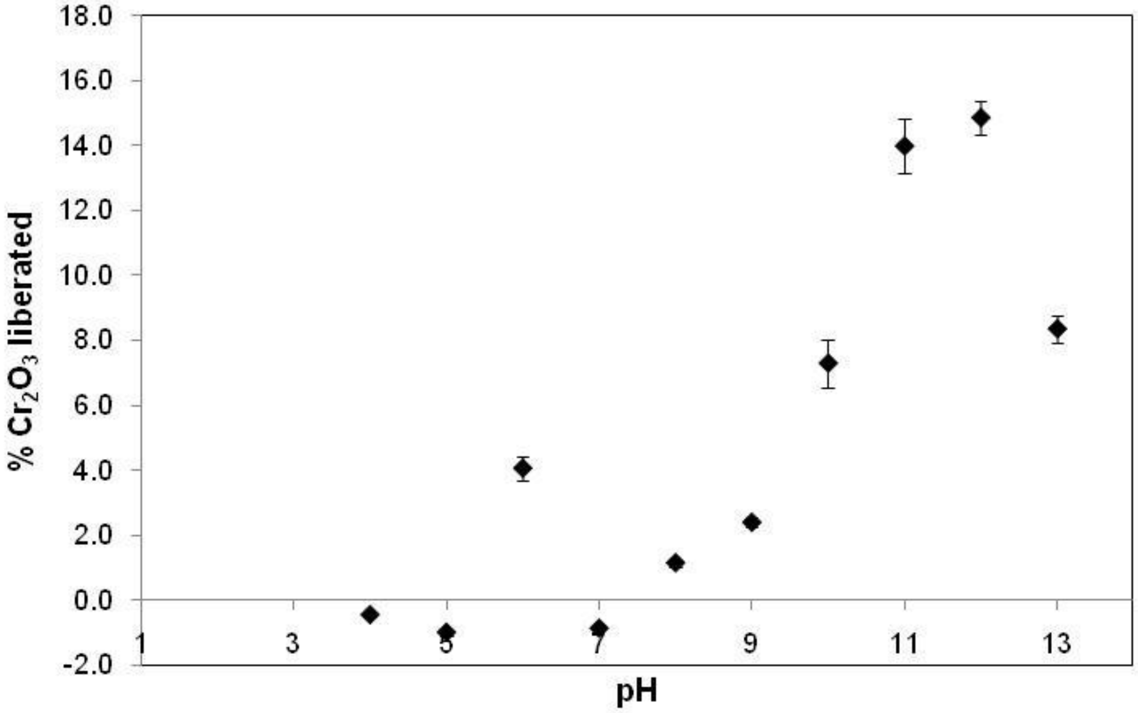

Figure 5.1: Cr_2O_3–liberation from ferrochromium slag during ozonation, as a function of pH. Solid loading = 5 g Cr–containing material per 100 mℓ; O_3 in O_2 gas = 0.0072 mg·mℓ$^{-1}$; ozonation contact time = 6 hours; T = 20 ± 0.5°C

From the results presented in Figures 5.1 it can been seen that an increase in pH resulted in increased Cr_2O_3–liberation. This was expected, since enhanced oxidation via the formation of the hydroxyl radical is obtained at higher pH values, as discussed in Par. 4.2. The maximum Cr_2O_3 that could be liberated was approximately 15% at pH 12. Due to the fact that the ferrochromium slag is a relatively heterogeneous material (Par. 4.1) some scattering of the results are evident (Figure 5.1).

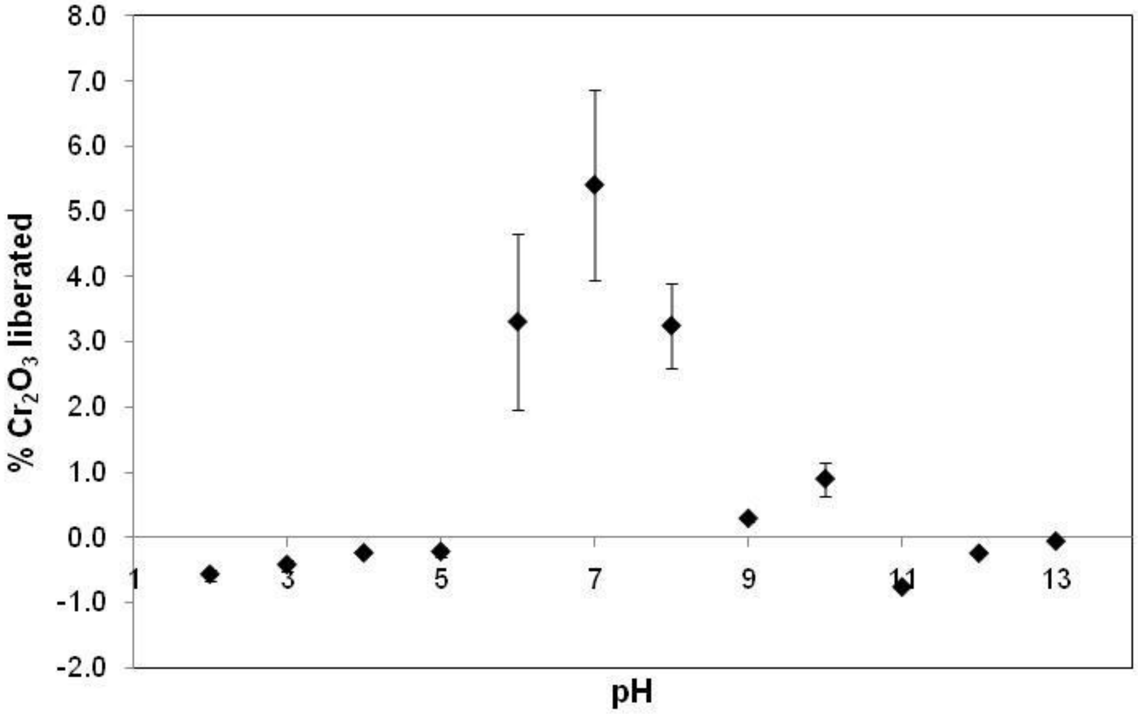

Figure 5.2: Cr_2O_3–liberation from UG2 ore during ozonation, as a function of pH. Solid loading = 5 g Cr–containing material per 100 mℓ; O_3 in O_2 gas = 0.0072 mg·mℓ$^{-1}$; ozonation contact time = 6 hours; T = 20 ± 0.5°C

Cr_2O_3–liberation from the UG2 was less successful (Figure 5.2), with a maximum Cr_2O_3–liberation of only approximately 5.5% achieved at pH 7. This was to be expected, since chromite is relatively inert due to its spinel crystal structure (Gu & Wills, 1988). The slag, where better Cr_2O_3–liberation was achieved (Figure 5.1), had passed through a pyrometallurgical process (liquid temperature of molten ferrochromium slag range from 1620 to 1750°C) hence the chromite structure had been destroyed. Interestingly though is the fact that Cr_2O_3–liberation for the UG2 ore peaked at pH 7 and not at higher pH levels as was found for Cr(VI) generation at lower concentrations in Chapter 4 (Figure 4.4).

5.4 Conclusions

The levels Cr_2O_3–liberation achieved in this exploratory work was relatively low. However the Cr_2O_3–liberation achieved for the ferrochromium slag is indicative that further work be pursued. Several steps can be considered in future studies, which would improve Cr_2O_3–liberation further. These are:

- Utilisation of a more powerful ozone generator. As discussed in Chapter 4 (Par 4.6) the ozone generator used could only achieve 0.0072 $\mathrm{mg{\cdot}m}\ell^{-1}$ O_2 gas.

- Finer milling of the solid materials. As indicated in Par 4.1 the d90 of the ferrochromium slag was 499.3 μm. Considering the Cr–liberation mechanism observed based on particle size (Par. 4.7) finer solid materials will most certainly results in better Cr_2O_3–liberation values.

- In this study ozonation was investigated. However, it is well known that advanced oxidation processes (AOP), i.e. ozonation with the addition of catalysts, hydrogen peroxide and/or UV radiation, achieves better oxidation that ozonation alone (Nawrocki & Kasprzyk-Hordern, 2010; Coca *et al.*, 2007; Selcuk, 2005; Gogate & Pandit, 2004; Beltrán, 2003). Thus, application of the AOP could further improve Cr_2O_3–liberation values.

We now know a thousand ways not to build a light bulb.

Thomas Alva Edison

CHAPTER 6

PROJECT EVALUATION

In this chapter...

The project is briefly evaluated based on the achievements and shortcomings. Future perspectives are identified.

6.1 Project evaluation and future perspectives

The project evaluation and future perspectives are structured around the objectives set in Chapter 1. The points listed below therefore correlate with the objectives set in Par. 1.2:

i. An in-depth literature survey was conducted in Chapter 2. It highlighted the importance of the chromium industry within the South African context (Par. 2.2). The processes utilised by these industries were characterised in Par. 2.3. The fact that relatively high volumes of waste materials are produced by these industries, each with unique characteristics (Par. 2.4), emphasised the need for further research to determine how these Cr–containing materials may affect the environment and how valuable Cr-units could be recovered from these waste materials. Since ozonation was specifically considered in this study as an oxidising process, additional emphasis was placed on the characterisation of it (Par. 2.7). The literature survey indicated that no studies have been conducted on the possible formation of Cr(VI) by ozonation in water treatment processes, nor has ozonation been considered as a means of recovering Cr-units from waste materials.

ii. The investigation on the formation of Cr(VI) from non-Cr(VI) Cr–containing materials oxidised with ozone in aqueous solution was successfully completed over a wide pH range ($2.0 \leq pH \leq 12.0$) (Chapter 4). This reaction was also studied as a function of O_3 gaseous concentration, solid material loading, ozonation contact time and water temperature. The results clearly indicated that Cr(VI) can be formed *in situ* during ozonation of water with non–Cr(VI) Cr–

containing materials present in suspension. pH has a significant influence on the formation of Cr(VI), with higher pH favouring Cr(VI) formation.

iii. The concentration of Cr(VI) formed in the water during the above-mentioned investigation is generally below the 50 ppb drinking water standard. Extreme conditions such as high solid loading and long ozonation contact time led to Cr(VI) concentrations exceeding drinking water standards. However, the experimental conditions employed in this study cannot be directly related to ozonation of drinking or waste water treatment plants since key process parameters e.g. solid loading, ozone concentrations and mixing efficiencies are typically different. Notwithstanding this limitation, it can be stated with confidence that Cr(VI) generation during water treatment by ozonation can be mitigated or totally eliminated by removal of suspended particulates containing chromium. Dissolved Cr(III) is much less likely to occur, although it can be expected to oxidise easier than the relatively inert chromite ore utilised as one of the case study Cr-containing materials. Additionally to removing suspended materials containing chromium prior to applying ozonation, if also became apparent that by controlling the pH of the water the oxidation of the Cr–containing materials can be mitigated, or even eliminated – lower pH resulted in lower Cr(VI) concentrations.

iv. From the results presented in Chapter 4 it was clear that Cr(VI) could be formed during the aqueous ozonation of Cr-containing materials. Consequently it was hypothesised that ozonation could possibly by used as a means of liberating valuable chromium units from waste materials. This possible recovery process was investigated as a function of pH with higher solid loadings and longer contact times (Chapter 5), if compared to the work that was relevant to the water treatment sector (Chapter 4). The results indicated that a maximum of 15% Cr_2O_3 could be liberated for the ferrochromium slag and 5.5% Cr_2O_3 from the UG2 ore.

v. As indicated above (point iv) relatively poor recoveries (expressed as Cr_2O_3 liberated) of Cr-units from waste materials were experimentally observed. However, the results indicated some potential. Several recommendations were made, which could improve the recovery of Cr-units via ozonation. These included the use of a better ozone generator (which was a limitation in this study) and the finer milling of the waste materials. The Cr-liberation mechanism observed in this study (Chapter 4) suggested that finer particles would be better suited to the Cr-recovery process. Additionally the results indicated that ozonation as a means of liberating chromium from waste materials is highly dependent on the nature of the Cr–containing waste material investigated. It follows from results that it is unlikely that unaltered chromite will be recovered in significant proportions via ozonation (e.g. ore residue), but altered chromite materials (e.g slag) might be better suited to such recovery processes. It was also suggested that the addition of catalysts, hydrogen peroxide and/or UV radiation, would improve the liberation of Cr_2O_3 further.

vi. Several future perspectives had already been stated in the above-mentioned points. Additionally it is suggested that the Cr(VI) formation via ozonation be investigated according to a classical kinetic mechanistic studies, to determine a possible chemical reaction mechanism for Cr(VI) formation with ozonation.

By considering the objectives stated (Par. 1.2) and the successful fulfilment of those objectives this study can be considered as successful. Obviously there were some limitation and shortcomings, as mentioned above, but these are sometimes unavoidable. Additionally a meaningful scientific contribution was made to understanding the Cr(VI) generation by ozonation.

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