LEACHABILITY OF NICKEL IN CEMENT WITH RICE HUSK ASH (RHA) USING WHOLE BLOCK LEACHING

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

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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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APPROVAL FOR SUBMISSION

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Specially dedicated to
my beloved grandmother, mother and father

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ABSTRACT

Nickel is a common heavy metal used in various electroplating and alloying industries and is present in the wastes they produced. There is no promising way to treat those waste nickel till now. Stabilization/ solidification (S/S) has been proposed be a good way to treat them. The aim of this research is to investigate the effectiveness of S/S of nickel in a cement-based system through Whole Block Leaching (WBL) test. In this study, ordinary Portland cement (OPC) was used as the primary binder and Rice Husk Ash (RHA) as a secondary binder with doping concentration of 10 000 ppm and 30 000 ppm of nickel ions. Acetic acid was used to simulate the landfill scenario in leachability tests for 1 hour, 4 hours, 7 hours, 14 hours, 1 day, 4 days, 7 days, 14 days and 28 days. The concentration of nickel and calcium in leachate was determined by ICP-OES. The mineral phase presence in cement block was identified through XRD and their morphology was observed through SEM. Furthermore, the pH of leachate was measured and related to the leachability of nickel in cement. Results showed that after 4 days of leaching time, the concentration of nickel leached was almost constant to 0.034 ppm for using pure OPC only; whereas 0.211 ppm for 5% RHA replacement. The calcium leached was below 1570 ppm after 28 days. Results shown that the leachability of nickel strongly depended on the pH of leachate. The leachability of nickel was high at low leachate's pH. This reveals that nickel hydroxide, $Ni(OH)_2$ may be formed in cement. XRD also indicates the presence of calcium hydroxide, $Ca(OH)_2$ in cement which formed during hydration reaction. Lastly, SEM has shown the increase of cement block porosity as the contact time increase. As a conclusion, the results proved that the S/S method can be one of the promising was to treat waste nickel produced in various industries.

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LIST OF SYMBOLS / ABBREVIATIONS

C_o	Initial concentration, mol/L or M
c/w	Binder-to-waste Ratio
K	Equilibrium constant
ppm	Part per million
w/b	Water-to-binder Ratio

BRC	Belite Rich Cement
BSE	Backscattering Electron
CBL	Crushed Block Leaching
CH	Calcium Hydroxide
CSH	Calcium Silicate Hydrate
EDX	Energy Dispersive X-ray
EXAFS	Extended X-ray Absorption Fine Structure
FAAS	Flame Atomic Absorption Spectroscopy
GGBS	Ground Granulated Blast Furnace Slag
HCP	Hardened Cement Paste
ICP-AES	Inductively Couple Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Couple Plasma-Mass Spectroscopy
ICP-OES	Inductively Couple Plasma-Optical Emission Spectroscopy
LDH	Layered Double Hydroxide
LFAS	Lime Fly Ash Sand
OPA	Oil Palm Ash
OPC	Ordinary Portland Cement
OWC	Oil Well Cement
PPC	Portland Pozzolana Cement
RHA	Rice Husk Ash
SEM	Scanning Electron Microscopy

SCE	Sequential Chemical Extraction
S/S	Stabilization/ solidification
TCLP	Toxicity Characteristic Leaching Procedure
UCS	Unconfined Compressive Strength
WBL	Whole Block Leaching
XAS	X-ray Absorption Spectroscopy
XRD	X-ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background

The presence of heavy metals in the environment is a serious environmental issue concerning both developing and developed countries. The amount of heavy metals such as Ni, Cr, Cu, Zn and Pb in the environment has soared substantially due to the increased of heavily-duty industries all over the world. Every year, various industrial activities such as mining and industrial smelting, pigment and paint, electroplating and metallurgical processes have released few thousand tons of these hazardous pollutants into the environment. The presence of heavy metals in the environment will definitely leads to air, land and aquatic pollutions. Excessive of heavy metals not only causing the acute health effects such as heavy metal poisoning, yet, chronologically, they may accumulate in the environment and make the ecosystem to be inhabitable for the future generation. Therefore, there must be a way to manage the disposal of heavy metal to ensure a sustainable growth of industrial development, at the same time maintain the health of the ecosystem.

In this study, nickel was chosen as the targeting heavy metal as it is one of the noxious agent used in many industries which can cause severe health problem as well as environmental pollution. As presented in U.S. Environmental Protection Agency’s Toxics Release Inventory (USEPA, 2015), the amount of nickel and nickel compound that have been released in year 2013 is 6 million pounds and 26 million pounds respectively. If all the nickel and nickel compounds are not being treated and dumped directly into the environment, no doubt, such amount of hazardous waste will cause inconceivable consequences on the entire ecosystem. Hence, the waste nickel should be properly disposed to minimize the amount of nickel that could enter into the environment.

There are several ways to dispose nickel such as neutralization, precipitation, redox reaction, landfill, incineration and stabilization/ solidification (Gilbert and Wendell, 2008). Each of these techniques are applying different principles and mechanisms, nevertheless the main goal is just to reduce the toxicity and mobility of nickel. In this study, the focus is on the stabilization/solidification (S/S) of nickel. S/S method is a technique that used to chemically inactivate the toxicity of nickel (i.e. stabilization) and physically entrap the nickel in a cementitious matrix (i.e. solidification).

1.2 Stabilization/ Solidification (S/S)

Stabilization/ solidification (S/S) is one of the crucial and increasingly attractive method used to treat discharged waste nickel before disposal. Solidification is a technique use to entrap the hazardous heavy metal within a monolith. This technique doesn’t necessarily require a chemical interaction between binder and wastes as the wastes are mechanically bonded within the cementitious matrix. The binder materials used to construct the solid matrix can be cement, clay, pozzolans as well as polymer (Hytiris, et al., 2015). As the wastes are solidified into monolithic form, the total surface area that exposed to leaching or extracting fluid reduced, thus keep the heavy metals from contacting the extracting fluid (Patel and Pandey, 2011). Not to mention that, the solidified waste is much easier for handling and transporting as compared to liquid or sludge waste.

Stabilization is a chemical treatment that mix additive with waste to bind the unstable hazardous waste, hence render its solubility and mobility so that it can be converted into a chemically inert or more stable form. The cement-based stabilization/ solidification is particularly effective in constraining the heavy metal’s mobility due to high pH of cement and thus greatly reduce the potential leaching of heavy metal from the cement (Spellman, 2010). During S/S, the nickel may react with the hydrated cement system in several ways or mechanisms such as precipitation, ion-exchange, adsorption, surface complexation, chemisorption, micro-encapsulation as well as passivation. Through the S/S method, the waste nickel discharged from industries can be prevented from entering the environment, hence reduce environmental pollutions. Besides, since cement is used in S/S technique as the primary binder, it is also a cost-effective method as the high strength end product may reuse as a potential construction material.

1.3 Cement

Cement plays a vital roles in the S/S of nickel because it acts as a primary binder to bind and restrict the mobility of nickel ions in the matrix. In the subsequence section, the types of cement, the raw materials, the processing steps and composition of cement will be described briefly. Then, the chemical reactions involve during hydration reaction will be explained. Lastly, the overview about the partial replacement of cement with rice hush ash (RHA) is discussed as well.

1.3.1 Types of Cement

The primary binder for S/S method is cement. Cement can be classified into several types, such as Ordinary Portland Cement (OPC), Portland Pozzolana Cement (PPC), Blast Furnace Slag Cement, Oil Well Cement (OWC) and so on. The various types of cement are classified based on the proportion of basic compounds in cement that is altered by using different raw materials and each of them are having unique characteristics. Among these, OPC was chosen as the binder in this study as it is the well-known or most common type of building material. It is widely used in many construction fields since it meets all the necessary physical and chemical requirements. Portland cement also known as hydraulic cement as it is not only hardens when it reacts with water but also develops water-resistance characteristic (Gambhir, 2013).

1.3.2 Raw Materials used for OPC Production

OPC usually made up from two major types of ingredients which are calcareous and argillaceous materials (Gupta, 2013). Calcareous materials are materials that contain a portion or more of calcium carbonate $CaCO_3$, for instance limestone, chalk and marl. On the other hand, argillaceous materials refer to minerals that consist clay-like component such as clay, shale and slate. Besides, there is also a small quantity of other ingredients such as iron ore or fly ash. By monitoring the proportion between these materials, the chemical combination of calcium, iron, silicon and, aluminium, magnesium and other elements can be well-controlled.

1.3.3 Manufacturing Process of OPC

Dry method is one of the common method used to produce OPC (Portland Cement Association, 2015). Firstly, the raw materials such as limestone, clay and other ingredients are crushed into a smaller size using hammer mills. These crushed rock is then homogenously mixed with iron ore or fly ash to form the raw meal or slurry. The Table 1.1 shows the composition of oxides present in raw meal.

Table 1.1: Oxides content in raw meal

Oxides	Percent Content (%)
CaO	60 – 65
SiO_2	17 – 25
Al_2O_3	3.5 – 9
Fe_2O_3	0.5 – 6.0
MgO	0.5 – 4.0
Alkalies (K_2O, Na_2O)	0.5 – 1.3
SO_3	1.0 - 2.0

Source: (Gambhir, 2013)

The raw meal is then sent to a rotary kiln. In rotary kiln, with blast of flame, the oxides will interact with each other to form clinker minerals when they are heated to high temperature. These compounds in clinker minerals are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). The Table 1.2 shows the proportion of four compounds in clinker.

Table 1.2: Clinker Minerals Content in OPC

Clinker Mineral	**Chemical Formula**	**Percent Content (%)**
C_3S	$3CaO·SiO_2$	25-50
C_2S	$2CaO·SiO_2$	20-45
C_3A	$3CaO·Al_2O_3$	5-12
C_4AF	$4CaO·Al_2O_3·Fe_2O_3$	6-12

Source: (Gambhir M. L., 2013)

The hot grey clinker balls, with the size of marbles are being cooled down by series of cooling process, followed by grinding into powder forms. Finally, these clinker powder mixed with gypsum, $CaSO_4$, which helps to regulate the setting in cement and improve soundness of cement, and some possible additive to form the final product of cement. The Figure 1.1 gives a clearer view about the manufacturing process.

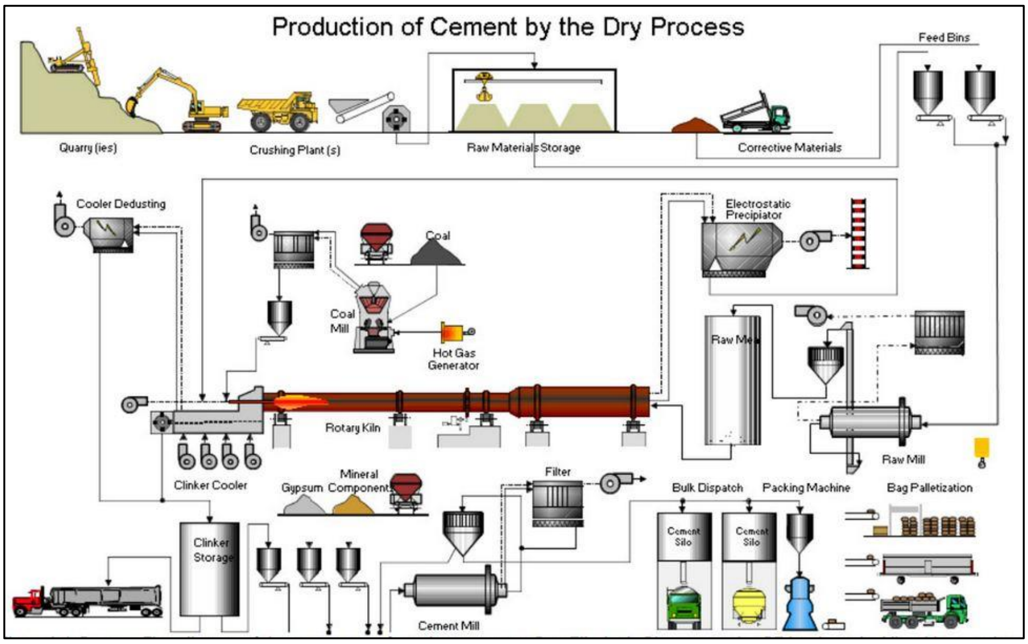


Figure 1.1: The Manufacturing Process of OPC

Source: (Afsar, 2012)

1.3.4 Hydration of Cement

Hydration of cement is a chemical process whereby the dry cement is mixed with water to form hard cement paste. The Figure 1.2 shows the chronological changes of cement's paste structure as five cement particles undergo hydration reaction.

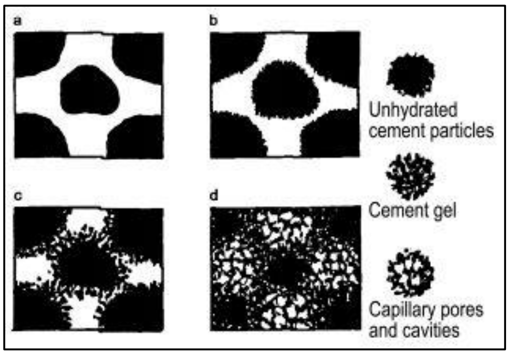


Figure 1.2: Structure of cement paste. a) Immediately after mixing; b) After a few minutes; c) Upon setting; d) After few months

Source: (Janz and Johansson, 2002)

During hydration process, among the four clinker minerals, two of the silicates which are C_3S and C_2S will form the same products which are calcium silicate hydrate (CSH), and calcium hydroxide (CH), $Ca(OH)_2$. Comparing C_3S and C_2S, C_3S has faster rate of reaction together with higher heat evolution which develops early strength. On the contrary, C_2S has slower rate of reaction but it provides much of the ultimate strength and greater resistance towards chemical attack (Mehta and Monteiro, 2014). In short, both of these silicates will give the overall hardening characteristic. The hydration reaction of C_3S and C_2S may be represented as:

$$2\ C_3S + 6\ H \rightarrow C_3S_2H_3 + 3\ CH \tag{1.1}$$

$$2\ C_2S + 4\ H \rightarrow C_3S_2H_3 + CH \tag{1.2}$$

where

C = Calcium oxide, CaO

H = Water, H_2O

S = Silica, SiO_2

$Ca(OH)_2$ produced during the formation of CSH is soluble in water and will leach out from cement to form porous in cement. Besides, C_3A will also react with water to form calcium aluminate hydrate (CAH), with even faster rate of reaction compared to the formation of CSH. Due to the fast rate of reaction, stiffening (i.e. loss of consistency) and setting (i.e. solidification) will happen in the cement paste (Mehta and Monteiro, 2014). Thus, gypsum, $CaSO_4$ is added to retard the fast hydration reaction of C_3A. The formation of CAH can be represented as

$$C_3A + 6\ H \rightarrow C_3AH_6 \tag{1.3}$$

where
A = Alumina, Al_2O_3
C = Calcium oxide, CaO
H = Water, H_2O

In a solution of gypsum and alkalies, the presence of sulphate ions contributed by gypsum and aluminate ions in the solution, will cause the precipitation of crystalline product called calcium aluminate trisulphate hydrate ($\mathrm{C_6A\bar{S}_3H_{32}}$) or the calcium aluminate monosulphate hydrate ($\mathrm{C_4A\bar{S}H_{18}}$) (Mehta and Monteiro, 2014). If the solution is saturated with calcium and hydroxyl ions, the former will form needle like structure called ettringite. The chemical reactions for the formation of ettringite and monosulphate are shown below.

Ettringite

$$[\mathrm{AlO_4}]^- + 3[\mathrm{SO_4}]^{2-} + 6[\mathrm{Ca}]^{2+} + \mathrm{aq.} \rightarrow \mathrm{C_6A\bar{S}_3H_{32}} \tag{1.4}$$

Monosulphate

$$[\mathrm{AlO_4}]^- + [\mathrm{SO_4}]^{2-} + 4[\mathrm{Ca}]^{2+} + \mathrm{aq.} \rightarrow \mathrm{C_4A\bar{S}H_{18}} \tag{1.5}$$

Because of the alkalinity of $Ca(OH)_2$, high pH in the cement can be maintained. This high pH of cement effectively confined the nickel in the insoluble form of hydroxide and carbonate salt within the cement. Undoubtedly, the effect of the nickel on the quality of cement must be studied as well because the properties and amount of additional materials that added into cement serve as a factor that could affect the porosity and the compressive strength of cement (Mehta and Monteiro, 2014). The treated cement must fulfil the basic requirement as specified by ASTM C 150, Standard Specification for Portland Cement.

1.4 Doped with Rice Husk Ash (RHA)

Besides using 100 % of OPC as binder, rice husk ash can also be used to partially replaced cement as secondary binder. As mention previously, the silica (SiO_2) in cement will combine with lime (CaO) in the presence of water to form calcium silicate hydrate (CSH), which contribute to the high strength characteristic of cement. However, as shown in Table 1.1, the amount of silica present in cement is comparative less than lime. Thus, there will be an excess of lime in cement once the reaction is completed. In order to use up the surplus lime, many of the cement manufacturers have utilize numerous types of pozzolonic materials such as fly ash, cement kiln dust, rice husk ash and etc. as the source of silica to react with the excess of lime to form more CSH, thus increase the compressive strength of cement.

Rice husk ash is chosen as the replacement binder because it is easily available, it provides the necessary source of silica and is a better way to dispose the useless rice husk instead of burning it off which causing environment pollution. Rice husk is the coating of paddy grain that removed from rice grain and is containing mainly of cellulose and lignin group with almost 20 % silica (Umeda, Kondoh and Michiura, 2007).

Figure 1.3: Rice Husk

Source: (KMEC, 2013)

Figure 1.4: Rice Husk Ash

Source: (WordPress, 2008)

Upon controlled burning, the cellulose and lignin of rice husk are lost, left behind the non-crystalline or amorphous silica in ash. This highly reactive amorphous silica formed in rice husk ash will react rapidly with calcium hydroxide, $Ca(OH)_2$ to form a secondary CSH linkage which contribute to the decrease of porosity and increase in compressive strength of cement (Chauhan and Kumar, 2013). Initially, nickel that doped into cement may somehow affect the physical properties of cement. However, due to the enhancement of rice hush ash on the cement's structural properties, it is believed that waste nickel can be safely entrapped in cementitious matrix without the loss of necessary compressive strength.

1.5 Hazardous of Nickel

In the following section, the usefulness of nickel will be discussed and this explains why the presence of nickel in the environment is unavoidable. Next, the sources and exposure routes of waste nickel, together with the consequences of hazardous nickel on both human and environment will be emphasized. From here, it can be seen that the study on the leachability of nickel from cement plays a vital roles in controlling the concentration of nickel presence in the ecosystem below the acceptable limit.

1.5.1 Useful of Nickel

Pure nickel is a hard metal with a silvery white colour and is having good conductivity of both heat and electricity. Nickel is very favour in combining with other metals such as copper, chromium, iron and zinc to form alloys. These nickel-containing alloys are characterized with good strength, ductility and resistance to heat and corrosion. Thus, they are very useful in the making of jewellery, coins and heat exchanger. In U.S., nearly half (46%) of the nickel was used in the nickel steel production, 34 % for nonferrous alloys and superalloys, 14% for electroplating and 6 % for other uses (Kuck, 2012). Nickel do combine with one or more types of element such as sulphur and oxygen to form nickel compound which can be used for nickel plating and catalyst. Both nickel and nickel compound are odourless and tasteless, yet it appears in different colour for different types of nickel compound. For example, the nickel compound used in this study is nickel nitrate, $Ni(NO_3)_2$ which appears in greenish-blue colour.

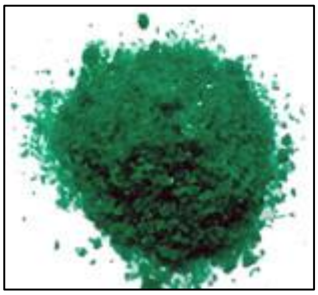


Figure 1.5: Nickel Nitrate

Source: (Minar, 2013)

1.5.2 Sources of Nickel

There are several ways of waste nickel to enter the environment. Since nickel is so versatile in many industries, the release or discharge of waste nickel into environment is unavoidable. Waste nickel is released into the atmosphere through the coal, fuel oil and diesel oil-burning power plant. Besides, the incineration of trash, sewage and miscellaneous waste also contribute to the concentration of nickel in ambient air (Rose and Cohrssen, 2011). Nickel that released through the stack of power plant will attached to the dust and water vapour in atmosphere that settle to the ground. These settled nickel will strongly attaches to particles containing manganese or iron and finally ends up in soil or sediment (ATSDR, 2005). These particles may also be washed off by rain into river and underground water. Meanwhile, nickel also released through the discharge of industrial wastewater especially from metal smelters.

1.5.3 Exposure Route to Nickel

Nickel in the environment can enter human body through breathing air, eating food, drinking water or smoking tobacco containing waste nickel (Anchorpoint Safety Inc., 2013). The nickel concentration in air is vary considerably but high amount of nickel was found from highly industrialized area. Occupational exposure through inhalation of dust or fumes is the main route and in work-related place has higher exposure of nickel compare to work-unrelated place. Due to the discharge of nickel-containing-wastewater into river, people may exposed to nickel through drinking water. Besides, dermal contact of water, soil or sediment containing waste nickel also contribute to the uptake of nickel.

1.5.4 Effect of Nickel on Health

Human expose to highly nickel-polluted area will cause several pathological effect. Most of the pathogenic effect of nickel are due to the interference with the metabolism of essential metals such as Ca(II), Zn(II) or Mg(II) (Cempel and Nikel, 2006). The most common harmful effect of exposure to nickel in human body is irritation. Approximate one-fifth of population are sensitive to nickel and cause allergic reaction as they touch those soil containing nickel. This dermatitis also known as “nickel itch” (ATSDR, 2005). High skin exposure of nickel may first cause skin eruption and followed by skin ulceration. Furthermore, there are few people who are hyper-sensitized to nickel will cause asthma attack. More seriously, as stated in 13th Report on Carcinogens (NTP, 2014) by U.S. Department of Health and Human Services Secretary, with sufficient studies on human carcinogenicity, nickel and certain nickel compounds are classified as reasonably anticipated to be a human carcinogen. The worker who works in nickel processing plant can develop chronic bronchitis, lung and nasal sinus cancer if they have breathed in nickel dust over a long period of time. Based on animal studies, high intake of nickel will affect the blood, kidney, stomach and immune system of rats and mice. Moreover, birth defects and reproduction problems also found in rats or mice that consume very high amount of nickel.

1.5.5 Effect of Nickel on Environment

Nickel is not only affect the human health but also shows some adverse effects on the environment. Nickel is uptake by plant through passive diffusion and active transport. Small amount of nickel is essential for plant metabolism, yet excessive amount of nickel is toxic to most of the plant. High concentration of nickel in soil or sediment will affect or damage the growth of plants by retarding seed sprouting. These nickel affects the digestion and mobilization of nutrients or food that reserve for seed germination (Ahmad and Ashraf, 2011). It also inhibits photosynthesis and nutrients absorption of roots. Additionally, the excess nickel also inhibit the growth of shoot and root which affects the branching development during vegetative stages. The stress of nickel reduce leaf blade area and leaf density. Ultimately, the overall yield of crops decrease due to poor plant development associated with the inhibition of supply of nutrient to reproductive parts (Chen, Huang and Liu, 2009). Besides, the surface water that containing high amount of nickel will reduce the growth rate of algae and thus affect the aquatic life.

1.6 Problem Statement

Nickel, as mentioned, is so useful in industry field, yet the adverse effect brought by discharge of waste nickel is noticeable as well. One of the proposed solution to solve this problem is to confine the waste nickel well in a solidified matrix through the stabilization/solidification method. However, there are few issues need to be considered when hazardous nickel is enclosed in the matrix.

First and foremost is the quantity of nickel that can be confined or trapped within a specific volume of cement without being leached out from the cement matrix. If the amount of nickel in cement is too much, the amount of binder may not be sufficient to entrap all the waste nickel, hence, the unbounded nickel may be released into the environment.

Leachability of nickel under different environmental conditions such as erosion caused by acid rain or acidic leachate when the solid matrix is disposed in landfill need to be concerned as well. As the cement block is in contact with acidic fluid, the effectiveness of S/S may be affected. Acid may dissolve the calcium on the surface or even deeper into the cement matrix. As a consequence, the nickel confined in the inner part of cement matrix may be released out from the cement. Thus, it is important to ensure that the concentration of nickel that leached out from the cement must below the acceptable concentration for discharge leachate under Environmental Quality Regulation.

Lastly, in most of the researches, they had studied the effect of replacing OPC with fly ash or bottom ash. Nevertheless, the research on the effect of RHA as a secondary binder in S/S method is not well-known. Some issues may arise when some portions of OPC have been replaced with RHA. Although the addition of RHA may increase the strength of cement contributed by its pozzolanic effect, yet, the physical properties of RHA may affect the effectiveness of S/S.

1.7 Aims and Objectives

The aim of this study is to examine the effectiveness of the stabilization/solidification of nickel in a cement-based system, thereby ensuring that solidification / stabilization is one of the promising way to dispose wasted nickel that discharged from heavily-duty industries. The main objectives of this research are:

- To study the factors affecting the leachability of nickel from cement-based system using Whole Block Leaching (WBL) test on nickel.
- To investigate the effect of different nickel doping concentration on its leachability.
- To clarify the relationship between pH of leachate and leaching time.
- To identify the relationship between pH of leachate with nickel and calcium leachability.
- To examine the effect of contact time on the leachability of nickel and calcium.
- To identify the mineral phases presence in cement block.
- To observe the morphology of cement block after WBL test.
- To study the effect of RHA on the leachability of nickel.

CHAPTER 2

LITERATURE REVIEW

2.1 Leaching

Although the high pH of cement is believed to reduce the mobility of nickel, somehow trace amount of the waste nickel may still release from cement through leaching. Thus, the leaching test is still need to be performed to ensure the amount of nickel that leached from cement doesn’t exceed the environmental limit after a long period of time. According to the Environmental Quality (Control of Pollution From Solid Waste Transfer Station and Landfill) Regulation 2009 which attached as Appendix B, the acceptable conditions for discharge of leachate for nickel is 0.20 mg/L.

2.1.1 Definition of Leaching

Leaching is also known as solid-liquid extraction where the solute contained in a solid matrix is removed by using a particular leachant (Dutta, 2009). Leachate is referring to the leachant that contains contaminants that leached from cement. In this case, nickel is the solute that contained in the solid matrix of cement and the leachant used is acetic acid. Under acidic condition, some constituents of cement and nickel may dissolve and the nickel might migrate from the internal cementitious matrix to external cement’s surface and finally enter the environment.

There are several factors that decide the amount of nickel leached into the leachate such as permeability and porosity of cement, the surface area of solid, the types and pH of leachant, the contact time, the solubility of nickel at certain pH and also the concentration of nickel initially presence in cement (LaGrega, Buckingham and Evans, 2001). In this study, some of the parameters will held constant while some of that will vary accordingly to study how those parameters affects the leachability of nickel from cement.

2.1.2 Types of Leaching Test

There are various types of leaching test that can be used to determine the leachability of heavy metals from cement. Leachability test can be categorized into two main groups which are extraction test (a.k.a static test) and dynamic test. For single extraction test, the leachant is contacting the solid matrix for a period of time without replacement or addition of leachant (Bone et al, 2004). The Figure 2.1 shows the schematic diagram of four main groups of extraction test.

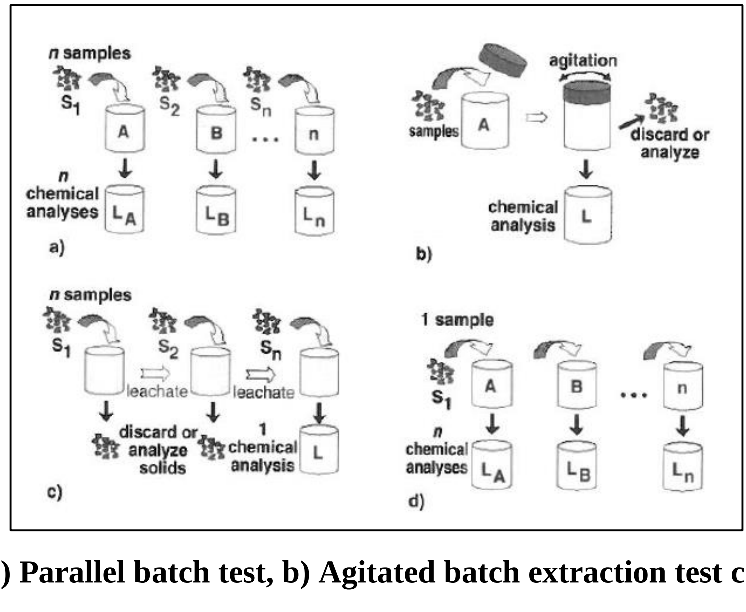


Figure 2.1: a) Parallel batch test, b) Agitated batch extraction test c) Concentration build-up test, d) Sequential chemical extraction test

Source: (Spence and Shi, 2005)

On the contrary, for dynamic test, the leachant is renewed continuously or intermittently to maintain high concentration gradient between the samples and leachant. The Figure 2.2 shows the schematic diagram of four main group of dynamic tests. Among the four tests, the tank leaching test can be considered as semi-dynamic test because the leachant are replaced after a certain period of time.

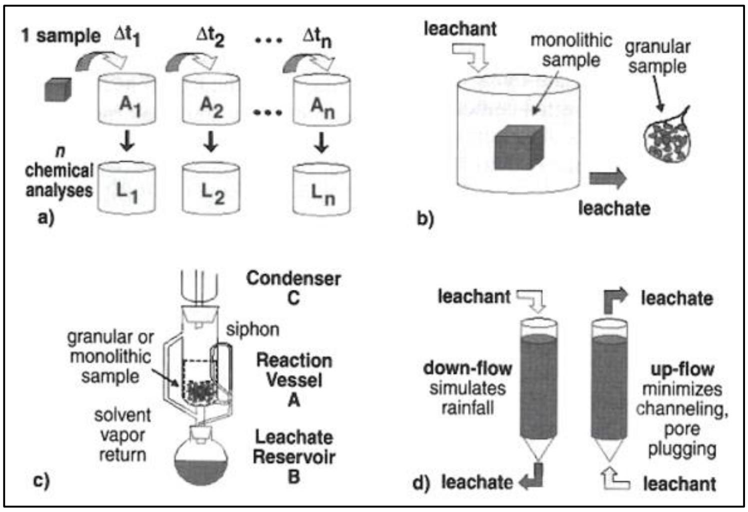


Figure 2.2: a) Tank leaching test, b) Flow around test, c) Soxhlet test, d) Flow through column test

Source: (Spence and Shi, 2005)

Whole block leaching (WBL) test and crushed block leaching (CBL) test are the examples of single extraction test in which their different is in term of the shape/ structure of the sample. WBL is aimed to simulate the short-term leaching condition of the sample (Yin, Shaaban and Mahmud, 2007). Cement that contains heavy metals is casted into a specified size (normally is cube shape) and placed into a leachant for a period of time. The leachant or extracting liquid can be deionized water, acetic acid or sulphuric acid depending on the objective of study. Since the cement cube is placed in a definite volume of leachant without any addition or replacement of leachant, therefore it can be considered as non-agitated batch extraction test. Not to mention that the WBL can also be considered as tank leaching test when the fresh leachant is replaced periodically to ensure a significant diffusive driving force between leachant and the solid matrix.

Crushed block leaching is aimed to simulate the worst-case scenario when the cement is being grinded, smashed, hit or crushed into smaller pieces during or after disposal (Zain, et al., 2004). In CBL test, instead of making the cement block intact, it is being crushed into smaller size and immersed in particular leachant. As compared to WBL, the contact surface area of the sample for CBL is significantly larger than WBL. Thus, it may having a higher chance for nickel to be leached from cement. CBL is also analogous to toxicity characteristic leaching procedure (TCLP) which adopted by U.S. Environmental Protection Agency. Normally for TCLP, the solidified samples are air-cured or water-cured for a specific period of time before being crushed into smaller pieces to allow the diffusion of water molecule through the channel before it undergoes hydration reaction with cementitious material to form CSH, hence enhance the strength development in cement (Yin, Wan Ali and Lim, 2008).

2.2 Factors Affecting the Leachability of Nickel

Over the years, many researchers have worked out different experiments to study the effects of various parameters or factors on the leachability of hazardous waste from cementitious matrix. Those factors including the types of binder used, the types of waste which containing nickel, the water to binder ratio, the binder to waste ratio, the different types of leachability test being performed including the structure or shape of specimen, the types of leachant used, the pH of leachant as well as the contact time between leachant and solidified samples.

2.2.1 Types of Cement and Waste Used and Their Relative Proportion

There are many types of cement, as discussed above, which can be used as the binder to solidify/ stabilize the hazardous waste nickel. Among them, Ordinary Portland Cement (OPC) is the most common type of binder that used by most of the researchers to study the leachability of nickel from cement. Besides, some additive or pozzolanic materials were also added to OPC to study their effects as well. There were also few researchers used different binders other than OPC to solidify the samples.

In most of the researches, the source of waste nickel that the researchers used were not produce analytically in laboratory, instead, they utilized the real waste which containing nickel, directly from real industries such as wastewater from electroplating industry. In order to review clearly the types of cement used corresponding to the types of waste they actually added into the cement, this section is divide into three sub-sections which are utilize OPC alone as binder, OPC with other additives as binder and binders other than OPC.

2.2.1.1 OPC as Binder

OPC contains mostly lime (CaO) and silica (SiO_2) is believed to have high performance in controlling the leachability of waste nickel from cement. In Malaysia, there are few researchers used only OPC as binder. Naganathan et al. (2013) studied the leaching behaviour of cementitious slurry made from bottom ash and quarry dust. They utilized OPC as the only binder to stabilize/ solidify bottom ash from industrial waste incineration plant and quarry dust from quarry plant, both containing trace amount of nickel. In their studies, they have varied the ratio of OPC to bottom ash and quarry ash and all the metals that leached out were below the threshold limit. In India, Minocha and his partner (2014) also investigate the solidification/fixation of nickel ions in OPC and they found that the nickel ions will get adsorbed in the cement and formed the insoluble nickel compound. The source of nickel ions that they utilized was the standard solution made from nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$).

Additionally, the OPC can also be used to restrict the mobility of waste nickel present in hazardous sludge from steel plating industry as done by Gupta and Surwade. In their research, up to 80 % of sludge can be stabilized by using only OPC as the binder. Furthermore, Kogbara et al. (2012) also done their studies on leachability of contaminants from soils treated with cement. In the experiment, 3000 mg/kg of each Zn, Ni, Pb, Cu and Cd was purposely added in a sandy soil with 10,000 mg/kg of diesel, and treated with OPC. In their findings, the concentration of Ni satisfied the leaching criteria which further prove the ability of OPC in immobilizing nickel within the cementitious matrix.

2.2.1.2 OPC with Other Additives

Instead of using OPC alone as binder, the OPC can incorporate with other materials as secondary binder to further enhance the leaching behaviour of nickel in cement. As done by Chindaprasirt et al. (2013), they used silica fume and fly ash as secondary binder to partially replace OPC by 10 % and 30 % by weight. The source of nickel was from wastewater from a nickel plating plant. They found that the solidified waste containing silica fume and fly ash was more effective in reducing the leachability as compared OPC alone. As compare between silica fume and fly ash, the silica fume shown a better result in reducing the leachability of nickel. Next, the OPC can also combined with belite rich cement (BRC) which made up from oyster shell, water treatment plant sludge, basic oxygen furnace slag and rice husk ash. Chen et al. (2011) has utilized different weight fraction of BRC and OPC to solidify electroplating sludge which contains several kinds of heavy metals. Almost all metals were found to be totally encapsulated within the blended cement.

Furthermore, Geosta which containing artificial zeolite, chloride and alkali can also act as a secondary stabilizing agent to solidify soil polluted with nickel (II) sulphate hexahydrate ($NiSO_4.6H2O$) with concentration of 2300 mg Ni/ kg soil. Hytiris et al. (2015) found that the optimum chemical efficiency was observed in a mixture of 10 wt% OPC with 1.4 wt% stabilizer. They have realized that zeolite can actually trap heavy metals by ion exchange in the zeolitic structure. Nevertheless, not all the additives that mixed with OPC could enhance the solidification/ stabilization of nickel. Experiment works done by Yin et al. (2007), they have partially replaced OPC with oil palm ash (OPA) to examine the immobilization of nickel hydroxide sludge collected from a chemical manufacturing plant. They found that, with the increased of OPA wt%, the nickel concentration in leachate increased indicates the nickel is more easily leached out from cement. Besides, the strength of cementitious matrix may also reduce due to the lack of calcium ions present in OPA (1.36 wt%) as compare to OPC (34.81 wt%). It is because calcium ions are the key component to form CSH which contribute to the hardening of cement block.

2.2.1.3 Binders Other Than OPC

Besides OPC, there are also other kinds of material that can be used to replace OPC to stabilize/ solidify the waste nickel. Patil and Zodape (2011) used more simple materials such as lime, sand and fly ash from thermal power plant as a binder to entrap the nickel contained in wastewater received from electroplating industry. With the right proportion between lime, sand and fly ash, this admixture can provide a better immobilization of heavy metal as compared to OPC. Kogbara and Al-Tabbaa (2011) also investigate the combination of 20 % hydrated lime with 80 % ground granulated blast furnace slag (GGBS) (lime-slag) for solidification/stabilization treatment of contaminated soil. The soil was spiked with different types of heavy metals including nickel. As compared to slag-cement (i.e. 10 % OPC mixed with 90 % GGBS), the lime-slag has shown a lower leachability of mobile metals such as cadmium, nickel and zinc although OPC was absence in lime-slag.

2.2.2 Effect of Water to Binder Ratio

Apart from binders, water is also an essential component to react with binder to form calcium silicate hydrate (CSH) during the cement hydration process. The amount of water needed is closely related with the amount of binder used to achieve an optimum chemical and physical performance of cementitious matrix. In most of the researches, the water-to-binder (w/b) ratio was fixed throughout the entire experiment and this ratio is depending on to the types of binder that used to solidify waste nickel. For instance, Napia et al. (2013) maintained a constant w/b ratio of 0.4 to ensure the workability of the cement paste.

Yet, there were also few researchers studied the effect of varying w/b ratio on the properties of the cement. One of the research showed that when the w/b ratio decreases, the porosity of the paste decreases as well (Laforest and Duchesne, 2007). In their research, most of the solidified block with 0.3 w/b ratio has shown a lesser amount of metal leached compared to that of 0.4. This indicated that as the w/b ratio decrease, the porosity will decrease, hence increased the retention of metals in the monolithic samples. Besides, there was another researcher who observed a different phenomenon as the w/b ratio increased. Opponent to Laforest and Duchesne, Kogbara et al. (2012) claimed that, the porosity of cement was actually decreased when w/b ratio increased. They observed that the decreased in porosity was due to the improvement of compactability of the cement sample as w/b ratio increased until optimum ratio is met. The more compact the cement sample, the more likely to have lower porosity of cement structure.

On the other hand, the pH of the leachate collected will decrease as the w/b ratio increased (Naganathan, Abdul Razak and Abdul Hamid, 2013). When the w/b ratio increases, the more water added, at the same time, the amount of cement reduce, causing dilution of alkaline substance such as $Ca(OH)_2$, hence reduce the pH of leachate. Finally, high w/b ratio decrease the hardening rate and eventually affect the strength of cement (Yin, Wan Ali and Lim, 2007). It was because the mixture doesn’t provide sufficient amount of CaO to react with the excess of water to sustain the building strength. In short, due to the limited researches on the effect of w/b ratio, the actual consequences on the effectiveness of S/S are not well-known.

2.2.3 Effect of Binder to Waste Ratio

In the S/S method, it is very important to monitor the proportion between binder and waste so that the waste nickel can be completely confined in the solidified matrix with the sufficient amount of binder. If the binder-to-waste (c/w) ratio is too small, the waste nickel may not be bonded strongly in the cementitious matrix and the strength may loss due to the lack of CSH produced. In most of the researches, the quantity of waste, thus the concentration of nickel, was varied to study on how it affects the leachability and mechanical strength of nickel-containing cement block.

In the Patel and Pandey (2012) research, they found that as the proportion of sludge increased (i.e. lower c/w ratio), the compressive strength of the cement block decreased because of the retardation of cement hydration caused by the increasing of waste. Besides, as the c/w ratio decreases, the pH of leachate decreases due to less amount of $Ca(OH)_2$ is produced in the cement during hydration process. Since the leachability of nickel from cement is depends on its solubility at the particular pH of leachate, as the pH dropped, more nickel will be dissolved out from the cement. This statement was agreed by Anastasiadou et al. (2012) which the stabilization rate increased as the c/w ratio increased. They also prove that the strength reduced as the cement loading decreased.

In addition, Chindaprasirt et al. (2013) has varied the plating sludge from 40 % to 60 % by weight of binder mixture comprise of cement and fly ash or silica fume. They found that the nickel concentration measured in leachate was increasing when percentage of sludge increases regardless the types of binder used in the experiments. Again, it showed the reduction of strength as the c/w ratio decreased. Next, from the studies of Hytiris et al. (2015), same phenomenon was observed which the amount of nickel released was lower for 10 % OPC mix design as compared to that of 5 % and 7.5 % mix design. The strength for 10 % OPC mix design was almost three times and four times higher when compared to 5 % and 7.5 % mix design respectively.

Lastly, the research done by Saeedi et al. (2010) has clearly explained the effect of c/w ratio on the leaching behaviour of metals. As they increased the c/w ratio from 0.5 to 1, the amount of metal leached was increased and after that decreased as ratio increase to 5. Considered the fact that, when the cement content decreases, the amount of water required also decreases. As a result, when the c/w ratio approaching 1, it was not only helpless in improving the leaching behaviour but also promote the release of nickel due to presence of excess water content in the mixture. Not to mention that, the increased of nickel released may also due to the lack of cement hydration products utilized to bound the waste materials. As a conclusion, the increase in cement percentage (i.e. c/w ratio) has improve the leachability of nickel and the strength developed in the cementitious matrix.

2.2.4 Effect of Leachability under Different Leaching Condition

As discussed in the previous part, generally there are many types of leachability test that can be used to evaluate the effectiveness of S/S of waste nickel. However, some of the tests are not represent the actual environment conditions and they are not suitable for regulatory purpose due to poor reproducible and long-time of duration (Bone et al., 2004). Besides, some of the tests are difficult to set up and perform, and hence the quality of the tests may be affected. In most of the researches, the leachability test they performed is the toxicity characteristic leaching procedure (TCLP) test. There were also limited number of researchers who tried out other tests such as the whole block leaching (WBL) and tank test. The different type of leaching test do affect the leachability of nickel because each types of leachability test will have the different leaching condition. For instance, the CBL simulate the worse-case scenario in which the condition where nickel may leach out easily from the cement, hence promote the leaching of nickel from cement.

In the studies of Anastasiadou et al. (2012), the TCLP test was performed to determine the leachability of nickel from cementitious matrix. Before the extraction test, the cement cube was cured for 1, 7, 14 and 28 days before being crushed into smaller size. The curing time is needed because water molecules required certain time to diffuse into pores of cementitious matrix to undergo hydration reaction before the formation of CSH. After curing and crushing, the sample was placed in a buffer solution of acetic acid and sodium hydroxide with pH 4.93 and liquid-to-solid ratio of 20. These mixture was shaken for 18 hours. The leachate collected was then tested by Inductively Couple Plasma-Mass Spectrometer (ICP-MS). From the results obtained, it shown that the stabilization rate was increased from the 1st day after solidified and reached maximum after 28 days.

Next, Chindaprasirt et al. (2013) also performed the TCLP test. However, the cement cube was cured in saturated lime water to complete the hydration and pozzolanic reaction. In their test, the curing time was even longer up to 90 days to ensure the cement paste has completed the hydration process and strength development. The leachant used is acetic acid solution with pH of 2.88. Once the sample has contacted with leachant for 18 hours, the leachate was collected and tested with Inductively Couple Plasma-Atomic Emission Spectrometer (ICP-AES). As shown in their results, the longer curing time did enhance the stability of the waste nickel in cement. The compressive strength was also observed to increase with longer curing time.

On top of TCLP, Saeedi et al. (2010) also carried out the sequential chemical extraction (SCE) test and testing on the alkalinity solubility and release as a function of pH to identify the leaching behaviours of the sample. For TCLP, the procedures were similar to the previous studies with curing time of 28 days in wet environment. The SCE test is performed by applying a series of increasingly more aggressive extracting solution successively. After the SCE test, the element can be categorized into five different fractions which are those exchangeable, bound to carbonates, bound to iron and manganese oxide, bound to organic matter and sulphide and residual fraction. The residual fraction is represent the least likely leachable of element and more than two-third of total leachable nickel was fell in this fraction. In their research, they also perform the testing on the alkalinity solubility and release as a function of pH to investigate the leaching characteristics of the cement sample over a wide range of pH value from 2 to 12. As a result, the leachability of metals decrease when the pH increases.

Additionally, there is also researcher who conducted whole block (WBL) and crushed block leaching (CBL) to study the leaching behaviour of nickel from solidified bottom ash and quarry dust (Naganathan, Abdul Razak and Abdul Hamid, 2013). For WBL, the extraction fluid used was deionized water to simulate the neutral precipitation. The leachant was not agitated and renewed after certain intervals up to 126 days. The concentration of nickel in leachate was determined by Inductively Couple Plasma-Optical Emission Spectrometer (ICP-OES). From the WBL test results, all the metals or metal compounds that leached out were below the regulatory limit.

Meanwhile, for CBL test, the method was followed the TCLP method. The cement blocks that have been cured for 28 days were crushed and mixed with acetic acid solution. Besides, they also used deionized water as extraction solution for CBL tests. In both acidic and neutral medium, the metals leached were within the threshold limit.

Lastly, Hytiris et al. (2015) performed the tank test to study the leaching behaviour of contaminated soil with cement and geosta. When performing the tank test, the 100 mm cube was cured for 28 days then the specimen was placed in a tank which filled with distilled water to achieve a liquid-to-solid ratio of 5. This method is almost similar to whole block leaching. The leachant was removed and replaced from time to time giving 128 days of total leaching time. After the leachate was collected, the Flame Atomic Absorption Spectrometer (FAAS) was performed to analyse the metals concentration presence in the leachate. In their findings, all the different mixture of cement and geosta did show a general trend where the amount of nickel leached from the mixture was keep decreasing after a long leaching time.

2.3 Interaction and Immobilization of Nickel in Cement

In the mechanism of solidification/ stabilization process normally involve a combination of encapsulation, precipitation, sorption, ion exchange and bonding. The nickel ions presence in waste may interact with the cementitious materials to form other compounds or phases and thus immobilized in the cementitious matrix. These interactions are initiated as the hydration process start, i.e. when anhydrous cement is mixed with water. During the hydration of cement, the dicalcium silicate (or alite), C_2S and tricalcium silicate (or belite), C_3S will react with water and decomposed to form calcium silica hydrated gel, CSH and calcium hydroxide (or portlandite), $Ca(OH)_2$ (Mehta and Monteiro, 2014).

From the research done by Vespa et al. (2006), they showed that there are two main types of CSH precipitates which are inner CSH and outer CSH. In their experiment, they have doped different concentration of nickel nitrate, $Ni(NO_3)_2$ into Portland cement to produce the sample called Ni-doped hardened cement paste (Ni-doped HCP). The purpose of their research was to examine the Ni uptake by cement in microscopy scale. From what they have done, the inner CSH and outer CSH can be identified through the backscattering electron (BSE) imaging. They found out that there was a bright rims form around the inner CSH phase in Ni-doped HCP whereas the bright rims was absence in non-doped HCP. This results showed that the Ni was accumulated in these Ni-rich region showing the bright rims.

Furthermore, they have investigated the Ni sorption onto hydrated portland cement through the analysis of X-ray Absorption Spectroscopy (XAS). They realized that most Ni(II) ions were mainly entrapped in Ni-Al layered double hydroxide (Ni-Al LDH) phase whereas some Ni(II) ions were precipitated as nickel hydroxides, including α-$Ni(OH)_2$ and β-$Ni(OH)_2$ in the system. In addition, through the results from μ-extended X-ray Absorption Fine Structure (μ-EXAFS) spectroscopy, they further confirmed the existence of Ni-Al LDH at the Ni-rich region in the sample doped with Ni.

In addition, Minocha and Goyal (2014) also found that the nickel added to the cement mortar was get adsorbed in the interstitial phase of cement, thus resulted in a very low leaching of nickel. They agreed that waste nickel will get immobilized through the Ni sorption as they realized some Ni was distributed throughout the CSH gel phase by studying the morphology of cement by using scanning electron microscope (SEM). The nickel was get adsorbed in the matrix and the CSH phase found is denser than cement without nickel loading.

Additionally, they found that nickel ion will precipitate to form insoluble nickel compound. In the research done by Chindaprasirt et al. (2013), they also suggested metals may react with $Ca(OH)_2$ to form insoluble compound in the form of metal hydroxides. The precipitation occurred when $Ca(OH)_2$ dissociated into Ca^{2+} and $2OH^-$ ions under aqueous condition (Yin et al., 2007). The presence of the hydroxyl ions have contribute to the alkalinity of the leachate. At high alkalinity, nickel hydroxide, $Ni(OH)_2$ complex may form through the reaction of Ni^{2+} and OH^- ion. Besides, in this high pH of the hydrated binder system, the nickel hydroxide may be ionized and reprecipitated as amorphous nickel complexes.

Next, the waste nickel can also be immobilized through the ion exchange mechanism. As studied by Aranda and Berenice (2008), the ion exchange process involve the cation exchange with the host cation from a clay soil. For instance, they have reported that large amount of calcium were leached due to the exchange of calcium cation with metal cation on the ion exchanger. In short, during S/S, most Ni are being adsorbed in the cement matrix or precipitated to form insoluble nickel hydroxide. The immobilization of nickel in the cementitious matrix is, on the other hand, due to the alkalinity nature and the buffering capacity contributed by $Ca(OH)_2$ and CSH (Malviya and Chaudhary, 2006).

2.4 pH and Leachability of Nickel

The immobilization of nickel is contributed by the alkalinity nature of cement to form the insoluble nickel hydroxide in the cement matrix. As long as the nickel hydroxide is safely encapsulated in the alkaline cement, then no nickel will be leached out from the cement. However, due to the acidic attacks in the real environment, the nickel hydroxide may dissolve and leach out from the cement. In other words, the leachability of nickel is depending on the pH of leachant and also the nickel hydroxide solubility at that particular pH (Malviya and Chaudhary, 2006). During the acid attack, the cement hydration products such as portlandite and CSH with high buffer capacity will actually neutralize the acidity of extraction fluid which lower the acid attack effect (Saeedi et al., 2010). This can be seen during the leachability test when acidic leachant is used. The pH of leachant is low initially but increase slowly as the leaching time increase. This is due to the dissolution of $Ca(OH)_2$ in the cement pores into the acid (Napia et al., 2012).

The Figure 2.3 showed the theoretical solubility of metal hydroxide at different pH value. As shown in Figure 2.3, the theoretical solubility of nickel hydroxide is the lowest at pH around 10 and increase drastically when pH drops. This further shows that nickel ion can be safely entrapped in the cement in the form of insoluble nickel hydroxide at high pH condition.

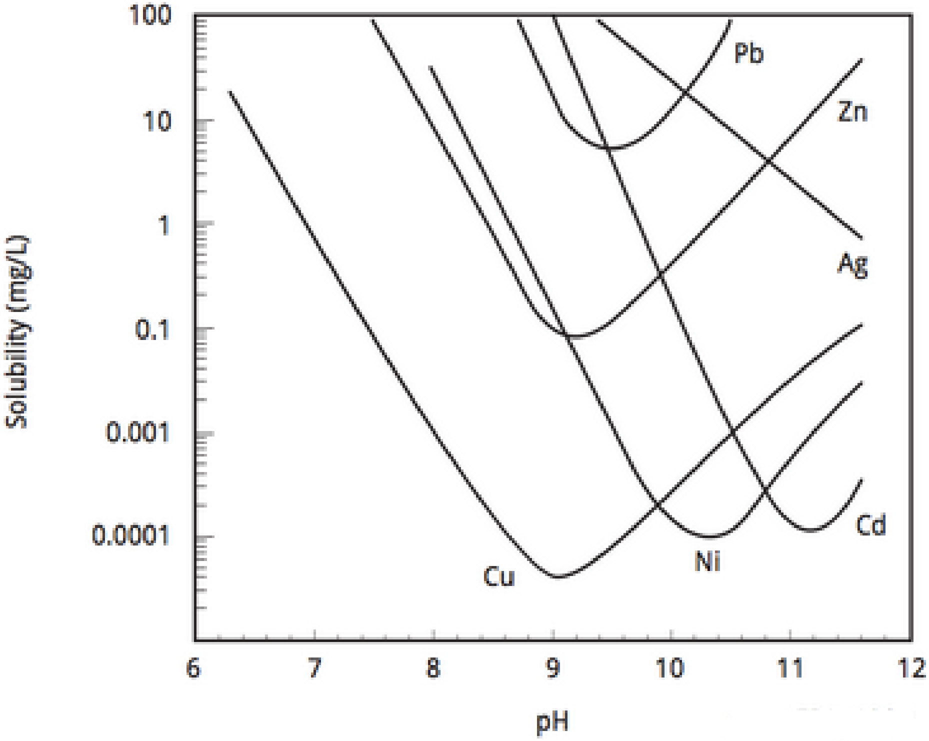


Figure 2.3: Theoretical Metal Hydroxide Solubility versus pH

Source: (EPA, 1983)

Most of the researches have shown the relationship between the leachability of nickel and the pH of leachant that contacting with solid matrix by carried out the experiments with various types of leachant and pH value. Kogbara and Abir (2011) who varied the pH of leachant to study the leachability of contaminant. They proved that the leachability of all metals (i.e. Cu, Cd, Pb, Ni and Zn) they have tested decreased when pH of leachant increases up to around pH 11. Besides, they also found that different binders will having different buffering capacities. When acid was added to slag-cement mixs (consists of OPC with furnace slag) it shows more significant effect on leachate pH as compared to lime-slag mixs (consists of hydrated lime with furnace slag). This indicated the slag-cement mixs was having lower buffering capacity and higher leachability of mobile nickel was observed.

Likewise, the similar trend was observed by Karamalidis and Voudrias (2011) who investigate the leachability of nickel in solidified refinery oil sludge and ash at pH 2 to 12. They realized that high Ni leaching was measured at pH 2 and diminished slowly as the pH of leachate increased. This research also showed that the solidified oily sludge are having different buffer capacity compare to solidified ash. The solidified ash were found to be more resistance towards the acid attack due to higher concentration of $Ca(OH)_2$ found in the matrix.

In the same manner, Song et al. (2013) also varied the pH value from 4 to 7 and 10 to study the release of heavy metals from solidified sewage sludge. From their findings, it can be observed that the metal leachability increased as pH decreased. On top of the high solubility of metal hydroxides at low pH, the acid erosion occurred at low pH condition caused the destruction of the matrix structure, thus further increased the leachability of nickel.

2.5 Effect of Nickel in Cement

As nickel are doped into the cement matrix, the interaction between nickel ion and cementitious materials will somehow exert some effects on the hydration reaction and the physical properties of the cement block. Most of the researchers have found that the main effects of heavy metals in cement are retardation of the cement hydration, the setting and curing of cement, hence lower the compressive strength of the cement matrix.

Experimental works observed that the unconfined compressive strength (UCS) for pure OPC mortar is much higher as compare to that of mortar with 50 wt% substitution of nickel hydroxide sludge (Yin et al., 2008). This showed that the presence of nickel in the cement can retard the cementation process which causing a significant drop in cement’s strength. Next, Chindaprasirt et al. (2013), have proven the effect of heavy metals on the physical properties of cement through SEM. When the percentage of sludge increased, the density of the matrix decreased. This can be explained by the inhibition of cement hydration due to the presence of heavy metals in sludge, causing the incomplete reaction of cement. As a result, the less dense cement block will show a lower compressive strength as compare to 100 % OPC block.

Additionally, the inhibition of cement hydration due to the presence of chemical sludge was revealed by Patel and Pandey (2012) through the XRD and SEM analysis. They found that the unreacted di- and tri-calcium silicate were present along with ettringite whereas the $Ca(OH)_2$ was not found. This revealed the retardation of cement hydration reaction since the di- and tri-calcium silicate were not reacted to form CSH and $Ca(OH)_2$. Through the SEM, they have observed that the sludge were coated everywhere on the cement's surface. The deposition may result in dense coating and it could be one of the factor which caused the inhibition of cement hydration.

In the research of Patil and Zodape (2011), the XRD pattern of lime fly ash sand (LFAS) cube containing nickel waste showed no evident on the presence of CSH. This clearly showed that the nickel have inhibited the formation of CSH. Due to the absence of CSH, the strength of LFAS may reduce.

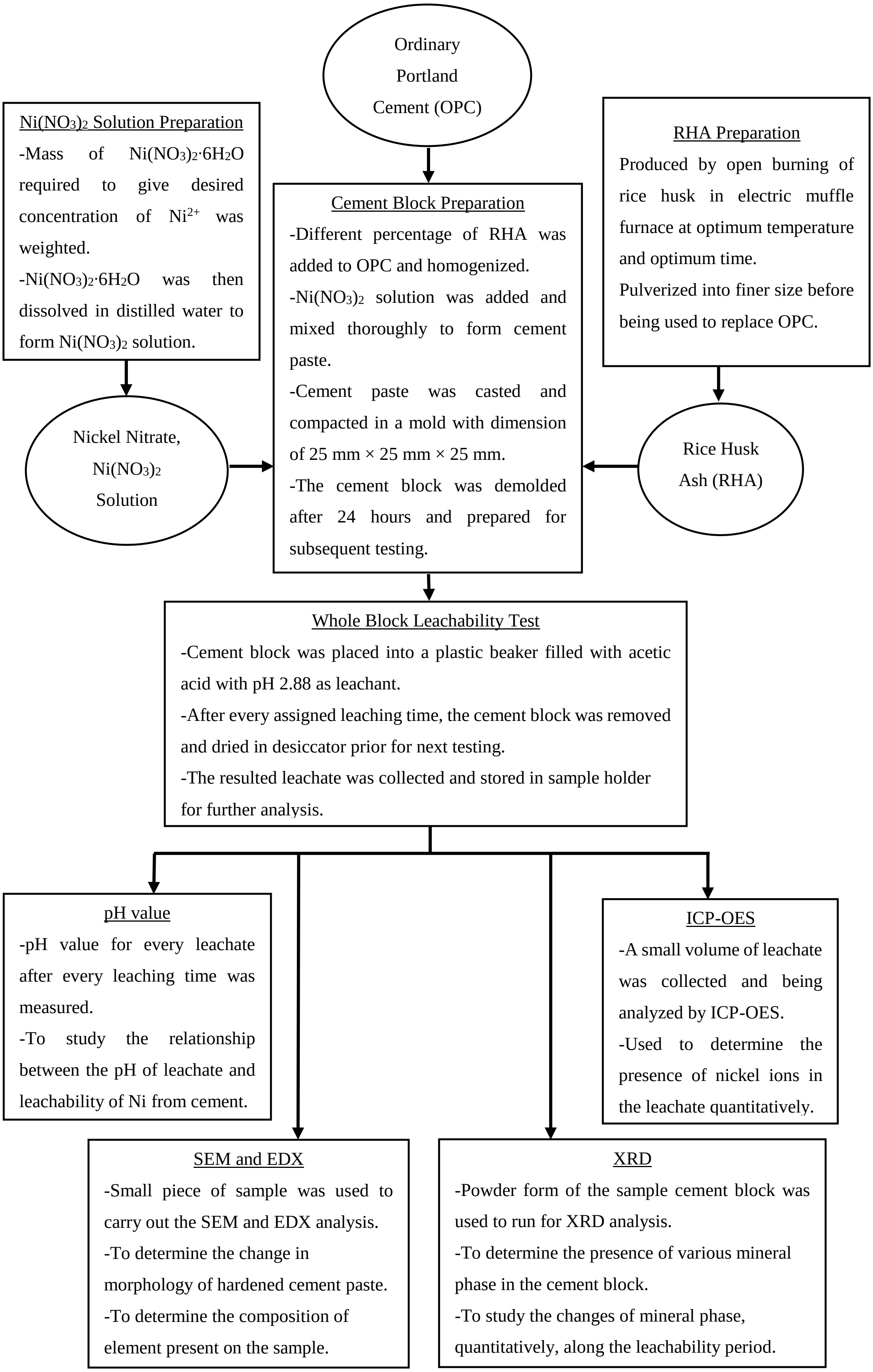
The researches being discussed were using different types of wastes which containing a mixture of various heavy metals including nickel. Some of the effects may contributed by the presence of certain heavy metals. Thus, it is not clear enough to study the effects solely based on the nickel ion itself. Yet, there were few researchers who utilized only the soluble nickel salt as the source of nickel ions. Hence, the effects on the chemical and physical properties solely based on nickel ions could be studied Minocha and Goyal (2014), who utilized nickel nitrate as source of nickel shown that the nickel has no greater effect on the cement properties. With the combination analysis of XRD and SEM, it has shown that the nickel doesn't give any effect on the hydration of cement but causes small retardation on the setting process. Lastly, Gineys et al. (2010) realized that the nickel has no significant effect on the compressive strength of the cement. However, they also found that nickel will cause some influence on the hydration of tricalcium silicate. Since the early-age compressive strength was mainly contributed by C_3S hydration, therefore a reduction of early-age compressive strength was observed.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

Research methodology shown in Figure 3.1 gives an overview about the experiments conducted in this research in order to determine the leachability of waste nickel from the cement block. Starting from samples preparation, such as rice husk ash preparation, acetic acid solution and cement block preparation, to the whole block leaching test, including each and every single analysis, the standard procedures were followed to maximize the accuracy, consistency and reliability of the experiment results while minimized the errors and risk incurred during the experiments. Under this section, the types of tests and analysis being performed in this research were explained as well.



$Ni(NO_3)_2$ Solution Preparation

-Mass of $Ni(NO_3)_2\cdot 6H_2O$ required to give desired concentration of Ni^{2+} was weighted.

-$Ni(NO_3)_2\cdot 6H_2O$ was then dissolved in distilled water to form $Ni(NO_3)_2$ solution.

Cement Block Preparation

-Different percentage of RHA was added to OPC and homogenized.

-$Ni(NO_3)_2$ solution was added and mixed thoroughly to form cement paste.

-Cement paste was casted and compacted in a mold with dimension of 25 mm × 25 mm × 25 mm.

-The cement block was demolded after 24 hours and prepared for subsequent testing.

RHA Preparation

Produced by open burning of rice husk in electric muffle furnace at optimum temperature and optimum time.

Pulverized into finer size before being used to replace OPC.

Whole Block Leachability Test

-Cement block was placed into a plastic beaker filled with acetic acid with pH 2.88 as leachant.

-After every assigned leaching time, the cement block was removed and dried in desiccator prior for next testing.

-The resulted leachate was collected and stored in sample holder for further analysis.

pH value

-pH value for every leachate after every leaching time was measured.

-To study the relationship between the pH of leachate and leachability of Ni from cement.

ICP-OES

-A small volume of leachate was collected and being analyzed by ICP-OES.

-Used to determine the presence of nickel ions in the leachate quantitatively.

SEM and EDX

-Small piece of sample was used to carry out the SEM and EDX analysis.

-To determine the change in morphology of hardened cement paste.

-To determine the composition of element present on the sample.

XRD

-Powder form of the sample cement block was used to run for XRD analysis.

-To determine the presence of various mineral phase in the cement block.

-To study the changes of mineral phase, quantitatively, along the leachability period.

Figure 3.1: Research Methodology

3.2 Materials and Apparatus used

The following listed the materials used throughout this research.

1) Ordinary Portland Cement (YTL Cap Orang Kuat)
2) Nickel (II) nitrate 6-hydrate., $Ni(NO_3)_2·6H_2O$ (Bendosen, Malaysia)
3) Calcium nitrate, $Ca(NO_3)_2·4H_2O$ (Bendosen, Malaysia)
4) 99.8 % acetic acid, CH_3COOH (Bendosen, Malaysia)
5) Nitric acid, HNO_3 (R&M Chemical, Malaysia)
6) Rice husk
7) Deionized water
8) Distilled water

The following listed the apparatus used throughout this research.

1) Beakers
2) Parafilm
3) Fishing string
4) Desiccator
5) Plastic mold
6) Centrifuge tube
7) Wooden stick
8) Glass rod
9) Cardboard
10) Crucible
11) Mortar and pestle
12) Bucket
13) Spatula
14) Electronic balance

3.3 Rice Husk Ash Preparation

The rice husk ash (RHA) was used in this research to partially replace the Ordinary Portland Cement (OPC) content in solidified cement block. The rice husk was collected from rice paddy in Kedah. The rice husk was cleaned and dried to remove any particulates that might contaminate the rice husk. After that, the rice husk was burnt in chamber furnace at a temperature of 600 °C for two hours and thirty minutes. This temperature was selected because at a temperature of 600 °C the entire cellulose and lignin group of rice husk will be destroyed and the silica is in the amorphous phase. At higher temperature, the crystalline cristobalite started to form which is undesired for solidification process (Chauhan and Kumar, 2013). The model of the chamber furnace is F62700 Furnace.

After burning for 2.5 hours, the brown colour rice husk has transformed into greyish-white colour of rice husk ash.

Figure 3.2: a) Rice Husk; b) Rice Husk Ash

The RHA was cooled down to room temperature before being grinded into smaller size. The larger form of RHA was pulverized by using mortar and pestle to reduce it size to the necessary fineness. Finally, the RHA was stored in a container prevent them in contact with atmosphere moisture.

3.4 Cement Block Preparation

In order to study the effect of different nickel concentration being doped in cement on its leachability, the concentration of nickel was varied. Besides, RHA was also added to partially replace the OPC to study on how it will affect the leachability of nickel from the cement block. The OPC used in this research was manufactured by YTL Cement Bhd branded Cap Orang Kuat.

In this research, two groups of binder's mixture with different composition (i.e. 100% OPC and 95% OPC + 5% RHA) were prepared. For each group of the mixture, nickel nitrate solution with 10 000 ppm and 30 000 ppm of nickel (II) ions, Ni^{2+} were added to the binder respectively. There was a control set for each group in which only distilled water was added to the mixture. The tree diagram below summarize the mix design that used in this research.

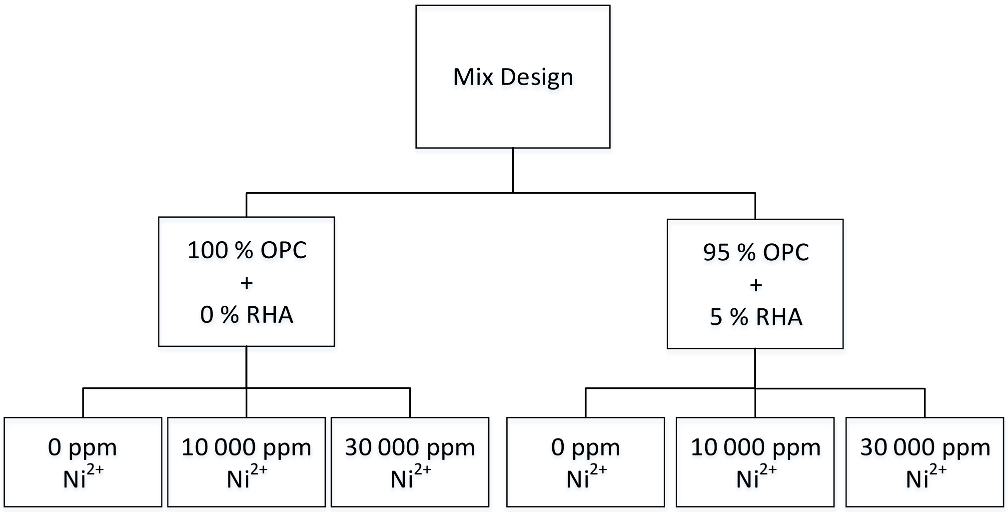


Figure 3.3: Tree Diagram of Different Mix Design

The Table 3.1 shows the notation for each design set that need to be prepared before being casted into a cube cement block.

Table 3.1: Notation of Mix Design

Sample	**Binder Mixture**		**Ni^{2+} (ppm)**	**Water-to-binder ratio**
	OPC (wt %)	**RHA (wt %)**		
100 OPC	100	0	0	0.33
100 OPC + 10k Ni	100	0	10 000	0.33
100 OPC + 30k Ni	100	0	30 000	0.33
95 OPC + 5 RHA	95	5	0	0.33
95 OPC + 5 RHA + 10k Ni	95	5	10 000	0.33
95 OPC + 5 RHA + 30k Ni	95	5	30 000	0.33

Note: 100 OPC + 10k Ni means 100 % OPC mixed with 10 000 ppm of Ni

Firstly, for the control set (i.e. 0ppm Ni^{2+}), the binder mixture was briefly homogenized prior to the addition of distilled water. The distilled water was then added to give a water-to-binder ratio (w/b) of 0.33 and followed by 10 minutes of mixing to ensure all the binders were perfectly mixed with water. The w/b ratio of 0.33 was chosen because it is high enough to provide sufficient hydration effect for the cement paste and low enough to prevent the excess of water present in the cement paste. Once the water was added, the hydration reaction initiated and slowly the mixture became a cement paste. Before the cement paste got hardened, it was poured into a 25 mm × 25 mm × 25 mm cardboard mold pre-coated with a layer of oil for easy demold. These cement paste was then compacted to ensure there was no air bubble present in the cement block. Next, the cement paste was covered with wet cloth and left for 24 hours. After one day, the hardened cement block was demolded and ready to be used for leachability test. For each mix design, a total of thirty duplicate cement cubes were made (three for one time interval with ten time intervals) to increase the accuracy of this experiment. The preparation procedure for the cement block that doped with nickel ions is almost similar to that for the control set. The only difference is just the distilled water being replaced with nickel nitrate solution that containing a specific amount of nickel ions.

3.5 Nickel Nitrate Solution Preparation

The nickel ions were doped into cement through the addition of nickel nitrate solution. The nickel (II) nitrate 6-hydrate, $Ni(NO_3)_2{\cdot}6H_2O$ was chosen as the source of nickel ions as it is soluble in water.

Depending on the concentration needed to be doped into the cement, the amount of nickel (II) nitrate 6-hydrate required was calculated as shown in Appendix C. After that, the weighted nickel (II) nitrate 6-hydrate was dissolved in distilled water to form nickel nitrate solution and being stored in Scott bottle for later use for cement block preparation.

3.6 Acetic Acid Preparation

The purity of the stock acetic acid used in this research was 99.8 wt%. This concentrated acetic acid was then diluted to obtain a desired pH of 2.88 before being used as a leachant. In order to prepare this acetic acid solution, the initial concentration of the concentrated acetic acid must be known and can be calculated as shown in Appendix D.

3.7 Whole Block Leachability Test Procedure

In this study, acetic acid was used as a leachant to simulate a landfill condition, so that the leachability of nickel from cement under a high acidic environment could be studied. The pH of the acetic acid prepared was about 2.88.

Firstly, the solidified cement block was tied on one end of fishing string and the other end was tied to a wooden stick with a length longer than the diameter of the beaker. At the same time, a 100 ml plastic beaker was prepared and poured with 60 ml of acetic acid. Next, the cement block was placed into the beaker so that it can immerse in the acetic acid. The acetic acid must fully covered the cement block. The purpose of tying the cement block with a fishing string is to ensure the cement block is floating in the acetic acid, hence maximized the contact area between cement and acetic acid.

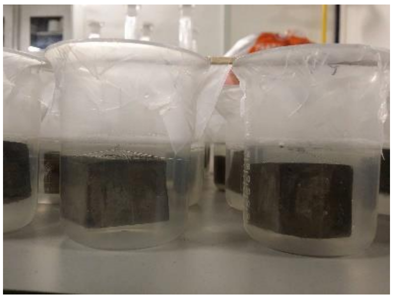


Figure 3.4: Whole Block Leachability Test

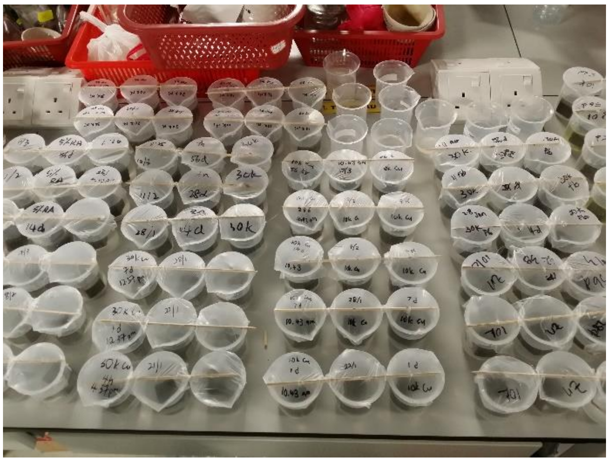


Figure 3.5: Whole Block Leachability Test for All Samples

The cement block was left in the acetic acid for 1 hr, 4 hrs, 7 hrs, 14 hrs, 1 day, 4 days, 7 days, 14 days, 28 days and 56 days. After each leaching time interval, the sample block was removed and dried in desiccator whereas the resulted leachate was collected for further analysis.

3.8 Characterization Techniques and Instrumentations

After the leachability test, some characterization techniques were performed on the leachate and cement block collected throughout the experiment. Thus, a set of data is available to be used to study on how well the cement can entrap nickel, keeping them from leaching out and get into the environment. There were several types of testing and instruments being used such as pH meter, Inductively Couple Plasma-Optical Emission Spectroscopy (ICP-OES), X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-ray (EDX).

3.8.1 pH meter

After each leaching time, the pH value of the resulted leachate was measured. The purpose of doing so is because the leachability and solubility of nickel is strongly depends on the pH of leachate.

The model of the pH meter used in this research was Sartorius pb-10. Before the measurement, the pH meter has to be calibrated by using buffer solution with pH 4, 7 and 10. After calibration, an enough volume of leachate was prepared and the pH probe was dipped into the leachate. The leachate volume must sufficiently immerse the tip of the pH probe. The pH value was read directly from the pH meter after the reading was stabilized for 5 seconds. After each measurement, the pH probe was rinsed with distilled water to ensure there was no impurities, trace acid or base remain on the probe. Finally, three (i.e. duplicate samples) pH value for each mix design at every leaching time were measured and the average value was reported.

3.8.2 Inductively Couple Plasma-Optical Emission Spectroscopy (ICP-OES)

In this study, the leachate collected were analysed by the Inductively Couple Plasma-Optical Emission Spectroscopy (ICP-OES). The ICP-OES plays a vital roles in this study to examine the present of nickel in the leachate quantitatively. The amount of nickel presence in the leachate directly reveals the information about the leachability of nickel from cement and whether the environmental acceptable limit has been fulfilled. In this research, the model of ICP-OES used was Optima 7000 DV.

ICP-OES is a very famous instrument being used to determine the trace elements in a sample. The principle of ICP-OES is based on the measurement of the emission of photons from atoms or ions once they have been excited and return to the ground state (Hou and Jones, 2000). The photons emitted carry the characteristic energies that are resulted from discrete energy level of the atoms or ions. By measuring the wavelength of the photons, the element from which it originated can be identified meanwhile the total number of photons represents the concentration of that particular element in the sample.

Before the samples were tested by ICP-OES, a few standard of nickel nitrate solution with known concentration of nickel ions that prepared through serial dilution method were analysed by ICP-OES to plot the calibration curve. This calibration curve was used to relate the intensity measured by ICP-OES with the concentration of nickel ions. From there, when a sample is analysed by ICP-OES, the intensity measured will be used to calculate the corresponding concentration of nickel ions present in the leachate.

3.8.3 X-ray Diffractometer (XRD)

Apart from analysing the leachate, the cement block was also being examined through some instruments. Upon the hydration process, there were several types of products being formed with unique crystalline phases in the cement block. The X-ray Diffraction (XRD) analysis used in this study was to study the phases, crystalline structure and the chemical compound or the possible mineral phase that might present in the cement block. XRD study the crystallographic structure of the material through the analysis of its diffraction pattern (Fultz and Howe, 2013). Besides, XRD can also be used to identify the unknown crystal in a sample by matching the position and intensity of the peaks from a database maintained by International Central for Diffraction Data (ICDD). Throughout this analysis, the effect of different mix design on the change in crystalline structure and phase can be studied.

The model of XRD used in this research was the Shimadzu XRD-6000 Diffractometer. Prior to the analysis, the cement block was crushed into powder form and filled into the sample holder of XRD. The X-ray tube used in this model was emitting the Cu-Kα X-ray. The voltage and current was set to 40 kV and 30 mA respectively. Furthermore, the sample was scanned through a scan range of $2\theta = 3^{o}$ to 70^{o} with a step of 0.02^{o} and steptime of 0.6 s, resultant a scan speed of 2^{o}/min.

3.8.4 Scanning Electron Microscopy (SEM) coupled with Energy-dispersive X-ray Spectroscopy (EDX)

Besides XRD, the cement block was also examined by the Scanning Electron Microscope (SEM) coupled with Energy Dispersion X-ray (EDX) as well. Through the observation from the SEM, the surface feature at the inner part of the cement block can be studied. The SEM revealed the information about the surface porosity of the cement block as well as showing the presence of mineral phase in the cement block as detected by the XRD. On the other hand, the EDX was used to determine the elements composition presence in the inner side of the cement block.

The analysis of SEM coupled with EDX was initiated as the electron beam stroked onto the sample. This interaction between the incident electron beams with the sample will result in the formation of backscattered electron, secondary electron, auger electron and x-ray. Each of these signals are detected by different detectors and they are carrying different information which is summarized in the table below (Mehta, 2012).

Table 3.2: Information carried by different signals

Signals	Information
Backscattered electron	Atomic number of element
Secondary electron	Topography of sample
Auger electron	Composition of sample
X-ray	Element identification

Hence, by examine the different signals resulted from the interactions, the information about the sample can be studied.

The model of SEM used in this study was Hitachi S-3400N.whereas the model of EDX is Apollo X which is part of the Ametek's Materials Analysis Division. The EDX is simply a detector that is attached together with SEM.

For SEM and EDX analysis, the cement block, instead of crushing down into powder form as for XRD, it was remained to be in pieces form. These pieces form of cement was then placed and adhered on the sample holder through the carbon tape. The samples was first run with EDX to determine the element composition on the surface of cement pieces. After that, for the SEM, the samples was gone through a pre-treatment process known as sputter coating through a sputter coater from Emitech.

Through the sputter coater, an ultra-thin (20 – 25 Å) coating of electrical-conducting metal such as gold and platinum was applied on the surface of the cement pieces. The purpose of doing so is to prevent the charging of specimen, to increase amount of secondary electron and to increase the signal to noise ratio. After that, the sample was ready to be observed through the SEM. The voltage was set to 15 kV with a magnification of 10 000 times.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Overview

Throughout a few months of experiment, the required results or data were collected from time to time and were tabulated in Appendices. This experiment started with the examination of the materials used, along the way observing the changes of the appearance of cement block and leachate during WBL test, until measurement of the pH and concentration of nickel presence in leachate. In this section, all the results collected were compiled and analysed thoroughly to study the effect of various factors on the leachability of nickel in the cement block.

4.2 Examination of the Material used

4.2.1 Ordinary Portland Cement (OPC)

Cement is the essential or core ingredient in the solidification/ stabilization technique. The high alkalinity of the cement contributes to the immobilization of waste nickel in cement-based system. As mention in the previous chapter, there are few major components presence in cement powder before the hydration reaction such as dicalcium silicate (C_2S), tricalcium silicate (C_3S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). After the hydration reaction as stipulated in

Equation (1.1) and (1.2), some of the C_2S and C_3S will react with water to form calcium silicate hydrate (CSH) and calcium hydroxide (CH). The presence of these crystalline mineral phases can be examined through the search-and-match technique of the X-ray Diffractometer (XRD).

In XRD, each of the crystalline mineral phase is possessing some characteristic peaks at certain diffraction angle (2θ).

Table 4.1: Diffraction angle for different mineral phase

Mineral Phase	2θ
CH or $Ca(OH)_2$	18.07°, 34.07°, 47.11°
C_2S or $2CaO{\cdot}SiO_2$	32.60°, 33.25°
C_3S or $3CaO{\cdot}SiO_2$	29.43°, 32.21°, 34.38°

The X-ray Diffractogram shown in Figure 4.1, gives a clear difference, in terms of the amount of mineral phase presence, between the cement powder before hydration reaction and the cement block after the hydration reaction.

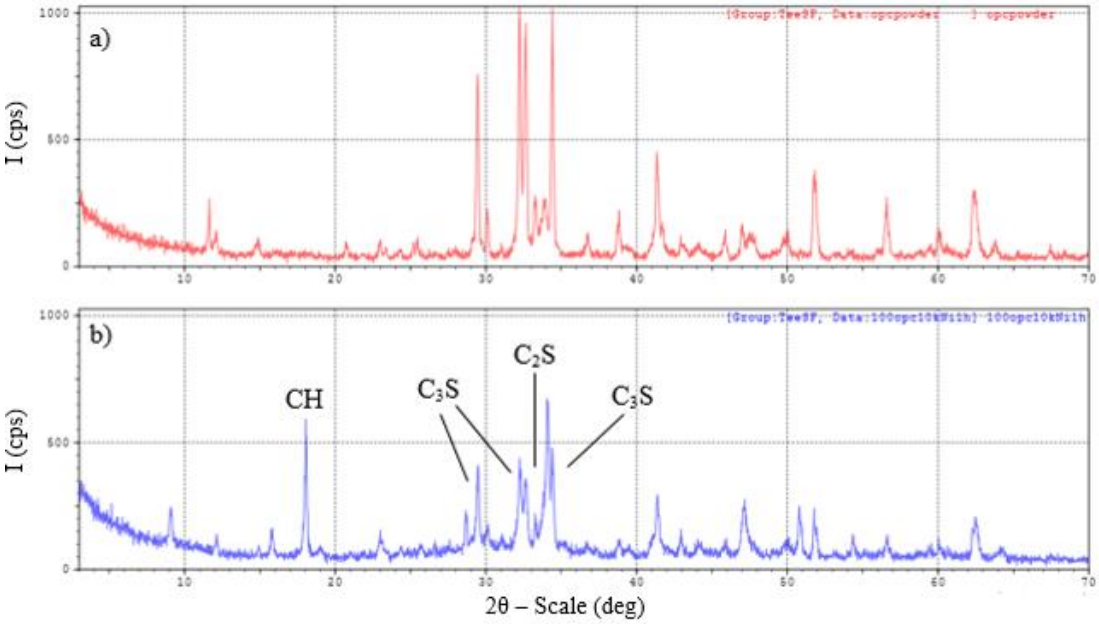


Figure 4.1: XRD for Cement a) Before Hydration Reaction; b) After Hydration Reaction

Before the hydration reaction, the diffractogram showed the distinctive peaks of C_2S and C_3S but without the presence of CH in the cement powder. This verified that before the hydration reaction, the major clinker minerals C_2S and C_3S was still presence in a very large amount in cement powder before they reacted with water to form CSH and CH. Once the cement powder mixed with water, the hydration reaction initiated. As reveal from Figure 4.1, the peak for CH appears with the decreased amount of C_2S and C_3S signified the hydration reaction of the clinkers mineral in cement. The diffractogram didn't shows the presence of CSH is because CSH do not have any long range order and only possess some weak and broad diffraction peaks (Gartner, Kurtis and Monteiro, 2000). In other words, the CSH is semi-crystalline in nature which is not able to be detected by XRD.

4.2.2 Rice Husk Ash (RHA)

Rice Husk Ash (RHA) was used in this research to partially replace the Ordinary Portland Cement (OPC) as a secondary binder. RHA which possess high content of silica is a very reactive pozzolanic materials which suitable to be used as active cement additive and for cement substitution. Yet, not all forms of RHA are suitable to be served as pozzolanic material. There are various researches who have proven that the RHA which containing amorphous silica will have higher pozzolanic effect than crystalline one (Soares *et al.*, 2015). The amorphous silica can be obtained by controlling the burning temperature and burning time of rice husk.

In this research, the RHA was burnt under 600 °C for 2.5 hours. Subsequently, this RHA was tested with XRD to determine the crystallinity of silica containing in the RHA. As shown in the diffractogram (Figure 4.2), there was a very broad peak rather than a sharp peak at $2\theta = 22^\circ$. This indicates that the silica in the RHA is in amorphous phase which fulfilled the requirement for highly active pozzolanic material (Xu *et al.*, 2015).

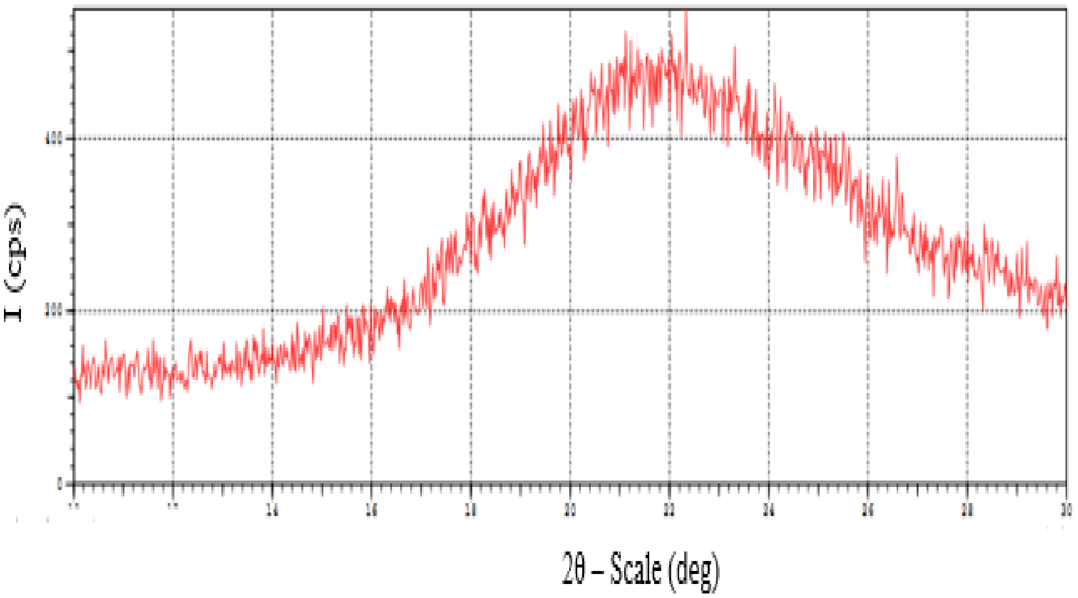


Figure 4.2: XRD for RHA Sample

4.3 Appearance of Cement Block and Leachate

Before the cement block was contacted with acetic acid, there was no obvious difference outlook between the cement block before and after nickel doping. After they have been immersed into acetic acid, there was not much changes for the block and leachate in the first two weeks. From 14 days onwards, the leachate became a slight cloudy which indicates the dissolution of calcium hydroxide in the leachate.

Besides, there was some white precipitate being found on the surface of leachate and the cement block. These white precipitate was collected and analysed through the XRD. From the XRD search-and-match result in Figure 4.3, it shows that the white crystalline material was calcium carbonate, $CaCO_3$.

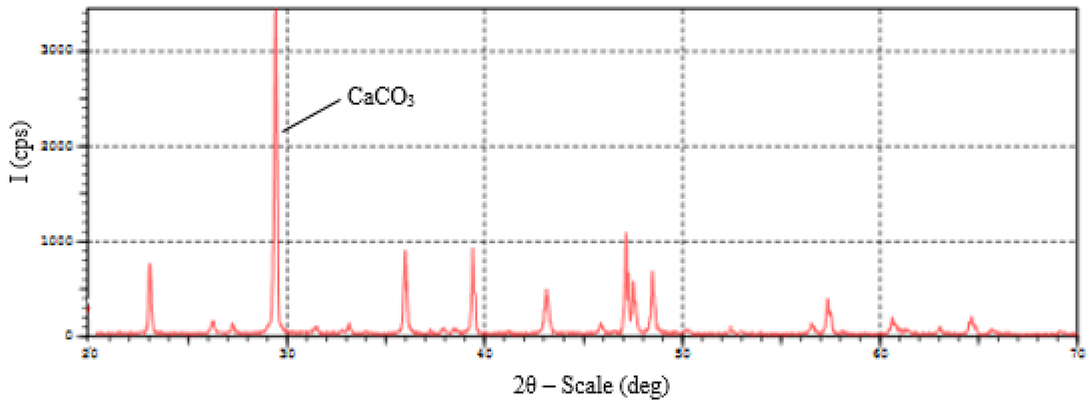


Figure 4.3: XRD for White Precipitate on Sample

The formation of calcium carbonate was not found in every sample but only for certain samples. This phenomenon may due to not properly seal or cover of the top of plastic beaker during the WBL test where the carbon dioxide, CO_2 in the atmosphere may have a chance to reacted with $Ca(OH)_2$ in the leachate to form $CaCO_3$ through the chemical equation (4.1) as shown below.

$$CO_2+Ca(OH)_2 \rightarrow CaCO_3+H_2O \tag{4.1}$$

Furthermore, during the time when cement block after WBL test has been crushed into pieces, it can be seen that the inner part of the cement block was darker in colour as compared to the surface. For the cement block which partially replaced with RHA, the presence of RHA at the inner part of cement block was significant due to big contrast in colour between light-grey colour RHA and dark-grey colour of cement.

4.4 pH Value of Leachate

The pH of leachate after every contact time was recorded and tabulated in Appendix E. The pH of leachate was measured because it has a direct effect on the leachability of nickel in cement. Since the leachate's pH was almost constant after 14 days (or 336 hr), the graph only plotted up to 14 days. This could further enhance the observation of the changes at the early stage.

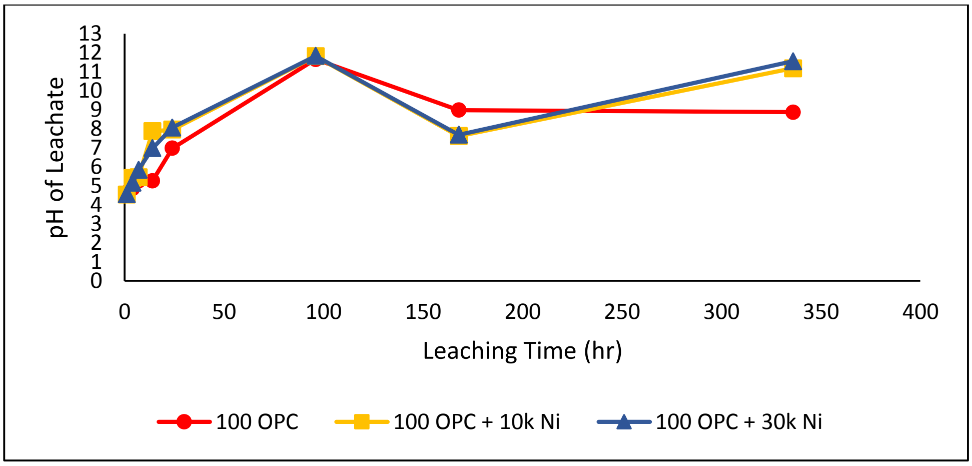


Figure 4.4: pH of Leachate versus Leaching Time for 100 % OPC

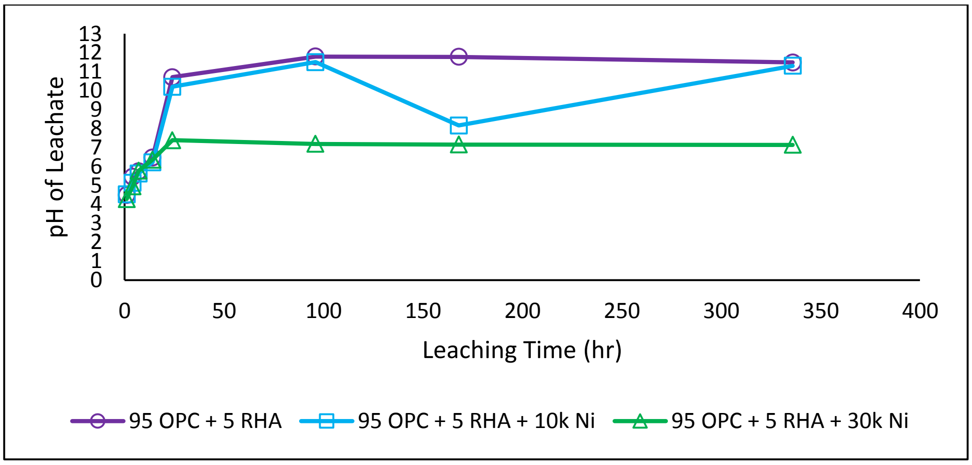


Figure 4.5: pH of Leachate versus Leaching Time for 95 % OPC

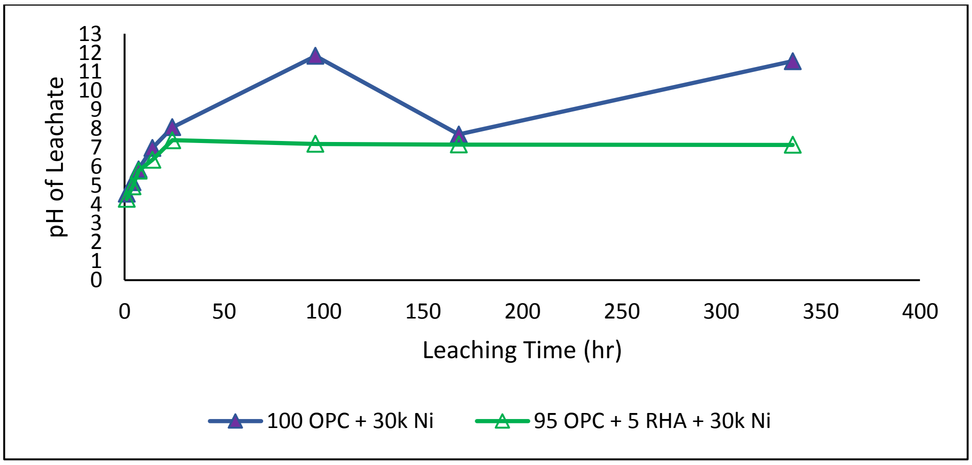


Figure 4.6: pH of Leachate versus Leaching Time Comparing between 100 % OPC and 95 % OPC

From Figure 4.4 and Figure 4.5, the pH of leachate followed almost similar trend during initial contact time regardless of the addition of RHA. The pH of leachate for all samples was low at the early time but increased gradually to pH 11 after 100 hours. The low pH of leachate was due to the presence of H^+ which formed from the dissociation of acetic acid, CH_3COOH.

$$CH_3COOH \leftrightarrow CH_3COO^- + H^+ \tag{4.2}$$

The pH was then increased due to the dissolution of CH in aqueous solution. During the hydration reaction, C_2S and C_3S will react with water to form CSH and CH in the cement. Subsequently, the CH was dissociated to form calcium ions, Ca^{2+} and hydroxide ions, OH^- under acidic condition. When the OH^- react with the H^+, amount of H^+ in leachate will reduce, hence the leachate's pH will increase.

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2\ OH^- \tag{4.3}$$

$$Ca^{2+} + 2\ OH^- + 2\ CH_3COO^- + 2\ H^+ \rightarrow Ca(CH_3COO)_2 + 2\ H_2O \tag{4.4}$$

At the early contact time, the pH was low due to not much of CH being formed just after the hydration reaction was happened. The amount of hydroxide ions dissociated was not enough to cover the acidic behaviour of acetic acid. However, as time goes on, more CH being produced. The high buffer capacity of CH started to neutralize the acidic acetic acid and slowly changed the pH of leachate from acidic to alkaline.

The Figure 4.4 shows that there was a drop of pH after 100 hours of contact time. This may due to the presence of atmosphere carbon dioxide. As stated in Equation 4.1, the CO_2 will react with $Ca(OH)_2$ in the leachate to form $CaCO_3$. This causes the reduction of OH^- in the leachate and lead to a drop of pH. After 160 hours of leaching time, the pH of leachate increased again. This may due to the rate of formation of OH^- through hydration reaction has overtook the rate of consumption of OH^- during the $CaCO_3$ formation. Finally when the CH in leachate reached the saturation point, the pH of leachate became almost constant as there was no excess hydroxide ions being produced.

In Figure 4.5, the pH of leachate for cement without nickel doping was higher than that with nickel doping. Meanwhile, the leachate’s pH for cement doped with 10000 ppm of Ni ions was higher than that for 30000 ppm of Ni ions. This may explain through the following equations,

$$2\ C_3S + 6\ H \rightarrow C_3S_2H_3 + 3\ CH \tag{1.1}$$

$$2\ C_2S + 4\ H \rightarrow C_3S_2H_3 + CH \tag{1.2}$$

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2\ OH^- \tag{4.3}$$

$$Ni^{2+} + 2\ OH^- \rightarrow Ni(OH)_2 \tag{4.4}$$

When the $Ca(OH)_2$ produced during hydration reaction (1.1) and (1.2) has dissociated into Ca^{2+} and OH^-, the OH^- will react with Ni^{2+} to form $Ni(OH)_2$ precipitate (Wang, Hung and Shammas, 2010). Due to the OH^- was consumed to form $Ni(OH)_2$ instead of to neutralize the H^+ from acetic acid, the pH of leachate will be lower. When more Ni^{2+} was added, more OH^- will be consumed lead to even lower pH of leachate.

As shown in Figure 4.6, when the composition of binder has changed, the pH value will be changed as well. This is simply because the amount of $Ca(OH)_2$ being produced has decreased. When 5 % of the OPC has been replaced by RHA, the calcium weight percent in the total blend of binders will decrease because the RHA do not contain any calcium. As the calcium weight percent has been reduced, the amount of CSH and CH produced will be reduced accordingly. Hence, less OH^- ions to neutralize the acetic acid, lead to a lower pH. In short, the higher the proportion of RHA in the mix design, the lower the pH of leachate.

4.5 Analysis for Control Set

As stated in methodology, there were two groups of binder's mixture namely 100 % OPC and 95 % OPC with 5 % RHA as replacement. For the control set, these binder's mixture were only mixed with pure distilled water. In other words, there was no nickel ions contained in the cement block. These control set was gone through the similar leachability test and analysis as well. In this section, some analysis were performed to examine the changes of structural properties and the chemical composition between the cement block made with pure OPC and with RHA replacement after different contact time.

4.5.1 XRD Analysis for Control Set

4.5.1.1 Effect of Contact Time on Mineral Phase in Cement Block

The Figure 4.7 showed the XRD diffractogram for cement block with pure OPC as binder after several leaching time.

There was a significant difference for the amount of CH presence in cement block after a long period of time. When comparing the diffractogram after 1 hour and 7 days of leaching time, it was found that the latter was having higher amount of CH compared to previous. This was because the hydration reaction was still ongoing during the WBL test. Meanwhile, the amount of C_3S and C_2S was decreasing along the leaching time which further signify the hydration reaction which converted C_2S and C_3S to CH. At the time when water was added to cement, the hydration reaction initiate and will continue as long as there is C_2S and C_3S presence in the cement.

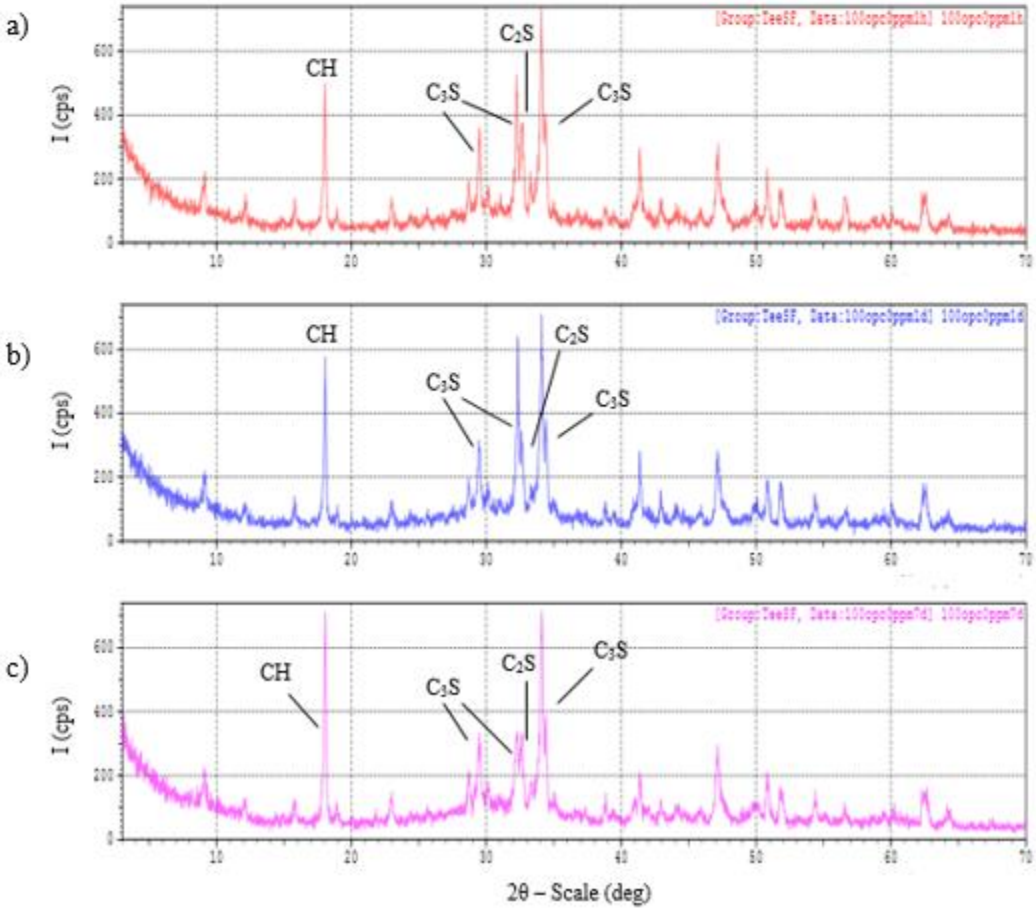


Figure 4.7: XRD Result for 100 % OPC After a) 1 hr; b) 1 day; c) 7 day of Leaching Time

4.5.1.2 Effect of Binder Composition on Mineral Phase of Cement Block

The XRD diffractogram (Figure 4.8) shows the different amount of mineral phase presence in the cement block of 100 % OPC and 100 % OPC + 5 % RHA after one hour contact with acetic acid.

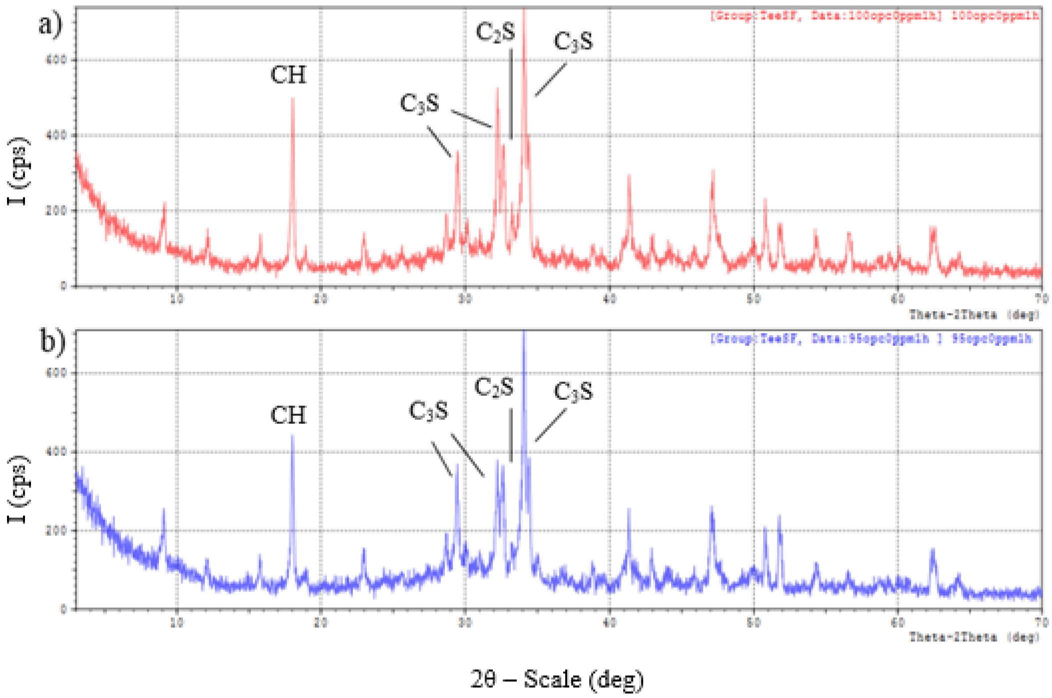


Figure 4.8: XRD for cement block with a) 100 % OPC; b) 95 % OPC + 5 % RHA after 1 hr Leaching Time

From Figure 4.8, the amount of CH, C_2S and C_3S was slightly higher for sample of 100 % OPC compared to that of 95 % OPC + 5 % RHA. This was because when 5 % of OPC being replaced with RHA, the amount of C_2S and C_3S which originally presence in the cement will be reduced by almost 5 % as well. Subsequently, causing the reduction of the CH produced during hydration reaction. The presence of RHA can also be seen through the EDX analysis.

4.5.2 EDX Analysis for Control Set

4.5.2.1 Effect of Contact Time on Cement Block Chemical Composition

The EDX result shown in Table 4.2 and Table 4.3 below was extracted from Appendix G. Initially, the weight percent (wt %) of calcium and oxygen atom was higher but decreased after 28 days. This was contradicted with the observation seen in Figure 4.7

where the XRD result shows that the $Ca(OH)_2$ was increasing along the contact time due to hydration reaction. This undesired result may due to different spotting area on the cement block.

Table 4.2: EDX Result for 100 % OPC after 1 h, 1 day, 7 days and 28 days of Leaching Time

Element	1 hour	1 day	7 days	28 days
Ca (wt %)	65.14	67.69	62.82	64.75
O (wt %)	15.27	12.88	16.79	14.08

Table 4.3: EDX Result for 95 % OPC + 5 % RHA after 1 h, 1 day, 7 days and 28 days of Leaching Time

Element	1 hour	1 day	7 days	28 days
Ca (wt %)	54.05	72.15	74.36	50.37
O (wt %)	23.38	8.74	8.38	13.70

When the EDX analysis was done on the outer part or surface of cement block, where it was contacting with acetic acid, the wt % of calcium and oxygen detected will be lesser as the acetic acid has dissolved the $Ca(OH)_2$ on the outer surface of cement block causing Ca and O leached out from cement block. On the other hand, if the EDX analysis was done on the inner part of cement block where the hydration reaction was still happening, then the amount of Ca and O will be higher as it is not eroded by acetic acid.

Hence, in this case, the EDX analysis maybe spotted on the outer surface of cement block whereas the XRD analysis was performed on the inner part of the cement block. The EDX result for different binder composition has shown almost similar result.

4.5.2.2 Effect of Binder Composition on Cement Block Chemical Composition

The EDX result shown in Figure 4.9 and Table 4.4 indicated the presence of excess silica in the sample contributed by RHA.

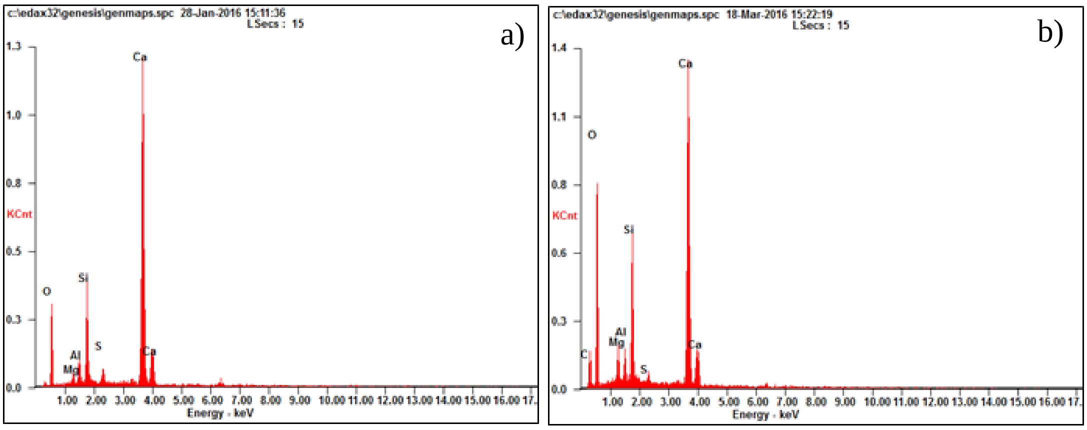


Figure 4.9: EDX Result for a) 100 % OPC; b) 95 % OPC + 5 % RHA after 1 h Leaching Time

Table 4.4: EDX Result for a) 100 % OPC; b) 95 % OPC + 5 % RHA after 1 h Leaching Time

Element	**100 % OPC**	**100 % OPC + 5 % RHA**
Ca (wt %)	65.14	54.05
O (wt %)	15.27	23.38
Si (wt %)	13.04	14.77

The amount of silicon and oxygen atom was higher when RHA was added to replace OPC. The increased in both Si and O atom indicates the presence of silica, SiO_2 in the cement block. Since RHA contains almost 20 % of silica, the sample which added with RHA will definitely increase the silica content in the cement block. (Umeda, Kondoh and Michiura, 2007). This replacement of OPC with RHA also reduce the Ca wt % in the cement block.

4.5.3 SEM Image for Control Set

Besides, the control cement block was scanned through the SEM to examine their morphology. As shown in the figure below, when the contact time was short at the early stage, there was not much of needle-liked ettringite being formed in the cement block as compared to that after 28 days of contact time.

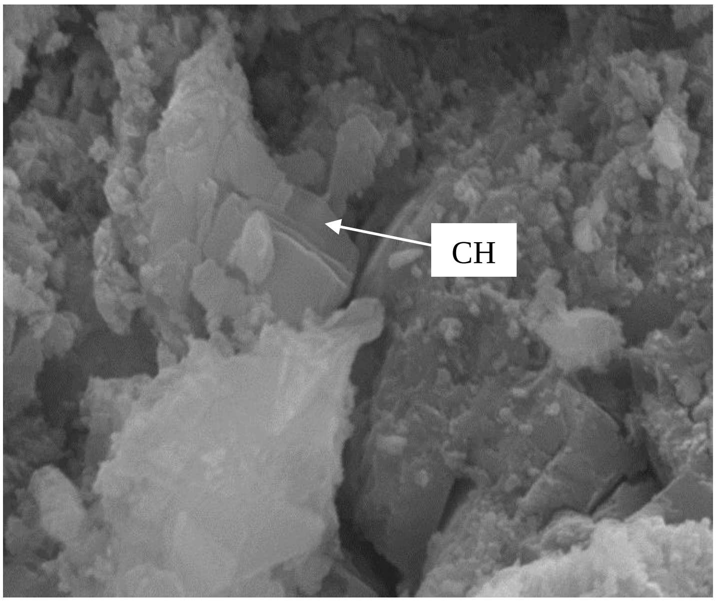


Figure 4.10: SEM Image of 100 % OPC after 1 h Leaching Time

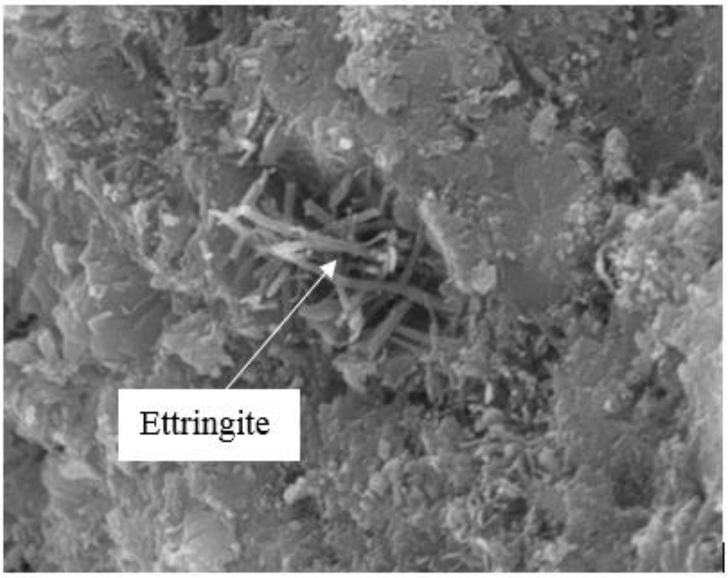


Figure 4.11: SEM Image of 100 % OPC after 28 days of Leaching Time

The porosity of cement block increased as the time of contact between acetic acid and cement block increased due to the cement block contacted with acetic acid for long period of time, more calcium hydroxide will be leached out from the cement block. The acetic acid may seep through the outer part of cement and gets into the inner side of cement block. This further increased the porosity inside the cement block to an extent where the acidity of acetic acid no longer be able to dissolve the CH. This can be seen for cement block with 5 % RHA replacement as well.

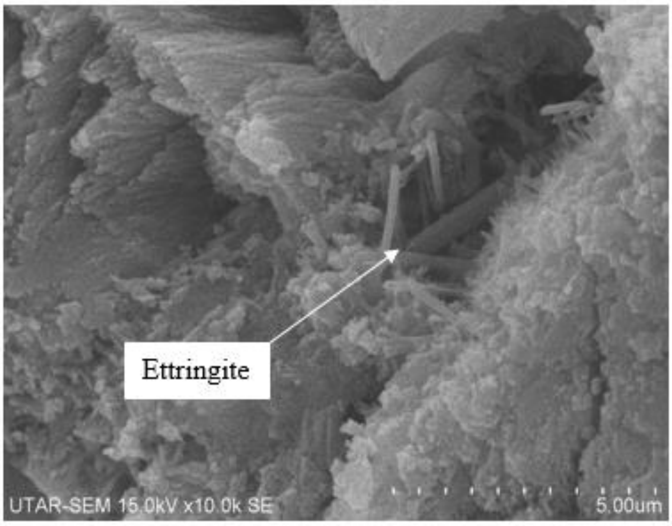


Figure 4.12: SEM Image for 95 % OPC + 5 % RHA after 1 h Leaching Time

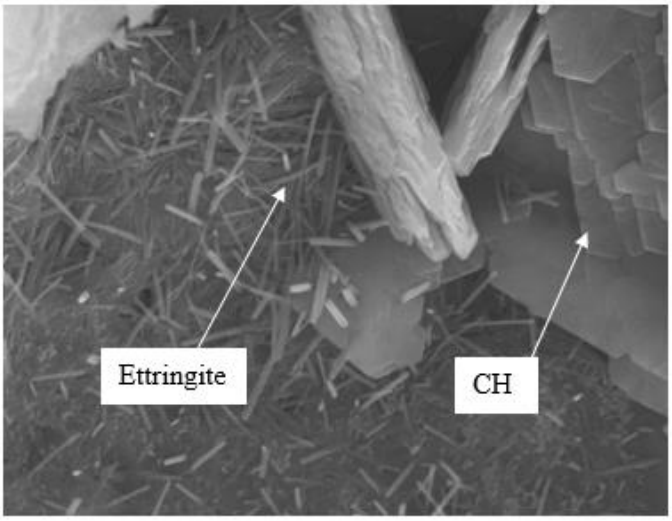


Figure 4.13: SEM Image for 95 % OPC + 5 % RHA after 28 days Leaching Time

4.6 Nickel-doped Cement Block

After the control sets have been studied, the cement block doped with 10 000 ppm and 30 000 ppm of nickel ions after the WBL test has been studied as well. The sample cement block were gone through the similar analysis steps as the control sets.

4.6.1 XRD Analysis for Ni-doped Cement Block

The Figure 4.14 showed the XRD diffractogram between cement block of 100 % OPC doped with 10 000 ppm Ni^{2+} and 30 000 ppm Ni^{2+}. This result has shown that as the amount of nickel ions doping increased, the CH formed in the cement block decreased. This is because during the preparation of cement block, same weight of nickel solution was added to cement powder to achieve water-to-binder ratio of 0.33, regardless of any concentration. Under the same weight, the nickel solution with higher concentration of nickel ions will have lesser amount of water molecule content. Since water is a key reactant for hydration reaction, as a result, less amount of CH will be produced through the hydration reaction.

In the diffractogram shown in Figure 4.14, the trace of nickel was not detected by XRD. This may due to the nickel complex presence in cement block was in amorphous phase (Chindaprasirt *et al.*, 2013). For XRD, the detector can only detect those mineral phase or compound which is crystalline. Hence, although the nickel may be trapped in the cement block, it might not be detected through XRD analysis.

The other reason of why nickel was not detected by XRD was due to the amount of nickel in cement block was too little as compare to those major mineral phases such as CH, C_2S and C_3S. The peaks of those major phase may have covered up the peak of nickel complex in a diffractogram. The tiny amount of nickel maybe detected through EDX analysis as shown in Figure 4.15.

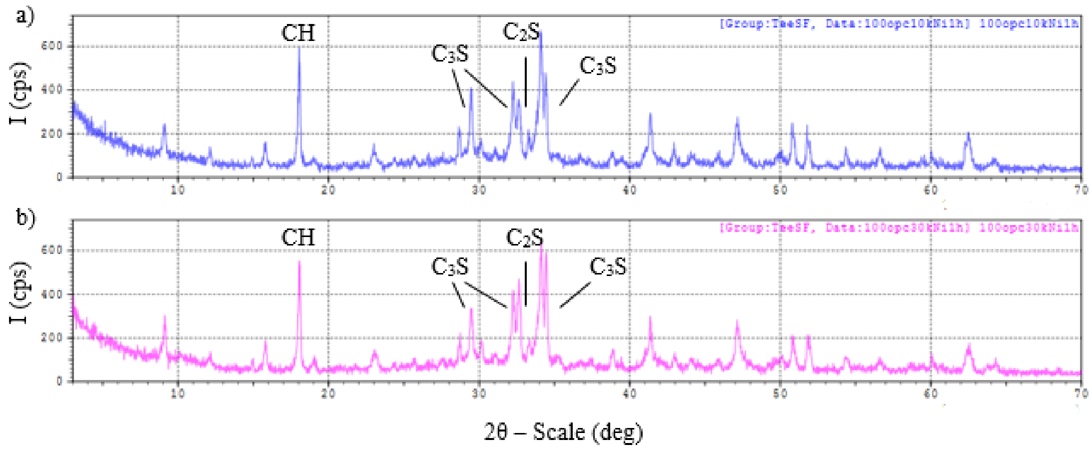


Figure 4.14: XRD for 100 % OPC doped with a) 10k ppm Ni; b) 30k ppm Ni after 1 h of Leaching Time

4.6.2 EDX Analysis for Ni-doped Cement Block

The EDX analysis can be used to determine the trace amount of nickel presence in cement block which cannot be detected by XRD.

Figure 4.15 shown nickel does exist in the cement block but only with very small amount as compared to other element such as Ca, O and Si. However, which form of nickel compound that actually presence in the cement block was not clear as the EDX result only shows the presence of Ni. The exact weight percent of Ni in cement block for both 100 % OPC and 95 % OPC + 5 % RHA was shown in Appendix G.

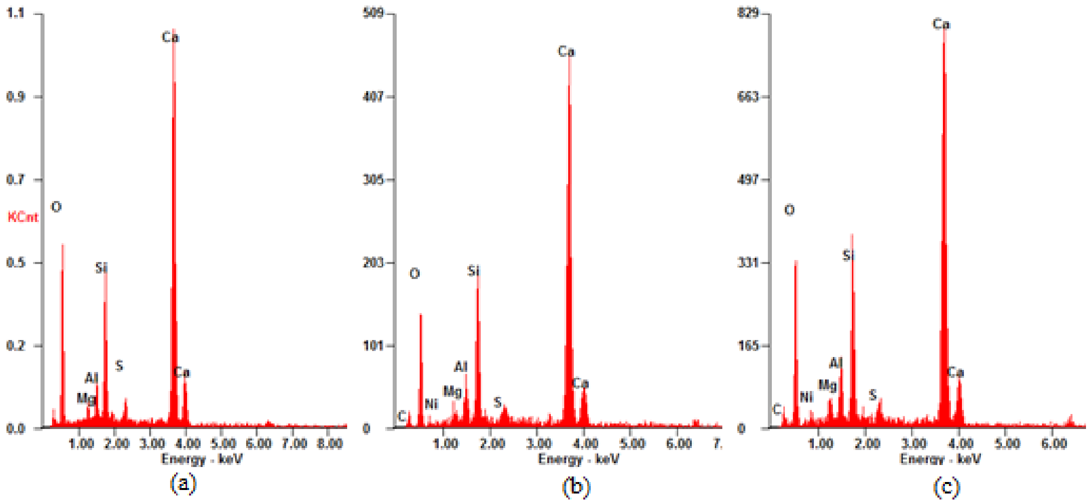


Figure 4.15: EDX Result for 100 % OPC for a) 0 ppm Ni; b) 10k ppm Ni; c) 30k ppm Ni after 1 h of Leaching Time

4.6.3 SEM Image for Ni-doped Cement Block

The SEM images below showed the changes of morphology of the cement block after doping with nickel.

As compare to Figure 4.10, the amount of CH found in cement block without nickel doping was higher than that with nickel doping. These images have proven that, the presence of nickel in cement may inhibit the hydration reaction of cement (Patel and Pandey, 2012). The inhibition of hydration reaction may reduce the formation of CH in the cement block as shown in Figure 4.16 and Figure 4.17

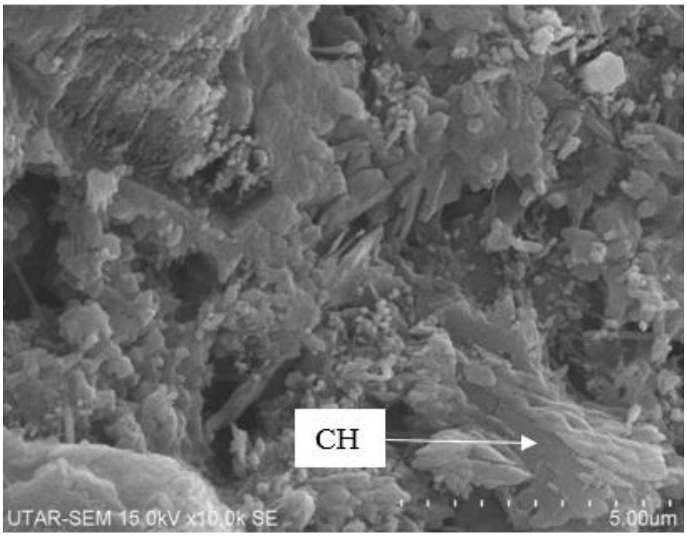


Figure 4.16: SEM Image for 100 % OPC + 10k ppm Ni after 1 h Leaching Time

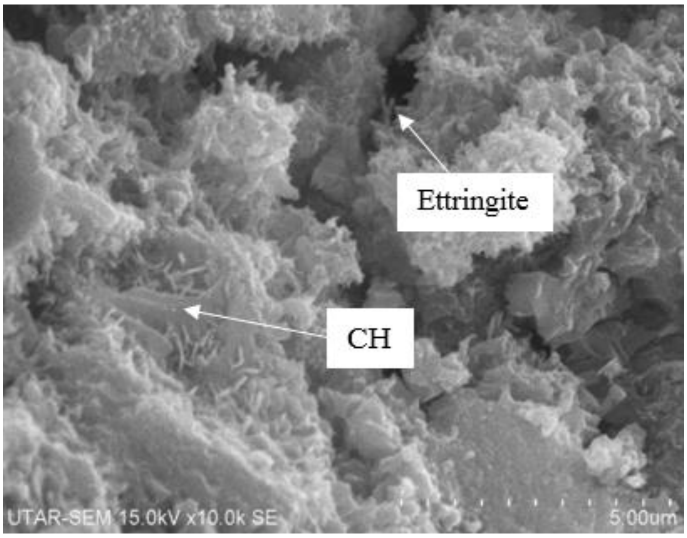


Figure 4.17: SEM Image for 100 % OPC + 30k ppm Ni after 1 h Leaching Time

The similar results have shown in Figure 4.18 and Figure 4.19 for cement block with 5 % replacement of RHA doped with 10k ppm and 30k ppm of Ni as compared to Figure 4.12 without Ni doping.

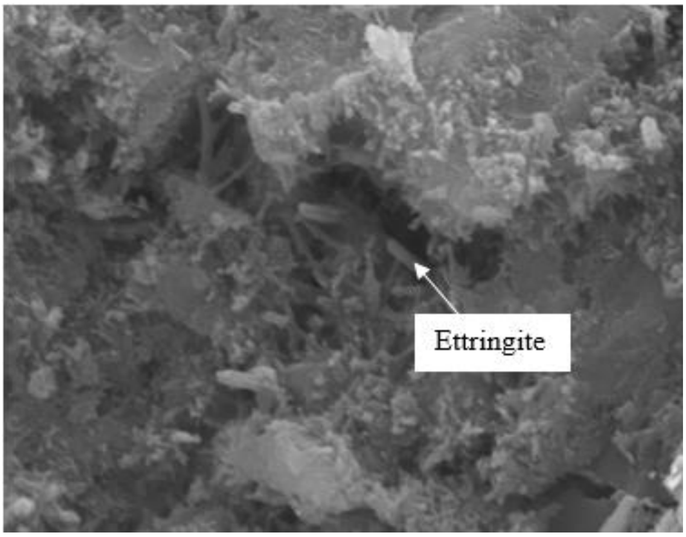


Figure 4.18: SEM Image for 95 % OPC + 5 % RHA 10k ppm Ni after 1 h Leaching Time

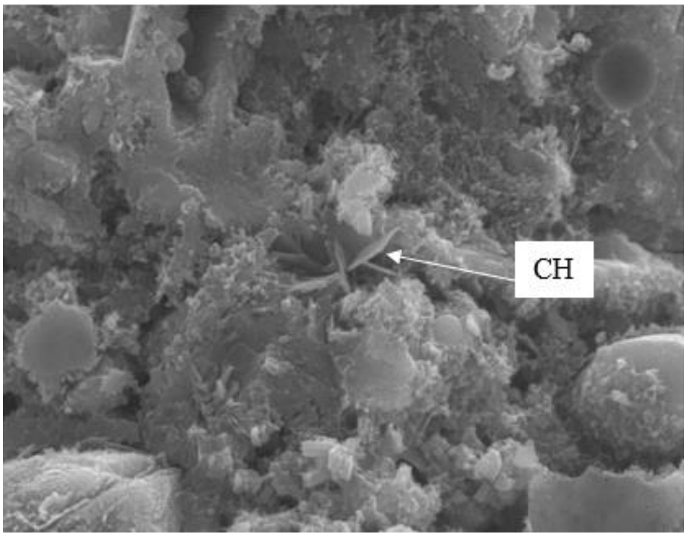
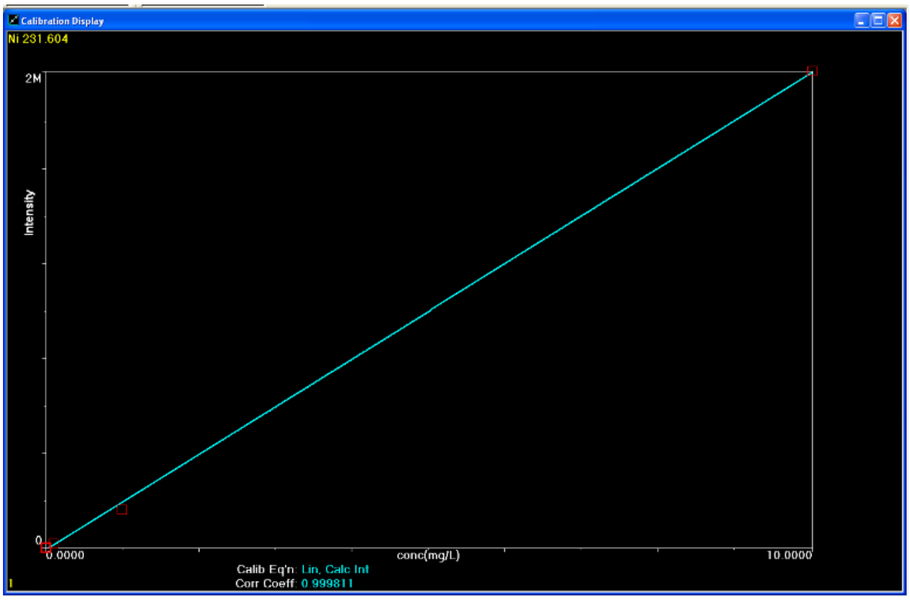


Figure 4.19: SEM Image for 95 % OPC + 5 % RHA 30k ppm Ni after 1 h Leaching Time

4.7 Leachability of Nickel

The leachability of nickel that depending on several factors such as binder's composition, pH of leachate and contacting time was examined in the following section. The concentration of nickel and calcium ions in leachate was measured by

ICP-OES and the results were tabulated in Appendix F. The calibration curve for nickel is also showed in Figure 4.20.



Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999811

Figure 4.20: Calibration Curve for Nickel

4.7.1 Effect of Nickel Doping Concentration, pH and Contact Time

The reason of selecting the Ni doping concentration of 10k ppm and 30k ppm, which considered as having a big gap, is to examine a more significant effect of doping concentration on the leachability of Ni in cement block.

There was more nickel being leached out from cement block doped with 30k ppm Ni ions at the early stage as compared to that for doping with 10k ppm Ni ions (Figure 4.21). This is because when the doping concentration of Ni increased, the amount of Ni contained in the cement block, as well as, on the surface increased. As the cement surface contacted with acetic acid, more nickel will be leached out from the surface of cement block. However, there was not much difference between 10k and 30k ppm of Ni ions doping after 96 hrs (or 4 days). Both were almost constant at concentration of 0.03 ppm.

During the early leaching time, the leachability rate was high and gradually reduced to a constant rate after a long period of contact time. This phenomena was closely related to the changes of leachate's pH along the contact time. As shown in Figure 4.4, the pH of leachate was affected by the contact time. The pH of leachate was relatively low initially and increased slowly along the leaching time. The leachability of nickel, yet, having an inverse relationship to the pH of leachate.

Referring to the graph shown in Figure 4.21, the highest amount of Ni (i.e. 3.64 ppm) being leached out was found during the first hour of leaching time where the leachate's pH was also at its lowest at 4.55. The leachate concentration has then gradually reduced to 0.03 ppm after long period of leaching time where the leachate's pH has reached and maintained at 11.

This inverse relationship between the pH of leachate and Ni leachability has proven the facts that the leachability is strongly relied on the pH of leachate. This result was tally with the graph of theoretical solubility of nickel hydroxide, $Ni(OH)_2$ at different pH as shown in Figure 2.3.

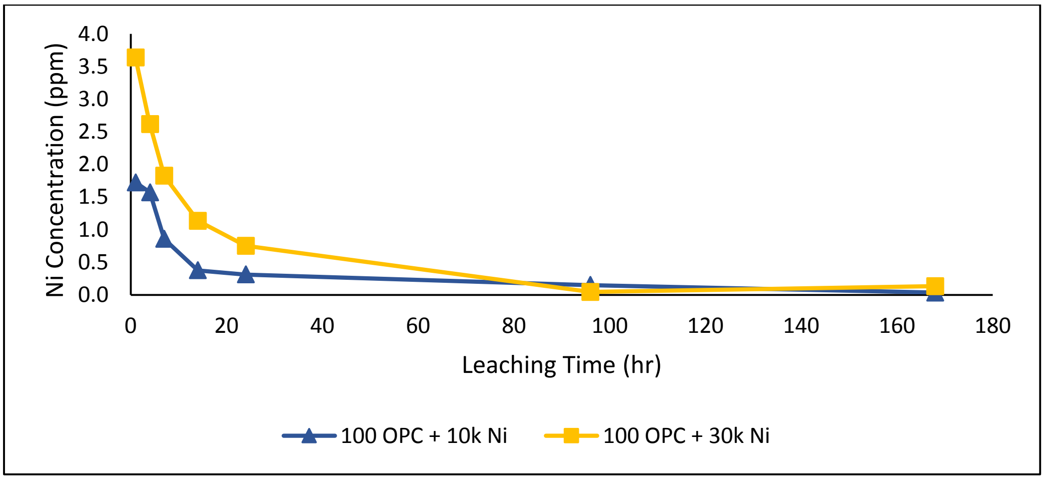


Figure 4.21: Ni Concentration in Leachate at Different Leaching Time for 100 % OPC

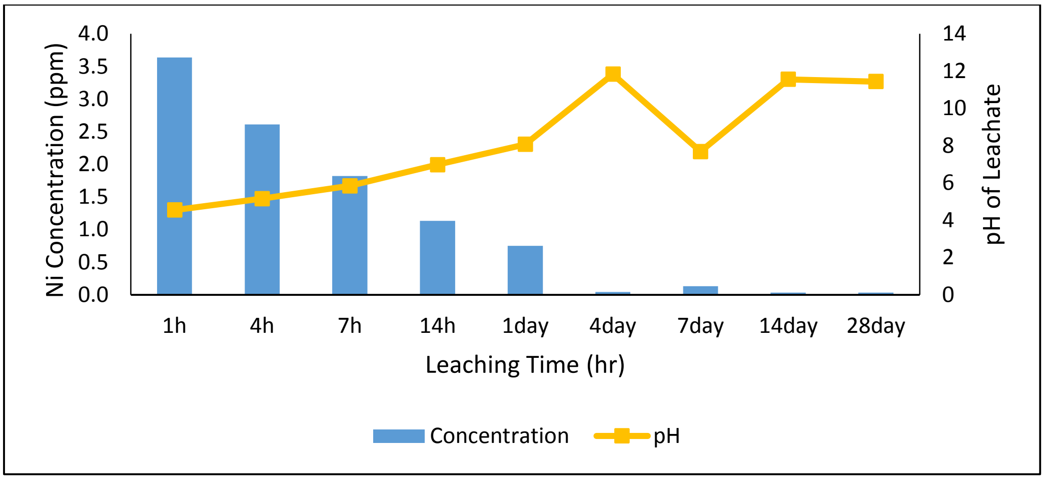


Figure 4.22: Ni Concentration and pH of Leachate versus Leaching Time for 100 % OPC + 30k Ni

The mechanism which immobilize the nickel ion is suggested to be precipitation. As stated by Yin *et al.* (2008), when the leachability of nickel is strongly depends on the pH, then the precipitation may be the main mechanism to immobilize the nickel in the cement block. At high pH, the nickel in the cement may presence in the form of insoluble nickel hydroxide. As the pH decreases, the $Ni(OH)_2$ may dissociated to form Ni^{2+} and OH^- and leached out from the cement matrix. Chindaprasirt *et al.*(2013), also suggested that the nickel may react with $Ca(OH)_2$ to form nickel hydroxide. Nickel hydroxide may subsequently transformed into nickel complexes which exists as amorphous phase. These nickel complexes may react with silicate matrix in the system (USEPA, 1993). The amorphous nickel complexes may adsorbed onto the S/S matrix as poorly crystallized precipitates and most probably to be entrapped within the matrix. In addition, the low leachability of nickel at latter stage may due to the adsorption of nickel in the interstitial phase of cement (Minocha and Goyal, 2014).

4.7.2 Effect of Replacement of RHA

The effect of the replacement of RHA on the leachability of nickel can be seen through the following figures. As shown in Figure 4.23 and Figure 4.24 below, the replacement of OPC with RHA has led to higher leaching of nickel as compared to pure OPC. This may due to the increase of porosity when RHA was added to replace OPC. Since the size of RHA is not as fine as the OPC powder, they cannot form a densely packed cement block as compared to 100 % OPC. The SEM image shown in Figure 4.25 and Figure 4.26 proved that the addition of RHA increased the porosity of the cement block.

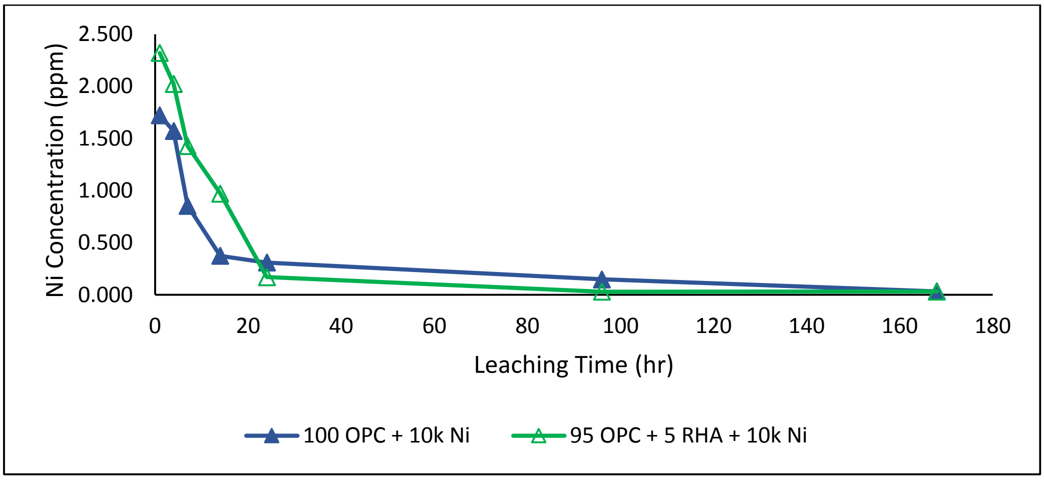


Figure 4.23: Ni Concentration versus Leaching Time for 100 % OPC + 10k Ni and 95 % OPC + 5 % RHA + 10k Ni

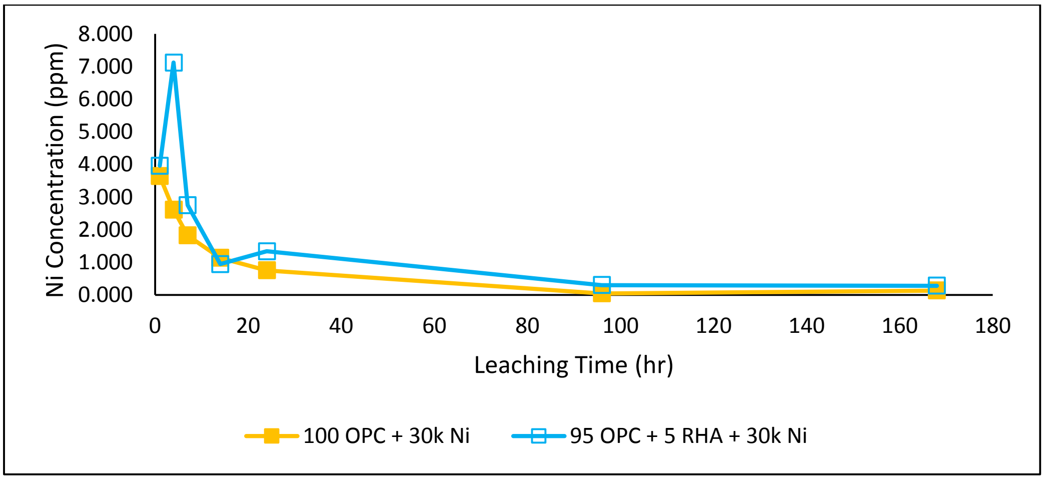


Figure 4.24: Ni Concentration versus Leaching Time for 100 % OPC + 30k Ni and 95 % OPC + 5 % RHA + 30k Ni

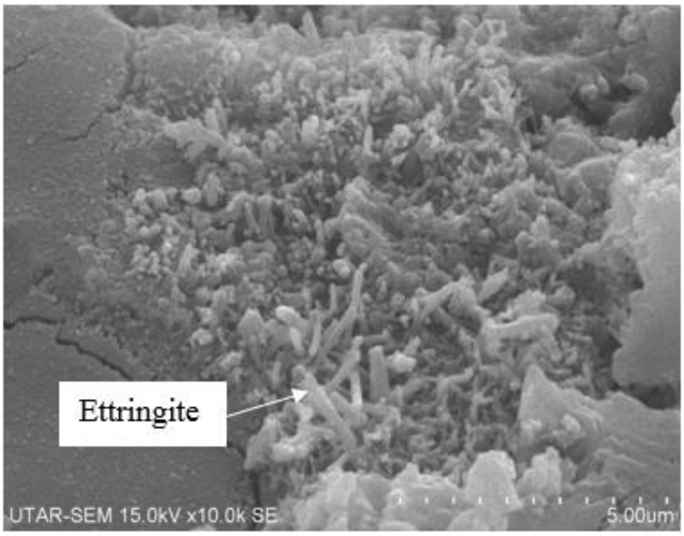


Figure 4.25: SEM Image for 100 % OPC + 10k Ni after 1 day Leaching Time

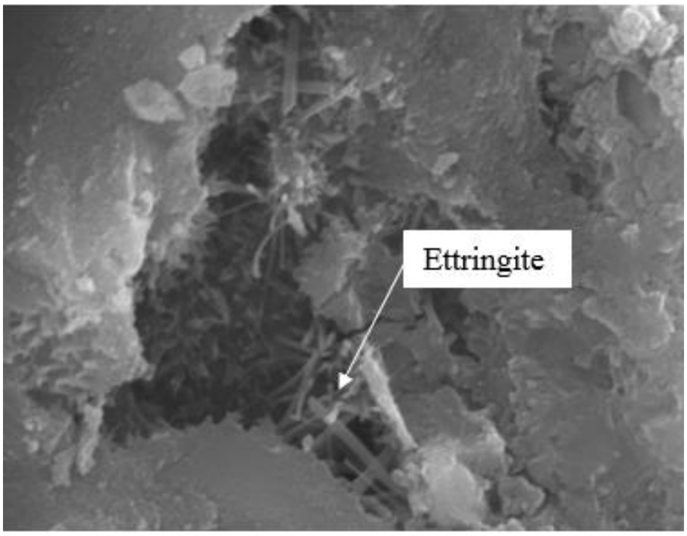


Figure 4.26: SEM Image for 95 % OPC + 5 % RHA + 10k Ni after 1 day Leaching Time

Furthermore, the replacement with RHA will reduce the calcium content in the cement which in other words, decreasing the pH of leachate (Yin *et al.*, 2008). As the pH of leachate decreases, more $Ni(OH)_2$ will be dissolved and leached out from the monolith. Eventually, combining both effect from high porosity of cement matrix and low pH of leachate will cause the sample with addition of RHA to have higher leachability of Ni^{2+} from the matrix. Nevertheless, this only happened at the early stage of leaching. After one week of leaching time, both sample with 100 % OPC and 95 % OPC + 5 % RHA were having very low amount of Ni leaching with concentration less than 0.2 ppm.

4.8 Leachability of Calcium

Apart from determining the nickel concentration in leachate, the calcium content was also being measured by ICP-OES. The purpose of measuring the calcium content in leachate is because calcium is the major builder of the cement block. During the leaching test, the acetic acid may corrode the surface or even deep inside the cement block. As this happens, the porosity of the cement block would increase significantly which in turns affecting the strength of the cement block.

As shown in Figure 4.27, all the mix design either doped with 10k ppm or 30k ppm of Ni ions were having the similar trend. During the first hour of leaching time, less amount of calcium was found in leachate. This was because the contact time was so short that the acetic acid only dissolve the calcium hydroxide on the surface of cement block. At the subsequent hours, the leachability rate of calcium was high because during this time, the leachate was still very acidic. The acidic leachate may go deep into the cement block to dissolve the calcium hydroxide in the cement block. After certain period, the acidic leachate has been neutralized by the hydroxide ions in the leachate. As the acidity of leachate reduced, the leachability of calcium decreased.

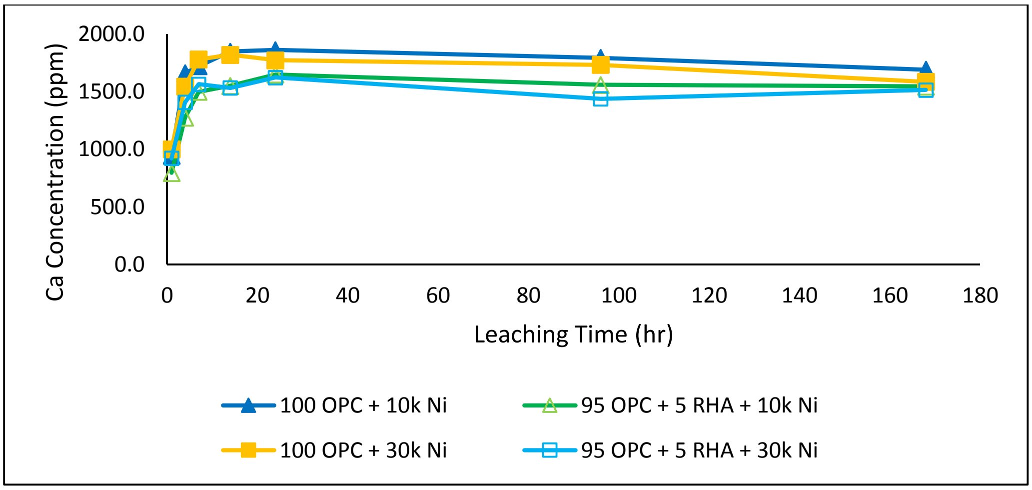


Figure 4.27: Calcium Leaching Concentration versus Leaching Time

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The aim and objectives in this study have been met throughout this research period. Firstly, the Whole Block Leaching (WBL) test with leaching time up to 28 days has been performed to study the leachability of nickel and the results obtained were satisfied. Some of the factors which brought about some effects to the leachability of nickel have been identified and monitored. Those factors are the amount of nickel doping, the leaching time, the pH of leachate and the composition of binders.

The concentration of nickel in leachate was measured by ICP-OES. The results have shown that the leach amount of nickel was highest at the early stage of leaching time but gradually reduced after 4 days. Besides, the leachability of nickel was higher when cement block has doped with higher concentration of nickel. Yet, after a long period of contact time, both of them has reached a constant concentration of 0.034 ppm.

Furthermore, the results also showed that the leachability of nickel was strongly depending on the pH of leachate. At the early leaching time, the leachability of nickel was high due to low pH of acetic acid. As time passed by, the calcium hydroxide, $Ca(OH)_2$ formed during hydration reaction has neutralized the acidity of acetic acid. The increase in leachate pH in turns reduce the leachability of nickel. Through this relationship, it can conclude that the nickel complex presence in the cement block is nickel hydroxide, $Ni(OH)_2$

On the contrary, the changes of the calcium concentration along the contact time was different from nickel. The amount of calcium in leachate was increased significantly within 1 day and maintain constant at around 1500 ppm after 1 day. This increased of calcium concentration was due to the dissolution of $Ca(OH)_2$ and calcium silicate hydrate (CSH) from cement block into leachate. The presence of hydroxide ions then increased the pH of leachate.

After the RHA have been used to replace OPC, the leachability of nickel was, in fact, increased. As shown in the results, the replacement of OPC by RHA has increased the concentration of nickel in leachate, after 28 days, from 0.034 ppm to 0.211 ppm. Meanwhile, the calcium concentration was reduced due to less OPC was used.

From the SEM images, it can be observed that the surface and inner part of cement block was eroded by the acidic leachate. The longer the leaching time, the higher the porosity of cement block.

As combining all the results obtained throughout this research, it can conclude that the nickel maybe safely entrapped into the cement-based system with a concentration less than 0.20 mg/L as required by the Environmental Quality Regulation. Although the replacement with RHA has increases the leachability of nickel and has just exceeded the environment regulation, the overall benefits that are given by RHA such as lower treatment cost can be considered as a compensation for this loss. In short, the stabilization/solidification technique may still considered to be effective for industries to treat waste nickel or even other kind of heavy metal.

5.2 Limitations and Recommendations

There were a few limitations in this research which can be improved or modified through some recommendation so that the results obtained will be more convincing and acceptable.

- The unconfined compressive strength test was not performed on the cement block after leachability test. The unconfined compressive strength of cement block must be measured in order to check whether they fulfilled certain construction requirement to sustain the pressure in landfill. The cement block dispose into landfill must withstand the harsh environment in landfill and not being crushed down. Some researchers have found that the addition of nickel will reduce the unconfined compressive strength of cement block. However, the addition of RHA may increase the strength which compensate the loss of strength due to presence of nickel.

- The size of mold made by cardboard was not consistent and it may deformed easily. In this research, the mold used to cast the cement block was made by cardboard and it will easily get soft and deform. When it is deformed, the size of cement block no longer be constant for each sample, this may lead to inaccurate result. Thus, it is recommended to use mold made by plastic or Perspex.

- The pure nickel used in this research may not represent the real industrial waste. In the real industrial waste, the nickel presence may not be pure nickel but it may presence in some other kind of nickel compound. Besides, the presence of other heavy metals in real industrial waste may affect the leachability of nickel. So, it is suggested to dope the real industrial waste into cement to study the leachability of nickel.

- The WBL test may not be able to simulate the real environment and conditions in landfill. WBL test only simulate the short-term scenario but not the worse-case scenario as can be simulated through the Toxicity Characteristic Leaching Procedure (TCLP) test. Furthermore, this research only use acetic acid to simulate landfill condition. It can be further extended to other conditions such as acid rain and normal rain. Through this extent, a more complete research will cover almost all the common scenario that the cement block may face.

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APPENDICES

APPENDIX A: Material Safety Data Sheet

APPENDIX B: Acceptable Conditions for Discharge of Leachate
(Environmental Quality Regulation 2009)

Environmental Quality (Control of Pollution From Solid Waste Transfer Station and Landfill) Regulations 2009
(PU(A) 433)

SECOND SCHEDULE
(Regulation 13)
ACCEPTABLE CONDITIONS FOR DISCHARGE OF LEACHATE

	Parameter (1)	Unit (2)	Standard (3)
(i)	Temperature	°C	40
(ii)	pH Value	-	6.0-9.0
(iii)	BOD_5 at 20°C	mg/L	20
(iv)	COD	mg/L	400
(v)	Suspended Solids	mg/L	50
(vi)	Ammoniacal Nitrogen		5
(vii)	Mercury	mg/L	0.005
(viii)	Cadmium	mg/L	0.01
(ix)	Chromium, Hexavalent	mg/L	0.05
(x)	Chromium, Trivalent	mg/L	0.20
(xi)	Arsenic	mg/L	0.05
(xii)	Cyanide	mg/L	0.05
(xiii)	Lead	mg/L	0.10
(xiv)	Copper	mg/L	0.20
(xv)	Manganese	mg/L	0.20
(xvi)	Nickel	mg/L	0.20
(xvii)	Tin	mg/L	0.20
(xviii)	Zinc	mg/L	2.0
(xix)	Boron	mg/L	1.0
(xx)	Iron (Fe)	mg/L	5.0
(xxi)	Silver	mg/L	0.10
(xxii)	Selenium	mg/L	0.02
(xxiii)	Barium	mg/L	1.0
(xxiv)	Fluoride	mg/L	2.0
(xxv)	Formaldehyde	mg/L	1.0
(xxvi)	Phenol	mg/L	0.001
(xxvii)	Sulphide	mg/L	0.50
(xxiii)	Oil and Grease	mg/L	5.0
(xxix)	Colour	ADMI*	100

ADMI- American Dye Manufactures Institute

APPENDIX C: Nickel Nitrate Solution Preparation

For 10k ppm of nickel ions, the mass of nickel (II) nitrate 6-hydrate required was calculated as follow,

Amount of nickel (II) ions required = 10000 ppm
Molecular weight of nickel = 58.6934 g/mol
Molecular weight of nickel (II) nitrate 6-hydrate = 290.79 g/mol

The parts per million (ppm) is equivalent to mg/L,

$$\begin{aligned}\text{Amount of nickel ions required} &= 10000\ \text{mg/L}\\ &= 10000\ \frac{\text{mg}}{\text{L}} \times \frac{\text{mol}}{58.6934\ \text{g}} \times \frac{\text{g}}{1000\ \text{mg}}\\ &= 0.1704\ \text{mol Ni}^{2+}/\text{L}\end{aligned}$$

Since every mole of nickel (II) nitrate 6-hydrate, $Ni(NO_3)_2{\cdot}6H_2O$ contains one mole of Ni^{2+} ions, thus

$$\begin{aligned}\text{Amount of nickel (II) nitrate 6-hydrate required} &= 0.1704\ \text{mol Ni}^{2+}/\text{L}\\ &= 0.1704\ \frac{\text{mol Ni}^{2+}}{\text{L}} \times \frac{\text{mol Ni(NO}_3)_2\cdot 6\text{H}_2\text{O}}{\text{mol Ni}^{2+}} \times \frac{290.79\ \text{g Ni(NO}_3)_2\cdot 6\text{H}_2\text{O}}{\text{mol Ni(NO}_3)_2\cdot 6\text{H}_2\text{O}}\\ &= \mathbf{49.5439\ g\ Ni(NO_3)_2{\cdot}6H_2O\ /L}\end{aligned}$$

By dissolving **49.5439 g** of nickel (II) nitrate 6-hydrate in 1 L of distilled water to achieve 10k ppm concentration of nickel (II) ions.

For 30k ppm of nickel (II) ions,

$$\begin{aligned}\text{Amount of nickel (II) ions required} &= 30000\ \text{mg/L}\\ &= 30000\ \frac{\text{mg}}{\text{L}} \times \frac{\text{mol}}{58.6934\ \text{g}} \times \frac{\text{g}}{1000\ \text{mg}}\\ &= 0.5111\ \text{mol Ni}^{2+}/\text{L}\end{aligned}$$

Since every mole of nickel (II) nitrate 6-hydrate, $Ni(NO_3)_2{\cdot}6H_2O$ contains one mole of Ni^{2+} ions, thus

Amount of nickel (II) nitrate 6-hydrate required = 0.5111 mol Ni^{2+}/L

$$= 0.5111\ \frac{\text{mol Ni}^{2+}}{\text{L}} \times \frac{\text{mol Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}}{\text{mol Ni}^{2+}} \times \frac{290.79\ \text{g Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}}{\text{mol Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}}$$

= **148.6317 g $Ni(NO_3)_2 \cdot 6H_2O$ /L**

Hence, **148.6317 g** of nickel (II) nitrate 6-hydrate was required to be dissolved in 1 L of distilled water for 30k ppm of nickel ion concentration.

APPENDIX D: Acetic Acid Preparation

The stoichiometric equation below shows the dissociation of acetic acid in water to form acetate ion and hydronium ion.

$$\mathrm{CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+}$$

The equilibrium constant of this dissociation can be expressed as,

$$K = \frac{[\mathrm{CH_3COO^-}][\mathrm{H_3O^+}]}{[\mathrm{CH_3COOH}][\mathrm{H_2O}]}$$

According to Bruce (2012), the water concentration is constant for all reactions happened in aqueous solution, therefore, the equilibrium constant can be expressed as a new constant known as acid dissociation constant, K_a. The hydronium ion, H_3O^+ can also express as hydrogen ion, H^+ as the H^+ ion would not stand alone and will form H_3O^+ with H_2O.

$$K_a = K[\mathrm{H_2O}] = \frac{[\mathrm{CH_3COO^-}][\mathrm{H^+}]}{[\mathrm{CH_3COOH}]}$$

As shown in the above stoichiometric equation, when one mole of acetic acid dissociate, one mole of acetate ion is produced together with one mole of hydrogen ion. Hence,

$$[\mathrm{CH_3COO^-}] = [\mathrm{H^+}]$$

Since acetic acid is a weak acid, it will not completely dissociate into ions, hence, some undissociate acetate ions will left behind in the solution. Let C_o be the initial concentration of acetic acid, hence,

$$K_a = \frac{[\mathrm{H^+}][\mathrm{H^+}]}{C_o - [\mathrm{H^+}]}$$

Yet, as compared to the initial concentration of acetic acid, the final concentration is so small and normally is negligible.

$$K_a = \frac{[\mathrm{H^+}]^2}{C_o}$$

In order to calculate the initial concentration of acetic acid, the concentration of H^+ must be known and it can be calculated from pH value.

$$\mathrm{pH} \quad = -\log[\mathrm{H^+}]$$

$[\mathrm{H}^+] = 10^{-\mathrm{pH}}$

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

$= 1.318\times 10^{-3}$ mol/L or M

From Bruce (2012), the K_a of acetic acid is 1.75×10^{-5}. Hence,

$$K_a = \frac{[\mathrm{H}^+]^2}{C_o}$$

$$C_o = \frac{[\mathrm{H}^+]^2}{K_a}$$

$$C_o = \frac{(1.318 \times 10^{-3})^2}{1.75 \times 10^{-5}}$$

= 0.100 mol/L or M

After knowing the concentration of acetic acid required to give pH 2.88, the volume of stock acetic acid can be calculated through dilution equation.

Purity of stock acetic acid	=	99.8 wt%
Molecular weight of acetic acid	=	60.052 g/mol
Density of acetic acid	=	1.05 g/cm^3

Concentration of stock acetic acid $= \frac{99.8\ \mathrm{g\ CH_3COOH}}{100\ \mathrm{g\ solution}} \times \frac{\mathrm{mol\ CH_3COOH}}{60.052\ \mathrm{g\ CH_3COOH}} \times \frac{1.05\ \mathrm{g\ solution}}{\mathrm{cm^3\ solution}} \times \frac{1000\ \mathrm{cm^3}}{1\ \mathrm{L}}$

= 17.450 mol CH_3COOH/ L or M

$M_1V_1 = M_2V_2$

$$V_1 = \frac{M_2V_2}{M_1}$$

$$= \frac{0.100\ \mathrm{M}(1000\ \mathrm{ml})}{17.450\ \mathrm{M}}$$

= **5.731 ml**

By diluting **5.731 ml** of stock acetic acid with distilled water to 1 L would result an acetic acid with pH of 2.88.

APPENDIX E: pH Value of Leachate

		pH of Leachate								
Duration / **Sample**	**Triplicate**	**1h**	**4h**	**7h**	**14h**	**1 d**	**4 d**	**7 d**	**14 d**	**28 d**
100 OPC	**1**	4.60	4.90	5.04	5.12	6.91	11.58	9.72	9.02	10.64
	2	4.67	4.74	5.25	5.29	8.37	11.69	8.62	8.77	10.74
	3	4.68	4.92	5.50	5.41	5.67	11.71	8.64	8.85	10.79
100 OPC + 10k Ni	**1**	4.51	5.36	5.25	5.79	7.83	11.74	7.59	11.27	11.21
	2	4.59	5.49	5.71	7.93	8.30	11.74	7.62	11.21	11.29
	3	4.53	5.40	5.41	9.90	7.74	11.99	7.67	11.10	11.11
100 OPC + 30k Ni	**1**	4.51	5.23	6.59	8.00	8.08	11.83	7.71	11.40	11.61
	2	4.56	5.03	5.49	7.15	8.32	11.80	7.65	11.42	11.32
	3	4.58	5.23	5.46	5.79	7.81	11.89	7.71	11.86	11.40
95 OPC + 5 RHA	**1**	4.47	5.48	6.26	6.25	11.31	11.68	11.74	11.47	7.16
	2	4.44	5.49	5.30	7.30	11.41	11.71	11.97	11.61	7.07
	3	4.58	5.38	5.64	5.85	9.43	12.03	11.66	11.39	7.21
95 OPC + 5 RHA + 10k Ni	**1**	4.55	5.04	6.19	5.57	10.68	11.59	11.49	11.49	7.05
	2	4.51	5.20	5.61	5.44	9.45	11.38	1.52	11.08	7.08
	3	4.51	5.18	5.09	7.65	10.48	11.55	11.47	11.37	7.08
95 OPC + 5 RHA + 30k Ni	**1**	4.35	4.92	5.81	6.94	7.58	7.17	7.05	7.14	7.26
	2	4.22	4.74	6.08	5.36	7.24	7.23	7.10	7.15	7.16
	3	4.27	5.20	5.43	6.76	7.33	7.17	7.32	7.13	7.21

Contact Time / Sample	Average pH Value of Leachate								
	1 h	**4 h**	**7 h**	**14 h**	**1 day**	**4 days**	**7 days**	**14 days**	**28 days**
100 OPC	4.65	4.85	5.26	5.27	6.98	11.66	8.99	8.88	10.72
100 OPC + 10k Ni	4.54	5.42	5.46	7.87	7.96	11.82	7.63	11.19	11.20
100 OPC + 30k Ni	4.55	5.16	5.85	6.98	8.07	11.84	7.69	11.56	11.44
95 OPC + 5 RHA + 0k Ni	4.50	5.45	5.73	6.47	10.72	11.81	11.79	11.49	7.15
95 OPC + 5 RHA + 10k Ni	4.52	5.14	5.63	6.22	10.20	11.51	8.16	11.31	7.07
95 OPC + 5 RHA + 30k Ni	4.28	4.95	5.77	6.35	7.38	7.19	7.16	7.14	7.21

APPENDIX F: ICP - OES Results of Leachate

		Ni Concentration in Leachate (ppm)								
Duration **Sample**	**Triplicate**	**1h**	**4h**	**7h**	**14h**	**1 d**	**4 d**	**7 d**	**14 d**	**28 d**
100 OPC + 10k Ni	**1**	1.552	1.505	0.873	0.552	0.258	0.093	0.038	0.032	0.032
	2	1.854	1.581	0.795	0.218	0.278	0.039	0.032	0.033	0.034
	3	1.767	1.628	0.899	0.354	0.394	0.316	0.030	0.031	0.036
100 OPC + 30k Ni	**1**	3.853	2.351	1.862	1.166	0.593	0.043	0.330	0.032	0.035
	2	3.495	2.595	1.949	1.406	1.265	0.034	0.034	0.033	0.034
	3	3.569	2.897	1.660	0.829	0.392	0.053	0.031	0.033	0.034
95 OPC + 5 RHA + 10k Ni	**1**	2.187	2.111	1.308	1.223	0.302	0.031	0.033	0.036	0.176
	2	2.165	1.973	1.415	0.480	0.089	0.032	0.032	0.035	0.163
	3	2.609	1.990	1.559	1.213	0.122	0.031	0.033	0.034	0.203
95 OPC + 5 RHA + 30k Ni	**1**	4.044	7.667	2.727	0.448	1.676	0.403	0.371	0.224	0.153
	2	3.549	6.217	2.852	2.023	0.380	0.258	0.229	0.242	0.278
	3	4.280	7.486	2.674	0.359	1.945	0.233	0.245	0.177	0.201

		Ca Concentration in Leachate (ppm)								
Duration **Sample**	**Triplicate**	**1h**	**4h**	**7h**	**14h**	**1 d**	**4 d**	**7 d**	**14 d**	**28 d**
100 OPC	**1**	938.2	1483.0	1687.0	1755.0	1954.0	1665.0	1639.0	1627.0	1405.0
	2	956.6	1475.0	1882.0	1722.0	4030.0	1823.0	1769.0	1573.0	1648.0
	3	889.0	1295.0	1503.0	1478.0	2060.0	2422.0	1790.0	1654.0	1656.0
100 OPC + 10k Ni	**1**	938.6	1668.0	1702.0	1916.0	1817.0	1811.0	1749.0	1554.0	1297.0
	2	979.8	1637.0	1809.0	1759.0	1903.0	1775.0	1684.0	1588.0	1297.0
	3	912.8	1675.0	1653.0	1869.0	1866.0	1796.0	1642.0	1706.0	1424.0
100 OPC + 30k Ni	**1**	948.4	1591.0	1751.0	1807.0	1866.0	1800.0	1553.0	1457.0	1268.0
	2	1034.0	1435.0	1692.0	1800.0	1647.0	1732.0	1581.0	1433.0	1280.0
	3	1019.0	1610.0	1897.0	1856.0	1808.0	1668.0	1624.0	1490.0	1286.0
95 OPC + 5 RHA	**1**	861.7	1471.0	1535.0	1470.0	1555.0	1494.0	1339.0	1962.0	1019.0
	2	798.1	1357.0	1454.0	1473.0	1563.0	1525.0	1341.0	1233.0	1284.0
	3	2631.0	1459.0	1399.0	773.3	1531.0	1457.0	1330.0	1236.0	1090.0
95 OPC + 5 RHA + 10k Ni	**1**	807.7	1307.0	1298.0	1480.0	1624.0	1542.0	1559.0	1199.0	1456.0
	2	772.9	1208.0	1682.0	1653.0	1677.0	1573.0	1586.0	1390.0	1305.0
	3	801.8	1308.0	1520.0	1521.0	1646.0	1562.0	1491.0	1327.0	1138.0
95 OPC + 5 RHA + 30k Ni	**1**	935.3	1436.0	1557.0	1637.0	1634.0	1487.0	1567.0	1212.0	860.2
	2	875.4	1295.0	1621.0	1351.0	1660.0	1476.0	1576.0	1195.0	1055.0
	3	954.4	1491.0	1516.0	1611.0	1576.0	1352.0	1402.0	1160.0	871.4

	Average Ni Concentration in Leachate (ppm)								
Contact Time **Sample**	**1 h**	**4 h**	**7 h**	**14 h**	**1 day**	**4 days**	**7 days**	**14 days**	**28 days**
100 OPC + 10k Ni	1.724	1.571	0.856	0.375	0.310	0.149	0.033	0.032	0.034
100 OPC + 30k Ni	3.639	2.614	1.824	1.134	0.750	0.043	0.132	0.033	0.034
95 OPC + 5 RHA + 10k Ni	2.320	2.025	1.427	0.972	0.171	0.031	0.033	0.035	0.181
95 OPC + 5 RHA + 30k Ni	3.958	7.123	2.751	0.943	1.334	0.298	0.282	0.214	0.211

	Average Ca Concentration in Leachate (ppm)								
Contact Time **Sample**	**1 h**	**4 h**	**7 h**	**14 h**	**1 day**	**4 days**	**7 days**	**14 days**	**28 days**
100 OPC	927.9	1417.7	1690.7	1651.7	2681.3	1970.0	1732.7	1618.0	1569.7
100 OPC + 10k Ni	943.7	1660.0	1721.3	1848.0	1862.0	1794.0	1691.7	1616.0	1339.3
100 OPC + 30k Ni	1000.5	1545.3	1780.0	1821.0	1773.7	1733.3	1586.0	1460.0	1278.0
95 OPC + 5 RHA	1430.3	1429.0	1462.7	1238.8	1549.7	1492.0	1336.7	1477.0	1131.0
95 OPC + 5 RHA + 10k Ni	794.1	1274.3	1500.0	1551.3	1649.0	1559.0	1545.3	1305.3	1299.7
95 OPC + 5 RHA + 30k Ni	921.7	1407.3	1564.7	1533.0	1623.3	1438.3	1515.0	1189.0	928.9

APPENDIX G: EDX Results of Cement Block

		Leaching Time			
Sample	**Elements**	**1 h**	**1 day**	**7 days**	**28 days**
100 % OPC + 0 ppm Ni	**Ca (wt %)**	65.14	67.69	62.82	64.75
	O (wt %)	15.27	12.88	16.79	14.08
	Si (wt %)	13.04	13.25	13.91	14.28
	Ni (wt %)	ND	ND	ND	ND
	Mg (wt %)	1.28	1.42	1.54	1.65
	Al (wt %)	3.16	3.10	3.23	3.52
100 % OPC + 10 ppm Ni	**Ca (wt %)**	63.70	70.98	66.26	73.97
	O (wt %)	13.51	10.66	12.19	8.90
	Si (wt %)	13.90	11.23	13.06	10.61
	Ni (wt %)	0.75	0.47	0.72	1.27
	Mg (wt %)	1.59	1.07	1.56	0.83
	Al (wt %)	3.46	2.89	3.21	2.26
100 % OPC + 30 ppm Ni	**Ca (wt %)**	59.53	79.71	64.63	50.26
	O (wt %)	17.33	8.28	14.89	15.45
	Si (wt %)	13.63	8.81	14.20	16.73
	Ni (wt %)	0.97	0.77	1.37	3.04
	Mg (wt %)	1.67	ND	ND	2.42
	Al (wt %)	3.49	2.00	4.02	4.02

**ND = Not Detected*

		Leaching Time			
Sample	**Elements**	**1 h**	**1 day**	**7 days**	**28 days**
95 % OPC + 5 % RHA + 0 ppm Ni	**Ca (wt %)**	54.05	59.42	74.36	50.37
	O (wt %)	23.38	8.74	8.38	13.70
	Si (wt %)	14.77	12.98	12.22	5.18
	Ni (wt %)	ND	ND	ND	ND
	Mg (wt %)	1.59	1.35	1.30	5.00
	Al (wt %)	2.48	2.98	2.36	13.47
95 % OPC + 5 % RHA + 10 ppm Ni	**Ca (wt %)**	65.85	45.50	74.21	48.47
	O (wt %)	11.79	14.85	7.61	13.51
	Si (wt %)	14.95	17.14	8.82	7.06
	Ni (wt %)	0.43	0.41	1.00	1.05
	Mg (wt %)	1.83	1.46	1.03	3.11
	Al (wt %)	2.24	2.88	2.43	26.81
95 % OPC + 5 % RHA + 30 ppm Ni	**Ca (wt %)**	66.57	48.36	73.24	75.74
	O (wt %)	10.01	13.09	7.22	6.63
	Si (wt %)	9.86	13.69	7.07	10.17
	Ni (wt %)	3.47	2.17	3.61	2.14
	Mg (wt %)	1.40	1.37	ND	0.81
	Al (wt %)	2.75	3.66	3.49	2.49

**ND = Not Detected*

APPENDIX H: FYP Poster Competition