EXPERIMENTAL INVESTIGATION AND GEOCHEMICAL MODELLING FOR INDUSTRIAL HAZARDOUS WASTE MATERIAL

Thesis

Submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

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DEPARTMENT OF CIVIL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY KARNATAKA,

SURATHKAL, MANGALORE - 575 025

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DECLARATION

by the Ph.D. Research Scholar

I hereby declare that the Research Thesis entitled, "**Experimental Investigation and Geochemical Modelling for Industrial Hazardous Waste Material"** which is being submitted to the National Institute of Technology Karnataka, Surathkal in partial fulfilment of the requirements for the award of the **Degree of Doctor of Philosophy in Civil Engineering** is a *bonafide report of the research work carried out by me.* The material contained in this Research Thesis has not been submitted to any University or Institution for the award of any degree.

(Krishnamurthy M. P.)

Place: NITK, Surathkal

Reg. No. 165076CV16F10

Date: 31st July, 2019

Department of Civil Engineering

CERTIFICATE

This is to *certify* that the Research Thesis entitled "**Experimental Investigation and Geochemical Modelling for Industrial Hazardous Waste Material"** submitted by **Krishnamurthy M P, (Reg. No.165076CV16F10)** as the record of the research work carried out by him is *accepted as the Research Thesis submission* in partial fulfillment of the requirements for the award of degree of Doctor of Philosophy.

Dr. C. P. Devatha	**Dr. K. Swaminathan**
Research Guide	Chairman-DRPC

ABSTRACT

Till the recent past the cities were small and sparsely populated and the amount of industrial solid waste generated is very less which was stored in the industrial backyards. Due to the rapid increase in population, urbanization and industries, it resulted in the generation of huge quantity of industrial solid waste with wide range of characteristics which when directly disposed on the dumpsite would directly or indirectly affect the surrounding environment and human health. The objectives set include understanding the leaching mechanisms (dissolution and sorption) from the industrial waste such as Ferrochrome Ash (FCA) and Biomedical Waste Bottom Ash (BMWBA), geochemical modelling of leached heavy metals were carried to identify the major oxidation states of leached mineral/metals from FCA and BMWBA and immobilization heavy metals present in the BMWBA using the Ground Granular Blast Furnace Slag (GGBFS). For FCA and BMWBA leaching experiments have been carried out to analyse the leaching concentration of metals such as Hg, Se, Co, Ni, Fe, As, Cd, Zn, Pb, Ca, Cu and Cr by adopting standard procedures viz. ASTM D3987-12, TCLP 1311 and USEPA 1313 (Under various pH conditions 3, 5, 7, 9 and 11) to assess the interactions. Geochemical modelling carried out using Visual MINTEQA 3.1 to recognize the dominant chemical species of redox sensitive metals in leachates. In this investigation, 0, 10, 20 and 30% of GGBFS was added to BMWBA to carried out the immobilization of heavy metals with the help of alkaline solutions (sodium silicate solution and sodium hydroxide solution). From the results of all the three leaching test methods for FCA found that Cr, As, Hg, and Se and BMWBA Hg, Pb, Se and As elements were leaching in very high concentrations. Geochemical modelling for leached concentrations of Ca, Cd, As, Cu, Cr, Fe, Ni, Se and Zn in the FCA and BMWBA were summarized based on their dominant oxide, hydroxide and carbonate minerals and leaching controlling solids for each element of interest. From the solidification/stabilization results shows that the compressive strength of overall mixture of BMWBA and GGBFS solidified matrices were between 0.75 to 10.52 MPa. The process of immobilizing heavy metals a physically encapsulated process, diffusion may cause cation should be substituted by another cation. The leaching test results of the solidified matrices show that the GGBFS addition was able to immobilize the toxic metals found in BMWBA.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
Ag	Silver
AL	Alkaline Solution
Al	Aluminium
Al_2O_3	Aluminium Oxide
ANC	Acid-base Neutralization Capacity
As	Arsenic
ASTM	American Society for Testing Materials
ATSDR	Agency for Toxic Substance and Disease Registry
Ba	Barium
BMWBA	Biomedical Waste Bottom Ash
BMW	Biomedical Waste
Cd	Cadmium
CPCB	Central Pollution Control Board
Co	Cobalt
Cr	Chromium
CLT	Column Leach Test
DNA	Deoxyribonucleic Acid
EU	European Union
EPA	Environmental Protection Agency
EDAX	Energy Dispersive X-Ray Analysis
Fe	Iron
FCA	Ferrochrome Ash
GGBFS	Ground Granulated Blast Furnace Slag
Hg	Mercury
IAP	Ion Activity Product
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
K	Potassium
Mg	Magnesium

Mn	Manganese
MSW	Municipal Solid Waste
MSWI	Municipal Solid Waste Incineration
MEP	Multiple Extraction Procedure
Na_2O	Sodium Oxide
NaOH	Sodium hydroxide
Ni	Nickel
OPC	Ordinary Portland Cement
ORP	Oxidation Reduction Potential
Pb	Lead
RPM	Rotation Per Minute
Se	Selenium
SEM	Scanning Electron Microscopy
SH	Sodium Hydroxide
SI	Saturation Index
SS	Sodium Silicate
S/S	Solidification/Stabilizations
SPLP	Synthetic Precipitation Leaching Procedure
TCLP	Toxicity Characteristic Leaching Procedure
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
XRD	X-Ray Diffraction
Zn	Zinc
ZPC	Zero Potential Charge

CHAPTER 1

INTRODUCTION

1.1 General

Past 200 years in world history has seen significant changes in the environment due to rapid urbanization and industrialization, which has projected the lifestyle of human beings to a higher level. However, on the parallel means has generated several issues related to the environment due to improper regulations on the product manufacturing and waste management especially by the industries. Major waste generating industries are thermal power plants (producing coal ash), integrated Iron and Steel mills (producing blast furnace slag and steel melting slag); among non-ferrous industries, aluminium, zinc, sugar industries, pulp and paper industries. Most preferred method of disposal for these wastes are Landfill or landfill followed by incineration. This ash thus dumped in landfill or used in any construction material may pose a threat when the heavy metals or hazardous substances in them leach into the environment.

Biomedical Waste Bottom ash (ash left after incineration of medical waste) and Ferrochrome ash (dust particles released during the ferrochrome production process) consists of harmful components such as Cd, Cr, Pb, Zn and Ni (Sofilic et al., 2004; Cohen and Petrie, 2005; Laforest and Duchesne, 2005). These components could cause serious environmental contamination if they leach in to soil, air or water.

India generates around 484 tons of biomedical waste per day of which 92.1% is treated by incineration, autoclaving, hydroplaning, plasma pyrolysis, microwaving and chemical disinfection methods (CPCB, 2016) and the remaining 7.9 % could not be treated properly (Bio-Medical Waste Management Rules, 2016) and is disposed in improper ways. Hence, there is a possibility that it affects the environmental system through the means of contaminated water bodies, leaching, soil pollution, etc. Though BMW rules are in force to come across upon serious policies to reduce the contamination levels due to biomedical waste; however, it is mainly classified as 85% non-infectious and 15% infectious / hazardous to the environment. The unscientific disposal of infectious material causes a serious threat to the surrounding environment.

It is considered as toxic waste since it may mobilize pathogenic activity and cause objectionable impacts on humans and the surrounding nature (Askarian et al., 2004).

Ferrochrome ash is produced globally around 12 to 16 million tonnes per annum (Richard, 2015). India is one of the largest ferrochrome producing country (Sahu et al., 2016). Apart from wasting large quantity of valuable land in the form of a dumping site, FCA also pollutes the ground water and nearby surface water sources by its leaching behaviour. The leaching behaviour of ferrochrome dust was investigated by pore water extrusion, sequential chemical extraction, equilibrium extraction and TCLP methods. Leaching behaviour of Cr and Zn was studied with various pH and L/S ratios (Cohen and Petrie, 2005). Even though it has been shown that FCA is a useful industrial by product in the construction practices, its potential impacts on environment must be considered for environmentally safe practices.

Various leaching studies were used till date to identify the behaviour of leaching materials, such as ASTM D 3987 (Standard Test Method for Shake Extraction of Solid Waste with Water), TCLP (Toxicity Characteristic Leaching Procedure), SPLP (Synthetic Precipitation Leaching Procedure) and so on. Using USEPA test results, geochemical analysis was conducted to know the dissolution/solubility of samples. Leaching potential of various wastes is influenced by various chemical factors. The chemical factors involve equilibrium and kinetic reactions which are faster and slower in reaction time, desorption properties of the constituent materials, pH of the waste dumped, liquid in non-aqueous phase, pH of the leachate and complexation with organic or inorganic materials.

Geochemical modelling is the exercise of the utilization of chemical kinetics and chemical thermodynamics, or both to identify the chemical interaction effects. Geochemical modelling is used in various field exercise, ecological protection remediation works (Zhu and Anderson, 2002). It is used in various field applications such as environmental protection and remediation, economic geology and petrochemical industries. Models can be built such as mobility and breakdown of pollutants in flowing surface and ground water, to know the composition of drinking water, the dissolution and formation of minerals and rocks in geologic formation in response to injection of carbon dioxide, steam or waste water and also generation of acidic water and leaching of heavy metals in mining waste deposits.

Several investigations (Mudd et al., 2004; van der Sloot and Dijkstra, 2004; Wang et al., 2004) have identified the controlling mechanisms for release of coal combustion residues like fly ash, i.e., Sorption control and Solubility control mechanisms. Earlier studies (Komonweeraket et al., 2015; Cetin and Aydilek, 2013) had adopted geochemical modelling for the various soil stabilization work and road embankment works, but very less study found in the cause of industrial hazardous waste management.

Komonweeraket et al. (2015a) investigated leaching governing mechanism of arsenic, barium, calcium, cadmium, magnesium, selenium and strontium from fly ash, soil and mixture of fly ash and soil identified at various pH range through geochemical modelling. The model prediction shows that leaching of magnesium and cadmium were governed by minerals of carbonates. Arsenic and selenium were governed by the sorption mechanism. Analogous to these (Komonweeraket et al., 2015b) and (Zhang et al., 2016) performed geochemical modelling for fly ash and MSW incineration fly ash and results obtained are in good agreement. Hence, it is proved that geochemical modelling is capable of predicting the speciation of soluble species. This supports the need for S/S is necessary technique to treat the industrial waste substance before disposal when they were tested for leaching with TCLP disposal guidelines.

Solidification/stabilization (S/S) utilizing Portland cement was developed in the 1950s for stabilizing nuclear waste, but the process was eventually expanded further for treating hazardous waste by the 1970s. The process has been identified by the USEPA as the best demonstrated available technology for 57 regulated hazardous wastes (Batchelor, 2006). S/S has been shown to be a viable treatment process for many heavy metals bearing solid wastes (Kumpienem et al., 2007; Mickley, 2008; Moon et al., 2009). S/S consists of two processes: solidification (improving physical properties of waste) and stabilization (converting contaminants to less mobile and toxic forms).

S/S is a pre-landfill hazardous waste management technique, which is used to treat of the various industrial hazardous material but specifically for the waste containing toxic heavy metals (Malviya and Chaudhary, 2006). The primary goal of the stabilisation is to minimise the leaching of toxic contaminates. While the solidification refers to the binding material like cement that is used to compress the hazardous substance to restrain toxic contaminates and decrease leaching of toxic heavy metals (Lam et al., 2010). The S/S of ash obtained from the municipal solid waste incineration plant were investigated by various researchers using the geopolymerization technique (Komnitsas et al., 2013; Lancellotti et al., 2010; Zheng et al., 2010; Galiano et al., 2011). However, there is a less evidence of studies on S/S of industrial ashes.

Solidification can increase waste strength and improve microstructure. S/S removes free liquids from waste through pozzolanic reactions and the S/S blocks will have a lower surface area/volume ratio compared to coal fly ash thereby significantly decreasing the surface area exposure to water in the landfill. The produced S/S solid will also be less permeable than other materials such as coal fly ash in the landfill; hence, water is more likely to flow around instead of through the material thereby decreasing leaching potential (Batchelor, 2006).

The goal of stabilization is to decrease the mobility and toxicity of contaminants. Contaminants in the dissolved phase are free to diffuse down a pore to the external environment. Precipitation and adsorption are two important mechanisms of heavy metal immobilization in S/S (Batchelor, 2006). In addition, coal fly ash contains a significant amount of Fe (III) and Al (III) oxides which can provide active sites for heavy metal sorption (Cornelis et al., 2008a; Garrabrants, 2010).

Oxyanions can also be chemically incorporated into mineral phases such as Friedel's salt or ettringite (Goni et al., 2001; Baur et al., 2003b; Chrysochoou et al., 2006; Matschei et al., 2007; Wu et al., 2010). pH has a significant impact on all the above mentioned immobilization mechanisms. Typically, S/S solids will have a high pH due to the high CaO content. The three most important cement minerals for heavy metal immobilization in S/S are monophase ($Ca_2(Al,Fe)(OH)_6).X\cdot xH_2O$), ettringite ($Ca_6Al_2(OH)_{12}(SO_4)_3\cdot 26H_2O$) and C-S-H (Keller, 2002). Monophases are denoted by the shorthand AFm-X in cement chemistry where X is an anion and ettringite is denoted by the shorthand AFt-SO4 (Goni et al., 2001; Matschei et al., 2007; Guerrero et al., 2009; Balonis et al., 2010; Wu et al., 2010).

The studies revealed that the heavy metal contamination due to leaching of bottom ash from the incineration plant/hospital is conventionally dealt by two major options, i.e., stabilization and solidification as reported in various literature. Hence, it is imperative to investigate its chemical composition which is one of the crucial factors that decides the leaching process to occur in different concentrations.

Nevertheless, leaching behaviour of BMA and FCA is studied by various authors but not investigated the controlling mechanism so as to adopt proper remedial measures. Therefore, knowledge towards the release of toxic/hazardous elements in the different environmental matrix is important in order to evaluate the behaviour of substances and the range of their impacts. With this as background, a through literature survey was done in line with the above discussion, objectives were derived from the gaps identified in the area and addressed appropriately.

1.2 Objectives of the study

The objectives of the proposed research work include:

- The leaching mechanisms of toxins/hazardous substances (dissolution and sorption) from FCA and BMWBA.
- The geochemical modelling of leached heavy metals to identify the major oxidation states of leached mineral/metals.
- To study the immobilization of heavy metals using the Ground Granulated Blast Furnace Slag (GGBFS).

1.3 Thesis outline

The thesis has been organized into six chapters as:

Chapter 1 is a general introduction and discusses the objectives and outline of the thesis.

Chapter 2 is the literature review on the leaching of toxic metals, leaching controlling mechanism, geochemical modelling and solidification/stabilization mechanisms.

Chapter 3 presents the materials and methods used for the experimental studies on leaching of industrial ashes and describes the experiments.

Chapter 4 presents results and discussion for a) leaching test conducted using various test methods and leaching controlling mechanisms b) geochemical modelling for leached toxic metals c) solidification/stabilization of toxic industrial ashes.

Chapter 5 outlines the conclusions and future scope of work.

CHAPTER 2

LITERATURE REVIEW

2.1 General

Due to ever increasing stringent regulation across the world on solid waste management, there is always a need for the researchers to work on different technologies and their up gradations to meet the requirements. Among various test methods are available to determine the toxic metal leaching and controlling mechanisms, and stabilization/solidification process is the best option for safe landfill disposal practice. In the present chapter efforts were made to present a summary of work being done in the current area of research to snap out the drawbacks or gaps.

2.2 Industrial hazardous waste

The current scenario of environmental problems faced is due to improper vision and planning of the products and wastes generated by the industries. Domestic solid waste management has become a herculean task for the majority of the communities around the world because of the improper planning and/or implementation of plans during the design stages of the communities.

Hazardous waste demands a special focus due to its potentially harmful nature and subsequent disastrous effects on the environment. Also, it has notable threats to human health. The hazardous wastes can be broadly distinguished as solid, liquid or gaseous form depending on its physical state. Based on the category of waste, the treatment and stabilization methods may be selected.

Ignitability, reactivity, corrosivity, toxicity are the four primary characteristics which separate hazardous wastes from other wastes in terms of all stages of handling and management.

Ignitability deals with the property of the waste to catch fire. Reactivity is the ability to react with any material and leads to the formation of some complex which is difficult to handle. Hazardous wastes are generally corrosive which is why it is difficult to handle and manage. They also have the tendency to harm the biological components of the environment to even the extent of fatality.

2.3 Toxic heavy metals and their mechanisms

Higher electrical conductivity, luster and pliability are the basic properties of the metals. Metals originate in the crust of the earth and their chemical structure varies from one place to another place. The distribution of metals in the surrounding environment is observed by the characteristics of the metal and by different environmental components (Babatunde, 2008; Khlifi and Hamza-Chaffai, 2010). 5 gm/cm^3 of density is considered while categorizing the heavy metals and the ill effects on the surrounding environment and human health risks are considered in this aspect (Jarup, 2003).

Heavy metals are important ecological and environmental contaminants and their toxicity is a major threat to the nutritional, evolutionary and ecological reasons (Sharma and Reddy, 2004; Jaishankar et al., 2013; Nagajyoti et al., 2010). Laxhmi and Kaushik (2019) remarked that heavy metals are non-biodegradable and cause long term threat to environment. Source of the heavy metals include urban runoff, sewage discharge, mining, industrial effluents, soil erosion, natural weathering and other aspects. Heavy metals reach the surrounding environment through various natural and human activities. (Morais et al., 2012). Heavy metals that are generally identified in wastewater are zinc, nickel, lead, copper, chromium, cadmium and lead all which cause dangers for the wellbeing of humans and the earth (Lambert et al., 2000). Thakur and Ojha (2010) studied the several rivers in Asia play a significant role in movement of sediments in rivers. Toxic pollutants from the coastal sediment particle by heavy metals can cause serious threat to the marine environment. Heavy metal pollution in food crops and their entry mechanism from the anthropogenic and natural sources resulting impacts on surrounding humans is as shown in Figure 2.1.

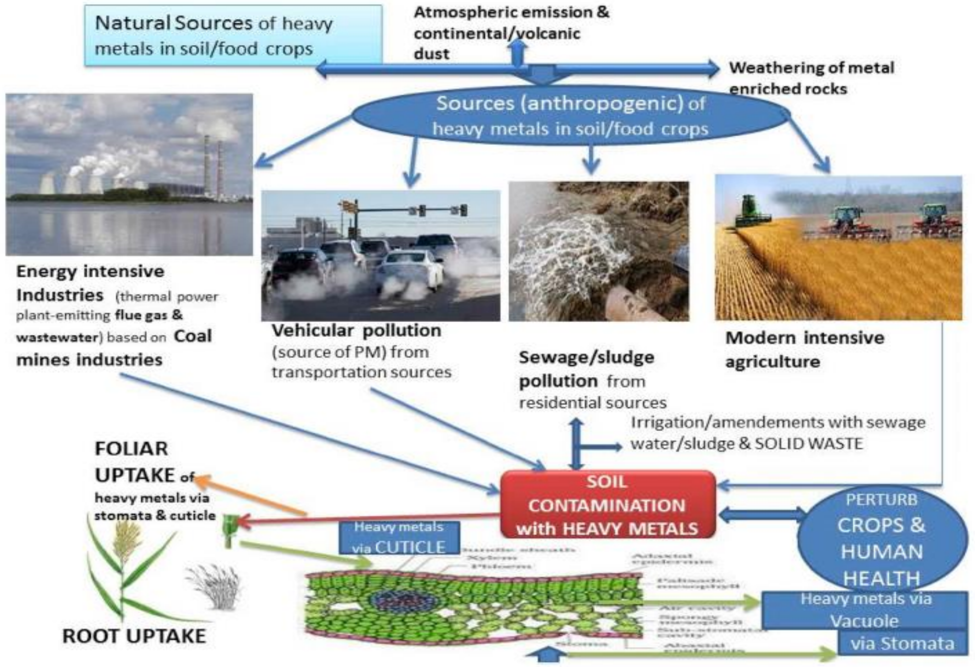


Figure 2.1 Heavy metal pollution in food crops and their entry mechanism from the anthropogenic and natural sources resulting impacts on surrounding humans (Rai et al. 2019)

Destructive endeavours or unintentional utilization by youngsters may likewise result in the acute poisoning problems (Saha et al., 1999; Mazumder, 2008; Rajagopal, 2013). Arsenic influences essentially the sulphydryl gathering of cells leading to failure of respiration of the cells and hence it can be called as a protoplastic poison (Gordon and Quastel, 1948).

2.3.1 Mechanism of arsenic toxicity

Unsafe inorganic arsenic mixes get methylated with the help of microorganisms, algae, fungi and people during its biotransformation to produce monomethylarsonic and dimethylarsinic acids. In this activity of biotransformation, the species of inorganic arsenic are enzymatically changed to methylated arsenicals that are the end metabolites and biomarker of continuing arsenic contact. The acid of the monomethylarsonic is the transitional product is observed to be exceptionally dangerous contrasted with other arsenicals, conceivably responsible carcinogenesis instigated by arsenic (Singh et al., 2007).

2.3.2 Lead

Lead is one of the significant dangerous metal and its extensive use has caused broad surrounding ecological and environmental pollution and human health issues across the globe. Lead is metal with brightness, silvery colour and somewhat bullish colour in dry climatic conditions. It starts to dis-colour once it contacts with surrounding air in the atmosphere, in this way framing a complex blend of mixes, contingent upon the individual conditions.

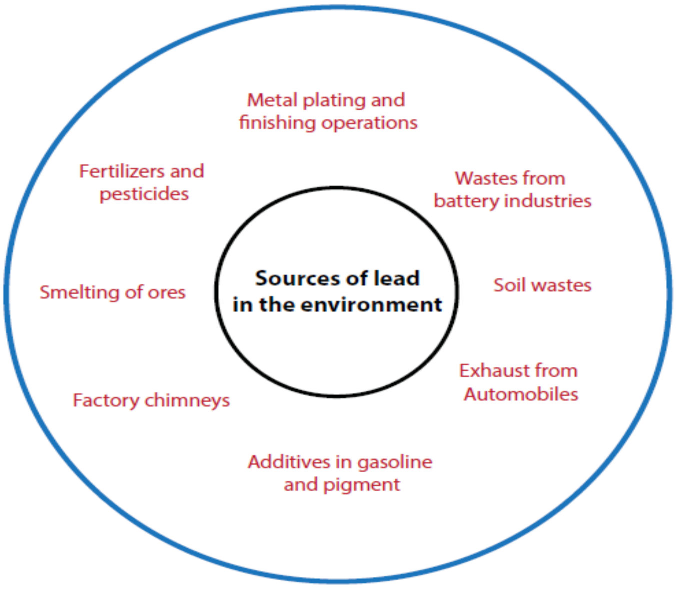


Figure 2.2 Lead contamination sources in the ecological system (Sharma and Dubey, 2005)

Figure 2.2 demonstrates different lead contamination sources in the ecological system (Sharma and Dubey, 2005). Exposing the lead to humans is mainly because of the industrial activities, contaminated drinking water consumption, smoking and food habits. The lead source may be the house paints, fuels, batteries and toys (Thurmer et al., 2002).

Around 100 - 200,000 tons of lead for every year is being discharged from vehicles in the United States. A certain quantity of this lead generated is inhaled by the plants, obsessed into the soil and streamed into the water sources, subsequently human exposure of lead is either because of the food or by the drinking water contamination (Goyer, 1990). Lead is a significantly poisonous toxic substance and it disturbs the different plant physiological activities. A plant with higher levels of the lead depositions gradually increase the generation of the species of reactive oxygen causing damage to the lipid membrane and finally leads to harm the chlorophyll and photosynthetic procedures and it impacts the plant growth to the maximum extent (Najeeb et al., 2014). Few experimental investigations show that lead is proficient of preventing the tea plants growth by diminishing the biomass, also spoils the quality of tea by changing its segmental nature (Yongsheng et al., 2011).

2.3.2 (a) Mechanism of lead toxicity

Lead is poisonous to the living cells in which the oxidative stress is caused by following the ionic system. The unevenness in creating the free radicals and production of antioxidants for detoxifying the intermediate reactants is due to the oxidative stress caused in the living cells.

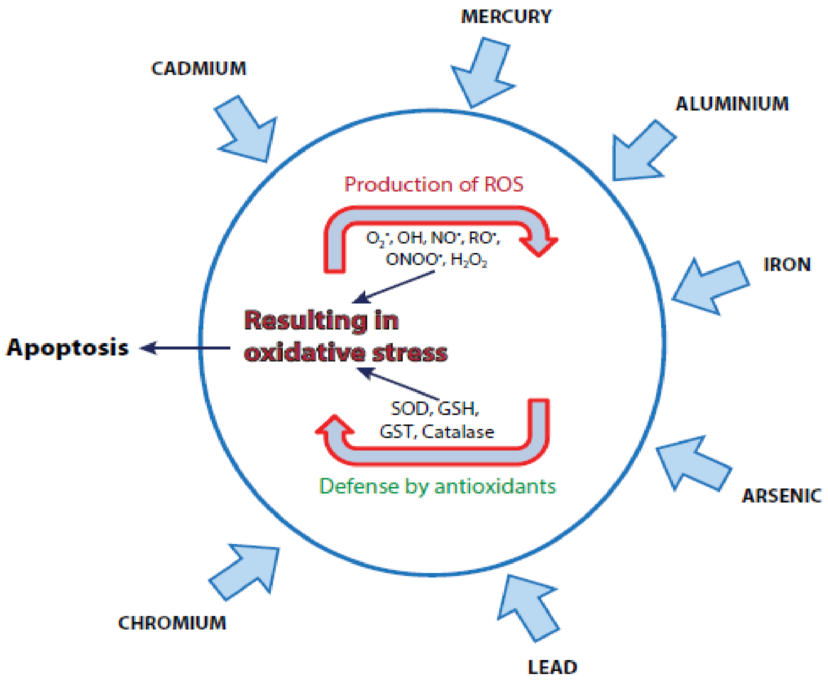


Figure 2.3 Heavy metals attacking the process of a living cell and the defence from the antioxidants along with the ROS production (Jaishankar et al., 2014)

Figure 2.3 demonstrates the heavy metals attacking the process of a living cell and the defence from the antioxidants along with the ROS production and the consequent resistance from the antioxidants. Glutathione is an antioxidant existing in the cells which protect from the free radicals, viz., H_2O_2. Affected by lead, in any case, the degree of the ROS increments and the degree of antioxidants diminishes.

The ionic lead toxicity mechanism happening because of the capacity of ions of lead to replacing other monovalent cations such as Na^+ and bivalent cations such as Mg^{+2}, Fe^{+2} and Ca^{+2} which disturbs the activity of biological metabolism of the living cell. Mechanism of lead ionic toxicity leads to substantial modification in the several biological activities for example release of neurotransmitters, ionic transportation, enzyme regulation, protein folding, apoptosis and maturation. Even calcium can be replaced with lead in picomolar concentration which influences the protein kinase C that manages the storage of memory and neural excitation (Flora et al., 2012).

2.3.3 Mercury

Mercury is a normally occurring metal, shiny and whitish silver colour, also it is an odourless metal. Mercury is extremely toxic metal and highly bio accumulative. Its essence adversely influences the places like marine area and thus numerous examinations are constituted for determining the dispersion of mercury in the water medium. Significant sources of contamination of mercury incorporate anthropogenic exercises, such as incineration plants, mining, agricultural activities and municipal wastewater discharge (Chen et al., 2012).

This metal is obtained in three forms such as organic compound, inorganic compound and metallic element, each one individually possesses the different toxicity. These kinds of mercury largely present in the various water sources like oceans, lakes and rivers wherein the microorganisms consume these and gets changed into methyl mercury, in the long run experiencing biomagnification making more damage to the lives in the oceans. Methyl mercury reaches humans through oceanic lives that are contaminated with mercury (Trasande et al., 2005). Mercury is utilized for various applications such as fluorescent lamps, catalyst, mercury arc lamps, hydrometers, pyrometers, barometers and thermometers. Also used in paper and pulp industries and battery components. Figure 2.4 shows the various applications of mercury in the world.

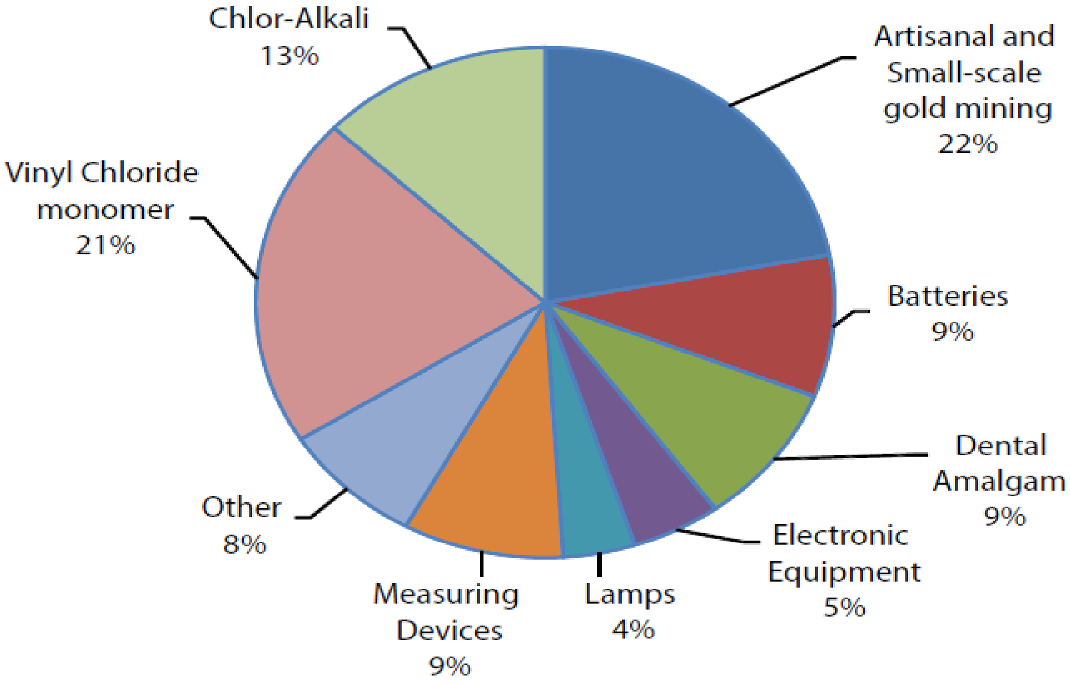


Figure 2.4 The various applications of mercury in the world (http://www.thegef. org/gef/greenline/april-2012/gef-and-mercury-challenge)

2.3.3 (a) Toxicity Mechanism of Mercury

Mercury is one of the significant toxic metals and its toxic nature is the typical reason for acute poisoning with instances of around 3,500 during the year 1997 as per the records of American Association of Poison Control Centres. Methyl mercury is a neuro-toxic substance that is accountable for the microtubule damage, accumulation of neurotoxic and lipid peroxidation for example glutamate, serotonin and aspartate (Patrick, 2002). The aggregate sum of mercury released into the atmosphere has been evaluated at 2,200 metric tonnes every year (Ferrara et al., 2000). It is evaluated that around 8 to 10 % of ladies in American has got level of mercury in them which may cause damages to nerves of their children, as per the National Academy of Science and Environmental Protection Agency (Haley, 2005). The animals exposed to mercury have witnessed the neurological issues and changes in the behaviour. One experimentation shows that the rabbits exposed to mercury of concentration 28.8 mg/m^3 for 1-13 weeks and identified the cellular degeneration, brain necrosis and pathological changes (Ashe et al., 1953).

Mercury mainly targets on the brain, also can debilitate any other organs and leads to nerves breakdown, muscles and kidney problems. It can disturb the membrane potential and cause intracellular calcium homeostasis (Patrick, 2002).

Asthma, bronchitis and respiratory problems appear because of the vapours of the mercury exposure. Mercury vapours may lead to health issues such as asthma, bronchitis and temporary respiration issues. Mercury shows a major role in harming the quaternary and tertiary protein structures and adjusts the cell work by connecting to sulfhydryl and selenohydryl that hampers the cell structure by experiencing response with methyl mercury. It additionally intercedes with the annihilation of endoplasmic reticulum, movement of common executioner cells and the procedure of interpretation and interpretation bringing about the vanishing of ribosomes (Bernhoft, 2013).

2.3.4 Cadmium

According to Agency for Toxic Substance and Disease Registry (ATSDR), the seventh most lethal substantial metal is cadmium. It is a result of the generation of zinc that people or living beings that are exposed to the surrounding environment or during work. When cadmium is consumed by people, it gets aggregated throughout their lifespan in the whole body.

Cadmium was utilized first in first world war as an alternative material for manufacturing paints as a colour pigment and tin. Nowadays, it is additionally utilized in the production of various alloys, rechargeable batteries and furthermore present in tobacco-based smoking. Around 3/4 times the cadmium present is utilized as an electrode component in batteries, the rest of the part is utilized in plastic stabilizer, pigments, plantings and coatings. People are exposed to cadmium essentially by inhalation or ingestion and can experience the ill effects of chronic and acute intoxications.

Cadmium spread in nature will stay in soils and silt for a very long while, Cadmium gets accumulated in the plants day by day and the same is concentrated across the food chain causing damage to major lives. According to the Agency for Toxic Substances and Disease Registry in the United States, excess of 5 lakh laborers are exposed to poisonous cadmium every year (Bernard, 2008; Mutlu et al., 2012). In

China, the complete area contaminated by this cadmium is in excess of 11 thousand hectares and its yearly measure of industrial discharge of this metal released into the surrounding environment is evaluated to be in excess of 680 tonnes. Ecological exposure of cadmium presentation is relatively more in Japan and China compared to other nations (Han et al., 2009). Cadmium is dominatingly determined in foods (vegetables and fruits) grown from the ground because of its tendency to move from soil to plants (Satarug et al., 2011). This metal is exceptionally dangerous and overwhelming one that is very much perceived for its bad impact on the enzymatic frameworks of cells (Irfan et al., 2013).

2.3.4 (a) Toxicity mechanism of cadmium

The cadmium toxicity mechanism is not explained very clearly, but its impact on living cells is well known (Patrick, 2003). Metallothionein is a rich protein to whose cysteine cadmium gets attached and its concentration increases by 3000 times. The cysteine-metallothionein complex leads to hepatotoxicity in the liver and after which it flows to the kidney wherein it causes nephrotoxicity by getting accumulated in the renal tissues. This metal can tie with histidine, glutamate, aspartate and cysteine ligands and can prompt iron lacking (Castagnetto et al., 2002). Cadmium can supplant zinc in the metallothionein, also inhibits from going about as a free extreme scrounger inside the cell, since the zinc and cadmium are is similar oxidation states.

2.3.5 Chromium

Chromium is the richest metal on this globe which stands seventh in its value (Mohanty and Patra, 2013). Chromium is obtained in a few oxidation states extending from Cr^{+2} to Cr^{+6} (Rodriguez et al., 2009). Common types of Cr are Cr^{+3} (trivalent) and Cr^{+6} (hexavalent), with the two states being dangerous to plants, animals as well as human beings (Mohanty and Patra, 2013).

Chromium is obtained normally by burning of coal and oil, catalyst, fertilizers, metal plating tanneries, oil well drillings, pigment oxidants, chromium steel, petroleum products obtaining from the ferro chromate refractory substances. Chromium is discharged into the earth through fertilizers and sewers (Ghani, 2011). Cr^{+3} is stable in its decreased structure and is water insoluble, but Cr^{+6} is soluble in water in its oxidized state and hence it is versatile (Wolinska et al., 2013). So as to decide the exercises of the metal ions, speciation of metals is significant where if there should be an occurrence of chromium, the oxidative type of Cr^{+3} isn't a basic pollutant of the ground water however Cr^{+6} has been observed to be dangerous for the people (Gurkan et al., 2017; Abhishek et al., 2018). Cervantes et al. (2001) studied that Cr^{+3} stays in the organic mass of the soil and oceanic condition as sulphates, oxides and hydroxides.

This metal is widely utilized in various manufacturing sectors, for example, paper and pulp industries, preservation of woods, tanning industries, production of pigments and paint industries, electroplating industries and metallurgy industries. These manufacturing industries assume a significant job in chromium contamination with bad impact on surrounding ecological and biological lives (Ghani, 2011). There is an increased scope for agricultural and industrial practices which increases the level of chromium hazardousness in the atmosphere. In the recent period, contamination of the atmosphere by chromium, Cr^{+6} has become prominent (Zayed and Terry, 2003).

Various contaminating toxic metals are released from the Tanneries and mixed into the surrounding water bodies (Nath et al., 2008). Because of the increased oxygen content in the atmosphere, Cr^{+3} is oxidized to Cr^{+6} which is incredibly poisonous and water dissolvable (Cervantes et al., 2001). The underground water in Tokyo had Cr^{+6} which was 2000 times more than the permissible limit during the year 1975 in the month of August (Zayed and Terry, 2003).

Chromium is in excess of 550 to 1500 ppm/Lts of ground water of India. The system of ultra-basic association and guidelines is not explained properly as the procedure of phytotoxicity by chromium in the aquatic condition is not studied fully (Chandra and Kulshreshtha, 2004). Centralization of chromium in the soil has increased with the release of industrial wastewater and thereby causing pollution of ground water (Bielicka et al., 2005). In the chromate industry, the chromium deposits and wastewater released from the industry shows chromium contamination to the surrounding environment. The present-day farming leads to the continuous release of Chromium into the earth by methods of chromium residues and wastewater system, bringing about soil contamination influencing the soil vegetable framework and disturbs the yield of vegetables (Duan et al., 2010). The plants getting affected by chromium will have a direct influence on the food chain and thus causing damage to the animal and human lives. Regular highlights because of Cr phytotoxicity are decreased in seed germination, biomass, chlorosis of leaf and reduction in the growth of roots. Toxicity of chromium is very significantly influencing the biological developments in various plants for example, grains, cereals, wheat, cauliflower and other vegetables. Chromium in poisonous quantity in plants causes necrosis and chlorosis (Ghani, 2011).

Cytochrome enzymes oxidase with the iron content, oxides of cytochrome, catalase and peroxides are strongly affected by the toxicity of chromium. The catalase action restored with enough supply of chromium in poisonous quantity has been considered concerning photosynthesis, nitrate reductase movement, pigments in photosynthetic and content of proteins in algae growth (Nath et al., 2008). Cr^{+3} requires a basic procedure for diffusion to get into the cell and doesn't rely upon a layer. Opposite to Cr^{+3}, Cr^{+6} can go through the membrane of a cell without much stretch (Chandra and Kulshreshtha, 2004).

2.3.5 (a) Toxicity mechanism of chromium

In the atmosphere, Cr^{+3} is normally nontoxic because of its weak permeability. Cr^{+6} is progressively dynamic in infiltrating the membrane of the cell through sections for isostructural and isoelectric anions, for example, HPO_4^{-2} and SO_4^{-2} channels.

Cr^{+6} is a strong oxidizing operator which can be decreased to produce ephemeral species of tetravalent and pentavalent Cr which are not quite the same as that of Cr^{+3}. The pentavalent structure is stabilized by glutathione and henceforth intracellular decrease of Cr^{+6} is viewed as a mechanism of detoxification when the decrease is far from the required target. In any case if the intracellular reduction of Cr^{+6} happens close to the target, it may serve for actuating chromium. The reaction among Cr^{+6} and natural reductants such as ascorbate and thiols that results in the generation of reactive oxygen species such as superoxide ion, hydroxyl radical and hydrogen peroxide eventually prompting the cell to undergo oxidative stress that causes harm to proteins and DNA (Stohs and Bagchi, 1995).

Dayan and Paine (2001) and Zhang (2011) investigated that Cr^{+6} has been observed to be significantly more hazardous than Cr^{+3}, as Cr^{+6} rapidly enters into the cells compared to Cr^{+3} and in the end diminished to Cr^{+3}. As per the International Agency for the Research on Cancer, Cr^{+6} acts as a carcinogenic product because of mutagenic properties.

2.3.6 Iron

According to Environmental Protection Agency (EPA) 1993 iron is one of the richest metals in the earth. Valko et al., (2005) studies show that iron is the most significant component for survival and growth of all living beings. Vuori (1995) investigated the iron is one of the major components for the organisms for example, enzymes (catalase and cytochromes) and algae. Phippen et al. (2008) studied that iron is one of the major transition metals for different biological oxidation reduction process because of the transformation between ferric (Fe^{+3}) and ferrous (Fe^{+2}). Valko et al. (2005) investigated that various sources of iron in the surface water is anthropogenic and majorly it is because of the mining exercise in that area. The generation of the acid of sulphur and release of the ferrous happens due to oxidation of iron pyrites.

According to EPA (1993), dissolved iron concentration in oceans is 0.6 nM or $33.5X10^{-9}$ mg/L. the concentration in fresh water is 5 μg/L. And, the concentration of iron in ground water is detected as 20 mg/L. Grazuleviciene et al. (2009) showed that Lithuania area several humans consumed higher concentration of iron via drinking water collected from the groundwater more than the permissible limit according to the European Union Directive.

2.3.6 (a) Toxicity mechanism of iron

The cells of mammalians will get influenced by the serious concentration of iron when the destructive free radicals are formed due to the failure of iron getting tied to the proteins. The gastrointestinal tract is affected by the corrosive effects due to the circling of unbound iron. The iron enters of the human body beyond the absorption limits and gets saturated. Such entered free ions will get into the cells of heart, liver and cerebrum and cause disturbance of oxidative phosphorylation. The ferric ion is formed from the ferrous ions which release hydrogen particles leading to acidity in metabolism activity. Also, the free ions can result in lipid peroxidation showing a serious threat to cellular organelles, mitochondria and microsomes (Albretsen, 2006).

2.4 Impact of toxicity of heavy metals on human health

Around thirty five metals cause worry to utilize in residential and occupational exposures and twenty three of which are highly toxic in nature: Lead, Tin, Silver, Zinc, Uranium, Vanadium, Thallium, Platinum, Nickel, Copper, Gold, Cobalt, Chromium, Mercury, Iron, Gallium, Manganese, Cerium, Cadmium, Tellurium, Antimony, Bismuth and Arsenic. (Mosby et al., 1996). Toxic metals are usually found in the earth's crust and the routine diet. In limited quantities, certain metals are required for keeping the health better, but in higher concentration they will become harmful. Table 2.1. shows the contamination of heavy metal from the various sources in global food crops.

Table 2.1 contamination of heavy metal from the various sources in global food crops

No	Food crops (fruits, vegetable and cereals etc)	Country	Concentration of metal In food crops based on Dry weight	Heavy metals contamination sources affecting on food chain	Reference
1	Radish	India	Cu 5.96 mg/kg and Zn 22.5 mg/kg	Various contamination sources	Arora et al. (2008)
2	Amaranthus	India	Cu 1.4 mg/kg, Cr 2.4 mg/kg, Zn 8 mg/kg and Pb 2.9 mg/kg	-	Chary et al. (2008)
3	Chenopodium sp., Brassica sp., leafy and root vegetables, grains	India	Pb 0.13 mg/kg, Cu 1.7-12.9 mg/kg, Zn 7.25-24.6 mg/kg, Pb 0.02-0.013 mg/kg, Cr 0.08-0.38 mg/kg,	Sewage effluent	Rattan et al. (2005)
4	Spinach	India	Ni 3.2 mg/kg, Cu 0.09 mg/kg, Cr 2.9 mg/kg, Pb 3.2 mg/kg, Zn 10 mg/kg and Cu 0.09 mg/kg	Inadequately treated sewage wastewater	Chary et al. (2008)
5	Lycopersicum esculentum L. (tomato), Triticum aestivum (wheat), radish, Allium sativum (garlic),	Pakisthan	Pb 0.91-3.96 mg/kg and Cr > 0.18 mg/kg	Heavy metal contaminated ground water	Khan et al. (2013)

	spinach, carrot, Capsicum annum, Coriandrum sativum (coriander), brinjal and okra				
6	Wheat, rice, potato, soybean (Glycine max) and corn (Zea mays)	Brazil	Below the standard limits hazardous to human health	Industrial/modern intensive urban agriculture	Branco Corguinha et al. (2015)
7	Grain, maize (Zea mays), radish (Raphanus sativus L), green cabbage, Brassica juncea L,turnip, spinach, cauliflower, brassica napus and lettuce	China	Pb 0.02–0.013 mg/kg, Cr 0.08–0.38 mg/kg,Cu 0.16–0.85 mg/kg, Zn 0.16–0.53 mg/kg	Sewage effluent (inadequately treated using a biological approach)	Khan et al. (2008a)
8	Lettuce (Lactuca sativa); a leafy food crop/vegetable	Spain	< 0.02 mg of Ni/kg, 0.005 mg of As/kg, <0.008 mg of Hg/kg and <0.005 mg of Cd/kg	Air (Particulate matter) from industries and vehicles	Ercilla-Montserrat et al. (2018)
9	Brassica sp., food grains, and leafy vegetables	Chaina	Pb 0.12–0.23 mg/kg, Cr 0.01–0.19 mg/kg,	Both sewage and industrial waste (from	Liu et al. (2005)

			Zn 0.42–0.95 mg/kg and Cu 0.15–0.86 mg/kg	smelter) drained into river water used for irrigation	
10	Rice and other paddy crops and vegetables	Australia (food crops imported from Bangladesh, India, Pakistan, Thailand, Italy, Canada and Egypt)	Rice: Cr 15–465 µg/kg, Pb 16–248 µg/kg, Cu 1.0–9.4 mg/kg, Zn 10.9–24.5 mg/kg, Cd 8.7–17.1 µg/kg, Co 7–42 µg/kg, Mn 61–356 µg/kg, Ni 61–356 µg/kg and Pb 670–16,500 µg/kg Vegetables: Cr 27–774 µg/kg, Cu 1–29 mg/kg Pb 35–495 µg/kg, Cd 3–370 µg/kg Zn 17–183 mg/kg, Mn 3–140 µg/kg, Ni 151–10,035 µg/kg and Pb 35–495 µg/kg	Arsenic and metal contaminated groundwater	Rahman et al. (2014)
11	Soybean	Argentina	Metals (Pb and Zn) well above Permissible limits	Industrial (battery) waste in soil	Blanco et al. (2017) and

					Rodriguez et al. (2014)
12	Radish	China	Cu 0.34 mg/kg, Ni 0.07 mg/kg, Cr 0.03 mg/kg, Cd 0.012 mg/kg, Pb 0.07 mg/kg and Zn 2.48 mg/kg	Inadequately treated wastewater	BoSong et al. (2009)
13	Industrially processed food stuffs (e.g. candy) and pharmaceuticals	USA, Portugal, Spain, England, Belgium and Chile	Cr (0.10–17.7 ppm), Cu (0.01–6.44 ppm), Zn (0.01–7.01 ppm), Zn (0.01–6.44 ppm) and Pb (0.03–7.21 ppm)	Industries/food processing industries/modern pesticides based agriculture	Gonzalez-Martin et al. (2018)
14	Potato	China	Cu 1.03 mg/kg, Pb 0.067 mg/kg Cr 0.03 mg/kg, Cd 0.015 mg/kg Zn 3.77 mg/kg and Ni 0.054 mg/kg	Inadequately treated urban wastewater	Song et al. (2009)
15	Potato/other foodstuffs	Egypt	Cu 0.83 mg/kg, Zn 7.16 mg/kg, Cd 0.02 mg/kg and Pb 0.08 mg/kg	Inadequately treated wastewater	El-Kady and Abdel-Wahhab (2018);

					Radwan and Salama (2006)
16	Cauliflower	Chaina	Cu 0.6 mg/kg, Pb 0.03 mg/kg Cr 0.02 mg/kg, Ni 0.68 mg/kg Zn 5.45 mg/kg and Cd 0.014 mg/kg	Urban wastewater	Song et al. (2009)
17	Lettuce (Lactuca sativa)	United States (Florida)	As 27.3 mg/kg	-	de Oliveira et al. (2017)
18	Chinese cabbage	Chaina	Cd 0.12–1.70 mg/kg	Pot experiment with exogenous supply of Cd	Junhe et al. (2017)

Jarup (2003) investigated the toxicity of heavy metal highly impact at the lower concentrations and harm the working of kidneys, liver, lungs, brain and blood organs. Long term exposure may cause neurological, muscular and physical illness. And some of the metals may cause cancer. Biochemical and physiological mechanism of toxic heavy metals pollution in food crops is as shown in Figure 2.5.

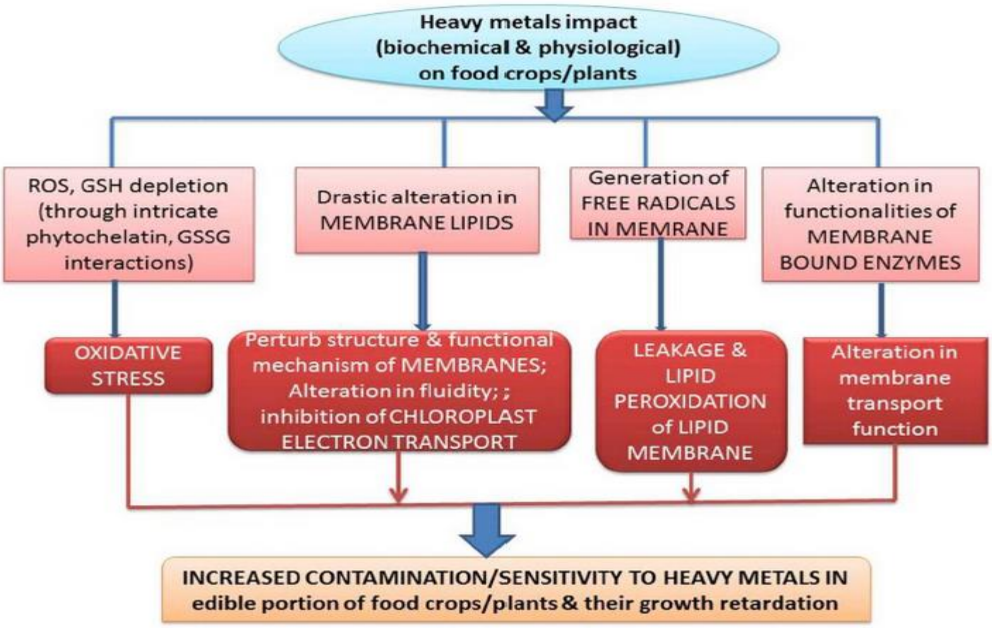


Figure 2.5 Biochemical and physiological mechanism of toxic heavy metals pollution in food crops (Rai et al., 2019)

Ferner (2001) investigated the poisonous levels of several heavy metals can be simply over the background concentration that is being available normally in nature. Consequently, exhaustive information of substantial metals is significant for permitting to give appropriate defensive measures against their extreme contact. Eco-toxicological impact of toxic heavy metal pollution in food crops and ultimately in human health is as shown in Figure 2.6.

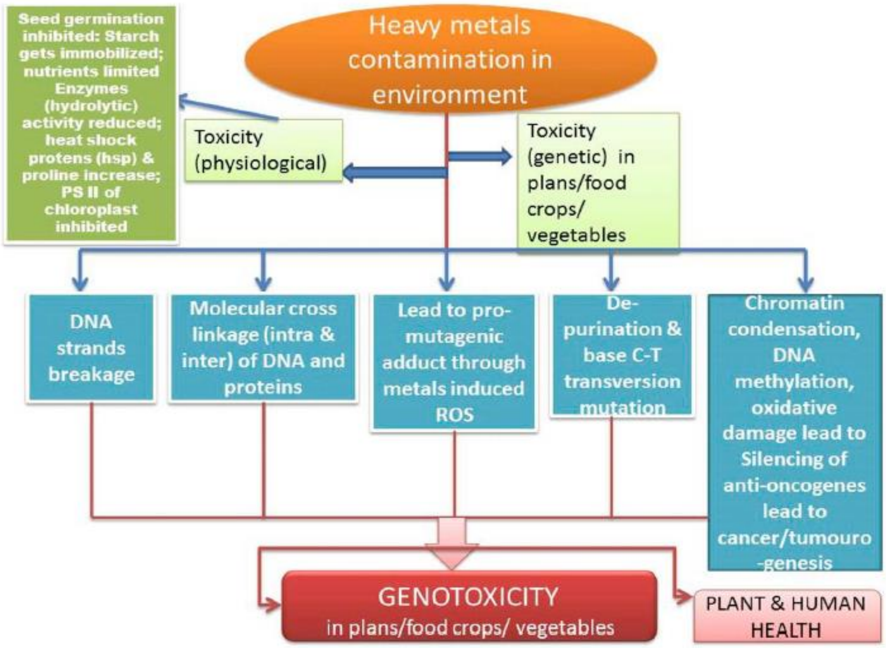


Figure 2.6 Eco-toxicological impact of toxic heavy metal pollution in food crops and ultimately in human health

2.4.1 Arsenic effects

Arsenic pollution has happened because of both regular geologic procedures and the exercises of humans. Anthropogenic activities include activities of human beings like mining and extracting of ores. The purifying procedures can discharge arsenic metal into the surrounding soil and air (Matschullat, 2000). The sources of arsenic can influence the nature of groundwater as well as surface water. Another way of groundwater pollution is through the geological sources, for example, minerals of arsenic. The sedimentary rocks are also the sources of arsenic (Smedley and Kinniburgh, 2002). Chowdhury et al. (2000) studied that the large portion of the drugs, paints, semiconductors and soaps contain arsenic. Also, arsenic present in higher amount certain fertilizer, insecticide and animal feedings. The inorganic types of arsenic, for example, arsenate and arsenite are observed to be more toxic to human beings. They are exceedingly carcinogenic and can reason for the liver damage, bladder, lung cancer and sin diseases. People are exposed to arsenic through water, air and food. More than thirty nations are suffering from an increased level of arsenic in the drinking water (Chowdhury et al., 2000). Hoque et al. (2011) found that the arsenic concentration in groundwater is 10 to 100 times the limit prescribed by the World

Health Organization (WHO) which is harmful to human health. Water may get polluted through inappropriately discarded arsenical insecticides, arsenic chemicals. Toxicity of arsenic can be either chronic or acute and arsenicosis is the name given for chronic arsenic toxicity. Martin and Griswold (2009) showed that the chronic toxicity of arsenic in human beings mainly focussed on manifestations of the skin due to its particularity in diagnosis. Keratosis and pigmentation are the skin problems that show chronic toxicity of arsenic (Martin and Griswold, 2009).

2.4.2 Lead effects

Human exercises, for example, burning of fossil fuel, mining manufacturing activities have resulted the lead accumulation in the environment. Lead is utilized for the formation of batteries, beauty care products, metal items, for example, solder, ammunitions, and pipes (Martin and Griswold, 2009). Gerhardsson et al., (2002) investigated that lead is exceptionally dangerous and consequently its utilization in different items, for example, gasoline and paints, has been significantly reduced these days. The fundamental sources of lead exposures are toxic paints, industrial emissions, contaminated soil, cosmetics and gasoline. Toxicity of lead causing poisoning of drinking water. The water may also get polluted due to the pipes of conveyance which are manufactured with lead (Brochin et al., 2014). As per EPA (Environmental Protection Agency), lead is a carcinogenic agent. Lead affects the human body in various parts. Lead circulation in the human body at first relies upon the blood stream into different human body tissues and around 95 % of lead is stored in skeletons as insoluble phosphate (Papanikolaou 2005).

Lead poisoning or toxicity of lead can be either chronic or acute. Chronic lead exposure can result in kidney damage, brain damage, muscular weakness, paralysis, hyperactivity, weight loss, dyslexia, allergies, autism, psychosis, birth defects and mental retardation. Acute exposure can cause sleeplessness, vertigo, hallucinations, arthritis, fatigue, renal dysfunction, abdominal pain and headache (Martin and Griswold, 2009).

2.4.3 Mercury effects

Mercury is observed as the most toxic metal on the earth. Mercury harming is mentioned to as pink dieses or acrodynia. Mercury is discharged into the surrounding atmosphere by the exercises of different industries, for example, caustic soda production industry, agriculture practice, paper and pulp industries and pharmaceuticals (Morais et al., 2012). Alina et al. (2012) showed that mercury can consolidate with various components and form inorganic and organic mercury. Exposure to raised degrees of metallic, inorganic and organic mercury can harm the kidneys, brain and foetus. Reilly (2007) investigated the presence of mercury in the majority of food and soft drinks in the range of < 1 to 50 μg/kg. In marine food items frequently observed at higher levels of mercury.

Table 2.2 Types of Toxicity of Mercury (Patric, 2002)

	Inorganic mercury	**Elemental mercury**	**Methyl mercury**
Sources	Demethylation of methyl mercury by intestinal microflora, Biological oxidation of mercury	Thermometers, incinerators, old latex paints, dental amalgams, fossil fuels	Poultry, fish and pesticides
Absorption	Dermal dose absorbed in animals (2–3%) and ingested dose absorbed (7–15%)	Vapor absorbed (75–85%)	Absorbed in the intestinal tract (95–100%)
Distribution	Accumulates in the kidney, present in brain neonates, does not cross blood-brain or placental barrier	Accumulates in brain and kidney, crosses blood-brain barrier and placental barrier, lipophilic, distributed throughout the body,	Accumulates in kidney and brain, readily crosses the barrier of blood and brain and the placental barrier, lipophilic, distributed throughout the body,
Excretion	Urine and faeces, saliva and sweat	Urine and faeces, saliva and sweat	Urine (10%), bile and feces (90%)
Reason for toxicity	Binding to thiols in structural proteins and enzymes	Inorganic mercury oxidation	Binding to thiols in enzymes, free radicals generation, structural proteins, demethylation to inorganic mercury

EPA has announced methyl mercury and mercuric chloride to be highly dangerous. The nerves of humans and animals are extremely sensitive to a wide range of mercury. Higher exposure to mercury can damage the functions of the brain, leads to shyness, irritability, memory problems, tremors. Exposure to mercury metallic vapours at higher levels for a shorter time can cause higher blood pressure, skin rashes, nausea, vomiting and lung damage. The fatigue problems associated with memory, tremors, headache, hair loss, depression, etc are the basic symptoms of mercury poisoning. Table 2.2 shows the types of mercury toxicity (Patric,2002).

2.4.4 Cadmium effects

Cadmium is a metal of the twentieth century. It is a by-product obtaining during the production of zinc. Rocks, soils, mineral fertilizers and coal having cadmium content. Applications of cadmium such as metals coating, pigments, batteries, making of plastics and largely used in the production of the electroplating (Martin and Griswold, 2009). Figure 2.7 presents a relative contribution of different sources to human cadmium exposure (Regoli, 2005).

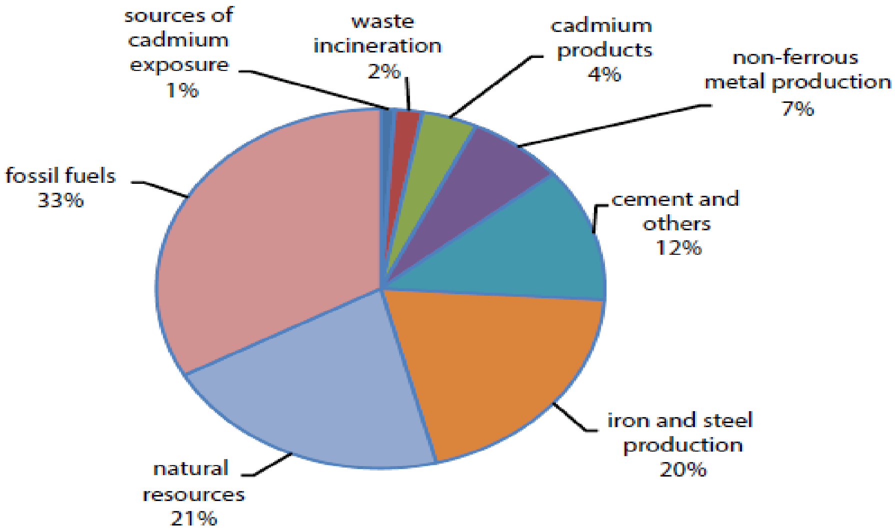


Figure 2.7 presents a relative contribution of different sources to human cadmium exposure (Regoli, 2005)

Cadmium and its mixes are named Group 1 cancer-causing agents for people by the International Agency for Research on Cancer (Henson and Chedrese, 2004).

Cadmium is discharged into the earth through regular exercises, for example, volcanic ejections, enduring, stream transport and a few human exercises, for example, mining, purifying, tobacco smoking, burning of metropolitan waste, and production of manures. Although cadmium discharges have been discernibly decreased in most industrialized nations, it is an outstanding wellspring of dread for laborers and individuals living in the contaminated territories. Cadmium can cause both intense what's more, unending inebriations (Chakraborty et al., 2013).

According to Henson and Chedrese (2004), cadmium and its mixes are named as Group 1 carcinogenic agents for people by the International Agency for Research on Cancer.

Cadmium is discharged into the earth through common exercises, for example, river transport, volcanic emissions, enduring and some human exercises, for example, smelting, smoking of tobacco, manufacturing of fertilizers, municipal solid waste incineration and mining activities. In spite of the fact that cadmium discharges have been recognizably decreased in most industrialized nations, it is a residual source of anxiety for specialists and individuals living in the contaminated regions. Cadmium can cause both chronic and acute (Chakraborty et al., 2013). Cadmium is extremely dangerous to the kidney and it stored in the proximal cylindrical cells in higher concentrations. Cadmium may be the reason for bone mineralization either through bone harm. Experimental studies conducted on people and living beings have uncovered that osteoporosis (skeletal harm) is a dangerous effect of cadmium exposure alongside disturbance in calcium digestion, the arrangement of renal stones and hypercalciuria. Breathing in larger amounts of cadmium can make serious harm to the lungs.

If cadmium is consumed in higher concentration, it can prompt stomach disturbance and case the vomiting. On extremely exposure long term at lesser concentration, it can be stored in the kidney lastly lead to kidney illness, damage to lungs and fragile bones (Bernard, 2008; Zhao., 2011). Cadmium and its mixes are very water dissolvable contrasted with different metals. Their bioavailability is extremely high and henceforth it tends to bioaccumulate. Cadmium long term exposure can cause morpho pathological variations in the kidneys. Smokers are more helpless for cadmium inebriation than non-smokers.

Tobacco is the principle source of cadmium take-up in smokers as tobacco plants, as different plants, can gather cadmium from the soil. Non-smokers are exposed to cadmium by means of food and drinking water. However, cadmium take-up in different ways is much lower (Mudgal et al., 2010). Figure 2.8 shows estimations of the toxicity of cadmium (Flora et al., 2008).

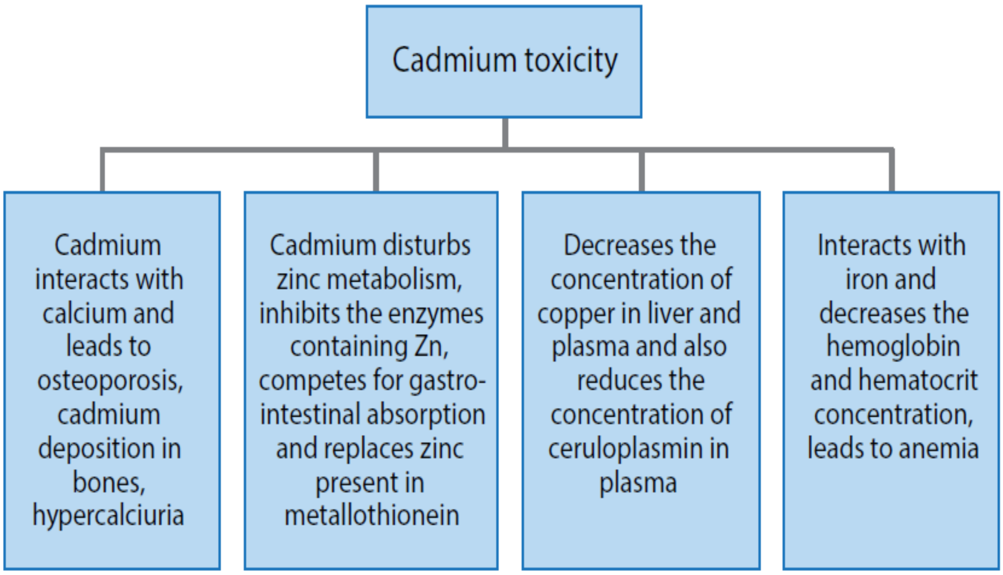


Figure 2.8 shows estimations of the toxicity of cadmium (Flora et al., 2008)

Cadmium interfaces with fundamental supplements through which it causes its lethality impacts. Experimental investigation in animals has appeared 50 percentage of cadmium gets absorbed in the lungs and less in the gastrointestinal tract. Reduced birth weights problems and premature birth arise if exposure of cadmium in very during the pregnancy (Henson and Chedrese, 2004).

2.4.5 Chromium effects

Chromium is available in soil, rocks, plants and animals. It is in the form of soil, water or gas. Chromium mixes are particularly steady in water residues. They can occur in a wide range of states, for example, divalent (Cr^{+2}), four-valent (Cr^{+4}), five-valent (Cr^{+5}) and hexavalent state (Cr^{+6}). Cr (VI) and Cr (III) are the steadiest structures and just their connection to human exposure is of high (Zhitkovich, 2005; Madhurambal et al., 2012).

Chromium (VI) mixes like lead chromate, strontium chromate, zinc chromate, calcium chromate are highly hazardous in nature and carcinogenic. Chromium (III) is a fundamental nutritional supplementary for living beings and people and has a significant job in glucose digestion.

The take-up of hexavalent chromium mixes through the airways and the digestive related tract is quicker than that of trivalent chromium mixes. Sources of chromium consist of the leather tanning, metal plating, wood preservative, paper and pulp industries, cement industries, rubber industries, pain pigments, metal alloys and metal coatings (Martin and Griswold, 2009).

Schroeder et al. (1970) announced that cigarettes having 390 g/kg of chromium, yet there has been no critical report distributed on the measure of chromium breathed in through smoking. At the point when broken skin interacts with any sort of chromium substances, a greatly penetrating hole will be formed. exposure to chromium mixes can outcome in the development of ulcers, which will persevere for months.

Ulcers on the nasal septum are regular if there should arise an occurrence of chromate laborers. Exposure to higher measures of chromium mixes in people can prompt the inhibition of erythrocyte glutathione reductase, which thusly brings down the ability to diminish methemoglobin to hemoglobin (Koutras et al., 1965; Schlatter and Kissling, 1973). Results acquired from various in vitro and in vivo trials have appeared chromate mixes can incite Deoxyribonucleic acid (DNA) harm in numerous various ways and can prompt the arrangement of DNA adducts, transcription of DNA, alterations in replication, sister chromate exchanges, and chromosomal aberrations (O'Brien et al., 2001; Matsumoto et al., 2006).

2.5 Leaching of toxic elements

Industrial wastes are hazardous in nature and cause potential damage to human health and the environment by leaching the heavy metals into the environment. Release of toxic pollutants has its impact on various aspects of our eco system like ground water and surrounding soil. Leaching of such pollutants also influences the vegetation and thereby spoils the food chain of various living beings (Carlson and Adriano, 1993). Major threats to the eco system are through water wherein the combustion residues will react with aqueous media. All such interactions have to be studied to understand the leaching of industrial wastes in short and long runs with respect to its reactivity (Bharagava,2019).

The leaching of industrial hazardous waste is like an acid titration process in a heterogeneous system. Industrial hazardous waste is not stable under natural conditions. This high temperature product is active in the subsurface environment especially in an aquatic environment. Different materials present in the residue gets dissolved when it is wet with water. The rates of dissolution are faster than the matrix phase when compared to that of the soluble minerals. The chemical properties of the surrounding atmosphere and the dissolution of the matrix phase modifies chemical properties of the soluble minerals. The carbon dioxide composition in the atmosphere and from the oxidation phenomena of organic acids and organic carbon neutralises the residue's alkalinity. Saturation state is reached by certain elements based on different secondary minerals such as amorphous SiO_2 and $Al(OH)_3$. metastable phases in the hazardous ash residues will be altered to form the assemblages of thermodynamically stable minerals. Any chemical reactions occurring can be resisted by the capacity of the residue to release the toxic elements and time duration needed for the same. To understand the changes in the combustion residue under different leaching conditions and on different time scales is therefore important for predicting its environmental impact.

Many reactions and processes are involved in the interactions between industrial hazardous waste and an aqueous solution. It is necessary to distinguish the major processes from other leaching processes, because these processes control the leaching environment and strongly affect the release of minor or trace toxic elements. In most cases, several reactions or processes may take place simultaneously and feed back to each other. Some of the reactions or processes are fast, and others are slow and time-dependent. A different approach may be required to describe a different type of processes, e.g. a thermodynamic consideration for the fast process, and a kinetic consideration for slow reactions. An integral understanding of the interactions between various processes is also critically important for a systematic assessment of the environmental impacts of industrial hazardous waste.

The emphasis of this study of industrial hazardous waste is on the major leaching processes which have been identified by experimental investigations. However, because most researchers pay more attention to the leaching of toxic elements which are directly related to the environmental impact of industrial hazardous waste, the major leaching processes have actually not been addressed very well. Even the acid-base reactions in the leaching of industrial hazardous waste have not been fully studied, especially with respect to their chemical kinetics and the influence of solute transport. Little is known so far about the long-term behaviour of industrial hazardous waste in utilisation and disposal. The major processes need to be understood first to provide insight into the leaching of trace elements. The relationship between the major leaching processes and release of toxic elements is as shown in Figure 2.9.

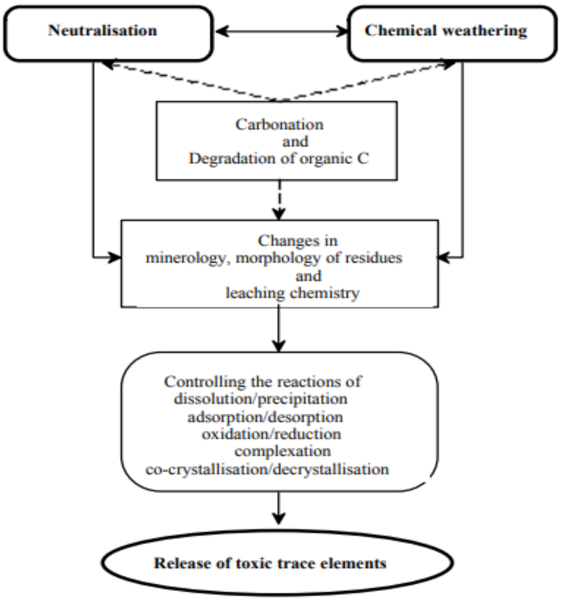


Figure 2.9 The relationship between the major leaching processes and release of toxic elements (Yan, 1998)

However, it is important to develop the quantitative models for describing different leaching methods of combustion residues (van der Sloot et al., 1997). Various leaching methods of combustion residues in case of natural disposal of wastes are as given in Table 2.3.

Table 2.3 The leaching processes of combustion residues in natural disposal

Time	Short term	Medium term	Long term
Major processes	wash-off	Carbonation, Neutralisation And the degradation of organic carbon	Carbonation And chemical weathering
Leaching characteristics	pH buffering built-up, rapid wash-off and first release peak occurs	consumption of ANC dissolving organic carbon	Phase alteration pH shift if any and dissolution of the matrix
Dissolved fraction	water-soluble	weak acid-solubl	the residues
Dissolved solid phases	soluble salts and species on the surface of particles	Metal oxides, part of the amorphous phases and Ca containing minerals	Glass phases
Potential reaction related to trace metals	dissolution/precipitatio complexation	dissolution/precipitatio n, adsorption/desorption and oxidation/reduction complexation	dissolution/precipitation, adsorption/desorption and co-crystallisation complexation

2.5.1 Biomedical waste bottom ash

Biomedical waste bottom ash (BMWBA) consists of toxic, infectious, and radioactive substances from hospitals, clinics and laboratories. Medical waste is highly potential for causing infection compared to any other type of waste. It led to environmental pollution and health issues due to the propagation of ailment by microorganisms as per World Health Organization (2017) reports. Developing countries are providing top priority for such waste management.

To handle hazardous BMWBA, the proper management system is required to be developed. Several techniques adopted including incineration, chemical disinfection; stem sterilization, microwave sanitation, superheated stem and dry heat disinfection are the best available methods for treating Biomedical waste (BMW). Literature reveals that incineration is the most widely accepted method for handling BMW because it reduces the volume by more than 95% and weight by 75%. It is carried out at a temperature of 850 °C which leaves two by-products of biomedical ash, i.e. bottom ash and fly ash (Ibanez et al., 2000). The practice of incineration of waste materials with metal contents leads to the release of heavy metals (lead, mercury and cadmium) in the environment. These ashes are hazardous in nature which may leach inorganic salts, heavy metals and organic compounds to the soil and hence can contaminate the soil and ground water in the vicinity of the waste dump (Tufail and Khalid, 2008). Bui et al., (2019) investigated the hospital waste water and found that toxic substance.

Leachability of heavy metals from biomedical ash were studied by various researchers (Lombardi et al., 1998; Idris and Saed, 2002; Rajor et al., 2012; Tzanakos et al., 2014) adopted standard procedures and is dealt in terms of the reuse of ash in agriculture, percentage replacement of cement and conventional aggregate material for road construction, and raw material for production of geopolymer. Zhao et al. (2010) investigated the leaching behaviour of hazardous elements present in the medical waste incinerated bottom ash by the TCLP method and found that the concentration of Al, Ca, Fe, Mg, Na, Ag, As, Cr, Ni, Sn and Sr were above the permissible limits.

Sabiha-Javied and Khalid (2008) investigated the medical waste incineration ash of the wastes from three hospitals and reported that the concentration of Zn, Cd, Cr, Ni and Cu in the ash were within the limits and the Pb concentration was exceptionally higher as per EPA, Canada. Azni et al. (2005) investigated medical incineration plant waste used as road and asphalt aggregate and analysed for trace elements according to EPA toxicity procedure by maintaining solid/liquid ration 1:16 at pH (3 and 5) for a day. Results reveal that Ni, As, Ag, Ba, Cd, Se, Cr, Hg, Pb and Cu concentrations were above permissible limits. Lombardi et al. (1998) studied leaching behaviour using the acetic acid method and found that Cu, Zn and Pb were above permissible limits and it can be strongly immobilized by cementitious materials.

2.5.2 Ferrochrome ash

Ferrochrome ash is a discarded waste substance obtained from the ferrochrome manufacturing sector. An enormous quantity of ferrochrome ash is generated and disposed of without any prior treatment, prevention or any remedial measures. Ferrochrome ash not only occupies large space of land but also a major threat to contaminate the surrounding soil and surrounding water bodies (Acharya and Patro, 2016). Annual production of ferrochrome is about 6.5 to 9.5 million tonnes globally. The production increasing at a rate of 2.8 to 3 % annually. For each million-tonne ferrochrome product average 1 to 1.2 million tonnes of solid waste generating from the gas cleaning plant of ferro alloy manufacturing industry (Acharya and Patro, 2015). The ferrochrome ash obtaining from the ferrochromium gas cleaning plant, ash particle is spherical in shape and having a diameter of the range in between 30 to 200 nm. This ferrochrome ash particle consists of silica, chromite, calcium, alumina and magnesium around which is having a thin layer of condensed volatile particles such as Cr(VI), Fe, Zn and. Ferrochromium is made by chromium and iron alloy, comprising of 40 to 80 % of chromium and remaining quantity of iron and carbon and other elements. Pyrometallurgically by carbothermic reduction of chromite ore ($FeO{\cdot}Cr_2O_3$) generating ferrochromium products. The dust particles released into the surrounding atmosphere during the ferrochrome production process are also significant contaminant sources because of its high levels of extractable harmful components which may cause serious environmental contamination. The majority of toxic metals are present in this fine dust particle such as Cd, Cr, Pb, Zn and Ni were reported in Sofilic et al., (2004); Cohen and Petrie (2005); Laforest and Duchesne (2005). Especially, it has been shown that the filtered fine dust particles or its sludge generating from the ferrochrome manufacturing industry consist of huge quantity of soluble hexavalent chromium Cr(VI) noted by Cohen and Petrie (1997).

A developed and developing society vastly depends upon energy and channelization of that energy into various resource yielding fields. It depends upon industrialization in which energy created from different sources are channelized into. But this energy creating, and energy consuming process has a huge amount of by-product which we conventionally termed as waste. If these wastes are not properly disposed, they may come across as a potential threat to not only to the environment but also to the society dwelling in the vicinity of the disposal ground. In these regards one of the greatest problems which have been faced by the thermal power generating plants and Ferroalloy producing industries are the ashes and slag that they produce during the intermediate phase of production, e.g., fly ash and ferrochrome ash. Generally fly ash is a by-product obtained from coal burning thermal power plants. Fly ash has negative environmental impacts as it is found to be an air pollutant and also has an adverse effect on the ground water sources lowering its drinking standards. In Turkey a survey has found that approximate fly ash production per year is about 18 million tons which is more than its total industrial waste. India also has a huge yield of fly ash per year which is approximated to be 80 million tons. In the entire world fly ash production is about 600 million tons which have now become a point of concern for various environmentalist. Ferrochrome ash and ferrochrome slag are waste obtained from Ferroalloy producing industries. When high carbon ferrochrome metal with Cr > 65% is produced in electric arc furnace by the carbothermal process at 1700°C, ferrochrome slag and ferrochrome ash are obtained. Disposal of this huge quantity of waste is the major problem that environmentalist is facing in these days. Hence, instead of disposing, they came across with an idea of recycling these waste products which reduces the load on the landfill as well as preserves natural resources. Research has shown that amongst many alternative use possibilities; enhancement of concrete and cement quality and stabilization of soil using these ashes have much more future scope and importance than any others. Here, this study solely focuses on detailed analyses of these ashes to find their future probable scope in concrete and stabilization process of soil. Recycling ensures three probable prospects such as reduce the number of new resources required, cuts down transportation and energy production cost and reduces the load on landfill areas (Gencel et al. 2012).

2.6 Types of leaching tests

Common batch leaching tests include extraction procedure (EP-Tox; US EPA Method 1310), Toxicity characteristics Leaching Procedure (TCLP; USEPA Method 1311), synthetic precipitation leaching procedure (SPLP; USEPA method 1312), waste extraction tests (WET; California code of regulations), American society for testing materials extraction tests (ASTM D 3987), and multiple extraction procedure (MEP; USEPA method 1320)(Tiwari et al., 2015). The batch test typically involves mixing size reduced waste with extraction solution and then agitating the mixture. These tests generally performed for a short period of time (typically for hours to days) and therefore are often called short term tests. The main differences among these tests are leaching solution, liquid to solid ratio and number of rotation and duration of extraction.

Baba and Kaya (2003) studied the leaching behaviour of Tuncbilek and Soma thermal power plants located in Turkey. Toxicity tests were conducted using two test methods such as toxicity characteristic leaching procedure (TCLP) and European committee for standardization (CEN) test methods. The experimental results show that the ash samples geochemical composition variation based on their burned coal composition. The ash samples were categorized as toxic waste with respect to TCLP analysis and categorized as non-toxic waste with respect to the CEN study.

Akar et al (2012) investigated short duration leaching test for Yenikoy coal fired power plant collected fly ash. Cr (VI), Zn, Pb, Ni, Mn, Cd, Co, Cu, Ca and Fe were analysed at various particle size fractions of fly ash by TCLP 1311 and ASTM D 3987-85 test procedure. The results reveal that calcium oxide concentration is very high and its directly influence on the concentration of trace elements leaching from flay ash and pH of the leaching solution. From TCLP procedure, Zn, Ni, Pb, Cu, Co and Cd mobility is very high. The heavy metals concentration from the fly ash leachates revels that particle size decrease, leaching concentration of elements increases. Except Cr (VI) remaining heavy metals are within the acceptable limit of landfill regulations.

Gharabaghi et al. (2013) investigated the leaching kinetics of Ni in H_2SO_4. Various parameter such as temperature, leaching duration, the concentration of H_2SO_4, particle size and solid-liquid ration were considered for the optimization of leaching and to identify the leaching kinetics. The experimental results revel that 96 % of Ni leaching was observed from the particle size 250µm, 30 minutes leaching time, solid to liquid ratio of 0.1 and 8 % of H_2SO_4.

Cetin and Aydilek (2013) investigated the two laboratory experiments such as column leach test (CLT) and water leach test (WLT) to determine the concentration of the Mo, Se, Mn and B leaching from fly ash and soil blends. The experimental results revels that increase the fly ash content in the leaching solution, pH of the leaching solution also increases with their heavy metal concentrations. The concentration of leaching was higher in WTL procedure compare to CLT with few exceptions. pH plays a significant role in leaching of Mo, Se, Mn and B, the concentration of leaching solution. Unburned carbon content not affecting much on leaching of heavy metals.

The simulation of normal leaching in the laboratory with respect to the field conditions is studied by Tiwari et al., 2013. Among various test methods available, the proper test method has to be selected to simulate it to the field conditions in a better way. This becomes challenging as the presence of toxic metals, their effects on disposal method, reusing options, etc have to be considered. Based on physical and chemical properties of the leaching material. Composition of the waste material, age of the material, area of dumping, surrounding environmental conditions have to be considered for selecting the leaching method perfectly.

Komonweeraket et al (2014) investigated the leaching behaviour of the Sr, Se, Ng, Cd, Ca, Ba and As from the coal fly ash and coal fly ash and soil blends were examined at various pH (2-14) condition via batch leaching experiments. The experimental results reveal that Sr, Mg, Cd, and Ca were controlled by cationic leaching pattern, Se and As controlled by the amphoteric leaching pattern. Various composition of fly ash, soil and fly ash blend were studied in the current investigation, results show the similarity in the behaviour leaching as a function of pH. The similarity is major because of the similar leaching controlling mechanisms i.e., sorption, dissolution, pH of the leachate, redox condition and solution-solid construction.

Jiao et al. (2016) determine the leaching mechanism of Cr, Cu, Pb and Zn in fly ash having a high amount of Ca collected from the municipal solid waste incineration plant, using sequential batch leaching procedure. Experiment results revel that Pb, Cu and Zn were controlled by sorption mechanism and Cd and Cr were controlled by the dissolution mechanism. Zn and Cu incorporate with the Ca bearing compounds via sorption/precipitation mechanism, while Pb incorporates with the phosphate and sulphate.

Zhang et al. (2016) studied the leaching mechanism of Ca, Na, K, Al, Cr, Ag, As, Zn, Mn, Cu, Ba, Cd, Pb, Se and So_4^{-2} from aged and fresh municipal solid waste incineration fly ash investigated using USEPA test method at various pH range (2-14). The experimental results show that cationic leaching pattern followed by the majority of metals. The high concentration of leached Al at extremely acidic and alkaline phase show amphoteric leaching pattern. Se and Ba leaching very higher at alkaline condition represent the oxyanionic leaching pattern.

Table 2.4 The major difference in-between a) ASTM D3987-12, b) TCLP 1311, c) USEPA 1313 test methods

Test Methods	**ASTM D3987-12 (Standard practice for shake extraction of solid waste with water)**	**TCLP method 1311 (Toxicity characteristic leaching procedure)**	**USEPA 1313 (Liquid-solid portioning as a function of extract pH using a serious of batch extraction procedure)**
Solid/ liquid ratio	1:20	1:20	1:10
Extraction fluid	Distilled water	Glacial acetic Acid and sodium hydroxide buffers	Target extraction fluid pH (3, 5, 7, 9 and 11) by adding nitric acid and

			potassium hydroxide buffers
Agitation time	18hours± 30 minutes	18hours± 30 minutes	18hours± 30 minutes
Agitation speed	29±2 rotation per minute	30±2 rotation per minute	28±2 rotation per minute
Filtering	Pressure filtering using 0.45µ filter paper used	Pressure filtering using 0.8µ filter paper used	Pressure filtering using 0.45µ filter paper used

Yilmaz (2016) investigated the leaching mechanism of three fly ash collected from various lower grade lignite fired stations. Leaching study conducted by using two test methods such as ASTM D 3987 and TCLP. The major and minor trace elements such as Se, Sb, Pb, Ni, Mo, Mn, Mg, Fe, Cu, Cr, Co, Cd, Ca, Ba, As and Ag were investigated. In both leaching test method major cationic element calcium found in very higher concentration. Surface morphology results show that stabilization of several toxic metals such as Sb, Se, Cr, and As elements convert into in the form of ettringite. The major difference in-between a) ASTM D3987-12, b) TCLP 1311, c) USEPA 1313 test methods as shown in Table 2.4.

2.7 Factors affecting leaching

Chemistry of the compounds in any material along with other physical and chemical properties influences the leaching potential of that material. Also, the surrounding atmosphere plays a role in deciding the leaching potential. (Kida et al., 1996: van der Sloot et al., 2003). Kosson et al. (2002) studied the effect of the presence of ions and dissolved organic carbon on the leaching which modifies the characteristics and composition of the solution and liquid-solid proportioning equilibrium.

2.7.1 pH

The pH of the material and the pH of the environment are key components influencing the release of numerous constituents for different sorts of materials, particularly for those whose release is solubility controlled or sorption controlled. pH has a strong impact since dissolution and sorption processes are pH dependent (van der Sloot and Dijkstra, 2004).

The pH at which leaching happens is influenced by the pH of the material, the pH of the environment, and the acid-base neutralization capacity of the material. The acid-base neutralization capacity determines how the pH changes over time under the influence of environment factors (van der Sloot and Dijkstra, 2004). However, Theis and Wirth (1977a) found that the leachate pH may become either basic or acidic when the fly ash content in the soil-fly ash mixture is increased. Factors that are believed to be responsible for this alteration are amorphous iron that is associated with the acid content, and soluble calcium that represents the alkaline component of fly ash.

The change in pH affects the release of heavy metals from fly ash by (a) increasing of dissolution and/or desorption of metal-bearing mineral phases under acidic conditions (Sauer et al. 2005); or (b) diminishing leaching due to precipitation and/or an increasing of partitioning into a solid phase at higher pH or under alkaline conditions (Sauve et al., 2000, Bin-Shafique et al., 2002, Wang et al., 2004).

2.7.1 (a) Effect of pH on solubility

Low pH generally favours the leaching of many metals from fly ashes (Rao et al. 2002). Leachability of metals (such as Cd, Cr, Zn, Pb, Hg and Ag) was also enhanced at the lower pH when an intensity of acid increased (Kirby and Rimstidt, 1994; Fleming et al., 1996). However, the alkaline nature of the ashes can diminish the release of metals from many coal fly ashes (Drakonaki et al., 1998).

The release of metals due to the dissolution of metal-bearing mineral phases under acidic conditions is attributed to the attack of hydrogen ion on the bonds of mineral oxides and other phases. The rate and concentration of leached metals are a function of the original abundance of metal-bearing mineral oxides, the oxide mineralogy of the ash, the spatial distribution of the oxides within ash particles, and the physical properties of ash particles (e.g. porosity) (Fleming et al., 1996).

When a solid oxide and hydroxide is in equilibrium with free ions in solution, the solubility is decreased linearly with increasing pH represented by decreasing free metal-ion concentration [Mez^+] in solution. However, this log [Mez^+]-pH diagram assumes that only uncomplexed species of metal ions and hydroxide ions are present.

The occurrence of hydroxo-metal complexes in equilibrium with solid must consider for evaluation of complete solubility (Stumm and Morgan, 1996).

In addition, the change in solution pH highly affects which solid phases control the release of elements. For instance, Al^{+3} activities in leachate from fly ash and flue gas desulfurization sludge are controlled by the solubility of $AlOHSO_4$ at low pH, by amorphous $Al(OH)_3$ at midrange pH (6-9), and by gibbsite at higher pH (Mattigod et al., 1990).

Under alkaline conditions, the leachability of many metals decrease as a result of increasing precipitation and/or adsorption (Mizutani et al., 1996). Divalent cations can react with hydroxide ion (OH-) and precipitate as metal hydroxides at high pH (Mizutani et al., 1996). Precipitation at high pH can completely remove Cu(II), Ni(II), Zn(II) and Pb(II) (Ricou et al., 1999). In contrast, amphoteric metals, such as Pb, Cr, Zn and Cu, can readily dissolve in leachate under both acidic and extremely alkaline conditions (Lim et al., 2004) and form complex ions and solutes (Mizutani et al., 1996). For example, the leaching test conducted by Lim et al. (2004) on clay-amended with combustion fly ash showed that amphoteric metals were least mobile at pH between 9 and 10 and their concentration increased significantly when the pH was outside this range.

2.7.1 (b) Effect of pH on sorption

Adsorption-desorption mechanisms play a significant role in the release of heavy metals from fly ashes when the equilibrium concentration of metals is far below the saturation concentration. Key factors affecting metal partitioning in fly ash include pH and surface physical-chemical characteristics of fly ash, including surface site densities, acidity constants, surface electrical characteristics, specific surface area, metal binding capacities, and metal binding strength (Wang et al., 2004).

Solution pH affects sorption on metal oxides by influencing the solid-phase surface and the speciation of the adsorbate in solution (Riemsdijk and Hiemstra, 1993). The metal oxide or hydroxide surfaces exhibit an amphoteric behaviour of which the surface can be either positively charged or negatively charged depending on the pH of the system. A change in the surface charge of the reactive solid phases results in a change in electrostatic repulsion or attraction that affects metal adsorption. The pH at which the mineral surface is neutral or uncharged is called the point of zero charges (ZPC) (Riemsdijk and Hiemstra, 1993).

Surface charge of oxides, hydroxides, phosphates, and carbonates is established mainly by ionization of surface groups. Typically, the surface of minerals is positively charged at low pH and negatively charged at high pH. In case proton is the only cation in the system, the positively charged is attributed to protonation, whereas the negatively charges were due to deprotonation. An example of the pH-dependent surface charge of silicate with increasing of pH can be described as $SiOH^{2+}$, SiOH, and SiO^- (Langmuir 1997). For fly ash, Wang et al. (2004) found that the surface of fly ash is positively charged when the solution pH is less than pHzpc and negatively charged when the solution pH is higher than pHzpc. Sorption of metals (Cd, Cr, Cu, Ni and Pb) increased with an increase in pH. All metals they studied were almost completely removed from the solution for pH greater than 8 (Wang et al., 2004).

2.7.1 (c) Reduction/Oxidation

The chemical form is important affecting leaching behaviour. Metals may be present in an oxidized or reduced form depending on the redox state of the metal and the environment. For instance, chromium may be present as CrO_4^{2-} or Cr^{3+} (van der Sloot and Dijkstra, 2004).

The redox condition of a solution is often reported in term of the redox potential (Eh), which indicates the tendency of a chemical species to accept or transfer electrons (Stumm and Morgan, 1996). Reducing conditions, indicated by low or negative Eh, have been reported for leachate from alkaline fly ash (Garavaglia and Caramuscio, 1994). However, the redox potential in coal waste field disposal sites has been reported vary widely from the very reduced condition for flue gas desulfurization (FGD) disposal site (EPRI, 1989), to a very oxidized condition in a fly ash field lysimeter containing chrome (Fruchter et al., 1990).

Electrochemical processes influence metal speciation and redox behaviour by modifying the nature of the metal itself, or by conversion of other species within the environment (Pohland et al., 1993). Many elements (e.g., As, Cr, Cu, Fe, Hg, Mn, Mo, Se, U, V and the actinide elements) may exist in more than one oxidation state (Davis et al., 1993), and oxidation state can dramatically affect solubility, toxicity, reactivity, and mobility (Fish, 1993). For example, leachability and mobility can differ orders of magnitude under oxidizing conditions and reducing conditions (Davis et al., 1993, van der Sloot et al., 1994).

The effect of redox condition on leachability varies depending on the chemical species. Leaching of some metals (e.g. As, V, Fe and Pb) increases significantly under reducing conditions, whereas leaching of other metals (e.g. Cr) increases under oxidizing conditions (Dusing et al., 1992). Other metals (e.g. Mo) are hardly affected under reducing environment (van der Sloot, 1991).

2.7.1 (d) Ionic Strength

The ionic strength of a solution influences both dissolution (van der Sloot and Dijkstra, 2004) and sorption of heavy metals (Impellitteri et al., 2001). The interaction of charged particles in solution deviates particles from ideal behaviour and affects the "effective concentration" or "activities" of particles for the reaction (Langmuir, 1997). The intensity of the interactions of the charged particles in solution depends on the charges of the ions and the total concentrations of ions in solution. These effects are embodied and expressed as ionic strength (Langmuir 1997). Since the solubility equilibrium is calculated from the "effective concentration" of each species in solution, the solubility equilibrium is strongly influenced by ionic strength. In contrast, an increasing in ionic strength decreases sorption of cations in soil systems, which is attributed to a decreasing in thickness of the reactive layer for cation sorption (Impellitteri et al., 2001).

2.8 Geochemical modelling

Geochemical modelling is the exercise of the utilization of chemical kinetics and chemical thermodynamics, or both to identify the chemical interaction effects the geological framework with the help of a computer. Geochemical modelling is used in various field exercise, ecological protection remediation works (Zhu and Anderson, 2002).

2.8.1 Development of geochemical modelling

Garrels and Thompson (1962) first applied chemical modelling to geochemistry at 25 °C and one atmosphere total pressure. Their calculation, computed by hand, is now known as an equilibrium model, which predicts species distributions, mineral saturation states, and gas fugacities from measurements of bulk solution composition. By removing small aliquots of solvent water from equilibrated spring water and repeatedly recalculating the species distribution, Garrels and Mackenzie (1967) simulated the reactions that occur as spring water evaporated. This coupling of mass transfer with an equilibrium model, known as a reaction path model, enabled geochemists to simulate reaction processes.

Helgeson (1968) introduced the first computer program to solve equilibrium and reaction path models. which he and co-workers used to model geological processes like weathering, sediment diagenesis, evaporation, hydrothermal alteration, and ore deposition (Helgeson et al., 1969). Later developments in geochemical modelling included reformulating the governing equations, first as ordinary differential equations, then later as algebraic equations. Additionally, chemical components came to be represented in models by aqueous species, minerals, and gases, rather than by the elements and electrons which make up the species, simplifying the governing equations and their numerical solution (Bethke, 2008).

2.8.2 Setting up a geochemical modelling

An aqueous system is uniquely defined by its chemical composition, temperature, and pressure (Anderson. 2009). Creating geochemical models of such systems begins by choosing the basis, the set of aqueous species, minerals, and gases which are used to write chemical reactions and express composition. The number of basis entries required equals the number of components in the system, which is fixed by the phase rule of thermodynamics. Typically, the basis is composed of water, each mineral in equilibrium with the system, each gas at known fugacity, and important aqueous species. Once the basis is defined, a modeler can solve for the equilibrium state, which is described by mass action and mass balance equations for each component (Bethke, 2008).

In finding the equilibrium state, a geochemical modeler solves for the distribution of mass of all species, minerals, and gases which can be formed from the basis. This includes the activity, activity coefficient, and concentration of aqueous species, the saturation state of minerals, and the fugacity of gases. Minerals with a saturation index (log Q/K) equal to zero are said to be in equilibrium with the fluid. Those with positive saturation indices are termed supersaturated, indicating they are favoured to precipitate from solution. A mineral is undersaturated if its saturation index is negative, indicating that it is favoured to dissolve (Anderson, 2009).

Geochemical modelers commonly create reaction path models to understand how systems respond to changes in composition, temperature, or pressure. By configuring the way mass and heat transfer are specified (i.e., open or closed systems), models can be used to represent a variety of geochemical processes. Reaction paths can assume chemical equilibrium, or they can incorporate kinetic rate laws to calculate the timing of reactions. In order to predict the distribution in space and time of the chemical reactions that occur along a flow path, geochemical models are increasingly being coupled with hydrologic models of mass and heat transport to form reactive transport models (Bethke, 2008). Specialized geochemical modelling programs that are designed as cross-linkable re-entrant software objects enable the construction of reactive transport models of any flow configuration.

Geochemical models can simulate various kind of reactions such as, oxidation and reduction reactions, sorption, surface complexation, ion exchange, aqueous complexation, acid base reactions, stable isotope fractionation, radioactive decay, and catalysed by enzymes.

Zhang et al. (2016) studied the leaching controlling mechanism with the help of geochemical modelling. Analyses results show that Ag, Se, As and Cr were governed by precipitation or dissolution mechanisms of their carbonate, sulphates and hydroxide minerals. Ag, Se and As not controlled by any solid phases, sorption leaching mechanism controlling leaching of these heavy melts in this current study. Also, soluble $BaCrO_4$ controlled leaching of Cr. The concentration of leached elements controlling mechanism was significantly not affecting by municipal solid waste incineration fly ash age.

Komonweeraket et al. (2015) investigated the major oxidation states of leached elements and describes their controlling mechanisms using computer software Geochemical Model MINTEQA2. The analysis results show that releases of elements were controlled by solubility. Hydroxide and oxide minerals governed the leaching of Cr, Zn, Fe and Al and Cu was governed by carbonate and oxide minerals.

Komonweeraket et al. (2015) investigated that leaching mechanism of Sr, Se, Mg, Cd, Ca, Ba and As from soil, fly ash and Soil-fly ash blends were identified at a various pH range 1.5 to 14 via geochemical analysis. the pH of the effluent solution, Eh (oxidation reduction potential) and metal concentration obtained from the pH static experiments were used as input data for geochemical analysis. The modelling results revels that release of metals (except Se and As) governed by the precipitation and dissolution of hydroxide, oxide, carbonate and sulphates solids. Analysis shows that Mg and Cd leaching were governed by the minerals of carbonate, and Sr, Ba and Ca were controlled by the minerals of sulphate and carbonates depending on the leachate of pH. Se and As were not controlled by the precipitation/dissolution of hydroxide or oxide minerals.

2.9 Stabilization/solidification of BMWBA using geopolymer

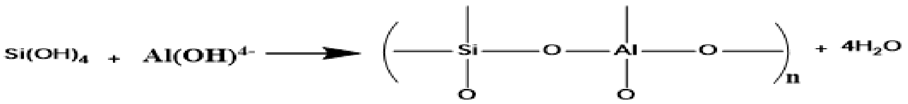
The term ‘geopolymer’ was invented by French researcher Prof. Joseph Davidovits in the year 1970s and its very useful for solid substance synthesized by the reaction of an alumina-silicate powder with an alkaline solution (Davidovits, 1991). Geopolymers are made by the formation of chain structure with the help of Al and Si ions. The chemical configuration of geopolymers substance similar to the natural zeolite, the only difference is in the morphology i,e amorphous microstructure instead of crystalline (Palomo et al., 1999; Xu and van Deventer, 2000). The polymerization process involves a substantially fast chemical reaction on Si-Al minerals under the highly alkaline condition, which results in a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds, as follows (Davidovits, 1999).

$$Mn[-(SiO_2)\ z\text{–}AlO_2]\ n.\ wH_2O$$

Where: M = the alkaline element or cation such as potassium, sodium or calcium; the symbol "–" indicates the presence of a bond, n is the degree of polycondensation or polymerization; z is 1, 2, 3 or higher, up to 32.

The schematic formation of geopolymer material can be shown as described by equation (2.1) and equation (2.2) (Davidovits, 1999). These formations indicate that all materials containing mostly Silicon (Si) and Aluminium (Al) can be processed to make the geopolymer material.

$$(Si_2O_5Al_2O_2)_n + H_2O + OH_2^- \longrightarrow Si(OH)_4 + Al(OH)^{4-} \quad \ldots (2.1)$$



$$Si(OH)_4 + Al(OH)^{4-} \longrightarrow (-Si-O-Al-O-)_n + 4H_2O \quad \ldots.(2.2)$$

Geopolymer consists of three formations (Davidovits, 1999, 2002). According to Davidovits, these structures can be of three types a) (–Si–O–Al–O–) poly(sialate), b) (Si–O–Al–O–Si–O) poly (sialate–siloxo), and c) (Si–O–Al–O–Si–O–Si–O) poly (sialate–disiloxo). Molecular Structure of Geopolymer as shown in Figure 2.10.

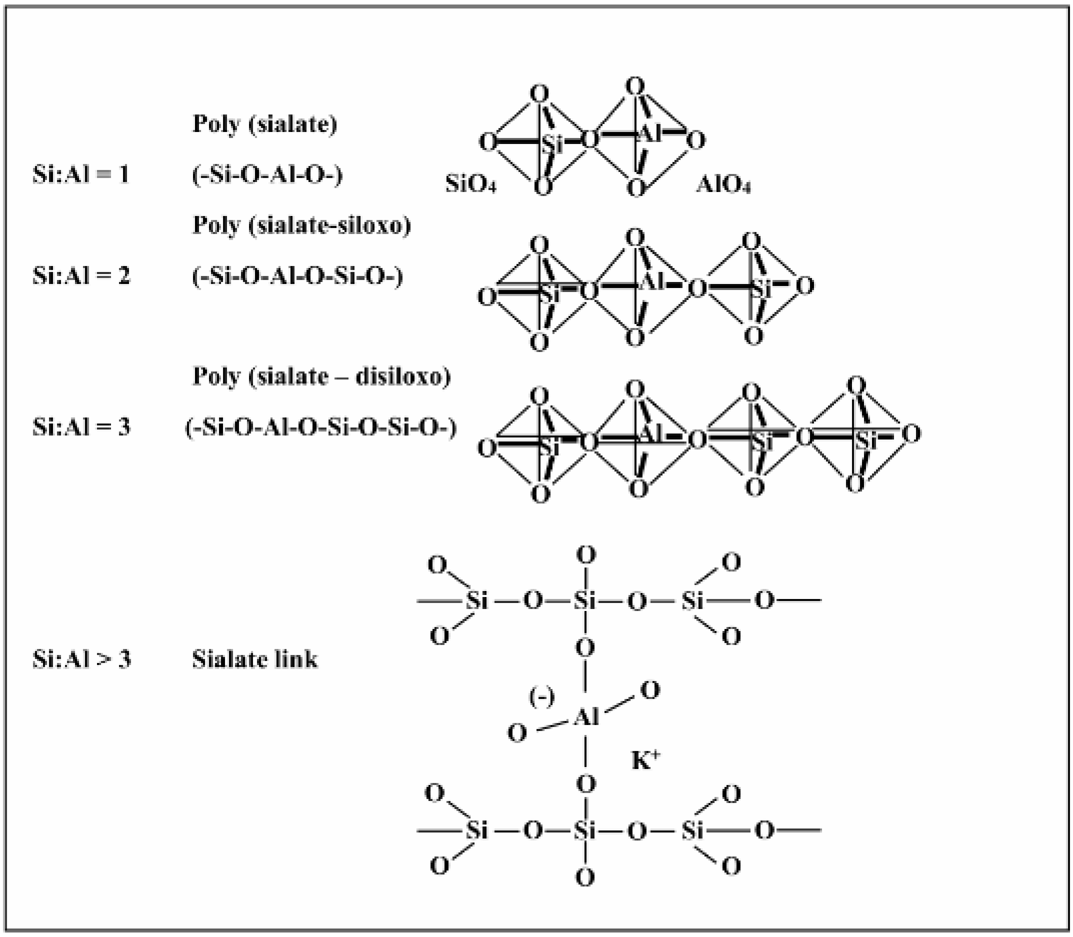


Figure 2.10 Molecular Structure of Geopolymer (Davidovits, 1999, 2002)

Duxson et al. (2007) have given a brief description of the conceptual model of geopolymerization as shown in Figure 2.11.

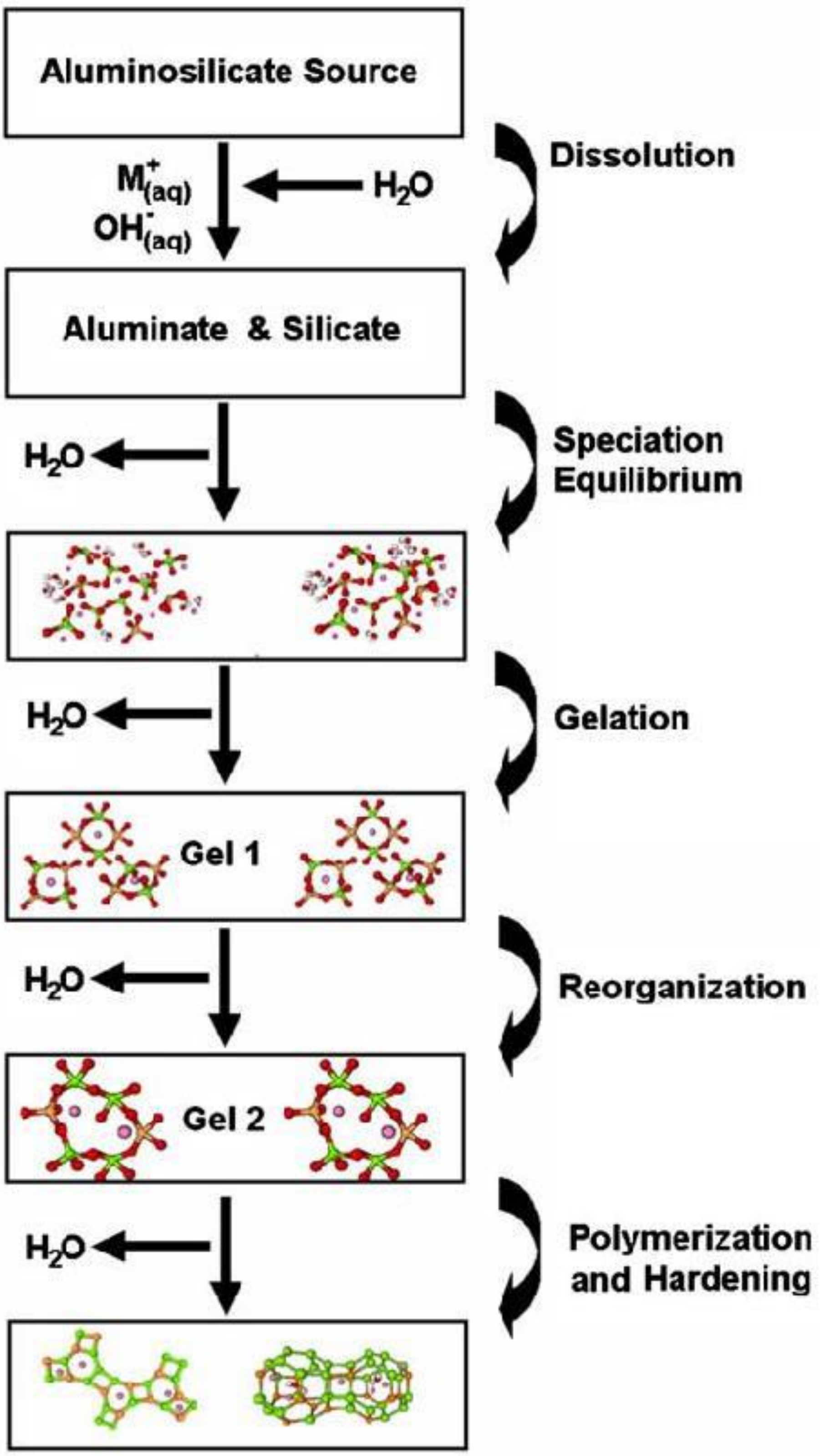


Figure 2.11 Model of geopolymerization (Duxson et al., 2007)

2.10 Factors affecting the properties of geopolymer mortar mixes

For twenty-five years, geopolymer science was studied in very few laboratories and institutions. But during the last ten years, research on geopolymer has increased extensively throughout the world. The challenges of using geopolymer, the methods to be adopted during mixing, the factors to be considered etc. noted from a brief review of previous studies on geopolymer mortar and concrete mixes is presented here. From the previous research work, it can be said that the factors, which play important role on the properties of geopolymer mortar mixes, are concentration of Sodium Hydroxide (SH) solution, ratio of Sodium Silicate (SS) solution to the SH solution, modulus of alkali activator, curing conditions, and alkali liquid to fly ash/slag ratio etc. The effect of these different factors on the properties of geopolymer mixes is going to be reviewed from the past studies.

2.10.1 Effect of alkaline solution

Alkaline solutions such as sodium/potassium hydroxide (NaOH/KOH) solution and soluble silicates have a significant role in the properties of geopolymer mortar mixes. The effect of the addition of chemical activators on the physical, mechanical, durability, shrinkage, and microstructural properties of geopolymers are discussed in this section.

Tzanakos et al. (2014) investigated that stabilization/solidification of hospital waste ash using sodium silicate, sodium hydroxide (10 molar) and metakaolin were mixed. Geopolymer matrices were cured for 24 hours at 50˚C. Leachability of toxic heavy metals and strength of the specimens were measured at 7 and 28 days. The effects of the additional calcium compounds were investigated. The experimental results reveal that hospital waste ash can be utilized as an alternative material to produce the geopolymers. The addition of the fly ash and calcium substance significantly improves the strength of the moulded cubes. Leaching test results show that the geopolymerization technique can reduce the concentration of the toxic heavy metals in the hospital waste ash.

Neto et al. (2008) studied drying shrinkage and autogenous shrinkage of mortar samples prepared with activated slag cement. Samples were prepared with the consideration of the Na_2O dosage of 2.5%, 3.5% and 4.5% by the mass of slag. Sodium silicate having silica modulus 1.7 was used in this study. Considerable increment of drying and autogenous shrinkage and early hydration were observed with the increase of silica in activator solution. They concluded that extensive water loss when the samples were exposed to the environment and less water loss due to the hydration process might be the reasons for drying shrinkage. Refinement of activated slag cement of porous system was marked as the reason for autogenous shrinkage.

Thockhom et al. (2009) studied the resistance of geopolymer mortar samples produced with different percentage level of Na_2O in alkali activator solution kept in 10% sulphuric acid solution for a period of 18 weeks. Na_2O content varied from 5% to 8 % of fly ash. The ratio of water to binder and ratio of sand to fly ash were kept as 0.33 and 1.0 respectively. Cast specimens were kept at 85°C for 48 hrs for heat curing. Based on their study, it is concluded that geopolymer specimens lost its alkalinity within 15 weeks in the above-mentioned acid solution. After keeping samples in acid solution, weight loss of the geopolymer samples showed less than Ordinary Portland Cement (OPC) samples.

Guo et al. (2010) carried out a study on compressive strength and microstructural characteristics of class C type of fly ash based geopolymer. The investigation was carried out at modulus of the mixed alkali activator 1.0, 1.5, 2.0 and 5% - 15% mixed alkali activator content by the mass of Na_2O to class C fly ash. The ratio of water to the class C fly ash was kept at 0.4 (by mass). The optimum modulus of mixed alkali activator was found to be 1.5 and content of alkali activator (by mass of Na_2O to fly ash) be 10% to get high compressive strength. From the microstructural analysis, they concluded that calcium silicate hydrate was formed along with geopolymeric gel i.e. sodium-poly (sialate-disiloxo) and some un-reacted spheres also observed.

Vargas et al. (2011) investigated the effects of the molar ratio (Na_2O/SiO_2) on the properties of alkali-activated fly ash geopolymer materials. 97% sodium hydroxide

(NaOH) was used as the alkaline activator in this study. The molar ratio was varied at 0.20, 0.30 and 0.40. High compression strength was observed for the mortar samples prepared with the alkali solution of molar ratio 0.40 and denser morphology was noticed for the samples of geopolymer prepared with the alkali solution of molar ratio 0.40.

Ridtirud et al. (2011) studied the effects of the concentration of sodium hydroxide (NaOH) solution and the ratio of sodium silicate (Na_2SiO_3) to sodium hydroxide solution on the shrinkage of fly ash based geopolymers. In this experiment, the ratio of sodium silicate to NaOH and the ratio of liquid to ash were used as 0.67 and 0.6 respectively. For this test, 40 °C temperature was used as the curing temperature of samples. Concentrations of NaOH Solution were taken as 7.5M, 10.0M, and 12.5M. Based on results, they concluded that the concentration of NaOH solution has little effect on compressive strength, but significant effects on shrinkage. High shrinkage was observed for geopolymer produced with 12.5M NaOH solution comparing to that with a lower NaOH concentration. In another phase, different ratios of sodium silicate to sodium hydroxide solution (0.33, 0.67, 1.0, 1.5, and 3.0) were taken to prepare the samples of geopolymer mortars for testing. Low drying shrinkage of geopolymers was observed for high sodium silicate to NaOH ratio of 3.0 as compared to other geopolymers produced with the other ratios of sodium silicate to NaOH (0.3 - 1.5). In another phase of this research work, the ratio of liquid to ash was varied as 0.4, 0.5, 0.6, and 0.7 for the preparation of geopolymer samples. Significant increase in shrinkage was found with the increase in the ratio of liquid to ash from 0.4 to 0.7.

Dutta et al. (2012) did a comparative study on the properties of geopolymer paste prepared with different alkali activators. Potassium hydroxide (KOH) and sodium hydroxide (NaOH) were used as alkali activators. Sodium silicate solution was added to hydroxide solution 3 hours before being used to prepare geopolymer specimens and SiO_2/Na_2O or SiO_2/K_2O ratio was maintained at 1 and 1.5. Cast specimens were kept at 85°C for 48 hours for curing. Experimental results show higher compressive strength for specimens activated by potassium hydroxide solution when the ratio SiO_2/K_2O is 1.5 and higher compressive strength for specimens activated by sodium hydroxide solution when the ratio SiO_2/Na_2O is 1. Samples activated by sodium hydroxide solution exhibited little lower early strength than the strength after 28 days for specimen prepared with potassium hydroxide solution. Significant increase in compressive strength was observed with time for specimens activated by sodium hydroxide solution.

Chindaprasirt et al. (2012) investigated the influence of silica and alumina contents on the physical properties of high calcium fly ash geopolymers. By adding nano-silica, RHA, or nano-alumina to mixes, the contents of silica and alumina varied whereas the control mix prepared with fly ash, sodium silicate, and sodium hydroxide solution in required quantities. In this experimental work, the contents of fly ash and water were kept constant in all mixes. Acceleration of setting of geopolymer was observed with the increase of alumina and silica both. The optimal SiO_2/Al_2O_3 ratio was found to be in the range of 3.20 - 3.70. Reduction in strength was also noticed while increasing the silica content ($SiO_2/Al_2O_3> 4.3$) for high calcium fly ash based geopolymers.

2.10.2 Curing conditions

Somna et al. (2011) concluded from their study that sodium hydroxide activated ground fly ash geopolymer paste can be produced with reasonable strength at room temperature. NaOH concentrations are mentioned as the attribute for the variation of the compressive strength and microstructure of the geopolymer pastes.

Pangdaeng et al. (2014) studied the influence of different curing conditions on the properties of high calcium fly ash based geopolymer when ordinary Portland cement was used as an additive. 10M sodium hydroxide (NaOH) and sodium silicate solution (15.32% Na_2O, 32.87% SiO_2, and 51.81% H_2O) were used as alkaline solutions throughout the experiment. In this experiment, the ratio of liquid alkaline to binder (L/B) and the ratio of sodium silicate to sodium hydroxide (Na_2SiO_3/NaOH) was maintained constant as 0.40 and 0.67 respectively. 50 mm × 50 mm × 50 mm cube samples fresh geopolymer pastes and mortars were covered with a damp cloth and vinyl sheet and kept in 23°C for 24 hrs. After de-moulding, samples were kept following different curing conditions: Vapour-proof membrane curing (after de-moulding, samples were kept with a vapor-proof membrane wrapping to avoid moisture loss and 19 kept at 23°C), temperature curing (samples cured at 40°C for 24 hours after wrapping with a plastic membrane to avoid moisture loss. After that the samples were demoulded and kept at 23°C), and wet curing (de-moulded samples were kept in water at 23°C until the day of testing). Results indicated high compressive strength at a later age for vapor-proof membrane curing and water curing. High early compressive strength was observed for temperature curing.

2.11 Summary of the literature

Several factors including the reaction type, the time scale of the leaching processes and the leaching environment must be considered in the assessment of major leaching processes. It is also necessary to use different approaches for different leaching scenarios. The methods used in this study are based on the interactions between the combustion residue and an aqueous solution, emphasising the leaching kinetics. Although experimental investigations provide important information on the leaching of combustion residues, geochemical modelling is essential to obtain an insight into the leaching processes. The experimental investigation combined with geochemical modelling is the basic method of assessing the leaching processes. It should be mentioned that geochemical models are often only tools to analyse the complicated processes and to predict their long-term behaviour when the processes involve times too long to perform laboratory experiments. Further, Ordinary Portland cement (OPC), metakaolin and lime were used as binder material/additive for the stabilization/solidification process for hazardous material. But OPC, metakaolin and lime were costlier material.

2.12 Gaps identified

From the review of literature in earlier sections, several research gaps have been found which are discussed in this section. Several leaching studies show they used only one standard test methods for leaching test to identify the various toxic heavy metals. Past studies have adopted geochemical modelling for the various soil stabilization work and road embankment works, but very less study found in the cause of hazardous waste management. Further, Ordinary Portland cement (OPC), metakaolin and lime were used as binder material/additive for the stabilization/solidification process for hazardous material. But OPC, metakaolin and lime were costlier material.

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 General

The details of the experimental programme in terms of materials, the experimental setup for determining the effect of different parameters, testing procedures for leaching and stabilisation process and input parameters for model development have been discussed in this chapter.

3.2 Materials

3.2.1 Sample collection

3.2.1 (a) Biomedical waste bottom ash

The Biomedical waste bottom ash (BMWBA) was collected from (Biomedical Waste management Services, nearby Mangalore) biomedical incineration plant. The ash consists of the incinerated radioactive, infectious and hazardous material (pharmaceuticals, body parts, human tissues, blood products) from the clinics, hospitals and laboratories. And, some of the unburnt substance such as sharp needles and syringes. The BMWBA is having very stringent odour and greyish black colour with a particle size below 2.36 mm and to be stored in an air-tight container. Hence handling biomedical ash for sample preparation and other experimental part is typically a tricky task. The samples were collected according to ASTM D6009 standard guidelines for sampling waste piles. Chemical composition of BMWBA is as shown in Table 3.1.

3.2.1 (b) Ferrochrome Ash

Ferrochrome ash (FCA) is a waste material obtained from the gas cleaning plant of the steel industry in the form of ash. Ferrochrome is the ferroalloy, i.e., an alloy with iron and chromium characteristics, around 50% to 70% of chromium will be present in it by its weight. The samples were collected according to the ASTM D6009 standard guidelines for sampling waste piles. Chemical composition of FCA is as shown in Table 3.1.

3.2.1 (c) Ground granulated blast furnace slag

Ground-granulated blast furnace slag (GGBFS) is a by-product generated in iron and steel industries. GGBFS is generated in the process of quenching the molten slag with water or steam after obtaining the slag from blast furnace. The material obtained after quenching is glassy in nature and this granular material is ground into fine powder. This processed glassy product is termed as GGBFS. Chemical composition of GGBFS is as shown in Table 3.1.

Table 3.1 Chemical Composition of BMWBA, FCA and GGBFS (Percentage by weight)

Constituents	BMWBA	FCA	GGBFS
SiO_2	20.2	23.5	31.23
CaO	39.6	0.49	33.7
Al_2O_3	9.2	34.13	16.6
Fe_2O_3	7.2	1.61	1.3
Na_2O	2.9	0.25	0.2
MgO	3.1	2.59	9.96
K_2O	0.8	33.8	0.06
SO_3	5.6	-	0.81
Cr_2O_3	-	2.64	-

3.2.1 (d) Alkaline solution

Alkaline solution is a combination of sodium silicate and sodium hydroxide chemicals. Sodium hydroxide is available in the form of flakes and sodium silicate in the form of solution. Composition of sodium silicate and sodium hydroxide in proper proportions and optimum dosage of sodium oxide and molarity of solutions must be worked out to arrive at proper mixing and binding. Sodium silicate solution has 8.5%Na_2O, 28.0%SiO_2 and63.5% water in the composition. In the current work, 98 % pure sodium hydroxide in the form of flakes was taken for the preparation of sodium hydroxide solution. The ratio of 1:2 of sodium silicate and sodium hydroxide was maintained. The mixture of sodium hydroxide and sodium silicate was prepared one day prior to the experiment (before 24 hours).

The number of moles of a solute in one litre of the solution is termed as Molarity which describes the concentration of the solution. In order to prepare one litre of 1M solution, one mole of solute is required to be dissolved into water. Therefore, to prepare

1M sodium hydroxide solution, 40g of sodium hydroxide pellets/flakes are required to be dissolved in water and made up to one litre sodium hydroxide solution. Similarly, to prepare one litre of 10M of NaOH solution 400 grams of sodium hydroxide pellets/flakes to be dissolved in distilled water.

3.3 Chemical and physical properties

3.3.1 Specific Gravity

The specific gravity of BMWBA, FCA and GGBFS was determined as per IS: 2386 (Part 3) - 1963 using density bottle method in which 1/3rd of the density bottle was filled with the ash/slag and the weight is noted down. The bottle is then filled with kerosene and weighed. Later, it is emptied and dried. Then, the clean density bottle is filled with kerosene and weighed. Specific gravity of BMWBA, FCA and GGBFS is reported in Table 3.2.

3.3.2 Blaine's fineness test

Blaine’s finesse test was conducted to identify the specific surface of material expressed in terms of m^2/kg according to ASTM C 204-11 (Table 3.2).

Table 3.2 Specific Gravity of BMWBA, FCA and GGBFS

Material	BMWBA	FCA	GGBFS
Specific gravity	2.61	2.72	2.90
Blaine's Fineness (cm^2/gm)	1550	5710	3575

3.3.3 pH

pH is one of the most significant factors in the current investigation. pH test is done to identify the state of acidity or alkalinity of the leached samples. The state of the samples needs to be known to identify its behaviour in different medium (acidic or alkaline mediums). The pH of the samples was measured with Hanna HI 4521 instrument.

3.3.4 Oxidation - reduction potential

Oxidation reduction potential (ORP) measures the affinity of chemical substances by virtue of which they gain and thereby loses electrons. It gives a fair idea about the oxidizing and anti-oxidizing strength of substances. ORP helps in studying oxidizing and reducing characteristics of water or soil thus defines the state of different chemicals or metals in water and in the soil. Some of the oxidizers are Hydrogen peroxide, Chlorine, Ozone, Chlorine di-oxide, Bromine and some of the reducers are Sodium sulphite, Sodium bisulphate and Hydrogen sulphite. Substances acquired from environment have complex chemical and physical characteristics and by doing ORP measurement one can differentiate these substances into Oxidizing and reducing regime. Oxidation- Reduction Potential is another important experiment to identify the redox reaction in the leached solution.

3.4 Methodology

3.4.1 Leaching tests

There are various standard methods available for the analysis of the leaching behaviour of samples. Leaching behaviour can be identified to some extent in the way of short term or long-term analysis. However, both will present the possibility of interaction of particles and leaching solution. To assess the interactions under various possible conditions, experiments have been carried out by three methods viz., a) ASTM D3987-12, b) TCLP 1311, c) USEPA 1313 (Under various pH conditions 3, 5, 7, 9 and 11) to determine the leaching potential.

3.4.1 (a) ASTM D3987-12 (Standard practice for shake extraction of solid waste with water)

In this study, laboratory distilled water is used as an extraction solution and oven dried BMWBA and FCA were used to identify the concentration of leaching of heavy metals. 10 grams of each of oven dried samples was weighed and transferred into 250 mL clean and dried conical flasks and 200 ml distilled water is added. Solid to liquid ratio by weight as 1:20 was maintained. Samples were agitated with rpm speed of 29±2 rotation per minute maintained for 18hours±30 minutes. After agitation, the samples were filtered using a high-pressure filter setup attached with 0.45µ filter paper. Samples were stored in 20 mL high density polyethene bottle and 1 mL of nitric acid was added as a preservative. Then the samples were stored in a refrigerator at 4^{o}C until heavy metal analysis will be done using inductively coupled plasma optical emission spectroscopy (ICP-OES). Pictorial demonstration of ASTM D3987-12 leaching testis as shown in Figure 3.1.

10 g of ash with 200 mL of distilled water

Rotary shaker and agitated at 29±2 RPM

vacuum filter using 0.45µ size filter paper

Figure 3.1 Pictorial demonstration of ASTM D3987-12 leaching test

3.4.1 (b) TCLP method 1311 (Toxicity characteristic leaching procedure)

In this investigation, the glacial acetic acid and sodium hydroxide buffers were used as extraction solution and oven dried BMWBA and FCA were used to determine the concentration of leaching of heavy metals. 10 grams of oven dried samples were measured using laboratory balance of 0.01grams accuracy, transferred into 250 mL clean and dried conical flask and 200 ml extraction solution (glacial acetic acid and sodium hydroxide buffers) was added. Solid to the liquid ratio by weight was 1:20. For each leaching test three trials were carried out and the average result was considered. Experimental procedure is repeated as explained in section 3.4.1.1. Samples were stored in 20 mL high density polyethene bottle and 1 mL of nitric acid was added as a preservative. Then the samples were stored in a refrigerator at 4°C until heavy metal analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES).

3.4.1 (c) USEPA 1313 (Liquid-solid portioning as a function of extract pH using a serious of batch extraction procedure)

In the present study, nitric acid and potassium hydroxide buffers were used to prepare different extraction solutions at pH of various range (3, 5, 7, 9 and 11). 10 grams of BMWBA and fresh and aged (one year) FCA oven dried samples were measured using laboratory balance of 0.01gram accuracy, transferred into 250 mL clean and dried conical flask and 100 ml extraction solution was added. Solid to the liquid ratio by weight was 1:10. For each leaching tests, three trials were carried out and the average result was considered. Experimental procedure is repeated as explained in section 3.4.1 (a) Then the samples were stored in a refrigerator at 4°C until heavy metal analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES).

3.5 Characterization study

Oven dried representative FCA and BMWBA samples were passed through a 425µ sieve and were examined. It is indeed important to determine the morphological features of the ashes to evaluate the toxicity levels. The surface morphology and its elemental configuration were examined by SEM equipped with EDAX analyser (EVO MA18 with oxford EDS(X-act)). The structural phase composition was determined by Rigaku – Minflex 600 XRD in the scanning angle from 20^0-80^0 with a scan speed of 1^0/ sec to indicate the presence of various minerals which leads to contamination.

3.6 Geochemical modelling

Chemical equilibrium model is used in this study by using Visual MINTEQ 3.1 for computing the solution’s composition in the natural water or in the laboratory. Visual MINTEQ 3.1 software running in two steps. Identifying the speciation’s in the leachate was first step, which was used to determine the major dominant oxidation states of the redox sensitive elements. Second step was determining the aqueous concentration of species in present in the leachate and the state of saturation of the leachates with respect to metals or minerals.

3.6.1 Dominant oxidation states

To identify the dominant oxidation states speciation of metals was identified by allowing the redox and aqueous complexation reactions and pH, Eh and USEPA 1313 leaching test results were used as input. When the redox couple and Eh are specified as equilibrium constraints, Visual MINTEQ 3.1 software will determine the sum of the element in each of the two oxidation states corresponding to the specified equilibrium Eh. Firstly, speciation of an element is known, the dominant oxidation sates was identified for the following redox sensitives elements such as Se, As, Cr, Cu and Fe. Ca, Mg, Cd, Zn, Hg having no redox and low sensitivity elements were observed in the leachate.

3.6.2 Calculations used in Visual MINTEQA 3.1 to determines speciation and saturation index

3.6.2 (a) Element speciation calculation

Equilibrium constraints – Equilibrium Eh and redox couple are specified and one member of the redox couple transfers the mass into other so that it leads to their activity ratio and the Nernst Equation is honoured at equilibrium (Allison et al., 1991).

$$\mathrm{E_h(volt)} = \mathrm{E^0} + \left(\frac{2.303*\mathrm{R}*\mathrm{T}}{\mathrm{nF}}\right)\log\left[\frac{\mathrm{a_{Ox}}}{\mathrm{a_{Red}}}\right]\text{........} \qquad (3.1)$$

Where,

F = Faraday constant = 23.061 kcal/volt g eq

T = Absolute Temperature

R = 0.001987 kcal/mol

a_{Ox}=Oxidized state's chemical activity

a_{Red}= Reduced states's chemical activity for the half-reaction presented as a reduction reaction as shown below,

$A + B + ne^- = C + D$

Oxidized state Reduced state

Nernst Factor: Term 2.303RT/F is 0.05916 volts.

i.e., Equilibrium constant is taken as $Fe^{+3} + e^- = Fe^{+2}$ (Redox Couple) and the Eh is specified when Fe^{+3} and Fe^{+2} are the components.

With respect to the specified equilibrium Eh, the amount of Iron present in both the oxidation states is determined by using Visual MINTEQA 3.1 software.

3.6.2 (b) Calculation of chemical activity

To consider the non-ideal effects in the solution, the activity co-efficient has to be estimated for the ionic species. For this purpose, the Davies equation was considered. As per Visual MINTEQA 3.1, the Davies equation is,

$$\log\gamma_i = -Az_i^2\left(\frac{(\sqrt{I}-(0.24*I))}{1+\sqrt{I}}\right)\text{........ (3.2)}$$

Where,

γi = The Activity Coefficient,

A = Constant,

zi = Charge on each species i,

I = Ionic strength of the solution

The Ionic Strength (I) is determined by using,

$$I_{i=1}^{m} = \frac{1}{2}\sum z_i^2 C_i \text{……..} (3.3)$$

Where,

Ci = Concentration of ion species i,

m = Number of charged species present in the solution,

z_i = Charge on species i.

The concentration of species *I* is related to the activity *Si* by the activity co-efficient γI for any species *I*.

$$\{S_i\} = \gamma\,[S_i] \text{……..} (3.4)$$

3.6.2 (c) Calculation of saturation index

For any mineral, saturation index is determined by,

$$SI = \log \frac{(IAP)}{K_{sp}} \text{……..} (3.5)$$

Where,

K_{sp}= Solubility product for the mineral (from theoretical thermodynamic data)

IAP =Ion Activity Product (from the mineral constituents which dissolved activities).

For each mineral, the solution is undersaturated or supersaturated when the saturation index value is positive and the precipitation of such mineral takes place. Similarly, the solution is undersaturated when the saturation index is negative and the dissolution of such a mineral may occur. If the saturation index becomes zero, the solution will be in equilibrium (K_{sp} = IAP) (Allison et al., 1991).

If SI > 0, mineral is supersaturated (IAP > K_{sp})

If $SI<K_{sp}$, mineral is undersaturated

If $SI = 0$, mineral is saturated ($IAP = K_{sp}$)

3.7 Stabilization / solidification of BMWBA

3.7.1 Casting of specimens

In this investigation, the mixture of 0%, 10%, 20% and 30% of GGBFS was added to BMWBA. Each of the proportional mixtures of GGBFS and BMWBA was dry mixed for 2 - 3 minutes using mechanical agitator. The prior prepared alkaline solution added and mixed for nearly 5 minutes using mechanical agitator. The mixture was now ready for pouring in the moulds. Cubes having dimension 50 mm×50 mm × 50 mm were cast to determine compressive strength geopolymer mortar mixes. The cube moulds were filled with fresh mortar and compaction was done by hand operations and then using a vibrating table. Figure 3.2 (a and b) represents the cast sample and de-moulded sample prepared from geopolymer mortar mixes.

(a) (b)

Figure 3.2 (a) Cast cube sample; (b) De-moulded cube sample

3.7.2 Demoulding of test specimens

The specimens cast were removed from the moulds after a day. Without damaging the specimens. The specimens were removed and kept for curing.

3.7.3 Curing of specimens

After careful de-moulding, the cubes were kept for ambient air curing. All cured cube samples were tested at the age of 3, 7, 28 and 56 days to determine the compressive strength of different proportion BMWBA geopolymer mortar mixes.

3.7.4 Compressive strength test

The compressive strength of concrete is given in terms of the characteristic compressive strength for the cubes tested at the different age of curing. The compressive strength test was conducted on cast cubes at 3 days, 7 days, 28 days, and 56 days of curing under different regimes. The average strength of three cube samples with different geopolymer mixes was reported as the compressive strength of the respective BMWBA based geopolymer mixes.

3.7.5 Leaching test for toxic metals

Leaching test is one of the important techniques to estimate the rate of toxic elements that may be released to the atmosphere. Toxicity characteristic leaching procedure (TCLP) method 1313 was used to test toxic metal leaching for the above samples. The extraction solution made by glacial acetic acid and sodium hydroxide buffers with 4.93±0.05 pH. Solid/liquid maintained as 1/20 ratio by weight was adopted. 10g of geopolymer sample was taken in 500mL volume beaker and mixed with 200mL of TCLP extraction solution. Rotary shaker was used to shake the solution at a constant speed of 30 ± 2 rotation per minute for 18hours ±30 minutes. After shaking, the suspensions were settled for 5 min and then the liquid phases were decanted. Later geopolymer slurry samples were filtered using a 0.8 borosilicate glass fibre filter. Filtered leachate samples were stored in a 20mL high-density polyethylene bottle and acidified with nitric acid. Subsequently, samples were stored in 4˚C in the refrigerator to avoid evaporation and volume change. The toxic metals were analyzed using (Agilent Technologies, model 7500cx) Inductively coupled plasma optical emission spectroscopy (ICP-OES).

3.8 Inductively coupled plasma optical emission spectroscopy working mechanism (ICP- OES)

The toxic heavy metal leachate sample is analysed by using ICP-OES in which the sample is passed to the spray chamber through a nebulizer using a peristaltic pump. The aerosol is made to get into the argon plasma which is the fourth state of the matter (after solid, liquid and gas). A cooled induction coil which allows the flow of high frequency AC current produces plasma at the end of a quartz torch. Electrons are accelerated into circular trajectory when the alternate magnetic field is induced. The hotter Plasma at 6000 to 7000 K gets stabled when the ionization of electrons takes place along with the collision between argon atoms. The plasma may reach even 10000 K in an induction zone. Ionization and atomization of the samples occur during the torch dissolvation. The electrons reach higher state of excitation when they receive higher thermal energy. Then, the electrons are dropped back to the ground state to liberate photons or light. Spectrometer is used to measure the emission spectrum of each elements. As per the calibrated value of concentration, the intensity of light on the wavelength is measured. The working principle of ICP-OES equipment is as shown in Figure 3.3.

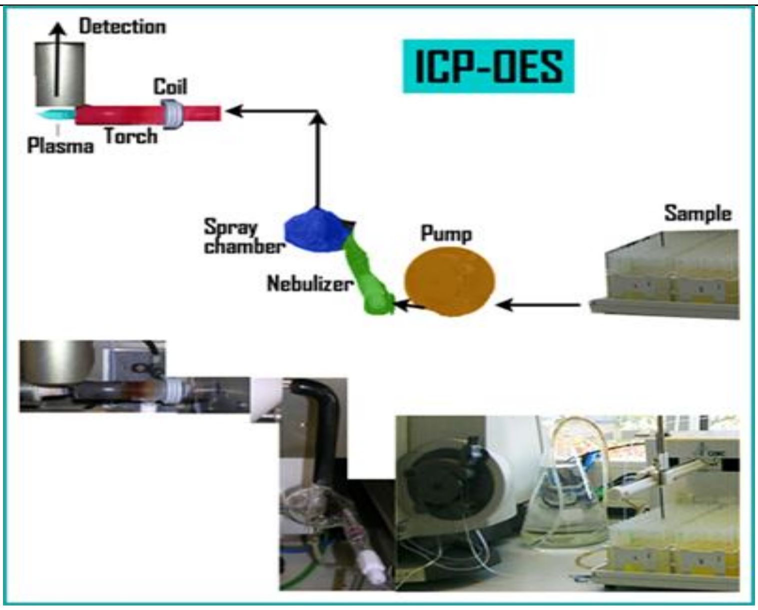


Figure 3.3 The graphical representation ICP-OES working mechanism (Source:https://www.ru.nl/science/gi/facilities-activities/elemental-analysis/icp-oes/)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 General

This chapter describes the results obtained by various leaching test methods. Further governing mechanism for elemental leaching of various heavy metals were presented. Effect of different parameters on workability, compressive strength and heavy metal leaching of different proportion of BMWBA geopolymer mixes are discussed in the following sections.

4.2 Leaching test results

4.2.1 BMWBA

The BMWBA leached samples were examined using ASTM D3987-12, TCLP method 1311 and USEPA 1313 test methods to analyse heavy metal concentrations such as Cr, Cd, Hg, Pb, Se, Co, Ni, Fe, As, Zn and Cu by ICP-OES. The ash is highly reactive when it exposes to atmosphere. Hence it is not viable to conduct the experiment for aged sample.

4.2.1 (a) Results of heavy metal leachates by various protocols: BMWBA

The leaching potential of BMWBA as per ASTM D3987-12 (pH : 6.7) is shown in Figure 4.1. It is inferred that concentration of Hg (4.37 mg/L) and As (8.53 mg/L) are high when compared to the regulatory limits are 0.2 mg/L, 5.0 mg/L respectively as per TCLP disposal limit. Other metals such as Se, Co, Ni, Fe, Cd, Zn, Pb, Ca, Cu and Cr were within the disposal limits. Similarly, leachate potential were experimented by TCLP method 1311 (pH : 4.9) and were depicted in Figure 4.2. It is observed that most of the metal concentrations (Se, Co, Ni, Fe, As, Cd, Zn, Pb, Ca, Cu and Cr) were within the desirable limits except Hg showed higher concentration of 4.61mg/L which is exceeding the TCLP disposal regulatory limit (0.2 mg/L).

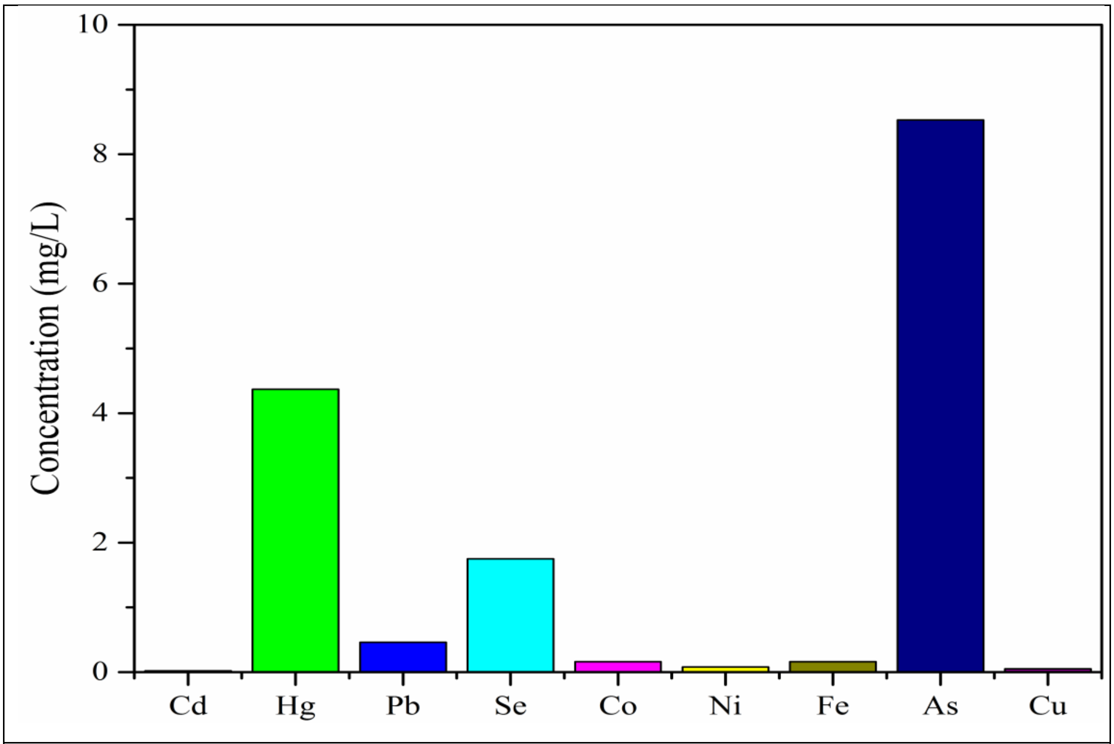


Figure 4.1 Leaching of metals from BMWBA (ASTM test procedure)

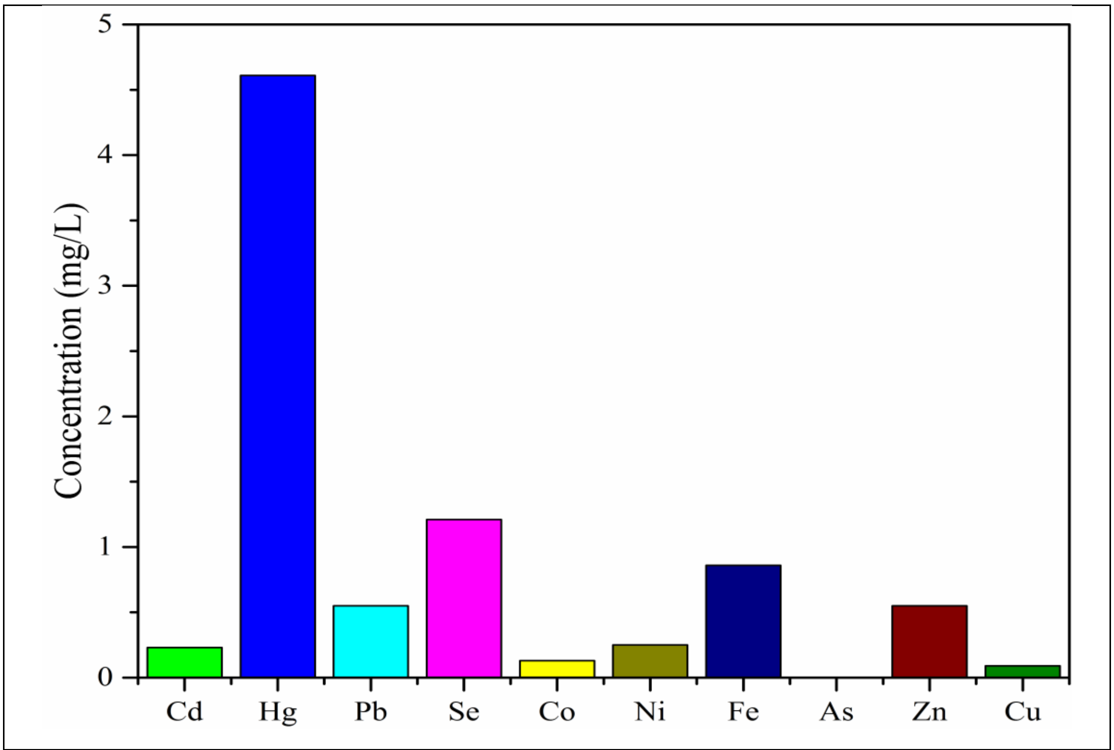


Figure 4.2 Leaching of metals from BMWBA (TCLP test procedure)

pH dependent leaching test was performed by USEPA 1313 method. It is inferred from the experimental results that Hg, Se and As were recognized to be toxic elements as per desirable standards that exist as oxyanions during the pH range of 3 to 11 is as shown in Figure 4.3. These oxyanionic elements Se and As (SeO_3^{2-},SeO_3^{-4} and AsO_3^{-4}) prevent adsorption on the surface of negatively charged BMWBA. Different species of Se and As have a dissimilar affinity for adsorption (surface interaction)/solid solution formation (ion incorporation) and are therefore accountable for the reactions to occur. Adsorption that occurred might be specific or non-specific (Komonweeraket et al., 2015c).

In USEPA leaching procedure, it is found that leaching of Hg (3.5 mg/L and 9.3 mg/L) at pH 3 and 11 and leaching of As (8.53 mg/L and 6.4 mg/L) at pH 7 and 9. Hence it is evident that from all three test procedures, leaching of Hg and As bound to fall under the category of hazardous material as it exceeds the TCLP disposal limits (As limit is 5 mg/L and Hg limit 0.2 mg/L). Hence it is evident that from all three test procedures, leaching of Hg and As bound to fall under the category of hazardous material as it exceeds the TCLP disposal limits (As limit is 5 mg/L and Hg limit 0.2 mg/L).

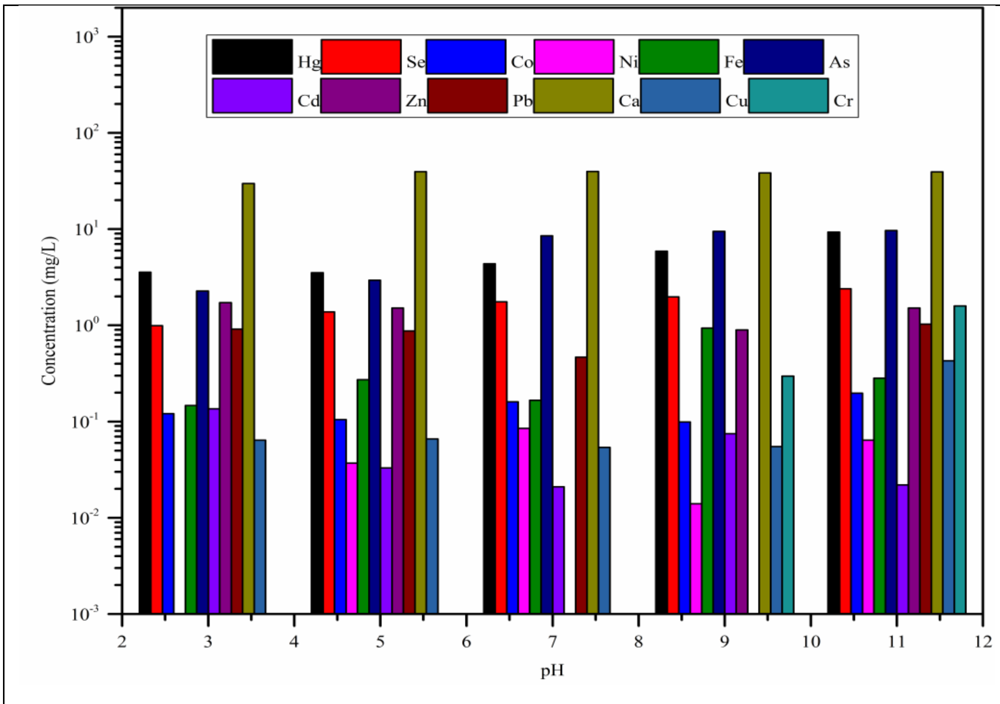


Figure 4.3 Metal concentrations for different pH for BMWBA (USEPA test procedure)

4.2.1 (b) Acid-base neutralization capacity

To identify the amount of acid or base required to achieve the equilibrium condition for BMWBA was investigated. Batch leaching experiments were conducted in the current investigation by adopting solid to liquid ratio as 1:10. Aliquots 1 M KOH and 2 M HNO_3 were mixed to prepare the target pH in the range of 3, 5, 7, 9 and 11; later, the mixture was kept in a shaker using a rotary shaker at 30 rotation per minute speed. The acid-base neutralization capacity (ANC) for BMWBA was demonstrated in Figure 4.4. The results indicate that for pH 3 and 5, during the initial period, shifting of the solution pH towards the alkalinity was very rapid and later reached equilibrium. For pH 9 and 11, it took a longer time to accomplish the equilibrium state due to a slow variation of pH towards alkalinity.

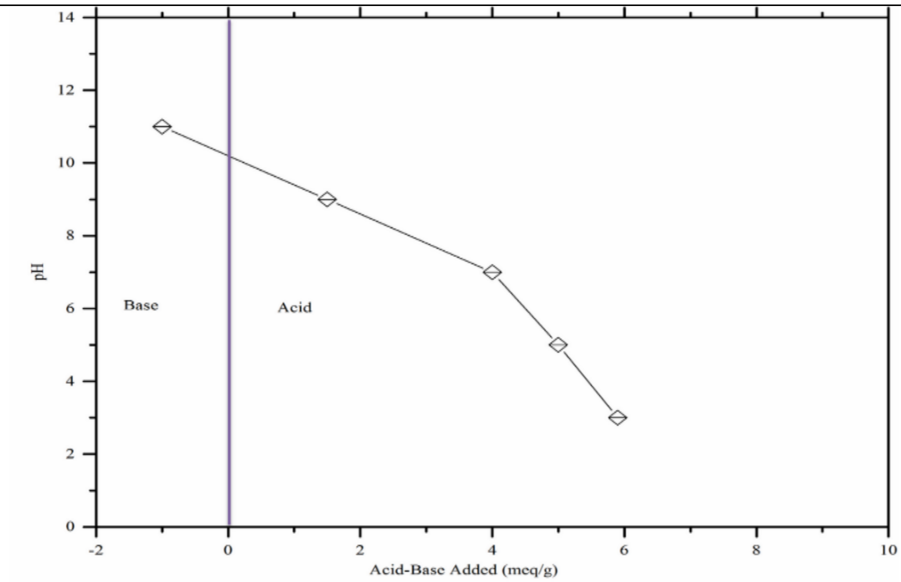


Figure 4.4 Acid neutralisation curve for BMWBA

4.2.1 (c) Leaching pattern of BMWBA

The conceptual example of leaching pattern as a function of pH is as shown in Figure 4.5.

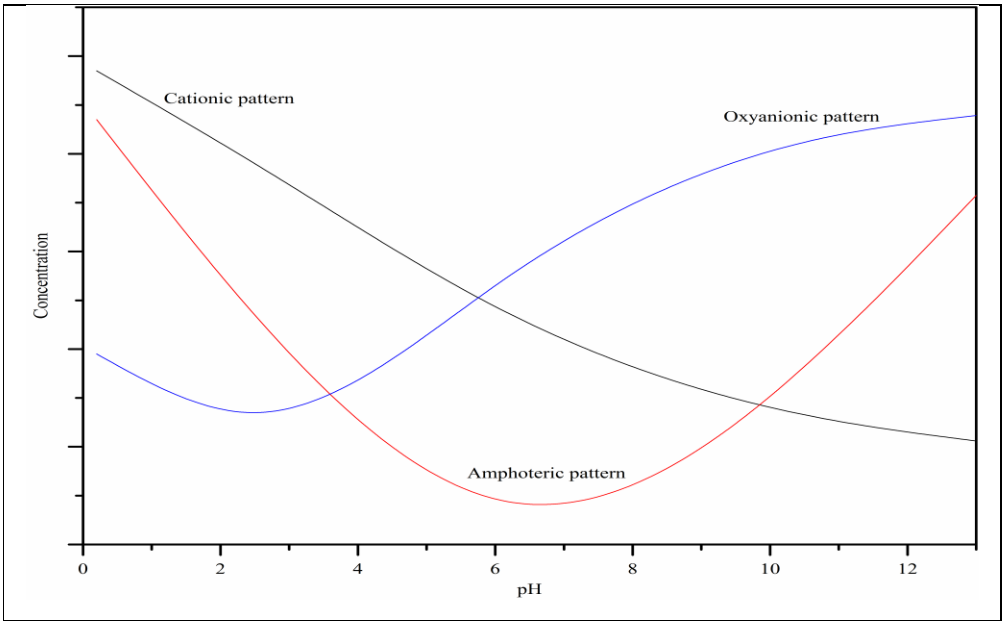


Figure 4.5 Conceptual example of leaching pattern as a function of pH

Fe, Cd, Zn, Pb, Ca, Co, Ni, Cr and Cu does not follow any exact pattern such as oxyanionic, cationic and amphoteric patterns. Increase in the concentration of element As and Hg follows oxyanionic pattern in this case, pH increment resulted in increasing of leaching concentration. Different species of Se and As have a dissimilar affinity for adsorption (surface interaction)/solid solution formation (ion incorporation) and are therefore accountable for the reactions to occur.

4.2.1 (d) BMWBA: discussion

Leaching behaviour of all the heavy metals were studied (Hg, Se, Co, Ni, Fe, As, Cd, Zn, Pb, Ca, Cu and Cr) at different pH levels (3, 5, 7, 9 and 11). It is inferred from the results that Hg, Se and As were recognized to be toxic elements as per desirable standards that exist as oxyanions during pH range of 3 to 11. These oxyanionic elements Se and As (SeO_3^{2-}, $SeO^3{}_4^-$ and $AsO^{3-}{}_4$) prevent adsorption on the surface of negatively charged BMA.

Different species of Se and As having dissimilar affinity for adsorption (surface interaction) /solid solution formation (ion incorporation) and therefore accountable for the reactions to occur. Adsorption occurred might be specific or non-specific (Komonweeraket et al., 2014). However solid solution formation falls under specific adsorption phenomenon which depends on geometry, charge and ion/molecule size. Further leaching concentration of the mentioned metals were well within the desirable limits in both acidic and alkaline environment.

4.2.2 FCA

The FCA leached samples were examined using ASTM D3987-12, TCLP method 1311 and USEPA 1313test methods to analyse metal concentrations such as Cr, Cd, Hg, Pb, Se, Co, Ni, Fe, As, Zn and Ca and Cu by ICP-OES.

4.2.2 (a) Results of heavy metal leachates by various protocols: FCA

It was observed from Figure 4.6 that the leaching of heavy metals Cr, Hg, Pb, As is not within the regulatory limits. Cr is leaching very high i.e.153.7 mg/L but the limit is only 5.0 mg/L. Toxic metals such as Hg, Pb and As are also showing higher concentration of about 9.76 mg/L, 6.58 mg/L and 12.66 mg/L respectively which exceeds the disposal limit. Other heavy metals Se, Co, Ni, Fe, Cd, Zn, Ca and Cu were within the limits. Results of TCLP procedure were presented in Figure 4.7. In this method, Cr, Hg and As is leaching high and the concentrations were observed as 123.3 mg/L, 7.87 mg/L and 7.12 mg/L.

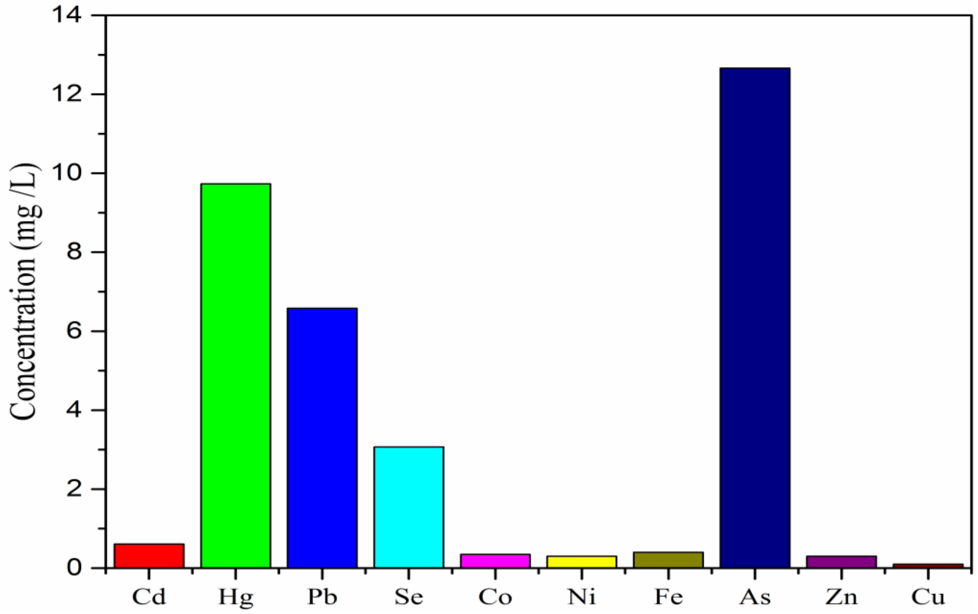


Figure 4.6 Leaching of metals from FCA (ASTM Test Procedure)

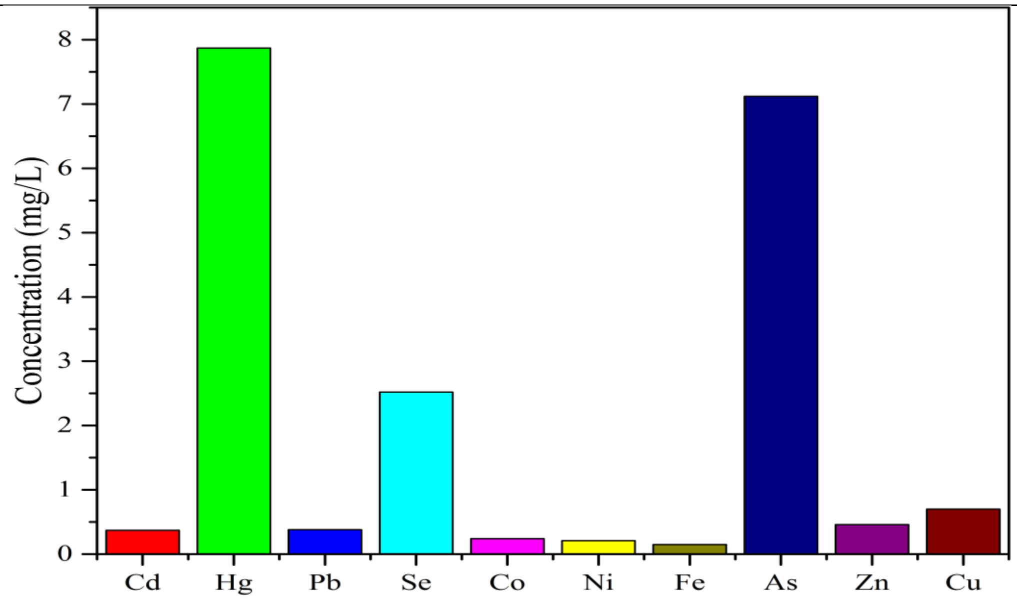


Figure 4.7 Leaching of metals from FCA (TCLP Test Procedure)

Leachate concentration by USEPA 1313 method for varying pH is portrayed in Figure 4.8. Hg is leaching more varying between 5.6 mg/L to 10.23 mg/L for pH variation from 3 to 11. As leaching concentration i.e., 10.6 mg/L to 11.19 mg/L for pH variation between 3 to 9. Cr is leaching extremely high, 153.2 mg/L at pH 3 and 98.39 mg/L at pH 11. Leaching behaviour of Co metal is less during acidic phase compared to the alkaline condition for all the FCA samples. Cu concentration is slightly higher in acidic condition. However, we have tested for identifying the form of availability of Cr in the sample as major available form such as Cr (III) and Cr (VI) in FCA sample. The sampling report indicated that concentration of Cr (VI) is 27.5 mg/L. Hence typically the industrial waste considered falls under the category of hazardous material and it needs further pre-treatment before disposal. Furthermore, it is clear that from all the three test protocols, leaching of Hg and As observed to be very high compared to the disposal limits.

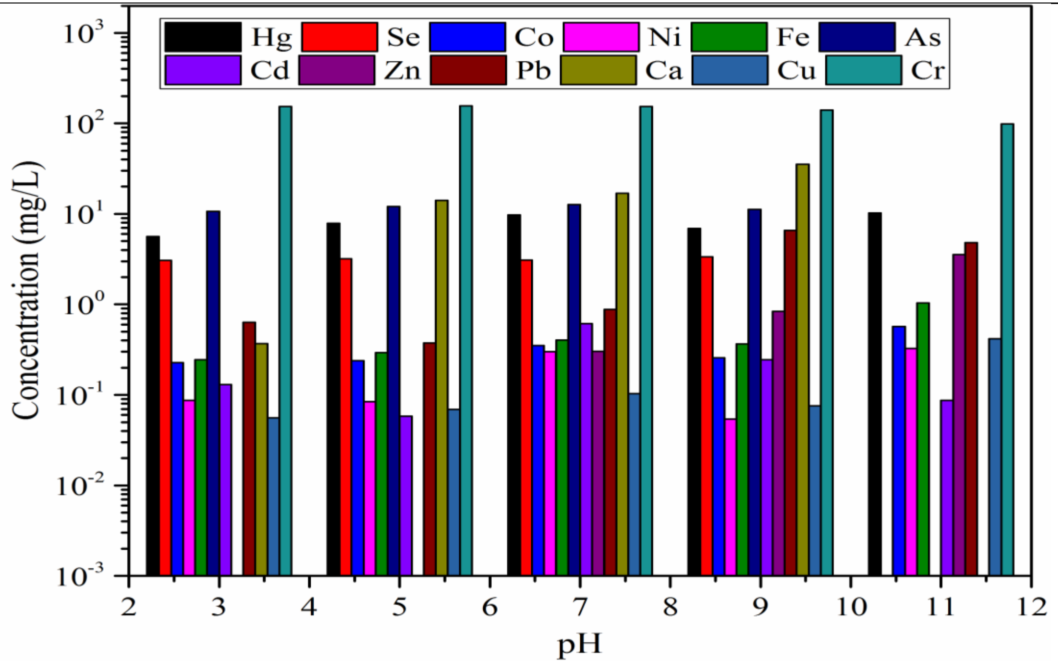


Figure 4.8 Metal concentrations for different pH (USEPA test procedure)

4.2.2 (b) Acid-base neutralization capacity

To identify the amount of acid or base required to achieve the equilibrium condition for FCA was investigated. The variation of pH when an acid or base is added to the sample is represented by using ANC curve. ANC is related to acid attack resistance that affects the matrix durability and thereby the contaminants of leaching. Also, ANC is the important property related to cementitious or waste system. (Giampaolo et al. 2002). The solid phases present which can resist a decrease in pH are identified as the plateau in the ANC curves (Isenburg and Moore, 1992). The original pH (natural pH of material without adding any acid/base buffer) of FCA samples was varied from 11.0 to 11.7. Batch leaching experiments were conducted by maintaining the solid to liquid ratio as 1:10. Sample preparation protocol for different pH was adopted as explained in section 4.2.1 (b). Surrounding environment have its influence on pH of the leachate which is indicated by the plateau of ANC curve at lower pH values (2 to 3).

The results of FCA (Figure 4.9) indicate that for pH 3 and 5, during the initial period shifting of the solution, pH towards the alkalinity was very rapid and later reached equilibrium. For pH 9 and 11, it took a longer time to accomplish the equilibrium state due to a slow variation of pH towards alkalinity. The lower pH of the particles in the dumping sites may be due to the aging effects (Kosson et al., 2014).

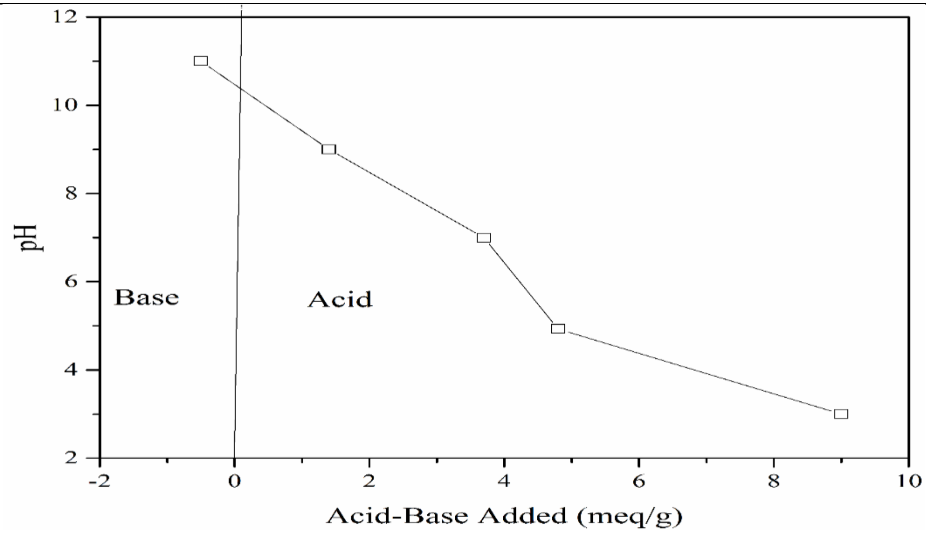


Figure 4.9 Acid neutralisation capacity for FCA

4.2.2 (c) Oxidation reduction potential

Oxidation Reduction Potential (ORP) measures the affinity of chemical substances by which they gain and thereby lose electrons. Substances acquired from environment have complex chemical and physical characteristics and by doing ORP measurement one can differentiate these substances into oxidizing and reducing regimes. Figure 4.10 shows the relationship between pH and ORP for FCA at different pH levels. The ORP of FCA was decreasing gradually with increase in pH and found to be negative (pH>9) for alkaline condition. It is inferred that the oxidising potential at lower pH level is more due to the presence of various oxides of FCA which is clear from the results obtained for leaching analysis by different methods. Also, it provides an idea on anti-oxidising strength of the substance. In this section, it is attempted to present the behaviour of ORP of FCA.

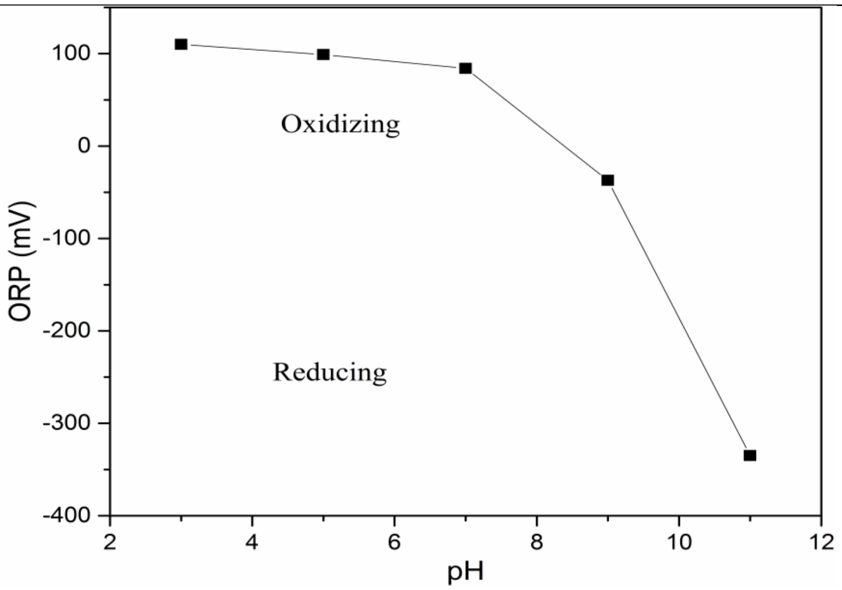


Figure 4.10 Oxidation-Reduction potential as a function of pH for leachates from FCA

4.2.2 (d) Leaching pattern of FCA

The difference in pH and concentration of leached effluent elements follow three leaching patterns, i.e., oxyanionic, cationic and amphoteric patterns (Komonweeraket et al., 2015). In case of oxyanionic leaching pattern, increase in pH causes increase in the effluent concentration of elements whereas increase in pH causes decrease in the effluent concentration of elements in case of cationic leaching pattern. In case of amphoteric leaching pattern, the concentration of effluent elements is high during acidic and alkaline conditions and minimal during neutral pH.

Hg, Se and As following in the oxyanionic leaching pattern. Fe, Cd, Zn, Pb, Ca, Co, Ni, Cr and Cu do not follow any exact pattern such as oxyanionic, cationic and amphoteric pattern. Analogous to current study by Cetin and Aydilek (2013); Fleming et al. (1996); Wang et al. (2004) investigated the leaching behaviour of metallic cations such as Cd, Pb, Zn, Ag, Mg, and Cr from fly ash of coal and reported as the mentioned elements follows cationic leaching pattern. The concentration of As and Se followed Oxyanionic leaching pattern for fly ash of coal in alkaline pH condition (Van der Sloot, 2007; Tiruta-barna, 2006).

4.3 FCA ageing factor

4.3.1 Leaching of trace metals

The concentration of selected trace metals with varying pH is as shown in Figure 4.11 Previous investigation shows that the behaviour of leaching of trace metals is sensitive to result in changes in the pH of the solution (Gitari et al, 2009; Mudd et al, 2004). Leaching behaviour of Co metal is less during acidic phase compared to the alkaline condition for all the FCA samples. At pH 11, concentration of fresh ashes is more than the concentration of aged ashes. Co does not follow any mentioned leaching pattern in this current investigation as shown in Figure 4.11 (a).

Cu does not follow any specified leaching pattern in the current study as shown in Figure 4.11 (b). Concentration of fresh FCA ash is slightly higher in acidic condition compared to the concentration of aged ash. Concentration of all the samples shows similar trend during pH 9. Muraka et al. (1991) found that the leaching behaviour of Cu is controlled by the oxides of Cu.

Fe metal which follows the oxyanionic leaching pattern is represented in Figure 4.11 (c). Fresh and aged samples were similar in acidic and neutral pH conditions, but during alkaline condition different values were observed.

Leaching behaviour of Zn from all the four samples follows similar trend. At lower pH, mild decrease in the concentration is observed and after pH 7 gradual decrease in the concentration is observed. Cationic leaching pattern of Zn is as shown in Figure 4.11 (d). Earlier studies show that the leaching behaviour of zinc is controlled by oxides and hydroxides of Zn (Zhang et al., 2016).

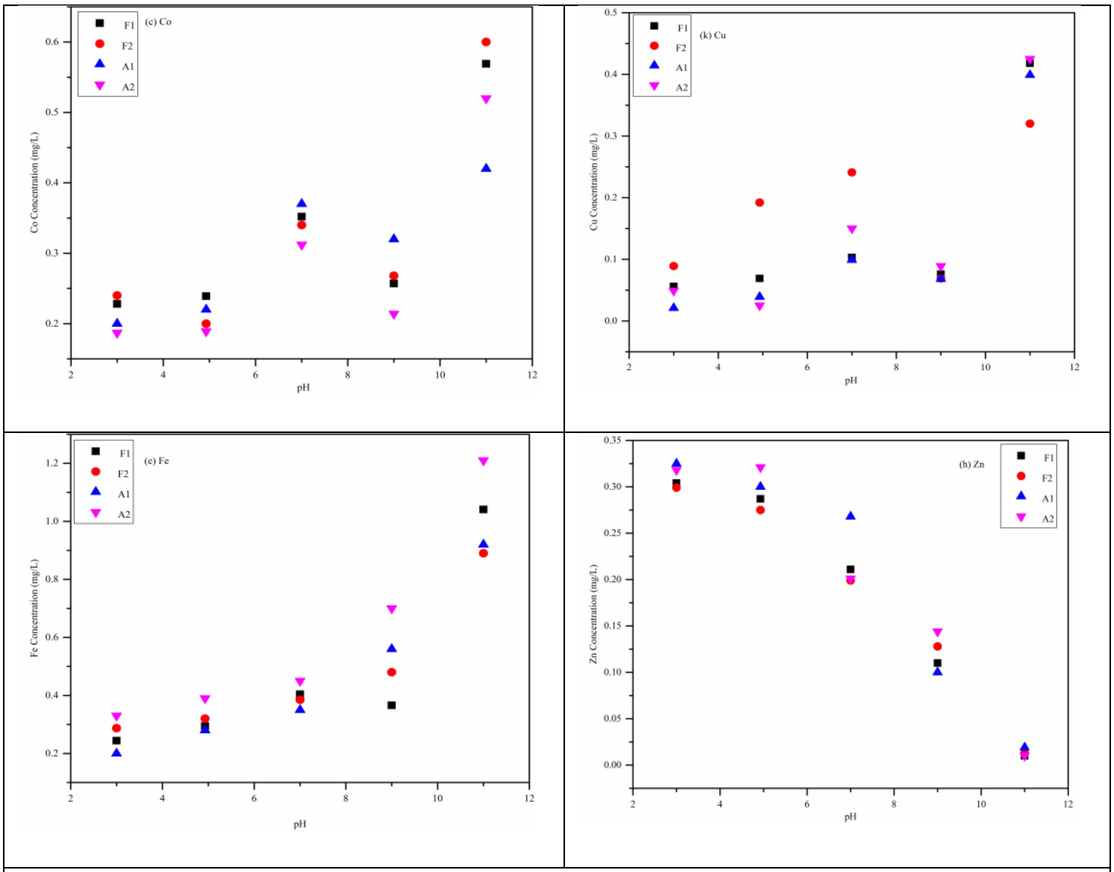


Figure 4.11 Trace metals concentration v/s pH of FCA ashes (a) Co, (b) Cu, (c) Fe, (d) Zn

4.3.2 Leaching of alkaline elements

The leaching behaviour of alkaline elements is as shown in Figure 4.12. Negative potentials are high against an electrode of hydrogen with noticeable electro positivity that are observed in Ca (Muraka et al., 1991). Ca does not follow any exact leaching pattern. Concentration of Ca in fresh and aged ashes shows similar trend. From acidic pH to neutral pH, there is a slight increase in the concentration from 6.8 to 17.2 mg/L for all the four samples. Maximum concentration was found at pH 9, i.e., 39 mg/L.

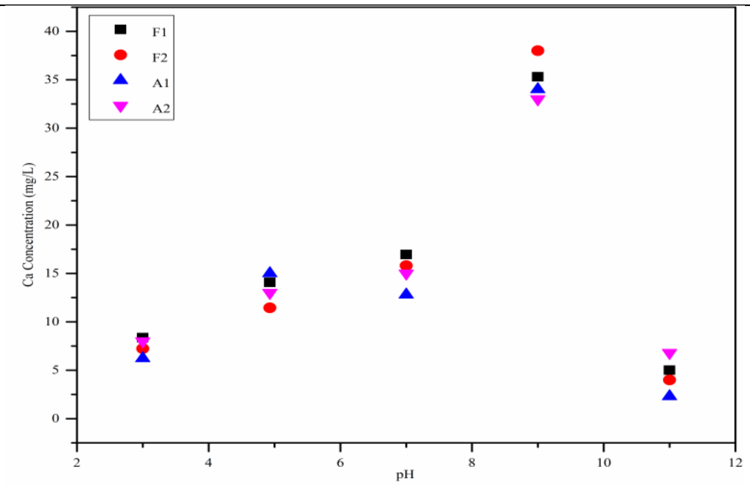


Figure 4.12 Concentration of alkaline element as a function of pH for FCA

4.3.3 Leaching of heavy metals

Concentration of heavy metals with respect to pH is presented in Figure 4.13. As metal follows oxyanionic leaching pattern. From Figure 4.13 (a), it is observed that the concentration of fresh ash leachate is more when compared to the concentration of aged ash, except at pH 9. The maximum leaching concentration for fresh and aged samples are found to be 13.46 and 12.89 mg/L respectively at pH 11.

Cd concentration for all the samples steadily decreases with increasing pH as shown in Figure 4.13 (b) and reaches 0.01 mg/L at pH 11. The Cd leaching behaviour follows the cationic pattern. Earlier studies show the similar trend (Komonweeraket et al., 2015; Tiruta-Barna et al., 2006) which claimed that the Cd leaching was increased in acidic condition because of the dissolution of metal bearing minerals.

The variation of concentration of Cr in the FCA samples when different pH values are considered is as shown in Figure 4.13 (c). Maximum concentration of Cr was found to be 156.18 and 155 mg/L for fresh and aged ashes respectively. Cr leaching behaviour during acidic and neutral phase found very high for all the samples, later gradually decrease with increase in pH. Cr follows cationic leaching behaviour. Earlier studies show that the Cr oxide governs the leaching behaviour of Cr (Mulugeta et al., 2011; Gitari et al., 2009).

Hg is following oxyanionic leaching pattern except pH 9 and it is as shown in Figure 4.13 (d). Maximum concentration of Hg obtained during pH 11 are 10.4 and 10.23 mg/L for aged and fresh ash samples respectively. All the four samples show similar leaching trend from acidic to alkaline phase.

Ni follows oxyanionic leaching pattern as presented in Figure 4.13 (e). During acidic phase, the concentration of Ni is found to be less compared to neutral and alkaline phases. Compared to fresh FCA ash sample, Ni leaching concentration is more in aged FCA ash samples.

The leaching behaviour of Pb for aged and fresh FCA is as shown in Figure 4.13 (f). Pb follows oxyanionic leaching pattern. Similar trend at acidic and neutral phase is observed and varies during alkaline phase. Maximum concentration is found to be 6.72 mg/L and 6.58mg/L for aged and fresh samples. Previous studies identified that the Pb element starts precipitating and forms lead hydroxide at effluent pH > 6 (Bektas et al., 2004).

Se does not show any specified leaching pattern as observed in Figure 4.13 (g). Leaching concentration of Se during acidic phase to neutral phase slightly decreases and later a sudden increase in concentration is observed in alkaline phase.

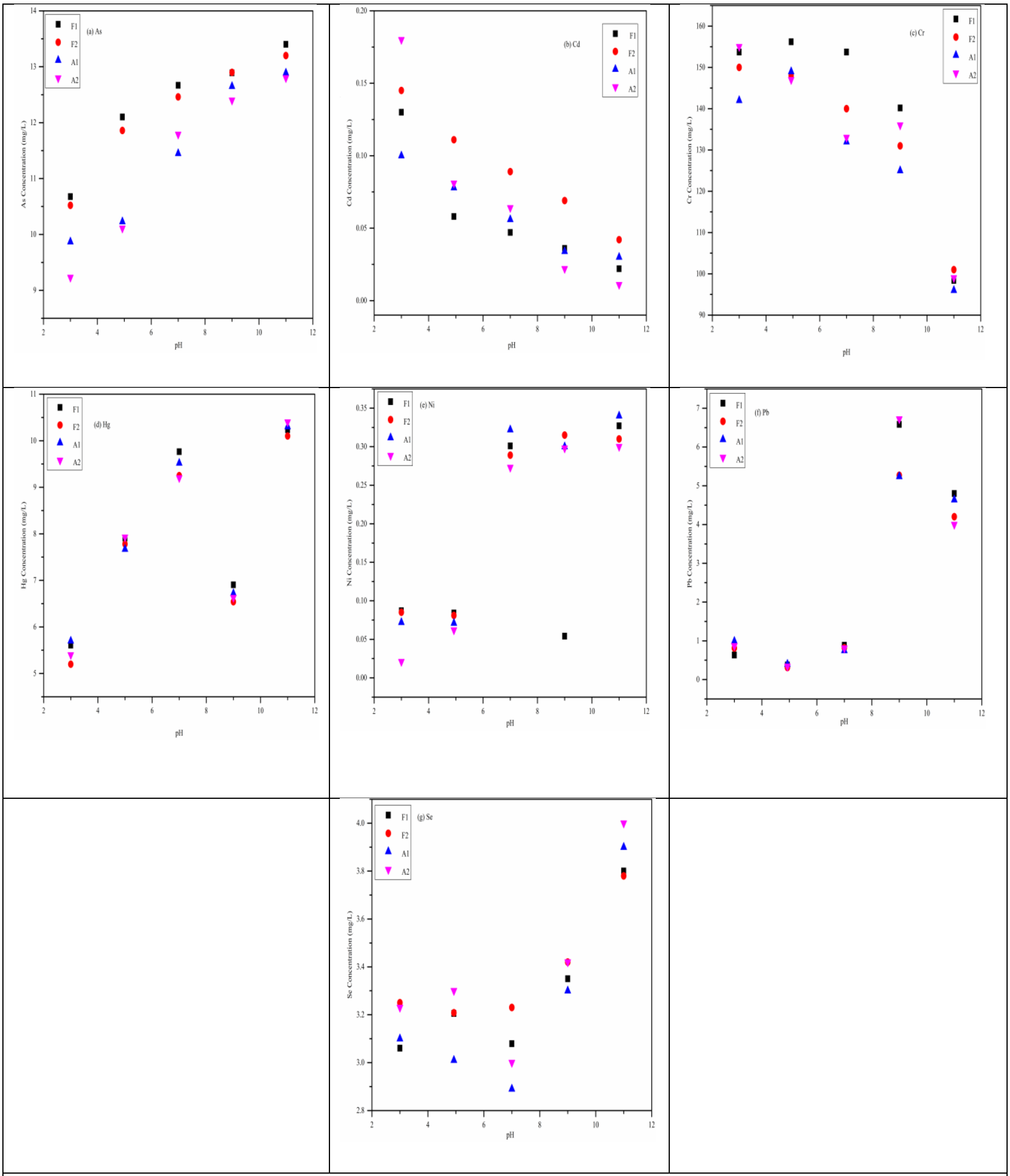


Figure 4.13 Concentration of heavy metal v/s pH of FCA ashes (a) As, (b) Cd, (c) Cr, (d) Hg, (e) Ni, (f) Pb, (g) Se

Leaching of toxic metals are heavily influenced by following factors such as particle size of ash, leaching temperature, leaching regent, solid/liquid ratio, rotation per minute during agitation, agitation time and pH of leaching solution. In the current investigation finds that leaching factors were not much affected in the current investigation and comparatively lower impacts on the toxic metal's concentrations for the FCA samples. The toxic metals concentrations were observed during the fresh and aged ash leaching experiments, ageing of ash having a very lower effect on the metal concentrations when compared with the fresh ash toxic metal concentrations.

Ageing of FCA samples did not alter the leaching mechanism, which was dependable with the lack of changes in the characteristics of FCA samples due to ageing process. Because of continuous drying and wetting process in the FCA landfill area may cause the minor variation in the metal concentration for fresh and aged FCA samples. The moisture evaporation during the drying process may increase the natural attenuation phenomena cause the toxic metals are able to be sorbed by the inner side of FCA particle mechanisms rather than outside FCA particle mechanism because of the loss of moisture content, making them become less reversibly sorbed.

During the ageing process FCA samples majorly affected by temperature and moisture in the atmosphere but these factors not affected on the leaching of toxic metals in the current investigation. But in this study moisture content and temperature cause the variation in the pH of the FCA samples we can observed. The original pH of fresh samples comparatively higher than the pH of aged ash samples. The lesser pH of the FCA samples in the dumping sites may be due the ageing effect (Kosson et al., 2005).

Results of the present investigation prove that there is no change in the leaching behaviour of fresh and aged ash samples. Overall, it has been found that the governing mechanism for leaching of heavy metals, trace metal and alkaline elements from FCA ash leachate do not change with aging samples over the duration and dump site location considered. The findings are supported by the study of Venegas et al. (2016) who observed that there was only little variation in cation exchange capacity and acid neutralization capacity, but the pH, dissolved organic carbon remained same after aging process. They observed very less differences in the physical and chemical properties of the organic amendments during the aging process (Venegas et al., 2016).

From the test results, maximum concentration of chromium leaching was found out to be 156.18 and 155 mg/L, concentration of arsenic 13.46 and 12.89 mg/L, concentration of mercury 10.23 and 10.4 mg/L and lead concentration were 6.58 and 6.72 mg/L for fresh and aged FCA ashes respectively. Therefore, Cr, As, Hg and Pb are identified as significant hazardous pollutants and must not be discharged without being solidified/stabilized.

Several factors including the leaching solution, the time scale of the leaching processes and the leaching environment must be considered in the assessment of major leaching processes. It is also necessary to use different approaches for different leaching scenarios. The methods used in this study are based on the interactions between the combustion residue (BMWBA and FCA) and an aqueous solution, emphasising the leaching kinetics. This supports the need for S/S of BMWBA and FCA wastes before disposal.

4.4 Characterization studies

The BMWBA and FCA are heterogeneous materials. The leaching characteristics therefore depend not only on the chemical composition of the BMWBA and FCA combustion residues but largely on its mineralogy and morphology. The critical evaluation of the information obtained from leaching tests aims to identify the major leaching mechanisms and processes.

Two major component silicon and calcium obtained for BMWBA, silica and potassium for FCA and silica, calcium and alumina for GGBFS. This feature indicates that the constituents of the four elements in the residues should play an important role in leaching chemistry. In addition, the major chemical compositions of the combustion residues are like those of some natural materials.

4.4.1 Chemical composition and morphology

4.4.1 (a) BMWBA

The morphological properties of BMWBA potentially affect the dissolution behaviour of material. SEM analysis of BMWBA sample depicts the morphological features is as shown in Figure 4.14 BMWBA is mainly composed of irregular shaped agglomerate particles in a wide range size and long needle-shaped (ettringite) crystals. Ettringite consists of completely unburned carbonaceous materials and a high amount of glassy phase particles. It is a crystalline, needle like formation with $(Al(OH)_6)^{3-}$ octahedra structure. It is associated with columns (Ca^{2+}) which runs parallel to needle axis while sulphate and water molecules are accommodated between them. The morphological characteristics including the ettringite formation obtained for BMWBA was similar on investigation of volcanic ash (Al-Bahar et al. 2017). The bulk chemical compositions vary for different combustion residues. Although the variation in some trace species may be as high as several orders of magnitude, the contents of predominant components in the residues usually differ only in a limited range (Theis and Gardner, 1990; Murarka et al., 1991; Goldin et al., 1992; Meima, 1997).

EDAX results demonstrates (Table 3.1 in section 3.2.1) that glassy phase was composed of high SiO_2, low Mg and K on the prismatic shaped particles. The high SiO_2 content also indicate that presence of quartz in the form of hexagonal shape. The percentage of major mineral constituents of BMA includes SiO_2 (20.2%), Al_2O_3 (9.2%), MgO (3.1%), Na_2O (2.9%), CaO (39.6%), Fe_2O_3(7.2%), SO_3 (5.6). The formation of ettringite is confirmed by the percentage of free lime (Cao), aluminium oxide (Al_2O_3), anhydrite ($CaSO_4$) and silicon dioxide (SiO_2) presence.

The presence of above constituents could react to form ettringite and it is written as follows:

$$CaO + Al_2O_3 + 3CaSO_4 + 32H_2O = Ca_6Al_2 (SO_4)_3(OH)_{12}.26H_2O$$

The higher content of CaO leads to formation of Ca^{2+} ions which may be replaced by metallic ions such as Fe^{2+}, Zn^{2+}, Mg^{2+}, Cd^{2+} etc. ions through leaching mechanism at alkaline pH condition.

Tashiro et al. (1977) studied the effects of Fe_2O_3, ZnO, Cr_2O_3, $Cu(OH)_2$ and $Pb_2O(OH)_2$ on the development of ettringite. The formation of crystal growth ettringite was encouraged due to the presence of heavy metals in the form of oxides and hydroxides in the material. Piantone et al. (2004) reveals that formation of solid solution in ettringite identified in alkaline waste (MSWI bottom ash) probably due to presence of several oxyanions of metals in it. Speiser et al. (2000) investigated that in majority of alkaline wastes (MSWI bottom ash) silica was present because of the calcium silicate hydrate (C-S-H) comprises of 50-60%. Analogous to early investigation, the BMWBA having 60% of C-S-H was obtained through EDAX analysis which could be the possible reason for formation of ettringite.

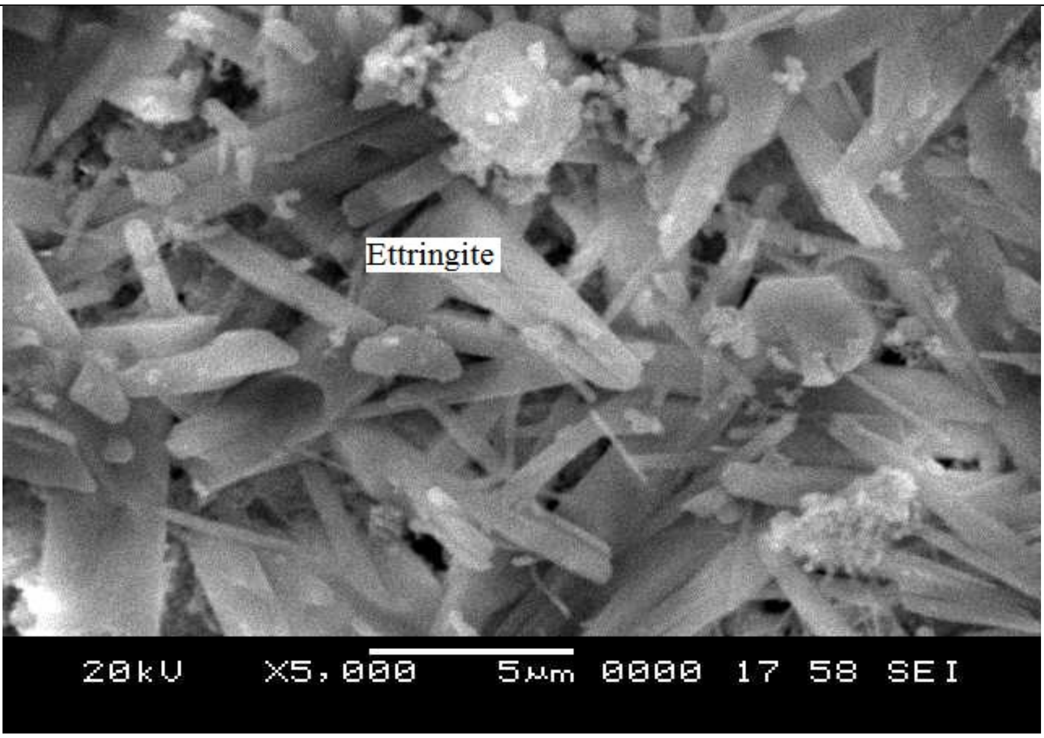


Figure 4.14 Scanning Electron Microscopic image of BMWBA

4.4.1 (b) FCA

Morphological features of FCA is presented in Figure 4.15 The morphology of FCA significantly affects the leaching behaviour of elements (Kersten, 1996). Mainly FCA is composed of particles of irregular shaped, minor square and hexagonal particles. SEM reveals and confirms the presence of glassy phase, unburned carbonaceous material and different mineral phases.

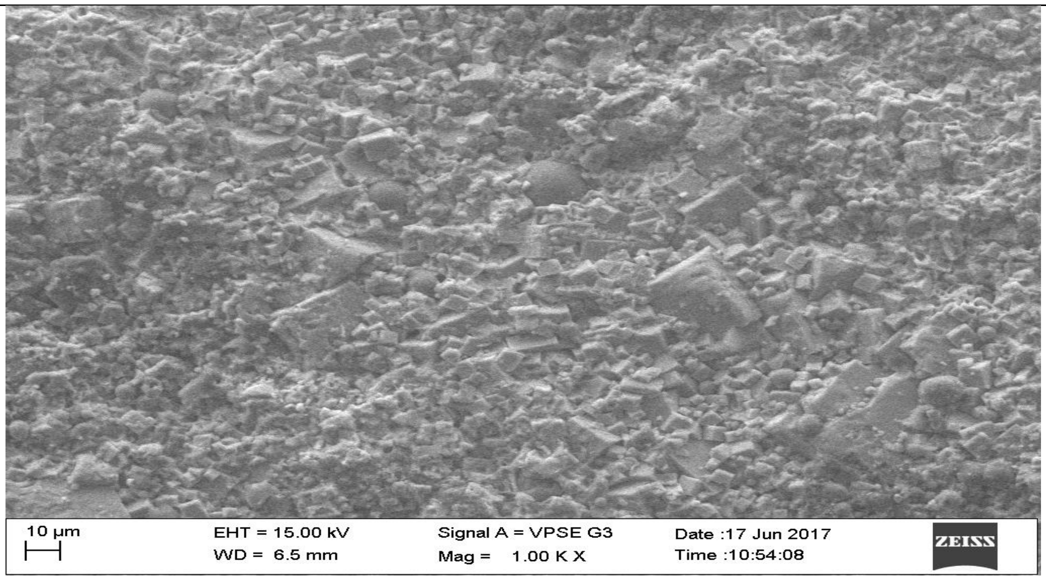


Figure 4.15 Scanning Electron Microscopic image of FCA

4.4.2 Mineralogy of combustion residues

The mineralogy of a combustion residue refers to both amorphous and crystalline phases or other mineral fractions in the residue. The leaching behaviour of BMWBA and FCA can be related to their mineralogical characteristics. More attention should be paid to the major phases which may control leaching chemistry and the host phases of toxic elements which directly associate with the release of the elements, in order to understand the leaching processes. Glass phases, ferrite spinel or other silicates are preferably formed in a high temperature combustion.

4.4.2 (a) Mineralogy of BMWBA

The XRD spectrum for of BMWBA is portrayed in Figure 4.16 The formation of crystal growth in ettringite was encouraged due to the presence of heavy metals in the form of oxides and hydroxides in the material. Piantone et al. (2004) reveals that the formation of a solid solution in ettringite identified in alkaline waste (MSWI bottom ash) is probably due to the presence of several oxyanions of metals in it. Speiser et al. (2000) investigated that in majority of alkaline wastes (MSWI bottom ash), silica was present because of the calcium silicate hydrate (C-S-H) comprising 50–60%. Analogous to early investigation, the BMA having 60% of C-S-H was obtained through EDAX analysis which could be a possible reason for the formation of ettringite.

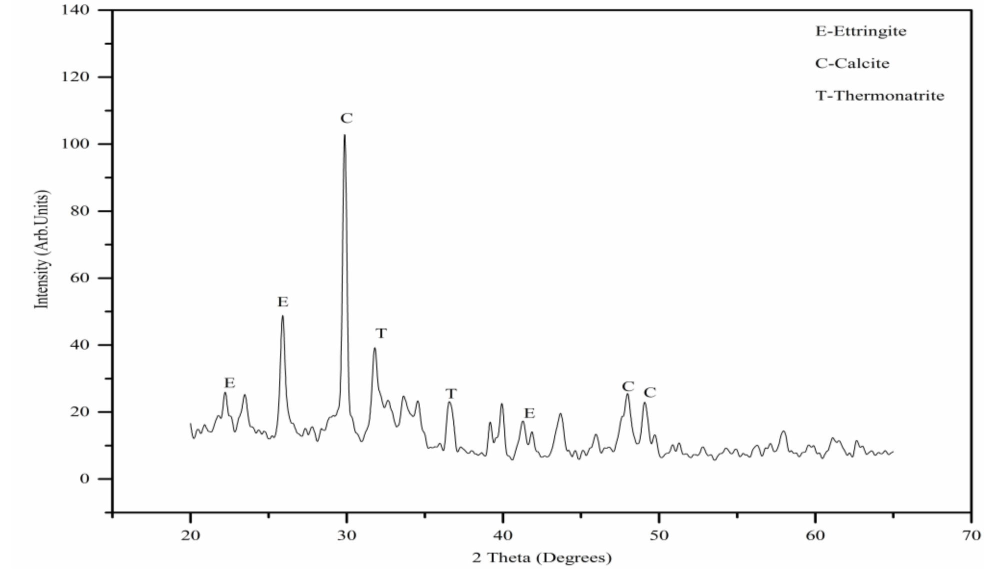


Figure 4.16 XRD spectrum for BMWBA

4.4.2 (b) Mineralogy of FCA

The XRD pattern of FCA from Figure 4.17 reveals the presence of various minerals such as, domeykite stilleitesyn, nickeline, mgriitesyn, arsenolamprite, modderitesyn, kamacite, mgriite and orcelite. Although this trend may not be the same for various Industrial hazardous waste, the major fraction of the residues is usually composed of amorphous phases of silicon, aluminium and iron such as the glasses, magnetic spinel and some aluminosilicates. It is widely accepted that an impure aluminosilicate glass constitutes the bulk of the coal fly ash matrix (Fisher and Natusch, 1979; Roy et al., 1985). It has been found that the glass content in MSWI bottom ash varies between 40 and 75% (Kirby and Rimstidt, 1993; Zevenbergen et al., 1994).

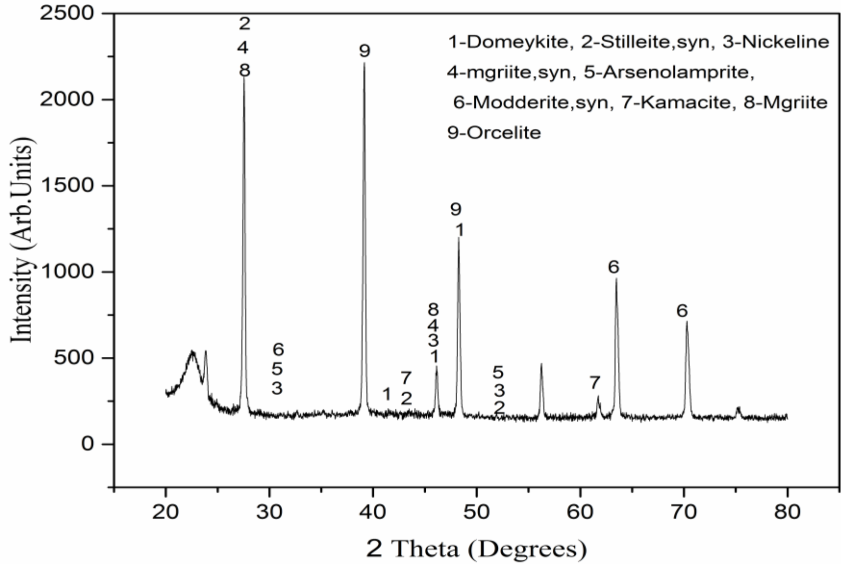


Figure 4.17 XRD spectrum for FCA

Most trace elements exist as a solid solution in the combustion residue. The leaching behaviours of these elements are usually determined by their host phases. In most cases, the glass phases and magnetic fraction in the combustion residues contain most of the potentially toxic trace elements. Most trace elements in the aluminosilicate matrix of ashes are concentrated in the glass phases, while the crystalline phases have low concentrations. The mullite-quartz phase, for example, is relatively pure than the glass phase. The glass phases and magnetic fraction are potentially the most important hosts for many toxic trace elements in the combustion residues.

4.5 Geochemical modelling analysis

Geochemical modelling was conducted for BMWBA and FCA to identify the major oxidation states of leached mineral/metals and to corroborate whether these leached components are controlled by sorption/solubility. Equilibrium was assumed between probable solubility governing compounds and leachate, adopting atmospheric CO_2 (3.16 × 10^{-4}atm) at 25° temperature. The concentration of leachate and pH of aqueous solution were used as input in Visual MINTEQA 3.1. Different redox species will exhibit different geochemical behaviours. A relationship was obtained between log activity of leached element oxidation and pH of the corresponding element. These relationships used to suggest to us the dominant associated process such as sorption/solubility-controlled elements of interest. In addition, metals/minerals will present the existing status like over or undersaturation with respect to the stability line achieved.

4.5.1 Predominant oxidation states

Speciation was determined by allowing redox and aqueous complexation reactions and using aqueous concentrations, pH and Eh data from the leaching tests as input. When the equilibrium Eh and redox couple (oxidized and reduced form) are specified as equilibrium constraints, Visual MINTEQA 3.1 will calculate the element in each of the two oxidation states corresponding to the specified equilibrium Eh. Once speciation of an element is known, the predominant oxidation state was determined for the following redox sensitive elements: As, Cr, Cu, Fe, and Se. Other elements observed in the leachate, including Ca, Cd and Zn have low or no redox sensitivity elements and were not included in the speciation determination.

4.5.2 Aqueous phase composition and saturation index calculation

Aqueous phase equilibrium composition and saturation index (SI) of all leachates with respect to solids or minerals were computed by allowing aqueous complexation reactions at fixed pH, as suggested by Apul et al. (2005). Input data included the leachate pH and aqueous concentration of the components. Components corresponding to the predominant oxidation states identified previously were selected for the simulations. The aqueous phase concentration analysis and the SI calculation (Table 4.1 include) were performed assuming equilibrium between the leachate and potential solubility-controlling minerals in the solid in an open system at 25˚C under the influence of atmospheric CO_2. Table 4.1 and 4.2 tabulates the saturation indices for minerals determined by using Visual MINTEQA 3.1 for BMWBA and FCA.

Table 4.1 Saturation indices for minerals calculated using Visual MINTEQA 3.1 for BMWBA

Solid/Mineral	Saturation Index				
	pH 3	pH 5	pH 7	pH 9	pH 11
Aragonite	-7.2	-5.3	0.2	2.23	1.6
Calcite	-7.3	-5.4	0.2	2.22	1.7
Portlandite	-20	-16.23	-12.6	-9.2	-9.8
Otavite	-7.2	-6.2	0.14	2.2	-3.9
$Cd(OH)_2$	-13.4	-10.3	-7.23	-4.1	-8.3
Malachite	-15.89	-7.46	0.12	0.3	-7.4
Tenorite	-8.34	-4.1	0.1	0.2	-5.2
$Hg\ (OH)_2$	-1.74	-1.24	-1.2	-0.7	-2.7
Hematite	6.3	12.5	16.3	20.1	15.2
Geothite	2.3	5.2	7.4	7.7	5.1
Feerihydrite	-0.2	2.4	2.8	3.7	2.9
$Pb\ (OH)_2$	-7.4	-5.3	0.23	-9.8	-4.9
$Pb_2O\ (OH)_2$	-25.4	-16.2	-10.1	-30.1	-15.6
Zincite	-9.9	-4.6	-12.3	1.4	-3.2
$Zn\ (CO)_3$	-9.6	-4.3	-11.9	1.1	-3.9

Table 4.2 Saturation indices for minerals calculated using Visual MINTEQA 3.1 for FCA

Solid/Mineral	Saturation Index				
	pH 3	pH 5	pH 7	pH 9	pH 11
Aragonite	-3.3	-0.12	2.3	4.9	4.7
Calcite	-3.24	0.17	2.24	4.78	4.7
Lime	-26.4	-24.2	-20.7	-19.2	-20.2
Otavite	-5.4	-2.6	1.1	-0.9	-5.1
Malachite	-4.7	0.1	2.3	-0.2	-5.2
Azurite	-4.8	5.2	9.4	-0.7	-9.6
Tenorite	-4.9	-0.2	0.6	1.2	-6.7
$Cr\ (OH)_3$	0.3	11.2	17.5	18.2	19.1
Cr_2O_3	0.1	5.1	7.6	7.8	7.62
Hematite	7.3	12.3	15.4	15.6	17.2
Maghemite	-0.3	0.3	0.1	2.5	0.2
$Ni\ (OH)_2$	-7.4	-4.9	2.5	-0.9	-0.7
$NiCO_3$	-2.42	2.4	4.9	5.6	5.5
Zincite	-	-	0.7	0.1	-0.2
Hydrozincite	-	-	15.1	10.2	-10.6

The conditions in the leaching test are assumed to be under the influence of atmospheric CO_2 (g), because slurries and leachates were exposed to the atmosphere during preparation procedures before the leaching test and during sample collection and filtration after the leaching test. Accordingly, the system in this study is assumed to be in equilibrium with the partial pressure of atmospheric CO_2 at $10^{-3.5}$ atm ($3.16\ x10^{-4}$ atm, or 32.02 N/m^2) (Langmuir, 1997). Mudd et al. (2004) showed that including the effect of CO_2 is important for the modelling study when the system is exposed to atmospheric CO_2 because CO_2 greatly affects the carbonate geochemistry in the leachate and the solubility-controlling solids.

4.5.3 Mechanism controlling leaching: BMWBA

Concentrations of Ca, Cd, Cu, Hg, Fe, Pb and Zn in the BMWBA leachates were found to be consistent with the dissolution/precipitation of solid/minerals. Table 4.3. summarizes the dominant oxidation state and controlling-solids for each element of interest. Oxide and hydroxide minerals apparently control leaching of Ca as Aragonite [$CaCO_3$], Calcite [$CaCO_3$], Portlandite [Ca $(OH)_2$]. Cd as Otavite [$CdCO_3$], Cadmium (II) hydroxide [$Cd(OH)_2$].Cu as Malachite[$Cu_2CO_3(OH)_2$] and Tenorite [CuO], Hg as Mercury (II) hydroxide [Hg $(OH)_2$], Fe as Hematite [Fe_2O_3], Geothite [FeO(OH)], Feerihydrite, Pb as Lead (II) hydroxide [Pb $(OH)_2$], [Pb_2O $(OH)_2$], Zn as Zincite [ZnO], Zinc (II) carbonate [Zn $(CO)_3$], Leaching of As and Se is not solubility-controlled and no geochemical reactions were elucidated based on the results from this study.

Table 4.3 Speciation and controlling solid for elements: BMWBA

Element	Speciation	Solubility controlling Solids
Ca	Ca(II)	Aragonite [$CaCO_3$], Calcite [$CaCO_3$], Portlandite [$Ca(OH)_2$]
Cd	Cd(II)	Otavite [$CdCO_3$], Cadmium (II) hydroxide [$Cd(OH)_2$]
As	As(V)	None
Cu	Cu(II)	Malachite[$Cu_2CO_3(OH)_2$], Tenorite [CuO]
Hg	Hg(II)	Mercury (II) hydroxide [Hg $(OH)_2$]
Fe	Fe(III)	Hematite [Fe_2O_3], Geothite [FeO(OH)], Feerihydrite
Pb	Pb(II)	Lead (II) hydroxide [Pb $(OH)_2$], [Pb_2O $(OH)_2$]
Se	Se(IV) or Se(VI)	None
Zn	Zn(II)	Zincite [ZnO], Zinc (II) carbonate [Zn $(CO)_3$]

Otavite and $Cd(OH)_2$ identified as solubility-controlling solids for Cd in the pH range between 3 and 11. The Cd^{+2} activity line reaches saturation at pH 5; a slight under saturation was observed at pH 3 and 9. It was due to the adsorption and slow dissolution of otavite and Cd $(OH)_2$ at pH 3 and 9 is as shown in Figure 4.18(a). Undersaturation was expected when solvable Cd Concentration is more than the adequate saturation with respect to the minerals. Further, oversaturation was observed at pH 7and 9. The obtained results agree with Komonweeraket et al. (2015b) who reported that otavite was the controlling leaching mineral speciation of Cd in coal combustible end products like fly ash and bottom ash.

Aragonite, calcite and portlandite were recognized as solubility-controlling minerals for Ca^{+2} in Figure.4.18(b). A slight undersaturation was observed at pH 3 and 11 because of insufficient minerals in the solids/incomplete dissolution of minerals. At pH 7 and 9, oversaturation of minerals occurred due to the presence of carbonate species. Similar results for calcite mineral was reported through geochemical modelling by Costa et al. (2016) for carbonated steel slag. The present study results were in accordance with Mudd et al. (2004) investigated that for fly ash during alkaline pH, carbonate minerals such as lime, calcite and aragonite are responsible for controlling the solubility of Ca.

Solubility-controlling solids for Zn were predicted as zincite and smithsonite $Zn(CO)_3$ formations as depicted (Figure.4.18(c)). A slight undersaturation was observed during neutral pH, oversaturation during pH 5 and 9. The possible reason could be due to Zn $(OH)_2$ formation during the sorption process to hydrous aluminium oxide in an alkaline environment.

Tentorite [CuO] and malachite [$Cu_2CO_3(OH)_2$] have comparable solubility-controlling solids for Cu (Figure. 4.18(d)). The obtained mineral speciation was confirmed as acquired by Kumpiene et al. (2016) who investigated thermally treated soil and Dijkstra et al. (2006) who examined MSWI bottom ash for copper.

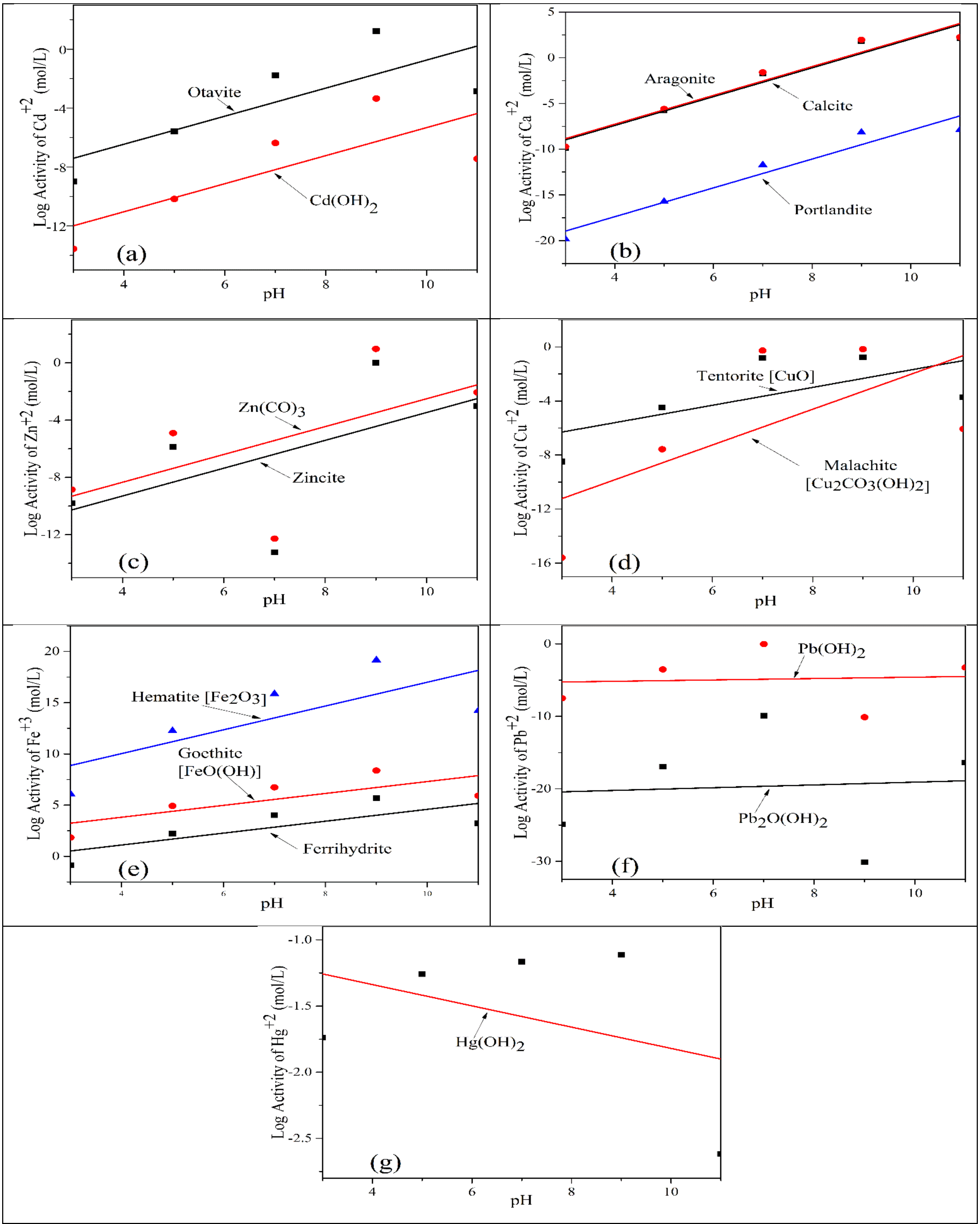


Figure 4.18 Log activity of metal ions a)Cd^{+2}, b)Ca^{+2}, c)Zn^{+2}, d)Cu^{+2}, e)Fe^{+3}, f) Pb^{+2} and g)Hg^{+2}

Iron is another important element and its solubility control depends on the formation of the minerals ferrihydrite, hematite and goethite as depicted in Figure. 4.18 (e). These minerals consist of oxides and hydroxides of iron which are accountable for the solubility process to occur.

Lead (II) hydroxide [$Pb(OH)_2$]and $Pb_2O(OH)_2$ were established as solubility controlling solids/minerals for Pb as shown in Figure. 4.18 (f) as it represents the presence of oxides and oxyhydroxides of the metal. Mercury (II) hydroxide [$Hg(OH)_2$] was indicated as solubility-governing solids for mercury as pH varies from acidic to alkaline as shown in Figure. 4.18 (g).

For As and Se, the dominating speciation is oxyanions, and hence, it can be concluded to fall under the sorption control process.

4.5.4 Mechanism controlling leaching of FCA

Concentrations of Ca, Cd, Cu, Cr, Fe, Ni and Zn in the FCA leachates were found to be consistent with the dissolution/precipitation of solid/minerals. Table 4.4 summarizes the dominant oxidation state and controlling-solids for each element of interest. Oxide and hydroxide minerals apparently control leaching of Ca as Lime [CaO], Cd as Cadmium hydroxide [$Cd(OH)_2$], Cu As Malachite [$Cu_2CO_3(OH)_2$], Azurite [$Cu_3(CO_3)(OH)_2$], and Amorphous Tenorite [CuO], Cr as Amorphous chromium(III) hydroxide [$Cr(OH)_3$], Crystalline chromium(III) oxide [Cr_2O_3], Fe as Hematite [Fe_2O_3] and Maghemite [Fe_2O_3], Ni as Amorphous nickel (II) hydroxide [$Ni(OH)_2$], Zn as Zincite [ZnO], Hydrozincite [$Zn_5(CO_3)_2(OH)_6$] and carbonate mineral present in Ca as Aragonite [$CaCO_3$], Calcite [$CaCO_3$], Cd as Otavite [$CdCO_3$], Ni as Soluble nickel (II) carbonate [$NiCO_3$]. Leaching of As and Se is not solubility-controlled and hence no geochemical reactions were obtained based on the results.

Table 4.4 Speciation and controlling solid for elements: FCA

Element	Speciation	Solubility controlling Solids
Ca	Ca(II)	Aragonite [$CaCO_3$], Calcite [$CaCO_3$], Lime [CaO]
Cd	Cd(II)	Otavite [$CdCO_3$]
As	As(V)	None
Cu	Cu(II)	Malachite[$Cu_2CO_3(OH)_2$],Azurite[$Cu_3(CO_3)_2(OH)_2$], Tenorite [CuO]
Cr	Cr(III)	Amorphous chromium(III) hydroxide [$Cr(OH)_3$], Crystalline chromium(III) oxide [Cr_2O_3]
Fe	Fe(III)	Hematite [Fe_2O_3], Maghemite [Fe_2O_3]
Ni	Ni(II)	Amorphous nickel (II) hydroxide [$Ni(OH)_2$] , Soluble nickel(II) carbonate [$NiCO_3$]
Se	Se(IV) or Se(VI)	None
Zn	Zn(II)	Zincite [ZnO], Hydrozincite [$Zn_5(CO_3)_2(OH)_6$]

4.5.4 (a) Oxide and hydroxide minerals

Fe, Cr, Zn, Cu and Ni are oxides and hydroxides solids/mineral obtained from the FCA leaching studies. When FCA meets water, dissolution and hydrolysis of these oxides occur, and ultimately metal hydroxide precipitates are formed.

Otavite [$CdCO_3$] was identified as potential solubility-controlling solids for Cd is as shown in Figure 4.19 (a). The findings are consistent with van der Sloot et al. (1996), who reports otavite as a controlling solid for Cd in leachates from MSWI bottom ash and from sewage amended soil. Eary et al. (1990) also suggested that the Cd concentrations are controlled by otavite for fly ash leachate in slightly acidic to alkaline pH condition.

Iron is another major element for which the leachate concentration is controlled by oxide mineral, Hematite [Fe_2O_3], Maghemite [Fe_2O_3] is as shown in Figure 4.19 (e). Rai et al. (1987a) reported that leaching of Fe from coal ash in short-term and long-term batch leaching experiments and is controlled by solubility of both Fe oxides.

Amorphous chromium (III) hydroxide [Cr $(OH)_3$] and crystalline chromium (III) oxide [Cr_2O_3] have comparable solubilities and are identified as potential controlling oxide and hydroxide solids for Cr (III) in this investigation is as shown in Figure 4.19 (g). Reardon (1995); Rai and Szelmeczka (1990) have reported that leaching of Cr (III) from fly ash is controlled by Cr $(OH)_3$. Chromium hydroxides are likely to be formed in the leachates, whereas Cr_2O_3 is originally present in the FCA.

Zincite [ZnO] and hydrozincite [$Zn_5(CO_3)_2(OH)_6$] were identified as potential controlling solids for Zn (II), although slight undersaturation with respect to these solids was observed in Figure 4.19 (c). Earlier investigation reported that zincite is a primary phase in fly ash (Theis et al., 1982) and has been reported to control leaching of Zn in fly ash leachate (Garavaglia and Caramuscio, 1994).

Similarly, Malachite [$Cu_2CO_3(OH)_2$] and Azurite [$Cu_3(CO_3)_2(OH)_2$] were identified as potential controlling solids for Cu (II), although slight undersaturation with respect to these solids was observed in Figure 4.19 (d). Tenorite has also been found as a common ore mineral under oxidizing conditions (Rai et al., 1987a) similar to the extraction conditions in this study. Tenorite as a controlling solid for Cu in fly ash leachates is also identified by Eary et al. (1990), Fruchter et al. (1990), Murarka et al. (1992), and Garavaglia and Caramuscio (1994).

4.5.4 (b) Carbonate minerals

Carbonate minerals were found to have a prominent role in controlling the leaching of Cd, Ca and Ni depending on the leachate pH is as shown in Figure 4.19 (a), (b) and (f). However, carbonate minerals became more important for highly alkaline pH (pH >10). Calcium is the major soluble elements leached from FCA.

Roy and Griffin (1984) concluded that anhydrite controls leaching of Ca from fly ashes, but Ca concentrations in highly alkaline solutions in contact with atmospheric $CO_2(g)$ are controlled by calcite solubility. Both calcite and aragonite control the leaching of Ca from coal fly ash when the system is in equilibrium with atmospheric $CO_2(g)$ (Mudd et al. 2004). Calcite and aragonite have been identified by other studies (Kirby and Rimstidt 1994) as one of important carbonate minerals controlling Ca in combustion fly ash and MSWI leachates.

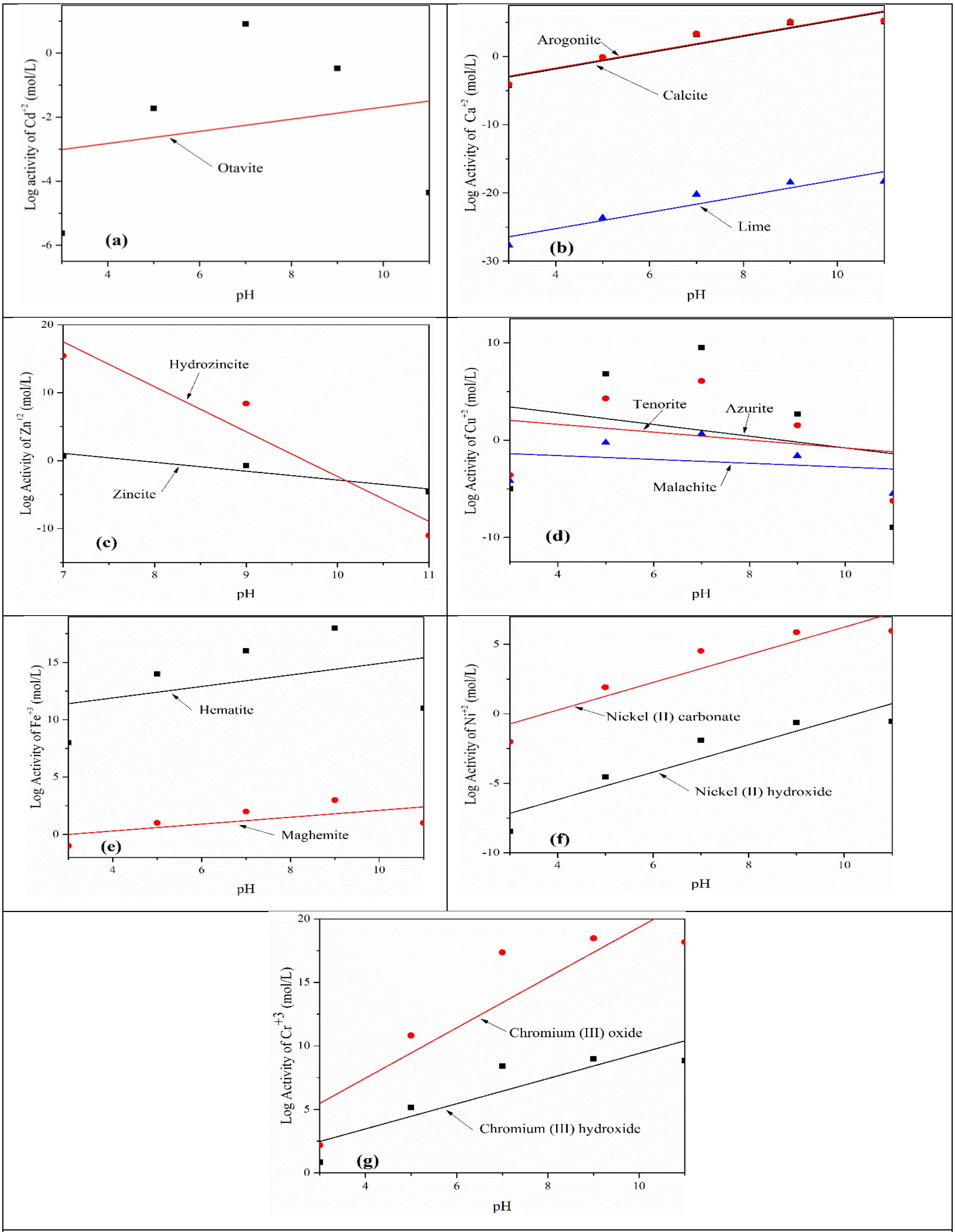


Figure 4.19 Log activity of metal ions a) Cd^{+2}, b) Ca^{+2}, c) Zn^{+2}, d) Cu^{+2}, e) Fe^{+3},f) Ni^{+2} and g) Cr^{+3}

4.6 Solidification / stabilization of BMWBA

4.6.1 Workability

Flow table test was conducted to determine the workability of geopolymer mortar mixes according to the guidelines given by IS: 5512-1983. Usually, BMWBA based geopolymer mortar mixes were sticky type in nature. Based on several trials of experimentation, the ratio of 0.4 was obtained (Alkaline solution/BMWBA) preferable for preparing the geopolymer mortar mixes.

4.6.2 Compressive strength

The trial mixtures with different proportion of GGBFS and BMWBA were sampled thrice and were averaged to arrive at compressive strength. The compressive strength of overall mixture of BMWBA and GGBFS solidified matrixes were between 0.75 to 10.52 MPa. The compressive strength obtained during 30% of GGBFS and 70% of BMWBA was 7.86 to 10.52 MPa. Similarly, with 20% and 10% of GGBFS in overall mixture resulted with 3.62 to 6.1 MPa and 1.25 to 2.8 MPa compressive strength. With 100% of BMWBA (0% GGBFS) the compressive strength declined to 0.75 to 1.8 MPa, this shows that the strength decreased as the percentage of GGBFS declined. Figure 4.20 Compressive Strength of BMWBA with GGBFS additives samples after 3, 7, 28 and 56 days of solidifications. The comparative strength of the solidified matrix with ash and cement loading resulted with similar result of decrease in the strength of the test matrix as the cement loading declined in the matrix (Padmi et al., 2009).

The compressive strength of the geopolymer is due to the bonds between the Si–O–Si, when the mixture is enriched by greater amounts of silicon leads to the increase in compressive strength (Songpiriyakij et al., 2010). In the current investigation from Table 3.1, it can be observed that GGBFS having maximum silicon content compare to BMWBA, therefore in this investigation results showing maximum compressive strength at 30% of GGBFS replacement. The compressive strength increases with the increase in calcium oxide and the proportion of SiO_2/Al_2O_3 in the geopolymer matrices.(Li and Liu, 2007; Yip et al., 2008) experimentally proved that the strength of the solid matrix will increase with the application of the blast furnace slag rich in CaO. The calcination process activates the material, which in turn converts crystalline into amorphous structure which store extra energy and induces the activity of geopolymer to increase the compressive strength (Khale and Chaudhary, 2007). Past studies have shown that variation in the proportion of the SiO_2/Al_2O_3 has a significant impact on the compressive strength (Silva and Sirivivatnanon, 2007; Fletcher et al., 2005;Duxson et al., 2005). However, a small variation in the initial molar concentrations of Na_2O, SiO_2/Al_2O_3 can dramatically change its long-term properties(Silva and Sagoe-crenstil, 2008). During the process of polycondensation, the presence of the chloride will cause the negative effect on solid matrix (Ferone et al., 2013). Chloride will retard the solidification of geopolymer gel (Lee and Deventer, 2002) and decreases the strength of the matrix due to the structural discontinuity within the gel (Lee and J, 2002).

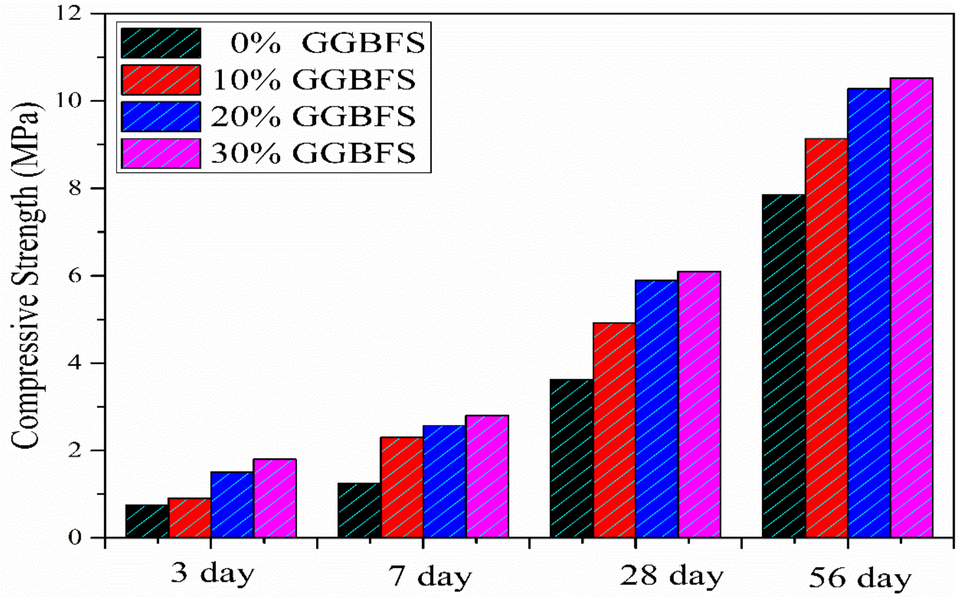
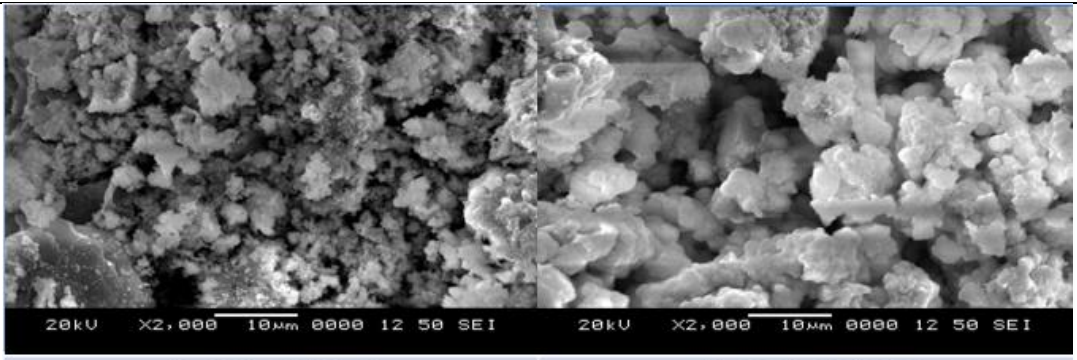


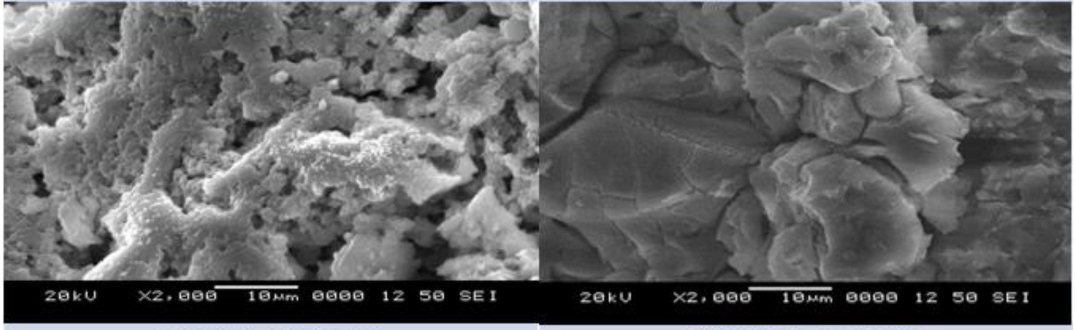
Figure 4.20 Compressive Strength of BMWBA with GGBFS additives after 3, 7, 28 and 56 days

4.6.3 Morphological analysis

Characterization is one of the technique to evaluate the efficiency of the solidification/stabilization (Batchelor, 2006). The microstructure analysis for the geopolymer paste was conducted with the various proportion of GGBFS (0%, 10%, 20% and 30%) and BMWBA from the failure surface of the moulded samples. The pictorial representation of the images of samples using SEM is presented in Figure 4.21 (a-d). The image from the SEM indicate that maximum replacement of BMWBA by GGBFS in the blends aids to form denser structure. This shows that increase in the GGBFS maximises the compressive strength. Increase in the quantity of GGBFS result with the higher occurrence of calcium silicate gel in the blends that provides highly dense structure. The clear evidence of the calcination process can be noted from the SEM image which shows the crystalline into amorphous structure with increase in GGBFS.



(a) 0% GGBFS **(b)10% GGBFS**



(c)20% GGBFS **(d)30% GGBFS**

Figure 4.21 Scanning electron microscopy images a) 0% GGBFS, b) 10% GGBFS, c) 20% GGBFS and d) 30% GGBFS

4.6.4 Leaching test for toxic metals

The process of immobilizing heavy metals in alkali-activated matrices during the stabilization of toxic materials has been extensively studied. This studies are well established as the geopolymerization plays an important role in waste management (Qian et al., 2003; Deja, 2002). The toxic metal immobilization mechanism is anticipated to be the fusion of chemical and physical reactions. Positively charged ions (Cation) may bonded into the mould through Si-O or Al-O bond or present in the structure holes to keep up electrical charge balance. A physically encapsulated process, diffusion may cause cation should be substituted by another cation (Jaarsveld et al., 1998). The rich content of CaO plays major role in the formation of cations (Ca^{2+}), which may exchange by metal ions such as Pb^{+2}, Zn^{+2}, Cd^{+2}, Mg^{+2} etc. ions during alkaline condition. Thus, during alkaline condition precipitation of lead ions (Pb^{+2}) may convert into lead hydroxides ($Pb\ (OH)_2$) or lead carbohydrates ($Pb\ (CO)_3$).

Table 4.5 Summary of TCLP leaching values after 3, 7, 28 and 56 days for solidified samples

Heavy metal		**Hg**	**Se**	**Co**	**Ni**	**Fe**	**As**	**Cd**	**Zn**	**Pb**	**Cu**	**Cr**
TCLP limit (mg/L)		**0.2**	**1**	**-**	**7**	**-**	**5**	**1**	**5**	**5**	**-**	**5**
3 day	0%GGBFS	0.02	0.04	0.01	0.4	0.2	0.01	ND	2.66	0.08	0.2	0.52
	10%GGBFS	ND	0.02	ND	0.2	0.1	0.01	ND	2.23	0.03	0.1	0.16
	20%GGBFS	ND	0.01	ND	0.2	0.1	0.01	ND	1.86	0.03	0.09	0.1
	30%GGBFS	ND	0.01	ND	0.2	0.1	ND	ND	1.08	0.02	0.07	0.05
7 day	0%GGBFS	0.01	0.03	0.01	0.3	0.2	0.01	ND	2.16	0.06	0.16	0.36
	10%GGBFS	ND	0.02	ND	0.2	0.1	0.01	ND	2.1	0.03	0.11	0.24
	20%GGBFS	ND	0.01	ND	0.2	0.1	0.01	ND	1.92	0.02	0.06	0.2
	30%GGBFS	ND	0.01	ND	0.2	0.1	ND	ND	1.64	0.01	0.05	0.1
28 day	0%GGBFS	0.01	0.03	0.01	0.3	0.1	0.01	ND	2.01	0.05	0.1	0.32
	10%GGBFS	ND	0.02	ND	0.2	0.1	0.01	ND	1.86	0.02	0.06	0.1
	20%GGBFS	ND	0.01	ND	0.2	0.1	0.01	ND	1.52	0.01	0.02	0.07
	30%GGBFS	ND	0.01	ND	0.1	0.1	ND	ND	1.02	0.01	0.02	0.05
56 day	0%GGBFS	ND	0.02	ND	0.2	0.1	0.01	ND	1.9	0.02	0.09	0.26
	10%GGBFS	ND	0.01	ND	0.1	0.1	0.01	ND	1.03	0.01	0.05	0.1
	20%GGBFS	ND	0.01	ND	0.1	ND	ND	ND	0.91	0.01	0.02	0.06
	30%GGBFS	ND	ND	ND	0.1	ND	ND	ND	0.72	ND	0.02	0.03

The leaching test results of the solidified matrices show that GGBFS addition was able to immobilize the toxic metals found in BMWBA. Table 4.5 reports the TCLP leaching text results, where the specimens were tested after 3, 7, 28 and 56 days of solidification of geopolymer matrices, are presented. The results obtained from the specimens were found to have lower concentration of toxic materials based on the permitted limits of TCLP disposal limits. This indicates that the geopolymerization process was able to reduce the toxic metals that are found in the leachate of BMWBA. Reduction of toxic metals' leaching potential was observed as the function of stabilization. The significant results on the basis of permitted limits was found to be on the 3rd day of leaching test. However, the stabilization rate increased to the maximum level at the 56th day of leaching experiment. This shows that increase in the period of stabilisation reduces the toxic metals in geopolymer solid matrix. The matrix with the best immobilization effectiveness has the littler pore opening and maximum compressive strength. Therefore, this is the phenomenon wherein the toxic metal immobilization is controlled by physical encapsulation of toxic metals.

CHAPTER 5

CONCLUSIONS

Based on the present study, the following conclusions are drawn:

Leaching of various toxic heavy metals was identified by three different test procedures (ASTM D3987-12, TCLP 1311, USEPA 1313). For BMWBA, Hg and As concentration was found exceed the disposal limit from all the three leaching test procedures. Similarly, for FCA, Cr, As and Hg were leaching in very high concentrations when compared to United States Environmental Protection Agency (USEPA) and European Union (EU) disposal limits. Hence it is not advised to discard these wastes at landfills without proper treatment.

- The leaching potential of BMWBA shows higher concentration of Hg and As at 4.37 mg/L, 8.53 mg/L from ASTM test procedure. In TCLP test procedure, higher concentration of Hg is 4.61mg/L. Similarly, in USEPA leaching procedure Hg leaches at 3.5 mg/L at pH 3 and 9.3 mg/L at pH 11 and As leaches at 8.53 mg/L at pH 7 and 6.4 mg/L at pH 9. From all the three test methods, the results of Hg and As shows higher concentrations compared to the TCLP disposal limits (As limit is 5 mg/L and Hg limit is 0.2 mg/L).
- The leaching potential of FCA shows higher concentration of Cr, Hg and As at 153.7 mg/L, 9.7 mg/L and 12.66 mg/L respectively in ASTM test procedure. In TCLP test procedure higher concentration of Cr is 156.18 mg/L, Hg is7.9mg/L and As is 12.01 mg/L. And, in USEPA leaching procedure Cr is leaching at the range of 153.7 mg/L to 98.3 mg/L at various pH range from 3 to 11. From all the three test methods. The results of Cr, Hg and As shows higher concentrations when compared to the TCLP disposal limits (Cr limit is 5 mg/L, As limit is 5 mg/L and Hg limit is 0.2 mg/L).

In the present study, leaching behaviour for fresh and aged samples (one year) of FCA was performed to assess the ageing factor. However, results showed that there is no much change in the leaching behaviour of fresh and aged ash samples for various metal leaching. Therefore, it can be deduced that the leaching mechanism for heavy metals, trace metals and alkaline elements does not get influenced by ageing effect.

Characterisation studies were carried out for both BMWBA and FCA to identify their mineralogy and morphology by SEM equipped with EDAX and XRD, however leaching of respective element depends also on its composition.

- BMWBA consists of irregular shaped particles which are agglomerated and long needle-shaped crystals. The percentage of major mineral constituents include SiO_2 (20.2%), Al_2O_3 (9.2%), MgO (3.1%), Na_2O (2.9%), CaO (39.6%), Fe_2O_3(7.2%), SO_3 (5.6). The formation of ettringite is confirmed by the presence of percentage of free lime (Cao), aluminium oxide (Al_2O_3), anhydrite ($CaSO_4$) and silicon dioxide (SiO_2). Further, XRD results reveal the presence of ettringite, calcite and thermonatrite as major minerals.
- Similarly, FCA is composed of particles of irregular shaped, minor square and hexagonal particles. SEM confirms the presence of glassy phase, unburned carbonaceous materials and different mineral phases. Various minerals present in FCA constitute domeykite, stilleitesyn, nickeline, mgriitesyn, arsenolamprite, modderitesyn, kamacite, mgriite and orcelite as obtained by XRD examination.

The leaching characteristics therefore depend not only on the chemical composition of the BMWBA and FCA combustion residues, but largely on its mineralogy and morphology. Hence, it provides much experimental evidence concerning the morphology and mineral composition that plays significant role in leaching process.

Leaching of toxic metals from BMWBA and FCA governed by sorption/solubility process was performed through geochemical modelling. The geochemical model, Visual MINTEQA 3.1 was used for modelling.

- Geochemical modelling discloses that Ca, Cu, Fe and Pb were controlled by the dissolution/precipitation process of BMWBA due to the presence of oxides, hydroxides and carbonates. Carbonate minerals mainly control the leaching of malachite in Cu, otavite in Cd and calcite and aragonite in Ca. As and Se were identified as dominant oxidation state-possessing metals and found to be redox-sensitive elements. As and Se leaching was occurred by sorption due to the presence of oxyanions and tend to be highly immobile in an alkaline condition.

- Geochemical modelling shows that leaching of Ca and Cd in FCA were mainly controlled by the carbonate minerals. As and Se were identified as dominant oxidation state-possessing metals and found to be redox-sensitive elements. Leaching of Zn, Fe, Cr and Cu were controlled by the oxides and hydroxides present in the minerals or metals.
- Geochemical modelling for leached concentrations of Ca, Cd, As, Cu, Cr, Fe, Ni, Se and Zn in the BMWBA and FCA was summarized based on their dominant oxide, hydroxide and carbonate minerals and leaching controlling solids for each elements of interest.

Solidification/Stabilization was attempted to achieve the reduction in leaching of toxic metals and also to reuse the considered waste material as a treatment option.

- In this process, BMWBA geopolymer was prepared by using alkaline activators (sodium silicate and sodium hydroxide) in the ratio of 1:2 along with GGBFS. Cubes were prepared for the mixture of 0%, 10%, 20% and 30% of GGBFS replacement to BMWBA geopolymer and was tested for strength aspect.
- The compressive strength obtained for 30% of GGBFS and 70% of BMWBA was 7.86 to 10.52 MPa. Similarly, with 20% and 10% of GGBFS in mixture resulted in 3.62 to 6.1 MPa and 1.25 to 2.8 MPa compressive strength respectively. With 100% of BMWBA (0% GGBFS), the compressive strength declined to 0.75 to 1.8 MPa. This shows that the strength declined as the percentage of GGBFS decreased. Therefore, it can be inferred that there is an increase in compressive strength from 0.75 Mpa to 10.5 Mpa when there is GGBFS replacement in BMWBA from 0 to 30%.

The compressive strength of the BMWBA geopolymer is due to the bonds between the Si–O–Si, when the mixture is enriched by greater amounts of silicon leads to the increase in compressive strength. The toxic metal immobilization mechanism is anticipated to be the fusion of chemical and physical reactions. Positively charged ions (Cation) might get bonded through Si-O or Al-O bond or present in the structural holes to keep up the electrical charge balance. A physically encapsulated process, diffusion might cause cation to be substituted by another cation. The rich content of CaO plays major role in the formation of cations (Ca^{2+}), which may get exchanged by metal ions such as Pb^{+2}, Zn^{+2}, Cd^{+2}, Mg^{+2}, etc. ions in alkaline condition.

The image from the SEM indicate that maximum replacement of BMWBA by GGBFS in the blends aids to form denser structure. This shows that increase in the GGBFS maximises the compressive strength. Increase in the quantity of GGBFS result in higher occurrence of calcium silicate gel in the blends that provides highly dense structure. The clear evidence of the calcination process can be noted from the SEM image which shows crystalline to amorphous structure with increase in GGBFS.

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2. Krishnamurthy M. P. and Devatha C. P. “Impact on Leaching Behaviour of Toxic Metals in Ferrochrome Ash with varying pH levels”. Journal of Material Cycles and Waste Management (Under review).

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