1.0 Introduction

Urbanization and population growth are responsible for high increasing rate of solid waste. Improper Municipal Solid Waste (MSW) disposal and management causes all types of pollution: air, soil, and water. Indiscriminate dumping of wastes contaminates surface and ground water supplies. In urban areas, MSW clogs drains, creating stagnant water for insect breeding and floods during rainy season. Uncontrolled burning of MSW and improper incineration contributes significantly to urban air pollution.

The U.S. Public Health Service identified 22 human diseases that are linked to improper MSW Management. Waste worker and pickers in developing countries are seldom protected from direct contact and injury, and the co-disposal of hazardous and medical wastes with MSW poses serious health threat. Exhaust fumes from waste collection vehicles, dust stemming from disposal practices and the open burning of waste also contribute to overall health problems. People know that poor sanitation affects their health, especially in developing and low-income countries, where the people are the most willing to pay for environmental improvements (Singh et al., 1998; Gupta et al., 1998).

Presently in India, annually total wastes of about 960 million tonnes is being generated as by products from industrial, mining, municipal, agricultural and other processes. Of these organic wastes from agricultural sources is about 350 million tonnes, inorganic waste of industrial and mining sectors is about 290 million tonnes and hazardous wastes of about 4.5 million tonnes are in nature. Advances in solid waste management resulted in alternative construction materials as a substitute to traditional materials like bricks, blocks, tiles, aggregates, ceramics, cement, lime, soil, timber and paint. Efforts are being made to safeguard the environment, by recycling different wastes and utilise them in value added applications. Due to the escalating growth in world population and large increase in waste production the generation of solid waste has become an increasingly important global issue over the last decade. The increase in solid waste generation poses numerous questions concerning the adequacy of conventional waste management systems and their environmental effects. Worldwide landfill disposal is the most commonly used waste management method
and new methods are required to reduce emissions from landfills. Landfills have served as ultimate waste receptors for municipal refuse, industrial residues, recycle discards and wastewater sludge.

Landfill still continues to be the major disposal route for solid waste disposal. Wastes in landfill experience high physical and biological changes resulting in solubilisation or suspension of high concentrations of organic matter in the form of landfill’s leachate. Source reduction and waste minimization, resource recovery and recycling, waste processing and treatment, combustion and land filling have all significantly affected the sufficiency of waste management systems. Landfill disposal is the most commonly employed waste management worldwide. Such landfill have served as ultimate waste receptors for municipal refuse, industrial or agricultural residues, wastewater sludge, incinerator ash, recycle discards, and/or treated hazardous wastes and have thereby promoted greater interest in landfill system innovation and advancement.

1.1. Solid wastes and its classification

Solid refers to non-soluble material such as agricultural refuse, industrial waste, mining residues, demolition waste, municipal garbage or even sewage sludge. Most of these kinds of wastes cannot be recycled or rehabilitated for further use.

Solid waste means any garbage, refuse, sludge from a wastewater treatment plant, water supply treatment plant or air pollution control facility and other discarded materials including solid, semi-solid, or contained gaseous material, resulting from industrial, commercial, mining and agricultural operations and from community activities, but does not include solid or dissolved materials in domestic sewage or solid or dissolved materials in irrigation return flows or industrial discharges that are point sources (Table 1.1).
<table>
<thead>
<tr>
<th>Source</th>
<th>Typical waste generators</th>
<th>Types of solid wastes</th>
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<tbody>
<tr>
<td>Residential</td>
<td>Single and multifamily dwellings</td>
<td>Food wastes, paper, cardboard, plastics, textiles, leather, yard wastes, wood, glass, metals, ashes, special wastes (e.g., bulky items, consumer electronics, white goods, batteries, oil, tires) and household hazardous wastes).</td>
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<tr>
<td>Industrial</td>
<td>Light and heavy manufacturing, fabrication, construction sites, power and chemical plants.</td>
<td>Housekeeping wastes, packaging, food wastes, construction and demolition materials, hazardous wastes, ashes, special wastes.</td>
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<tr>
<td>Commercial</td>
<td>Stores, hotels, restaurants, markets, office buildings, etc.</td>
<td>Paper, cardboard, plastics, wood, food wastes, glass, metals, special wastes, hazardous wastes.</td>
</tr>
<tr>
<td>Institutional</td>
<td>Schools, hospitals, prisons, government centres.</td>
<td>Same as commercial.</td>
</tr>
<tr>
<td>Construction and demolition</td>
<td>New construction sites, road repair, renovation sites, demolition of buildings</td>
<td>Wood, steel, concrete, dirt, etc.</td>
</tr>
<tr>
<td>Municipal services</td>
<td>Street cleaning, landscaping, parks, beaches, other recreational areas, water and wastewater treatment plants.</td>
<td>Street sweepings; landscape and tree trimmings; general wastes from parks, beaches, and other recreational areas; sludge.</td>
</tr>
<tr>
<td>Process (manufacturing, etc.)</td>
<td>Heavy and light manufacturing, refineries, chemical plants, power plants,</td>
<td>Industrial process wastes, scrap materials, off-specification products, tailings.</td>
</tr>
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</table>
Agriculture

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<tr>
<th>Mineral extraction and processing.</th>
<th>Spoiled food wastes, agricultural wastes, hazardous wastes (e.g., pesticides).</th>
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<td>Crops, orchards, vineyards, feedlots, farms.</td>
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1.1.1. Types of solid waste

Solid waste can be classified into different types depending on their source:

a) Household waste is generally classified as municipal waste

b) Industrial waste as hazardous waste

c) Biomedical waste or hospital waste as infectious waste

Municipal solid waste (MSW) consists of household waste, construction and demolition debris, sanitation residue and waste from streets. This garbage is generated mainly from residential and commercial complexes. With rising urbanization and change in lifestyle and food habits, the amount of MSW has been increasing rapidly. In 1947 cities and towns in India generated an estimated 6 million tonnes of solid waste; in 1997 it was about 48 million tonnes. More than 25% of the generated MSW is not properly collected, 70% of the Indian cities lack adequate capacity to transport it and there are no sanitary landfills to dispose of the waste. The existing landfills are neither well equipped nor well managed and are not lined properly to protect against contamination of soil and groundwater.

Over the last few years, the consumer market has grown rapidly by packing the products in cans, aluminium foils, plastics, and other such non biodegradable items that cause harm to the environment. In India, some municipal areas have banned the use of plastics and they seem to have achieved success. One positive note is that in many large cities, shops have begun packing items in reusable or biodegradable bags. Certain biodegradable items can also be composted and reused. In fact proper handling of the biodegradable waste will considerably lessen the burden of solid waste that each city has to tackle.
b) Hazardous waste:

Industrial and hospital waste is considered hazardous as they may contain toxic substances. Certain types of household waste are also hazardous. Hazardous wastes could be highly toxic to humans, animals, and plants; are corrosive, highly inflammable or explosive and react when exposed to certain things e.g. gases. India generates around 7 million tonnes of hazardous wastes every year, most of which is concentrated in four states: Andhra Pradesh, Bihar, Uttar Pradesh, and Tamil Nadu. Household wastes that can be categorized as hazardous waste include old batteries, shoe polish, paint tins, old medicines and medicine bottles. In the industrial sector, the major generators of hazardous waste are the metal, chemical, paper, pesticide, dye, refining and rubber goods industries.

c) Hospital waste:

Hospital waste is generated during the diagnosis, treatment, or immunization of human beings or animals or in research activities in these fields or in the production or testing of biological. It may include wastes like sharps, soiled waste, disposables, anatomical waste, cultures, discarded medicines, chemical wastes, etc. These are in the form of disposable syringes, swabs, bandages, body fluids, human excreta, etc. This waste is highly infectious and can be a serious threat to human health if not managed in a scientific and discriminate manner. It has been roughly estimated that of the 4 kg of waste generated in a hospital at least 1 kg would be infected.

Survey carried out by various agencies shows that the health care establishments in India are not giving due attention to their waste management. After the notification of the Bio-medical Waste (Handling and Management) Rules, 1998, these establishments are slowly streamlining the process of waste segregation, collection, treatment, and disposal. Many of the larger hospitals have either installed the treatment facilities or are in the process of installing the treatment facilities.
1.1.2. Health impacts of solid waste

Modernization and progress has its share of disadvantages and one of the main aspects of concern is the pollution it is causing to the earth – be it land, air, and water. With increase in the global population and the rising demand for food and other essentials, there has been a rise in the amount of waste being generated daily by each household. This waste is ultimately thrown into municipal waste collection centres from where it is collected by the area municipalities to be further thrown into the landfills and dumps. However, either due to resource crunch or inefficient infrastructure, not all of this waste gets collected and transported to the final dumpsites. At this stage the management and disposal is improperly done, it can cause serious impacts on health and problems to the surrounding environment.

Waste that is not properly managed especially excreta and other liquid and solid waste from households and the community are the serious health hazard which leads to the spread of infectious diseases. Unattended waste lying around attracts flies, rats, and other creatures that in turn spread disease. Normally it is the wet waste that decomposes and releases a bad odour. This leads to unhygienic conditions and thereby to a rise in the health problems. The plague outbreak in Surat is a good example of a city suffering due to the callous attitude of the local body in maintaining cleanliness in the city. Plastic waste is another cause for ill health. Thus excessive solid waste that is generated should be controlled by taking certain preventive measures.

The group at risk from the unscientific disposal of solid waste includes the population in areas where there is no proper waste disposal method, especially the pre-school children, waste workers and workers in facilities producing toxic and infectious material. Other high-risk group include population living close to a waste dump and those, whose water supply has become contaminated either due to waste dumping or leakage from landfill sites. Uncollected solid waste also increases risk of injury and infection.

In particular, organic domestic waste poses a serious threat, since they ferment, creating conditions favourable to the survival and growth of microbial pathogens. Direct handling of solid waste can result in various types of infectious and
chronic diseases with the waste workers and the rag pickers being the most vulnerable.

Exposure to hazardous waste can affect human health, children being more vulnerable to these pollutants. In fact, direct exposure can lead to diseases through chemical exposure as the release of chemical waste into the environment leads to chemical poisoning. Many studies have been carried out in various parts of the world to establish a connection between health and hazardous waste.

Waste from agriculture and industries can also cause serious health risks. Other than this, co-disposal of industrial hazardous waste with municipal waste can expose people to chemical and radioactive hazards. Uncollected solid waste can also obstruct storm water runoff, resulting in the forming of stagnant water bodies that become the breeding ground of disease. Waste dumped near a water source also causes contamination of the water body or the ground water source. Direct dumping of untreated waste in rivers, seas and lakes are resulting in the accumulation of toxic substances in the food chain through the plants and animals that feed on it.

Certain chemicals like mercury, cyanides, lead are highly toxic on exposure to human health and can lead to death. Disposal of health care’s and Waste requires special attention overcoming major health hazard. Several precautionary measures have to be taken for the disposal of solid waste to neighbourhood landfill. Landfill sites should be well lined and walled to ensure that, leakage is avoided to nearby ground water sources. Recycling of materials should be carried out.

Proper methods of waste disposal have to be undertaken to ensure that it does not affect the environment around the area or cause health hazards to the people living there. At the household-level proper segregation of waste has to be done and it should be ensured that all organic matter is kept aside for composting, which is undoubtedly the best method for the correct disposal of this segment of the waste. In fact, the organic part of the waste that is generated decomposes more easily, attracts insects and causes disease. Organic waste can be composted and then used as a fertilizer.
1.2. Heavy Metals in solid waste

Modern civilization is completely dependent on a large range of metals for all aspect of daily life. There is a long history associated between metals and human development. Heavy metal pollution not only affects the production and quality of crops, but also influences the quality of the atmosphere, water bodies and threatens the health, life of animal and human being (Marzieh, 2010). Heavy metals are environmentally problematic substances due to their high persistence and toxic effects (Esakku et al., 2003). Landfills accumulate large amounts of heavy metals and therefore contribute greatly to the risk potential (Hellweg et al., 2001). Municipal solid waste (MSW) is the waste, which is most commonly used in composting. It is an extremely heterogeneous material in its geometry, (Flyhammar, P (1997)). It may, moreover contain high concentrations of Pb, Cu, Cd and Zn has been shown by several studies (Flyhammar,P(1998)). Consequently, subsequent applications of MSW compost rich in heavy metals to agricultural soils may cause heavy metals accumulation to toxic levels (King, L.D et al.,(1990)) : Veeken,A et al.,(2002)).

Heavy metals appear in the MSW stream from a variety of sources. Batteries, consumer electronics, ceramics, light bulbs, house dust and paint chips; lead foils etc., all introduce metal contaminants into the solid waste stream. Composts made from the organic material in solid waste will inevitably contain these elements, although at low concentrations after most contaminants have been removed. In modern era human civilization has progressed with production of waste which also changes in quality and quantity. In early 20th century management of MSW by open dumping on land was common practice. Solid waste management is a worldwide phenomenon.

Thousands of millions of MSW are produced every year. Waste management and utilization strategies are major concern in many countries. Every year MSW incineration generates large quantities of solid residues, such as bottom ash and fly ash. In many countries the Air Pollution Control (APC) residues must be handled as toxic waste. Worldwide many attempts have been made to treat this residue in order to reduce the leaching of heavy metals on global level in various concepts like minimization of solid waste, recycling and reuse, source separation etc., emerging for management of MSW. These materials require extensive handling and particularly
residue from incineration of MSW systems is problematic due to its high content of readily leachable heavy metals (Chandler, et al., 1997).

1.3. MSW site in Mysore – an overview

Mysore is one of the largest cities in Karnataka. Mysore was the capital of Mysore state until 1956, when the capital was shifted from Mysore to Bangalore. Mysore is spread over an area of about 128 sq. km with the growing population at a faster rate due to the influx of many service industry activities, the generation of municipal waste both garbage and sewage has been on the rise. Anthropogenic activities in society generate large quantities of wastes posing a problem for their disposal. Improper disposal leads to spreading of diseases and unhygienic condition besides spoiling the aesthetics. The city has several major and small industries present in Nanjangud 20Km away from the Mysore city together with many educational and commercial establishments. In India, every year 30.3 million tons of Municipal solid waste is generated. This equates to about 350gms of waste per person on average.

1.4. Steel Authority of India Limited, Visvesvaraya Iron and Steel Plant (VISL), Bhadravathi, Karnataka State- an overview

It is a unit of Steel Authority of India Limited, involved in the production of alloy steels and pig iron. It is located in the city of Bhadravathi, Karnataka, India. The Visveswaraya Iron and Steel Limited at Bhadravathi (formerly known as the Mysore Iron and Steel Ltd.) were set up in 1923 by the princely state of Mysore with the assistance of M/S Peri and Marshall Co. (USA). It is now a steel plant under the jurisdiction of the Steel Authority of India Limited. Visvesvaraya Iron & Steel Plant was established with 1000 Employees and were the Manufacturer of Alloy Steel, Alloy Steel Pipes, Alloy Steel Pipe Fittings, Alloy Steel Tube, and Alloy Steel Bars. The plant was taken over by the Central Government in 1962. The localisation of the plant is controlled by the availability of rich silicon iron ores of Kemmangundi mines in the Bababudan hills (Chikmagalur district). The reserves are estimated at 25-60 million tonnes with Fe contents from 55-64 percent.

The plant is located 17 km east of Shimoga on the Birur-Shimoga branch line of the Southern Railway. It enjoys the facility of the vast market of the southern India.
The plant meets its demands of limestone from the Bhandigunda deposits at a distance of 20.8 km; manganese and chromite from a distance of 48 km; charcoal from the nearby forests of the Malnad area; electricity from the Jog hydroelectric and Shravati power projects. The hydral power has now replaced charcoal in the smelting process.

The plant was initially designed to produce 24,500 tons of pig iron which has now been increased to 21 lakh tones of pig iron and 77,000 tons of alloy and special steel. In 1978-79 produced 1.13 lakh tones of ingot steel. The plant is one of the major producers of alloy and special steel in the country. In addition it also supplies spun-pipe, ferro-silicon, cement, mild steel and castings, etc.

1.5. Waste Generated in Steel Industry: Causes and Effects

1.5.1. Cause of Waste Generation

The Steel industry is considered as resource intensive and pollution prone. Production of steel involves several operations. It starts from naturally occurring raw materials like coal, iron ores & fluxes to produce hot metal in blast furnace, convert hot metal into steel and subsequently to go for rolling of steel into finished product. Several other activities including production of refractory aerosol performed in varying magnitude inside the steel works. A large quantity of waste is generated as a sequel to such Activities. To make one-tonne of crude steel even with good raw materials and efficient operation, 5 tonnes of air, 2.8 tonnes of raw materials and 2.5 tonnes of water are required. These will produce in addition to 1 tonne of crude steel, 8 tonnes of moist laden gases and 0.5 tonne of solid wastes (Lean, 1990). However, in SAIL plants, this figure varies from 820-1,200Kg/tonne of crude steel—which is very high (Prothia and Roy, 1993). In a steel industry, all the three types of waste materials (gaseous, liquid and solid) are generated. The generation of gaseous waste material is the highest but the management of solid waste material is the most intricate. The steel plants of the seventies were characterized by higher waste generation rates associated with massive dumps around the steel works resulting in serious land, water and air pollution. Over the years, due to technological changes in steel making and strict environmental regulations and legislation, emphasis on raw material quality and emergence of new markets coupled with innovative ideas of waste reduction and rescue have resulted in drastic reduction in the quantity of waste generated in steel
works from 1,200 Kg to less than 200 Kg per tonne of crude steel and recycling rates have reached 95-97% in some parts of the world. However, the solid waste generation presently in Indian steel industry is in range of 600-1,200 Kg/tonne of crude steel and recycling rate varies between 40-70% which lead to higher production costs, lower productivity and further environmental degradation.

The steel plant solid wastes have been broadly classified into categories:

(a) Solid waste generated from process units.

(b) Solid waste generated from pollution control equipment.

Generation of solid waste from process units mainly depends on quality of raw materials and technology adopted. The primary reason for high waste generation in Indian steel Industry is the poor quality of raw materials i.e. Iron ore and coal. High ash content of coal leads to increased coke consumption in blast furnace causing increased slag generation. Further, higher ash content of coal leads to increased fly ash generation in power plant. The high alumina content of iron ore increases the coke rate volume in blast furnace. Technological and operational discipline can bring down hot metal’s silicon and sulphur level, which will in turn reduce the slag rate per tonne of crude steel. Other technological improvements like high blast furnace temperature, higher top pressure; use of prepared burden, injection into blast furnace etc. will reduce the coke consumption rate which will ultimately reduce the slag volume. Similarly, continuous charging technologies for electric arc furnaces can reduce the volume of dust discharge by as much as 40%. Scrap in the pre-heater traps the dust and returns it to the furnace thereby increasing the steel yield. By adopting Electric Arc Furnace (EAF) of steel making the solid wastes generated from blast furnace process will be drastically reduced constituting major quantum of solid waste generation from an integrated steel plant. Similarly the COREX iron making process eliminates the need for coke making and coke oven gas by product recovery plants. Solid wastes generated from process units are generally characterized by their uniform size and composition, low moisture content and high levels of Fe, Ca, C etc., which makes these waste suitable for recycling within the plant premises or to be sold out to consuming industries. Solid waste generation from pollution control equipment mainly depends on type of control equipment i.e. dry/wet, efficiency of the equipment
and quality of raw materials. To improve the work zone air quality, highly efficient deducing systems have been installed to capture secondary emissions that were previously discharged to the environment. This environmental protection measures are relating to air and water lead to the accumulation of sludge and dusts rendering their reuse cumbersome. These dusts and sludge coming out of the pollution control equipment are grouped under hazardous waste. Pollution control measures can make the recycling of certain substances impossible due to their fine to ultra-fine grain size. Dusts and sludge generated from flue gas and pollution control units vary in size and composition.

1.5.2. Effects on Environment

The process of industrialization and continuous exploitation of earth resources for sustainable growth of civilization has depleted the non-renewable resources of the earth thereby adversely affecting the environment. An integrated steel plant unit exhausts several harmful dusts, fumes and substances that are quite injurious to human health, vegetation, crops, landscape, animals, machine life etc. Such discharges contaminate and damage inland waters, environment, soil, food, human settlement and even flora and fauna. Therefore, these wastes could not be left uncared for and that is why threshold limits for such harmful substances have been fixed and industries are required to adhere to these norms.

1.6. Bottom Ash

1.6.1. Definition and Classification of Bottom Ash

Bottom ash, the solid residue from electric power generation process, represents the coarser size fraction which falls to the bottom of the combustion boiler. The combustion technologies and furnace type determines the characteristics of the material generated.

In dry pulverized bottom furnaces, ashes are collected as dry solids before complete melting occurs. These solid particles are collected in a collection hopper and removed by high-pressure water jets and conveyed to a disposal pond or a decant basin for dewatering, crushing, and stockpiling for disposal or use (Hecht and Duvall, 1975). This type of bottom ash is known as dry bottom ash. Material is dark gray in
colour and has porous, granular sand like appearance. On the other hand, the coarser ash obtained from wet boilers is called as boiler slag. During coal combustion, bottom ash is kept in molten state and tapped off as liquid. Molten material flows into the hopper where quenching water is held. When the molten slag comes in contact with water, it starts to crystallize and then forms pellets. Boiler slag consists of hard, black, angular and having glassy-like appearance materials (Coal Bottom Ash/Boiler Slag, 2009).

1.6.2. General Characterization of Bottom Ashes

Bottom ash is the most significant by-product from waste incineration (Chandler et al., 1997). It is a slagged and granular material containing mostly lithophilic elements. Hence, elements like Si, Ca, Fe and Cr are more significant than elements with higher vapour pressures, e.g. Hg and Cd. Despite the depletion of volatile elements, the content of easily leachable salts and heavy metals is often 10-100 times higher than in natural soils or in the lithosphere (Chandler et al., 1997).

Bottom ashes from different plants are generally very similar despite the different origins (Chimenos et al., 1999; Eusden et al., 1999). The mineral content is typically classified within the same few main categories (i.e. inorganic residue, melt-products, glasses, metallic components, and unburned materials such as ceramics and rocks (Eusden et al., 1999; Speiser et al., 2000). The morphology, mineralogy and alkalinity are all very important factors for the physical and chemical characteristics of bottom ashes. These properties can, however, be hard to classify because the bottom ashes are often very inhomogeneous. It contains, a great number of mineral phases spread in different particles with variant textures and morphologies. The mineral phases have been investigated in several studies in order to elucidate the leaching properties and the weathering processes (e.g. Chanders et al., 1997 and references therein: Chimenos et al., 1999; Speiser et al., 2000).

Minerals such as quartz, calcite, gypsum, hematite and various silicates to name a few have been identified in these studies. Bottom ashes typically have a high initial pH (pH 11-12.5) due to the presence of Ca (OH)$_2$ and alkali metal hydroxides (Johnson et al., 1995; Chandler et al., 1997). The equilibrium pH will, however, decrease as a consequence of natural weathering reactions, for instance when CO$_2$
from the atmosphere reacts with the hydroxides and forms carbonates (Chandler et al., 1997; Steenari et al., 1999). This means that the leaching properties change considerably as a consequence of the altered pH conditions (Chandler et al., 1997; Meima and Comans, 1999). Also the neo-formation of phases may change the leaching properties if they are capable of binding foreign elements, such as the formation of clays and iron oxides (Meima and Comans, 1999; Speiser et al., 2000).

It flows from the furnace with molten slag floating on its upper surface, when the blast furnace is tapped to release the molten iron. These two materials are separated using a weir, the molten iron being channeled to a holding vessel and the molten slag to a point where it is to be treated further. The final form of the blast furnace slag is dependent on the method of cooling. There are four main types of blast furnace slag: granulated; air-cooled; expanded and pelletised. Chemically, the blast furnace slag contains mainly silica (30–35 %), calcium oxide (28–35 %), magnesium oxide (1–6 %) and Al₂O₃/Fe₂O₃ 1.8–2.5 %. Due to its low iron content it can be safely used in the manufacture of cement. Two types of blast furnace slag such as air-cooled slag and granulated slag are being generated from the steel plants. The specific gravity of the slag is approximately 2.90 with its bulk density varying in the range of 1,200–1,300 kg/m³. The colour of granulated slag is whitish. The air-cooled slag is used as aggregate in road making while the granulated slag is used for cement manufacturing. Its use as aggregate in concrete is not very usual although it has no behavioural problems, and there has been little research work done on the subject. Because of their more porous structure, blast furnace slag aggregates have lower thermal conductivities than conventional aggregates. Their insulating value is of particular advantage in applications such as frost tapers (transition treatments in pavement sub-grades between frost susceptible and non-frost susceptible soils) or pavement base courses over frost-susceptible soils. The granulated blast furnace slag is formed due to rapid quenching of molten slag, which converts it into a glassy state. Granulated slag possesses cementitious properties if it is ground finely. The size and physical properties of granulated blast furnace slag varies, depending on the chemical composition and method of production. Numerous studies are available on the properties of cement and concrete containing ground blast furnace slag as a latent hydraulic material. Slag cement is the hydraulic cement that results when molten slag
from an iron blast furnace is rapidly quenched with water, dried and ground to a fine powder.

1.6.3. Physical Properties of Bottom Ash

Like fly ash, physical properties of bottom ash depend on the coal type, preparation before combustion and temperature of combustion. Bottom ash displays physical properties similar to that of natural sands (Kumar et al., 2004). Bottom ash has a high porous surface, large particle size, angular shape and glassy texture. Bottom ash particles range in size from a fine gravel to a fine sand (Kumar et al., 2004). The ash is usually a well-graded material; yet, the particle size distribution of ash samples obtained from the same power at different times can display variations (Kumar et al., 2004). Bottom ash particles tend to range in size between 50.8 mm and 0.075 mm (Churchill and Amirkhanian, 1999).

1.6.4. Chemical Composition of Bottom Ash

Chemically, coal bottom ash has similar properties to fly ash and composition of bottom ash particles is controlled by the source of coal. Three predominant oxides are silicon dioxide ($\text{SiO}_2$), aluminium oxide ($\text{Al}_2\text{O}_3$) and ferric oxide ($\text{Fe}_2\text{O}_3$). Calcium oxide ($\text{CaO}$), magnesium oxide ($\text{MgO}$), sodium oxide ($\text{Na}_2\text{O}_3$), potassium oxide ($\text{K}_2\text{O}$), sulfur trioxide ($\text{SO}_3$) and other minor oxides such as $\text{P}_2\text{O}_5$, TO$_2$ also occurs in lower amounts. Bottom ash which originally comes from lignite or sub-bituminous coals has a higher percentage of calcium than that of derived from anthracite or bituminous coals. There can also be some percentage of carbon particulate resulting from incomplete combustion.

Bottom ash and boiler slag could exhibit corrosive properties due to salt content and low pH. The potential for corrosion of metal components that would come in contact with boiler slag could be a concern and should be tested when bottom ash or boiler slag is used in embankment, backfill, sub base, or in a base course (Ke and Lowell, 1992). Information pertinent to this issue can be found in ACAA Technical Bulletin TB 51 Underground Corrosion of Metals in Bottom Ash Backfills. Testing to indicate potential corrosivity of boiler slag (or bottom ash) should evaluate pH, electrical resistivity and soluble chlorides and sulfates (Ke and Lowell, 1992).
Materials are judged to be noncorrosive if the pH exceeds 5.5, the electrical resistivity is greater than 1,500 ohm-centimetre, the soluble chloride content is less than 200 ppm, or the soluble sulfate content is less than 1,000 ppm (Ke and Lowell, 1992).

1.7. Heavy Metals and their Health effects

Heavy metals are elements having atomic weights between 63.546 to 200.590 and specific gravity greater than 4.0. Living organisms require trace amounts of some heavy metals including Co, Cu, Fe, Mn, Mo, V, Sr and Zn. They are known as essential metals but their excessive levels can be detrimental to organisms. Heavy metals including Hg, Cr, Cd, As, Pb, Sr, etc. are non-essential metals and considered to be great threat for aquatic life as well as humans, plants and other animal’s life. These toxic metal ions are directly released into natural water by various industrial applications and by other human activities. They exist in surface water in colloidal, particulate and dissolved forms although dissolved concentration is very low and are generally ions or unionized organometallic chelates or complexes.

Heavy metals are considered to be one of the main sources of pollution in the environment, because of their significant effect on the ecological quality. The main sources of heavy metal pollution in the environment are manmade effects including combustion of fossil fuels, mining activities, wastewater discharges of manufacturing industries and waste disposal. High levels of heavy metals in the sediments and soils may pass to the aquatic environment, groundwater and plants through the transfer processes and reach to the animals and humans. Therefore, the use of simple and accurate methods for monitoring heavy metals has a great importance among the environmental studies.

1.7.1. Cadmium

Cadmium is the 48th element in the periodic table and occurs naturally in the environment as Cd$^{2+}$ and rarely as Cd$^+$. The metallurgical, electroplating, pigment, fertilizers, batteries, mining and electroplating industries is major contributors to the increase of Cd in the environment (Gupta et al., 2009, and Sharma et al., 2009). Ziemacki et al. (1989) reported that Cd emissions in Europe have been closely linked
to Zn production. The steel industry, volcanic eruptions and waste incineration pose the most problems.

Its toxicity is linked with reproduction problem because it affects sperm and reduces birth weight. It is a potential carcinogen and seems to be a causal factor in cardiovascular diseases and hypertension. Large concentrations of Cadmium in the soil are associated with parent material (black slates) and most are manmade (burning of fossil fuels, application of fertilizers, sewage sludge, and plastic waste). Exposure to cadmium over a long period leads to kidney failure and also plays a role in the development of hypertension and prostate cancer. High levels of cadmium in the body can also lead to death. Cadmium has been reported to be the most toxic element easily taken up by plants (Ahmaruzzaman, 2011; Fu and Wang, 2011; and Bruce, 1990).

1.7.2. Copper

Copper, the 29th element in the periodic table is employed in metal finishing, paint, chemical, Mining, wood manufacturing, fertilizer and electrical industries. It exists in nature in two oxidation states: Cu\(^+\) or Cu\(^{2+}\) (Hu, 2006).

Copper is needed for metabolic processes but the central nervous system, hepatic and renal regions of living organism are affected by high levels of copper in the body. Conditions such as irritations in the eyes, nose and mouth, cramps, convulsions and sometimes death have been reported to be associated with high levels of copper in the tissues of living organisms. (Ahmaruzzaman 2011; Fu and Wang 2011; Paulino et al., 2006, Sharma et al., 2009). According to Patterson (1985) there is a strong connection between pH and the amount of copper available in waste water.

1.7.3. Nickel

Nickel and its compounds are widely used in modern industry such as electroplating, battery, alloy production and dye industries, due to its unique chemical and physical properties; the plating industry is recorded to be the most significant contributor of nickel in waste (Hu, 2006; Jin et al., 2006 and Patterson, 1985).
1.7.4. **Lead**

Lead, a very common element associated with the mining, waste incineration, pesticide, paint, battery, fuel and photographic industries, has been described as the most significant of toxic metals. The element occurs in the earth crust primarily as galena (PbS) but also occurs in other minerals such as cerrusite (PbCO$_3$) and anglesite (PbSO$_4$). Together with the sulfides of zinc, copper and iron, lead sulfide is highly associated with gold and silver ores. It occurs naturally in two oxidation states, +4 and +2 with the latter being the prevailing one (Reeder, *et al.*, 2006).

This has been known to be toxic since the 2nd century BC in Greece. It is a widespread contaminant in soils. Lead poisoning is one of the most prevalent public health problems in many parts of the world. It was the first metal to be linked with failures in reproduction. It can cross the placenta easily. It also affects the brain, causing hyperactivity and deficiency in the fine motor functions, thus, it results in damage to the brain. The nervous systems of children are especially sensitive to Pb leading to retardation. It is also cardiotoxic and contributes to cardiomyopathy (disease of the heart muscle leading to the enlargement of the heart). Lead's toxicological and neurological effects on living organisms include dizziness, anaemia, hallucination, brain dysfunction, high blood pressure, renal, liver, and reproductive system damage as well as weakness of muscles (Ahmaruzzaman, 2011; Fu and Wang, 2011; Reeder *et al.*, 2006; Gupta and Ali, 2004; and Naseem and Tahir, 2001).

1.7.5. **Zinc**

The paint, pharmaceutical, plastic, newsprint, galvanizing and zinc plating industries are responsible for the release of zinc into the environment. Although essential for human health due to its regulation of biochemical processes and importance to the proper physiological functioning of living tissues, an excess of zinc in living organisms results in retardation of growth, skin irritations, nausea, restlessness and lung disorders (Ahmaruzzaman, 2011; Fu and Wang, 2011; Sharma *et al.*, 2009).
1.7.6. Chromium

Chromium is a chemical element which has the symbol Cr and atomic number 24. It is the first element in Group 6. It is a steely-gray, lustrous, hard and brittle metal which takes a high polish, resists tarnishing, and has a high melting point. The name of the element is derived from the Greek word, Chroma, meaning color, because many of its compounds are intensely colored. Chromium is remarkable for its magnetic properties; it is the only elemental solid which shows antiferro magnetic ordering at room temperatures.

It is required for carbohydrate and lipid metabolism and the utilization of amino acids. Its biological function is also closely associated with that of insulin and most Cr-stimulated reactions depends on insulin. However, excessive amount can cause toxicity. Toxic levels are common in soils applied with sewage sludge.

1.8. Iron Oxides

Iron is the fourth most abundant element in the earth’s crust and the second most abundant metal (Schwertmann and Cornell, 1991; Jambor and Dutrizac, 1998). It occurs as Fe$^{+2}$ and Fe$^{+3}$ in a diversity of minerals including many types of iron oxides. The iron oxides are in fact oxides, hydroxides or oxihydroxides, but here they are commonly referred to as iron oxides. Most of the compounds are thermodynamically stable in natural systems (e.g. goethite, hematite, magnetite) while others can be designated as intermediates only ((ferrihydrite, maghemite); Jambor and Dutrizac, 1998). The different iron oxides have all their own characteristics and qualities, governed by the mineral structure.


The mineral structure of the iron oxides controls the stability, the surface area, the porosity, the dissolution rate, formation and transformation kinetics of each compound (Cornell and Schwertmann, 1996). Ferrihydrite is found in many systems. It occurs in nature in waters and sediments, in soils, in mine waste and acid mine drainage and even in meteorites (Cornell and Schwertmann, 1996; Jambor and Dutrizac, 1998). The incidence of ferrihydrite is often underestimated due to difficulties in the specific characterization (Jambor and Dutrizac, 1998). Ferrihydrite is
a poorly ordered oxihydroxide, which is typically present as small and aggregated grains (Cornell and Schwertmann, 1996). The Fe$^{+3}$ ions are spread randomly over the structure that moreover holds a great number of vacancies (Cornell and Schwertmann, 1996). This combination has made it hard to agree on a specific crystal structure, and the chemistry of ferrihydrite has, consequently, never been defined precisely (Jambor and Dutrizac, 1998). The degree of ordering in ferrihydrite is variable but it has two extremes. The best-crystallized material shows six X-ray diffraction lines, whereas the less ordered shows only two. Ferrihydrite is thermodynamically meta-stable and will over time transform into more stable members of the group, typically hematite and goethite, unless stabilized in some way (Cornell and Schwertmann, 1996). Ferrihydrite has a high adsorptive capacity and an extensive specific surface area and it can, thus, hold back large amounts of foreign ions by sorption. Ions may, in addition, be held back by sorption to “inner surfaces” in the aggregated particles, and their release is, thus, additionally limited by diffusion. Substitution of foreign cations in the ferrihydrite structure has never been proven even though a great number of metal-holding co precipitates have been studied (Cornell and Schwertmann, 1996; Jambor and Dutrizac, 1998).

1.8.2. Goethite

Goethite is frequently found in nature. It is one of the thermodynamically most stable iron oxides at ambient temperatures and it is, for this reason, often found as an end product of many transformations. Goethite can form directly in solution via a nucleation- crystal growth process, e.g. from ferrihydrite via dissolution and re-precipitation (Schwertmann and Cornell, 1991). It is generally formed in competition with hematite in aqueous systems. The resultant ratio between the goethite and the hematite depends on factors like pH, temperature and ionic strength of the solution .Foreign cations like Al, Cd, Co, Cr, Cu, Mn, Ni and Zn can readily replace Fe in the goethite structure by substitution (Lim-Nunez and Gilkes, 1987; Gerth, 1990; Singh and Gilkes, 1992; Cornell and Schwertmann, 1996).
1.8.3. Hematite

The red hematite is often found in nature, particularly in tropical or subtropical soils. Like goethite, hematite is extremely stable and hence, often the end member of transformations of other iron oxides. Hematite can form in several ways but one common way implies an internal rearrangement and dehydra-
tion of ferrihydrite (Schwertmann and Cornell, 1991). In aqueous systems, hematite generally forms in competition with goethite. Also a thermal dehydration can generate a phase of hematite, depending on the redox conditions. Foreign cations like Al, Cu, Cr, and Mn can substitute for Fe in hematite (Lim-Nunez and Gilkes, 1987; Singh and Gilkes, 1992; Cornell and Schwertmann, 1996).

1.8.4. Maghemite

Maghemite is invariably found in soils, primarily in the tropics and the subtropics. As the word says, maghemite is a combination of magnetite and hematite. It holds the structure of magnetite and the composition of hematite and it can, consequently, be considered a fully oxidized magnetite (Cornell and Schwertmann, 1996). Maghemite can form by heating magnetite in an oxidizing atmosphere. Maghemite integrates foreign cations like Al, Co, Cu, Cr, Mn, Ni, and Zn (Sidhu et al., 1980; Sidhu, 1988; Schwertmann and Taylor, 1989).

1.8.5. Magnetite

The presence of magnetite in nature is often a result of biological processes, but it can also have a lithogenic origin (Schwertmann and Cornell, 1991). Magnetite has the structure of an inverse spinel and it differs from most other iron oxides in that it contains both Fe$^{+2}$ and Fe$^{+3}$. Magnetite can form directly by oxidative hydrolysis of Fe$^{+2}$solution, and heating of Fe$^{+3}$ compounds under strongly reducing conditions can also lead to the formation of magnetite. Magnetite is often non-stoichiometric and both divalent and trivalent cations, such as Al, Cd, Co, Cr, Cu, Ni, Mn and Zn are integrated with ease (Sidhu et al., 1978, 1980; Sidhu, 1988; Cornell and Giovanoli, 1989; Schwertmann and Cornell, 1991; Cornell and Schwertmann 1996; Gillot et al., 1999).
1.9. Transformation of Iron Oxides

One of the fascinating features of the iron oxides is the variety of interconversions between the different phases. This means that processes like thermal treatment; weathering and natural aging processes can induce changes in the mineralogy that possibly affect the phase characteristics, including the ability to bind metals. The transformation from one compound to another requires the rearrangement of atoms in the structure. This may take place either via internal solid state rearrangement (like the formation of hematite from ferrihydrite) or from solution via dissolution and re-precipitation (such as the formation of goethite from ferrihydrite; Cornell and Schwertmann, 1996).

1.9.1. Natural Aging and Weathering Reactions

In nature, iron is introduced into the environment during rock weathering. Most of the Fe is located in silicates or in sulfides such as pyrite, FeS$_2$ (Schwertmann and Cornell, 1991). When these compounds gradually decompose, Fe$^{3+}$ oxides with low solubility form. These weathering and aging processes all go on slowly but continuously in nature. Like the primary host material, the freshly precipitated iron oxides will also undergo aging and weathering reactions. The iron may, for instance remobilize if it dissolves in an acidic environment or if it is reduced microbiologically under anaerobic conditions. Later, it will re-precipitate and possibly form ferrihydrite. Depending on the external conditions, this ferrihydrite either dissolves again or it transforms into other compounds. If crystalline compounds eventually form, they are more likely to remain stable. The crystalline phases are thermodynamically favoured over ferrihydrite. Their solubility products are orders of magnitude lower and they are less likely reduced microbiologically, partly because of their smaller specific surface areas (Munch and Ottow, 1980; Cornell and Schwertmann, 1996; Postma and Jakobsen, 1996; Roden and Zachara, 1996).

1.9.2. Thermal Treatment of Iron Oxides

By studying thermally induced transformations, processes related to natural aging can be examined. The elevated temperature will speed up the aging reactions, but new reactions that would not have been seen at ambient temperature may also
occur. Hence, the processes that take place can hardly be argued to reflect natural aging at ambient temperature perfectly and the higher the treatment temperature, the greater are the differences. Thermal dehydroxylation typically takes place at 140-500°C depending on the nature of the compound, the crystallinity, the extent of isomorphous substitution and any chemical impurities (Cornell and Schwertmann, 1996). At temperatures well above 100 ºC no water persists and the transformation can, therefore, only take place via solid state diffusion. This normally implies that hematite, magnetite or maghemite form, depending on the redox conditions. However, an anhydrous analogue of ferrihydrite may also form if the parent ferrihydrite is substituted. If water is present in the system, dissolution and re-precipitation can also occur, and goethite may form. Hence, when iron oxides are studied at elevated temperatures one must distinguish sharply between systems containing water and perfectly dry systems obtained at elevated temperatures (Stanjek and Weidler, 1992).

1.9.3. Factors Affecting the Transformation

Natural transformations in aqueous media and thermal transformations are both to a large extent controlled by external conditions. A few of these are outlined in the following. The rate of transformation and the properties of the end product can be affected. In aqueous suspensions, goethite and hematite form from ferrihydrite via two mutually competitive processes. This means that factors like pH, ionic strength, temperature, and association with foreign elements have a great influence on the composition of the end product (e.g. Torrent and Guzman, 1982; Schwertmann and Taylor, 1989; Schwertmann and Murad, 1983; Cornell et al., 1987; Cornell and Schwertmann, 1996). The formation of hematite is promoted by factors that induce the aggregation and formation of ferrihydrite, such as an increase in the ionic strength or a pH near the point of zero charge (approximately pH 8). The formation of goethite is, on the contrary, favoured by factors that increase the dissolution, e.g. a high or a low pH. Apart from regulating the reaction towards goethite, a high pH also increases the rate of transformation (Schwertmann and Murad, 1983; Ford et al., 1999).

The association with foreign elements can affect the transformation in that the rate typically decreases or that the formation of one specific compound is favoured. Hence, contaminating ions can delay expected transformations simply by stabilizing
the original structure (Torrent and Guzman, 1982; Cornell and Schwertmann, 1996; Jambora and Dutrizac, 1998; Baltpurvins et al., 1997), and a meta-stable phase like ferrihydrite, therefore, can exist for very long periods. Particularly Si has been found to hinder the transformation of ferrihydrite into more well-ordered phases (Schwertmann and Thalmann, 1976; Cornell et al., 1987; Cornell and Schwertmann, 1996; Jambor and Dutrizac, 1998; Glasauer et al., 2000), but several metals have also been found to delay the required structural rearrangement (Cornell and Giovanoli, 1987, 1989; Cornell and Schwertmann, 1996; Giovanoli and Cornell, 1992; Cornell et al., 1992; Ford and Farley, 1994; Sun et al., 1996; Jambor and Dutrizac, 1998; Martínez and McBride, 1998; Sidhu, 1988; Ford et al., 1999). Si in ferrihydrite increases, moreover, the temperature at which the ferrihydrite converts to hematite by hundreds of degrees (Carlson and Schwertmann, 1981; Vempati and Loeppert, 1989; Childs et al., 1993; Zhao et al., 1994; Glasauer et al., 2000, Sørensen and Bender Koch, 2001).

Higher temperatures generally favour the formation of hematite over goethite (Cornell and Giovanoli, 1985; Schwertmann and Taylor, 1989; Cornell and Schwertmann, 1996). Fe can be present in a divalent or a trivalent state in the iron oxides. This means that if the temperature is raised sufficiently; the presence of organic matter can change the identity of the end products if it causes reducing conditions. Hence, minerals containing Fe$^{3+}$ prior to the thermal treatment (e.g. ferrihydrite) can be reduced chemically if the conditions are appropriate. Iron oxide minerals holding Fe$^{2+}$ (e.g. magnetite) will then form instead of hematite (Cornell and Schwertmann, 1996; Campbell et al., 1997). In air, magnetite is readily oxidized to maghemite, and at elevated temperatures the reaction proceeds to hematite (Cornell and Schwertmann, 1996). This means that if the content of organic matter in a heated sample is limited, hematite and maghemite may form from ferrihydrite via magnetite (Sørensen et al., 2000b; Sørensen and Bender Koch, 2001).

Iron oxides exist in many forms in nature. Magnetite (Fe$_3$O$_4$), maghemite (γ-Fe$_2$O$_3$) and hematite (α-Fe$_2$O$_3$) are the most common forms (Cornel and Schwertmann, 1996; Chan and Ellis, 2004). In recent years, the synthesis and utilization of iron oxide Nanomaterial with nanoparticles properties and functions have been widely studied, due to their size in nano-range, high surface area to volume ratios and super paramagnetism (McHenry and Laughlin, 2000; Afkhami, et al., 2010; Pan, et al., 2010). Particularly the easy synthesis, coating or modification and the ability to control or manipulate matter on an atomic scale could provide unparalleled versatility (Boyer, et al., 2010; Dias, et al., 2011). Additionally the iron oxide Nanoparticles with low toxicity, chemical inertness and biocompatibility show a tremendous potential in combination with biotechnology (Huang, et al., 2003; Roco, 2003; Gupta and Gupta, 2005).

The unique properties, which account for the application of iron oxide Nanomaterial as well as the considerable differences among iron oxide bulk materials, (Bystrzejewski, et al., 2009; Selvan, et al., 2010). It is reported that preparation methods and surface coating mediums play a key role in determining the size distribution, morphology, magnetic properties and surface chemistry of non-materials (Jeong, et al., 2007; Machala, et al., 2007). Many researchers have been focusing their efforts on developing chemical and physical methods for the synthesis of Nanoparticles (Dias, et al., 2011). Recently a variety of synthesis approaches have been developed to produce high quality Nanoparticles (Hassanjani, et al., 2011), nano-ovals (Zhong and Cao, 2010), nanobelts (Fan, et al., 2011) and nanorings (Gotić, et al., 2011) or other nanostructures. The three most important published routes for the synthesis of super paramagnetism iron oxide Nanoparticles (SPIONs), summarized by Mahmoudi, et al., (2011). Advances in Nanoparticle synthesis enable the precise control of surface active sites by manufacturing monodisperse and shape controlled iron oxide Nanoparticles (Bautista, et al., 2005; Li and Somorjai, 2010). Generally, non-materials should be stable to avoid aggregation and endow a low deposition rate, in order to assure their reactivity and mobility (Schrick, et al., 2004; Kanel, et al., 2007).
Hematite ($\alpha$-Fe$_2$O$_3$) Nanoparticle is the most thermodynamically stable iron oxide phase and is of particular interest because of its high resistance to corrosion, low processing cost and non-toxicity. This multifunctional material has therefore been investigated extensively for a variety of applications including photo-catalysis, gas sensing, magnetic recording, drug delivery, tissue repair engineering and magnetic resonance imaging, along with its use in lithium-ion batteries, spin electronic devices and pigments. In particular, the magnetic properties of $\alpha$-Fe$_2$O$_3$ have attracted much interest over the past decades.

Goethite ($\alpha$-FeOOH) nanoparticle is one of the most important iron compounds. It has got several technological applications like catalyst, gas sensors, and magnetic recording media. Goethite shows a strong affinity for contaminants such as heavy metals ions and organic pollutants.

1.1. Speciation of Heavy Metal and its Importance.

In a widely understood analysis of the environment there exists a need to determine not only total concentrations of elements in examined samples, but also concentrations of various forms in which these elements could exist. Speciation analysis gives us answers to such questions. Speciation plays a very important role in chemical analysis and in particular concerns about samples connected with environmental analysis (sediments, soils, waters).

The safety of sludge in relation to their metal content is usually assessed by studying the total metal contents. However, this implies that all forms of the metal have the same impact on the environment (Vanni et. al., 1994). To establish the true environmental impact of the sludge it is necessary to know the distribution of the metals in the different metal fractions since the form in which the metal is present determines its behaviour and mobilisation. Therefore, since the availability of a metal depends on the chemical form in which it is present, it has been suggested that the speciation of trace elements be taken into account (Davidson et. al., 1994).
The speciation is a discipline of Analytical Chemistry. The International Union for Pure and Applied Chemistry (IUPAC) has published guidelines or recommendations for the definition of speciation analysis:

- Speciation analysis is the analytical activity of identifying and/or measuring the quantities of one or more individual chemical species in a sample.

- The chemical species are specific forms of an element defined as to isotopic composition, electronic or oxidation state and/or complex or molecular structure.

- The speciation of an element is the distribution of an element amongst defined chemical species in a system.

- In case that it is not possible to determine the concentration of the different individual chemical species that sum up the total concentration of an element in a given matrix, that means it is impossible to determine the speciation, it is a useful practice to do fractionation instead.

- Fractionation is the process of classification of an analyte or a group of analytes from a certain sample according to physical (e.g. size, solubility) or chemical (e.g. bonding, reactivity) properties.

1.11.1. Speciation analysis as a tool to enhance the quality of life

Speciation analysis provides the information necessary to describe the effects of active species which is not available from the results of total trace element determinations. It is therefore predictable, that the concepts based on total trace element determination, such as

- Trace element determination

- Toxicity of elements

- Essentiality of elements

- Metals as environmental pollutants and workplace hazards

- Trace metals in human health and nutrition
Will be replaced gradually by the more meaningful concepts using the information of speciation that means

- Trace element speciation
- Toxicity of element species
- Essentiality of element species
- Element species as environmental pollutants and workplace hazards
- Trace element species in human health and nutrition

The additional information is very useful to direct actions enhancing the quality of products, improving production processes, reducing health risks associated with toxic species, leading to improved understanding of life and better control for the environment.

1.11.2. Problems to be solved by Speciation

The major challenge of speciation analysis is the isolation, separation and quantification of the species leaving the original compound intact, which may be in some kind of equilibrium state with other species present in the sample. While it would be most logical to do the species analysis on-site, in real-time by probing the original “sample” in its natural environment, most of the available tools today require to collect a sample and to analyse it after some sample pre-treatment in the laboratory. It is clear that such practical approach has distinct drawbacks with respect to possible species transformation during analysis. It also requires a high degree of awareness for possible transformations when designing meaningful sample conservation and pre-treatment procedures. A particular difficult issue is the extraction of compounds of interest from a solid sample while preserving the molecular identity of the analyte.

At present, existing methodologies are rather complex and not easy to adapt for routine applications. Further, commercially available instrumentation is rather limited to very few techniques (LC-ICP-MS, GC-MIP-OES). The dissemination of the analytical methods from specialised analytical chemistry laboratories to routine laboratories is not evident. New developments in this area try to fill this gap by
providing commercial tools for specific speciation problems, such as an automated speciation analyser (ASA) for mercury speciation.

The comments on the speciation weakness are clear that, procedures is not in the measurement process itself, but occurs in the steps prior to the determination. More rugged and reliable analytical methods and instrumentation have to be developed. Additionally certified reference materials, inter-comparison studies and proficiency testing are some of the steps that could help in pinpointing weaknesses and problems in the overall analytical process.

1.12. Speciation of Heavy Metals in Solid waste byproduct

The chemical forms of a metal or speciation allows the estimation of heavy metal bonding strength, different natures of the metals, either in free ionic form or complexed by organic matter or incorporated in the mineral fraction of the sample. The pH was decreased due of acid production during the composting process, which accelerated the mobilization of heavy metals; especially those in mobile fractions. The “total” content of elements in the waste has been measured by chemical extraction with HNO$_3$ and HCl. The heavy metal binding forms in the solid phase were analysed by using a sequential extraction method. This method is based on the method developed by Tessier and co-workers (Tessier et al., 1979).

1.13. Scope of the Study:

It is well known from geochemistry that heavy metals are often associated with iron oxides, and that they to a large extent control the cycling of heavy metals in nature (Johnson, 1986; Schwertmann and Taylor, 1989; Singh and Gilkes, 1992; Cornell and Schwertmann, 1996; Stumm and Morgan, 1996; Tessier et al., 1996). The fresh iron oxide precipitate in Ferrox stabilized products can be expected to posses the same properties as the natural compounds and they are, therefore, assumed to limit the leaching of metals.

Iron oxides are present in many inter-convertible forms. The different compounds can be altered by changes in the outer physical or chemical conditions or via natural aging reactions. The iron oxides all provide very well binding properties for heavy metals when the metals either sorb to surfaces or substitute for Fe in the
bulk structure. Consequently, heavy metals are frequently found associated with iron oxides in nature.

The binding of metals and the association with iron oxides depend partly on the properties of the specific metals and partly on the iron oxide compounds. Therefore, the sorption properties, the size, and the valency determine whether a metal ion is retained by sorption or integrated into the iron oxide structure by substitution for iron. Ferrihydrite has a large sorption capacity and it can bind a considerable amount of heavy metals. However, a transformation to more ordered structures in most cases implies segregation and ejection of any integrated metals. In addition, desorption of sorbed elements is initiated as a consequence of the smaller surface area that typically is a consequence of the conversion. This means that the ability to immobilize metals is reduced after the transformation and that the metals, subsequently, release more readily in an aquatic environment.

A characteristic fraction of each element is integrated into stable phases in the products while the remainder is either present in more reactive phases or sorbed to surfaces. The latter and easily available fraction presumably controls the equilibrium concentration of the leachate, if the stabilized product comes into contact with water. Metals integrated into stable solid phases (e.g. iron oxides) will, on the other hand, only release if the host phase dissolves. This is only expected to take place under very extreme conditions (e.g. under strongly reducing or acidic conditions). The binding of Pb, in particular, is controlled by surface sorption whereas the retention of Cd and Cr is caused partly by sorption and partly by stable solid phases – possibly substituted iron oxide phases.

Iron is the fourth most abundant element in the earth’s crust and the second most abundant metal (Schwertmann and Cornell, 1991; Jambor and Dutrizac, 1998). It occurs as Fe (II) and Fe (III) in a diversity of minerals including many types of iron oxides. The iron oxides are in fact oxides, hydroxides or oxihydroxides, but here they are commonly referred as iron oxides. Most of the compounds are thermodynamically stable in natural systems (e.g. goethite, hematite, magnetite) while others can be designated as intermediates only (ferrihydrite, maghemite; Jambor and Dutrizac, 1998). The different iron oxides have all their own characteristics and qualities,
governed by the mineral structure. Iron oxides have been examined in a great number of studies over many years and it is not the scope of this chapter to summarize all the findings.

**Table 1.2. Properties of some iron oxides (Cornell and Schwertmann, 1996)**

<table>
<thead>
<tr>
<th>Iron Oxide</th>
<th>Structural Formula</th>
<th>Surface area (m²/g)</th>
<th>Substitution ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrihydrite</td>
<td>Fe₉Ho₈.4H₂O</td>
<td>100-400</td>
<td>-</td>
</tr>
<tr>
<td>Goethite</td>
<td>α-FeOOH</td>
<td>8-200</td>
<td>Ni(II), Zn(II), Ga(III), Cd(II), Al(II), Cr(III), Mn(III), Co(III)</td>
</tr>
<tr>
<td>Hematite</td>
<td>α-Fe₂O₃</td>
<td>2-90</td>
<td>Al(III), Cr(III), Mn(III), Rh(III), Ga(III), Cu(III), Ge(IV), Sn(IV), Si(IV), Ti(IV)</td>
</tr>
<tr>
<td>Maghemite</td>
<td>γ-Fe₂O₃</td>
<td>8-130</td>
<td>Al(III)</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe₃O₄</td>
<td>4-100</td>
<td>Al(III), Mn(III), Ni(II), Cu(II), Co(II), Zn(II), Ca(II), Ge(IV)</td>
</tr>
</tbody>
</table>

The mineral structure of the iron oxides controls the stability, the surface area, the porosity, the dissolution rate, and the formation and transformation kinetics of each compound (Cornell and Schwertmann, 1996).

Ferrihydrite is found in many systems. It occurs in nature in waters and sediments, in soils, in mine waste and acid mine drainage, and even in meteorites (Cornell and Schwertmann, 1996; Jambor and Dutrizac, 1998). The incidence of ferrihydrite is often underestimated due to difficulties in the specific characterization (Jambor and Dutrizac, 1998). Ferrihydrite is a poorly ordered oxihydroxide, which is typically present as small and aggregated grains (Cornell and Schwertmann, 1996). The Fe⁺³ ions are spread randomly over the structure that moreover holds a great number of vacancies (Cornell and Schwertmann, 1996). This combination has made it hard to agree on a specific crystal structure, and the chemistry of ferrihydrite has,
consequently, never been defined precisely (Jambor and Dutrizac, 1998). One example is given in Table 1.2 but several other formulas have been proposed. Ferrihydrite has a high adsorptive capacity and an extensive specific surface area, and it can, thus, hold back large amounts of foreign ions by sorption. Ions may, in addition, be held back by sorption to “inner surfaces” in the aggregated particles and their release is, thus, additionally limited by diffusion. Substitution of foreign cations in the ferrihydrite structure has never been proven even though a great number of metal-holding co precipitates have been studied (Cornell and Schwertmann, 1996; Jambor and Dutrizac, 1998). Ferrihydrite forms through rapid precipitation and oxidation of aqueous Fe (II), particularly in complex and contaminated systems.

Goethite is frequently found in nature. It is one of the thermodynamically most stable iron oxides at ambient temperatures and it is, for this reason, often found as an end product of many transformations. Goethite can form directly in solution via a nucleation-crystal growth process, e.g. from ferrihydrite via dissolution and re-precipitation (Schwertmann and Cornell, 1991). It is generally formed in competition with hematite in aqueous systems. The resultant ratio between the goethite and the hematite depends on factors like pH, temperature and ionic strength of the solution. Foreign cations like Al, Cd, Co, Cr, Cu, Mn, Ni and Zn can readily replace Fe in the goethite structure by substitution (Lim-Nunez and Gilkes, 1987; Gerth, 1990; Singh and Gilkes, 1992; Cornell and Schwertmann, 1996).

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Maghemite is invariably found in soils, primarily in the tropics and the subtropics. As the word says, maghemite is a combination of magnetite and hematite. It holds the structure of magnetite and the composition of hematite and it can, consequently, be considered a fully oxidized magnetite (Cornell and Schwertmann, 1996). Maghemite can form by heating magnetite in an oxidizing atmosphere. This formation of maghemite from magnetite requires the ejection of 11% Fe, and it holds, therefore, vacancies in the structure (Schwertmann and Cornell, 1991). Maghemite integrates foreign cations like Al, Co, Cu, Cr, Mn, Ni, and Zn (Sidhu et al., 1980; Sidhu, 1988; Schwertmann and Taylor, 1989).

The presence of magnetite in nature is often a result of biological processes, but it can also have a lithogenic origin (Schwertmann and Cornell, 1991). Magnetite has the structure of an inverse spinel and it differs from most other iron oxides in that it contains both Fe$^{+2}$ and Fe$^{+3}$. Magnetite can form directly by oxidative hydrolysis of a Fe$^{+2}$ solution, and heating of Fe$^{+3}$ compounds under strongly reducing conditions can also lead to the formation of magnetite. Magnetite is often non-stoichiometric and both divalent and trivalent cations, such as Al, Cd, Co, Cr, Cu, Ni, Mn and Zn, are integrated with ease (Sidhu et al., 1978, 1980; Sidhu, 1988; Cornell and Giovanoli, 1989; Schwertmann and Cornell, 1991; Cornell and Schwertmann 1996; Gillot et al., 1999).

One of the fascinating features of the iron oxides is the variety of interconversions between the different phases. This means that processes like thermal treatment; weathering and natural aging processes can induce changes in the mineralogy that possibly affect the phase characteristics, including the ability to bind metals. The transformation from one compound to another requires the rearrangement of atoms in the structure. This may take place either via internal solid state rearrangement (like the formation of hematite from ferrihydrite) or from solution via dissolution and re-precipitation (such as the formation of goethite from ferrihydrite (Cornell and Schwertmann, 1996).
1.14. Objectives

In the present study, an attempt has been made to study the transformation reactions of iron oxides and their metal binding properties and also iron oxide was synthesized using hydrothermal method, since most of the iron oxide compound minerals are formed in the nature by hydrothermal process. Iron oxides were used to treat the heavy metal in solid waste incineration by-product, industrial bottom ash. The chemistry of by-products of incineration of solid waste residue is very complex and a great number of mechanisms and phases will present. Speciation of heavy metals will reveal the binding capacity of heavy metals on to the iron oxides. Hence, they can provide information about the long-term stability of the products and also about the future fate of the associated heavy metals.

The primary aim of these efforts has able to reach a stable product that can be land filled safely. Secondly, any possibility for the utilization of stabilized by-product of incineration of solid waste residue has been examined.

This work has, accordingly, been done in order to find four main objectives:

The main objectives of this research work are:

- The synthesis of iron oxide by using hydrothermal method to treat solid waste incineration byproduct residues.

- Special interest on immobilize the heavy metal by using iron oxides as stabilizing agent.

- Different iron oxides were used to treat the heavy metal in solid waste incineration byproduct and to examine, how long the heavy metals remain associated with the iron oxide by heavy metal speciation process.

- Examined the possibility of utilizing the stabilized byproduct of incineration residue.