LEACHABILITY OF CHROMIUM IN CEMENT USING WHOLE BLOCK LEACHING

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A project report submitted in partial fulfilment of the
requirements for the award of the degree of
Bachelor of Engineering (Hons.) of Chemical Engineering

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May 2016

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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I certify that this project report entitled **"LEACHABILITY OF CHROMIUM IN CEMENT USING WHOLE BLOCK LEACHING"** was prepared by **LIM SI KAI** has met the required standard for submission in partial fulfilment of the equirements for the award of the degree of Bachelor (Hons.) of Chemical Engineering at Universiti Tunku Abdul Rahman.

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ABSTRACT

Industrial revolution make possible for consumer product being manufactured in bulk concurrently generate massive amount of heavy metals bearing waste, hence it is necessary to develop convenient, efficient, and cost effective remediation technologies to cope with increasing demand to treat heavy metal bearing waste. In this study, effectiveness of stabilization and solidification to reduce leachability of chromium pollution was studied using whole block leaching method. Sodium chromate was served as the source of hexavalent chromium in this experiment. Cement cube samples are doped with RHA and sodium chromate and immersed in acetic acid for contact time of 1h, 4h, 7h, 14h, 1d, 4d, 7d, 14d and 28d. Cement cube were removed from acetic acid after specific immerse duration lapsed. This finding showed ordinary Portland cement (OPC) cable to reduce chromium (VI) ions into chromium (III) ions in leachate which later on deposited within cement cube matrix. Results revealed that concentration of chromium increased drastically after contact time of one day subsequently reduced. EDX and XRD results showed that chromium precipitate in cement cube as chromium (III) compound such as iron chromium oxide and chromium oxide. Other than that, XRD revealed white precipitate found on the surface of cement cube indeed was calcium carbonate. Lastly, RHA reduced cement cube hydraulic conductivity hence lessen calcium leachability. For control samples, pH of leachate increased from pH 2.88 to pH 12 subsequently remained constant. As a conclusion, OPC effectively reduced leachability of chromium yet did not comply with Malaysia regulatory standard of 0.05 ppm.

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LIST OF SYMBOLS / ABBREVIATIONS

ASTM	American Society for Testing Materials
CH	Calcium Hydroxide
Cr (VI)	Hexavalent Chromium
Cr (III)	Trivalent Chromium
CS	Calcium Silicate
C-S-H	Calcium Silicate Hydrate
d	day
DWLP	Deionized Water Leaching Procedure
h	hour
EDX	Energy Dispersive X-ray Spectroscopy
ICP-OES	Inductive Coupled Plasma Optical Emission Spectroscopy
MSWI	Municipal Solid Waste Incineration
OPC	Ordinary Portland Cement
PCLT	Pancake Column Leach Test
Ppb	Part per Billion
Ppm	Part per Million
prEn	Pitting Resistance Equivalent Number
RHA	Rice Husk Ash
SBLT	Sequential Batch Leaching Test
SEM	Scanning Electron Microscopy
SPLP	Synthetic Precipitation Leaching Procedure
S/S	Solidification/stabilization
TCLP	Toxicity Characteristic Leaching Procedure
XRD	X-Ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background

Industrial revolution improved mankind living standards and enhances civilization. Population growth leads to intensive demand for resources caused depletion of resources encourage people to look for better alternative. Industrial revolution make possible for consumer product being manufactured in bulk quantity continuously at the same time spawned massive amount of waste. Other than that, commercial product eventually turned into massive amount of municipal waste at the end of life cycle, resulting in unpredictable dissemination of toxic substances into environment. Generation of waste increased significantly since year 1960 to 2013 (Bobby, 2014), over 250 million tons of municipal solid waste was generated daily, without taking hazardous waste generation into consideration (Tibi, 2014).

Catastrophic historical incidents often reported due to poor waste management, such as the Minamata disease caused by improper methyl mercury containing waste disposal in Japan around 1960 (Timothy and Jane, 2001). In addition, abandoned mining site such as the Tui mine, New Zealand continuously leached heavy metal from the tailings, carried downstream by Tunakohoia River and flow through the centre of Te Aroha Town for four years after the mine closed (Ministry of the Environment, ND). These events draw worldwide attention to develop efficient and cost effective way to handle and treat hazardous waste.

Table 1.1 shows some global sites which suffer from severe heavy metal pollution due to leaching of heavy metals. Several waste management system developed to cope with large amount of waste, for example landfill, incineration, composting and etc. However, the final disposal form of heavy metal in these facilities remains mobile and unstable likely to enter environment via leaching process.

Table 1.1: Heavy Metal Polluted Sites All Around the Globe (Bobby Miller, 2014)

Heavy Metal Carrier	Major Origin / Location
Municipal Incineration Bottom and Fly Ash	Japan
Electroplating Sludge	India
Medical Waste Fly Ash	China
Leather Industry Waste Water	European Union
Municipal Wastewater Treatment Plants	United State of America
Rural Agricultural Cultivation and Fertilization	South Africa
Industrial Waste Water	Industry Zone
Soil Contamination	Road Runoff

In contrast to organic pollutant, heavy metal neither biodegrade nor destroy once it is discharged into environment, consequently accumulated up to high concentration and threatened all forms of life although it may be biological essential trace element (Conor, 2004). The mobility, bioavailability and toxicity of heavy metal vary with environment parameter and play an important role in selection of remediation technologies. Due to bulky usage of heavy metal in industries, and agriculture applications, exposure to heavy metal has increases significantly over years. Solidification/stabilization (S/S) technology is one of the cost effective and efficient ways to remediate heavy metal pollution (Anand, 2000). Thus, leachability of heavy metal from S/S matrix deserves further study in 21st century.

S/S is one of those famous remedial technologies which restrict mobility of heavy metal in ecosystem by encapsulate it within S/S matrix. Cement is commonly deploys as binder for S/S technique due several outstanding reasons such as ability to facilitate the reduction of some contaminant, ability to reduce toxicity of contaminant, reduce hazardous constituent solubility by chemical fixation, lower down the hydraulic conductivity of heavy metal, encapsulate waste unit with impermeable coating and chemically fix free liquids (Robert, 2001).

1.2 Fundamentals of Leaching

Leaching is defined as s process which soluble compounds in solid matrix, such as heavy metal or fertilizers are dissolved into a contacting water phase by percolation or dissolution into leachate (US EPA, 2000). These dissolved constituent may carry downstream through porous medium such as aquifer and soil by diffusion or by convection, eventually remain highly mobile in environment. The extents to which the heavy metal dissolves into contacting liquid phase rely on the duration of contact time, chemical, physical and biological factors.

The composition and concentration of heavy metal in leachate will directly influence water quality. Underground and surface water as well as soil are environmental resources that are primary influenced by industrial development through infiltration of leachate from solid waste and landfill. In contrast to ground water, surface water continuously dilutes pollutants that reach it. A stagnant plume of pollutant from ground water may take years to flush (Shrivastava and Mishra, 2011), thus it is critical to estimate their potential for chemical transformation in soil and its movement ability into deeper soil layers and eventually into groundwater. Associated risks of heavy metal run off is assessable by leaching test, which quantifies the possibility of contaminant from solidify mass being released into environment, for example toxicity characteristic leaching procedure (TCLP), synthetic precipitation leaching procedure (SPLP) and pancake column leaching test (PCLT).

Figure 1.1 shows the water balance at a hypothetical landfill site. Run off of surface water through landfilling material from unsaturated zone to saturated zone dissociate heavy metal and other contaminant, bring along with them to saturated zone where groundwater is. The contaminated ground water up takes for industrial usage or domestic usage, exposed population to heavy metal. Run off of contaminants rich leachate from dump site, infiltration of moisture and groundwater intrusion, finally discharge into surface water structure like river. Finally, contaminants enter population food chain through ingestion of aquatic flora and fauna besides drinking water.

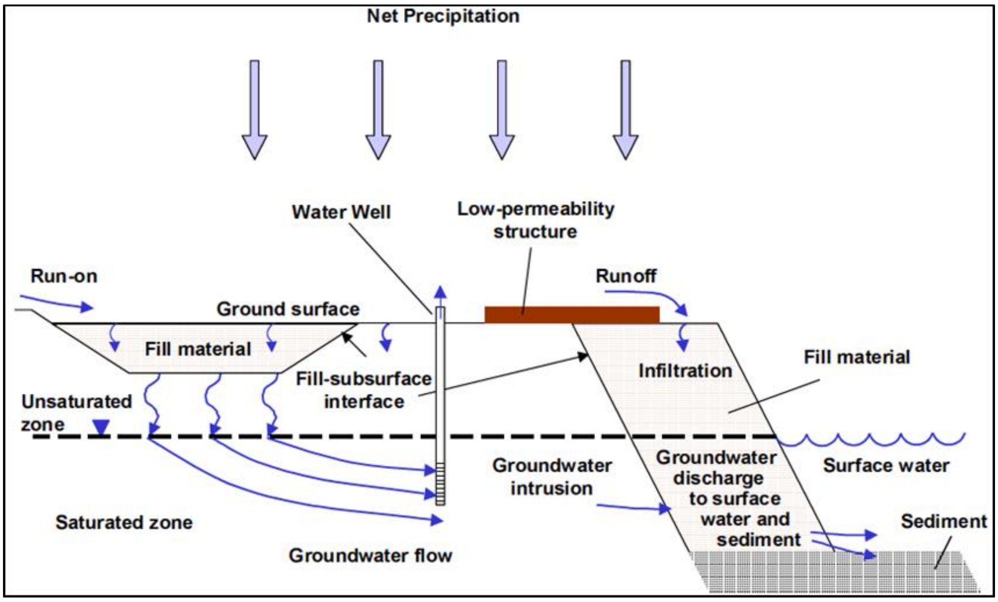

Figure 1.1: Water Balance at a Hypothetical Fill Site (Science Applications International Corporation, 2003)

1.2.1 Categories of Leaching

Throughout the years, various leaching procedures have been standardized for quantification of the release of contaminant into environment at the same time serve as standard to examine discharge of contaminant for compliance within regulatory limit. Leaching of heavy metal from S/S matrix depends on various factors, such as geometry and permeability of S/S matrix, exposed surface area, flow rate of the leaching fluid, temperature during leachability test and others.

Merit by complex mechanism, several proper methods should be chosen so that the leachability of heavy metal in dumpsite, landfill as well as runoff could be studied precisely. For example, toxicity characteristic leaching procedure (TCLP) is design to determine whether a waste is characteristically considered hazardous. Although some researcher conclude that TCLP consistently under predict concentration of arsenic, fluoride and selenium in leachate, over predict concentration of barium. Therefore, combination of several tests is necessary for precise modelling which aimed to give an overview of heavy metal behaviour in environment.

Principally there are four phases in preparing and analysing leachate, known as sample preparation, leaching stage, leachate pre-treatment and leachate analysis (Philip., 2004). Sample preparation may comprise of particle size reduction and dilution of samples and others. Agitation method and the mode of contact with the solid matrix defined during sample leaching stage. Pre-treatment of leachate such as decantation, centrifugation or filtration is carried out to obtain leachate properties which are appropriate for instrumental analysis. Finally, the leachates which are ready will be sent for instrumental analysis to characterize role of heavy metal in leachate.

In general, leaching can be categorized into static or dynamic diffusion test shown in Figure 1.2. Static methods can be further classified into crushed block leaching method which comprise of TCLP, SCLP and deionized water leaching procedure (DWLP) whereas monolithic leaching test is represented by whole block leaching method. On the other hand, dynamic method can sort into 3 groups, which is serial batch leaching test, flow around leaching test and flow through leaching test (Hans, 2014). As a whole, 16 type of leaching test methods are classify and implement based on the climate and local environment. These sixteen types of leaching methods are attached in Appendix A.

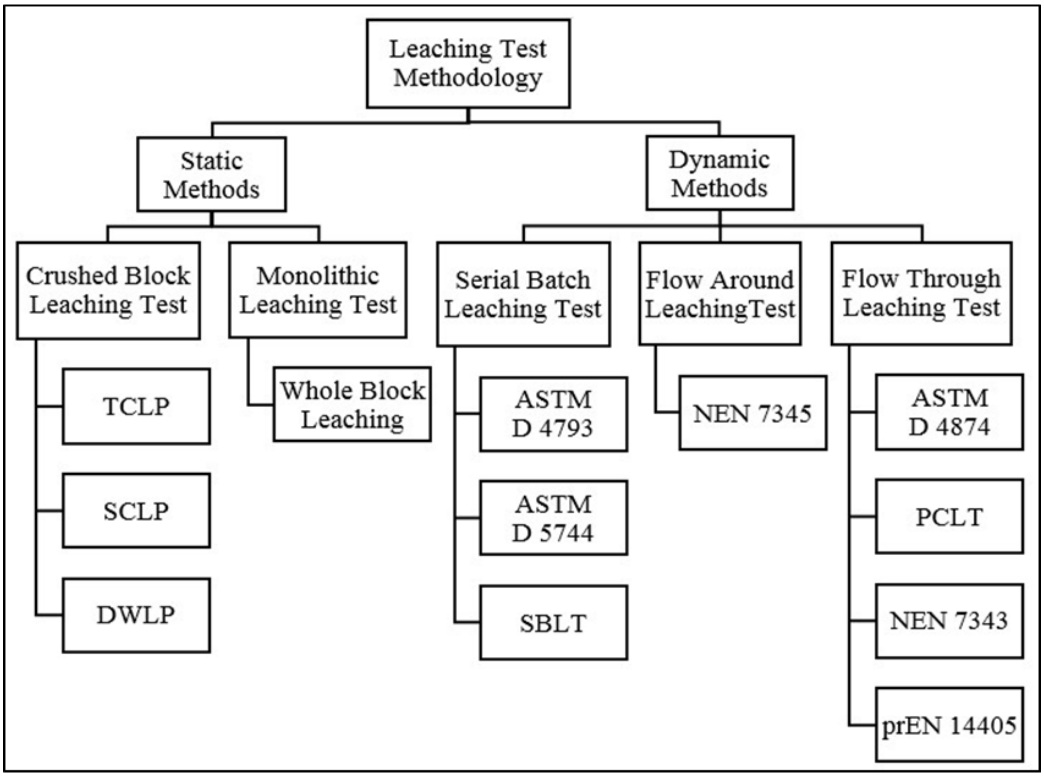

Figure 1.2: Categories of Leaching Test Methodology

1.2.2 Leachate Regulatory Level

Practically, municipal waste is sent to incinerator for volume reduction up to 80%, save lots of handling space (Chalita and Shabbir, 2007). The incombustible ash send to hazardous waste landfill with multiple layers of polyethylene liners which capable to reduce leachability of contaminant into environment. Combination of incineration and landfilling effectively and efficiently reduce the requirement for intensive treatment but require huge capacity of valuable land. Yet, part of municipal waste which is rich in certain heavy metal subject to leach from municipal landfill lead adverse effect to environment and population health Thus, leaching limit values serve as a standard to identify the tolerance of particular waste for landfilling.

Appendix B1 shows standard criteria for discharge of leachate propose by Ministry of Natural Resources and Environment, Malaysia.

Appendix B2 shows regulation limit for the use of heavy metals as building material in Belgium while Table 1.2 shows chromium (total) regulatory limit introduced by various countries. Two approaches are developed for quantifying and evaluation of regulatory limit which in milligram of heavy metal per litter of leachate or milligram of heavy metal per kilogram of dry mass. Evaluation based on milligram of pollutant per litter of leachate basis do not account effect of total mass of waste, considered safe as the permissible leaching concentration is below the limit. On the other side, evaluation that based on milligram of pollutant per initial dry mass of waste basis gives an overall and more complete assessment whereas normally have a higher value compared to per litter basis. From other point of view, the lower the limit the stringent the regulatory criteria. Thus, Italy leaching criteria by leaching test EN 12457 is much stringent than acceptable conditions for discharge of leachate introduced by Malaysia.

Table 1.2: Chromium (total) Regulatory Limits Introduce by Respective Government

County	Unit	Leaching Regulatory Limit
Malaysia	mg/l leachate	0.25
Austria	mg/kg dry matter	40
Italy	mg/l leachate	0.05
France	mg/kg dry matter	10
Sweden	mg/kg dry matter	40

1.3 Problem Statement

Recently, severe chromium contamination caused by various industries such as tanning and chrome plating industry has received attention. Groundwater and soil are primarily influenced by illegal dumping of chromium containing waste. Chromite ore processing residue, run off of chromium from municipal solid waste incinerator MSWI bottom ash, electroplating sludge, discharge of wood preserving chemical chromate copper arsenate are the main anthropogenic chromium sources. Application of chromium compound cover consumer products ranging from household product to steel and construction piece, exert great risk to environment and society. Due to its great stability and mobility, chromium (VI) neither decay nor destroy once discharged into natural environment, but tended to bio-accumulate in organism. Among numerous technique for leachability control, S/S is an efficient and cost effective technology by means of limit mobility chromium ions within inert matrix to reduce its bioavaibility in ecosystem, thus deserve further investigation and study.

Ordinary Portland Cement (OPC) capable to form calcium silicate hydrates (C-S-H) gel which is efficient in reducing leachability of heavy metal. Reaction between OPC and silica containing substances known as pozzolan material further improve formation of C-S-H gel. Rice husk ash (RHA) contains up to 95% of silica and economically available in Malaysia provide an interesting alternative to substitute sand. However, its application and reactivity in remediation of leachability remain unknown. Thus, this study aimed to reveal the effectiveness in remediation of heavy metal leachability by applying RHA as pozzolanic additive together with OPC as setting agent.

1.4 Aim and Objectives

The aim of this project is to study the leachability of chromium in cement cube and the effect of RHA as pozzolanic additive. Moreover, to fulfil the mentioned aim following objectives are listed below:

1. To determine leachability of chromium and calcium from samples.

2. To investigate changes of pH over contact period.

3. To identify compound present in cement matrix using X-ray diffractometer (XRD)

4. To examine microstructure of cement matrix by scanning electron microscopy (SEM).

5. To inspect elemental composition of cement cube samples using energy dispersive X-ray spectroscopy (EDX)

CHAPTER 2

LITERATURE REVIEW

2.1 Migration of Heavy Metal in the Natural Environment

Heavy metal defined as natural metallic chemical element with specific gravity greater than 5 which capable to damage living things even at low concentrations (James and Stephen, 2004). Heavy metals such as zinc, chromium, mercury and others neither degrade nor destroy in the environment, consequently tend to bio-accumulate in organism (European Commission, 2002). Natural weathering of soil and rocks breakdown inert bonded heavy metal and discharge into rivers and lakes in acceptable low concentration. Conversely, mining, electroplating operation, smelting and others anthropogenic activities increase local level of heavy metal discharge drastically such as chromium, nickel, arsenic and cobalt, prime to pollution issue. Acid rain that dissociate heavy metal from soil, or even industrial and consumer waste run off discharge heavy metal into lakes, streams and other water structures. Figure 2.1 shows the entire route of heavy metal processing origin from its source to waste, each steps exhibit potential to discharge heavy metal into environment.

Diverse pollutant sources such as industrial and agricultural activity lead to dispersion of pollutant which impossible to be recovers and collect. As heavy metal neither degrades nor destroy in environment, lead to permanent environmental effect. Radiation is the only way to break down heavy metal, else it will last forever and migrate around ecosystem by movement of water and air currents. Toxicity of heavy metal may differ according to the species, habitat, exposure and others factor.

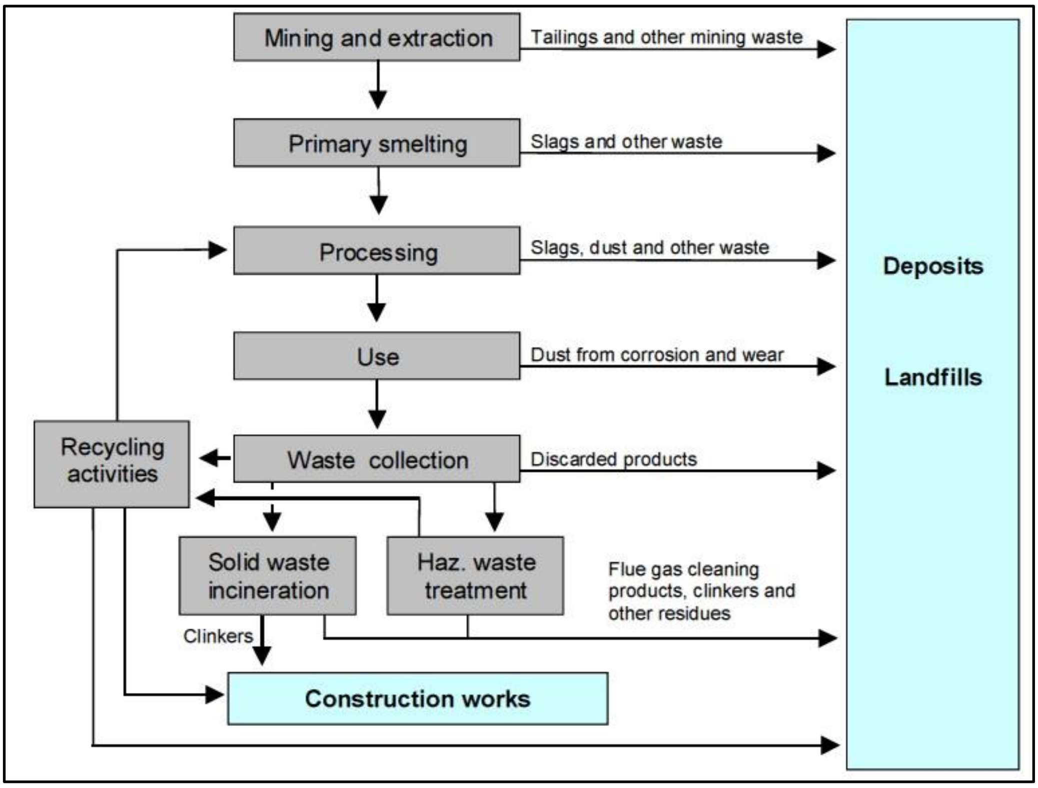

Figure 2.1: Illustration of Heavy Metals Source to Waste (US EPA, 2000)

In aquatic system, heavy metal is readily absorbed via direct uptake as free ions which interact and alter the metabolism of aquatic life. However, potential toxicity is variable among fishes, invertebrates and aquatic plants. Sub-lethal effects have been reported, for examples the impair development and reproduction of fish and stunt growth of aquatic invertebrate. Terrestrial inveterate and plant are relatively insensitive to heavy metal, do not show any adverse chronic effect.

On the other hand, bioaccumulation in organism occurs through ingestion of contaminated food or water. Organism tends to accumulate heavy metal compound quicker than rate it is broken down or excreted (Eco USA., ND). High concentration of heavy metal deposit in tissue might lead to organ failure. It is known that high concentration of heavy metal in living things lead to metal poisoning. However, trace amount of heavy metals complex ion play essential roles to maintain the metabolism for human health, as shown in Table 2.1 (Rodrigo, et al., 2010).

Table 2.1: Physiological Roles of Heavy Metal in Human

Heavy Metal	Role	Description
Copper	Co-factor in enzymes	Both copper and cobalt play an important role in central nervous system function, melanin synthesis and iron metabolism by alter the synthesis of numerous enzymes such as cytochrome oxidase, superoxide dismutase, ferro-oxidase and others.
Cobalt	Coenzyme	
Iron	Compulsory element for haematopoiesis	Presence of iron is compulsory for haematopoiesis, a synthesis process of red blood cells. It stains the haemoglobin red and enable them to bind with oxygen and transport throughout the whole body.
Selenium	Production of glutathione peroxidase	Glutathione peroxidase acts as a biological antioxidant that guards cell membranes, lipids, nucleic acids and proteins from oxidant molecules.
Chromium	Supplements	Potentiates the action of insulin in diabetes patients with impaired glucose tolerance to reduce blood sugar level.

Heavy metals such as mercury, cadmium, arsenic, and lead, are extremely toxic at any level. Contrary, nickel, copper, and zinc are compulsory in trace amounts, yet poisonous at elevated amounts too.

2.1.1 Overview of Chromium in the Environment

Chromium is one of the group 6 transition elements, showing typical transition element properties for example having various physical colours and oxidation states. Trivalent chromium and hexavalent chromium are the most common oxidation state available on the earth crush. Physically, trivalent chromium gives green colour solution while hexavalent chromium gives yellow - orange colour solution. Owing to the active industrial application of hexavalent chromium, contaminated sites increase dramatically recent years. Dams, underground water supply wells in addition to other surface or subsurface water sources are affected by hexavalent chromium. As with majority of environmental challenges, questions of science always compete with financial interests and public responses. Hence, there is still uncertainty to accomplish leaching level that consider safe to environment and health with affordable cost. Shown in Table 1.2, diverse level of contaminant is introduced by governments, common agreement has not been grasped.

2.1.1.1 Application of Chromium

Thousands of consumer product such as stainless steel, alloys, dye, magnetic tapes, paint, wood impregnation and more require chromium compounds in manufacturing process. Chromate of zinc, lead and barium give the pigments of zinc yellow, zinc green, lemon chrome, chrome orange, chrome yellow and chrome red. Chromium chemicals enhance the bright colour of buildings and automobiles beside capable achieve permanent stain colours of fabrics. Moreover, dyeing and tanning process utilize chromic acid and chrome alum too. Dichromate ion is widely use in photography and photoengraving.

Chromium superior properties such as chemically inert, heat resistance and hardness overtake nickel and dominate in plating application, deploy widely in manufacturing of bricks for furnace lining. Chromium is entitle for “guardian metal”

(Janes and Stephen, 2004). Alloy with 10% of chromium safeguard steel from corrosion. Rust resistance iron yielding stainless steel which prompt to replace conventional iron. Chromium based specialize steels characterize as tarnish resistant, bright and hard (Pierre-Jean, 2004). It support growth of modern industry as the properties of ferroalloys greatly improved.

2.1.1.2 Exposure Pathway

Daily chromium exposure route can be categorized into ingestion and dermal contact while inhalation of chromium mainly contributes by occupational exposure (OSHA, 2009). Bathing or washing in chromium contaminated water and ingestion of contaminated water believe to affect public health.

As a whole, hexavalent chromium is much toxic than that of trivalent chromium, proven to cause a number of adverse effects ranging from irritation to development cancer. Occupational expose via inhalation could lead to lung cancer. Hexavalent chromium show significant mutagenic and carcinogenic effect (National Toxicology Program, 2015). Exposure of both trivalent chromium and hexavalent chromium compounds is companion with allergic responds such as dermatitis and asthma. On the other hand, hexavalent chromium tends to accumulate in embryos compare to trivalent chromium when parental generation of tested animal injected high level of chromium. Hexavalent chromium classified by US Environmental Protection Agency (US EPA) as carcinogenic substances.

From other point of view, dispersed chromium affect all living things in the environment, especially the hexavalent form. Presence of hexavalent chromium in environment mainly contributes by human activity. It is relatively stable in water and air possess tendency to disperse further downstream or downwind. Most microorganism show toxic effect once expose to 0.05 to 12 mg of chromium per kilogram of medium such as suppress protein synthesis and photosynthesis, hence alter population size and growth rate (European Commission, 2002). High concentration of chromium accumulates in fish tissue as well as aquatic invertebrates such as worms and snail. Concentration as low as 0.01mg hexavalent chromium per litre is adequate to affect the reproduction of water flea, Daphnia. 0.05 mg hexavalent chromium per litre is more than enough to cause lethal effect to several aquatic and terrestrial invertebrates. Although plants do not show any acute chromium toxicity, it is believe that main influence of chromium intoxication is similar to iron deficiency, chlorosis. Trivalent chromium is an essential trace nutrient, suggested to consume 100 µg/day. As mention in Table 2.1 it is compulsory for regulation of blood glucose level by alter metabolism of insulin. On the other hand, all plants contain certain amount of chromium, but inconclusive weather it is essential or not (Rodrigo, 2010). Due to distinct properties between trivalent chromium and hexavalent chromium, hence it must consider separately.

2.1.1.3 Fundamentals of Chromium Chemistry

Oxides and ions form of chromium are the most abundant chromium compounds on the earth's crust as compared to metallic chromium which are rarely found as free element in nature. This is due to the surface of chromium react aggressively with atmospheric oxygen subsequently forming a dense, nonporous and strong trivalent chromium oxide. Chromium is one of the principal compounds in metallic colouring and give colouring for some gems, ruby and emeralds too.

By nature, chromium present as insoluble trivalent complex which bound to particulate, once come in contact with manganese (IV) dioxide it oxidize to highly soluble hexavalent chromium which occur naturally in aquifer material. On the other hand, low pH and other reducing condition of aquifer reduce hexavalent chromium to trivalent chromium. Similar to carbon cycle, chromium is a trace nutrient and uptake by flora and fauna through transpiration or nourishment eventually free the element into soil upon death (US EPA, 2000). Instinctively, chromium exist a balance in environment, forming a chromium cycle, but the balance is disturb by anthropogenic activities nowadays, show in Figure 2.2. Massive discharge of industrial chromium compound disrupted chromium balance consequently lead to significant increase of hexavalent chromium in drinking water source, put environment and human health in great risk. Hexavalent chromium identified as a human carcinogen by US EPA possess high mobility than trivalent chromium due to high solubility and tough to remove from water. Thus, numerous treatment technologies developed aim for solution and remediation purpose.

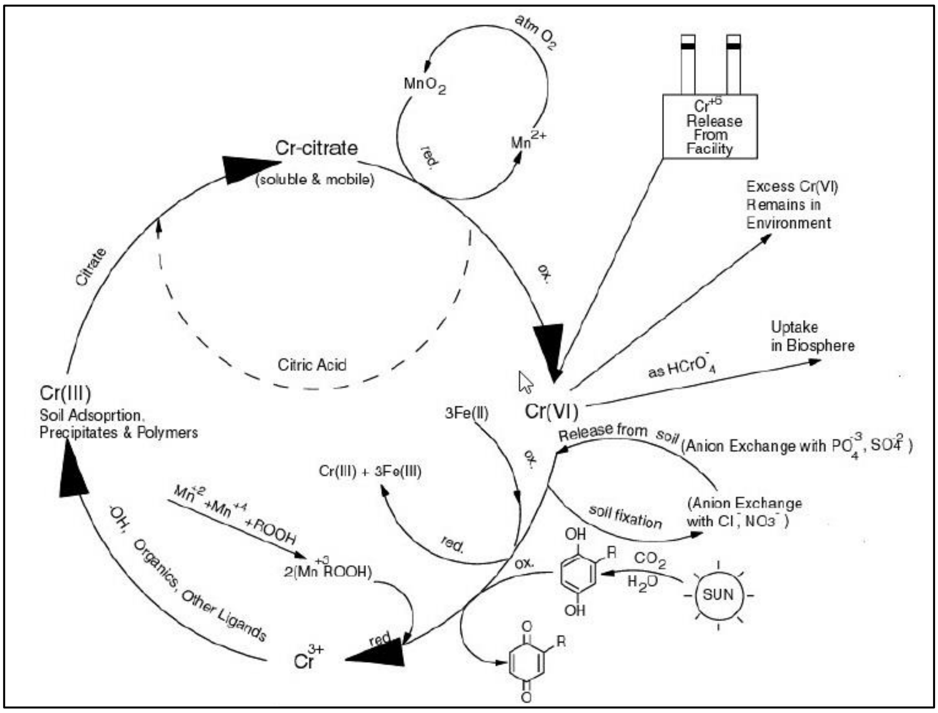

Figure 2.2: Illustration of chromium cycle (US EPA, 2000)

2.1.2 Concept of Treatment Technologies

Successful treatment technologies for remediating hexavalent chromium have been demonstrated and classify in to three categories: toxicity reduction process, destruction or removal treatments and containment technologies. S/S falls under containment technologies. Knowledge and understanding of flexibility in remediation design, geochemical properties of contaminated soil matrix, site particular conditions, biogeochemical properties of chromium and ingenuity in optimization play a crucial role in determining effective treatment method, not adhere to step by step method (James and Stephen, 2004). As summary, reduction of chromium toxicity can be accomplish by reducing hexavalent chromium to trivalent form subsequently removing them from water or soil and lastly confine trivalent chromium within a selected matrix is the focus of S/S remediation technologies.

2.1.2.1 Toxicity Reduction Methods

Mathematical product of inherent toxicity and exposure determine the carcinogenic effects on exposed species. Thus toxicity reduction methods capable to remediate pollution issue by reducing heavy metal toxicity (Elisabeth, 2004). Alleviate health impacts of chromium can be achieve by reducing hexavalent chromium to trivalent chromium which is biologically unavailable. The transformation can be done either by geochemical process or add in chemicals such as iron fillings or ferrate directly to contaminated site or promote selective microbial biological activity by manipulating environmental condition.

2.1.2.2 Destruction and Removal Methods

Generally, energy requires to transform chromium atomic nucleus to another element would be mammoth, thus destruction is not practical in remediation technologies. However, removal of chromium from drinking water source could easily done by reverse osmosis or ion exchange by granular activated carbon (Elisabeth, 2004). Extraction of chromium from contaminated groundwater by means of ex-situ treatment and separation of chromium from soil by soil washing or solvent extraction are the conventional removal methods.

2.1.2.3 Containment Methods and Fundamentals of Solidification/Stabilization (S/S) Technology

Containment technologies aim to inhibit dispersion and spreading of contaminant into larger areas. Encapsulation, precipitation, biostabilization and S/S are technologies develop under containment method. In-situ permeable reactive barrier isolating and immobilize chromium, yet zero effort is done to reduce the concentration of chromium within the containment zone.

S/S known as a handling method that encapsulates chromium ions within an inert matrix, for example fixation of chromium (III) compound by using cement (US EPA, 2000). Lime and Portland cement leach more chromium compare to slag-modified cement which leachability increase as slag content decrease. S/S performs best at shallow contaminated site with maximum depth of 2 to 5 meter. Moreover, among all remediation technologies, S/S is the best available technology for chromium remediation.

Fixation of chromium in cement involves deposition reaction to confine chromium species within cement cube matrix. Thus preliminary study of cement properties such as chemical composition is necessary for better understanding of S/S reaction mechanism. Ordinary Portland cement (OPC) is versatile and suitable for wide range of application, such as construction of general purpose buildings, civil engineering works and others. Lime bearing materials such as limestone account for almost 70 percent of raw materials for manufacturing of Portland cement while the rest made up of argillaceous materials such as iron, silica and aluminium. Composition of Portland cement shown in Table 2.2 (Shaswata, et al., 2014), loss on ignition (LOI) represent the carbon content presence in Portland cement. Furthermore, calcium oxide, silicon dioxide and aluminium oxide are the principle component. These principle component suspected to react with chromium in the solidify matrix, show in equation 2.1.

$$Cr_{\mathrm{a}}B_{\mathrm{b}\,\mathrm{(solid)}} \leftrightarrow \mathrm{a}Cr^{\mathrm{b}+}{}_{\mathrm{(aqueous)}} + \mathrm{b}B^{\mathrm{a}+}{}_{\mathrm{(aqueous)}} \qquad (2.1)$$

Table 2.2: Composition of Ordinary Portland cement

Chemical Compound	Composition (%)
CaO	61.42
SiO_2	18.62
Al_2O_3	4.75
LOI	3.55
MgO	3.21
Fe_2O_3	3.02
SO_4	2.29
Na_2O	1.51
K_2O	1.42

Nevertheless, deposited chromium compound in solidify matrix may leach out to the contacting liquid phase as ions until equilibrium is reach. Thus, concentration of chromium in leachate plays an important role in determining effectiveness of S/S treatment.

2.2 Fundamentals of Cement Chemistry

Cement is manufacture from burned lime stone, $CaCO_3$ which react readily with water to form slake lime or calcium hydroxide (CH). Mixture of slake lime and sand give mortar structure consist of calcium silicate gel (C-S-H). The solidify matrix possess certain degree of open porosity where deposited heavy metal subject to leaching. Addition of clay during cement manufacture process gives raise to grained anhydrous aluminosilicate (dehydroxylated kaolin) after firing. Aluminosilicate react with portion of slake lime after addition of water to form silicate gel, show in equation 2.2.

$$Al_2Si_2O_7 + Ca(OH)_2 + H_2O \rightarrow \text{C-S-H} \qquad (2.2)$$

Studies confirm that C-S-H enhance bonding by filling the pores that incapable to be done by slake lime alone. By reduce its porosity, hydraulic conductivity may greatly reduce which might alter heavy metal leachability. Hence, C-S-H containing cement tend to reduce leachability besides possess higher strength.

2.2.1 Hydration of Cement

Portland cement consist of approximately two third of lime bearing materials and one third of argillaceous materials such as lime stone and silica or alumina respectively. Major compounds of Portland cement consist of tricalcium silicate C_3S, dicalcium silicate C_2S, tricalcium aluminate C_3A, tetracalcium aluminoferrite C_4AF and Gypsum CSH_2. Addition of water induces series of hydration reaction (Chen, 2004). Common name introduce by Cement Chemist Notation, CCN is shown in Table 2.3.

Table 2.3: Important Common Name Introduce by Cement Chemist Notation, CCN

Common mane	Abbreviation introduce by CCN	Approximate Formula
Water	H	H_2O
Gypsum	CSH_2	$CaSO \cdot 2H_2O$
Tricalcium Aluminate	C_3A	$Ca_3Al_2O_6$
Ettringite	$C_6AS_3H_{32}$	$(CaO)_6(Al_2O_3)(SO_3)_3 \cdot 32H_2O$
Calcium Silicate Hydrates	$C_3S_2H_3$	$3CaO \cdot 2SiO_2 \cdot 3H_2O$
Lime	CH	$Ca(OH)_2$
Tricalcium Silicate	C_3S	$3CaO \cdot SiO_2$
Dicalcium Silicate	C_2S	$2CaO \cdot SiO2$

There are 6 major reactions which some of them are interrelated. First of all, hydration of cement initiate by reaction between gypsum and tricalcium aluminate in the presence of water to give ettringite. At the same time, calcium silicate hydrates and lime is formed after hydration of tricalcium silicate, subsequently induce ettringite turn into monosulfate aluminate hydrate crystal. Besides that, dicalcium silicate or belite react with water converted into calcium silicate hydrates too, similar to reaction of tricalcium silicate. Ratio of gypsum and tricalcium aluminate determines the conversion of ettringtie formed during early stage. Hydration to yield ettringite favours at high tricalcium aluminate ratio. The crystallographic structures of ettringtie are needle like and elongated.

Calcium silicate hydrogel with formula of $1.7CaO \cdot SiO_2 \cdot 2.1H_2O$ together with calcium hydroxide are the most abundant hydration product. It capable to customize continues layer that hold cement particle together into a cohesive block. Contrary, others hydration products do not possess strong bonding with the phases in contact with hence do not contribute much to the strength development, although it is intrinsically strong (Thomas, et al., 2003). One of C-S-H gel possess unique characteristic that shows two types of morphology. Low density C-S-H tend to occupy space which originally filled by water while dense morphology appears in areas initially occupy by cement particles. Since silica gel capable to grow into porous space during curing, high density C-S-H is less important than low density C-S-H. Well fabricate C-S-H gel has a Ca/Si ratio ranging between 1.8 ~ 2.0.

2.2.2 Pozzolanic Reaction

Reduction of excess calcium hydroxide can be achieved by reaction with slag or ash which is rich in silica. The alkaline calcium hydroxide react readily with acidic silicate compound to give C-S-H gel. Pozzolanic substances refer to water insoluble silicates which contain oxyanionic silicon (SiO_3^{2-}). There are quite a number of these substances originate from waste such as fly ash, slag or rice husk ash (RHA) (Stanley, 2008). These material are not cementitious by their own, but can be activated by addition of lime while Portland cement often applies as a setting agent.

RHA is highly porous, make it light weight and attain very high external surface area. Rice husk contain about 22.24% silica and unusually high in its ash, ranging from 92% to 95% silica (Nornikman, et al., 2009). Rice Husk is one of the main agricultural wastes in Malaysia which traditionally openly burn in field or truck out from field and dump. Due to extremely high content of silica in the ashes, it is an outstandingly additive technically besides than economical feasible. Silica content reacts with OPC to breed cementitious composition. Burning rice husk under controlled temperature below 800 ˚C harvest ashes compose of amorphous silica. Burning of rice husk at temperature between 500 ˚C to 700 ˚C for more than 12 hours yield ash without crystalline substances and high reactivity. At the same temperature, short burning duration yield high carbon content. Reaction between rice husk ash and OPC and its effectiveness to remediate leachability of heavy metal still remain unclear (Ghassan and Hilmi, 2010.).

2.3 Leachability of Chromium from Municipal Solid Waste Incinerator Bottom Ash

Heavy metal plays an important role in industrial application. Improper disposal and leakage of chemicals often lead to severe contamination causes irreversible adverse effect to the environment and population. Frequent environment and health issue reported due to over exposure of heavy metal attract concern of research teams.

There were 67 municipal solid waste incinerators (MSWI) allocated in China. According to 2005 statistics, total municipal solid waste treatment capacity of these facilities as high as 22010 tonnes per day (National Bureau of Statistics of China, 2006). Two large scale incineration plant located in Shanghai, one of the central city of China, treat approximate 2700 tonnes of municipal solid waste per day raising public attention. 85% to 90% of MSWI residue is made up of bottom ash while the rest constitute air pollution control residue (Zhang, 2006). Disposal of bottom ash become an issue as heavy metal retain in bottom ash is considerable, ranging from 61% to 94% except for cadmium (Zhang, et al, 2007).

Bottom ash samples from both MSWI were collected by Hua Zhang research team to study leachability behaviour and factors influence leachability of heavy metal from MSWI bottom ash. State Environmental Protection Administration of China establishes standard test method for evaluating leaching toxicity of waste. 1 litre of distilled water is mix with one hundred grams of each sample and tumble at 30 ± 2 rpm for 18 h. 0.45 µm membrane is utilize to vacuum filter the mixture and leachate was analysed using atomic adsorption spectrometry. The leachability of heavy metal from bottom ash verified to be relatively low compare to the limits values for hazardous waste. Chromium is one of the major pollutants present in bottom ash. Study shows that toxicity of chromium effectively reduces by S/S treatment and comply with regulatory limit. Hua Zhang research team conclude that leachability of chromium could be improved by cement S/S method.

In contrast to landfill, MSWI offer immediate volume reduction up to 90% advantage, which is particularly practical for populated country or area where land is precious and rare (Bethanis, et al., 2002). Severe environmental issue occur if MSWI ash does not treat properly. One of the approaches for MSWI ash disposal is by add into construction materials and practice by Belgium, the regulatory limit show in Appendix B2. In order to improve physical properties of stabilized matrix, MSWI fly and bottom ash use as additive in cement and the environmental impact is assess by leaching test (Kosson, et al., 2002).

On the other hand, MSWI bottom ash samples was took from mechanical waste pre-treatment centres in Latvia, Belgium and treat with standard procedure (Arina and Orupe, 2012). The 6 samples for leaching test compose of 50 wt.% spiked soil with copper sulphate, 35 wt.% MSWI bottom ash and 15 wt.% of Portland cement class 500 (Juris Burlakovs, et al, 2013). The leachate was filtered over a 0.45 µm sieve and the content of filtrate was determined by ICP-MS detected content of chromium in bottom ash ranging from 6.5 mg/kg to 117 mg/kg. S/S matrix is effective to treat heavy metal and negligible amount of heavy metal presence in leachate. Leaching of all heavy metal is comply with the regulatory limit for the use of heavy metal containing cement as building material in Belgium, concluded it is consider safe to utilize MSWI bottom ash as building material.

As a summary, although amount of heavy metal constitute in MSWI bottom ash is considerable, but fixation with cement using S/S technique capable to reduce its leachability to a safe level. Thus, by substitute MSWI bottom ash with RHA which consist of zero initial heavy metal and more silica constituent is believe to have better performance in reducing the leachability of chromium.

2.4 Relationship between Chromium Concentration and pH of Leachate

In general, heavy metals display lowest mobility at high pH whereas increasing mobility as pH decreases (Kosmulski, 2004). It is well known that pH play a crucial role in determining the mobility of chromium, however the relationship of pH with leachability of heavy metal and detail mechanism still subjecte to debate. Thus by varying parameters, researchers try to relate pH with leachability.

2.4.1 Study of Leachate pH as a Function of Time

By simulate the pH change of landfill leachate, chromium behaviour changes with time studied by Hui-Hu Liu and Shu Xun Sang by using Plexiglas columns for landfill dynamic leaching simulation.

By the reason of original adjusted phase and the transitional phase of S/S in landfill were short, pH of leachate vary dramatically at the beginning of test for all samples. The microbial activity release metabolic waste such as organic acids lowering leachate pH. Significant dissolution of heavy metal tends to occur at low pH (Valérie and Rudy, 2007). Short acidification duration is probably due to the difference in landfilling environment such as anaerobic condition which alter microbial activity. The significant decrement of pH which remain for a short period and goes up indicate the methanogenic phase of landfill started. At the end, landfill will reach mature stage where pH tends to stable ranging from 6 to 8.

Furthermore, ICP-OES analysis concludes that leaching concentration of chromium, arsenic and mercury usually decrease at first, then slowly increase. Leaching concentration of chromium got its first peak within 10 days and reaches its second peak at 40 days of experiment while its minimum appears at 50 days of experiment. Chromium is easier to dissolute in neutral environment and easier to leach in acidic environment (Hui-Hu and Shu-Xun, 2008).

2.4.2 Equilibrium of Chromium Species at Different pH

Chromium principally presents as trivalent or hexavalent form, which behave differently base on physio-chemical, biochemical and chemical properties. Thus, it is necessary to determine bioavailability of each chromium ions prior determination of toxicity. The objectives of research works carryout by Darko and co-workers were to investigate the distribution of chromium species between soil and leachate and the factors affecting them. Samples and synthetic rain water is prepare prior column leaching test. A correlation was observed by manipulating experiment parameters. Geochemical modelling calculations by Visual MINTEQ model gives states of trivalent and hexavalent chromium over pH, shown in Figure 2.3 and Figure 2.4.

Figure 2.3 shows that trivalent chromium ions dominate in acidic environment, largely presence as $Cr(OH)^{2+}$ for pH smaller than 4.5. Trivalent chromium species exist as insoluble $Cr(OH)_3$ species, particularly at pH 9. Moreover, soluble polyhydroxyl species present in minor constituent, they are $Cr(OH)_2^+$ and

$Cr(OH)_4^-$ ions. Figure 2.4 shows that dominate hexavalent chromium species are $HCrO_4^-$ and $Cr_2O_7^{2-}$ at pH lower than 6.5. Concentration of $HCrO_4^-$ species decrease rapidly with increment of pH and approaches to zero at pH equal to 8. Hexavalent chromium prefer species of CrO_4^{2-} when pH larger than 6.5 and is the only form in high alkaline conditions.

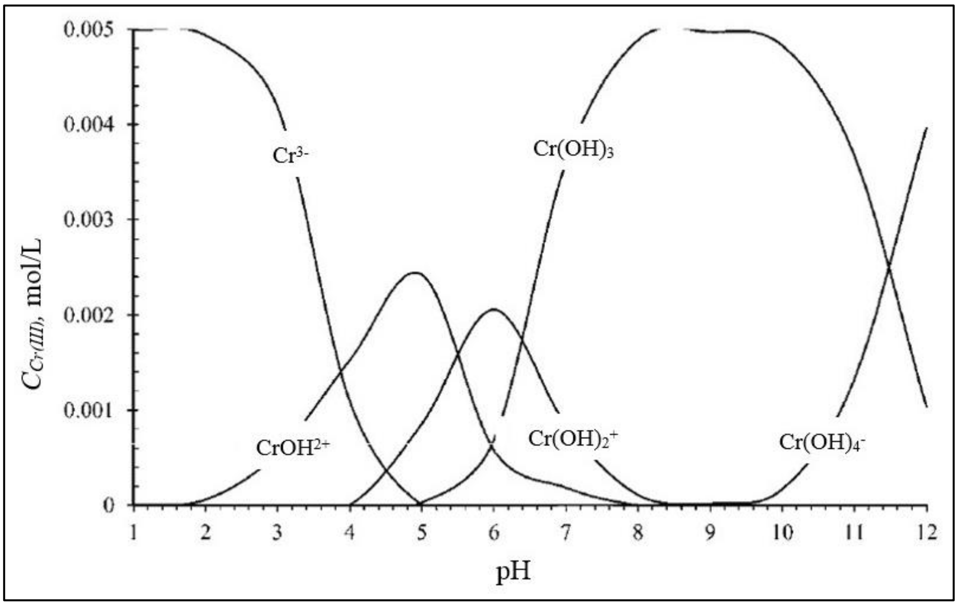

Figure 2.3: The Speciation Diagram of Trivalent Chromium as a Function of pH (Darko et al., 2000)

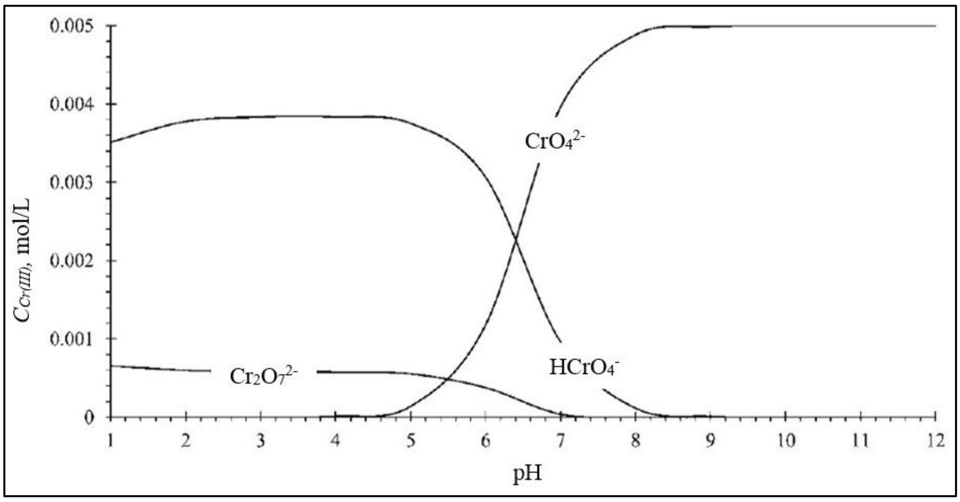

Figure 2.4: The Speciation Diagram of Hexavalent Chromium as a Function of pH (Darko et al., 2000)

Further study is continued by investigating the distribution of chromium species between precipitated, dissolve and sorbed phases. The objective of further study is to figure out the dominant species that principally dissolve does play a crucial role in quantifying toxicity of chromium in leachate. The fraction of dissolved hexavalent chromium as high as 100% compare to negligible dissolved amount of trivalent chromium, 0.966%. 99.034% of trivalent chromium is sorbed as immobilize form. On the other words, hexavalent form of chromium is highly mobilized in the environment, for example high concentration of hexavalent chromium in soil from the road runoff possesses a great risk to contaminate ground and surface water bodies. Thus, proper treatment or remediation is necessary to reduce the exposure of hexavalent chromium.

2.5 Relationship between Chromium Concentration and Redox Potential (Eh) of Leachate

Figure 2.5 shows Eh-pH diagram for chromium. Although it show the boundary separating one species from another is district, concentration, temperature, pressure and others parameter may affect the existence of chromium species. By measuring the pH and Eh of leachate, researcher may capable to predict species of chromium ions present in leachate, hence giving an overview on the leachable species (Salihu et al., 2000).

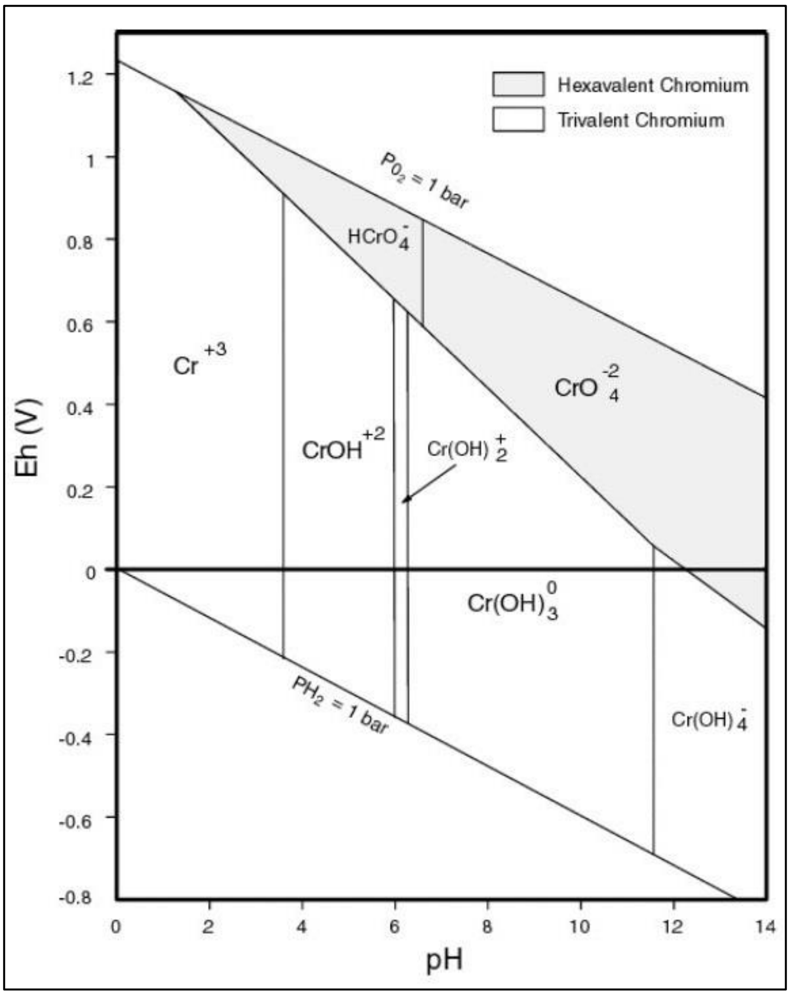

Figure 2.5: Eh-pH Diagram for Chromium (Salihu et al., 2000)

CHAPTER 3

METHODOLOGY

3.1 General Procedure Description

Leachability of chromium was determined by whole block leaching method, characterized monolithic leaching test. The blocks were casted into prefect cube and remain its geometry throughout experiment procedure. These blocks were immersed in 60 ml dilute acetic acid solution with pH equals to 2.88. The pH 2.88 was a standard introduced by US EPA to characterize whether a waste disposable in landfill (Roger and Caijun, 2004). Two buffer solutions, with pH equal to 2.88 and 4.93 were introduced by US EPA 1311 method whereas targeted to simulate landfill condition for alkaline waste and neutral to acidic waste respectively. As cement block consist predominant metal hydroxide and oxide, it is basic in nature and pH 2.88 was applied. (ALS Environment, 2000). Instrumental results were evaluated by triplicate method to ensure the reproducibility and reliability. Figure 3.1 showed top view of immersed cement cube samples.

Other than that, several variables were manipulated. First of all, each experiment set was subjected to 9 submerge duration vary from 1 hour, 4 hours, 7 hours, 14 hours, 1 day, 4 days, 7 days, 14 days to 28 days. Cement block doped with vary chromium concentration of 0 ppm, 10k ppm and 30k ppm was introduced for each duration. 0 ppm set was served as a standard control group.

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Figure 3.1: Cement Cube Samples in Contact with Acetic Acid

In order to study the leachability of chromium in the presence of additional binder, RHA was added into cement. OPC was mix with 5 weight percentage of RHA for samples with 10k ppm and 30k ppm chromium doping prior to casting and leaching test, including the control experiment set of 0 ppm. These configurations gave 6 sets of experiment sample comprised of different composition. Each set was subjected to 9 duration by triplicate thus sum up to 162 cubes to be cast. Table 3.1 showed an overview for the combination of different parameter and label to be used in following session.

Table 3.1: Specification and Labelling of Cement Cube Samples

Concentration of Chromium (ppm)	Ratio of OPC to RHA by weight	Binder to Water Ratio	Experiment Set Labeling
0	100/0	7:3.3	0ppm Cr - 100% OPC
	95/5	7:3.3	0ppm Cr - 95% OPC 5% RHA
10k	100/0	7:3.3	10k ppm Cr - 100% OPC
	95/5	7:3.3	10k ppm Cr - 95% OPC 5% RHA
30k	100/0	7:3.3	30k ppm Cr - 100% OPC
	95/5	7:3.3	30k ppm Cr - 95% OPC 5% RHA

Experiment generated both aqueous and solid phase samples namely leachate and cubes. Leachate was sent to inductively coupled plasma optical emission spectroscopy (ICP-OES) for metallic concentration determination, subsequently pH determination. Lastly, one of the blocks was crushed into flake and sent for scanning electron microscope (SEM) analysis, aimed to obtain surface morphology concurrently with energy dispersive X-ray spectroscopy (EDX) testing to gain elemental information. The remaining was crushed into powder for compositional determination by X-Ray Diffraction (XRD) analysis.

3.1.1 Preparation of Cement Blocks

Ordinary Portland Cement (OPC) was casted into cubes with scale 25mm x 25mm x 25mm shown in Figure 3.2 by using cupboard mold. These cubes are suspended in 60 ml of acetic acid solution with pH 2.88 ± 0.5. Properties of the solution and cube at distinct duration were studied by using instrument listed in Section 3.2.

Figure 3.2: Cement Cubes

The cubes were prepared by mixing cement and distill water according to weight ratio of 7:3.3; while cubes with 10,000 ppm and 30,000 ppm of chromium (VI) doping were prepared by using sodium chromate 4-hydrate solution instead of distilled water. Chemical was purchased from Synertec Enterprise Sdn Bhd. Chromium present as many forms, for example oxide, hydroxide and others.

However sodium chromate hydrate was chosen as the source for chromium (VI) ions just because sodium salts are completely soluble in water, dissociate chromium ions which responsible for reaction with cement. Other than that it is easily available in commercial. Sample calculation for preparation of 10k ppm chromium in cement was demonstrated in Appendix C.

Calculation found that 10k ppm of chromium solution equivalent to 45.01 gram of sodium chromate hydrate dissolved in 1 litter of distilled water. The same calculation procedure applied for preparation of 30k ppm solution, which required 135.04 gram of sodium chromate 4-hydrate in 1 liter of distilled water. The solution composed of chromium is then mix with cement to give a paste according to ratio of cement to solution equal to 7:3.3. From here, a paste was obtained, subsequently cured. For cubes required RHA doping, 50 gram of RHA was mixed with 1 kilogram of cement powder before and turned in to paste followed by curing process.

3.1.2 Preparation of RHA

Rice husk was burned in Barnstead Thermolyne 62700 chamber furnace at 600 ˚C for 2 hours and 30 minutes. It turned from a brown husk into white fluffy ash. Rice husk ash originated from Kedah paddy field. Figure 3.3 show the transformation of rice husk.

Figure 3.3: Transformation of Rice Husk into Ash

3.1.3 Flow Chart for Experimental Procedure

Figure 3.4 illustrated general procedure to be done throughout experiment. First of all, specific concentration of chromium (VI) solution for example 10k ppm or 30k ppm prepared by dissolving sodium chromate into distilled water. Prepared mould for casting before experiment was started. If RHA was required as dopant, mix 50 grams of RHA with 1 kilogram of OPC. After that mix solution with OPC gave a paste and subsequently casted into cubes. Other than that, prepared dilute acetic acid solution with pH 2.88 before leaching test was started. Leaching was started once harden cement cubes submerged into acetic acid and count down for the timing to remove cubes from the acetic acid. Solution remained in beaker was leachate and subjected to inductively coupled plasma optical emission spectroscopy (ICP-OES) test and pH test. On the other hand cement cubes was sent to X-ray diffraction (XRD) test, scanning electron microscope (SEM) test and energy dispersive X-ray spectroscopy (EDX) test.

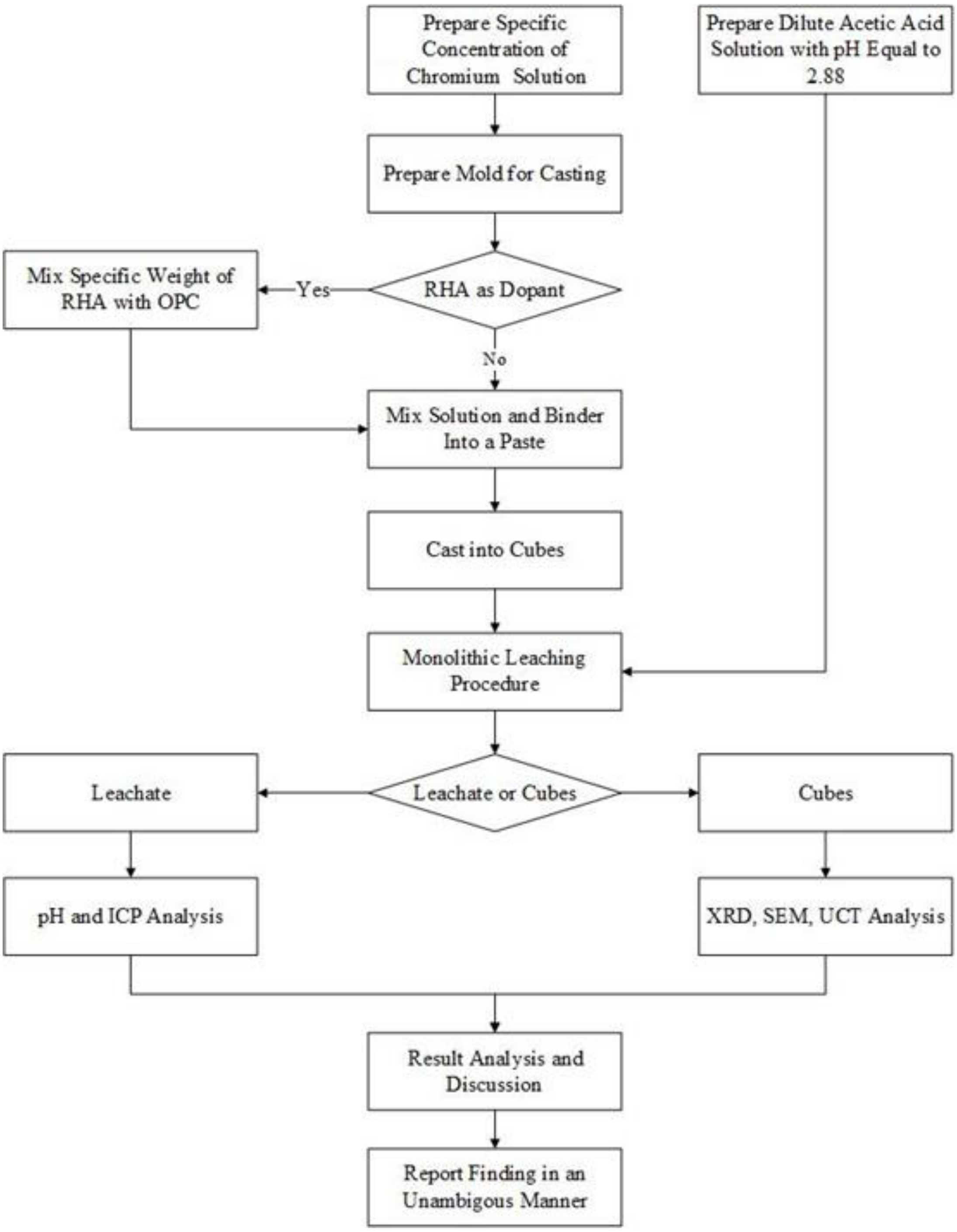


Figure 3.4: Experiment Procedure Flow Chart

3.2 Instrumental Analysis

All leachate samples sent for ICP-OES and pH test while solid samples comprised of cement cubes subjected to SEM, EDX and XRD test.

3.2.1 Leachate pH Determination

Normally, a pH meter consists of a probe which made up of two electrodes, one is a reference electrode and the other is a glass sensor electrode. The potential difference from these electrode pass to a meter by mean of electrical signal and display as reading in pH units. The reference electrode are hollow tubes comprising a silver chloride wire which suspended in potassium chloride solution, the same configuration goes for another electrode. The difference between them characterizes by non-conducting plastic or glass is use to made bulb for reference electrode whereas glass sensor electrode consist of a special glass membrane which coated with metal salts and silica. Hydrogen ions in sample solution replace some of the metal salts gives a minute potential difference across the glass bulb. The potential difference is compared with the reference solution with pH 7, which subsequently pick up by silver wire and pass to a pH meter for display purpose after amplify the minute potential difference. The voltage increment is proportional to the concentration of hydrogen ions. Increment hydrogen ions indicate an increase in acidity, pH meter will show lower reading. On the other hand, voltage decrement is proportional to the concentration of hydroxide ions. The more alkaline the solution is, the larger the voltage increment, lead to a rise in pH reading. pH meter needs to calibrate before use. This can be done by dipping probe into a buffer solution then follow standard operating procedure base on specification provided by manufacturer. Sartorious pH meter was used for pH determination which required calibration of pH 7, 4 and lastly 10 before carry out measurement.

3.2.2 X-Ray Diffraction (XRD) Analysis

XRD analysis has two ways to perform, either in the domain of single crystal or powder form. Shimadzu XRD-6000 Diffractometer used for sample analysis. Single crystal technique capable to solve the complete structure of crystalline material. On the other hand, powder diffraction technique commonly deployed to identify unknown substances, by comparing diffraction data against a database hold by International Centre Diffraction Data (ICDD), or formerly known as Joint Committee on Powder Diffraction Standards (JCPDS). Besides, powder diffraction is also a common method for determination of crystallographic structure, strains and crystallite size in crystalline materials. For this study, samples were prepared in powder form, aim to determine unknown compound.

However, XRD does possess some flaws too. It cannot detect particles that are either too small or amorphous. Besides that, one can never be sure that there are no other phases present than the ones detected with XRD, thus require EDX for elemental determination.

3.2.3 Scanning Electron Microscope (SEM) Analysis

SEM is a scientific instrument that use a focus beam of electrons to image the sample and gain meaningful data such as topography, morphology, composition and crystallographic information, Hitachi S-3400N serve for this purpose on the other hand SC7620 sputter was responsible to coat gold on the specimen surface prior SEM test. Interaction between the incident electron beams gives variety of effect, such as backscattered electrons, secondary electron, auger electrons and others. Different operation mode is applied to get information on each of them. This electron is originate from an electron source such as electron gun, through an opening in Whenelt cap which subsequently focus and sheer by magnetic lens before shoot to the sample. Ultimately, various materials is subjected to vary electrical potential for generation of electron to avoid degradation of samples or burn. It depends on the information target to gain too.

3.2.4 Inductively Coupled Plasma Optical Emission Spectrometry (ICO-OES) Analysis

Inductively coupled plasma optical emission spectrometry model Optima 7000 DV by PerkinElmer capable to determine concentration of metal in a given solution. It can analyse all kinds of solution with high specificity, rapid testing cycle and multi-element capability, ranging from dilute acids to high salt concentration.

The sample, which must be in a liquid form, is pumped at 1 mL/min (usually with a peristaltic pump) into a nebulizer, where it is converted into a fine aerosol with argon gas at about 1 L/min. The fine droplets of the aerosol, which represent only 1 - 2% of the sample, are separated from larger droplets using a spray chamber. The fine aerosol then emerges from the exit tube of the spray chamber and is transported into the plasma torch via a sample injector.

CHAPTER 4

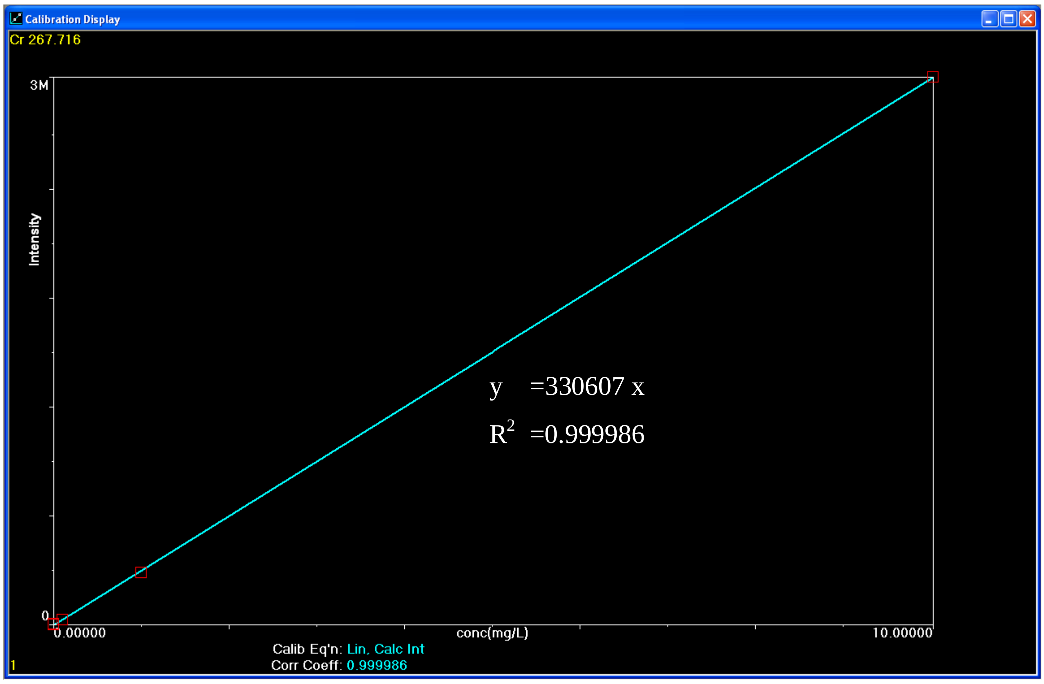
RESULTS AND DISCUSSION

4.1 Identification of Leachate Concentration by Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Leachate collected at vary duration was subjected to ICP-OES test for quantitative determination of calcium and chromium concentration. Triplicate samples applied for analysis, average and standard deviation were calculated based on value collected. Before samples subjected to analysis, all of them were diluted for 100 times. Such dilution was necessary to establish linear relationship between light intensity and concentration. According to Beer's Law, linear relationship between intensity-concentration calibration curve was limited and only be true for analyte within low concentration. Working beyond linear range would lead to drastic deviation of results.

4.1.1 Leachability of Chromium

Data for 0ppm Cr - 100% OPC, 10k ppm Cr - 100% OPC and 30k ppm Cr - 100% OPC were tabulated in Appendix E1 while 0ppm Cr - 95% OPC 5% RHA, 10k ppm Cr - 95% OPC 5% RHA and 30k ppm Cr - 95% OPC 5% RHA were tabulated in Appendix E2. In order to cope Beer's Law deviation, standard used for chromium calibration was 0.1ppb, 1 ppb, 10 ppb, 100 ppb, 1 ppm and 10 ppm respectively. Last but not least, standard calibrated by way of low concentration capable to achieve impressive precision with correction coefficient approximate 1, which is 0.999986, as shows in Figure 4.1.



Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999986

Figure 4.1: Chromium ICP-OES Calibration Curve

Beer's Law states that concentration of analyte is directly proportional to the quantity of light absorbed by a substance dissolved in a fully transmitting solvent, which is the basic working principle of spectroscopy. However, this law does not apply for solution with high concentration. At high concentration, stronger electrostatics and intermolecular interactions possess by analyte due to closer space between them, subsequently alter the linearity of molar absorptivity thus induced the concentration measurement to deviate from actual value. In order to solve this problem, dilution factor of 100 was implement and delivered value within linear working range below 10 ppm. Initially dilution factor of 10 was used however gave rejected results.

Figure 4.2 shows standard deviation for 30k ppm - 100% OPC and 30k ppm - 95% OPC 5% RHA samples were significant however 0 ppm Cr - 100% OPC and 0 ppm Cr - 95% OPC 5% RHA samples gave precise value. The precision was not a coincident and will be discuss in following session. Chromium concentration in leachate for both 10k ppm and 30k ppm doped samples declined steadily after fluctuation within time frame of 24 hours subsequently tend to stabilize after 28 days. Figure 4.3 shows concentration of chromium in leachate after 4 days of submerge duration, 30k ppm Cr - 95% OPC 5% RHA samples reached identical concentration with 0 ppm Cr - 95% OPC 5% RHA. Last but not least, by comparing Figure 4.2 and Figure 4.3, both 0ppm Cr - 100% OPC and 0ppm Cr - 95% OPC 5% RHA samples at every immerse period showed a constant value of 0.577 ± 0.002 ppm.

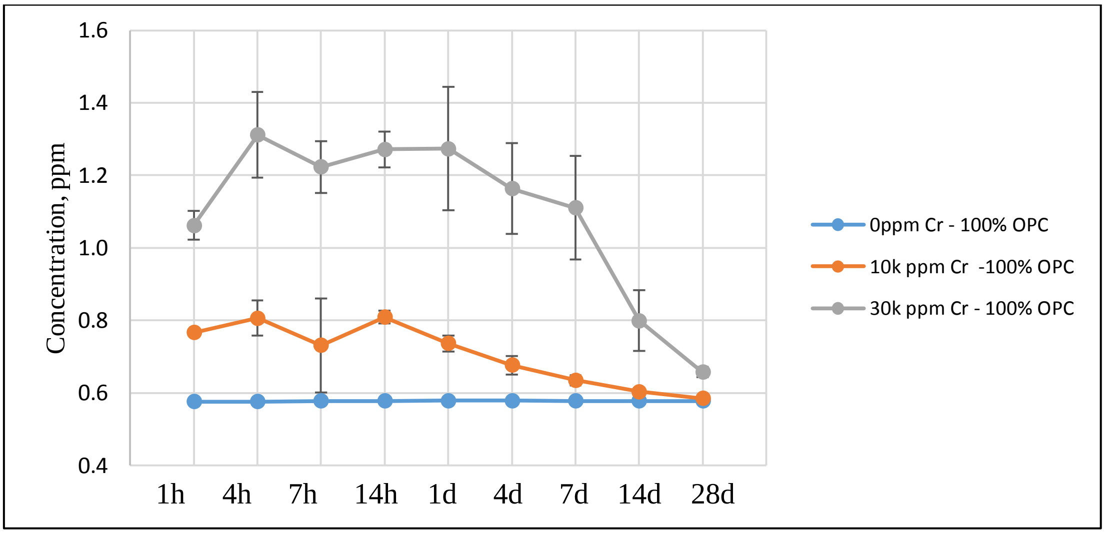


Figure 4.2: Standard Deviation and General Trend for 100% OPC Samples Data

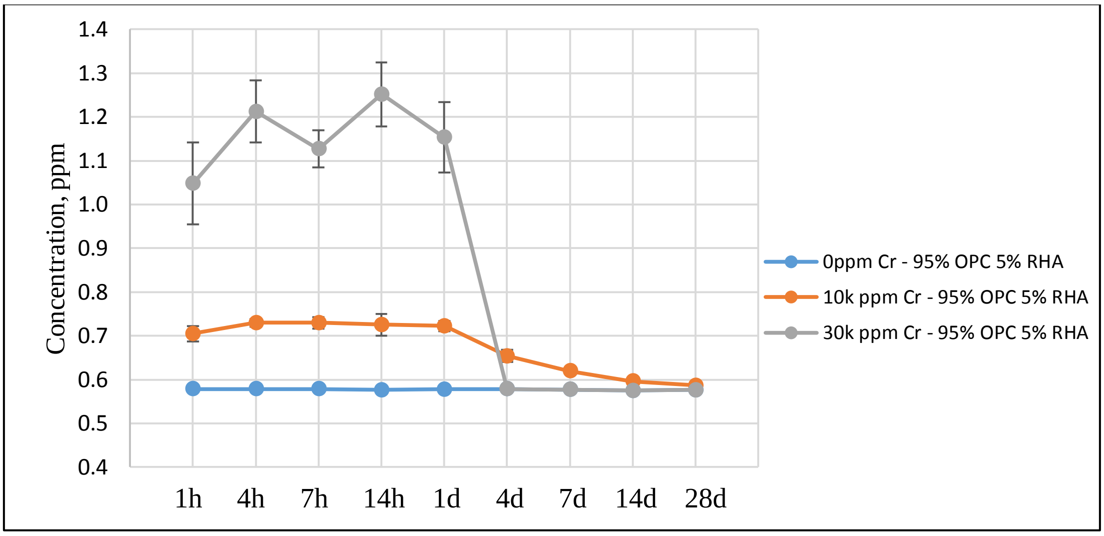
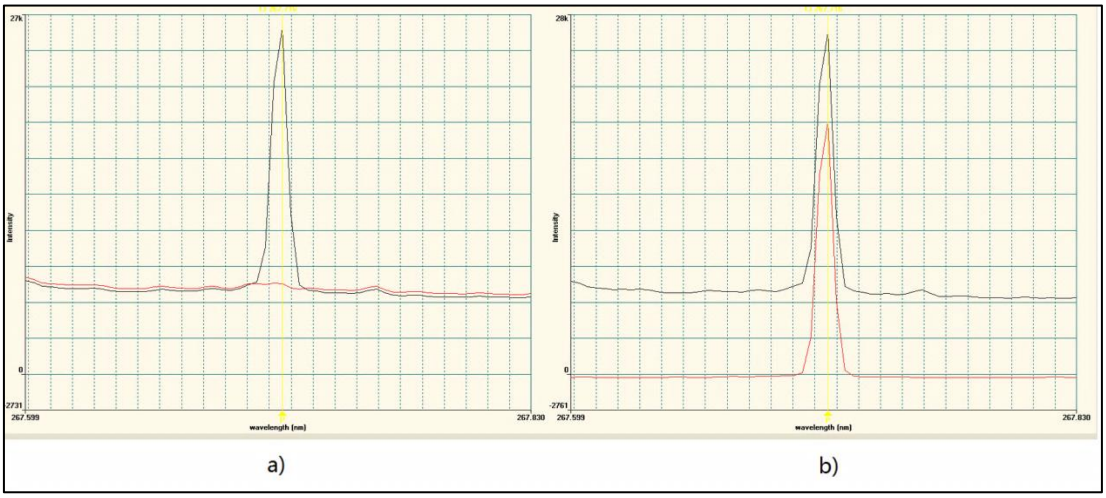


Figure 4.3: Standard Deviation and General Trend for 95% OPC Groups Data

High precision of 0 ppm Cr - 100% OPC and 0 ppm Cr - 95% OPC 5% RHA with value of 0.577 ± 0.002 ppm indeed was the background of chromium. Both of them neither doped with chromium nor OPC contain chromium, there was no room for chromium to leach into solution. On the other words, an additional value of 0.577 ± 0.002 ppm was caused by background signal.

Figure 4.4 a) shows the black peak was added on top of the background which represented by the horizontal red line, while Figure 4.4 b) shows a red peak which represent actual peak intensity after subtraction of background, decreased around 26.3 % which was absolutely not acceptable. The red peak in Figure 4.4 b) reflects the actual concentration of chromium in leachate.



a)

b)

Figure 4.4: Background of Chromium Signal

Correction of chromium concentration could be done by subtraction of sample light intensity with background light intensity, followed by substitution into calibration curve. Direct subtraction of measured concentration would not work and this was the reason to obtain high correction coefficient calibration curve. Effect of background ominously affected precision of 30k ppm-95% OPC data, particularly started from 4 days submerge duration. Based on Figure 4.3, 30k ppm-95% OPC samples after 4 days retain identical concentration with 0 ppm-95% OPC samples which was due to back ground signal, indicate no chromium presence in the leachate. Indeed, it was not. Figure 4.5 shows leachate collected on 4 days after immerse in acetic acid was in light yellow colour, hence chromium (VI) ions was present. In order to determine actual concentration, correction of chromium concentration must be done.

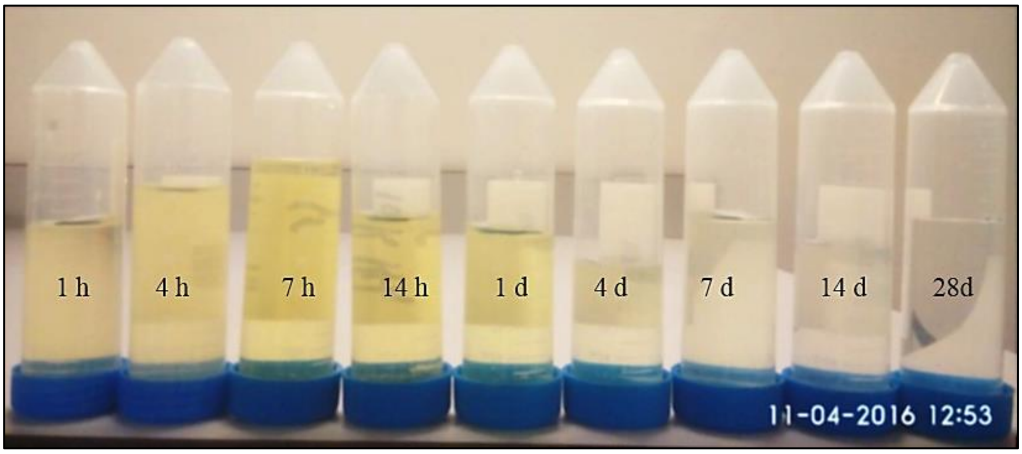


Figure 4.5: Colour Intensity of Leachate Collected at Various Period

RHA + CH → C-S-H (4.1)

whereas: RHA denote rice husk ash;
CH denote calcium hydroxide
C-S-H denote calcium silicate hydrate

Appendix E3 shows adjusted chromium concentration for all triplicate samples while Appendix E4 shows actual chromium concentration for all triplicate samples. Actual concentration calculated by multiplying adjusted chromium concentration with dilution factor of 100 times. Table 4.1 shows adjusted actual average actual chromium concentration base on triplicate samples run by ICP-OES and plotted in Figure 4.6, enabled comparison between Concentration of chromium increased drastically at initial stage and prompted to decline after reached its maximum. Significant amount of sodium chromate was leached within 1day. 10k ppm Cr - 100% OPC, 10k ppm Cr - 95% OPC 5% RHA, 30k ppm Cr - 100% OPC and 10k ppm Cr - 95% OPC 5% RHA data. 30k ppm Cr - 100% OPC samples chromium concentration higher than 10k ppm Cr - 100% OPC samples at any period, the same goes for 95% OPC groups 5% RHA samples. This effect was logical, the more doping it was larger capacity for it to be leached into leachate. On the other hand, samples with RHA doping always display lower chromium concentration in leachate, except 30k ppm Cr - 95% OPC 5% RHA with immerse duration of 14 and

28 days samples. The main reason for reduction of chromium leachability for sample with RHA doping was due to additional formation of C-S-H within cement cubes. Formation of C-S-H could lead to pores filling by short fibres or lamellar phases of hydrated calcium silicate. Addition of RHA capable to react with calcium hydroxide and amount to additional C-S-H, showed in equation 4.1. With additional C-S-H structure, cement became further compact and hence less chromium to be leached to the acetic acid.

Table 4.1: Average Actual Chromium Concentration in ppm

Triplicate Numbering	10k ppm Cr		30k ppm Cr	
	100% OPC	95% OPC 5% RHA	100% OPC	95% OPC 5% RHA
1 h	19.10	48.64	12.64	46.97
4 h	23.03	73.55	15.16	63.46
7 h	15.26	64.46	15.15	54.87
14 h	23.11	69.27	14.90	67.52
1 d	15.74	69.44	14.47	57.54
4 d	9.74	58.45	7.61	46.00
7 d	5.69	53.21	4.28	35.16
14 d	2.53	14.63	2.11	23.23
28 d	0.68	15.41	1.03	11.46

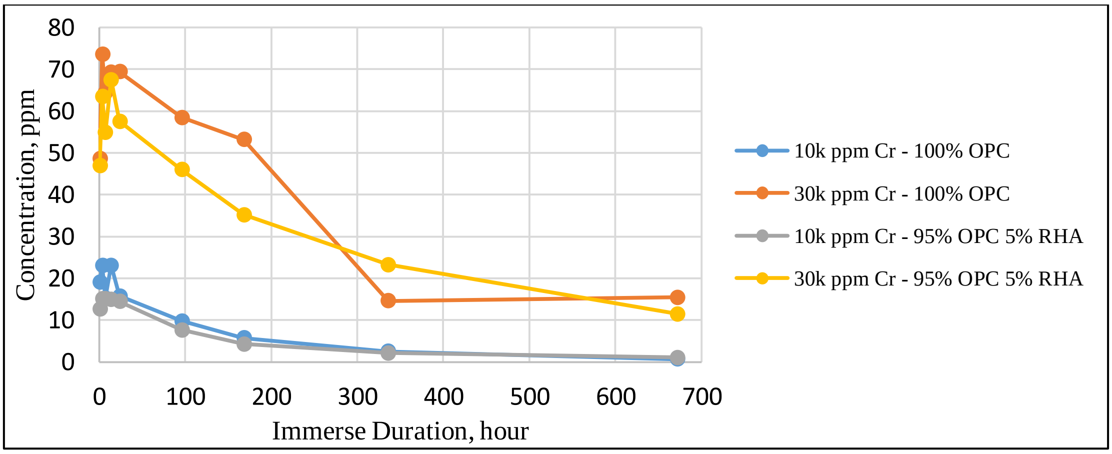


Figure 4.6: Adjusted Average Chromium Concentration over Time

In order to quantify effectiveness of whole block leaching to treat hazardous waste, mass and percentage of chromium leached calculated. 10k ppm Cr - 100% OPC samples as example, 330 g of 10k ppm sodium chromate solution was mixed with 670 g of OPC to give 1kg of paste and sufficient to cast approximate 35 cubes. This was equivalent to 94.286 mg of chromium doped in the respective cubes. On the other hand, 282.86 mg of chromium doped in 30k ppm samples. Total mass of chromium leached calculated by multiplying measured chromium concentration with 0.60 litter which represented volume of acetic acid in beaker, showed in Table 4.2. Table 4.3 converted mass of chromium leached at various periods to percentage.

Table 4.2: Mass of Chromium Leached into Leachate

Triplicate Numbering	10k ppm Cr		30k ppm Cr	
	100% OPC	95% OPC 5% RHA	100% OPC	95% OPC 5% RHA
1 h	1.146	0.758	2.918	2.818
4 h	1.382	0.910	4.413	3.808
7 h	0.916	0.909	3.867	3.292
14 h	1.387	0.894	4.156	4.051
1 d	0.944	0.868	4.166	3.452
4 d	0.585	0.457	3.507	2.760
7 d	0.341	0.257	3.192	2.110
14 d	0.152	0.127	0.878	1.394
28 d	0.041	0.062	0.311	0.687

Comparison could be made by using Figure 4.7. It shown 10k ppm Cr - 100% OPC samples without RHA doping leached maximum of 1.387 mg (1.47 %) chromium, higher than 10k ppm Cr - 95% OPC 5% RHA samples which doped with RHA of 0.910 mg (0.96 %), with a different of 0.477 mg. The same case applied for 30k ppm chromium doping samples whereas sample doped with RHA gave 4.051 mg (1.43 %) chromium leached and sample without RHA doping of 4.413 mg (1.56%). This finding coincided with conclusion found on Figure 4.6. Due to addition of RHA, more C-S-H was form hence reduced cement hydraulic conductivity consequently reduce leachability of chromium.

Table 4.3: Percentage of Chromium Leached

Triplicate Numbering	10k ppm Cr		30k ppm Cr	
	100% OPC	95% OPC 5% RHA	100% OPC	95% OPC 5% RHA
1 h	1.22	0.80	1.03	1.00
4 h	1.47	0.96	1.56	1.35
7h	0.97	0.96	1.37	1.16
14 h	1.47	0.95	1.47	1.43
1 d	1.00	0.92	1.47	1.22
4 d	0.62	0.48	1.24	0.98
7 d	0.36	0.27	1.13	0.75
14 d	0.16	0.13	0.31	0.49
28 d	0.04	0.07	0.11	0.24

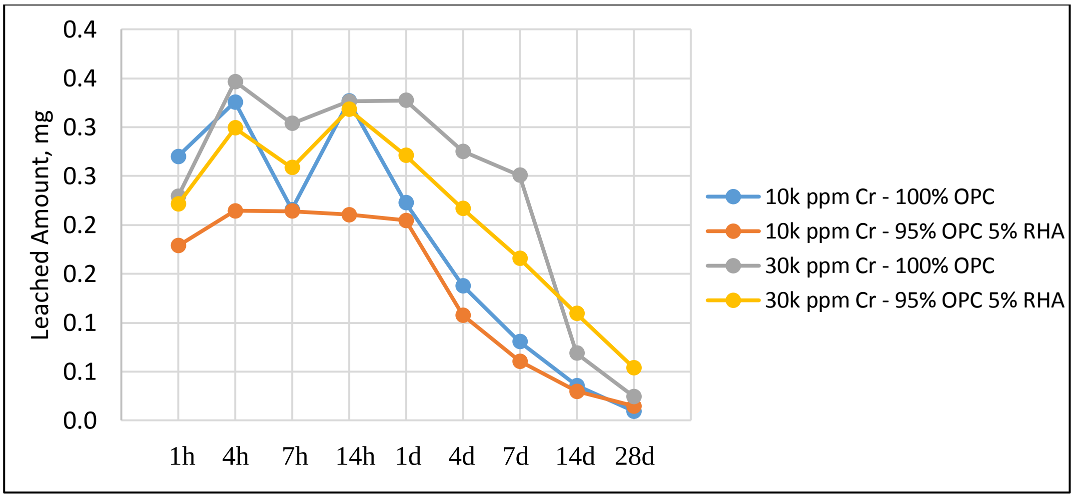


Figure 4.7: Mass of Chromium Leached over Period

As a summary, although whole block leaching test reveal competency of OPC to treat chromium reached effectiveness of more than 98.5 % by reduction and precipitation of chromium within cement cubes matrix, the leachate concentration of chromium did not comply with the regulatory limit stated in “A Guide For Investor” enforced by Ministry of Natural Resources and Environment Malaysia of 0.05 mg/L.

4.1.2 Leachability of Calcium

Figure 4.8 shows background for calcium signal which was negligible compare to chromium's. Hence, detected calcium concentration gave by ICP-OES could directly implemented into analysis.

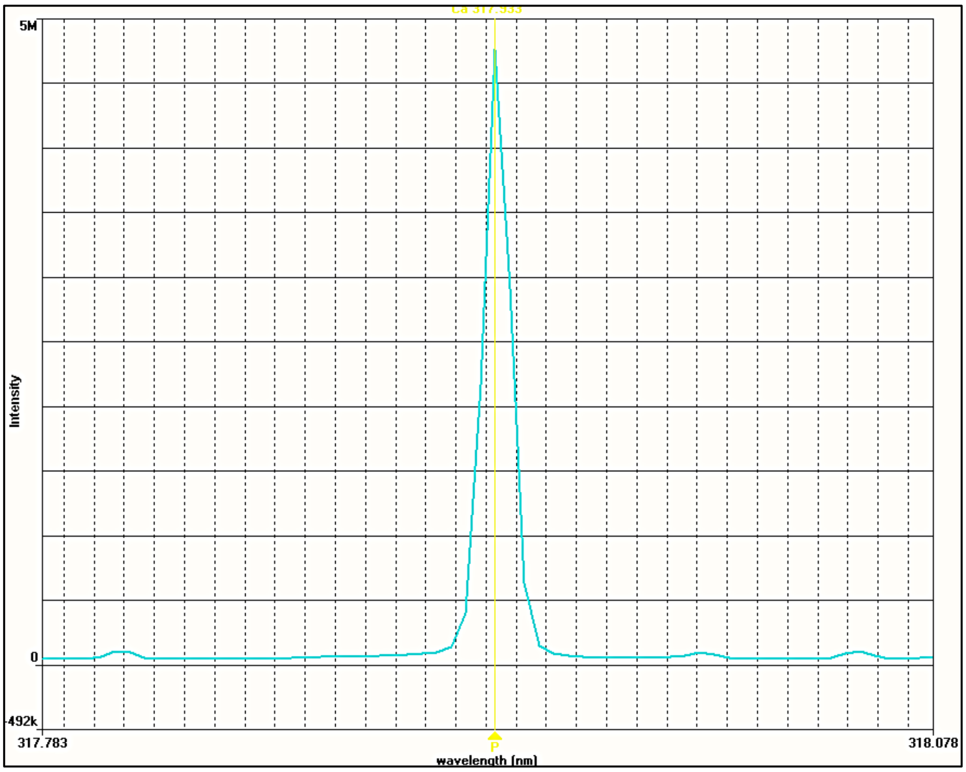


Figure 4.8: Background of Calcium Signal

Appendix F2 tabulate calcium concentration raw data while Table 4.4 shows average calcium concentration and plotted in Figure 4.9. All samples showed a general trend, calcium concentration reached its maximum value either at 14 hours or 1 day which was consider fast enough owing to rapidly attack of acetic acid on cement cube matrix, subsequently exposed inner surface to acetic acid. After 1 day it reduced steadily and maintain at certain level. CH which was a product of cement hydration reaction dissociated into ions and leaked into leachate. Positive gradient in the graph implies CH within the blocks continuously leached out at significant rate before 1 day lapsed. Dissociated calcium ions reacted with carbonic acid formed by reaction between water and carbon dioxide subsequently converted into insoluble calcium carbonate species, deposited on the surface of cement cubes and interface between leachate and air, shown in Figure 4.10. Calcium concentration tend to decrease resulted in negative gradient for all samples after 1day provided rate of deposition greater than rate of dissociation. On the other hand, samples doped with RHA reduced calcium leachability, typical example shown in Figure 4.9. RHA is one of the good pozzolanic materials which capable to react with CH during hydration of cement and form C-S-H, as describe by equation 4.1. Since part of CH is used up in the reaction, the fraction that leachable greatly reduced.

As a conclusion, RHA capable to reduced leachability of calcium by converting CH to C-S-H.

Table 4.4: Average Calcium Concentration

Duration	0 ppm		10k ppm		30k ppm	
	100% OPC	95% OPC	100% OPC	95% OPC	100% OPC	95% OPC
1 h	928	830	1166	885	942	727
4 h	1418	1429	1627	1586	1484	1190
7 h	1691	1463	1733	1395	1433	1382
14 h	1652	1472	1809	1536	1485	1295
1 d	2007	1550	1792	1555	1347	1347
4 d	1744	1492	1664	1464	1210	1224
7 d	1733	1337	1707	1589	1016	1185
14 d	1618	1235	1417	1451	814	1183
28 d	1570	1131	1232	1417	695	1018

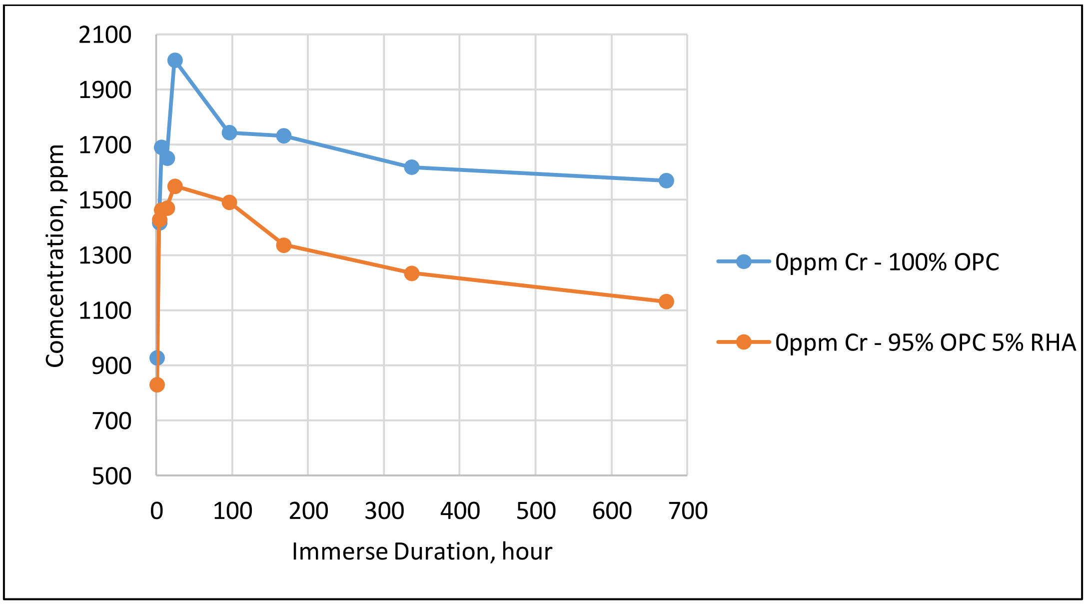


Figure 4.9: Average Calcium Concentration over Time for 0ppm Groups

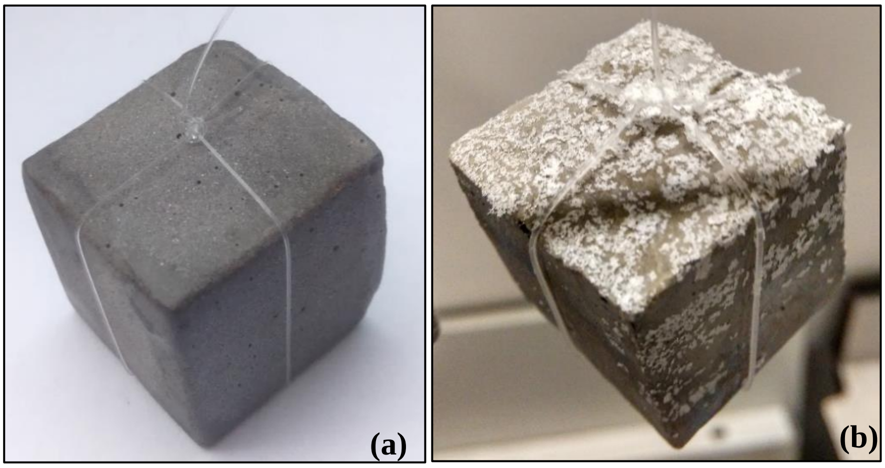


Figure 4.10: Precipitation of Calcium Carbonate (a) Before submerge into acetic acid (b) After 7 days of contact time with acetic acid

4.2 Changes of pH over Contact Period

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \tag{4.2}$$

$$CO_{2(aq)} + H_2O \leftrightarrow H_3CO_3^- + H^+ \tag{4.3}$$

$$H_3CO_3^- \leftrightarrow CO_3^{-2} + H^+ \tag{4.4}$$

$$Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^- \tag{4.5}$$

$$Ca^{2+} + CO_3^{-2} \rightarrow CaCO_3 \tag{4.6}$$

$$Ca^{2+} + H_3CO_3^- \rightarrow Ca(H_3CO_3^-)_2 \tag{4.7}$$

Equation 4.1 to equation 4.5 disclosed carbonisation mechanism. Equation 4.1 to equation 4.3 illustrated atmospheric carbon dioxide dissociation pathway into carbonate ions while equation 4.4 showed dissociation of calcium hydroxide originate from cement hydration process. All of them were reversible reaction except equation 4.5 which characterise carbonization, calcium ions react with carbonate ions and form calcium carbonate precipitate.

Figure 4.11 shows distribution of carbonate species over pH. High pH switched equilibrium in favour of carbonate ions while pH ranging from 6 until 10 switched equilibrium toward bicarbonate ions (James and Stephen, 2004). Both of them capable to react with calcium ions successively and turned into calcium carbonate (equation 4.6) or calcium bicarbonate (equation 4.7) respectively. Calcium carbonate was insoluble in water with pKa of 9.0, leaned towards saturation at pH 9 and precipitated. On the other hand, calcium bicarbonate were soluble in water, especially at pH 8.

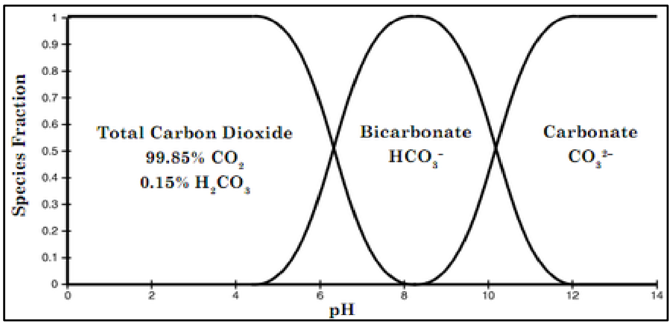


Figure 4.11: Distribution of Carbonate Species versus pH (James and Stephen, 2004)

Since cement was alkaline in nature, it undergoes neutralization with acetic acid. This reaction completed rapidly within few hours and pH of leachate raised significantly from 2.88 to 7. After than that, increment of pH until 12 was mainly due to dissociation of CH from cement cubes. 0 ppm Cr - 100% OPC samples showed greatest calcium dissociation capacity, leached 2007 ppm within 1 day, signified highest calcium leachability among other experimental groups. Sudden dissociation of CH boosted pH of leachate up to 12, represented saturation pKa of CH. Due to rapid dissociation, equilibrium between carbonate ions and bicarbonate ions being disturbed. Calcium ions in excess reacted with carbonate ions formed calcium carbonate precipitate, leaving unreacted calcium ions. It is critical to take note exhausted carbonate ion will replenished by dissociation of bicarbonate ions, via equation 4.4. Similar case applied for bicarbonate ions which replenished by dissociation of aqueous carbon dioxide followed equation 4.3. Hence, equilibrium to spawn carbonate ions required stages, unreacted calcium ions had no choice consequently formed calcium bicarbonate since carbonate ions exhausted. Calcium bicarbonate in the leachate saturated at pH 9. Saturated leachate did not permit further dissociation of calcium hydroxide thus leachate pH maintain at 9. As soon as carbonaceous equilibrium established and carbonate ions was restored, calcium bicarbonate converted into calcium carbonate precipitate. Due to precipitation of calcium carbonate, calcium ions in leachate no longer saturated, enable calcium hydroxide to resume its dissolution. Dissolution of calcium hydroxide gave raise to hydroxide group and caused pH increased near to 12 again. Above explanation best fit to Figure 4.12, which illustrate pH changes of 0 ppm Cr - 100% OPC samples.

On the other hand, 10k ppm Cr - 100% OPC and 30k ppm Cr - 100% OPC showed similar trend, which pH increased to 12 after 4 days and maintained until end of experiment at 28 days showed in Figure 4.13. Maximum calcium concentration for both of them were 1809 ppm and 1485 ppm respectively, lower than 0 ppm Cr - 100% OPC. The reason behind this was quite simple, sodium chromate which highly soluble in water competed with calcium hydroxide during dissolution and diffusion stage, migrated from cement cubes matrix to the surface of cubes subsequently leached into the leachate. Moderate released of calcium ions concentration did not interrupt carbonate and bicarbonate ions equilibrium. This statement supported with observation which white precipitate (calcium carbonate) formed by 10k ppm Cr - 100% OPC and 30k ppm Cr - 100% OPC samples came with less amount and smaller size compared to 0 ppm Cr - 100% OPC samples.

As a conclusion, pH development of leachate largely influenced by equilibrium between calcium ions and carbonate ions species. Neutralization process took place in the early stage raised pH of leachate to 7 subsequently saturation of CH and calcium carbonate tend to happen at pH 12 and 9 respectively. Triplicate pH raw data was listed in Appendix F.

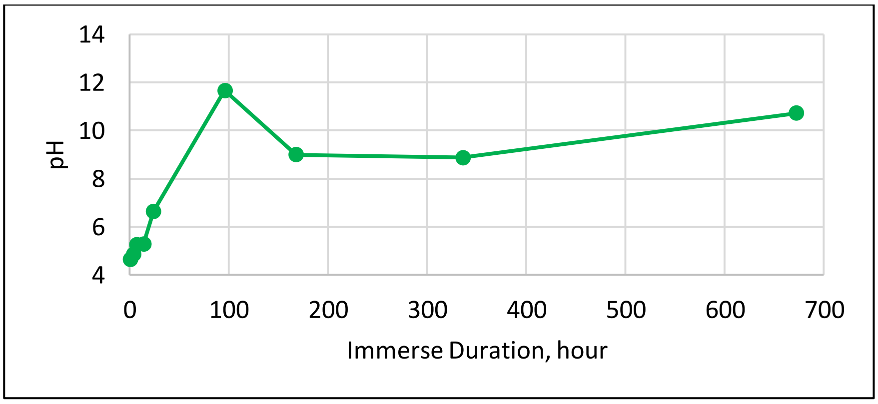


Figure 4.12: pH versus Immerse Duration for 0 ppm Cr - 100% OPC

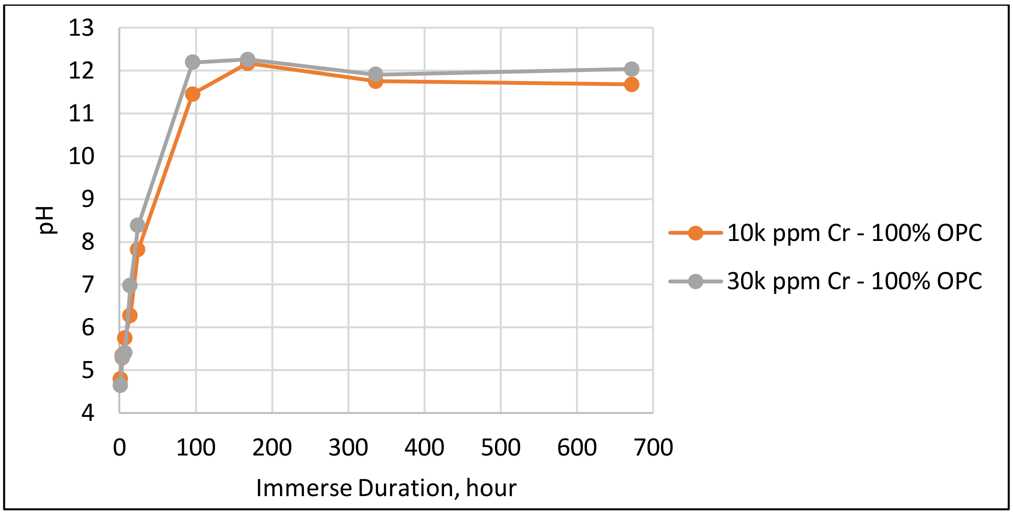


Figure 4.13: pH versus Immerse Duration for 10k ppm Cr - 100% OPC and 30k ppm Cr - 100% OPC

4.3 X-Ray Diffraction (XRD) Analysis

Changes in crystalline phases of cement with and without RHA and chromium (VI) doping were investigated using XRD. The most prominent peak in 10k ppm Cr - 100% OPC samples after 1 hour of immerse duration were those of CH at 2θ of 18.0˚ and 34.1˚ showed in Figure 4.14, CS at 2θ of 32.6˚ showed in Figure 4.15 and C-S-H at 2θ of 29.2˚ showed in Figure 4.16 (Mleza and Hajjaji, 2012). One of the characteristic peak of CH and CS at 2θ of 34.1˚ and 34.5˚ respectively overlapped due to peak broadening effect, hence peak around 34.˚ and 34.6˚ do not carry interpretable information. Other than that, calcium aluminium silicate, calcium magnesium aluminium, potassium calcium silicate, calcium carbonate and other minor compounds was detected.

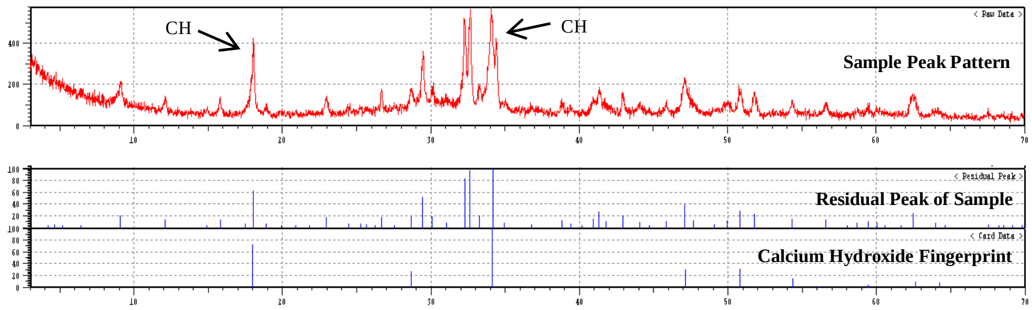


Figure 4.14: Matching of 1 hour Immerse Duration 10k ppm Cr - 100% OPC Sample Peak Data with Calcium Hydroxide Fingerprint

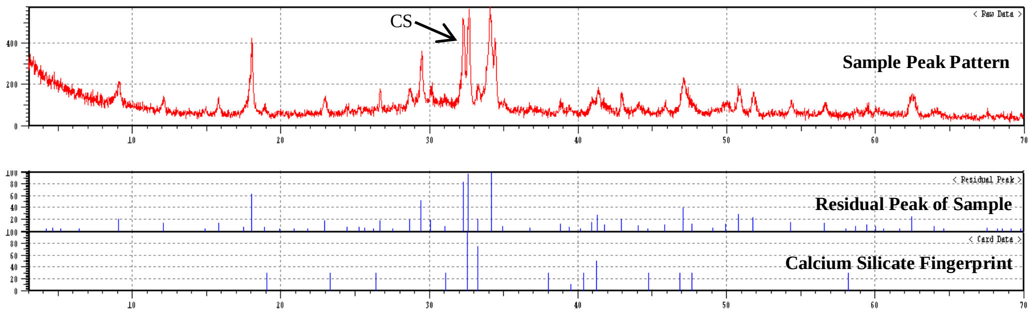


Figure 4.15: Matching of 1 hour Immerse Duration 10k ppm Cr - 100% OPC Sample Peak Data with Calcium Silicate Fingerprint

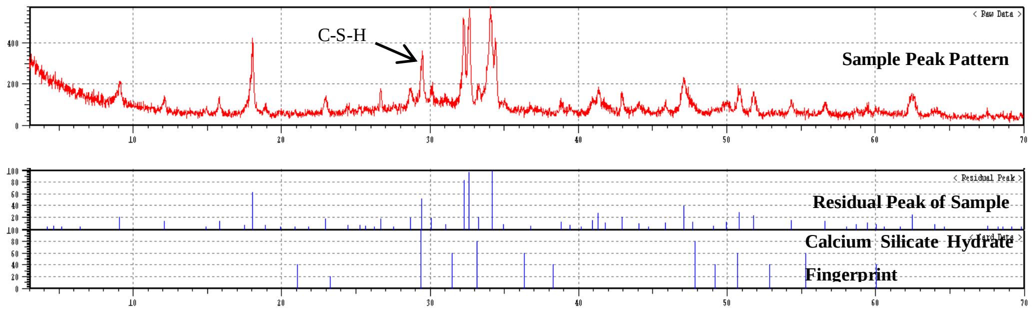


Figure 4.16: Matching of 1 hour Immerse Duration 10k ppm Cr - 100% OPC Sample Peak Data with Calcium Silicate Hydrate Fingerprint

Table 4.5 summarize CH, CS and C-S-H peak height (CPS) for samples with immerse duration of 1 h and 28 days. Generally, CPS of CH increased from 1 hour to 28 days due to propagation of cement hydration, for example 10k ppm Cr - 95% OPC 5% RHA sample peak data show increment from 410 CPS to 600 CPS. It took 28 days for this increment because cement hydration was a slow reaction and required months to complete. On the contrary, CS which was reactant for cement hydration being used up, hence CPS showed decline trend, observable in 10k ppm Cr - 95% OPC 5% RHA sample peak pattern from 400 CPS to 300 CPS. CPS of C-S-H fluctuated between 300 CPS to 400 CPS due to its poor crystallinity and principally existed in the form of amorphous.

As a summary, abundance of CH increased while contrary CS decreed as time lapsed.

Table 4.5: Summarized Peak Height (CPS)

Samples	Duration	CH	C-S-H	CS
10k ppm Cr -100% OPC	1 hour	420	360	600
	28 days	560	360	380
10k ppm Cr -95% OPC 5% RHA	1 hour	410	360	780
	28 days	600	300	340
30k ppm Cr -100% OPC	1 hour	300	400	400
	28 days	460	300	480
30k ppm Cr -95% OPC 5% RHA	1 hour	300	340	400
	28 days	480	360	300

Samples with high sodium chromate doping (30,000 ppm) gave smaller CPS reading of CH compared to samples with low sodium chromate doping (10,000 ppm) no matter with or without RHA. It is due to reaction between CH and chromate ions, gave raise to formation of calcium chromate which should be identified at 2θ of 32.3 and 35.2. However calcium chromate peak was drawn by broadening of calcium silicate peak at 2θ of 32.6 and calcium hydroxide at 2θ of 33.3 peak.

Samples peak pattern of 10k ppm Cr - 100% OPC after 1 day immerse duration showed similarity with fingerprint of chromium (III) oxide, indicated by Figure 4.17 (a). Postulated reduction of chromium (VI) ions and precipitation of chromium (III) ions took place after 1 days of submerge duration. Moreover, matching of 7 days immerse duration 10k ppm Cr - 100% OPC Sample Peak Data illustrated in Figure 4.17 (b) shows presence of additional chromium (III) compound, iron chromium oxide being formed. This finding cross checked and gave a good reason why leachate chromium (VI) concentration from ICP-OES analysis dwindled after 1 day.

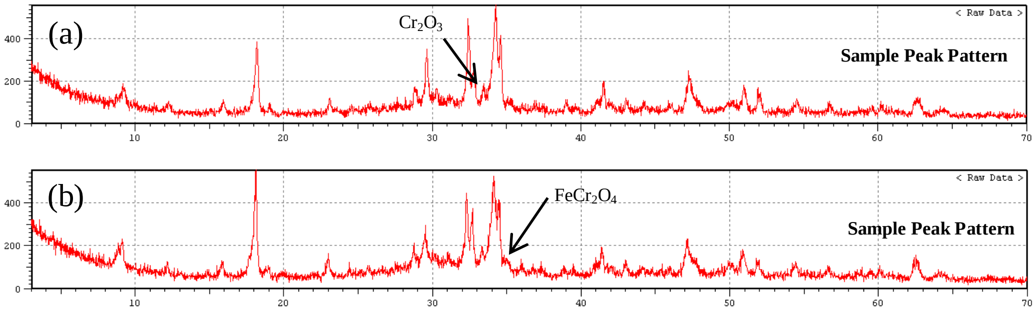


Figure 4.17: Chromium Compound Matching (a) 10k ppm Cr - 100% OPC Chromium Oxide Peak Data with 1 day Immerse Duration. (b) 10k ppm Cr - 100% OPC Iron Chromium Oxide Peak Data with 7 day Immerse Duration

30k ppm Cr - 100% OPC XRD results were quite similar with 10k ppm Cr - 100% OPC, except CPS of iron chromium oxide increased, point toward improved bulkiness of iron chromium oxide. Formation of iron chromium oxide reflected successful precipitation of chromium (III) ions. The more iron chromium oxide could be detected, the lesser chromium (VI) remain in leachate. This finding further proved hypothesis of iron oxide capable to serve as a reduction agent to reduce chromium (VI) to chromium (III), subsequently precipitated as iron chromium (III) compound. Hypothesis made during ICP-OES results analysis which suspected chromium (VI) concentration in leachate dwindled due to precipitation of insoluble chromium (III) oxide complexes within matrix of cubes was accurate.

As a short conclusion, effect of chromium precipitation for all samples started from first day after immersed. Iron chromium oxide, chromium oxide are the main chromium (III) compound found. Other than that, samples that collected after 28 days of immerse duration showed presence of additional chromium (III) compound species, such as sodium chromium oxide, magnesium aluminium chromium (clinochloree-1mii) phases, sodium chromium oxide found in minor quantity. 30k ppm Cr - 95% OPC 5% RHA samples at 28 days detected unique occurrence of chromium (III) carbide that do not soluble in water (Wang and Vipulanandan, 2000).

White crystal precipitated on cement cube samples was sent to XRD test. Figure 4.18 shows residual peak of white precipitate fit perfectly with calcium carbonate fingerprint. This finding indicate dissociated calcium ions eventually precipitate as calcium carbonate, reflect ICP-OES results which showed decreasing calcium concentration after 1 day of submerge duration.

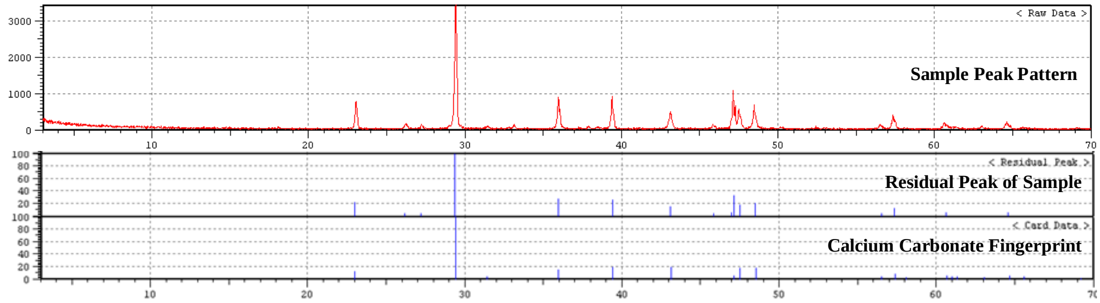


Figure 4.18: Matching of White Precipitate Peak Data with Calcium Carbonate Fingerprint

4.4 Scanning Electron Microscope (SEM) Analysis

Total 5 features could be easily determined based on morphology of cement cube, namely Ettringite, CH, C-S-H, RHA and precipitate. Ettringite characterized by its needle like geometry while CH appeared as pellet structure, results of calcium silicate hydrolysis after hours of curing. C-S-H morphology development can be classified into 3 stages. In early stages it formed a mesh similar to honey comb, subsequently massive structure consisting of interspersed and packed thin crystals and finally pore filling by short lamellar hydrated calcium silicate. The final stage of pope filling could take up to few days to several months (Ylmen, et al., 2009). RHA is distinguished by geometry of sphere. At the same times, deposition of large and small chromium crystal were dispersed in the harden cement cube.

Figure 4.19 shows tobemorite which was a calcium silicate hydrate mineral compound, C-S-H and RHA features (Arandigoyen, et al., 2007). Since submerge duration was merely 1 day, precipitate was hardly found.

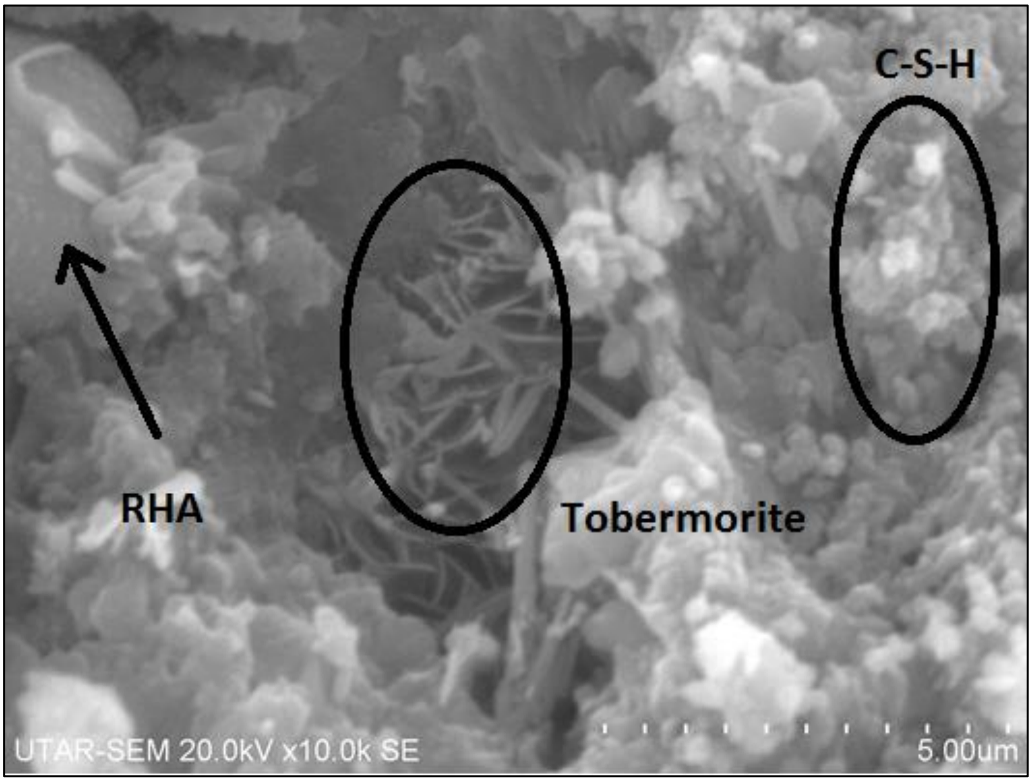


Figure 4.19: Morphology of 10k ppm Cr - 100% OPC after Immersed in Acetic Acid for 1 day

Figure 4.20 shows clear structure of ettringite. This specimen had gone through submerge duration of 28 days, chromium (III) compound was precipitated on the cement cube matrix. Figure 4.21 and Figure 4.22 give clear chromium (III) compound precipitate and RHA morphology.

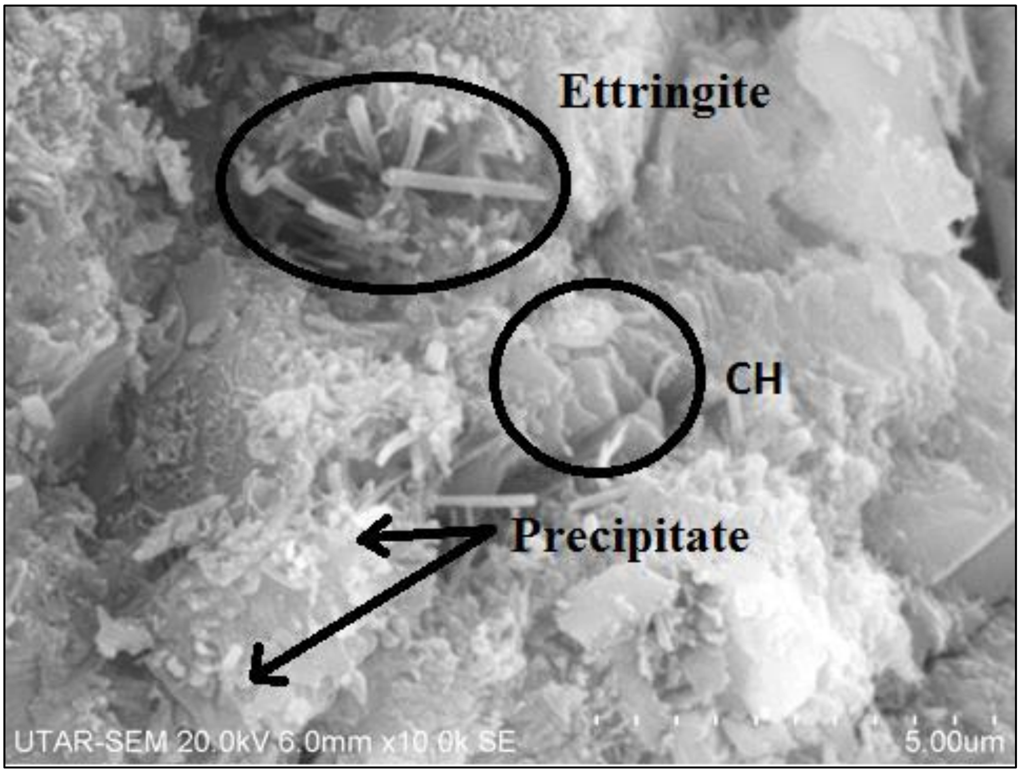


Figure 4.20: Morphology of 10k ppm Cr - 100% OPC after Immersed in Acetic Acid for 28 days

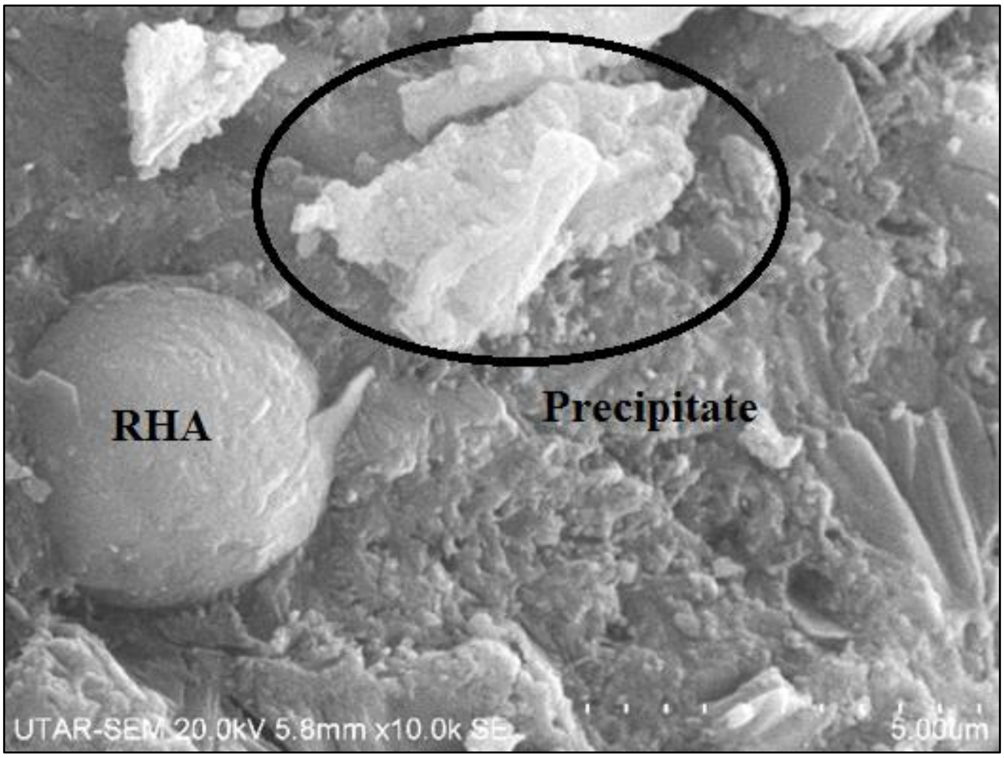


Figure 4.21: Morphology of 10k ppm Cr - 95% OPC 5% RHA after Immersed in Acetic acid for 28 days

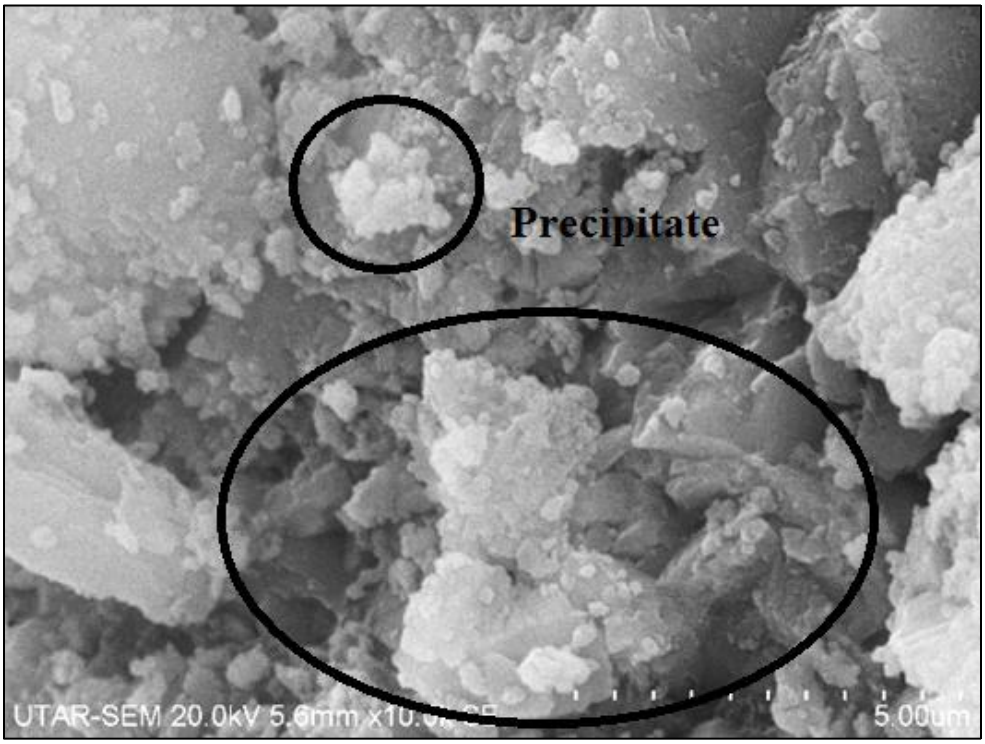


Figure 4.22: Morphology of 30k ppm Cr - 95% OPC 5% RHA after Immersed in Acetic acid for 28 days

4.5 Energy Dispersive X-ray Spectroscopy (EDX) Analysis

EDX was run to cross check XRD results qualitatively. EDX results uphold conclusion of chromium precipitate did presence in cement cube matrix and results was listed in Appendix H. Without any doubt, calcium was the most abundant element follow by silica and oxygen due to massive amount of CH and C-S-H being form, both of them are principle compound of cement hydration (Mleza and Hajjaji, 2012). Although results reveal that percentage of chromium was relatively small, but it did deposited within cement cube framework.

4.6 Postulated Leaching Mechanism

Figure 4.24 shows flow diagrams for major reaction took place throughout the whole experiment, such as hydration of cement, pozzolanic reaction, dissociation of compound, carbonation of calcium ions and reduction of chromium (VI) ions. The leachability mechanism involved development that could be classified into 2 stages. Reaction at stage 1 shared common characteristic, which interest compound were dissociated into ionic species for subsequent reaction at stage 2. For compounds that did not dissociated into ions and remained inert within cement cube matrix, hence did not involve in leachability studies. At the end of stage 2, transformation of ionic species into insoluble form by precipitation capable to reduce concentration of calcium and chromium (VI) ions existed in leachate. On the other word leachability of calcium and chromium was reduced. Following discussion integrated results from ICP-OES, pH and XRD, analysis.

First of all, addition of water with OPC induced hydration process to take place. CS turned into C-S-H and CH. CH take-up portion of the calcium from CS. Formation of CH is undesirable due to capability of CH to leach out from the cement cube matrix caused losses of calcium ions which was responsible for formation of C-S-H. Generally, high fraction of C-S-H was prerequisite to obtain superior properties of concrete (Mohamed and Abdul, 2008).

In order to reduce leachability of calcium by means of lowering hydraulic conductivity of cement cube via formation of C-S-H, 5 wt% of RHA was added into OPC and the performance was quite impressive. ICP-OES results showed that leachability of calcium in samples doped with RHA reduced by 22.79%. High silica content of RHA, ranging 92% to 95% (Nornikman, et al., 2009) entitled it to become a decent pozzolans. Pozzolans possesses no or little cementitious value but capable to reacted with calcium hydroxide in the presence of water at ordinary room temperature subsequently gave raise to compounds possessing cementitious properties, for example C-S-H and improved cement or concrete properties. RHA behave like a supplement to enhance cement properties.

Once sample cubes immersed into acetic acid solution, acidic condition attacked alkaline cement cube matrix, neutralization occur and soluble compound leached to the acetic acid. As shown in Figure 4.24, CH was dissociated into calcium and hydroxide at the same time iron oxide dissociated into iron (II), iron (III) and hydroxide ions. On the other hand, sodium chromate dissociated into sodium and chromate ions. Neutralization was a rapid reaction, hence it raised pH of leachate from 2.88 to 7 rapidly in the early stage and subsequently pH reached 12 due to saturation of calcium hydroxide ions.

At the same time, carbon dioxide originated from atmospheric air dissolved into the alkaline leachate at the end formed carbonate ions. This could be done in three steps, dissolved of carbon dioxide in leachate at first, followed by transformation of dissolved carbon dioxide into bicarbonate ions and hydrogen ions. Lastly bicarbonate ions transformed in to carbonate ions. All three reactions were reversible reaction.

At stage 2, calcium ions react with carbonate ions and form calcium carbonate, an insoluble compound that precipitated on the surface of cement cubes and the interface between leachate and air, shown in Figure 4.23. Deposition of calcium carbonate caused two major phenomenons, concentration of calcium in leachate was reduced and pH drops to 9. Once rate of deposition of calcium carbonate faster than rate of dissociation of CH, net calcium ions concentration within the control volume would decrease, hence leachability of calcium reduced. On the other hand, pH dropped due to reduction in hydroxide ions. For each mole of calcium ions deposited as calcium carbonate, it required 2 moles of hydroxide ions. pH tend to stabilize at 9 due to saturation of calcium bicarbonate instead of calcium hydroxide at pH 12.

Figure 4.23: Calcium Carbonate Precipitate on Cement Cubes

During stage 1, iron oxide gave raise to concentration of iron (II) ions while dissociating into leachate. At the same time sodium chromate dissociated into dichromate ions. Both iron (II) ions and dichromate ions undergo redox reaction at stage 2. Iron (II) served as a reducing agent and oxidized into iron (III) while chromium (VI) was reduced to kinetically inert chromium (III). Reduction of chromium (VI) to chromium (III) initiated impulsive solubility drop, induced precipitation of chromium (III) complex such as iron chromium hydroxide and chromium hydroxide. Based on XRD analysis, both of the compounds did found in cement cube matrix. This finding tally with literature review that pH ranging 6.5 to 11.5 favour deposition of chromium (III) hydroxide that insoluble in water, refer Figure 2.3 for specification diagram of chromium (III) species.

As a short summary, leachability study required consistence monitoring and supervising over a period of time and involved many discrete reaction. Since OPC contained various compound, for those did not play an active role in affecting the leachability of chromium (VI) did not stated in Figure 4.24.

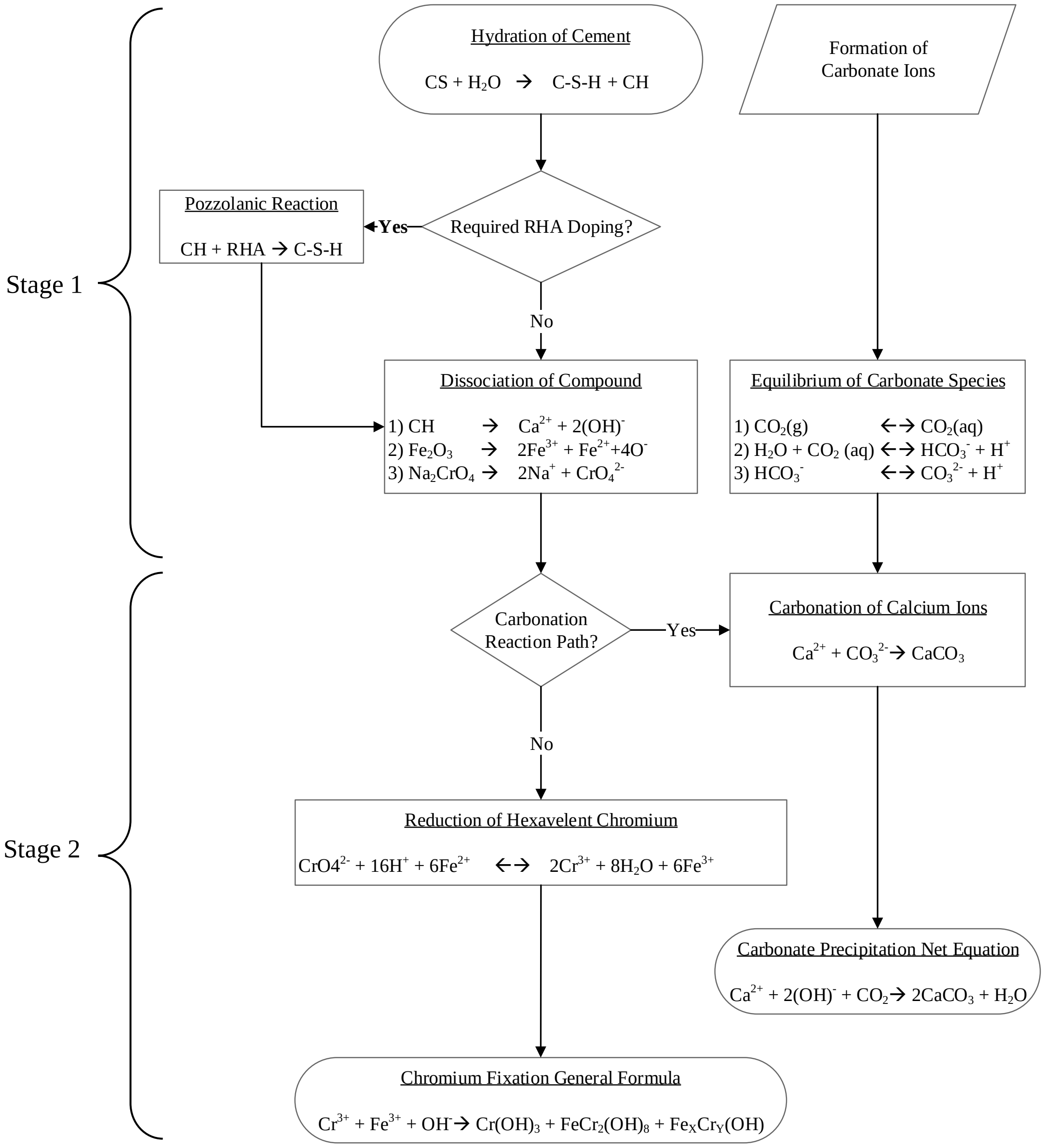


Figure 4.24: Postulated Basic Chromium and Calcium Leachability Mechanism for This Study

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Ordinary Portland cement has the potential in control leachability of chromium (VI) ions by converting them into inert insoluble chromium (III) deposit, such as iron chromium hydroxide and chromium hydroxide. However, none of the chromium (VI) concentration in leachate sample comply with the regulatory limit enforce by Ministry of Natural Resources and Environment Malaysia of 0.05 mg/L, stated in “A Guide For Investor”. Concentrations of chromium (VI) ions in all samples were more than 0.6 ppm according to ICP-OES analysis. This indicated that none of the experiment parameter competence to meet safety requirement yet showed great potential for further improvement as leached percentage of chromium was around 1 wt%. Nonetheless, calcium showed increasing leachability at the early stage but decreased later on due to formation of calcium carbonate precipitate.

pH of leachate at early stage tend to maintain at pH 12 at due to saturation of calcium hydroxide subsequently dropped to pH 9 at transition state between 7 to 14 days, provided carbonate ions was exhausted and calcium bicarbonate was the predominant species. Carbonate equilibrium might re-established after some delay and pH might increase to pH 12 again. Reaction between bicarbonate ions and carbonate ions are reversible process.

Nonetheless, XRD results revealed sample doped with RHA capable to confine of calcium within cement framework via formation of extra calcium silicate hydrate between reaction of CH and RHA. Chromium oxide and iron chromium oxide were detected for samples with immerse duration more than 1 day, indicated deposition of chromium (III) started at 1 day after leaching started. It was found that the longer of the immerse duration, the more different types of chromium complexes such as sodium chromium oxide, magnesium aluminium chromium and chromium carbide were formed.

SEM showed typical cement hydration microstructure of ettringite, CH, C-S-H, and tobemorite. Other than that, morphology of chromium deposition and RHA could be observed. Results showed that the long the submerge duration, the larger the crystal like chromium deposit was.

EDX elemental qualitative analysis spectacled chromium species presence in sample cubes, XRD results disclosed chromium compound in fact were chromium hydroxide and iron chromium oxide, tally with postulated leaching mechanism.

5.2 Recommendations

First recommendation will be increase weight percentage of RHA with respect to OPC. Although current studies which sample dope with RHA show reduction of calcium concentration in leachate, to what extend such reduction could achieve still remain mystery. From experimental data, the addition of RHA in excess use up portion calcium hydroxide in cement cube matrix by transformation to C-S-H which gives better cement properties besides inhibit leachability of calcium since soluble CH does not presence.

Experimental finding showed capability of iron oxide to reduce leachability of chromium was remarkable. OPC merely contain 3.02% of iron oxide by itself yet these small amounts of iron oxide capable to retain chromium doping up to 98.5%, provided enough time must be given. Hence, the effect of iron oxide doping can be justified in the further study. With extra iron doping capable to boost reduction kinetic of chromium (VI) hope to conclude a rapid reduction even in early stage.

Lastly, it is critical to determine presence of chromium (III) species in leachate. One of the methods is via ionic chromatography test. Differential charges between chromium (VI) and chromium (III) enable qualitative determination as both of them interact differently with ionic chromatography column and cause difference in retention time. Chromium (III) characterization conjugate with chromium (VI) analysis enable complete assessment of risk associated with exposure of chromium bearing contaminant by consider effect of total chromium concentration. besides that, it would be grateful to replace inductive coupled plasma optical emission spectroscopy (ICP-OES) with graphite furnace atomic absorption spectroscopy (GF-AAS).

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APPENDICES

Appendix A : Leaching Test Methods

TCLP	Toxicity Characteristic Leaching Procedure
SPLP	Synthetic Precipitation Leaching Procedure
DRET	Dredge Elutriate Test
NEN 7341	Availability Test
ASTM D 3987	Standard Test Method for Shake Extraction of Solid Waste with Water
ASTM D 6234	Standard Method for Shake Extraction of Mining Waste by the SPLP
SET	Standard Elutriate Test
EN 12457/1-4	Compliance Test for Granular Waste Sludge
Sequential Batch Tests	
SBLT	Sequential Batch Leachate Test
ASTM D 4793	Standard Test Method for Sequential Batch Extraction of Waste with Water
ASTM D 5744	Standard Test Method for Accelerated Weathering of Solid Materials Using a Modified Humidity Cell
Flow Through Test	
PCLT	Pancake Column Leach Test
prEN 14405	Up Flow Percolation Test
ASTM D 4874	Standard Test Method for Leaching Solid Waste in a Column Apparatus
NEN 7343	Column Test
Flow Around Test	
NEN 7345	Tank Leach Test

Appendix B: Leaching Regulation and Limits

Appendix B1: Malaysia Leaching Criteria

No.	Parameter	Unit	Standard Limit
1.	Temperature	˚C	40
2.	pH Value	-	6.0 – 9.0
3.	BOD_5 at 20 ˚C	mg/L	20
4.	COD	mg/L	400
5.	Suspended Solid	mg/L	50
6.	Ammoniacal Nitrogen	mg/L	5
7.	Mercury	mg/L	0.005
8.	Cadmium	mg/L	0.01
9.	Chromium, Hexavalent	mg/L	0.05
10.	Chromium, Trivalent	mg/L	0.20
11.	Arsenic	mg/L	0.05
12.	Cyanide	mg/L	0.05
13.	Lead	mg/L	0.10
14.	Copper	mg/L	0.20
15.	Manganese	mg/L	0.20
16.	Nickel	mg/L	0.20
17.	Tin	mg/L	0.20
18.	Zinc	mg/L	2.0
19.	Boron	mg/L	1.0
20.	Iron (Ferric)	mg/L	5.0
21.	Silver	mg/L	0.10
22.	Selenium	mg/L	0.02
23.	Barium	mg/L	1.0
24.	Fluoride	mg/L	2.0

Appendix B2: Regulatory Limit for the Use of Heavy Metal as Building Material in Belgium.

Parameters	Total Concentration (mg/kg dry substance)
Arsenic(As)	250
Cadmium (Cd)	10
Chromium (Cr)	1250
Copper (Cu)	375
Mercury (Hg)	5
Lead (Pb)	1250
Znc (Zn)	1250
Nickel (Ni)	250
Extractable Organohalogen Compounds (EOX)	10
Hexane	1
Heptanes	25
Mineral oil	1000
Octane	90
Polychlorinated biphenyls (PCB)	0.5

Appendix C: Heavy Metal Concentration Sample Calculation

Molar mass of chromium is equivalent to 51.9961 g/mol whereas nitrogen and oxygen atom is 14.0067 g/mol and 15.9994 g/mol respectively (Skoog, et al., 2004). 10k ppm of chromium as example.

10k ppm of chromium in solution
= 10k mg of chromium (III) ion per liter of distilled water
= $\frac{10 \times 10^{-3} \times 10^{3} g}{51.9961\ g/mole}$ per liter of distilled water
= $1.92 \times 10^{-1}\ \frac{\text{mol}}{\text{liter}}$

Chromium (III) nitrate, Cr $(NO_3)_3$ require,
= $1.92 \times 10^{-1}\ \frac{\text{mol}}{\text{liter}} \times \{51.9961\ +\ 3\ [14.0067\ +\ (15.9994 \times\ 3)]\ \}\frac{\text{g}}{\text{mol}}$
= $1.92 \times 10^{-1}\,\frac{\text{mol}}{\text{liter}} \times 238.0108\,\frac{\text{g}}{\text{mol}}$
= $45.7\,\frac{\text{g}}{\text{liter}}$

Appendix D : pH 2.88 Acetic Acid Calculation

Assume partial dissociation of acetic acid, given by

$$HA \rightarrow H^+ + A^-$$

$pH = -\log[H^+]$ --- Equation 1

$K_a = \frac{[H^+][A^-]}{[HA]}$ --- Equation 2

Whereas

HA denote acetic acid,

H^+ denote hydrogen cation,

A^- denote acetic acid anion,

K_a denote acid dissociation constant at 25 ˚C.

Given K_a of acetic acid equal to 1.75×10^{-5} (Skoog, et al., 2004) and pH of acetic solution is 2.88. Assume α is the concentration of acetic acid.

From Equation 2:

$$pH = -\log[H^+]$$

$$2.88 = -\log[H^+]$$

$$[H^+] = 10^{-2.88}$$

$$[H^+] = 1.32 \times 10^{-3}$$

From Equation 3:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$1.75 \times 10^{-5} = \frac{[1.32 \times 10^{-3}][1.32 \times 10^{-3}]}{[\alpha - 1.32 \times 10^{-3}]}$$

$$\alpha = 0.10\,M$$

Appendix E : Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) Data

Appendix E1: Chromium Concentration Raw Data for 100% OPC Samples.

Triplicate Numbering	0ppm Cr - 100% OPC		10k ppm Cr - 100% OPC		30k ppm Cr - 100% OPC	
	Intensity	Concentration (ppm)	Intensity	Concentration (ppm)	Intensity	Concentration (ppm)
1h @1	322.4	0.576	62235.60	0.763	167836.20	1.082
1h @2	315.70	0.576	64916.20	0.771	145861.30	1.016
1h @3	346.10	0.576	63226.50	0.766	169664.20	1.088
4h @1	349.70	0.576	67759.60	0.780	287269.60	1.444
4h @2	440.00	0.576	66965.10	0.777	231076.90	1.274
4h @3	321.80	0.576	94849.00	0.862	212255.10	1.217
7h @1	1112.50	0.578	73917.70	0.798	200027.00	1.180
7h @2	1273.30	0.578	2323.00	0.582	241498.30	1.305
7h @3	1315.90	0.579	78804.60	0.813	201481.60	1.184
14h @1	1109.00	0.578	83142.70	0.826	211200.20	1.214
14h @2	1270.40	0.578	71270.90	0.790	239516.90	1.299
14h @3	1333.40	0.579	78542.50	0.812	240052.80	1.301
1d @1	1563.80	0.579	52794.30	0.734	176835.40	1.110
1d @2	1328.80	0.579	61363.50	0.760	227232.50	1.262
1d @3	1488.10	0.579	46332.60	0.715	289035.90	1.449

4d @1	1284.80	0.579	42165.60	0.702	157491.70	1.051
4d @2	1525.30	0.579	33362.20	0.676	239201.20	1.298
4d @3	1292.10	0.579	25209.20	0.651	187090.60	1.141
7d @1	1197.80	0.578	14383.50	0.618	150334.60	1.029
7d @2	1252.20	0.578	22995.80	0.644	149601.80	1.027
7d @3	1205.20	0.578	22697.50	0.643	231443.10	1.275
14d @1	1214.40	0.578	10355.40	0.606	70272.40	0.787
14d @2	1145.20	0.578	7443.30	0.597	29546.80	0.722
14d @3	1182.80	0.578	10806.70	0.607	48790.30	0.888
28d @1	1188.50	0.578	2341.70	0.582	21915.30	0.664
28d @2	1113.50	0.578	3782.00	0.586	30847.00	0.641
28d @3	1235.60	0.578	4188.90	0.587	103582.60	0.668

Appendix E2: Chromium Concentration Raw Data for 95% OPC 5% RHA Samples.

Triplicate Numbering	0ppm Cr - 95% OPC 5% RHA		10k ppm Cr - 95% OPC 5% RHA		30k ppm Cr- 95% OPC 5% RHA	
	Intensity	Concentration (ppm)	Intensity	Concentration (ppm)	Intensity	Concentration (ppm)
1h @1	955.70	0.578	38069.20	0.690	138219.70	0.993
1h @2	994.40	0.578	49390.40	0.724	192184.00	1.156
1h @3	1691.30	0.580	41523.70	0.700	139074.50	0.995
4h @1	1015.70	0.578	48349.00	0.721	196297.40	1.168
4h @2	1520.40	0.579	54007.70	0.738	198904.00	1.176
4h @3	1024.50	0.578	51570.10	0.731	237798.10	1.294
7h @1	1695.50	0.580	46744.00	0.716	190283.20	1.150
7h @2	938.50	0.577	51703.10	0.731	166397.50	1.078
7h @3	1001.80	0.578	55438.00	0.742	191208.90	1.153
14h @1	112.30	0.575	47459.50	0.718	203782.90	1.191
14h @2	923.70	0.577	43245.00	0.705	250704.60	1.333
14h @3	960.50	0.578	59029.20	0.753	217158.10	1.232
1d @1	992.00	0.578	49938.10	0.726	163315.30	1.069
1d @2	904.70	0.577	44543.20	0.709	216203.60	1.229
1d @3	1200.10	0.578	52158.50	0.732	194254.70	1.162
4d @1	959.10	0.578	31545.00	0.670	111581.60	0.578
4d @2	1618.00	0.580	23092.30	0.644	158627.60	0.580
4d @3	843.70	0.577	24306.50	0.648	189404.30	0.577

7d @1	697.00	0.577	14274.90	0.618	115306.60	0.577
7d @2	994.70	0.578	15485.10	0.621	134676.60	0.578
7d @3	681.30	0.577	15107.30	0.620	101156.90	0.577
14d @1	-6.60	0.575	8090.60	0.599	83391.90	0.575
14d @2	-37.70	0.575	5998.20	0.593	65174.00	0.575
14d @3	107.70	0.575	6912.30	0.596	81904.60	0.575
28d @1	-4.50	0.575	2764.60	0.583	40026.20	0.575
28d @2	647.20	0.577	4150.60	0.587	32466.10	0.577
28d @3	730.70	0.577	4711.70	0.589	42522.50	0.577

Appendix E3: Adjusted ICP-OES Chromium Concentration

Triplicate Numbering	10k ppm Cr - 100% OPC		10k ppm Cr - 95% OPC 5% RHA		30k ppm Cr - 100% OPC		30k ppm Cr - 95% OPC 5% RHA	
	Adjusted Intensity	Concentration (ppm)	Adjusted Intensity	Concentration (ppm)	Adjusted Intensity	Concentration (ppm)	Adjusted Intensity	Concentration (ppm)
1h @1	61913.20	0.187	37113.50	0.112	167513.80	0.507	137264.00	0.415
1h @2	64600.50	0.195	48396.00	0.146	145545.60	0.440	191189.60	0.578
1h @3	62880.40	0.190	39832.40	0.120	169318.10	0.512	137383.20	0.416
4h @1	67409.90	0.204	47333.30	0.143	286919.90	0.868	195281.70	0.591
4h @2	66525.10	0.201	52487.30	0.159	230636.90	0.698	197383.60	0.597
4h @3	94527.20	0.286	50545.60	0.153	211933.30	0.641	236773.60	0.716
7h @1	72805.20	0.220	45048.50	0.136	198914.50	0.602	188587.70	0.570
7h @2	1049.70	0.003	50764.60	0.154	240225.00	0.727	165459.00	0.500
7h @3	77488.70	0.234	54436.20	0.165	200165.70	0.605	190207.10	0.575
14h @1	82033.70	0.248	47347.20	0.143	210091.20	0.635	203670.60	0.616
14h @2	70000.50	0.212	42321.30	0.128	238246.50	0.721	249780.90	0.756
14h @3	77209.10	0.234	58068.70	0.176	238719.40	0.722	216197.60	0.654
1d @1	51230.50	0.155	48946.10	0.148	175271.60	0.530	162323.30	0.491
1d @2	60034.70	0.182	43638.50	0.132	225903.70	0.683	215298.90	0.651
1d @3	44844.50	0.136	50958.40	0.154	287547.80	0.870	193054.60	0.584

4d @1	40880.80	0.124	30585.90	0.093	156206.90	0.472	110622.50	0.335
4d @2	31836.90	0.096	21474.30	0.065	237675.90	0.719	157009.60	0.475
4d @3	23917.10	0.072	23462.80	0.071	185798.50	0.562	188560.60	0.570
7d @1	13185.70	0.040	13577.90	0.041	149136.80	0.451	114609.60	0.347
7d @2	21743.60	0.066	14490.40	0.044	148349.60	0.449	133681.90	0.404
7d @3	21492.30	0.065	14426.00	0.044	230237.90	0.696	100475.60	0.304
14d @1	9141.00	0.028	8097.20	0.024	69058.00	0.209	83398.50	0.252
14d @2	6298.10	0.019	6035.90	0.018	28401.60	0.086	65211.70	0.197
14d @3	9623.90	0.029	6804.60	0.021	47607.50	0.144	81796.90	0.247
28d @1	1153.20	0.003	2769.10	0.008	20726.80	0.063	40030.70	0.121
28d @2	2668.50	0.008	3503.40	0.011	29733.50	0.090	31818.90	0.096
28d @3	2953.30	0.009	3981.00	0.012	102347.00	0.310	41791.80	0.126

Appendix E4: Actual Chromium Concentration, ppm

Triplicate Numbering	10k ppm Cr - 100% OPC	10k ppm Cr - 95% OPC 5% RHA	30k ppm Cr - 100% OPC	30k ppm Cr - 95% OPC 5% RHA
1h @1	18.73	11.23	50.67	41.52
1h @2	19.54	14.64	44.02	57.83
1h @3	19.02	12.05	51.21	41.55
4h @1	20.39	14.32	86.79	59.07
4h @2	20.12	15.88	69.76	59.70
4h @3	28.59	15.29	64.10	71.62
7h @1	22.02	13.63	60.17	57.04
7h @2	0.32	15.35	72.66	50.05
7h @3	23.44	16.47	60.54	57.53
14h @1	24.81	14.32	63.55	61.61
14h @2	21.17	12.80	72.06	75.55
14h @3	23.35	17.56	72.21	65.39
1d @1	15.50	14.80	53.02	49.10
1d @2	18.16	13.20	68.33	65.12
1d @3	13.56	15.41	86.98	58.39
4d @1	12.37	9.25	47.25	33.46
4d @2	9.63	6.50	71.89	47.49
4d @3	7.23	7.10	56.20	57.03
7d @1	3.99	4.11	45.11	34.67
7d @2	6.58	4.38	44.87	40.44
7d @3	6.50	4.36	69.64	30.39
14d @1	2.76	2.45	20.89	25.23
14d @2	1.91	1.83	8.59	19.72
14d @3	2.91	2.06	14.40	24.74
28d @1	0.35	0.84	6.27	12.11
28d @2	0.81	1.06	8.99	9.62
28d @3	0.89	1.20	30.96	12.64

Appendix E5: Calcium Concentration Raw Data.

Triplicate Numbering	0ppm Cr – 100% OPC	0ppm Cr - 95% OPC 5% RHA	10k ppm Cr - 100% OPC	10k ppm Cr - 95% OPC 5% RHA	30k ppm Cr- 100% OPC	30k ppm Cr- 95% OPC 5% RHA
1h @1	9.382	8.617	12.080	8.522	9.872	7.272
1h @2	9.566	7.981	11.140	8.579	9.043	12.930
1h @3	8.890	26.310	11.770	9.451	9.351	17.210
4h @1	14.830	14.710	16.130	22.620	1.647	11.510
4h @2	14.750	13.570	15.820	14.300	14.470	12.290
4h @3	12.950	14.590	16.850	17.420	15.210	23.760
7h @1	16.870	15.350	18.310	14.000	14.680	15.610
7h @2	18.820	14.540	16.350	13.110	14.450	25.310
7h @3	15.030	13.990	17.320	14.740	13.860	12.030
14h @1	17.550	14.700	19.130	15.260	15.890	12.400
14h @2	17.220	14.730	17.190	15.460	14.380	20.830
14h @3	14.780	7.722	17.950	18.690	14.290	13.490
1d @1	19.540	15.550	18.680	16.160	12.740	12.990
1d @2	40.300	15.630	17.850	14.940	14.410	13.790
1d @3	20.600	15.310	17.230	21.010	13.260	13.620

4d @1	16.650	14.940	17.850	14.740	11.140	19.450
4d @2	18.230	15.250	16.510	14.540	12.560	11.690
4d @3	24.220	14.570	15.570	19.200	12.610	12.790
7d @1	16.390	13.390	16.270	14.940	9.595	12.280
7d @2	17.690	13.410	16.330	22.170	14.010	12.140
7d @3	17.900	13.300	18.600	16.830	10.720	11.120
14d @1	16.270	19.620	14.200	13.860	6.864	12.820
14d @2	15.730	12.330	14.250	15.160	10.060	10.830
14d @3	16.540	12.360	14.070	11.860	7.484	9.638
28d @1	14.050	10.190	13.540	9.747	8.234	14.320
28d @2	16.480	12.840	11.230	12.420	6.692	10.180
28d @3	16.560	10.900	12.190	15.910	5.914	16.890

Appendix F pH Changes over Time

Appendix F1: Variation of pH over Period.

Duration	0ppm Cr		10k ppm Cr		30k ppm Cr	
	100% OPC	95% OPC 5% RHA	100% OPC	95% OPC 5% RHA	100% OPC	95% OPC 5% RHA
1h @1	4.60	4.47	4.79	4.46	4.63	4.42
1h @2	4.67	4.44	4.78	4.47	4.66	4.44
1h @3	4.68	4.58	4.79	4.45	4.64	4.57
4h @1	4.90	5.48	5.51	5.37	5.17	5.17
4h @2	4.74	5.49	5.32	5.07	5.47	5.02
4h @3	4.92	5.38	5.20	5.33	5.22	5.23
7h @1	5.04	6.26	5.37	5.14	5.34	5.25
7h @2	5.25	5.30	6.01	5.54	5.40	4.95
7h @3	5.50	5.64	5.88	5.54	5.47	5.31
14h @1	5.12	6.25	7.04	9.45	6.64	5.70
14h @2	5.29	6.30	5.77	9.68	7.88	5.74
14h @3	5.41	5.85	6.02	8.47	6.41	7.09

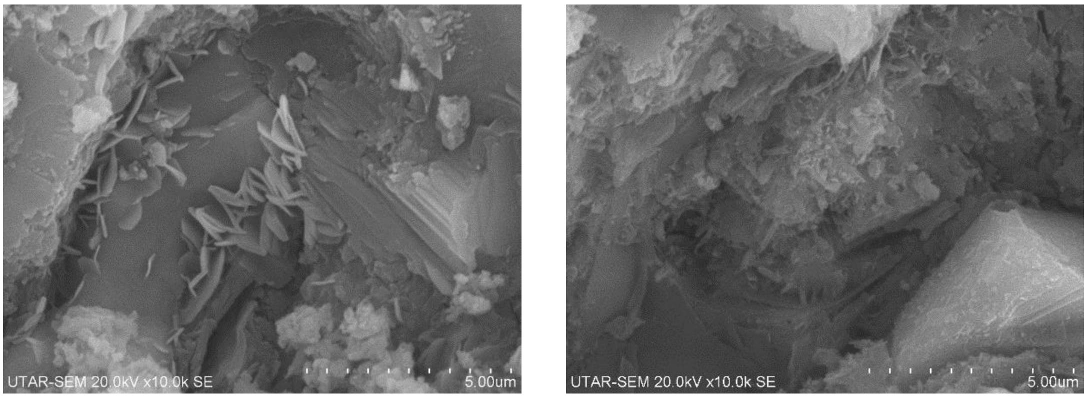
1d @1	6.91	11.31	7.74	9.01	8.48	11.81
1d @2	7.37	11.41	8.05	9.96	8.17	11.63
1d @3	5.67	10.43	7.64	10.17	8.49	11.76
4d @1	11.58	11.68	11.40	10.91	12.39	7.40
4d @2	11.69	11.71	11.44	11.50	12.08	7.06
4d @3	11.71	12.03	11.53	11.38	12.11	7.28
7d @1	9.72	11.74	12.20	11.69	12.48	7.69
7d @2	8.62	11.97	12.27	11.84	12.13	7.14
7d @3	8.64	11.66	12.04	11.68	12.19	7.01
14d @1	9.02	11.47	11.68	11.97	11.88	7.07
14d @2	8.77	11.61	11.84	11.83	12.12	7.31
14d @3	8.85	11.39	11.75	11.47	11.73	7.27
28d @1	10.64	7.16	11.47	7.22	11.85	11.18
28d @2	10.74	7.07	11.51	6.95	11.93	10.54
28d @3	10.79	7.21`	12.06	7.25	12.33	11.24

Appendix F2: Average pH over period

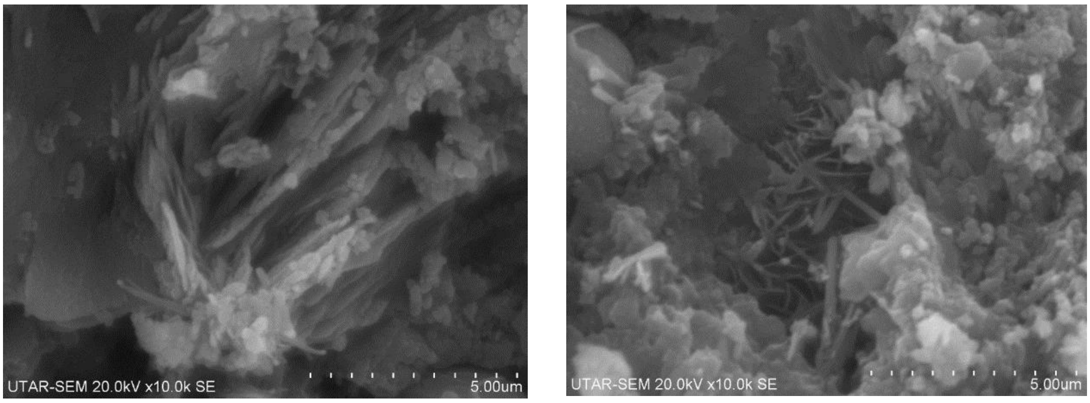
Duration	0ppm Cr		10k ppm Cr		30k ppm Cr	
	100% OPC	95% OPC 5% RHA	100% OPC	95% OPC 5% RHA	100% OPC	95% OPC 5% RHA
1h	4.65	4.50	4.79	4.46	4.64	4.48
4h	4.85	5.45	5.34	5.26	5.29	5.14
7h	5.26	5.73	5.75	5.41	5.40	5.17
14h	5.27	6.13	6.28	9.20	6.98	6.18
1d	6.65	11.05	7.81	9.71	8.38	11.73
4d	11.66	11.81	11.46	11.26	12.19	7.25
7d	8.99	11.79	12.17	11.74	12.27	7.28
14d	8.88	11.49	11.76	11.76	11.91	7.22
28d	10.72	7.15	11.68	7.14	12.04	10.99

Appendix G：Scanning Electron Microscope (SEM) Micrograph

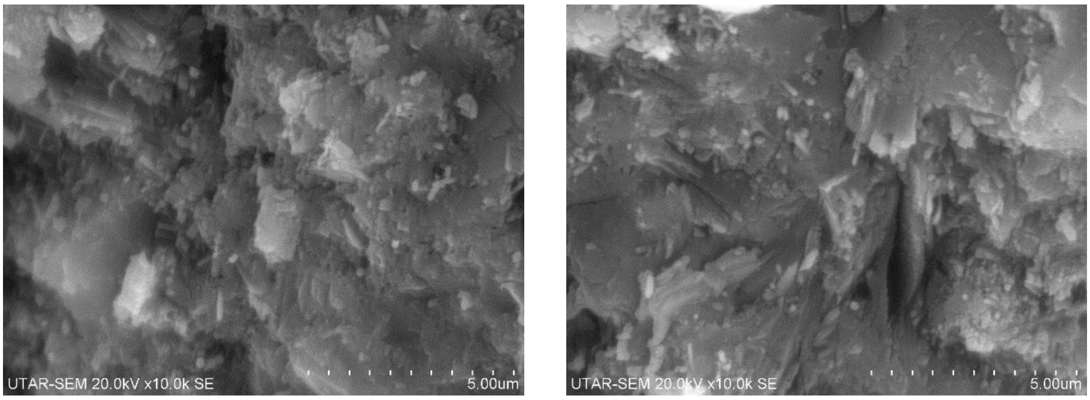
10k ppm-100% OPC@1hour



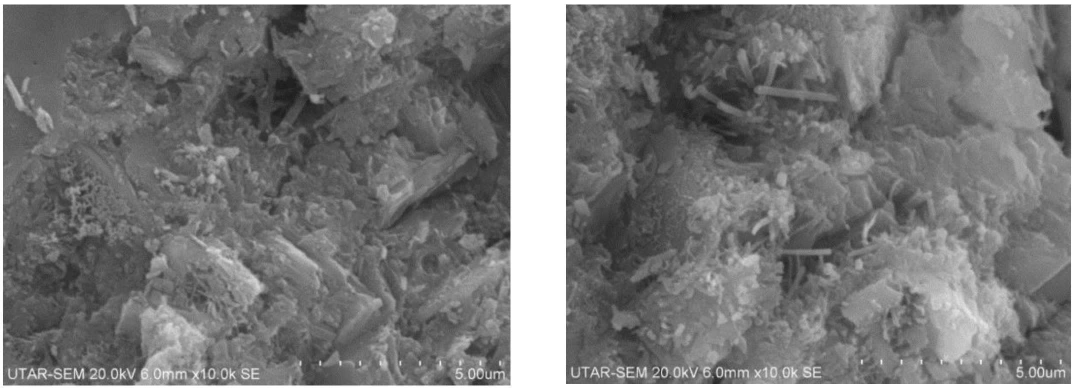
10k ppm-100% OPC@1day



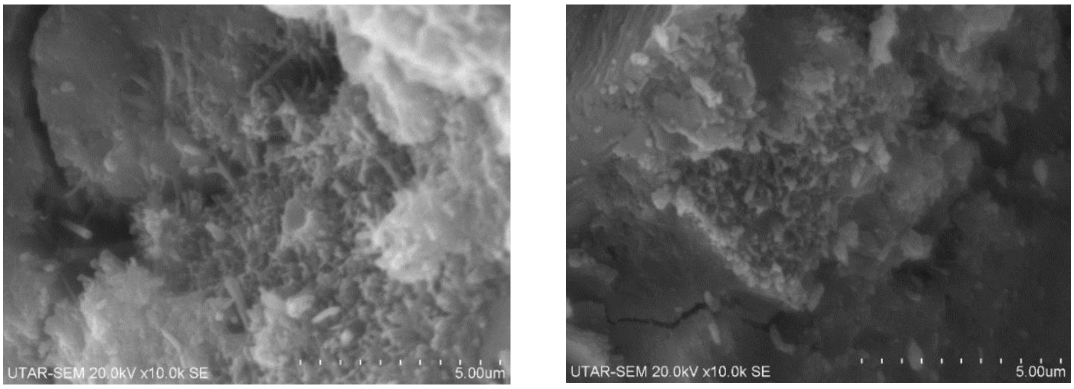
10k ppm-100% OPC@7day



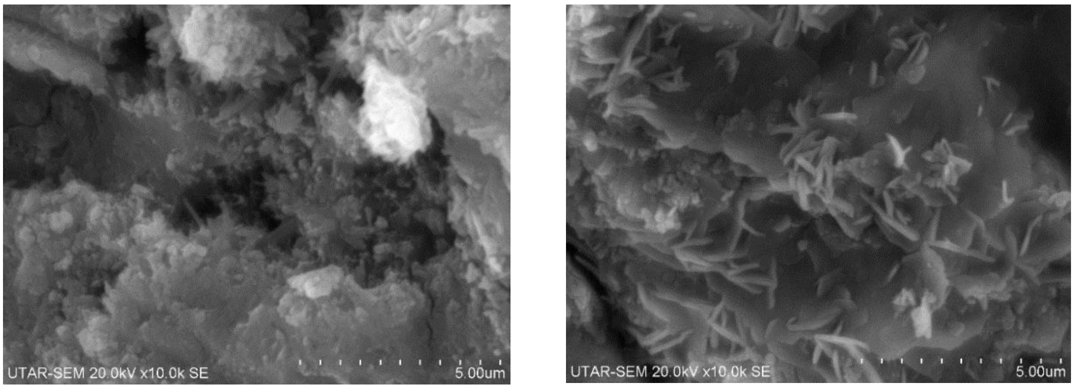
10k ppm-100% OPC@28day



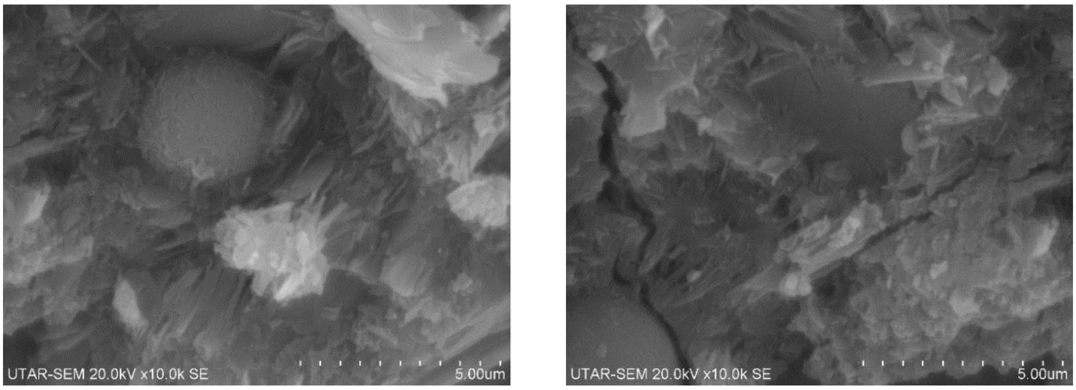
30k ppm-100% OPC@1hour



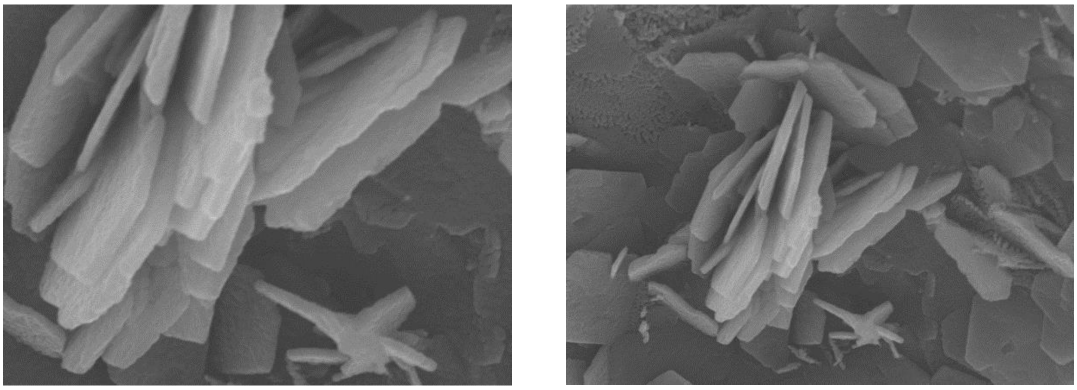
30k ppm-100% OPC@1day



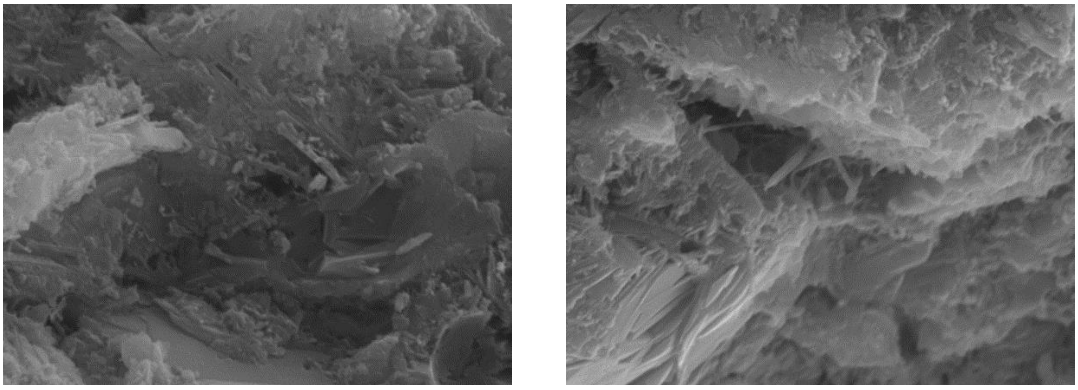
30k ppm-100% OPC@7day



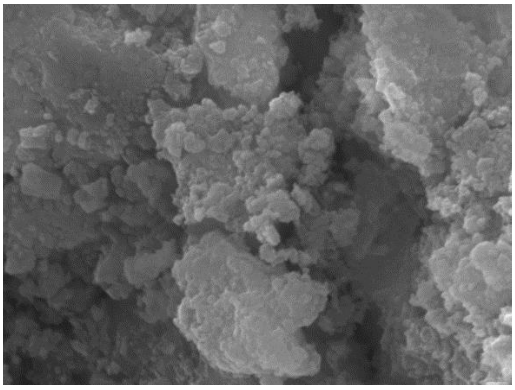
30k ppm-100% OPC@28day



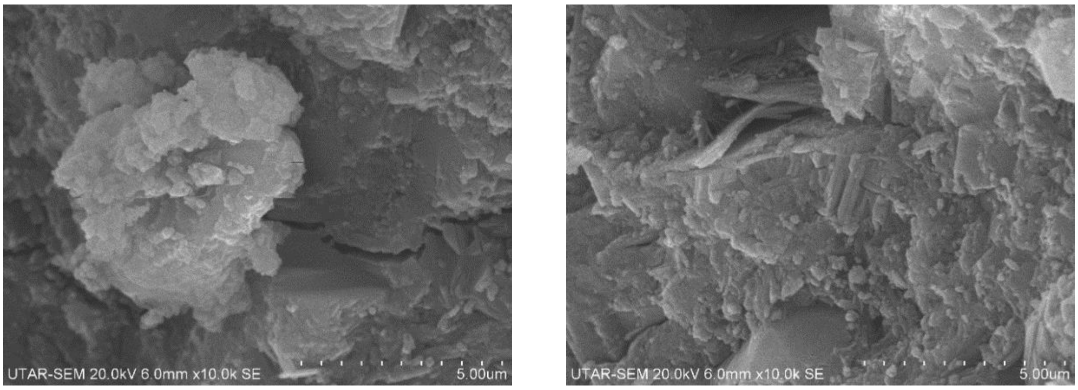
10k ppm-95% OPC@1hour



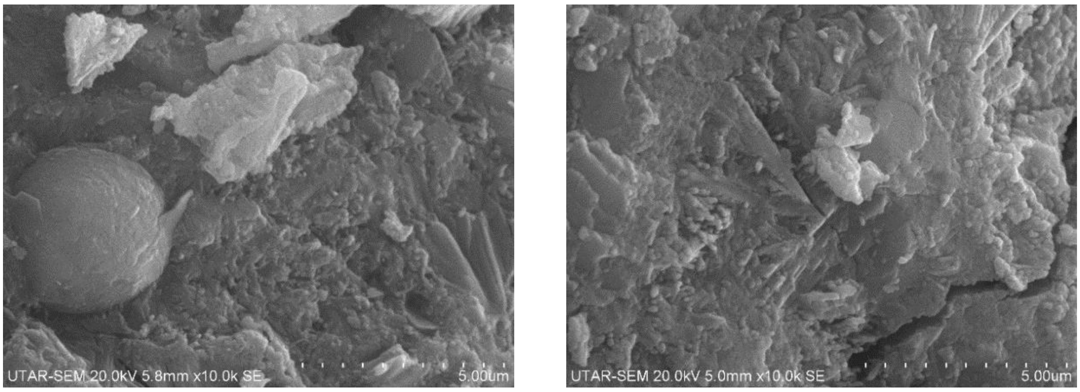
10k ppm-95% OPC@1day



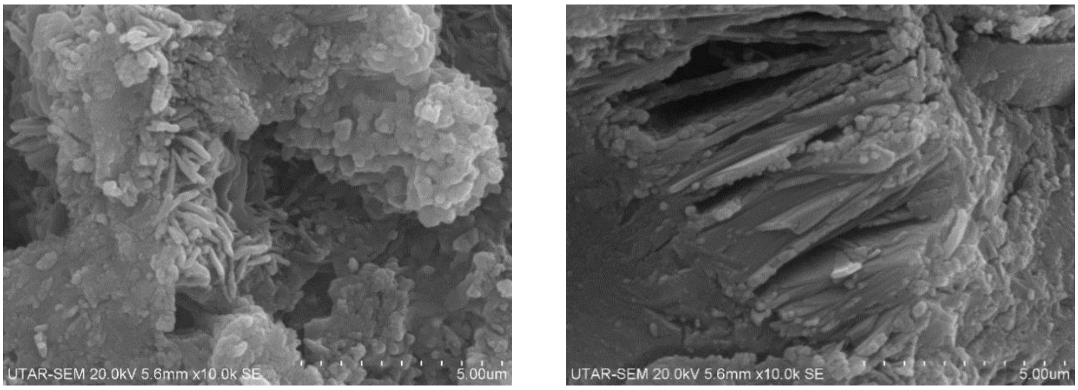
10k ppm-95% OPC@7day



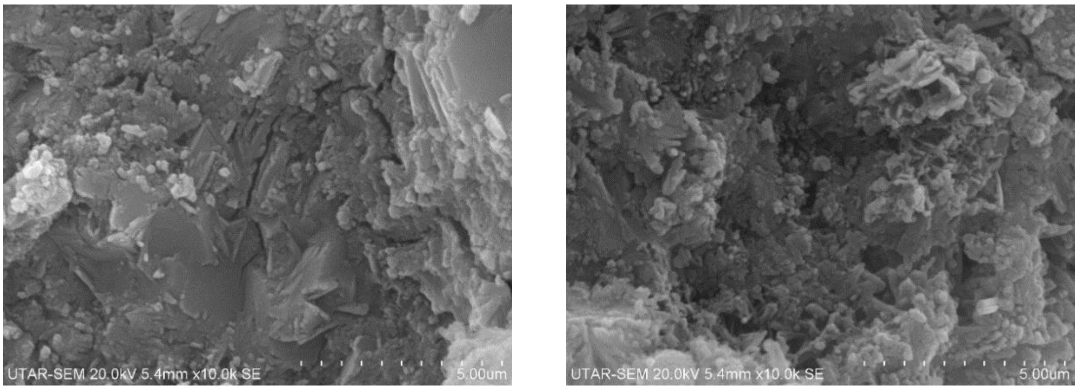
10k ppm-95% OPC@28day



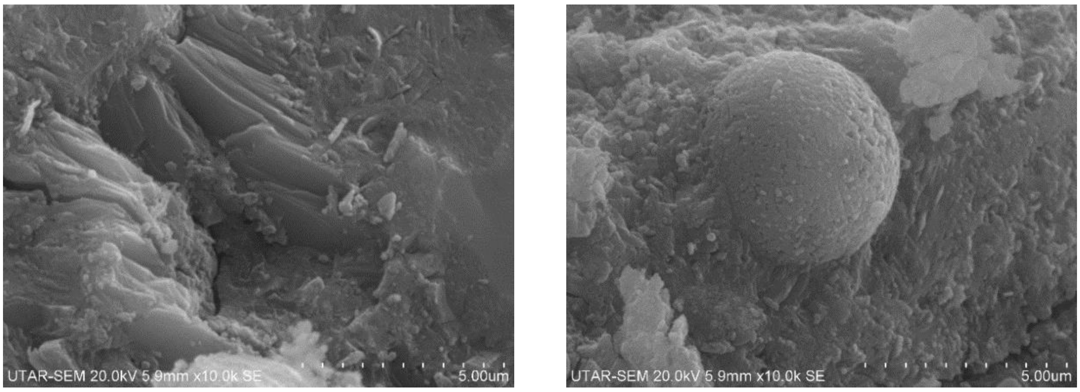
30k ppm-95% OPC@1hour



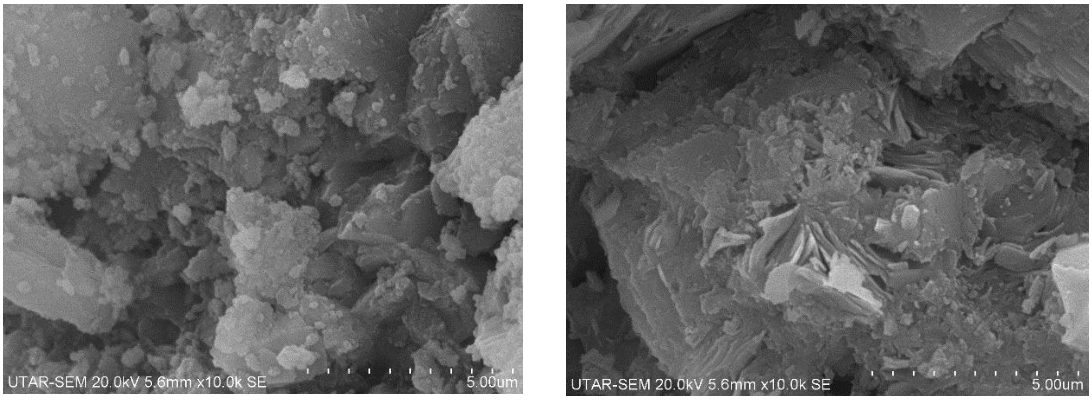
30k ppm-95% OPC@1day



30k ppm-95% OPC@7day



30k ppm-95% OPC@28day



Appendix H : Energy Dispersive X-ray Spectroscopy (EDX) Data

Sample	Duration	Calcium			Oxygen			Silicon			Chromium		
		1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
10k ppm Cr - 100% OPC	1h	63.93	58.21	60.77	13.56	17.97	15.75	12.13	12.29	12.95	1.07	1.06	0.91
	1d	56.25	64.90	67.90	17.74	14.09	10.95	13.31	11.71	11.34	1.17	1.01	1.21
	7d	61.01	53.96	58.50	14.40	17.53	18.79	13.53	15.07	14.16	1.34	0.94	1.18
	28d	61.24	65.04	65.24	18.31	16.03	15.50	14.16	13.13	13.53	1.04	0.97	1.00
30k ppm Cr - 100% OPC	1h	58.65	57.88	62.31	18.26	19.21	13.96	13.04	13.24	11.81	1.74	1.85	1.85
	1d	59.00	56.86	62.08	16.50	22.37	15.38	12.64	10.51	11.91	1.75	1.15	2.37
	7d	55.14	58.90	61.67	20.89	18.60	13.60	12.55	11.42	13.76	1.53	1.82	2.05
	28d	74.97	84.46	74.97	9.20	3.76	9.20	10.50	6.23	10.50	0.91	1.09	0.91
10k ppm Cr - 95% OPC 5% RHA	1h	63.92	65.58	63.02	12.95	12.53	13.55	15.45	13.61	14.55	0.75	1.44	0.95
	1d	43.08	30.84	37.42	19.09	23.37	18.92	27.62	34.50	30.95	0.59	0.91	1.07
	7d	59.04	60.21	58.75	18.30	17.37	18.40	16.19	14.71	16.42	0.70	1.12	0.72
	28d	59.25	54.51	57.76	17.47	19.52	17.67	15.57	18.87	16.82	0.74	0.66	1.00
30k ppm Cr - 95% OPC 5% RHA	1h	66.77	67.29	62.60	14.87	14.64	17.09	11.90	8.45	9.47	0.47	1.04	1.56
	1d	63.12	57.09	64.86	10.56	13.60	12.51	14.96	17.92	12.04	2.37	2.56	2.28
	7d	63.52	60.51	59.22	12.42	16.14	13.99	14.36	12.30	14.98	1.74	1.78	2.12
	28d	59.62	64.44	56.24	14.44	12.53	19.43	11.35	13.36	14.23	1.44	0.76	0.55
0 ppm Cr - 100% OPC	1h	70.96	63.58	60.89	10.94	16.89	17.99	12.20	13.07	13.85			
	1d	67.33	68.41	67.32	12.44	13.85	12.34	13.86	11.90	13.99			
	7d	64.14	63.40	60.93	17.38	16.13	16.85	12.86	13.46	15.42			
	28d	68.64	63.39	62.22	11.20	14.78	16.27	13.70	14.85	14.29			
0 ppm Cr - 95% OPC 5% RHA	1h	56.71	52.88	52.55	22.24	23.47	24.44	13.86	16.61	13.85			
	1d	73.40	73.06	69.99	8.06	8.25	9.92	12.74	13.13	13.06			
	7d	72.71	74.87	75.51	8.86	8.55	7.73	12.61	11.89	12.16			
	28d	81.92	66.73	2.46	9.14	7.66	24.36	6.64	7.59	1.30			

Appendix I: Material Safety Data Sheet