Hexavalent chromium analysis, reduction and stabilization in cement and concrete

A dissertation submitted to the faculty of science, University of Witwatersrand, in fulfilment of the requirements for the degree of Master of Science.

by

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Declaration

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

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(Signature of Candidate)

_____ Day of _____ 2007

Abstract

Hexavalent chromium is one of the toxic contaminants unavoidably widespread in the environment that exists in cement and concrete. Cement producers need to determine and control the content of hexavalent chromium, hence this study investigated the effect of environmental parameters on the leachability, stability and reduction of Cr(VI) in different types of concrete. Concrete cubes were made with different cement mixtures, and in some cases, reducing agents were added. The bulk and designed surface leaching experiments that simulated different environmental conditions were devised for leaching of Cr(VI). The Cr(VI) content in cement and concrete leachate solution was determined using optimized Adsorptive Stripping Voltammetry method which proved to be very sensitive and selective. Parameters like addition of MnO_2, aging of concrete, increase of temperature, UV variation and decrease in pH enhanced the leachability of Cr(VI). Cement type also affected the Cr(VI) stabilization. Attempts to stabilize Cr(VI) included addition of humic acid which proved to be not effective while the addition of ferrous sulfate was successful in reducing and stabilizing Cr(VI) in concrete.

Dedication

To my grandparents;

Mrs A. Khanyile

and

Mr E. M. Khanyile (1920 - 2002)

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The list of abbreviations used in the project

AdSV - adsorptive stripping voltammetry

Cr(III) - trivalent chromium

Cr(VI) - hexavalent chromium

Cr - chromium

DTPA - diethyl-triamine pentaacetic acid

EPA – environmental protection agency

$FeSO_4.7H_2O$ - ferrous sulfate heptahydrate

HA - humic acids

HMDE - Hanging mercury drop electrode

HSC - high strength Portland cement

MC - milled clinker

MnO_2 – manganese dioxide

TCLP – toxicity characteristic leaching procedures

UV - ultraviolet

Vis - visible

CHAPTER 1

Introduction

1.1 Trace metals speciation in the environment

Trace metals can be found throughout all the ecosystems hence they are natural components of the geosphere. They are naturally distributed differently in the environment by geochemical cycles. As a result of rain, trace metals found in ores and rocks dissolved and are transported into streams and rivers. They can then be deposited into the soil, or finally transported to the oceans where they can be precipitated as sediments. Some of the trace metals are essential to human health and some are toxic.

Speciation is the determination of the individual concentrations of different physico-chemical forms of an element which together make up the total concentration of the metal in the sample (Ali and Aboul – Enein, 2006; Florence, 1986). It allows the differentiation between oxidation states, coordinated and uncoordinated ions, cationic, anionic and neutral forms. Metals can exist in a range of physiochemical forms in environmental samples, including hydrated metal ions, inorganic and organic complexes, and adsorbed on organic and inorganic colloidal particles. The transport and fate of a metal ion varies with its physicochemical form. The most toxic forms are usually hydrated metal ions and labile complexes and the least toxic are strongly bound metal complexes and metal adsorbed on colloidal particles.

Chemical speciation specifies the transformation and the distribution of species or the analytical activity of both identifying chemical species and measuring their distribution. The different forms of an element exhibit different toxicities and mobilities in the environment (Ali and Aboul – Enein, 2006). It is clearly of importance to be able to distinguish between the individual species present in a particular sample. Measurements of total metal concentrations are well established but it is not easy to measure just the toxic form (Morrison et al., 1989).

There are two types of speciation, namely; physical and chemical speciation. Physical speciation is important for the understanding of sorption and migration phenomenon of heavy metals in a terrestrial system. Chemical speciation can be divided into four main different groups presented in figure 1.1.

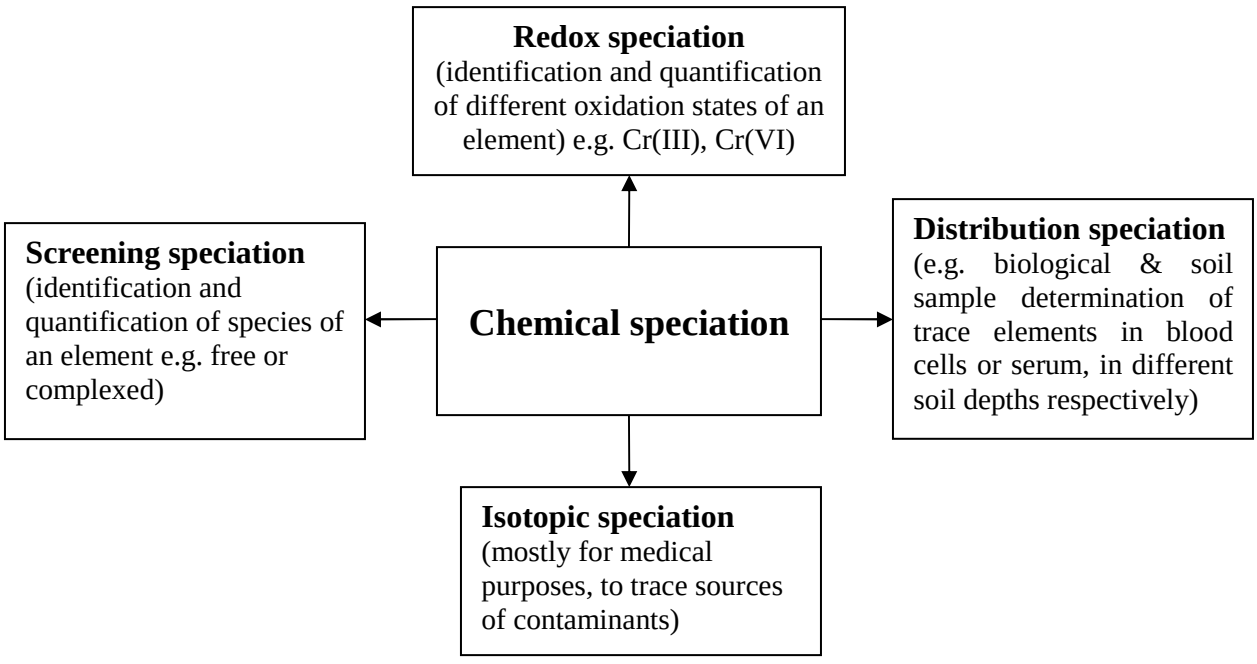

Figure 1.1 Main classes of chemical speciation (Templeton et al., 2000)

In order to understand the sorption and migration phenomena of heavy metals in the environmental system, speciation studies are crucial. The determination of trace metals species in the environmental samples is complicated due to matrix effects and low concentrations (Ali and Aboul – Enein, 2006). Therefore, errors can easily arise from contamination or loss of trace metal ions. In soils and sediments, determination of trace metals may involve soluble and suspended fractionation processes, identification and quantification of different forms present after extraction or derivatization (Florence, 1986).

1.2 Chromium speciation

Chromium speciation does not only influence its toxicity, but also the mobility of chromium depends on its chemical form, therefore detailed knowledge of each chromium species rather than the total chromium level is required to properly evaluate physiological and toxicological effects of chromium, its chemical transformation in water, soil and transport in the environment (El – Shahawi et al., 2005; Bobrowski et al., 2004; Bartlett and James 1988).

1.2.1 Chemistry of Chromium

Chromium was discovered in 1797, by Louis Vauquelin, in France. It is the 24th element in the periodic table (transition metal), atomic weight of 51.996. Chromium is a steel-gray, lustrous and hard metal.

Chromium can exist in several chemical forms displaying different oxidation states from zero to six, but in the natural environment, only trivalent and hexavalent chromium are

stable (Skovbjerg et al., 2006; Zayed and Terry, 2003). Cr(III) is the most stable state in water with a standard potential of -1.74V as shown in figure 1.2, therefore a considerable amount of energy would be needed to convert it to lower or higher oxidation states. The chromium oxidation sates of I – III all have negative potentials thus oxidation is favored and whereas with oxidation states of IV – VI all have positive potentials thus reduction is favored.

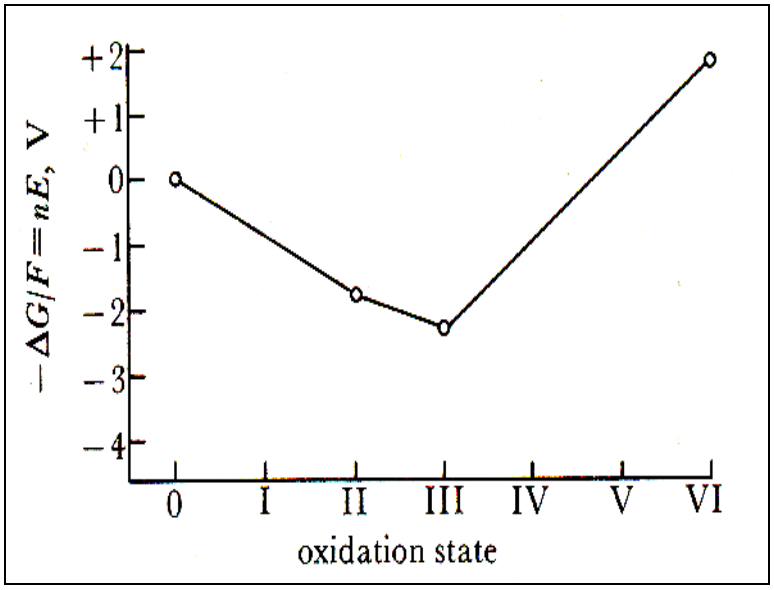

Figure 1.2 The oxidation state free energy diagram for chromium (Shriver et al., 1994)

Figure1.2 illustrates that Cr(VI) in acidic solution has a very high positive redox potential (~ 1.38V) which denotes that it is strongly oxidizing and unstable in the presence of electron donors. Oxidation of Cr(II) to Cr(III) occurs in basic solutions. Powerful reducing agents such as hydrazine, hydrosulfide, etc are utilized in preparation of Cr(III) from Cr(VI).

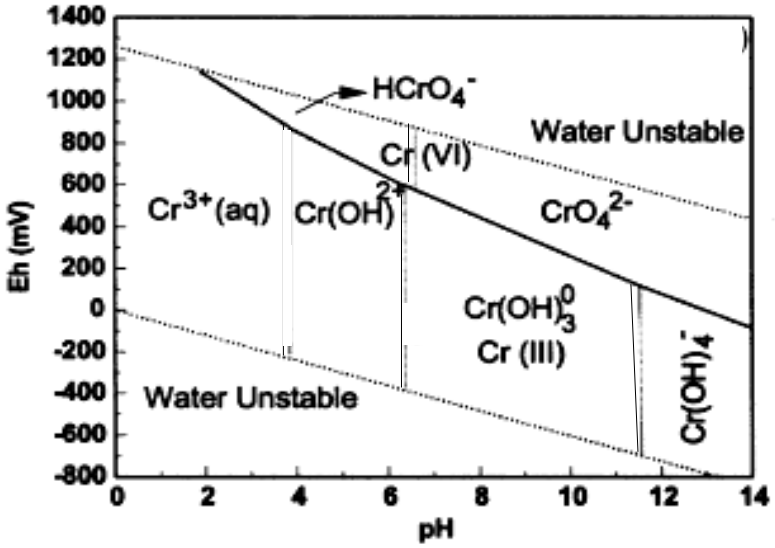

Figure 1.3 Pourbaix diagram for chromium species (Rai et al., 1987).

The Pourbaix diagram (figure 1.3), show the determinant chromium species in aerated diluted aqueous solutions in the absence of any complexing agents except water and hydroxide ion. The figure also show conditions of pH and potential under which chromium species are thermodynamically stable provided they exist in diluted aqueous solution, in the presence of air and absence of any complexing agent, other than water and hydroxide ion. These conditions are ideal, they do not consider the kinetic constraints which exist in the environment, and therefore its actual form may differ from that predicted by this diagram.

Trivalent chromium has 3d- electrons that are in a high spin state in an octahedral complex. The crystal stabilization for Cr(III) is the highest for all transition metals (Pearson, 1996). This set of characteristics result in the formation of strong kinetically inert complexes and a high stability of the hydration ion sphere which impose limitations on the mechanism of electron transfer reactions. Cr(III) is strongly hydrolyzed in aqueous

solutions and readily forms compounds such as $Cr(OH)_3$ and $(Cr,Fe)(OH)_3$. The predominant species in the pH range 6.5 – 10.5 is $Cr(OH)_3$ according to reported hydrolysis constants (Rai et al., 1987). Cr(III) has a very low solubility and a strong tendency to adsorb onto surfaces (Sass and Rai, 1987). The relatively low solubilities of $Cr(OH)_3$ and $(Cr, Fe)(OH)_3$ limit Cr(III) concentrations to less than the drinking water limit over much of the pH range of environmental interest.

The forms of chromium and their concentrations present in any environmental conditions are determined by different chemical and physical processes such as redox reactions hydrolysis, complexation and adsorption. The complexity of the processes that governs chromium speciation prompts further investigation and the refinement of reliable analytical methods.

When donor atoms are bound in a macro molecular system, such as humic acids, the Cr(III) complexes are less mobile due to complexation with liquids found in natural systems. Chromium is expected to be removed from the solution as $Cr(OH)_3$ precipitate, or in the presence of Fe(III), removed as $(Cr_x, Fe_{1-x})(OH)_3$ form, (where x is the mole fraction of Cr) (Rai et al., 1987; Deshpande et al., 2005). During hydrolysis of Cr(III) as the pH increases, the $Cr(H_2O)_6^{3+}$ which is a moderately strong acid, deprotonates into $Cr(OH)^{2+}$ and $Cr(OH)_3$ successively within pH 4 – 10.

Hexavalent chromium forms anionic oxy-compounds that also have an adsorption affinity for certain proton – specific mineral surfaces, although their adsorption is limited in natural aqueous systems by the presence of competing anions like sulfate (Zachara et al., 1987). The distribution of Cr(VI) species depends on pH, redox potential and total Cr(III)

concentration. The main aqueous species of Cr(VI) are $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$. Figure 1.3 shows that Cr(VI) is stable at positive redox potential in an alkaline medium (like in concrete environment) and is a strongly oxidizing agent that occurs as the orange dichromate ion $Cr_2O_7^{2-}$. At pH>6, CrO_4^{2-} is the major species, whereas at pH<6 $HCrO_4^-$ dominates. Below pH 4, H_2CrO_4 is the dominating Cr(VI) species (Tandon et al., 1984; Cotton and Wilkinson, 1980). Under alkaline conditions $Cr_2O_7^{2-}$ is present in high concentration. (Cotton and Wilkinson, 1980).

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \qquad K = 10^{-5.9} \qquad (1, 1)$$

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \qquad K = 4.1 \qquad (1, 2)$$

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^- \qquad K = 10^{-2.2} \qquad (1, 3)$$

In natural systems, there are few oxidants capable of oxidising Cr (III) to Cr(VI) because of high redox potential of the Cr(VI)/ Cr(III) couple. Oxidation of Cr(III) by dissolved oxygen and manganese has been reported (Eary and Rai, 1987; Bartlett and James, 1979; Nakayama et al., 1981; Saleh et al., 1989, Johnson and Xyla, 1991).

1.2.2 Toxicity and effects of chromium species

Metal toxicity is defined as a process whereby an organism cannot tolerate the additional metal concentration by direct usage or storage (Morrison et al., 1989). It is determined by several factors: compound-related (dose and duration of exposure, route of exposure, physical and chemical form of metal), characteristic of the organism (genetic factor, sex,

age, species, lifestyle and physiological state) diet and environmental conditions (Rose, 1983).

Trivalent chromium is essential for animal and human health at trace levels (Ali and Aboul – Enein, 2006). It plays a role in the potentiation of insulin, gene expression and nucleic acid metabolism (Irwin, 1997). Cr (III) is a nutrient element used for the control of glucose and lipid metabolism in cell membranes. Cr(III) is readily available from our diets. According to the National Academy of Science (El-Shahawi et al, 2005; Irwin, 1997), a safe, adequate daily intake of chromium is 50 to 200 micrograms per day. Food sources which have high chromium content include cereals, meat, fresh vegetables, fish, bread and beer (Anderson, 1989). Cr (III) deficiency could result in impaired fertility, elevated percent body fat, cardiovascular disease and maturity-onset diabetes (WHO, 1996).

Hexavalent chromium is highly toxic and is a known human carcinogen and mutagen (Irwin, 1997; Lide, 1998; Frias and Sa'nchez de Rojas, 1995; Potgieter et al., 2003; Kristiansen et al., 1997; Pillay et al., 2003; Bartlett and James, 1979; Mori et al, 2001; El-Shahawi et al, 2005; Deshpande et al., 2005; Ali and Aboul – Enein, 2006; Skovbjerg et al., 2006). Cr(VI) easily penetrates biological membranes and due to its strong oxidizing ability, physical contact can lead to corrosion and irritation. The structural similarity of CrO_4^{2-} to SO_4^{2-} makes it overcome the cellular permeability barrier, and oxidatively damage DNA due to the production of more transient Cr(V) and Cr(VI) species. It is important to note that the toxic effects of Cr(VI) are dependant on the duration of exposure and the dose. Skin contact with Cr(VI) can cause two types of dermatitis,

namely; primary irritant dermatitis and an immunological type IV response in sensitive individuals. Inhalation exposure includes the following effects; chronic rhinitis, congestion, hyperemia, chronic bronchitis and ulceration of the nasal mucosa. Inhalation of Cr(VI) particulates has also been associated with cancer (Lide, 1998; www.atsdr.cdc.gov). Other toxic effects of Cr(VI) include: renal tubular necrosis, mild liver abnormalities and occupational exposure has been associated with increased lung cancer mortality.

1.3 Chromium in cement and cement products

Chromium is a naturally occurring element in natural environment found in rocks, animals, plants, soil, and in volcanic dust and gases. High amounts of chromium are found naturally in minerals, namely chromite which is common and crocoite which is extremely rare (Viljoen & Reimond, 1999). However, only the trivalent, iron chromite ($FeCr_2O_4$) occurs in substantial quantities so that it can be mined (Barnhart, 1997). Chromium enters the environment mainly through the natural weathering of chromite ores. The most elevated concentrations of Cr(VI) found in the environment are the result of industrial pollution (Barnhart, 1997). Chromium ores are mined today in South Africa, Zimbabwe, Finland, India, Kazakhstan and the Philippines and a total of 14 million tonnes of chromite ore is extracted.

The most common sources of chromium emissions to the environment include: cement producing plants, combustion of natural gas, oil and coal, metal finishing industry, (e.g.

chrome plating), chemical manufacturing industry, (e.g.: dyes for paints, leather tanning, rubber and plastic products), incineration of council refuse and sewage sludge, manufacturers of pharmaceuticals (wood, stone, clay and glass products), electrical and aircraft manufacturers, steam and air conditioning supply services (Lide, 1998).

The interest in chromium speciation in cement especially in South African environment originates from the fact that the major source of chromium is mineralogical, basically in all cement ingredients. RSA and Russia account for more than half of the world chromite production while most of all the worlds known chromium reserves are located in the South Eastern region of the continent of Africa. South Africa has about 68.3% and Zimbabwe with about 11% of the reserves. In addition to that, South Africa ranks 8th in the world in iron ore production and is the worlds leading exporter of chromium and manganese ferro-alloys (Viljoen & Reinold, 1999).

Chromium exists as a trace element primarily from the raw materials utilized in cement manufacture. The chromium is mainly in form of Cr (III), which is inert and insoluble, but during the clinkerisation process, the Cr (III) can partly be oxidized to Cr (VI) (Frìas and Sànchez de Rojas, 2002). It is generally assumed that all hexavalent chromium present as chromate is likely to be water soluble which may not always be the case (Frìas and Sànchez de Rojas, 1995; Borros et al., 2004; Potgieter et al., 2003; Yamaguchi et al, 2006; Laforest and Duchesne, 2005). The pure gypsum employed in cement manufacture consists of chromate which is normally low or negligible.

The chemical speciation of chromium in environmental systems depends upon oxygen content, presence of organic matter, pH, solubility, nature of other chemical species, and

many other factors of solution chemistry. The processes that control the environmental chemistry of chromium include redox transformation, precipitation/dissolution, and adsorption / desorption reactions. Commonly occurring reductants, such as ferrous iron and organic material, can transform Cr(VI) to Cr(III), but manganese oxides are the only inorganic oxidants found in the environment that cause the rapid oxidation of Cr(III) to Cr(VI) (Rai et al., 1987).

Chromium compounds have never been deliberately added to cement (except in China to adjust concrete setting time) (Kristiansen et al., 1997). Historically it has typically contained approximately 50 parts per million (ppm) of chromium in its hexavalent state (Kristiansen et al., 1997). The hexavalent chromium arise from the oxidation of traces of trivalent chromium in the raw materials - chromium compounds occur naturally in the Earth's crust, so raw materials do contain chromium. This could be a serious problem for cement producing companies in South Africa where chromium is found at higher levels that most other countries.

The production of Portland cement clinker in rotary cement kilns uses many sources of calcium, aluminum, silicon and iron oxides as raw materials. Chromium is always present in the charge as an inessential element. On average, 16 ppm of chromium is found in limestone and 100 ppm in clay (Barros et al., 2004). 80 ppm in char and 50 ppm is found in oils, which are fuels used in rotary cement kilns. Another source of chromium is the contamination from abrasive wear that happens on the cast iron balls used during the milling of the raw material in ball mills and mineral admixtures (accelerators and retarders) (Frias and Sa´nchez de Rojas, 1995). The use of bauxite as a source of alumina

may also increase the amount of chromium in the final product. In concrete structures, stainless steel is sometimes used to strengthen buildings. Stainless steel is known to contain approximately 10 % chromium.

The main concern in the cement application is the potential leaching of hexavalent chromium from concrete structures such as water reservoirs, transport pipes, buildings, which can lead to contamination of groundwater (Potgieter et al., 2003).

The amount of chromium in cement is under scrutiny world-wide. In Europe, new restrictions on the amount of Cr(VI) in cement came into force on 17 January 2005.The Control of Substances Hazardous to Health (Amendment) Regulations 2004 (COSHH, 2004) prohibits the supply or use of cement which has a Cr(VI) concentration of more than 2 parts per million. In addition, information on safe shelf life must be provided, since most reducing agents are effective for a certain period. The restriction will apply to a wide range of products that contain cement such as mortars, grouts, tile adhesives etc.

The legislation is being introduced to alleviate the toxic effects of chromium (e.g.allergic contact dermatitis, a potentially serious condition that can lead to permanent disability, which can occur when wet cement containing Cr(VI) comes into contact with the skin). While construction workers such as bricklayers, tile layers, and workers laying concrete floors are likely to be at most risk, this condition can occur to members of the public who use cement or products containing cement without taking proper precautions.

1.3.1 Cement and concrete

Over six billion tons of concrete are made each year, amounting to the equivalent of one ton for every person on Earth, and powers a US$35 billion industry which employs over two million workers in the United States alone (www.bamburicement.com). Over 55,000 miles of freeways and highways in America are made of this material. China currently consumes 40 % of world cement production. South Africa is the third largest cement consumer in Africa, following Egypt and Algeria, and accounts for about 14 % of all cement consumed in Africa (Coakley and Dolley, 1997).

Cement

The word cement refers to powdered materials which have strong adhesive qualities of hydraulic binders when combined with water. Cement is a material used for bonding other materials together, and as a binder in concrete. These materials are more properly known as hydraulic cements, the hydraulic binders are non-metallic inorganic materials that react with water and then harden fast to form durable and volumetrically stable materials. (Mantel, 1991)

Cement Additions

Fly ash is a by-product of coal-fire electric generating plants; it is used to partially replace Portland cement by up to 40 % by weight. *Ground granulated blast furnace slag* is a by-product of steel making, it is used to partially replace Portland cement by up to 50 % by weight. *Silica fume* is a by-product of the production of silicon and ferrosilicon alloys, it is used to increase strength and durability of concrete**.**

1.3.2 Cement manufacture and concrete properties

The manufacturing process involves: quarrying, mixing, grinding, burning, and milling (Mantel, 1991). The figure 1.4 illustrates the manufacturing process and it sets out all the five stages involved.

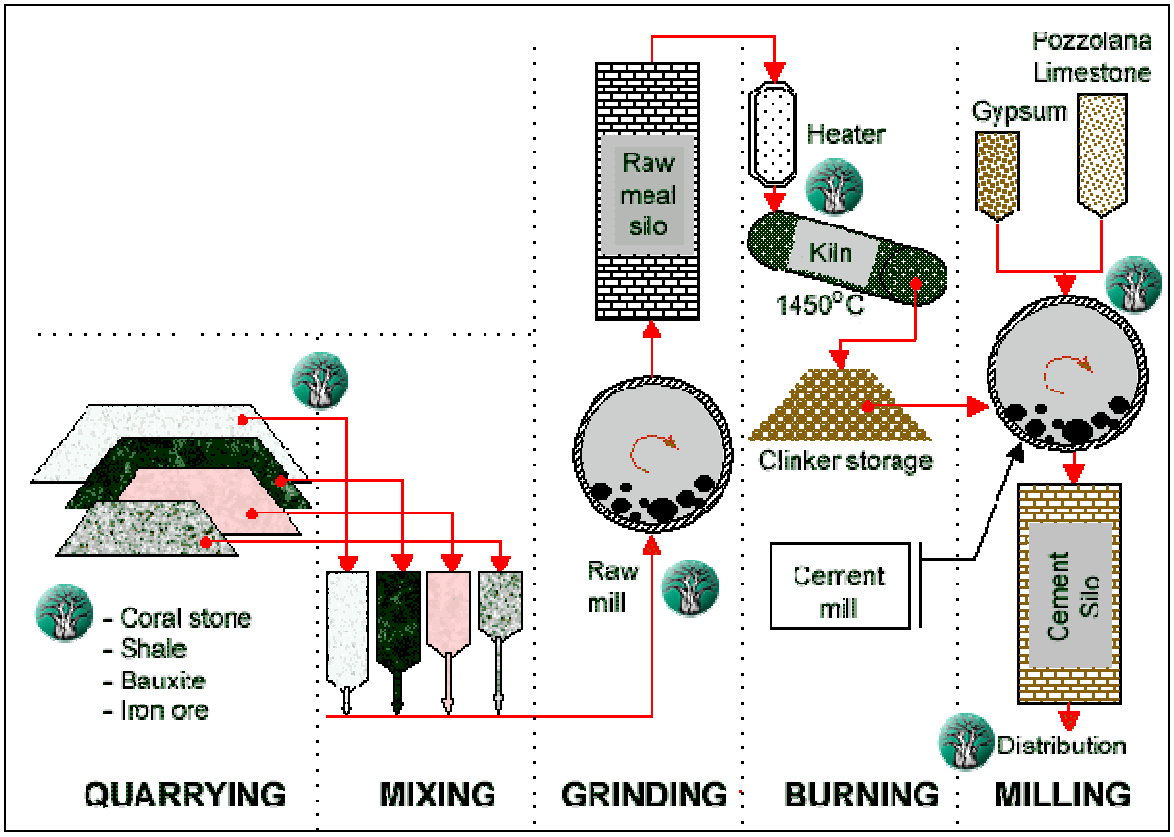

Figure 1.4 Cement manufacturing process (www.bamburicement.com)

Quarrying/mining is where the economic extraction of a chemically consistent raw material (raw mixture) is done. The most commonly used raw materials are; limestone /coral stone, shells, and chalk or marl combined with shale, clay, slate or blast furnace slag, silica sand, iron ore and gypsum. The raw materials are then crushed to smaller particles less than 19 mm.

Mixing – Where the raw materials are crushed to a fine powder so as to achieve the required particle-size for optimal fuel efficiency in the cement kiln and strength in the final concrete product. The coarse particles are separated from the fine particles and returned to the mill for further grinding whilst the fine particles are transferred to a blending silo.

Grinding - In the raw mill, all the raw materials used to produce clinker are milled together in calculated ratios to produce a fine powder. The meal in the blending silo is the fine powder content mixed properly before they are sent to the kiln feed silo.

Burning – The raw meal is fed into the kiln and burned at a temperature of 900 ^{0}C at the entrance of the kiln and 1450 ^{0}C at the lowest zone using oil and / or coal, in this stage clinker is prepared and it consists of; hard, grey, spherical nodules with diameters ranging from 0.32 – 5.0 cm. The clinker is then cooled down by blowing cold air through a special chamber. In the lower-temperature part of the kiln, calcium carbonate (limestone) turns into calcium oxide (lime) and carbon dioxide. In the high-temperature part, calcium oxides and silicates react to form dicalcium and tricalcium silicates (C_2S C_3S). Small amounts of tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) are also formed.

Milling - Clinker is fed into a ball mill where it is ground into a fine powder, then a small amount of gypsum is added to the clinker, which is mixed with other additives like pozzolan and filler added to the mill depending on the type of cement being manufactured (final cement product). The gypsum is added to slow down the setting of the cement.

Table 1.1 Typical constituents for Portland clinker and Portland cement as per cement industry style. (Mantel, 1991)

Clinker	Weight %	Cement	Weight %
Tricalcium silicate $(CaO)_3.SiO_2$, C_3S	45-65 %	Calcium oxide, CaO, C	62-67 %
Dicalcium silicate $(CaO)_2.SiO_2$, C_2S	15-30 %	Silicon oxide, SiO_2, S	20-25 %
Tricalcium aluminate $(CaO)_3.Al_2O_3$, C_3A	1-8 %	Aluminium oxide, Al_2O_3	3-7 %
Tetracalcium aluminoferrite $(CaO)_4.Al_2O_3.Fe_2O_3$, C_4AF	8-15 %	Ferric oxide, Fe_2O_3	2-5 %
Gypsum $CaSO_4$	1-3 %	Sulfate	

The high temperatures of the kilns provide oxidative conditions that oxidize naturally occurring Cr(III) in the raw materials to the toxic Cr(VI). The high energy requirements (~1700 J/g) and the release of significant amounts of carbon dioxide make cement production a concern for global warming. Cement manufacturing emits 0.2 Pg C/yr as CO_2. (1 Pg = 1 billion metric tons.) In addition, Portland cement plants have been identified by the USEPA as major sources of hazardous air pollutants (HAP) emissions, including hydrocarbons, hydrochloric acid (HCl), and polychlorinated dibenzo-*p*-dioxins and polychlorinated furans (PCDD/F) (Sidhu et al., 2001).

Concrete

Concrete is a mixture of a binding agent (generally cement) bonding materials together such as fine aggregate (sand), coarse aggregate (gravel/stones), and water. A typical composition is about 7-15 % cement, 14-21 % water and the rest aggregate. The primary properties of concrete are workability before hardening, strong in compression and stays strong for extremely long timescales. Concrete can be cast in almost any shape desired, and once hardened, can become a structural (load bearing) element. Concrete is used for our modern global infrastructure because it is used to build roads, houses, dams, water treatment systems, schools, hospitals and many other structures that stand today.

Characteristics of concrete

The *water/cement ratio* (w/c) of the mixture has a control over the final properties of the concrete. The water/cement ratio is the relative weight of the water to the cement in the mixture. The w/c ratio gives control over strength and workability. A mixture with a high w/c will be more workable than a mixture with a low w/c: it will flow easier. Typical values of w/c are between 0.35 and 0.40 because they give a good amount of workability without sacrificing a lot of strength (http://en.wikipedia.org/wiki/Concrete).

Durability is the ability of concrete to last a long time without significant deterioration. Concrete is virtually the only material used for the construction of wastewater transportation and treatment facilities because of its ability to resist corrosion caused by the highly aggressive contaminants in the wastewater stream as well as the chemicals added to treat these waste products.

Concrete admixtures

Admixtures are organic or non-organic materials in the form of solids or fluids that are added to the concrete to give it certain characteristics. In normal use the admixtures make up less than 5 % of the cement weight and are added to the concrete at the time of batching/mixing. The most used types of admixtures are: *Accelerators*: Speed up the hydration (strengthening) of the concrete. *Retarders*: Slow the hydration of concrete. *Air-entrainers:* Add and distributes tiny air bubbles to the concrete, which reduces damage due to freeze-thaw cycles. *Plasticizers*: are used to increase the workability of concrete, allowing it be placed more easily with less compactive effort. *Superplasticisers* allow a properly designed concrete to flow around congested reinforcing bars. Alternatively, they can be used to reduce the water content of a concrete (termed water reducers) yet maintain the original workability. This improves its strength and durability characteristics *Pigments*: Change the colour of concrete for aesthetics.

Factors contributing to concrete destruction

As the concrete sets, the *water* evaporates and leaves behind some voids in the concrete. These voids weaken the concrete and results in cracks and small holes in the surface. When corrosives, water, and freezing water gets into these gaps, the material is eroded and the strength of the concrete is weakened.

Excessive amounts of *sulfates* in soil and water can attack and destroy a concrete that is not properly designed. Sulfates (e.g. calcium sulfate, sodium sulfate and magnesium sulfate) can attack concrete by reacting with hydrated compounds in the hardened cement paste. These reactions can induce sufficient pressure to cause disintegration of the

concrete. High alkalinity of concrete results in an adhering protective layer (Fe_2O_3) of the embedded steel. *Chloride ions* can penetrate and depassivate this protective layer and initiate corrosion. Sulfates and chlorides in seawater require the use of low permeability concrete to minimize steel corrosion and sulfate attack.

Alkali-Silica Reaction is an expansive reaction between reactive forms of silica in aggregates and potassium and sodium alkalis, mostly from cement, but also from aggregates, pozzolans, admixtures, and mixing water. The reactivity is potentially harmful only when it produces significant expansion. It is characterized by a network of cracks, closed or spalling joints, or movement of portions of a structure.

The most potentially *destructive weathering factor* is freezing and thawing while the concrete is wet, particularly in the presence of de-icing chemicals. Deterioration is caused by freezing of water and subsequent expansion in the paste and the aggregate particles.

The calcium hydroxide present in concrete are attacked by *carbon dioxide* from the air and are converted to calcium carbonate, the is process called *carbonation*. The carbonation process results in lowering of the pH to about 7and thus decrease of the porosity of the concrete and increases the concrete strength, of non reinforced concrete. It is a serious disadvantage in reinforced concrete, as the pH of carbonated concrete drops to about 9 - 10; a value below the passivation threshold of steel. Chemical fixation of waste in cement based materials, attributed to the solubility reduction of metals at high pH, can be ruined (Macias et al., 1997; http://en.wikipedia.org/wiki/Concrete).

CHAPTER 2

Aims and objective of the study

In Europe, there is a restriction on the amount of Cr(VI) in cement which prohibits the supply or use of cement which has a Cr(VI) concentration of more than 2 parts per million (COSHH, 2004) due to its carcinogenic effects on human health (mainly cement dermatitis). Chromium levels and speciation must be constantly monitored to ensure minimal environmental impact (Frìas and Sànchez de Rojas, 2002). Holcim (SA), (an international company) as well as most of the worlds cement producers is embarking on this study to find an efficient Cr(VI) immobilizing and reducing agent in South African climatic conditions. South African raw materials for cement are likely to be far richer in chromium than those of other parts of the world (Viljoen and Reimond, 1999). In a study on SA cements by Potgieter et al. (2003), reported their data for water soluble Cr(VI) to be approximately 26.6 ± 3.1µg/g which is far higher than the European standards.

Cr(VI) is cannot be removed from the raw cement economically, but must be reduced to Cr(III) (Kristiansen et al., 1997 Yu et al., 2005; Potgieter et al., 2003; Wang and Vipulanandan, 2000). Even if Cr(VI) can be successfully reduced to Cr(III) in the cement manufacturing process there exist a significant risk of re-oxidation during post production. Exposure of cements and concrete to substances such as manganese oxide, which is highly abundant in SA environment can lead to oxidation of Cr (III) to Cr (VI).

The leaching in SA conditions described by Potgieter et al (2003), involved boiling for 10 minutes, cooled and treated an ultrasonic bath for 2 minutes, which is not close to

environmental leaching of Cr(VI), and there is a serious potential of oxidizing Cr(III) by boiling the samples hence increasing the error (Korolczuk and Grabarczyk, 2005; etc). The other methods including the standard TCLP method of leaching is too harsh for cementitious material as it is acidic ~ pH 4, Li et al., 2001, Rauret et al., 1999) The concrete needs to be crushed to a fine powder which deviate the procedure more from reality. Therefore a better method is necessary. Methods of analysis have their own drawbacks which have been discussed in the literature e.g. higher detection limit which is a problem with low Cr(VI) content AAS (Potgieter, 2003).

The objectives of this project include:

- The identification and optimisation of a method for the determination for chromium species in concrete samples.
- The comparison of locally developed chromium analysis standard method with European standard method.
- Determination of hexavalent chromium and total chromium in different kinds of cements and in concrete.
- To investigate the mobility and leachability of hexavalent chromium in cement and in concrete samples (surface reactions).
- To investigate the conditions resulting in the re-oxidation of chromium in cement and concrete. (Effects of cement components (MnO_2 and Fe_2O_3), temperature, pH).
- To investigate possible technologies for reduction of Cr (VI) to Cr (III) and the potential of immobilization / stabilization of Cr (VI) in cement matrix.

CHAPTER 3

Literature review

3.1 Aspects of Hexavalent chromium determination

Due to the different toxicity of chromium species, total chromium measurement cannot be used to determine the actual environmental impact. Thus, chemical speciation of chromium in environmental samples is necessary to accurately assess pollution levels (El-Shahawi et al, 2005). Recently there is an upsurge of interest for rapid and sensitive analytical methods for the determination and speciation of chemical forms of toxic metal ions in environmental samples.

Trivalent chromium has lower human toxicity and is also less environmentally mobile due to its low solubility and its tendency to be less absorbed or complexed by organic molecules making its disposal an acceptable environmental risk (Pillay et al., 2003; Rinehart et al., 1997; Bartlett and James, 1979). With its large positive charge, Cr(III) is attracted to negatively charged soil particles, and has been found to associate with the smallest size fractions in soils. Thus, Cr(III) is less mobile in soils than Cr(VI).

Hexavalent chromium is an oxyanion commonly occurring as relatively water soluble chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$). In temperate region soils, where negatively charged clay minerals predominate, these Cr(VI) anions are repelled by the negative charge on the soil particles (Pettine et al., 1998; Rinehart et al., 1997; Zachara et al., 1987). Due to the charge repulsion and the solubility of the Cr(VI) compounds, hexavalent chromium compared to Cr(VI) is quite mobile in soils, hence, in concrete. The

Cr(VI) form is a strong oxidizer which makes it the more toxic form to biological systems.

Most publications pertaining to chromium speciation in environmental samples are in aqueous environments. Determination of Cr(VI) especially in solid samples is regarded as one of the most challenging speciation tasks due to inter-conversions between Cr(VI) and Cr(III) in the course of the analytical process. (El-Shahawi et al, 2005; Yamaguchi et al., 2006; Borai et al., 2002 ; Mori et al, 2001; Kristiansen et al., 1997; Frias and Sa´nchez de Rojas, 1995; Bartlett and James, 1979).

In acidic solutions, especially in the presence of dissolved organic compounds and sulfides, there exists a risk of Cr(VI) reduction to Cr(III). In an alkaline medium on the contrary, Cr(III) oxidation may occur (Pettine et al., 1998). Hence, the selection of an appropriate analytical method should take into account: the type of matrix (natural water, effluents, cements, sediments, biological materials, etc.), the concentration level of the chromium forms and the presence of substances, which may disturb the chemical equilibrium between the chromium oxidation states (Bobrowski et al., 2004; Yamaguchi et al., 2006).

Although much research has been focused on the separation and detection of dissolved chromium species in aqueous mixtures or in relatively clean liquid environmental samples, the chemical process of solubilization, digestion and/or extraction of Cr(VI) in solid-waste materials has not been adequately addressed. The usual acid digestion for preparation of solids is inappropriate because Cr(VI) is reduced in acidic media if any reductants, such as organics or oxidizable inorganics, are present, and this is typically

true for environmental samples. The cement matrix is complicated and contains a variety of chromium interacting elements such as Mn, Fe and etc. (Borai et al, 2002; Yamaguchi et al., 2005; Kristiansen et al, 1997).

In order to determine the oxidation states of chromium in solid samples by most analytical techniques, it is required that prior to the analytical determination, the chromium must be extracted from the solid, as has been recently described by several authors (Korolczuk and Grabarczyk, 2005; Borai et al, 2002; Yamaguchi et al., 2005). The chemistry involved in such extraction steps or in the total dissolution of the solid can be a significant source of uncertainty and error in the determination of chromium oxidation states, depending on the nature of the solid material under investigation.

Cement may contain traces of reducing agents, which are inefficient, for example, sulfates and organics depending on the kind of cement (Toregö, 2006). Organics does not reduce Cr(VI) in alkaline solution, but when the cement extract is acidified during standard routine analysis, Cr(VI) is reduced, giving rise to a false-negative result (Kristiansen et al., 1997). In view of this, the Danish Working Environment Service demanded a revision of the Danish standard method for the determination of extractable chromate in cement.

There are a variety of the instrumental techniques for chromium trace determination in liquid samples which may be divided into two main groups: namely; (a) Valence specific, spectrophotometric methods with diphenylcarbazide or adsorptive stripping voltammetry (AdSV), mainly utilizing the catalytic system Cr(III)–diethylenetriammine-pentaacetic

acid (DTPA)–NO_3. The above methods are based on the different ability of complex formation by Cr(III) and Cr(VI).

(b) Valence-non-specific methods based on the preliminary valence-specific separation of both chromium forms or on selective removing of one chromium species from the sample and subsequent, non-specific measurement of the separated form by means of AAS, ICP-AES or ICP-MS (Bobrowski et al., 2004). Several methods for chromium determination based on coprecipitation, ion exchange, and solvent extraction, followed by spectrometric, chromatographic, and electrochemical detection, have been developed for the speciation of chromium in environmental samples (Talebi, 2003) but not necessarily for concrete leachate samples.

UV/VIS spectrophotometry the method prescribed by European Union (EU) for Cr(VI) analysis in cement (Klemm, 1994). Adsorptive stripping voltammetry is the most sensitive, convenient and cost effective analytical methods for detection and quantification Cr(VI) for routine application, and can simultaneously be used to analyze other related metals in aqueous samples (Bobrowski et al., 1997; Thomas et al., 2002; Bobrowski et al., 2004).

A high-performance liquid chromatographic method with diode array detection based on the chelating agent ammonium pyrrolidine dithiocarbamate has been developed for the analysis of chromium species (Cr^{3+}, CrO_4^{2-} and $Cr_2O_7^{2-}$) (Borai et al., 2002). The method was found capable for discriminating not only between Cr(III,VI), but also between the chemical forms of chromium(VI): CrO_4^{2-} and $Cr_2O_7^{2-}$. Another study (El-Shahawi et al,

2005), described a simultaneous, convenient and low cost solvent extraction spectrophotometric procedure for the chemical speciation of chromium(III,VI) in water samples employing $TPAs^{+}Cl^{-}$ and/or $TPP^{+}Br^{-}$ as ion-pair reagents.

In the study of the effect of Cr(VI) on a solid sediments and its leachability, (Morales-Muñoz et al., 2004) where extraction was followed by analysis using UV-Vis spectroscopy with DPC. In another study by Weng and Vipulanandum (2000), X-ray diffraction was used and found to be a useful analytical technique which does not change the physical form of sample and also characterizes the crystalline phases of the solidified sample. Information from such studies was used to obtain the immobilization mechanisms and reactions occurring in the solidification / stabilization process.

The content of Cr(VI) in cement has been estimated as soluble Cr(VI). Yamaguchi et al (2006) cited that Japan's JCAS I-51 and Germany's TRGS613 analytical methods for determination of soluble Cr(VI) have been widely published. According to the JCAS I-51, the soluble Cr(VI) is determined by a kind of leaching test using deionized water, a high *L*/*S* (leachate to sample ratio = 100) and a short duration (~10 min). However, some part of Cr(VI), which is contained in the solid solution of the calcium silicate minerals, cannot be detected in this short leaching time (Wang and Vipulanandan 2000; Yamaguchi et al., 2006).

In another application hexavalent chromium was determined (as chromate) by ion chromatography (IC), as described in US Environmental Protection Agency (EPA) Method (Thomas et al., 2002). This method specifies the use of a high- capacity IonPac

AS7 anion-exchange column and UV–Vis detection after post column reaction with diphenylcarbazide for the analysis of chromate in drinking water, groundwater and industrial wastewater effluents. This method permits a detection limit of 0.4 ppb.

In a study of Cr(III) oxidation to Cr(VI) in a stainless steel slag (Kilau and Shah, 1984; Pillay et al., 2003), evidence was presented that the slag compositions undergo atmospheric oxidation of trivalent to hexavalent chromium at ambient temperatures. It was also reported that stainless steel slag has a composition that favours formation of calcium chromite ($CaO\text{-}Cr_2O_3$) and the role played by the calcium oxide in the reaction and other environmental conditions were investigated. These results were also confirmed in another study where atmospheric oxygen, moisture, slag particle size and larger amount of CaO increased the rate of the oxidation reaction. The leached solution was analyzed for hexavalent chromium using UV/VIS spectrophotometry with diphenylcarbazide.

An ideal extraction method would extract the metal efficiently without converting metal ions from one oxidation state to another. Although much research has been focused on the extraction and detection of chromium species in liquid samples such as natural and waste waters, the extraction of Cr(VI) from soil samples requires an additional effort. The difficulty in determining Cr(VI) species in solid samples arises from the possible changes taking place in the chromium oxidation state (Morales-Muñoz et al., 2004; Korolczuk and Grabarczyk, 2005; Yamaguchi et al., 2005).

The multi-element ICP-AES and the AAS methods require the use of expensive apparatus, not always available in industrial laboratories, the sensitivity of the ICP-AES

method and that of flame AAS method is not always sufficient to determine the concentration of metal ions on the 0.1 - 10 ppb level (Bobrowski et al., 1997; El-Shahawi et al, 2005). The Graphite furnace atomic absorption spectrometry (GFAAS) method has the appropriate sensitivity; however, the presence of great amounts of sodium and calcium ions in the leaching solutions may pose some problems with accurate determination of toxic metals traces by this method.

The determination of chromium by (EU) spectrophotometric method based on oxidation of organic compounds and formation of ion associates has the disadvantage of high blank value, it suffers severe interference from Fe(III), Mo(VI), Cu(II) and Hg(II) (Narayana and Cherian; 2005). The Adsorptive stripping voltammetric method (AdSV), used in many countries as the standard method for the determination of the traces of some heavy metals in waters and leachates, is free from these limitations and is perfectly suitable for Cr(VI) determination in the presence of an excess of sodium, calcium, magnesium, iron and aluminum ions which cannot be excluded in cement and concrete samples.

A major problem is however the lack of a reliable analytical method to extract or leach the Cr(VI) species successfully from the solid cementitious matrix, without affecting the dynamic character of the ion. Most publications connected with chromium speciation in environmental samples, are dealing with liquid samples, like natural and waste waters, while selective determinations of chromium species in solid samples have not been well described especially for concrete samples.

3.2 Leachability of Hexavalent chromium in cement materials

Leaching is the process by which contaminants are transferred from a stabilized matrix to liquid medium, such as water or other solutions. A number of studies proved that the leachability of metals in waste materials is controlled by the solubility of metal compounds in the leachate (Malviya and Chaudhary, 2006).

The main aspect in respect of the environmental impacts of cement-based materials is the leaching of heavy metals when they are in contact with environmental waters, e.g. rain or groundwater. Cement materials including fly ash contain trace amounts of heavy metals and other toxic inorganic components, hence, there is pollution occurring due to the elution of the metals or components to environment, from construction works in which cement and fly ash containing materials are applied (Yu et al.2005; Mori et al., 2001). In addition, the rising concern is how to assess and prevent or reduce their release to the environment.

The main concern to cement producers is the potential leaching of hexavalent chromium from cement and concrete used in building structures such as water reservoirs, transport pipes, buildings, etc, which can lead to contamination of ground and surface waters (Potgieter et al., 2003). The possible processes that may be responsible for the release of Cr(VI) from chromite containing materials include; desorption of sorbed Cr(VI), conversion of Cr(III) to Cr(VI) and dissolution of Cr(VI) – containing solid phases (Geelhoed et al., 2003; Geelhoed, 2002). Chromate ions adsorb to positively charged

surfaces of oxides, hydroxides and clay minerals, but at high pH, these surfaces will be negatively charged, therefore it is unlikely that the release of Cr(VI) will be from desorption. Most of the fraction of total chromium exists as Cr(III), that indicates the importance of oxidation kinetics on the speciation of chromium.

The most popular leaching methods used are static tank methods, which consist of placing monolithic samples made up of the paste (water/cement) , mortar (cement /sand / water), or concrete in a tightly closed plastic container with distilled water or a weak solution of nitric acid (pH = 4) (Bobrowski et al., 1997; Yu et al., 2005). This method allows investigations at arbitrary time intervals. The leaching after a definite time period or when only made up to volume medium may be exchanged after taking samples of the solution for investigation.

Another popular method of leaching heavy metals from mortars pastes and concretes is the DEV-S4 method (Yu et al., 2005). It consists of shaking with water, under some definite conditions, suitably prepared chips of the material to obtain a clear filtrate in which the contents of the selected elements as well as its pH and conductivity are determined. In many laboratories performing leaching tests simulating natural environments, different modifications of these methods are used.

In order to obtain information for the stabilization of hexavalent chromium in cement, the leaching behaviour of chromium in cement matrix must be investigated. Batch leaching experiments have been conducted on soil using simulated rainwater as a leaching solution with a pH adjusted to cover a wide rage from 2.0 to 12.0 (Thomas et al., 2002; Morales-Muñoz et al., 2004). The sample was leached with 1M NaOH and the leached solutions

were then analysed for chromium as chromite using X-ray spectromicroscopy analysis (Rose et al., 2003). No Cr(VI) was detected at pH less than 2.5, which may be attributed to absorption of Cr(VI) into the soil surface or its reduction by organic matter or ferrous ions. A considerable amount of Cr(VI) was leached between pH 4.5 to 12.

It has been recently learned that cement treated soils do leach hexavalent chromium (Frias and Sa'nchez de Rojas, 1995; Borros et al., 2004, Li et al., 2001) and that chromates are among allergens that are unavoidably widespread in the environment. It is imperative that analytical technologies be developed to reduce or eradicate Cr(VI) in cement applications and in the entire environment.

Sodium carbonate dissolution method was applied to determine the amount of hexavalent chromium in the raw materials of cement (limestone and gypsum below detection level) (Potgieter et al., 2003). It was found that Cr(VI) was at detectable level and higher, which proves that the chromium present in cement clinker is mainly due to contamination during the process. Sodium carbonate was successfully used for the leaching of hexavalent chromium in a cement matrix. There are few different leaching procedures for the determination of chromium at µg/g level from concrete matrix. In the same experiment, HNO_3 was used for total amount of chromium, de-ionized water for water soluble Cr(VI) and Na_2CO_3 for total content of Cr(VI). Alkaline leaching is ideal conditions for cement samples because of the alkaline pH of cement, even it in its application.

The leaching method using sodium carbonate results in a very basic environment and simulates the pH range that normally prevails during hydration of cement. Therefore

much higher values were obtained for hexavalent chromium in this environment which illustrates more realistically the potential hazardous environment in which cement manufacturers and cement users are exposed to. The water leaching method which simulate true environmental effect in case of rain showed that water – soluble Cr(VI) values are less than those of Na_2CO_3 leaching method. The results showed that 30 – 80 % of the total chromium content of cement clinker existed in the hexavalent form (Potgieter et al., 2003; Weng and Vipulanandan 2000). The extraction method, which involves the treatment of solid samples with a Na_2CO_3 solution is able to convert all insoluble compounds of Cr(VI) to soluble ones, is well known in classical wet analytical chemistry, and all of the other common metals, including Cr(III), precipitate as insoluble carbonates, oxides, hydroxides, or basic carbonates.

In another study (Trezza and Ferraiuelo, 2003), leaching tests were carried out on the 1, 3 and 6 months aged hydrate pastes using the toxicity characteristic leaching procedure (TCLP). A sample was ground to a powder with a particle size < 0.5 mm and leached in water and in acetic acid solution (pH = 3). Two hundred milliliters of water or solution was added to the 10 g sample in a bottle. The bottle and its contents were agitated in a rotary shaker for 18 h. The leached solution was analyzed and the Cr(VI) concentrations were reported. Cr(VI) was determined by colorimetric tests using a Lasa 20 equipment (Lee et al., 1995; Barros et al., 2004; Idachaba et al., 2002). The results obtained pointed out the importance of the factors related to the leaching tests, shaking time, the fineness of the specimens (Frias et al et al., 1994; Idachaba et al., 2002).

It was cited in the PCA report which summarized the determination methods for Cr(VI), Ellis and Freeman's method using Na_2SO_4 solution to leach the Cr(VI) from cement detected the highest Cr(VI) concentration. However, this method left a large amount of insoluble residue, so it is hard to believe that all of Cr(VI) in the cement was dissolved (Yamaguchi et al., 2006).

Another direct and precise method for the leaching of total Cr(VI) in cement samples was optimized by Yamaguchi et al., (2006) followed by the determination of the Cr(VI) concentration using UV-Vis spectrophotometry. The method consisted of digestion of 1.00 g sample with 10 ml HCl and the solution was neutralized using NH_4OH followed by filtration to remove Fe which interferes with diphenylcarbazide method of analysis.

In Japan, approximately ten percent of the total cement produced is used as a soil stabilizer for construction (Yamaguchi et al., 2006). It was found that the leachability of Cr(VI) from soils stabilized by cement was high in some cases. In one case, with a "volcanic cohesive soil", it was estimated that the amount of leached Cr(VI) from the stabilized soil was much higher than that which could be accounted for by the "soluble Cr(VI)" determined in the cement using the standard methods.

The amount of metal ions in leachant solution depended on the amount and kind of the immobilized metals. (e.g. low Chromium concentrations and in the case of chromium content from 20 µg/L to some hundreds mg/L Cr(VI)). In order to determine such concentrations, it is necessary to apply sensitive instrumental methods such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP AES) or adsorptive stripping voltammetry (Bobrowski et al., 1997).

Yu et al. (2005) reported that heavy metals are leached from cement mortars and solidified fly ash cement. The leachability of the tested heavy metals depended largely on the leachant pH and the leaching test method (Dermatas and Moon, 2006). The leaching of heavy metals is enhanced at lower pH. The tank method extracts less heavy metal compared to the shacking test method.

Many researchers have studied mechanisms of chromium immobilization in cemented media in the absence of an apparent reductive pretreatment. Palomo and Palacios (2003) used Portland cement and fly ash as stabilizing agents to evaluate chromium immobilization mechanisms. They found that the formation of $CaCrO_4$, which is highly insoluble, in a cement system accounted for low Cr leachability, while the formation of $Na_2CrO_4 \cdot 4H_2O$, which is highly soluble, in fly ash systems accounted for high Cr(VI) leachability. Wang and Vipulanandan (2000) also studied Cr leachability by using Portland cement. In their study, the formation of $CaCrO_4 \cdot 2H_2O$ was observed using X-ray diffraction (XRD) analyses. They also concluded that the immobilization of Cr(VI) was achieved due to formation of $CaCrO_4 \cdot 2H_2O$.

3.3 Oxidation of trivalent chromium

The oxidation and reduction reactions of chromium in soil and natural water are dependent on the presence of oxidants and reductants, respectively. The main oxidants of Cr(III) to Cr(VI) in soils are manganese oxides and molecular oxygen (Bartlett, 1979; Bartlett and James, 1988; Kim et al, 2002).

The forms of manganese oxides that commonly occur in the soil are Birnessite, todorokite, and lithiophorite. Pyrolusite was represented in a reagent grade chemical standard and has been used in earlier published papers on Cr oxidation. The birnessite, todorokite, and lithiophorite samples contained silica, smectite, and kaolinite that indicate the model minerals formed under weathering conditions similar to those for the Mn oxides in soils. Thus their kinetic properties should be relevant to soil systems. The rate of oxidation was greater for todorokite and birnessite that contained the most quadrivalent Mn and least for lithiophorite that contained a greater proportion of trivalent Mn determined by x-ray photoelectron spectroscopy (XPS) (Kim et al., 2002).

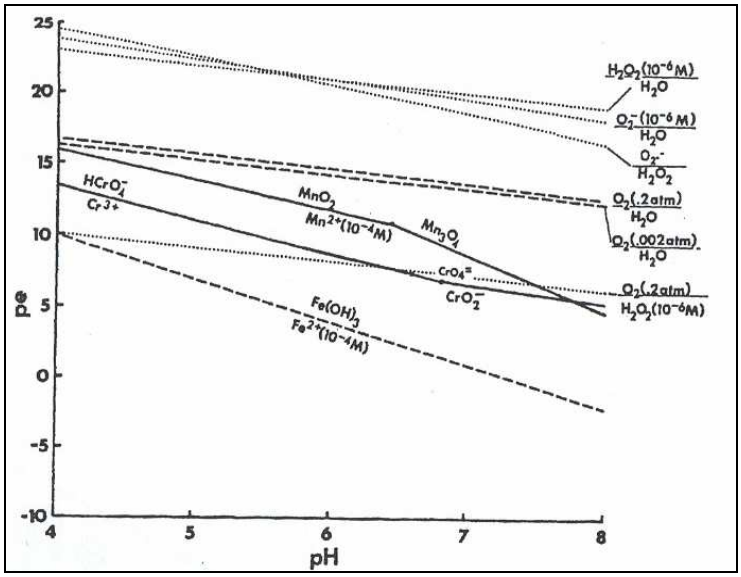

Figure 3.1 Relationship between pe and pH at 25^0C for various redox couples (Bartlett, 1979)

As shown in the Figure 2.1, the relative positions on the pe or Eh scale of redox couples signifies the stability of the reduced or oxidized species (Evangelou, 1998; Bartlett, 1979). For example, because MnO_2 (MnO_2 / Mn^{2+}) redox plateau is above that of Fe

(Fe^{2+} / Fe^{3+}), it reveals that MnO_2 has the potential to oxidize Fe^{2+} to Fe^{3+} throughout the pH range. In the process Mn^{2+} is produced. MnO_2 can also oxidize Cr^{3+} to Cr^{6+}, but at a pH < 8.

The oxidation of Cr(III) to Cr(VI) by Mn oxides in an aqueous system is complex and several factors have been credited with influencing the extent and rates of the processes involved. Adsorption mechanisms of Cr(III) on Mn oxides, is in competition with other cations such as Al and Fe for adsorption sites, mechanism of electron transfer, and desorption and readsorption of produced Cr(VI) and Mn(II) have been reported as controlling factors for the kinetics and the oxidation capacity of Mn oxides (Eary and Rai, 1987; Fendorf and Zasoski, 1992; Kim et al., 2002). Other factors include; pH, initial Cr(III) concentration, and the ratio of surface area of Mn oxide to solution volume also determine the kinetics and oxidation capacity (Eary and Rai, 1987). Manganese oxides have a high adsorption capacity for metal ions, thus potentially providing a local surface environment in soils and solid waste in which the coupled process of aqueous Cr (III) oxidation and manganese oxide reduction may take place.

Chromium oxidation by several synthetic Mn oxides in aqueous systems has been reported: pyrolusite (ß-MnO_2), birnessite (Na, K, Mg, Ca) {[Mn(IV, III)}]$_2O_4)\cdot nH_2O$, buserite ($Na_4Mn_{14}O_{27}\cdot 9H_2O$), manganite (γ-MnOOH), and hausmanite (Mn_3O_4) (Kim et al., 2002; Zasoski and Chung, 1992).

The kinetics of Cr oxidation are faster than originally thought, suggesting that the factors influencing Cr(VI)/Cr(III) ratios in natural systems deserve further investigation (Pettine

et al., 1994). Under natural conditions, the overall reaction involving MnO_2 and Cr(III) is represented by the following equation (2, 1),

$$Cr^{3+} + 1.5\ \delta\text{-}MnO_2 + H_2O = HCrO_4^- + 1.5\ Mn^{2+} + H^+ \qquad (2, 1)$$

The forward reaction is thermodynamically favorable under conditions reflective of surface environmental conditions, but not standard conditions (Fendorf and Zasoski, 1992). The extent of Cr(III) oxidation is limited probably by an ionic Cr(VI) adsorption in acidic solution and by $Cr(OH)_3$ (s) precipitation in neutral to alkaline solutions.

Small amounts of chromium are oxidized by O_2 at pH values greater than 9 and these conditions are prevalent in cement applications. Manganese oxides appeared to be the principle oxidising agent for Cr(III) in environmental systems (Rinehart et al., 1997; Fendorf and Zasoski, 1992).

Cr (III) is oxidised to Cr (VI) more readily in soils with high elemental contents of manganese as compared to other soils (Bartlett & James 1979). Cement contains approximately 1% manganese oxide, it is expected that with increase in the amount of MnO_2 in cement, there will be high amounts of chromium (VI) leached from cement and its application. May be with XRF elemental analysis, but it is locked up in solid solution and cannot be equated to free MnO_2 as it is in the literature experiments. Schroeder and Lee reported that a considerable amount of aqueous Cr (III) present in lake waters can be converted to Cr (VI) by reaction with an unspecified form of manganese oxide. In alkaline environments, such as sea water at pH 8.1, Nakayama et al. (1981) found that Cr (III) was oxidised by MnOOH(s) and therefore wet cement is no exception.

3.4 Reduction and immobilization of hexavalent chromium

Ascribable to increasing environmental and health-related concerns, the amount of hexavalent chromium found in cement is under increasing scrutiny. Various strategies have been evaluated to deal with the problem of chromium accumulation in the environment from different sources and the associated health standards. Some of the approaches include chemical reduction of Cr(VI) to the less toxic Cr(III), biological reduction of Cr(VI) to Cr(III) using micro organisms and immobilization of chromium in a solid matrix (Barros et al., 2004).

The reduction of Cr(VI) present in the alkaline media of cement is considered as a desirable step leading up to an effective chromium immobilization mechanism. The vast majority of the technologies reviewed involve the use of inorganic additives (lime, fly ash, slag, etc) to cement with the aim to provide the cement kind that can effectively stabilize the leachable Cr(VI). Most published data show that there was limited success in the Cr(VI) immobilization (Rinehart et al., 1997; Dermatas and Moon, 2006; Palomo and Palacios, 2003; Trezza and Ferraiuelo, 2003). This can be explained by the fact that in an alkaline environment the reduction of Cr (VI) is not generally favored (Geelhoed et al., 2003). The presence of fly ash, also blast furnace slag in cements, especially when high in sulfates, has been shown to be slightly effective in immobilizing Cr(VI) (Kidness et al., 1994; Rinehart et al., 1997).

Removal of Cr(VI) by chemical reduction from industrial wastewater involves a two-step process, reduction of hexavalent chromium under acidic conditions (usually pH > 3) and the precipitation of trivalent chromium as hydroxyl species. Most reducing agents are only effective under acidic conditions, especially organic compounds (Nakayama et al, 1981; Pettine et al., 2002), which limits the number of reducing agents that can be applied to the alkaline cement samples. However, some (such as H_2S, SO_2) exhibit toxicity themselves and introduce additional problems (Xu et al., 2004).

A survey of possible Cr(VI) reducing agents including ascorbic acid (Xu et al., 2004), hydrogen sulfide (Kim et al, 2001), hydrogen peroxide (Pettine et al., 2002), sodium thiosulfate, sodium dithionite, sodium metabisulfite, iron (II) sulfate and iron(II)-ammonium sulfate (Laskowski, 1996; Skovbjerg et al., 2006) were investigated. It was found that most of the indicated reducing agents need a far too high dosage and yield very poor results. Sodium dithionite has a problem since it is not storable in humid surroundings.

Iron (II) sulfate ($FeSO_4 \cdot 7H_2O$) is obtained from the production of titanium dioxide (Laskowski, 1996). Milled iron titanium ore (e.g. ilmenite $FeTiO_3$) is broken down with sulfuric acid. During the process iron (II)-sulfate crystallizes as a green salt. The granulated salt with a content of iron (II)-sulfate of approximately 50 % by mass contains 6 to 7 moles of crystallization water (hexa-heptahydrate). It was reported that approximately 0.35% (w/w) $FeSO_4 \cdot 7H_2O$, is enough to reduce 20 µg Cr(VI) /g cement (Laskowski, 1996). The addition of iron sulfate provides no technical side effect to the concrete (Fregert et al., 1979; Laskowski, 1996; Laforest and Duchesne, 2005). Only

iron(II) sulfate achieved, at even low dosage, reduction of hexavalent chromium over the entire pH range. In a suspension of cement, iron (II) sulfate and water, the main chemical reaction that takes place is the following equation (2, 2).

$$Cr^{6+} + 3Fe^{2+} \rightarrow Cr^{3+} + 3Fe^{3+} \qquad (2, 2)$$

In Scandinavia, the amount of hexavalent chromium allowed in Portland cement is limited to 2ppm. This is generally accomplished by intergrinding clinker and gypsum with a ferrous sulphate (Laskowski, 1996).

Studies in a cement plant in California showed that more than half of the hexavalent chromium in the cement was contributed by the grinding media in the finish mill (Mori et al., 2001; Laskowski, 1996). Attempts to reduce the chromium to its benign trivalent form with ferrous sulfate failed in full-scale trial grinds, due to oxidation of the ferrous iron. This indicates that further research is needed to find better methods for introducing ferrous sulfate into the cement or to develop more stable reducing agents.

There are several methods that are used to remove heavy metals from waste waters, which include; chemical precipitation, membrane filtration, ion exchange and adsorption. The adsorbents that are commonly recommended for the removal of heavy metals in aqueous media are alumina, silica, and activated carbon (Benhammou et al., 2005). Adsorption of chromium complexes such as $HCrO^{-}_{4,}$ and CrO^{2-}_{4} on clay minerals is generally weak which is explained by permanent negative charge that these materials contain.

Cr(VI) reduction in natural water by some solid reductants such as ferrochrome slag, copper smelter slag, steel wool, pyrite, synthetic iron sulphide and siderite has been studied which are cheap materials (Erdema et al., 2005; Laforest and Duchesne, 2005). A relatively small percentage of ferrochrome slag material finds its application in cement.

It has been indicated that other solid wastes such as bag filter dust or its sludge produced during the ferrochromium production contain high levels of soluble hexavalant chromium (Pillay et al., 2003). Cr(VI) reduction by using ferrochromium slag which contains iron and chromium mostly in metallic state as reductants was investigated. Further, oxide and silicate matrix of slag may partly adsorb chromates. Additionally, after reduction, in a following step another portion of slag may be used to neutralize the reduced solution in order to precipitate Cr(III) formed (Erdema et al., 2005).

Erdema et al. 2005, demonstrated that the reduction of Cr(VI) and the precipitation of Cr(III) in water was achieved where Fe(II) was used as a reducing agent. The source of Fe(II) was fine Ferrochromium Slag. The reduction of Cr(VI) by Ferrochrome Slag is strongly governed by the amount of acid (H_2SO_4). Consequently, it can be stated that the use of ferrochromium slag for the removal of Cr(VI) from waters may be a cost-effective alternative.

There is another kind of slag (SiMn slag) coming from the silico–manganese industry which is characterized by its high manganese content, compared with traditional (blastfurnace) slags. The possible chemical and technical viability of using SiMn slag as pozzolanic material in blended cements is still under investigation (Frias et al., 2006).

This show that cement production takes many sources of raw material of which it hazards in cement and concrete undergo investigations.

Humic acids (HAs) are natural compounds that are widely distributed in nature, still of unknown structure, are intensively studied. HAs and related fulvic acids (FAs) occur in soils, natural waters, marine and lake sediments, peat, lignin, brown coal and other natural deposits (Evangelou, 1998; Pokorna et al., 2000; Fetsch and Havel, 1998). The basic structural units of HAs are aromatic rings of two- or three-phenol type, which are connected by such groups as –COOH, –O–, –CH2–, –NH–, _N–, –S–, and usually contain two free hydroxyl groups (Pokorna et al., 2000). The HAs containing functional groups (–COOH, –OH, $–NH_2$, etc.) can influence the bonding distribution of cations in trace metals in the environment (Lubal et al., 1998; Evangelou, 1998). Each of these functional groups has reductive and adsorptive properties. The adsorptive property of these groups is due to the electrostatic forces between them and Cr(VI) or Cr(III) species (Daneshvar et al., 2002). Complexation of trace metals with HAs can cause a decrease in the metal's toxicity (e.g. copper) or an increase in its solubility (e.g. iron).

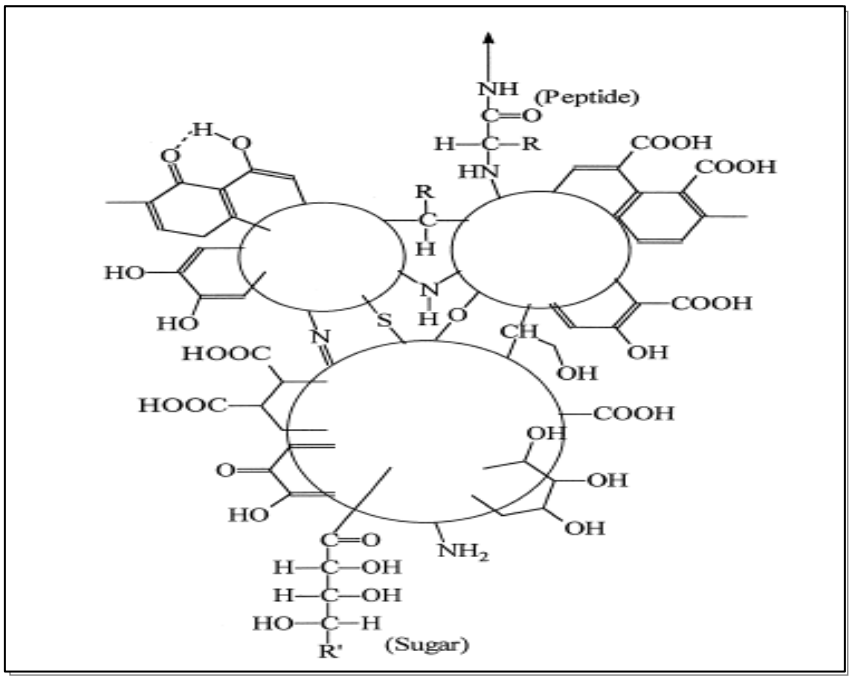

Figure 3.2 Proposed hypothetical structure of humic acids (Fetsch and Havel, 1998)

Humic acids are reported to reduce Cr(VI) under acidic conditions to trivalent chromium (Pettine, 1998; Pettine et al., 2002). Humic acids are reported to bind and cage metal ions irreversibly (Fetsch and Havel., 1998). This information prompts the study of humic acids in the immobilization of chromium in cement, since it is reported that Cr(III) in the cement has the possibility of being oxidized to Cr(VI) under natural environmental conditions (Eary and Rai, 1987).

3.5 Kinetics and mechanism of chromium oxidation and reduction

The kinetics of the chromium redox reactions which ultimately control the distribution of hexavalent and trivalent chromium complicate its transportation because each species

exhibit a unique sorptive response to changes in physio – chemical conditions (Weng et al. 1994; Lee et al., 2005).

Chromium(VI) exists in an anionic form in natural waters and its adsorption to oxide surfaces is readily reversible and varies inversely with pH and concentrations of competing anions (Pillay et al., 2003; Rinehart et al., 1997; Weng et al., 1994; Bartlett et al., 1979). In contrast Cr(III) is cationic, its sorption tends to increase with pH, owing to coordination with inner sphere complexes, and its absorption from oxide surfaces is slow.

Direct oxidation of Cr(III) to Cr(VI) in aqueous solutions at natural pH levels 4 – 9 by dissolved oxygen is known to occur with reaction half lives of the order of years. The rate of oxidation tends to increase with alkalinity (Pillay et al., 2003; Kilau and Shah., 1984; Lee et al., 1995). Rapid oxidation has been observed in highly alkaline conditions at pH 12 and higher (Petersen, 1998), although such conditions are rarely found in the natural environment except in cement.

In general, the rates of most reactions involving Cr(VI) decrease with increasing pH because either the rate-determining step in the reaction is acid catalyzed or the reaction involves forms of Cr(VI) that are present at significant concentrations only under acidic conditions (e.g., H_2CrO_4).

Cr(VI) reduction by Fe(II) depends upon the pH, temperature, and amounts of Fe(II). The half-life of Cr(VI) can range from several minutes to several months under typical conditions. The rates of Cr(VI) reduction increase with pH and temperature because the concentrations of highly reactive hydroxylated forms of Fe(II) increase (Sedlak and

Chan, 1997; Pettine et al., 1998). The rate of Cr (VI) reduction is also determined by the amount of Fe(II) which, in turn, is determined by the rates of Fe(III) reduction and Fe (II) re-oxidation reactions. When excess Fe (II) was added to Cr (VI)-containing solutions, Cr (VI) rapidly reacted with Fe (II) at pH values between 6.0 and 9.0 (Schroeder and Lee, 1975; Eary and Rai, 1988; Kieber and Helz, 1992). The effect of pH on the rate of reduction of Cr(VI) can be expressed by the following relationship:

$$-d\,[Cr(VI)]/\,dt = k[Cr(VI)][Fe(II)] \qquad (2, 3)$$

The rates of reduction of Cr (VI) with Fe (II) decrease over the pH range 1.5 to 4.5, and approximately constant at 4.5 – 5.0 and increase from 5.0 – 8.7. The reaction rate is first order with respect to both reactants. The rates at low pH range are not significantly influenced by ionic strength and temperature at 25 ^{0}C (Pettine et al., 1998; Sedlak and Chan, 1997).

The pH is a key factor that affects the rate and the extent of Cr (VI) reduction in sub soils. Cr (VI) may be effectively reduced in acidic soils simply because acidic conditions enhance the rate of release of Fe (II) species from soil minerals for reaction with aqueous Cr(VI) species, and also increase the rate of Cr (VI) reduction by organic matter (Eary and Rai, 1989, 1991) and sulfide (Pettine et al., 1994) but the reactions are extremely slow under the conditions encountered in the environment.

In general, the oxidation of Cr (III) to Cr (VI) is a very slow process at pH above 5 (Eary and Rai, 1987). The rate of Cr oxidation may be enhanced by other chemicals that may be introduced to the contaminated sample. The kinetics of the oxidation of Cr(III) with H_2O_2

was studied by Pattine (2002) who found that the oxidation rate was half times of 45 days with 0.1 µM H_2O_2 which were lower than those of 95 days previously reported for the oxidation of Cr(III) by particulate MnO_2 (Eary and Rai, 87). Lately, the kinetics of reduction of Cr(VI) by H_2S was found to be half times in NaCl media ranging from 0.5 to 500 days at 1 mM and 1 µM, respectively (Pettine, 1994, 2002). Fendorf and Zasoski (1992) reported that the oxidation of Cr(III) by MnO, occurred over a range of pH and Cr(III) concentrations. However, they found that as pH and Cr(III) concentrations increased, the amount of Cr (III) oxidized to Cr (VI) decreased.

Constant leaching of Cr (VI) in appreciable amounts were observed from column lysimeter filled with stainless steel slag over a 2 year period, where the reaction started slowly and concentrations increased thereafter (Bartlett and James, 1979; Pillay et al., 2003). It makes the sample aging factor to be the most important in the leaching behavior of Cr(VI) from soil and concrete stabilized waste. The following equation (2.4) was proposed for solid state oxidation of trivalent chromium.

$$Cr_2O_3 + CaO + 1.5\,O_2 \rightarrow 2CaCrO_4 \qquad (2, 4)$$

However, there is still not enough information to quantify the rates (Pillay et al., 2003; Kilau and Shah., 1984).

Kinetics of chromium transformations under typical environmental conditions were systematically evaluated using batch and column experiments (Guha et al., 2001; Benhammou et al. 2005). Oxidation and reduction reactions were evaluated in water systems. Reduction of hexavalent chromium by organics in sediments and soils, or the

oxidation of trivalent chromium by manganese oxide were much slower and clearly exhibited kinetic restrictions. Slow trivalent chromium oxidation was reported in one of the natural waters and sediments with half-lives ranging from 2 – 9 years and the extent of Cr (III) oxidation did not exceed 15 % of the initial Cr that was present.

Some research indicates that bacteria accelerate the oxidation of Cr (III) to Cr (VI) either directly or through the production of oxidized Mn (Murray et al., 2004). In addition, microorganisms can mediate the reduction of Cr (VI) to Cr (III) either directly or indirectly via the production of Fe (II), an inorganic reductant of Cr(VI). Therefore, microbially-mediated reactions are likely important in the redox cycling of Cr during the production, ageing, and transport of high Cr soils (Kim et al., 2002; Murray et al., 2004).

CHAPTER 4

Analytical techniques used

This chapter discuss the analytical techniques used in this project, their principles and analytical procedures.

4.1 Spectrophotometric techniques

Spectroscopic methods are still the mostly utilised techniques for metal ion speciation due to inexpensive application and simplicity (Ali and Aboul-Enein, 2006). The main goal of spectroscopic techniques is detection, not separation. The techniques include; UV-Visible and ICP-OES.

4.1.1 Inductively coupled plasma optical emission spectroscopy (ICP-OES)

ICP-OES analytical technique, offers many advantages including; high sensitivity with very low detection limits, good precision and detection of nearly all elements (Montaser, 1992; Ali and Aboul-Enein 2006).

In principle, the ICP-OES uses the concept that light has a dual nature, that is, it can behave like a wave and also like a particle. Light consists of particles, their energy being proportional to the wavelength. Spectral analysis makes use of the fact that the occurrence of certain lines serves as proof of the presence of certain elements (Harris, 2003).

Atomic spectroscopy is based on the measurement of the amount of electromagnetic radiation that is absorbed or emitted by an analyte atom to determine its concentration in a sample (Bradford and Cook, 1997).

The most common sample delivery system consists of a peristaltic pump and capillary tube to deliver a constant flow of analyte liquid into a nebuliser, Figure 4.1. The nebuliser turns the analyte liquid into droplets. The largest droplets fall out into a drain in the bottom of a spray chamber and the finer droplets are carried by gas into the IC plasma.

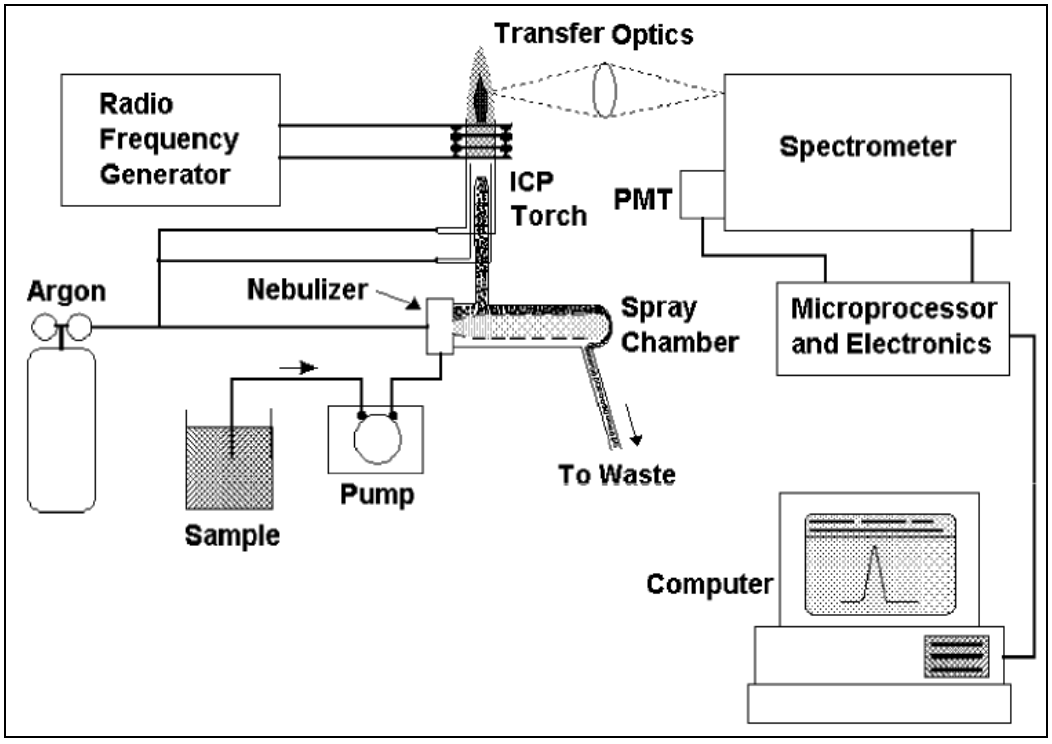

Figure 4.1 Schematic diagram of a typical ICP-OES instrument (Arcinus, 2000)

In the ICP-OES, plasma is used as an energy source, needed to atomize and ionize the samples to allow radiation emission, producing heat of 5500 K - 10 000 K, enough to ionize and excite most analyte atoms. Molecular interferences are greatly reduced with this excitation source. The element type is determined based on the position of the photon rays, and the content of each element is determined based on the rays intensities.

Argon gas is supplied to the torch coil, and high frequency electric current is applied to the work coil at the tip of the torch tube in order to generate plasma. Using the electromagnetic field created in the torch tube by the high frequency current, argon gas is ionized and plasma is generated. Solution samples are introduced into the plasma in an atomized state (Boumans, 1996).

4.1.1.1 ICP-OES instrumentation

ICP-OES was used to analyze cement and concrete for total chromium content as well as 0ther total elements in those samples (Bobrowski et al., 1997). The ICP - OES Ciros with a charged coupled device detector was from Spectro Analytical Instruments, Inc. (Kleve, Germany). The system was purged with high purity Argon gas. The optimized instrument parameters were for chromium and other heavy metals analysis: plasma power of 1200 W, coolant flow rate 12.0 L min^{-1}, auxiliary flow rate 1.0 L min^{-1}, nebulizer flow rate of 1.0 mL min^{-1} at wavelength of 257.610 nm. The system was controlled with Smart Analyzer Windows software. The instrumental parameters that were used are listed in appendix B.

4.1.1.2 Total chromium determination procedure using ICP-OES

Sample preparation for ICP-OES involves acid digestion of the cement samples using microwave assisted digestion.

Microwave digestion

Total digestion for the determination of total metal concentration was done by dissolving of about 0.100 g of solid cements and crushed concrete cubes (including the coarse aggregate) with the following acids;

- 5 ml HNO_3
- 3.0 ml HF (later dissolved in 18 ml boric acid)

An Anton Paar Multiwave microwave sample preparation system with Rotor XF100-8 was used to digest the samples. The digestion time was 65 minutes and then neutralized in 18 ml boric acid. The resulting solution was qualitatively transferred into a 100 ml volumetric flask and then diluted to the mark with water before for ICP analysis.

4.1.2 UV/VIS spectrophotometry

UV-Vis absorption spectroscopy is considered to be one of the oldest physical methods used for quantitative analysis of organic and inorganic species (Ali and Aboul-Enein, 2006). The determination of the analyte is carried out by the absorption of radiation at a fixed value of wavelength (540 nm) called λ_{max}. The spectrophotometer involves the sources of light, filter or monochromator (to select a narrow band from wavelengths of continuous spectra), sample holder and a detector (Ali and Aboul – Enein, 2006), Figure

4.2. The source of light are tungsten and deuterium for visible and UV radiation. The detector electronically measures the intensity of the light striking it. A sample is placed in the light path, and the instrument compares the intensity of the light going through the sample (I) to the intensity observed without the sample (I_o).

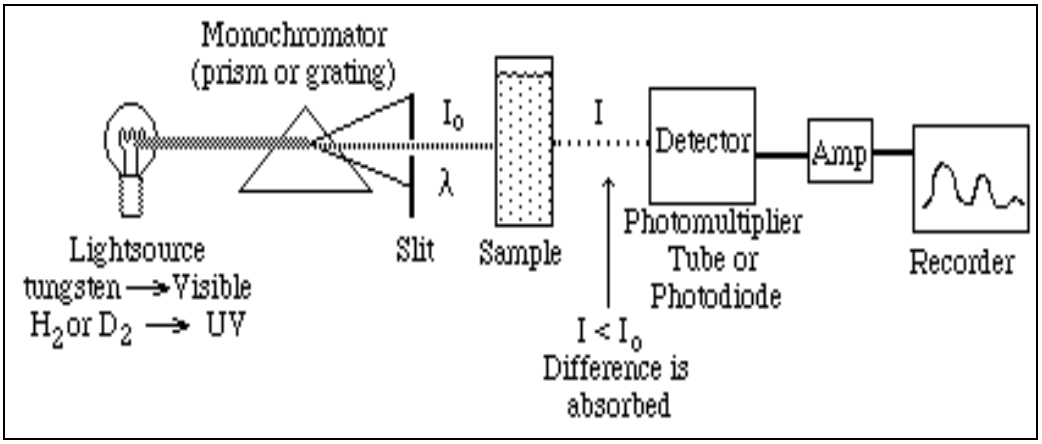

Figure 4.2 Single Beam UV-Vis spectrophotometer (Ali and Aboul – Enein, 2006)

The effect is measured either as Transmittance (T, the percentage of light that goes through the sample) or as the Absorbance (A - representing the amount of light absorbed by the sample) $T = 100 \times (I / I_0)$

$$A = -\log_{10}(T / 100) = \log_{10}(I / I_0)$$

Beer's Law states that at constant path length, the absorbance is directly proportional to the concentration of absorbing material. The equations combined in the Beer-Lambert Law: $A = \varepsilon c l$

l is the path length, c is the concentration, and ε is a constant which depends on the wavelength of the light, the absorbing material, and the medium (solvent and other components). The constant ε is called molar absorbtivity coefficient.

Visible light represents a very narrow section of this range with wavelengths between 380 nm for blue light to around 780 nm for red light, figure 4.2. Shorter wavelengths fall into the ultraviolet region and longer wavelengths are in the infrared region.

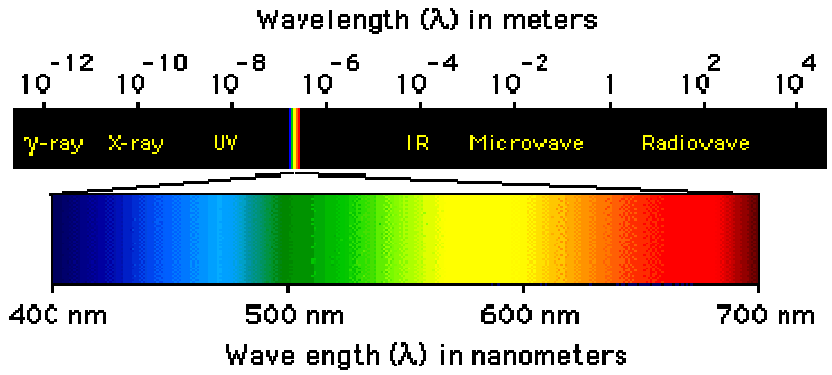

Figure 4.3 Electromagnetic spectrum (Harris, 2003)

White light is a mixture of all of the wavelengths in the visible range. When light strikes an object, it may be reflected, absorbed, transmitted, or diffracted. A prism or a diffraction grating separates white light into its various colours. If some of the light is absorbed, the reflected or transmitted light has the complementary colour of the absorbed light.

Normally, metals ions are detected by visible spectroscopy after colour development with some suitable reagent. The method is based on the formation of a complex with an organic compound (diphenylcarbazide) characterized with colour change. The most

commonly used organic reagent for Cr(VI) determination is diphenylcarbazide but it suffers serious interference from Fe(III), Mo(VI), Cu(II) and Hg(II) and the formed complex is stable for 30 minutes in the presence of a phosphate buffer (Narayana and Cherian, 2005).

4.1.2.1 UV/VIS spectrophotometric instrumentation

A (VARIAN) Cary 50 Conc UV-Vis spectrophotometer, coupled to Cary WinUV software was used for all photometric analysis. Small quartz cuvettes with a path length of 10 mm were used as samples vessels for analysis. Absorbance was measured at a wavelength of 540 nm.

4.1.2.2 Cr(VI) determination procedure using UV-Vis spectrophotometry

*Reagent*s

0.04 M and 4.0 M HCl, acetone, 1.5 – diphenylcarbazide indicator solution, 5.0 mg/L Cr(VI) stock solution and analytes.

UV-Vis Spectrophotometric analysis

The UV/Vis spetrophotometric method, described by the European committee for standardization (Draft prEN 196-10), for determination of the water soluble Cr (VI) content of cement. The indicator solution was weekly prepared by dissolving 0.250 g of 1.5 – diphenylcarbazide in 50 ml acetone in a 100 ml volumetric flask and made up to the mark with deionised water. Standard chromate solution was prepared by dissolving 0.1414 g dried potassium dichromate dried to constant mass at (140 +/- 5 ^{0}C) in a litre flask and made up to the mark with deionised water (50 mg Cr(VI) stock solution). 50 ml

of the stock solution was then transferred into 500 ml flask and made up to the mark with deionised water (5.0 mg Cr(VI) stock solution).

The following standard solutions 0.1, 0.2, 0.5, 1.0, and 1.5 ppm Cr(VI) were prepared in 50 ml volumetric flasks by transferring 1.0, 2.0, 5.0, 10 and 15 ml respectively, of the 5 mg Cr(VI) stock solution to each flask. 5.0 ml of Indicator solution and 5 ml of 0.04 M HCl were added to each flask and made up to the mark with deionised water. A blank was prepared following the same procedure, without addition of standard solution. Absorbance values were measured against the procedural blank at 540 nm, 15-30 minutes after addition of indicator solution. A calibration curve was constructed by the measured absorbance values against the concentration of Cr(VI).

Sample preparation involved the addition of 5 ml sample, 5.0 ml indicator solution and 20 ml deionised water to a 50 ml volumetric flask. The pH of this mixture was adjusted to 2.5 by addition of 4.0 M HCl. The resulting solution was made up to the mark with deionised water. The absorbance of the solution was measured after 15 – 30 minutes at 540 nm. The above procedure was applied to the leachate solutions.

4.2 Voltammetric techniques

The polarographic and voltammetric analysis method have been an important aid for many years, particularly for trace analysis. The elegance of these techniques is based on their high accuracy and extremely low quantification limit even at parts per trillion levels (ppt), and the possibility of carrying out multi-element analysis. The voltammetric

technique may certainly be a good alternative to spectroscopy: it does not need expensive equipment and require very small sample volumes (Ali and Aboul – Enein, 2006; Locatellia and Torsi 2004; Bobrowski et al., 2004), but skills are required to operate the voltammetry instrument.

Voltammetry is a collection of analytical techniques in which the relationship between current and voltage is observed during electrochemical processes. When voltammetry is conducted with a mercury electrode it is called polarography (Harris, 2003). Polarography is a branch of voltammetry, where a relationship between potential and current is characterized through the use of a dropping mercury electrode (working electrode).

The technique is used to analyse an electroactive chemical species (that is, one that can be oxidised or reduced). The potential of the electrode is the controlled parameter that causes the chemical species to be oxidised or reduced. The current produced, known as the Faradic current, is due to electron transfers which occur during oxidation or reduction on the electrode surface and is proportional to concentration of the analyte (Skoog et al., 1992; Harris, 2003). The current is measured between working electrode and an inert auxiliary electrode, while the voltage is measured between the working electrode and the reference electrode.

Electrochemical equipment

The voltammetric cell consists of the analyte dissolved in a solvent, a non reactive ionic electrolyte, and three electrodes (Figure 4.3). The material of the cell (glass, Teflon, polyethylene) is selected to minimize reaction with the sample.

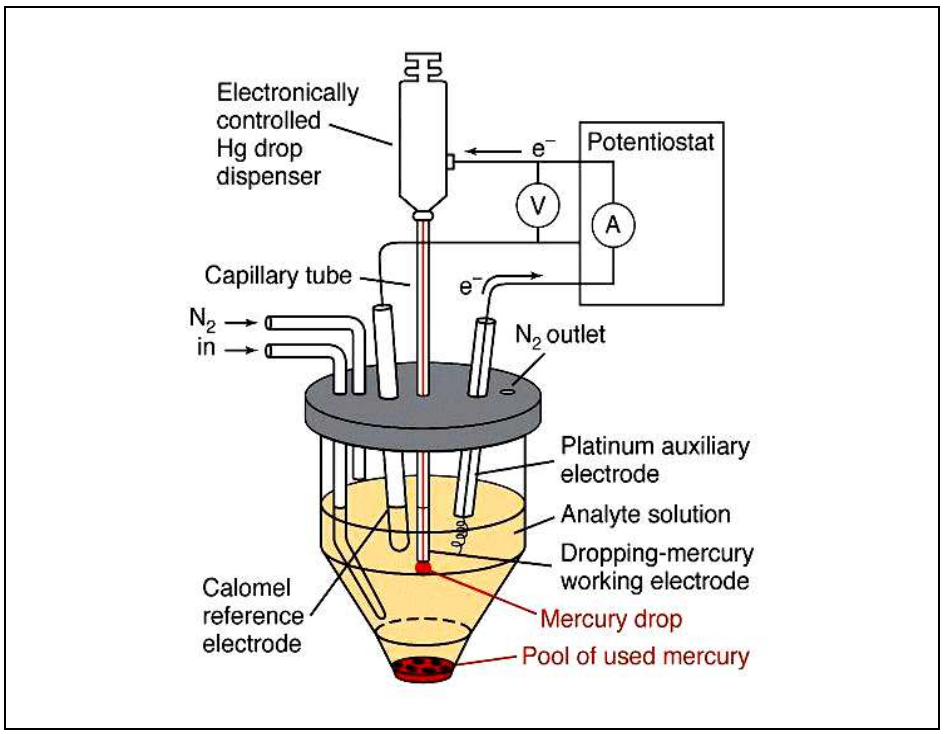

Figure 4.4 Typical three electrode polarographic cell (Harris, 2003)

The three electrodes include:

- *Working electrode* whose potential is varied with time. It is also where redox reaction takes place. It is used to monitor the response of the analyte. Its small size ensures that a high current density develops at its surface. Mercury is mostly preferred because it displays a wide negative potential range (because it is difficult to reduce hydrogen ion or water at the mercury surface), its surface is readily regenerated by producing a new drop or film, and many metal ions can be reversibly reduced into it.
- *Reference electrode* whose potential is fixed throughout the experiment. It must be a completely depolarisable electrode. The most commonly used reference electrodes for aqueous solutions are the calomel electrode, with potential determined by the reaction.

$Hg_2Cl_2(s) + 2e^- = 2\,Hg(l) + 2\,Cl^-$

And the silver/silver chloride electrode (Ag/AgCl), with potential determined by the reaction $AgCl(s) + e^- = Ag(s) + Cl^-$.

- *Auxiliary electrode* (can be a platinum wire or glassy carbon) that serves to conduct electricity from the signal source through the solution to the working electrode. It controls the potential applied to the WE and completes the circuit for carrying the current generated by the process occurring at the WE.

There are many different types of working electrodes that can be used in voltammetry. Some the most common types are: disk electrode, hanging mercury drop electrode, dropping mercury electrode and static mercury dropping electrode (Skoog et al., 1996).

Stripping Voltammetry

Electrochemical stripping analysis is one of the most powerful analytical methods and it is certainly the most sensitive and selective electrochemical analytical technique for determining inorganic species (heavy metals) and organic species. The concentration of metal ions up to 10^{-10} M can be detected by this technique, it can be used for metal ion speciation without extra sample preparation (Ali and Aboul-Enein, 2006). The high detection capability is achieved by the use of an enrichment step before the electrochemical determination itself. Dissolved air and oxygen are the interferents in this technique.

The stripping process involves two steps; the analyte species in the sample solution is concentrated onto or into a working electrode and the preconcentrated analyte is measured from the electrode by the application of a potential scan. Any number of

potential waveforms (differential pulse, square wave, linear sweep, or staircase) can be used for the stripping step. The most common are differential pulse and square wave due to the discrimination against charging current. However, square wave has the added advantages of faster scan rate and increased sensitivity relative to differential pulse.

The enrichment of analyte at a stationary mercury electrode (drop or film) can be carried out according to three most commonly used variations which are anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV), and adsorptive stripping voltammetry (AdSV).

Anodic Stripping Voltammetry

ASV enables multi-element analysis and has a practical detection limit in the part per-trillion ranges. Metal ions in the sample solution are concentrated into a mercury electrode during a given time period by application of a sufficient negative potential. These amalgamated metals are then stripped (oxidized) out of the mercury by scanning the applied potential in the positive direction. The resulting peak currents are proportional to the concentration of each metal in the sample solution, with the position of the peak potential specific to each metal. The use of thin Hg films or Hg microelectrodes along with pulse techniques such as square-wave voltammetry can substantially lower the limits of detection of ASV.

Cathodic stripping voltammetry

CSV is effectively the electrochemical inverse of ASV, where the analyte of interest is accumulated as an oxidized species (rather than reduced as in anodic stripping voltammetry) on the electrode at a positive potential, and then quantified during the

stripping step as the electrode potential is swept cathodically. In summary, the working electrode behaves as an anode during deposition and as a cathode during stripping (Skoog et al., 1992; Paneli et al., 1993; Kalvoda and Kopanica, 1989).

4.2.1 Adsorptive Stripping Voltammetric methods

The primary difference between AdSV and the other stripping methods is that the preconcentration step of the analyte is accomplished by adsorption on the electrode surface or by specific reactions at chemically modified electrodes rather than accumulation by electrolysis (Kalvoda and Kopanica, 1989; Kounaves, 1995). The adsorbed species is quantified by using a Voltammetric technique such as DPV or SWV in either the negative or positive direction to give a peak-shaped Voltammetric response with amplitude proportional to concentration.

Cathodic Adsorptive Stripping Voltammetry

Cathodic adsorptive stripping methods differ from cathodic stripping by the fact that in AdSV, the preconcentration step, involves a suitable complexing ligand, which forms a stable complex with the metal species of interest and is accumulated by adsorption on the working electrode surface. In CAS, a hanging mercury drop is employed and deposition of the analyte then occurs by physical adsorption on the surface rather than by electrolytic deposition. The stirring rate becomes a more important factor in AdSV (good stirring results in rapid adsorption).

4.2.2 AdSV instrumentation

A 757 VA computrace instrument (Metrohm Ltd, CH-9101 Herisau, Switzerland) was used for AdSV measurements. The three electrodes system used consisted of: reference

electrode a Metrohm 6.0728.0X0 Ag/AgCl electrode, the auxiliary electrode a Metrohm 6.1247.000 glassy carbon electrode, and the working electrode a Metrohm 6.1246.020 Mercury Electrode in the Hanging Drop Mode. The system was controlled with 6.6032.100 VA Computrance software 2.0 The pH was measured using a Beckman 50 pH meter with HI 1330 pH electrode to measure the pH of the sample (Hanna Instruments). The instrumental parameters that were used are listed in appendix 1.

4.2.3 Adsorptive stripping voltammetric analysis for Cr(VI)

In AdSV, the determination of chromium involves formation of a chelate with an organic ligand that is adsorbed on the hanging dropping mercury and the reduction current of the accumulated complex is recorded. Several chromium complexing ligands have been used; chlorodiaminetetraacetic acid (CDTA), diethylenetriammine pentaacetic acid (DTPA) (Zaresbki, 1977; Bobrowski et al., 2004), Cupferron (Elleuout et al., 1992) and pyrocatechol violet (PCV) (Domínguez and Arcos, 2000), etc. The highest sensitivity for the determination of Cr(VI) was achieved by the application DTPA in acetate supporting electrolyte and nitrate in CAdSV (Cukrowska and Dube, 2001). The method used in this research was previously optimized in our laboratory at the University of Witwatersrand and found to be very efficient and applicable to industrial and natural waters in South Africa.

The experimental procedure for Cr determination is based on the preconcetration of Cr(III)-DTPA complex by adsorption at HMDE at the potential of -1.0 V. The Cr(III) is freshly produced during adsorption step by reduction of the dissolved Cr(VI) at the electrode surface at -1.0V deposition potential and forms a complex with DTPA. This

complex is adsorbed on the hanging mercury drop and produces a peak at -1.25V. The Cr(III) will then be reduced to Cr(II) due to the presence of nitrate ions owing to chemical re-oxidation of Cr(II) to Cr(III) (catalytic effect) which is reduced on the electrode surface. During the stripping step the current measured is due to the reduction of Cr(III) to Cr(II). The concentration of $NaNO_3$, DTPA and CH_3COONa and the pH are factors that have an influence on the peak current.

4.2.3.1 Solutions for AdSV

All solutions were prepared using de-ionized water. The 1000 mg l^{-1} of Cr (VI) stock solution was made by dissolving 0.2828 g potassium dichromate (Associated Chemical Enterprises) in 100 ml de-ionized water and was stable for a week when kept at 4 ^{o}C. The Cr(VI) standard solutions for use in AdSV and in recovery studies in the cement and concrete leachates were made from that stock solution and prepared on a daily basis. The background electrolyte used in the AdSV was made by mixing (1.950 g) 0.045 M DTPA, (1.642 g) 0.2 M CH_3COONa and (21.302g) 2.5 M $NaNO_3$ in a 100 ml volumetric flask.

4.2.3.2 Procedure

The adsorptive stripping voltammetry method, described previously (Golimowski et al.1985; Korolczuk et al.1999; Cukrowska and Dube, 2001), was used for final determination of Cr (VI) concentration. Before sample analysis, a blank solution (de-ionized water) was analyzed to examine contamination present. Then 2.5 ml of sample (leachate) and 2.5 ml mixture of background electrolyte (consisting of 0.045 M DTPA, 0.5 M CH_3COONa and 2.5 M $NaNO_3$) were added to the voltammetric cell and diluted with 5 ml of ultra pure water such that the total volume in the polarographic cell is 10 ml.

The pH was adjusted to approximately 6.20 (±0.01) using 40 % NaOH or 1M $HNO_{3.}$ The mixture was then purged with nitrogen for 300s to remove dissolved oxygen. The instrumental parameters used for the analysis were (Cukrowska and Dube, 2001): deposition potential of -1.0 V, equilibration time of 15 s with signal scanned at 0.030 Vs^{-1} from -1.0 to 1.4 V; frequency 50 Hz and pulse amplitude of 50 mV. The determination of Cr(VI) in each sample was achieved by three standard additions at reduced purging time. Samples with higher chromium concentration were diluted to maintain the concentration within the linearity region.

4.3 Other instrumentation

Reagents and cement samples were accurately weighed using a Precis 180 A balance (Precis balances Ltd., Buckinghamshire). A concrete crushing machine was used to crush concrete cubes. Tenius Compression Testing Equipment (CTE), 1000 kN capacity used for the determination of concrete strength. A rotor mixer was used for the mixing and homogenization of the cement and concrete material. A 500W UV mercury lamp was used for oxidation of Cr(III) to Cr(VI) during the leaching of concrete cubes.

4.4 Materials used in the study

All cement samples were obtained from HOLCIM in 50 kg bags. The samples materials included; MC - “OPC” cement; for OPC stands for “Ordinary Portland Cement”, HSC01

- “Portland Slag-01 cement, HSC02 - “Portland Slag-02 cement, Fly ash - “Portland ash cement, Limestone - “Portland-limestone cement and Composite cement was a mixture of Portland-limestone and Portland ash cement. Pure Cr slag (Calsiment). All the samples were high strength cement. Granite sand and 13 mm crushed stones were also provided by HOLCIM.

Reagents

All the chemicals used throughout this work were of analytical grade. All the glassware was soaked in 1M nitric acid prepared from 55 % nitric acid (Saarchem Pty Ltd, Johannesburg, South Africa) at least for 24 hours. All utensils were rinsed before use with ultra pure water with resistivity of 18.5 $M\mu cm^{-1}$ obtained from a Milli-Q-R10 (Millipore, Bedford, MA, USA). Fume cupboards were used when transferring or preparing volatile reagents.

The chemicals used were: Iron (II) sulfate, sodium nitrate and potassium dichromate from Saarchem. Iron oxide, Manganese dioxide, acetic acid, sodium acetate, 1.5 diphenylcarbazide and DTPA from Merck. Sodium hydroxide was obtained from Holpro Lovasz.

CHAPTER 5

Results and discussion

5.1 Methods of sample preparation, treatment and analysis

5.1.1 Sample preparation

All cementitious materials were obtained from HOLCIM (SA) and were described in Chapter 4.4.

Each 50 kg bag of cement was poured into a clean, dried rotating mixer and homogenized for 15 minutes; the required mass was then measured into a clean 10 L plastic container. This was done to make sure that the analysis is a true representative of the 50 kg cement sample and to minimize contamination during sampling and preparation. The different kinds of cement were used to build concrete cubes that were used as experimental samples in this study.

Preparation of concrete cubes

1000 cm^3 concrete cubes were cast using each type of cement namely; High strength cements (limestone, fly ash, slag, composite and clinker) with the same proportion or ratio of concrete constituents (water, crushed stones, sand) and also the same ratio of water and cement (w/c = 0.5) (Table 5.1). The workable concrete mixture was thoroughly mixed using an electric mixer, then filled into a metal 1000 cm^3 mould, and left to solidify overnight. The cubes were removed from the mould and then cured in water for 3 days, and then they were ready for leaching analysis. The cubes were cured for 3days because by then the cube could have acquired enough strength. The drying of the surface

was not prevented as it was part of the environmental conditions concrete is exposed to on its application, it was controlled. Some of the cubes built from each cement type mix were tested for concrete strength and water sorptivity up to 28 days of curing.

Table 5.1 Mixing design for concrete cubes made of different types of cement.

Materials	Amount
Water (291)	4.33L
Cement (52.5)	8.44 kg
Granite sand (850)	13.67 kg
Stone (750)	12.80 kg

The rest of the cubes were painted using epoxy paint around the sides to provide a watertight seal leaving one side of the cube as the test surface as shown in Figure 5.1. The epoxy paint allows controlled exposure of one side surface to specified leaching conditions. These concrete cubes were then tested for the leachability of Cr(VI) under different environmental conditions.

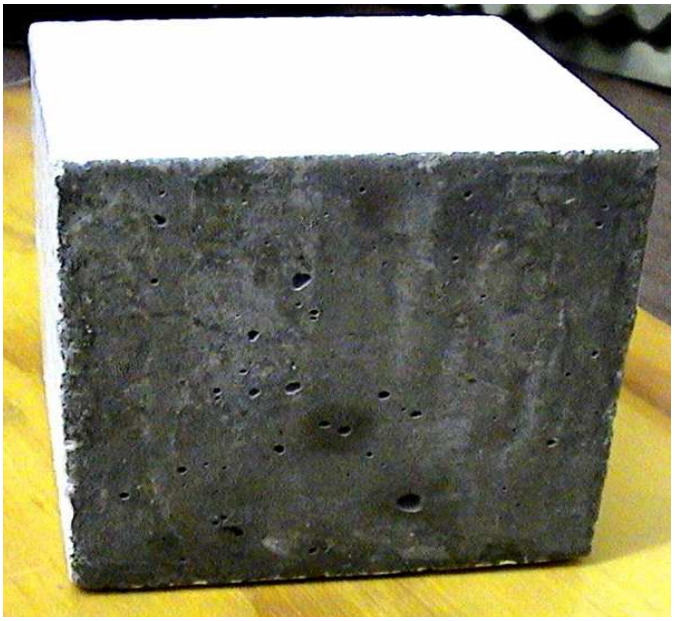

Figure 5.1 Concrete cube prepared for surface leaching for Cr(VI) content.

The exposed surface was leached for Cr(VI) with treated deionised water over a period of 5 days. The leaching of the cubes were done for 5 day because changes in the leachability occurred before the 5 days. The leachate was refrigerated at 4^0C and analysed for water soluble Cr(VI) using AdSV within 24 hours.

125 cm^3 concrete cubes were also made according to the same mix design proportions as in Table 5.1, with some additives such as reducing agents ($FeSO_4$, Humic acids) and cement constituents (MnO_2, Fe_2O_3) in varied amounts. These cubes surfaces were not epoxidised to increase surface area for leaching and were used for batch leaching and surface experiments.

5.2 Physical characterization of the concrete

In the study of the leachability and mobility of Cr(VI) in cement and concrete, it is imperative to consider the physical properties which can indirectly affect the speciation

chemistry of Cr(VI). The physical properties tested included; concrete compression strength, water sorptivity and porosity for the concrete cubes.

5.2.1 Concrete strength test

The most common measure of concrete strength is the compressive strength, determined in either a cube test or a cylinder test. In this study the cube test was used to measure compressive concrete strength using the 100 Mpa capacity Tenius Compression Testing Equipment (CTE). The cube test is most commonly used for determining concrete strength in Europe and the rest of the world. A 1000 cm^3 concrete cube was cast and cured for 28 days and then compressed between two parallel faces. The stress at failure is the compressive strength of the concrete (Ballim, 1993).

5.2.1.1Determination of concrete strength

The concrete strength test results are tabulated in Table 5.2, for cubes tested after 28 days of curing according to the method described above (Ballim et al., 1993). The concrete cubes made with MC cement were the strongest whereas the cubes made with limestone and composite cements were the weakest. The different kinds of cement were found to have different compressive strength and they can be used for different in construction applications.

The difference in the concrete compressive strength is depended on the different kinds of cement used. The different types of cement are characterised by the different admixtures and additives (slag, fly ash, limestone and etc.) which dilutes the cement and influences the rate and degree of hydration.

Table 5.2 Results on concrete strength for 1000 cm^3 cubes made with different types of cements.

Concrete cube	Mass /kg	Strengths /MPa
HSC - limestone	2.472 ± 0.095	42.26 ± 2.954
HSC – Fly ash	2.441 ± 0.058	50.52 ± 4.590
HSC - Composite	2.432 ± 0.029	33.22 ± 7.289
HSC02 - slag	2.469 ± 0.006	54.50 ± 4.742
HSC01	2.505 ± 0.014	57.70 ± 4.163
MC	2.499 ± 0.011	60.70 ± 6.110

5.2.2 Water sorptivity and porosity test

The sorptivity test measures the rate of capillary water absorption through dry or partially dry materials (Hall, 1989; Ballim, 1993). The principle of the method is that a concrete specimen has one surface in contact with water while the others are sealed and water ingress into a non-saturated concrete structure due to sorption, driven by the capillary forces. The tests were carried out using the guidelines provided by Alexandra et al., (1999) and Ballim (1993) for measuring the initial rate of absorption of concrete. A thick concrete disc of 50 mm diameter x 20 mm length was cored out from a 1000 cm^3 cube and used as the test specimen. The specimens were oven dried at 110^0C for different drying periods so that all the specimens showed a similar change in mass per day (0.5 %) and then they were left to cool in dry conditions for 24 hours.

The test included placing of the concrete specimen on $Ca(OH)_2$ wetted paper towel for 30 minutes in a desiccator, then patting it once on a damp piece of adsorbent paper and the mass of the specimen was weighed at fixed time intervals (3, 5, 7, 12, 20 and 25 minutes) during the test. The specimen should appear wet, but not have free water on the test surface. This kind of drying of the test specimen is a critical part of the test because the sorptivity is dependent on the initial moisture content of the testing unit.

5.2.2.1 Determination of water sorptivity and porosity

The test was carried out according to the method described above and the results are tabulated in Table 5.3.

Cubes made with MC cement had the highest water sorptivity and porosity whereas those made with HSC01 had the least. Water sorptivity indicates the number of interconnected pores of the right size to promote capillary suction which facilitates leaching of heavy metals. It plays a crucial role in the elution of heavy metals from the cement matrix. It has been shown that concrete with higher porosity tend to leach higher metal concentrations due to high surface area available for the leaching process (Togerö, 2006).

Table 5.3 Water sorptivity and permeability of concrete cubes tested after 28 days

Concrete cubes	Sorptivity (mm/ hr)	Porosity (%)
1. HSC01	8.50	14.3
2. MC	9.80	17.2
3. HSC02- slag	9.96	15.6

5.3 Laboratory Method (AdSV) optimization and validation

The AdSV method is well optimized when the polarograms give stable signals and highest sensitivity coupled with the best shape. This is achieved by optimizing the following parameters; ligand concentration, deposition potential, deposition time, pH of the solution, peak evolution time and buffer concentration.

The AdSV analytical procedure involving DTPA was previously optimized mainly for natural water samples (Baussemart et al., 1992; Korolczuk, 2000; Cukrowska and Dube, 2001) and therefore, can be applicable to water leachate. The concentration of the nitrate buffer which catalyses the electrochemical reaction was reported by Zebereski (1997) that it showed no significant influence and therefore the literature value was adopted. The variation of DTPA concentrations showed that the peak current of chromium increased proportionally and attained a relatively stable maximum value between 0.004 M and 0.005M concentrations. The optimum value of the DTPA concentration was chosen to be 0.0045 M DTPA and was without any interference from anions and cations (Dube, 2001).

The limit of detection and the limit of quantification were calculated by the traditional method, which takes into account the uncertainties of the slope and the intercept of the calibration plot that were 3 and 10 fold multiply the blank standard deviation (Bobrowski et al., 2004).The limit of detection found was 0.0288 ppb that was obtained from analysis of blank 7 times then blank standard deviation was obtained (LOD = 3 x SD =3 x 0.0069). The quantification limits was 0.069 ppb (QL = 10 x SD = 10x 0.0069). The minimum Cr(VI) content in blank was 0.19 ppb.

The optimized method proved to be very sensitive and selective for the determination of Cr(VI). The method showed resistance to a variety of interferences including iron, calcium and sulfates (Dube, 2001), which are persistent in cement samples.

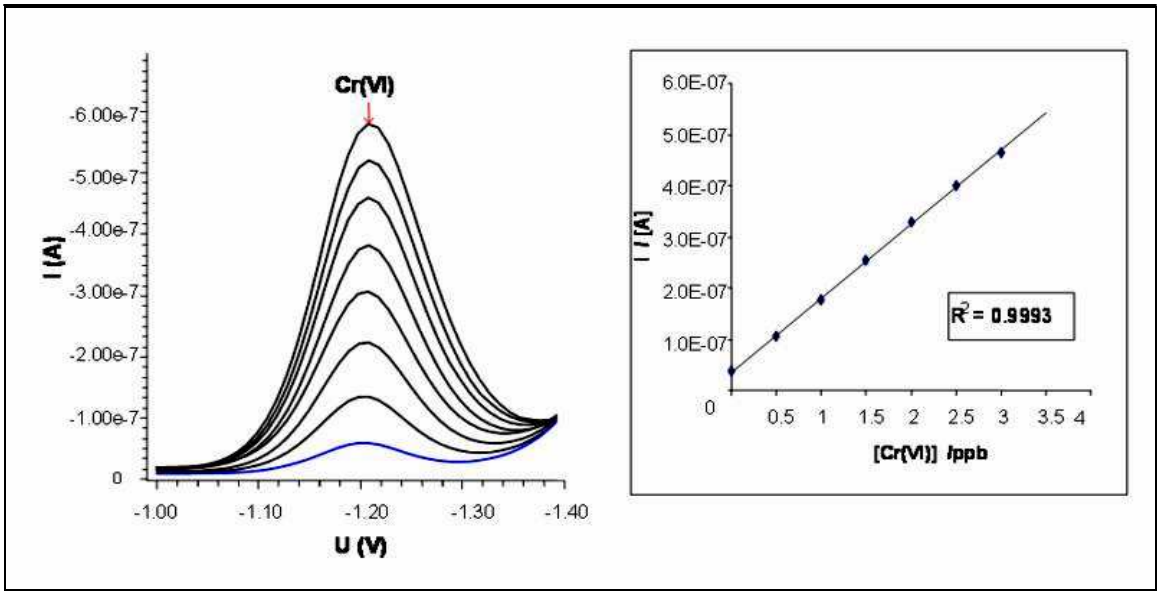

Figure 5.2 AdSV curves and a calibration plot for Cr(VI) at low concentration level. Curves for 0 - 4 ppb Cr(VI) in 0.2 M sodium acetate, 0.045 M DTPA and 2.5 M $NaNO_3$ pH = 6.2, E_{acc} = -0.950 to 1.40 V, t_{acc} = 60s.

Figure 5.2 shows the optimized parameters set for the Cr(VI) determination throughout the project which are as follows: 0.2 M sodium acetate, 0.045 M DTPA, 2.5 M $NaNO_3$ and pH = 6.2. Hence, AdSV can be successfully used for direct determination of Cr(VI) without any special treatment of the samples. This direct measurement of chromium species in samples minimizes the problem of disturbing the stability of chromium speciation, which is experienced in other techniques.

5.4 Comparison of AdSV (laboratory std method) and UV-Vis spectrophotometry (EU and EPA std method)

5.4.1 Method validation

There are may methods available for determination of Cr(VI), but all have their drawbacks such UV-Vis spectroscopy which has little (Kristiansen et al., 1977). It is important to find the correct method for the determination for Cr(VI) in the cement samples. Such methods are characterized by low detection limit, high accuracy, precision, minimal interferences, specificity and selectivity.

In order to determine if the results from both instruments are viable, standards are analyzed exactly as samples and by determining their recovery. Therefore these results can be considered reliable. Slight differences can exist between the results obtained for the standards and those for the real samples due to the difference in sample matrix.

In the recovery experiments, the sample standard solutions were done in triplicate and analyzed using the AdSV and UV-Vis spectrophotometry, the results in Table 5.4 were obtained by both methods as described in Chapter 4.

The Cr(VI) standard recoveries from AdSV method were between 96 – 102 %, which was a good recovery. The precision, accuracy and repeatability of the results were quite good as shown by the standard deviation.

Table 5.4 Recovery for Cr(VI) standards by AdSV

Sample std /ppm	AdSV Cr(VI) recovered /ppm, s	AdSV Recovery %	UV-Vis Cr(VI) recovered /ppm , s	UV-Vis recovery %
1.0	0.98 ± 0.03	98	2.0 ± 0.00	200
2.0	1.92 ± 0.14	96	3.0 ± 0.00	150
5.0	4.87 ± 0.40	97	6.0 ± 0.00	120
10.0	9.60 ± 0.66	96	9.8 ± 0.58	98
20.0	20.3 ± 2.08	102	20.1± 0.12	101

The UV-Vis spectroscopic method showed poor recovery, especially at lower Cr(VI) concentrations. The lower values were highly exaggerated. The accuracy was poor at lower concentrations, but the precision and repeatability were good.

Recovery of Cr(VI) from real samples

The recovery experiments were then carried out with spiked cement leachate samples. AdSV and UV-Vis methods were validated using cement leachate samples from HOLCIM company with known amounts of Cr(VI). The recovery of Cr(VI) spiked to leachate samples ranged from 80 to 120 % for UV-Vis spectrophotometry and approximately 95 % for AdSV, as indicated in tables 5.5 and 5.6 before accounting for the dilution factor.

Table 5.5 Results for the recovery of 0.5 ppm Cr(VI) standard spiked on the selected cement leachate samples determined with UV-Vis spectrophotometry

Cement leachate	Cr(VI)/ppm before spiked	Cr(VI) /ppm after spiked	% recovery
A2	0.8	1.4	120
B1	0.5	1.0	100
C2	0.3	0.7	80

The recovery was lower with lower concentrations of Cr(VI) in the samples, which confirms that the values were exaggerated at those concentrations where the standard samples were to account for the difference in the Cr(VI) values.

Table 5.6 Results for the recovery of 1 ppb Cr(VI) standard spiked on selected cement leachate samples and determined with AdSV method.

Cement leachate	Cr(VI)/ppb before spike	Cr(VI) /ppb after spike	% recovery
A2	1.30	2.25	95
B1	3.56	4.50	94
C2	1.10	2.05	95

The recoveries on real samples were also in agreement with the results found with the standard recoveries above. Similar results were reported by several authors (Bobrowski et al., 2004, 1997). Such results were expected, and the inefficiency of the UV-Vis

technique can be attributed to the high blank value of diphenylcarbazide and interferences by iron, aluminum, and other metals (Kristiansen et al., 1997). These interfering metal ions are more abundant in South African environments compared to rest of the world, which is the reason that they are not taken care of in the European UV-Vis spectroscopy standard method. These metals are unavoidably widespread in the cement and concrete leachate samples. Therefore, this method is not ideal for Cr(VI) determination in such samples.

5.5 Determination of hexavalent chromium in real cement leachate samples using AdSV and UV-Vis spectrophotometry

Cement leachate batch samples from HOLCIM were analyzed with both methods just to obtain the range and some comparison. The results are presented in Figure 5.3. There was an agreement with the results obtained with both techniques at intermediate Cr(VI) concentrations as seen in Figure 5.3, but with lower concentrations there was greater deviation as expected, which manifests because UV-Vis method fails with lower concentrations, found in the cement leachate samples.

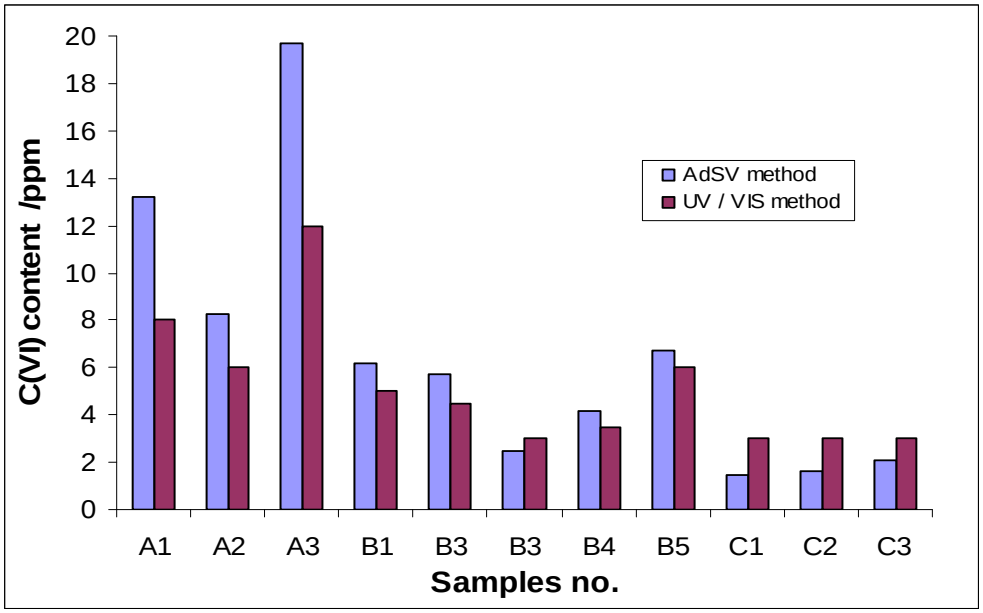

Figure 5.3 Determination for Cr(VI) content in cement samples using AdSV and UV/VIS method (refer to appendix 3 for the table of results). Labels (A, B, C) refer to different batch leachate samples from Holcim analyzed for Cr(VI) content from different samples.

The validation experiments for the analytical techniques showed that catalytic adsorptive stripping voltammetry gives more reliable results over the entire concentration range without any interference. It showed satisfactory accuracy, high sensitivity and simplicity. AdSV was found to be the most accurate compared to UV-Vis spectroscopy method for the detection of Cr(VI) content in leachate cement samples that are characterized with low Cr(VI) concentrations. For the above mentioned reasons, the AdSV method was used for Cr(VI) determination for the rest of the study in the Chapters that follows.

5.6 Leaching tests

5.6.1 Batch extraction procedure

In order to determine Cr(VI) in solid samples extraction followed by determination is necessary. Extraction under alkaline condition is ideal and recommended for chromium speciation in different cement samples because it minimizes reduction of Cr(VI) or oxidation of Cr(III) (Safavi et al., 2006; Yamaguchi et al., 2006; Potgieteret al., 2003). It also simulates the conditions prevalent during cement hydration.

The concrete cubes were crushed and sieved to (75µm) particle sizes and then approximately 1.00 g concrete powder and cement were leached with 20 ml of 0.1 M Na_2CO_3 (Yamaguchi et al., 2005; Potgieter, 2003; Cukrowska and Dube, 2001; Dermatas and Moon, 2006). According to the modified Toxicity Characteristic Leaching Procedures (TCLP) tests (Dermatas and Moon, 2006), the mixture was agitated at 18 rpm on a platform shaker for 24 hours, then filtered using a gravitational filter through a 0.45 µm filter paper and made up to the mark of 100 ml in a volumetric flask, then finally stored in a refrigerator at 4^0C and analyzed for Cr(VI) content within 24 hours using AdSV. (Some samples with higher Cr(VI) concentration were further diluted to maintain concentration in the linearity region of the analytical method).

5.6.1.1 Determination of Cr(VI) in cements and concrete after leaching

The results obtained from the sodium carbonate leaching method described previously are presented in Table 5.7. They indicate that the amount of Cr(VI) extracted depend on the type of cement used. It was shown that the total amount of Cr(VI) in fly ash cement and concrete was generally higher compared to the other types of high strength cement.

The Cr(VI) content in fly ash originated from the burning of coal (Toregö, 2006). Limestone cement and concrete consist of the least Cr(VI) content, similar findings were obtained in another study (Togero, 2006). Slag cement also contains higher Cr(VI) which is attributed to the ferrochrome slag included in the cement.

The batch experiment are done to provide an estimate of the Cr(VI) content in the different types of cements used in the building the concrete cubes and to compare the values obtained with our designed methods.

Table 5.7 Cr(VI) content in cements and concrete leached with Na_2CO_3 and analyzed using AdSV as described in chapter 4. (Refer to appendix 1 for AdSV parameters).

Samples	**Cr (VI) content** /ppm
HSC - Composite	14.6 ± 1.10
HSC - Limestone	8.6 ± 0.46
HSC - Fly ash	17.3 ± 0.71
HSC - Slag	13.1 ± 1.94
MC - Cement	14.3 ± 0.53
Cube - Composite	7.3 ± 0.32
Cube -Limestone	3.8 ± 0.07
Cube - Fly ash	14.4 ± 0.53
Cube - Slag	13.2 ± 0.28
Cube - Clinker	9.2 ± 0.28

The variation that may exist with Cr(VI) leachability on the concrete cubes could be attributed to the different elements and compounds present in the different types of cement which might have interacted with the speciation of interest.

5.6.1.2 The total chromium concentrations and other metals in cements and concrete cubes.

The results in Table 5.8 present the total chromium and other heavy metals concentrations in different types of concrete cubes, determined by ICP-OES after microwave acid digestion. The table shows other metals which are always present in chromium ore and they can interfere with the analysis of chromium

The fly ash cement consisted of the highest concentration of total chromium compared to the other types cements, followed by slag and composite, MC was the least (Table 5.5). The results indicate that the cement manufacturing process and the raw materials are not the only source of chromium in cement and cement products but, also the types of cement additives. The results obtained were in the proximity of the certified value, 137 mg/kg (Potgieter et al., 2003). These results are in agreement with those for Cr(VI) content leached using 0.1 M Sodium carbonate.

In the study of the leachability of Cr(VI) from concrete, it is crucial to evaluate the total chromium content and the hexavalent chromium present in a sample. It was reported that the amount of Cr(VI) leached from the concrete sample is proportional to the total chromium but there is a large gap existing between Cr(VI) and total chromium (Wang and Vipulanandan, 2000; van der Sloot, 2000).

Table 5.8 Total Chromium content and other metals in the different types of cement and concrete cubes [ppm].

	Cr	**Mn**	**Fe**	**Al**	**Cd**	**Cu**	**Pb**
1. HSC - limestone	**79**	4 900	64 600	43000	23	110	70
2. HSC - composite	**111**	3 200	13 500	32 600	17	30	71
3. HSC – Fly ash	**124**	700	16 800	18 900	8	17	71
4. M - Clinker	**59**	3 300	12 800	15 800	23	137	17
5. HSC - slag	**111**	1 104	31 100	10 500	10	94	58
5. Cube - limestone	**58**	105	18 000	7 200	8	76	74
6. Cube - composite	**82**	2 300	31 300	19 600	11	97	80
7. Cube – Fly ash	**68**	1 010	21 100	21 900	20	117	83

(Refer to appendix 2 for ICP-OES parameters)

With increased understanding of the leaching behavior of cement from different origins, where large differences in the Cr(VI) released exist in spite of marginal differences in total concentration, the use of total concentration as a criterion for quality control of cement is unacceptable.

5.6.2 Surface leaching procedures

There were two methods used; (A) laboratory designed surface leaching method and (B) modified static tank method (Bobrowski et al., 1997; Yu et al., 2005)

(A) The surface leaching method (laboratory designed) is further divided into surface *immersed* and *sprayed*. (1). The surface *sprayed* method consisted of placing 1000 cm^3 concrete cube samples in a closed beaker to prevent evaporation. A total volume of 250 ml of the pH adjusted de-ionized water was circulated continuously while sprayed on the side surface of the cube with the aid of a peristaltic pump and a T-shaped glass funnel (to evenly spray the concrete surface) (Figure 5.4). This method allows investigation at arbitrary time intervals. A 5 ml leachate was sampled for analysis every 24 hours for a leaching period of 5 days. This experimental setup simulates leaching on concrete buildings and other cement structures by natural rain. (2). In the surface *immersed* method, the test surface of the cube was immersed in the 250 ml leaching solution which was continuously agitated with a stirrer. Sampling was done as in A(1) above.

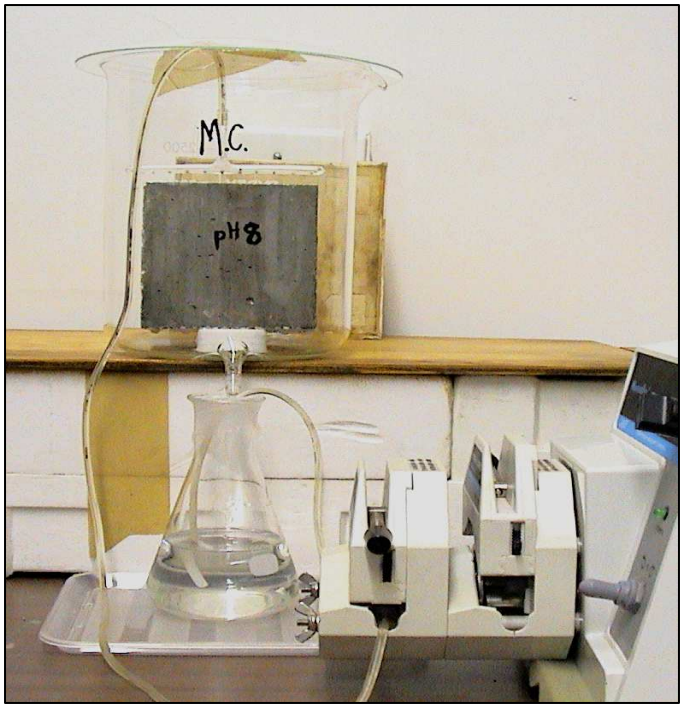

Figure 5.4 The designed experimental setup for continuous leaching of Cr(VI).

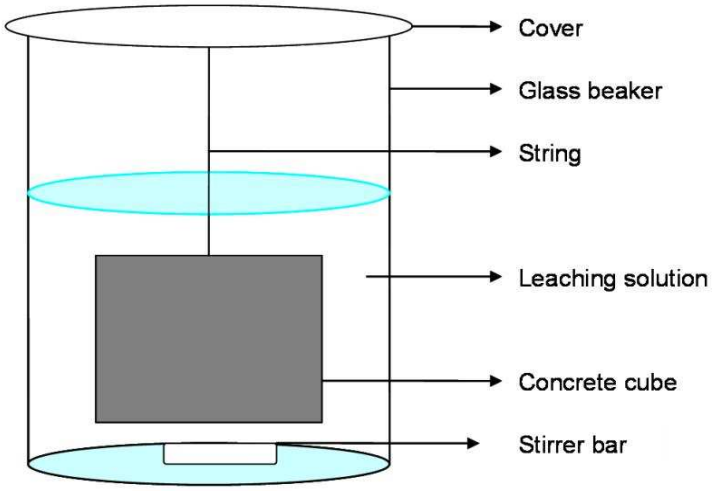

Figure 5.5 Leaching set up for the 125 cm^3 concrete cubes (modified tank method).

(B) In many laboratories performing leaching tests simulating natural environments. Different modifications of static tank methods are used (Yu et al., 2005). In this work, the modified static tank leaching method involved 125 cm^3 concrete cubes submerged in continuously stirred deionized water at adjusted pH with a magnetic stirrer, under

definitely controlled conditions (e.g. temperature) as illustrated in Figure 5.5. The leachate solution was sampled at 24 hours time interval to determined Cr(VI) content.

5.6.3 Comparison of designed surface leaching methods

5.3.3.1 Immersed surface and sprayed surface

The surface leaching method is where the concrete test surface is sprayed (*not immersed*) with leaching solution (Figure 5.4). The method simulates leaching of heavy metals from building structures by rain water. The surface *immersed* leaching method is where the cube side surface is immersed into leaching solution. The method simulates environmental leaching of heavy metals by natural and sea water, where concrete structures are used as bridges, tanks, pipes etc.

Evaluation of both leaching methods is advisable for the holistic understanding of leachability of heavy metals in all aspects of concrete matrix applications in the environment.

Figure 5.6 show the Cr(VI) content leached from 1000 cm^3 concrete made with fly ash cement. The cube was leached for a period of 5 days with deionized water at pH 10. (maintained with 40 % NaOH). Refer to the Appendix 3 for the table of results used in the Figure 5.6, the same applies to the Figures in the following chapters.

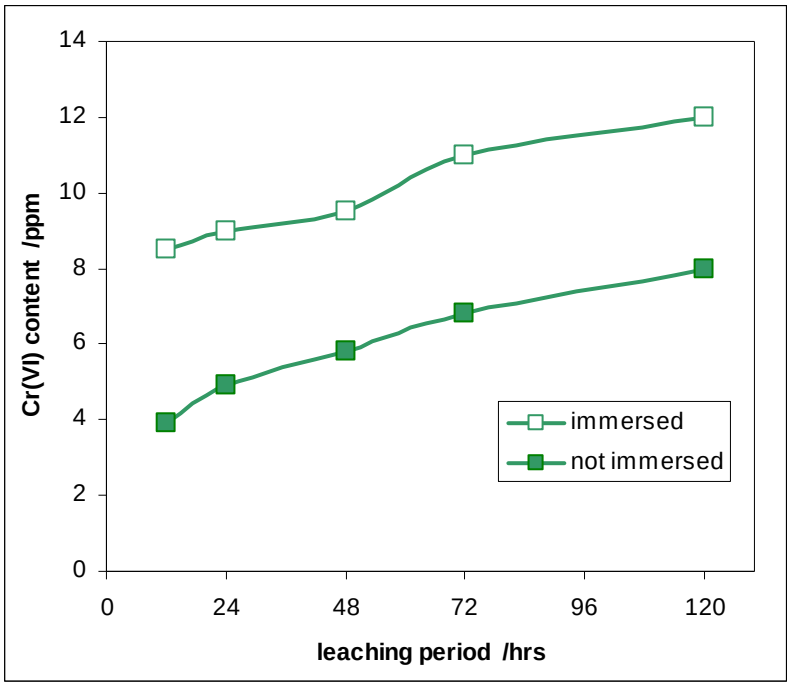

Figure 5.6 Cr(VI) content leached by immersing or spraying the test side surface of the concrete cube.

The results show that the immersed surface leaching compared to the sprayed surface (designed) method leaches more Cr(VI) because the cube has more surface contact with the leaching solution, facilitating diffusion of Cr(VI). The same results were obtained on cubes made with limestone cement. Yu et al. (2005) found similar results when they compared tank and shaken extraction leaching methods on a concrete matrix. According to the results, the amount of Cr(VI) leached from concrete surface is influenced by the leaching method. The different leaching methods represent different ways in which concrete is used in the environment.

Concrete cubes subjected to time dependent leaching showed uniform leaching patterns where the amount of the Cr(VI) in the leachate increased with the leaching period (Figure 5.6). This is attributed to continuous oxidation and leaching of chromium from the

concrete matrix under the specified conditions. The leaching of Cr(VI) occurs in a two step process. Firstly, the loosely surface bonded Cr(VI) was washed out into the leaching solution during the first few hours. Secondly, diffusion controlled transport resulted in a small increase of Cr(VI) in the leachate with time. These findings are in agreement with those reported in similar studies by several authors (Wang and Vipulanandan, 2000; van der Sloot, 2005; Dermatas and Moon, 2006), hence different leaching methods elute the metal content to different extent.

5.7 Environmental parameters that increases the leachability of Cr(VI) from concrete

Treatment of concrete cubes with parameters that affect the leachability of Cr(VI) allows the evaluation of the environmental risk posed by real world application of concrete. The following parameters are proposed to accelerate the leachability of Cr(VI) in concrete surfaces; leachate pH, UV radiation, temperature, concrete aging time, presence of chromium oxidizing agents. Hence, they can increase the risk of Cr(VI) pollution of the environmental waters.

5.7.1 The effect of pH

Concrete finds application under different pH conditions ranging from acidic to alkaline pH. The aim of this investigation was to determine the leaching and immobilization behaviour of Cr(VI) under specific aggressive pH conditions with the use of leaching tests.

5.7.1.1 Leaching at pH 4

Acidic leaching tests simulate more severe environmental conditions that concrete products are likely to encounter in real-world applications but most possibly in contaminated soils (e.g. acid mine drainage and acid rain).

The leaching for Cr(VI) from 1000 cm^3 concrete made with different kinds of cements with deionized water which was maintained at pH 4 using 1 M H_2SO_4. The leaching was carried out as described in Section 5.3.2a and results for Cr(VI) content are presented in Figure 5.7.

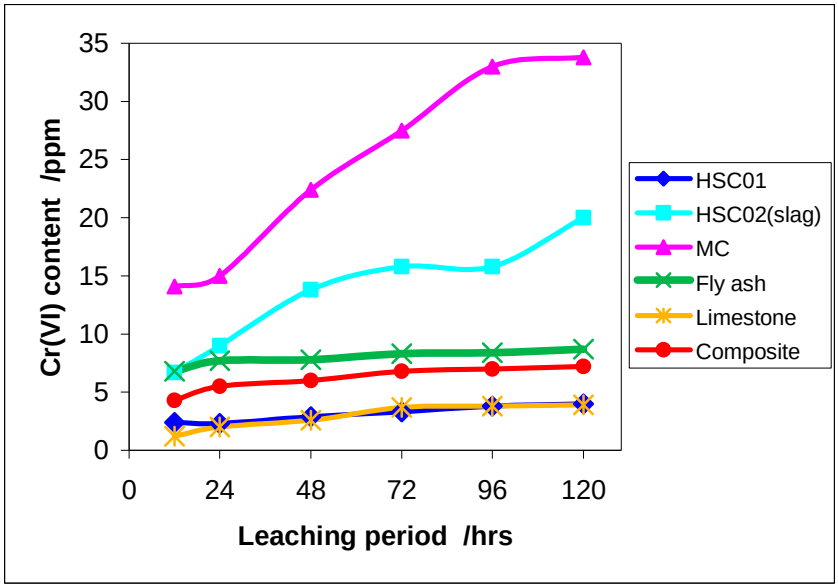

Figure 5.7 Cr(VI) content in leachate versus leaching period at pH = 4 leached on the side surface of concrete cubes of different cements.

The leaching curves show relatively uniform leaching patterns, where the amount of the Cr(VI) in the leachate increases with the leaching period in all types of cements. The increase in Cr(VI) leachability with increasing leaching period was due to oxidation of Cr(III) to Cr(VI) in the concrete and also the diffusion of Cr(VI) from the concrete to the leachate solutions. The rate of this oxidation reaction will be dependent on the penetration of atmospheric oxygen (Pillay et al., 2003).

It was evident from the results that different kinds of cements had different capabilities of leaching and immobilization of Cr(VI) in the concrete matrix. The concrete cubes made of MC were observed to leach higher Cr(VI) concentrations than the cubes made with other cements in the sequence; HSC02 (slag) > Fly ash > composite > HSC01 > limestone.

In a study of leaching of heavy metals (Yu et al., 2005), it was reported that at lower pH, the leaching of heavy metals was enhanced. At the leachate pH levels of 4, metals are highly soluble (Webster and Loehr, 1996) which in turn can also influence the mobility and speciation of chromium in many different ways. However, the main influence of pH on leachability is dependent on particular metal solubility properties.

5.7.1.2 Leaching at pH 8

Leachability in the alkaline range (pH 7 - 11) is most relevant from an environmental point of view, since those are the conditions prevailing in the cement hydration. It is therefore, more relevant to study the influence of alkaline pH on the Cr(VI) leachability.

A similar leaching investigation as the above was undertaken at pH 8. The pH was maintained using 40 % (w/v) NaOH. Figure 5.8 shows the Cr(VI) concentrations obtained after leaching of the concrete cubes made of the different kinds of cement.

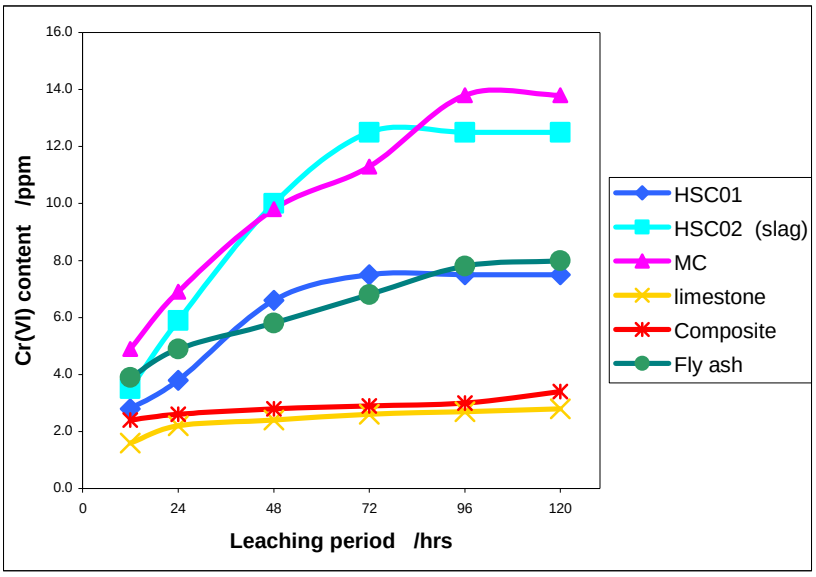

Figure 5.8 Cr(VI) content in leachate versus leaching period at pH = 8 leached on the side surface of concrete cubes of different cements

The alkaline leaching results in Figure 5.8 show an increase in Cr(VI) content with an increase in leaching period, which was in agreement with the leaching results in acidic pH. Alkaline leaching of the concrete cubes also followed the same trends with the amount of Cr(VI) leached in acidic conditions: MC > HSC02(slag) > fly ash > HSC01 > composite > limestone. Frìas and Sànchez de Rojas (2002) also reported similar results. The amount of Cr(VI) in the leachate increased with decreasing pH with the all the different kinds of cements and the opposite results were obtained with HSC01 and limestone cubes.

In this study, it was observed that only the concrete cubes made with HSC01 and limestone, leached higher Cr(VI) with higher leachate pH which is in agreement with literature (Geelhoed et al.,2002). According to the chemistry of chromium, it is expected that higher concentration of Cr(VI) is leached in alkaline conditions because chromate ions adsorb onto positively charged surfaces of oxides, hydroxide and clay minerals, whereby at this high pH these surfaces will be negatively charged (Geelhoed et al.,2002). Limestone and HSC01 concrete happen to immobilize Cr(VI) better compared to the MC and HSC02 concrete.

The concretes made from the other types of cements presented opposite results. It is evident that in acidic pH, higher amounts of Cr(VI) are leached in cubes made with MC, HSC02(slag), fly ash and composite. This means that lower pH accelerates Cr(VI) leachability. Similar results were reported by the following authors; van der Sloot (2000) and Wang and Vipulanandan (2000). This could be due to the influence of different additives and admixtures in the different kinds of cements, which might consist of

elements or compounds that can interact or interfere with the chemistry of chromium speciation and the acid neutralization capacity of the concrete plays a role. Also that solubility of many metal ions in a particular concrete increases with the decrease in pH. The stability of chromium in cement matrices is due to formation of $CaCrO_4$ which is insoluble in water, but its elution is due to formation of Na_2CrO_4 which is highly soluble. The formation of the different chromates differs with different types of cements and is likely to be dependent on pH.

There were many factors that were involved with the leachability of Cr(VI) in the concrete cubes other than pH. The higher Cr(VI) concentrations could also be attributed to physical properties of the concrete cubes, for example MC cubes have the highest porosity, therefore higher surface area for the leaching of Cr(VI) (Togerö, 2006). Elevated concentration Cr(VI) in the leaching of different cement materials could also be due to cement additives some of which consisted of elevated chromium content (e.g. slag, fly ash), and compounds with capabilities of reducing (e.g. Fe(II)) and immobilizing or mobilizing Cr(VI) (e.g. limestone) in the concrete (Dermatas and Moon, 2006).

This study show that the leachability and immobility of Cr(VI) bears largely on leachate pH, as well as the type of cement and corresponding metal hydroxide solubility controlled process (Malviya and Chaudhary, 2006).

5.7.2 The effect of temperature

South Africa experiences warmer temperatures compared to most European countries and this might increase the risk of Cr(VI) pollution through leaching. Temperature is known to play an important role in the oxidation of chromium in nature (Sedlack and Chan,

1997). The study was aimed at investigating the influence of temperature on the leachability of Cr(VI) in a concrete matrix.

The leaching for Cr(VI) in 125 cm^3 HSC01 concrete cubes was carried out as described in the previous chapter (Section 5.3.2.b) at different temperatures (20, 30, 40^{0}C). Figure 5.9 shows the results for Cr(VI) content leached with deionized water maintained at pH 10 by addition of 40 % NaOH.

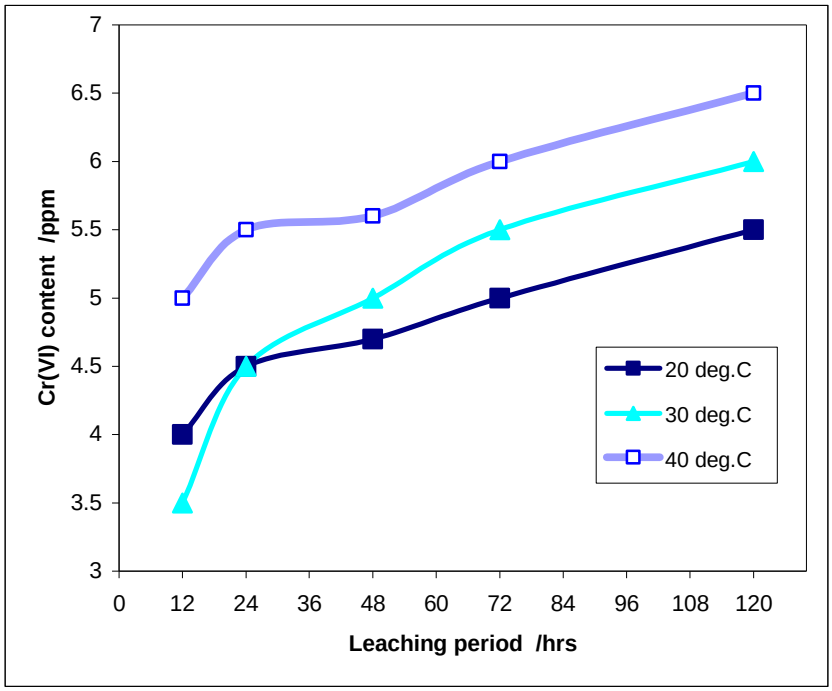

Figure 5.9 Cr(VI) content leached at pH 10 from HSC01 concrete cubes at different temperatures.

It is evident that there was a slight increase in Cr(VI) content in the leachate with increase in leaching temperature. These results shows that temperature positively affect the Cr(III) oxidation reaction to a certain extent. These results are in agreement with an investigation by Sedlack and Chan (1997), where they found that the rate of the reaction increased by a

factor less than two. The effect of temperature on the rate of the reaction can be attributed to the redox chemistry of Fe that occurs as the temperature changes.

5.7.3 The effect of UV radiation

South African climate is characterized by high UV radiation, hence concrete in building structures is also subjected to the radiation. It is therefore, very important to evaluate the effect of radiation on the leachability of Cr(VI) in concrete.

The irradiation experiment involved 125 cm^3 HSC01 concrete cubes which were continuously wetted with deionised water while under UV irradiation with a 500 watts UV lamp for six hours. This was followed by leaching for Cr(VI) content at pH 10 according to Section 5.3.2.b. Figure 5.10 shows the results obtained.

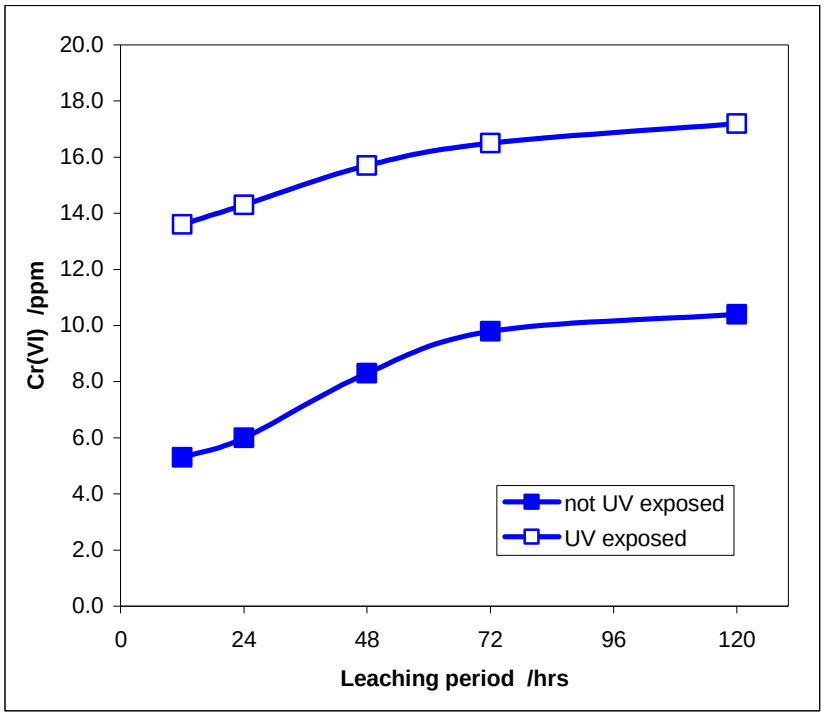

Figure 5.10 Cr(VI) content leached from HSC01 concrete cubes after UV irradiation

Figure 5.10 shows that a steady state is reached after 72 hours of leaching and almost all the chromium in the leachate was in its highly oxidized state, Cr(VI), since the gradient of the curve was lower with UV radiation. The results showed elevated concentrations of Cr(VI) leached after UV exposure. It can be deduced that UV irradiation accelerates Cr(VI) leachability by the oxidation of Cr(III) that exist in concrete. These results are in agreement with those reported by Bobrowski et al (2004) that UV is an oxidizing agent that oxidizes Cr(III) to Cr(VI). These results show that there is a risk of Cr(III) oxidation in the environment attributed to high UV radiation.

5.7.4 The effect of Addition of MnO_2 to concrete

Manganese compounds are unavoidably distributed everywhere in South African environments and therefore always there in concrete. Manganese oxides have been reported to play a very important role in the oxidation of Cr(III) (Kim et al., 2002; Battlet & James, 1979), hence its influence in Cr(VI) leachability in concrete is expected. The effect of MnO_2 was investigated at extreme pH conditions prevailing in cement and concrete to obtain its effect.

There are different kinds of manganese oxides that occur in the natural environment which includes; birnessite, todorokite, Pyrolusite and lithiophorite. They are reported to influence the oxidation of Cr(III) at different rates, greater for todorokite and birnessite that contained the most quadrivalent Mn and least for lithiophorite that contained a greater proportion of trivalent Mn (Kim et al., 2002). Pyrolusite (reagent grade chemical standard) was used in the experiment.

The 125 cm^3 HSC01 concrete cubes made with manganese oxide, added as a cement additive in different proportions (0.1, 0.5, 1.0 and 2.5 %) were leached for Cr(VI). The leaching experiment for Cr(VI) content was done as prescribed in Section 5.3.2b at pH 12. The results are shown in Figure 5.11 and tabulated in the Appendix.

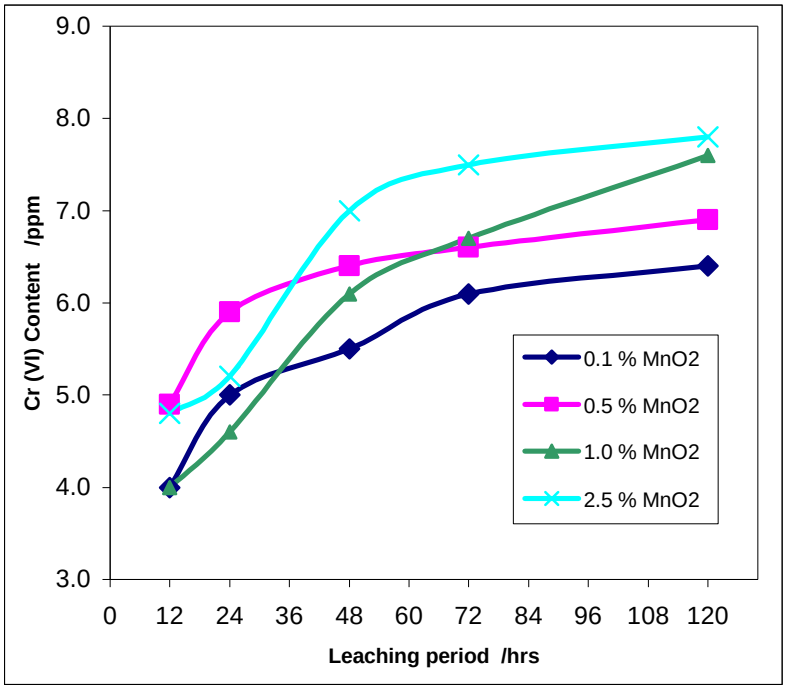

Figure 5.11 Cr(VI) Content in concrete cubes with different amount of MnO_2 leached at pH = 12.

The results in Figure 5.11 show that there was a non negligible increase in the amount of Cr(VI) leached with an increase in the amount of MnO_2 added to the concrete cube. This meant that manganese oxides positively influence the oxidation of Cr(III) to a certain extent. These findings are in agreement with those reported by several authors (Kim et al., 2002; Rinehart et al., 1997; Rai et al., 1987). Addition of manganese oxides to cements will increase the oxidation of Cr(III) to Cr(VI) (Kim et al., 2002), hence increase

the concentration of Cr(VI) since it affects the redox chemistry of chromium. The effect of MnO_2 in concrete leachability of Cr(VI) will finally depend on the type of MnO_2 present since the different types exhibit different activity on the oxidation of Cr(III).

5.7.5 The effect of aging of the concrete cubes

The kinetics of chromium oxidation and reduction was reported to be very slow under natural conditions depending on a number of factors (Pillay et al., 2003). Aging of the prepared concrete cube appeared to be a very important parameter to evaluate in this study.

Figure 5.12 show the results for Cr(VI) content leached from 125 cm^3 concrete cubes made with HSC01 and left to age under normal air oxidation for 1 and 10 days after curing. The leaching was carried out at extremely alkaline pH 10 as described in Section 5.3.2b.

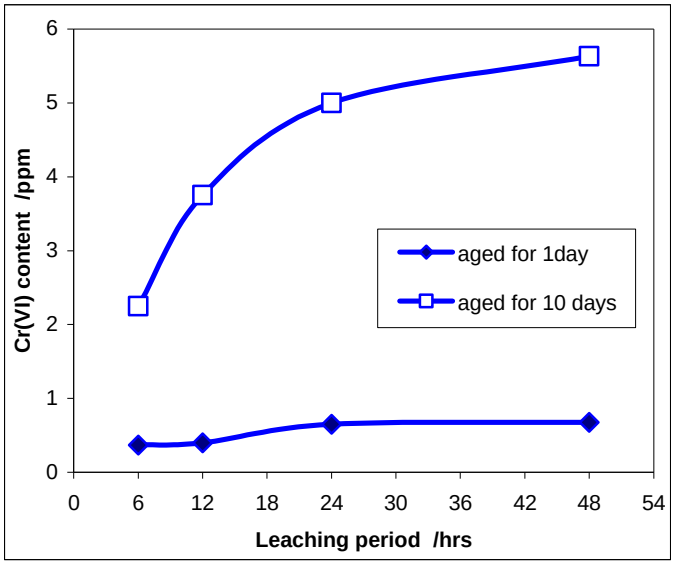

Figure 5.12 Cr(VI) content in HSC01 concrete cube leached at pH = 10 after ageing at room conditions.

The amount of Cr(VI) leached from cubes that were aged for 10 days compared to the one aged for 1 day was approximately 5 times higher (Figure 5.12). Aging and drying of concrete played a major role in the leaching of Cr(VI). Aging provides a pathway for the oxidation of Cr(III) in the presence of oxidants such as MnO_2 naturally existing in cements and the concrete mixture. These results are in agreement with the studies undertaken by Pillay et al (2003) which showed the rate of Cr(III) oxidation under environmental conditions is faster than anticipated.

5.8 Treatment of concrete that stabilizes Cr(VI)

One of the aims of this investigation was to find a way of reducing or immobilizing Cr(VI) in cement and concrete. The following additives were evaluated in this study; ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) and humic acids (HA).

5.8.1 Addition of Humic acids to the concrete cubes

HA was reported to have high binding capacity for Cr(III) and Cr(VI) reducing ability (Davies et al., 1997; Fetsch et al., 1998; Pettine, 1998; Pettine et al., 2002). This prompted its investigation in the immobilization and reduction of chromium in cement and concrete products.

The addition of humic acid as a concrete admixture provides technical side effects to the concrete. The leaching for Cr(VI) experiment was carried out as described in Section 5.3.2 b, at pH 8. From the results it is seen that with the addition of humic acid, the setting time for the concrete was delayed to about 10 days instead of 24 hours which makes it unusable in practice, and also greatly deteriorated the quality of the concrete

(strengths and colour, Figure 5.13). The reason could be that HA caged water molecules and other elements that are responsible for the physical properties of concrete.

Figure 5.13 HSC01 concrete cubes consisting different amount of HA: no HA, 2.5 % HA and 5 % HA, respectively.

The results that were obtained were opposite to what was expected according to literature whereby the HA was reported to bind Cr(III) and other metals irreversibly. Therefore, preventing any Cr(VI) resulting from the oxidation of Cr(III) (Fetsch and Havel., 1998). The addition of humic acid was supposed to immobilize Cr(VI) in the concrete. It was a positive proof that HA did not immobilize the Cr(VI)".

The results showed increase of Cr(VI) elution with the addition of HA. Addition of HA increases the porosity and resulted in enhanced surface area for the leaching of chromium as shown in Figure 5.13.

Chromate ions adsorb onto positively charged surfaces of minerals, but at high pH, these surfaces will be negatively charged. This could explain why humic acid is not binding

Cr(VI) in cement as expected since cement has a very high pH (Geelhoed, 2002). Cr(VI) reduction with HA has been reported at acidic pH, with a half life of 3.6 hours at pH 2 (Pettine et al., 2002). Based on results in this study, humic acid is not supposed to be used in cement or concrete as a stabilizing agent for chromium.

5.8.2 Addition of $FeSO_4 \cdot 7H_2O$ to the concrete cubes

The reduction behavior of Cr(VI) was also investigated by using ferrous sulfate addition, since previous research has conclusively established that ferrous iron is a highly effective Cr(VI) reductant (Laskowski, 1996; Klemm**,**1994; Sedlak and Chan, 1997; Kim et al., 2002) in cement.

The addition of iron sulfate did not interfere with the binding properties of the cement. There was no difference in the colour of the concrete cubes with or without the ferrous sulfate, there was no change was observed with their setting time. This showed that ferrous sulfate had no technical effect on the properties of cement (Laskowski, 1996). This is one of the requirements for an immobilizing or reducing agent.

The Figure 5.14 shows results for Cr(VI) content leached from 125 cm^3 concrete cubes consisting of different amount of ferrous sulfate ($FeSO_4 \cdot 7H_2O$). The leaching was carried out as described Section 5.3.2b. The results are tabulated in the Appendix.

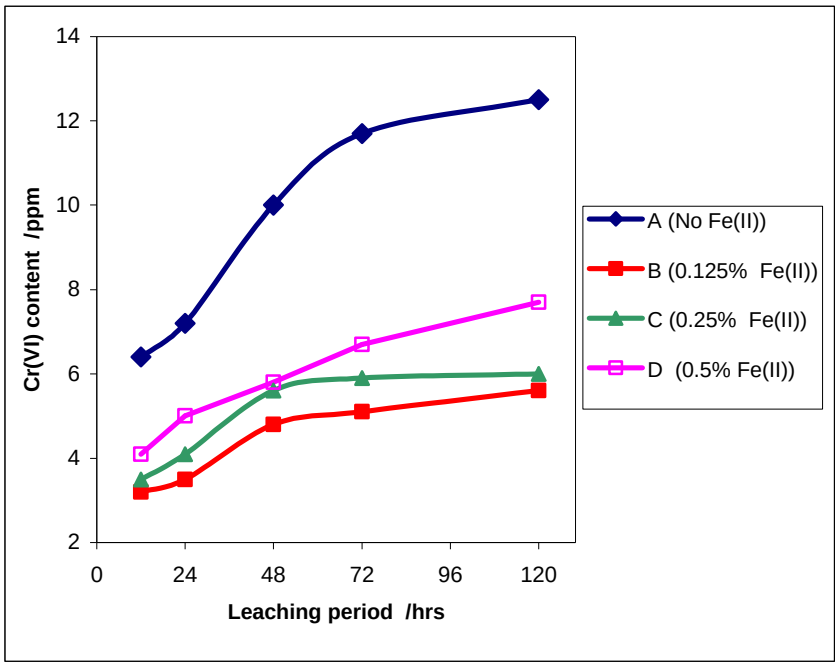

Figure 5.14 Cr(VI) content leached from concrete cubes containing $FeSO_4 \cdot 7H_2O$

From the results, it is observed that on addition of the ferrous sulfate, the amount of Cr(VI) leached from the concrete cubes decreases considerably (Figure 5.14). The results demonstrate that ferrous sulfate in concrete had successfully reduced Cr(VI) to a certain extent. Cr(VI) was reduced by more than 50 % by addition of 0.13 % ferrous sulfate. However, with an increase of the amount of the reducing agent, reducing efficiency deteriorates. The reason could be due to the precipitation of $Fe(OH)_2$ and reduction of the surface active sites for the reaction. Laskowski, (1996) reported that 0.35 % (w/w) iron sulfate was enough to reduce 20 mg Cr(VI) / kg cement. The difference with the results of this work could be due to the different types of cement used and the different environmental conditions (e.g. climate) which also contribute to the redox chemistry of chromium.

Most importantly in South African conditions, it is possible that ferrous sulfates doesn't achieve 100 % reduction of Cr(VI) in cement and concrete because the factors affecting the reaction are more severe (UV, temperatures, Mn levels) in this country compared to other parts of the world (e.g. Europe). Hence, the ferrous sulfate can be oxidized to ferric oxide which is inactive. There is also the risk of re-oxidation of Cr(III) in the concrete matrix.

There is still insufficient information on the mechanism of Cr(VI) reduction with iron sulfates, and the reason why, specific ferrous sulfate content in the cement gives optimum results. There is no obvious relationship with the stoichiometry of the reduction equation.

$$Cr^{6+} + 3Fe^{2+} \rightarrow Cr^{3+} + 3Fe^{3+}$$

It has been reported that only the ferrous sulfate salts are successful in reduction of hexavalent chromium in cement and cement materials compared to other ferrous salts (Laskowski, 1996). One of the reasons could be that cement contain mineral (e.g. hydrocalumite) which is known to have ionic exchange properties of chromate for sulfate (Geelhoed et al., 2003).

It is evident from the results that ferrous sulfate is still the best Cr(VI) immobilizer or reductant in cement and concrete to a certain extent. It is imperative that other methods Cr(VI) reduction are discovered to solve the problem of chromium contamination in the country and to meet the European standard of 2 ppm Cr(VI) content in cement to compete in global markets.

CHAPTER 6

Conclusions and recommendations

6.1 Conclusions

The precise determination method of Cr(VI) in concrete was developed based on surface leaching. The designed test simulates environmental conditions for concrete as a building material. This method allows investigation at arbitrary conditions and time intervals. Different parameters were varied including; temperature, aging time, UV radiation, which have been shown to have an effect on the oxidation of Cr(III). An increase of these parameters increased the amount of Cr(VI) leached from the concrete matrix. The addition of manganese oxide have been shown to increase the amount of Cr(VI) leached from the concrete cubes, which is attributed to oxidation of chromium. The leaching of Cr(VI) was also shown to depend largely on the leachant pH, where acidic pH increased the leachability of Cr(VI) but opposite results were observed in alkaline conditions.

The leaching of Cr(VI) from concrete is highly dependent on the different types of cement used since they consist of different Cr(VI) oxidizing, reducing or mobilizing and immobilizing agents. Their capacity to leach Cr(VI) was found to be in this order, starting with the highest to the lowest; MC > HSCO1 > HSCO2(slag) > Fly ash > composite > limestone. This means that concrete made with limestone stabilizes Cr(VI) better compared to those made of other kinds of mixes (e.g. MC, slag and fly ash).

Physical properties of concrete play a very important role in the leachability of Cr(VI). The concretes that had higher porosity and sorptivity were found to facilitate Cr(VI)

leachability to some extent and that was manifested with MC concrete leaching the highest amount of Cr(VI). HSC01 concrete had the least water sorptivity and porosity hence it leached the least amount of Cr(VI) at lower pH.

In the study of agents resulting in the reduction and immobilization of Cr(VI) in cement and concrete, humic acids addition was to be ineffective, instead it interfered with the concrete physical properties which included deterioration of the quality of the concrete.

Ferrous sulfate played a major role in the reduction and stabilization of Cr(VI) in concrete, a dosage of approximately 0.13 % (w/w) gave optimum activity. The addition of ferrous sulfate was observed not interfere with the mechanical properties of the cement and concrete, therefore it is still the best Cr(VI) stabilizing agent.

The optimised adsorptive stripping voltammetric method was successfully used for the analysis of Cr(VI) content in cement and concrete leachate samples. It was shown to be a very sensitive and selective method for Cr(VI) analysis and allows extremely low quantification limit. The UV-Vis spectrometry was found not to be sensitive enough for Cr(VI) analysis in cement leachate samples since it was shown to have a poor accuracy and suffered from interferences, and had higher quantification limits for the low Cr(VI) concentrations in cement leachate samples.

6.2 Recommendations

- The developed method for Cr(VI) determination in concrete can be used in industrial applications.

- The use of limestone concrete is advised because it was shown to immobilize Cr(VI) best compared to the tasted concretes.
- Addition of Fe(II) to concrete is recommended since it successfully reduces and immobilizes Cr(VI) in concrete to a certain extent.

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Appendix 1 Summary of parameters used in AdSV procedure for the determination of Cr(VI)

Initial purging time:	300 s
Deposition potential:	–1.0 V
Deposition time:	60 s
Equilibration time:	10 s
Differential pulse scan:	from –1.0 V to –1.4 V
Scan rate:	30 mV s-1,
Frequency:	50 Hz
Pulse amplitude:	50 mV.
Number of additions:	3
Peak position:	1.25 ± 0.05
Electrode:	HMDE

Appendix 2 Summary of instrument parameters used in Microwave and ICP – OES

(i) Microwave parameters for digestion

Power:	1200 watts
Ramp:	15 minutes
Fan1 hold:	15 minutes
Fan2 hold:	20 minutes
Rate:	0.5 bar /s
Process max power:	60 bar

(ii) ICP –OES Parameters

Plasma power:	1300 w
Pump step:	2
Coolant flow:	13.0 $Lmin^{-1}$
Auxiliary flow:	1.0 $Lmin^{-1}$
Heating:	1

Appendix 3 Tables of results for the Cr(VI) content determined from cement and concrete leachate samples

Table 3A.1 Cr(VI) content leached with deionised water at pH 10 by surface immersing and surface spraying of the concrete cube made with limestone cement.

Leaching period /hrs	**Immersed surface leaching** Cr(VI) /ppm	**Surface leaching** Cr(VI) /ppm
12	4.5	1.6
24	5.0	2.2
48	5.5	2.4
72	5.6	2.6
120	6.0	2.8

Table 3A.2 Cr(VI) analysis of the leached 11 cement samples using AdSV method and UV method.

samples	Cr(VI) content /ppm AdSV method			Cr(VI) content /ppm UV method		
	1	2	**Av**	1	2	**Av**
A1	13.8	12.5	**13.2**	8.0	8.0	**8.0**
A2	8.1	8.4	**8.3**	6.0	6.0	**6.0**
A3	19.0	20.3	**19.7**	12.0	12.0	**12.0**
B1	6.3	6.1	**6.2**	5.0	5.0	**5.0**
B2	5.6	5.9	**5.7**	4.0	5.0	**4.5**
B3	2.5	2.5	**2.5**	3.0	3.0	**3.0**
B4	4.1	4.3	**4.2**	3.0	4.0	**3.5**
B5	6.9	6.5	**6.7**	6.0	6.0	**6.0**
C1	1.5	1.5	**1.5**	3.0	3.0	**3.0**
C2	1.5	1.6	**1.6**	3.0	3.0	**3.0**
C3	2.0	2.1	**2.1**	3.0	3.0	**3.0**

Table 3A.3 Cr(VI) content leached from the side surface of a 1000 cm^3 concrete at pH 4.

Leaching period /hrs	HSC01	HSC02 (slag)	MC	Fly ash	Limestone	Composite
	Cr(VI) /ppm	Cr(VI) /ppm	Cr(VI) /ppm	Cr(VI) /ppm	Cr(VI) /ppm	Cr(VI) /ppm
12	2.4	6.7	14.1	6.8	1.2	4.3
24	2.3	9.0	15.0	7.7	2.0	5.5
48	2.9	13.8	22.4	7.8	2.6	6.0
72	3.3	15.8	27.5	8.3	3.7	6.8
96	3.8	15.8	33.0	8.4	3.8	7.0
120	4.0	20.0	33.8	8.7	3.9	7.2

Table 3A.4 Cr(VI) content leached from the side surface of a 1000 cm^3 concrete at pH 8.

Leaching period /hrs	HSC01	HSC02 (slag)	MC	Fly ash	Limestone	Composite
	Cr(VI) /ppm	Cr(VI) /ppm	Cr(VI) /ppm	Cr(VI) /ppm	Cr(VI) /ppm	Cr(VI) /ppm
12	2.8	3.5	4.9	3.9	1.6	2.4
24	3.8	5.9	6.9	4.9	2.2	2.6
48	6.6	10.0	9.8	5.8	2.4	2.8
72	7.5	12.5	11.3	6.8	2.6	2.9
96	7.5	12.5	13.8	7.8	2.7	3
120	7.5	12.5	13.8	8	2.8	3.4

Table 3A.5 Cr(VI) content leached from cubes at different temperatures at pH 10.

Leaching time /hrs	**Temp. 20^0C** Cr(VI) /ppm	**Temp. 30^0C** Cr(VI) /ppm	**Temp. 40^0C** Cr(VI) /ppm
12	4.0	3.5	5.0
24	4.5	4.5	5.5
48	4.7	5.0	5.6
72	5.0	5.5	6.0
120	5.5	6.0	6.5

Table 3A.6 Cr(VI) content in concrete cubes leached at pH 10 after six hours of UV irradiation over a period of time.

leaching period /hrs	**not UV exposed** Cr(VI) /ppm	**UV exposed** Cr(VI) /ppm
12	5.3	13.6
24	6.0	14.3
48	8.3	15.7
72	9.8	16.5
120	10.4	17.2

Table 3A.7 Cr(VI) content in concrete cubes with MnO_2 leached at pH 12 over a period of time.

Leaching time /hrs	**0.1 % MnO_2 cube** Cr(VI) /ppm	**0.5 % MnO_2 cube** Cr(VI) /ppm	**1.0 % MnO_2 cube** Cr(VI) /ppm	**2.5 % MnO_2 cube** Cr(VI) /ppm
12	4.0	4.9	4.0	4.8
24	5.0	5.9	4.6	5.2
48	5.5	6.4	6.1	7.0
72	6.1	6.6	6.7	7.5
120	6.4	6.9	7.6	7.8

Table 3A.8 Cr(VI) content from HSC01 concrete cubes leached at pH 10 after 1 and 10 days of aging at normal room conditions.

Leaching period /hrs	**Aged for 1 day** Cr(VI) /ppm	**Aged for 10 days** Cr(VI) /ppm
6	0.37	2.25
12	0.40	3.75
24	0.65	5.00
48	0.68	5.63

Table 3A.9 Cr(VI) content leached at pH 10 from concrete cubes consisting of $FeSO_4.7H_2O$

Leaching time /hrs	**A** **No Fe(II)** Cr(VI) /ppm	**B** **0.1 % Fe(II)** Cr(VI) /ppm	**C** **0.25 % Fe(II)** Cr(VI) /ppm	**D** **0.5 % Fe(II)** Cr(VI) /ppm
12	6.4	3.2	3.5	4.1
24	7.2	3.5	4.1	5.0
48	10.0	4.8	5.6	5.8
72	11.7	5.1	5.9	6.7
120	12.5	5.6	6.0	7.7