“INVESTIGATION OF LEACHING CHARACTERISTICS OF ROLLING MILL ASH”

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Submitted By

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CERTIFICATE

I hereby declare the work which is being presented in this report entitled **"INVESTIGATION OF LEACHING CHARACTERISTICS OF ROLLING MILL ASH"** in partial fulfillment of the requirements for the award of degree of Master of Engineering (Thermal Engineering) submitted in Mechanical Engineering Department of Thapar University, Patiala, is a authentic work carried out by me under the supervision of Mr. Satish Kumar and refer other researcher's work which is duly mentioned in the reference section.

To the best of my knowledge, the matter embodied in this thesis has not been submitted to any other university/ institute for award of any degree or diploma.

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ABSTRACT

The ash produced by power stations and Steel Industries containing heavy metals which is hazardous to environment as well as for human health. The Leaching characteristics of ash depend upon the number of parameters such as types of coal, temperature, pH, time. In the present study our main concern is to investigate “The leaching behavior of Steel Rolling Mill Ash Samples” which can contain heavy metals if it is leached out then it can be harmful for the environment, human health and marine life etc. So it is mandatory to prevent the release of heavy metals to environment. For the prevention point of view it is better to release the heavy metal from ash before land filling.

In this thesis different leaching method were used to recover heavy metals from rolling mill ash samples. The results of these methods shown that the TCLP (Toxicity Characteristic Leaching Procedure) -1311 test recovered the more element as compare to the ASTM (American Society of testing material) test Methods. But all these methods are applicable for the extraction of heavy metals from rolling mill ash samples. Three samples of Rolling mill ash were collected from JTL Industries, Boparai Steel Rolling Mill, Laxami Steel Limited (Mandi Gobindgarh) located in Punjab. The Physical characteristics of fly ash determined by Scanning Electron Microscope (SEM) / Energy Dispersive Microscope (EDS) and X-ray Diffraction (XRD). The leaching Samples for the concentration of heavy metal in Leachates & Aqueous Solution analyzed by Atomic Absorption Spectrophotometer (AAS). By the results we can conclude that Lead, Cadmium, Iron as found above the permissible limit in most of the samples.

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Nomenclature

TCLP - Toxicity Characteristic Leaching Procedure

ASTM - American Society of Testing and Materials

pH - Potential of Hydrogen

Mn - Manganese

Zn - Zinc

Fe - Iron

Ca - Calcium

Cd - Cadmium

Co - Cobalt

Ni - Nickel

Cu - Copper

Pb - Lead

Cr - Chromium

Al - Aluminum

FBA - Furnace Bottom Ash

CaO - Calcium Oxide

ppm - Parts Per Million

C - Carbon

O - Oxygen

Si - Selenium

Greek Symbols

μ - Micron

CHAPTER 1 INTRODUCTION

Millions tons of coal are burnt in thermal power plants and the Industries like, Steel, Power, Cement, Sponge Iron, Paper etc. across the world. The quality of coal used varies widely from one country to another. It can vary with the location of coal mine and in some cases the quality of coal can vary between the upper and lower seams in a mine. This variation can be in terms of both the calorific value of the coal and the quantity of unburnt residue produce when it's burnt in a boiler. The quantity of ash generated and its collection at various locations is influenced by the ash content of the raw coal.

Most of the small scale steel re-rolling mills in India are based on pulverized coal (fuel) for heating of raw materials like mild steel scrap, ingot etc. There are around 1200 rolling mills in India out of which around 300 steel re-rolling mills are operating in the state of Punjab where around 4 million tons per annum of steel products are rolled using 2,44,000 MT pulverized coal as fuel worth Rs. 3400 million.

This information has been taken from the published article "Demonstration of heat recovery system in rerolling mills" by Punjab state Council for science and technology.

1.1 TYPES OF COAL USED IN INDUSTRY & THERMAL PLANTS

1.1.1 Coking Coal

When coal is heated in absence of air through the through coherent bead, free from volatile matters called coke. These types of coal having coking properties. These types of coals are used in steel making and metallurgical industries and also used for the manufacturing of hard coke manufacturing.

1.1.2 Semi Coking Coal

When coal heated in the absence of air from coherent bead it’ll not so strong so it cannot be fed directly in the blast furnace. So these types of coals are blended with coking coal in ample proportion to convert in to coke. These types of coals having less coking properties as compare to coking coal. These type of coal used as bendable coal in merchant coke manufacturing and steel making industries.

1.1.3 Non-Coking Coal

These Coals are without coking properties known as Non- Coking Coal. These types of coals are used in thermal power stations. Also used for brick manufacturing, paper, glass, cement, fertilizer industries and for other heating purpose.

1.1.4 Hard Coal

This type of coke is made from coking / semi-coking coal through carbonization process. Hard Coke mostly used in metallurgical industries and also used in the industries those are utilizing furnaces.

1.2 ASH GENERATION

The coal in the as “received” condition is first pulverized in the grinding mills to obtain pulverized coal. During the burning of the coal glassy droplets of ash are produced. Some of these particles impinge on the furnace wall and at high temperature the particles can fuse together to form deposits of slag. Built up of thick layer of ash on a furnace wall increases resistance to heat transfer process thus reducing the thermal efficiency of boiler. In order to minimize the effects of ash built up, these deposits are periodically blown off by soot blowers. The dislodged lumps fall in to the ash hoers at the bottom and this is generally referred to as Furnace Bottom Ash (FBA) or Simply Bottom Ash.

1.3 FLY ASH

Fly ash generally the by- product produced due to the combustion process . It is actually captured from the chimneys of coal fired plants. The ‘fine’ ash fraction is carried upwards with the flue gases and captured by ESP before reaching the atmosphere. This material is known as Pulverized Fuel Ash (PFA) or ‘fly ash’. It is composed mainly of extremely fine, smooth as glass sphere and looks like as cement.

1.4 CLASSIFICATION OF FLY ASH

1.4.1 On the basis of Calcium Oxide (CaO) %

a) Class C (High CaO content >20%, Sub bituminous coal or lignite)

b) Class F (Low CaO < 20% content, Bituminous Coal)

1.4.2 On the basis of pH

a) Slightly alkaline (6.5-7.5)

b) Moderately alkaline (7.5-8.5)

c) Highly alkaline (>8.5)

According to ASTM (American Society of Testing and Materials)) standards, bituminous and sub bituminous coal in India produces class C and class F ash with higher degree of self hardening capacity **(Baba et al. 2004)**

In India, fly ash is generally highly alkaline due to low sulphur content of coal and presence of hydroxides and carbonates of calcium and magnesium.

1.5 PHYSICAL CHARACTERISTICS OF FLY ASH

Generally the fly ash properties can vary from samples to sample. Some of the physical properties are as follow:

1.5.1 Size Distribution

Fly ash is the part of combustion residue with very small particle size. Fly ash carried away by flue gases. It generally consists of fine glassy type particles fall with the range of (2µm – 74µm). According to the Unified Soil Classification System the soil is defined as “fine grained” soil if greater than 50% by weight ash samples pass through the No. 200 sieve (74 µm).

1.5.2 Morphology

Morphology defines the structure of the particle. This study is very useful in understanding the physical properties and leaching behavior of fly ash. The morphological classes are based on shape, opacity etc. Some of the classes of morphology are opaque, nano - opaque, Sphere , rounded , Cenospheres (Hollow Spheres) etc.

1.5.3 Surface Area

Surface area of the particle is also an important parameter because it hold or control the absorption capacity. Generally surface area of particle varies inversely to particle size i.e. larger the surface area smaller the particle size. Particles over 74µm have the irregular shapes these shapes are deviates from spherical to irregular sponge shapes. The large particle mostly contains high carbonaceous content which shows the incomplete combustion.

1.5.4 Density

It’s defines as mass per unit area. Density is also affected by compaction. Fly ash the lower bulk density. When fly ash added to soil it’ll also the decrease the density of soil.

1.6 CHEMICAL PROPERTIES OF FLY ASH

1.6.1 pH

pH value of fly ash depend upon the coal source . Fly ash may be acidic or alkaline Acidic fly ash effects aquatic environment. So its very important point of concern with low pH value of ash should have the higher environmental effects.

1.6.2 Solubility

Generally the fly ash contains insoluble glassy particles. The Solubility of trace element and other component greatly impacted the composition of any leachates. It is very difficult to predict the solubility of content in fly ash. Leachates may greatly vary with the pH value which is the dominant parameter to control the solubility of constituents in the fly ash.

1.6.3 Toxicity

It was observed most of the toxic elements are not detectable in an alkaline solution so far the tracing toxic element solution should be acidic.

1.7 ENVIRONMENT IMPACT OF FLY ASH

1.7.1 Groundwater Contamination

Since coal contains heavy trace elements such as boron, cadmium, chromium, arsenic, barium, beryllium, molybdenum and mercury, thallium, selenium, molybdenum and mercury therefore its ash will continue to contain these trace metals and therefore these trace metals cannot be dumped or stored where rainwater can leach the metals.

1.7.2 Spills of Bulk Storage

Generally fly ash is stored in solar ponds or in land filling in bulk; mostly it is stored in wet form instead of dry so that fugitive dust can be minimized. Generally the solar ponds are very large and stable for long time, but any break of their bund walls will be effect the surrounding area rapid and on a massive scale.

1.7.3 Contaminants

Fly ash contains heavy metals and other substances that are known to be harmful to health above the higher range quantities. Potentially toxic heavy elements in coal include barium, chromium, arsenic, beryllium, cadmium, lead, mercury, lead, mercury, nickel etc. The National Academy of Sciences noted in 2007 that the presence of high contaminant levels in many CCR (coal combustion residue) leachates may create human health and ecological concerns (**Duyusen et al., 2011)**

1.7.4 Exposure Concerns

Crystalline silica and lime when used along with toxic chemicals are exposure to fly ash through inhalation of minute or very fine particle of dust and drinking water may well present health risks. Fine crystalline silica present in fly ash has been linked with lung damage, Another fly ash component of some concern is lime (CaO). This chemical reacts with water (H_2O) to form calcium hydroxide [$Ca(OH)_2$], giving fly ash a pH somewhere between 10 and 12, a medium to strong base. This can also cause lung damage if present in sufficient quantities.

1.8 TRACING ELEMENTS OF FLY ASH & ITS ENVIRONMENTAL, HEALTH EFECTS

1.8.1 Zinc (Zn)

Zn is shiny bluish white metal .Zn is the 23rd most available element available on the earth crust. It’s brittle and crystalline at ambient temperature. But when it is heated at temperature (110°C-150°C) it becomes malleable and ductile. It is literally reactive when it comes in the contact with oxygen and other non – metals. When it react with diluted acids it release Hydrogen. Water is highly contaminated with Zn due the higher concentration of Zn in industrial waste water and combustibles. When the waste sludge is directly dumped in the pond without any precautionary measures it may contaminated the above ground soil and underground water also. Zn also increases the acidity of the river water as well as underground water which is very dangerous for the marine life. The WHO (World health organization) stated a limit of Zn in water is 5mg Zn^{2+}/L. If the Zn is found in the higher range in soil only a limited plants are able to survive. That’s why where the Zn industries are located there is not to much plant diversity. Zn is trace element and very necessary for the human health. When human absorb little quantity of Zn can experience of decreased sense of smell and taste, a loss of appetite or hunger and skin sores. With the shortage of Zn birth defects are occurring. Even the human body can handle with large quantity of Zn. The higher range of Zn also creates the health problem such as skin irritation, anemia, vomiting etc. Very high level of Zn can disturb the protein metabolism cause arteriosclerosis, damage the pancreas and also effect the new born baby health.

1.8.2 Iron (Fe)

It is 10th clement which is mostly available in the universe. Fe is shiny, malleable, ductile and silver grey metal. It is exist in the four from of crystalline. It lusts in moist air but not in dry air Iron dissolve quickly of readily in dilate acids. Fe is chemically Fe is almost essential for the living things i.e. microorganism to humans. Human body can absorb Iron from see food instead plant foods. Iron is important parameter for hemoglobin. Iron is the red color agent in blood that supplies oxygen through the bodies. Iron can cause choriodities (the pigmented vascular layer of eye ball between retina and sclera) retinitis, etc. if it contacts the issues .Excessive inhalation of Iron oxides or dust may create the problem of siderosis (lung disease) which is observed by an X-ray change. Excessive inhalation may also increase the risk of lung cancer. 50% of marine animal death may occur due to exposure to the Iron by any route other inhalation. The deficiency of Iron leads to anemia instead of normal brain functioning depends upon the Iron. Iron may hazardous for the environment special attention for the plant , air and water. Generally plants contain between 200 to 300 ppm Iron (dry mass) when soil contains little iron, or little Iron concentration in water then there is problem persist in to plant growth. Plant growth does not depend only upon the percentage of Iron content in soil, it also depends on the pH values because if pH is higher is leads with iron precipitation. Iron is harmful if its content less than the limit (5-20ppm) at the time of feeding to plants. When Iron exceeds to the higher limit it is stored in liver then bone marrows have higher amount of Iron. When Iron deficit in human bodies leads to anemia, loss of concentration, causes of concentration disorder. The permissible limit of Iron in water is 200 ppm.

1.8.3 Calcium (Ca)

Ca is the most available metal in the earth crust.Ca is softer than aluminum and harder than sodium It's lesser chemically reactive as compare to other alkaline metals when it contact with air make oxide and nitride coating it prevents corrosion. Calcium is present in very large quantity in the human body. It is the main content of teeth as well as for bones. Calcium has several metabolic functions. It is necessary component for Skelton preservation and teeth. Leak of Calcium may leads to Osteoporosis diseases related to bones becomes slowly porous and heal. Calcium phosphide is toxic in nature and very harmful for the aquatic plants.Calcium is important parameter for the water harness. It is mainly stabilize the pH of water due to its buffering quality.

1.8.4 Cadmium (Cd)

Cadmium is a lustrous very malleable ductile and silver which metal It is very soft metal even though to be easily cut with simple Knife. But it tarnish when it explore to air 'It is easily soluble in acids but not is alkaline. Human uptake this element mainly through the sea foods. People those are living in industrial Area or near hazardous waste sites they are mostly suffering from lung disease if higher content of cadmium may occur in body if will accumulate in kidney and them damage the filtering mechanism. Health effect from cadmium are damage the central nervous system, DNA damage Psychological disorder etc. Cadmium may enter to the soil through burning of fossil fuels and waste combustions. Cadmium may cover longer distances when it absorb by sludge. This Cadmium rich sludge or soil may pollute the underground and surface water. Cadmium may absorb by organic matter in soil, when Cadmium in present in soil it is extremely dangerous for growing plans and for animals two those are depending upon or vegetative foods. Cadmium found in very high amount in cows because they are eating multiple plants. Salt water organism is grater resistant to cadmium poisoning as compare to fresh water.

1.8.5 Cobalt (Co)

It is hard, brittle, shiny, silver white element like Fe it can magnetized. This element is highly chemically active making many compounds. As cobalt is highly dispersed in environment human may be take it through air drinking and eating. Cobalt is not freely present in environment but when it’s particles are not found with soil it may take up by plants or animals Cobalt stimulates the production of red cells in blood. By higher concentration of plant various diseases are occur like Vomiting, vision problem, Heart problem, thyroid damage. Some other diseases are also occurring due to ratio above Cobalt isotopes this can cause hair loss, sterility, bleeding etc. Cobalt may settle or the land through wind which contains Cobalt dust and also enters to water when water rain water pass through the rock or soil containing Cobalt. Cobalt can’t be destroyed if it enters to the environment. It may reacts with other elements absorb by water, soil easily.

1.8.6 Nickel (Ni)

It is malleable and ductile metal. It is used for the coating purpose. It is good conductor of electricity and heat. It forms complex compound i.e. generally bluish or green. Nickel slowly dissolves in diluted acids. People may expose with nickel through the drinking water, air inhalation, Skin contact, vegetables those are grown on polluted soil. Plants can accumulate nickel. In small quantity nickel is essential for human but higher quantity may be problematic for human health. Intake of large quantity of nickel may create the various problems such as lungs embolism, heart disorder, asthma, birth defects and respiratory failure. Nickel is released in the atmosphere through power stations and incinerators. It will than settle down on ground then reaction with rainwater. It‘ll contaminate ground water it’ll highly mobile in acidic water. It also impacts the marine life also. Nickel tetra carbonyl is insoluable in water. Generally Ni is soluable in water at temperature (20°C). Nickel chloride is highly soluable in water. Nickel is required nutritional diet for many organisms. But it may be toxic if it persists in larger quantity.

1.8.7 Copper (Cu)

Cu is reddish metal having cubic crystalline structure. It is good conductor of electricity as well as of heat. It has low chemical reactivity. When it contact with moist air it creates a coating on it in green color known as patina. Long term contact with Cu can create the irritation on the nose, eyes and mouth. Excessive concentration of Cu may lead damage to liver and kidney. Cu may travel long distances in surface water. It can’t break down in environment due to that it accumulates in animals and plants when it exists in soil. On rich Cu soil only limited no. of plants can survive. Due to this reason very low greenery persist near the Cu disposing industries. Its serious threat for the production of farmlands.

1.8.8 Lead (Pb)

Lead is a lustrous metal. It is soft, ductile and malleable. It is poor conductor of electricity. Its resistant to corrosion but tarnish when it contacts with the moist air. Pb may have the most harmful effect on human health. The food like Sea food, vegetables, meat, grains, wine etc. contain huge amount of lead. By corroded pipe line of drinking water as well as of supply water pile lead can enter in the ground water. It is mostly happen when the water is acidic in nature. Due to this reason the water treatment plants are required to adjust the pH level of water. By high value of lead uptake may create the several unwanted effects such as Anemia, Blood pressure problem, Miscarriage, Kidney failure, Sperm damage. It is also create the problem among the diminishing of learning ability among the children. It can also effect the nervous system of new born baby by entering through the placenta of mother. Lead may enter in water and soil mostly through the pipe lines. Lead mostly accumulates in soil organism as well as in water organisms. With the interference of lead the functioning of Phytoplankton can disturb. Phytoplankton is very important source of oxygen supply in larger sea animals. Near highways and industrial area higher concentrated lead soil found. This type of soil organism may suffer from the lead poisoning.

1.8.9 Manganese (Mn)

Mn is very hard and brittle metal. It is pinkish grey in appearance. It is easily oxidized but very hard to melt. If it is used in powdered form it is burn in the presence of oxygen. It dissolves in the diluted acids. It act as iron (highly rusted) when it reacts with water.

When manganese presence in higher limits in human body then survival for human life is very difficult.It can effect in the brain and respiratory tract. It can also effect the central nervous system of the human which may cause of permanent disability. Due to shortage of manganese some other effects may occur such as skin problem, birth defects, Neurological symptoms, Blood clotting etc. Manganese compound naturally exists in soil and little particle of Mn found in water. Manganese contents found in air due to industrial pollution.When Mn used as pesticides then it is enter in the soil. Mn is essential for the animals for their metabolism , bone formation. By many laboratory test it is prove the higher side of Mn may poisoning even though also create the tumor among the animals. When pH of soil is low Mn deficiency found in the soil.

1.8.10 Chromium (Cr)

Chromium is lustrous, brittle and hard metal. It is not tarnish in air and gives green chromic oxides when it is heated. It is impermeable with oxygen and protect the metal. Chromium contents are higher in the environment due the industrial applications (Textile, Leather, Chemical Manufacturing etc.) Through the combustion of coal, waste disposal is enter in the soil and through soil it' is enter in ground water. During in presence of water is absorb on sediments become immobile. Cr(iii) naturally persist in vegetables , fruit, grain, meat etc. when food is stored in steel tank then the percentage of chromium is higher. Those people working in steel textile, steel manufacturing industries may have to exposure to Cr(iv). The health problems occur due to Cr(iv) such as Lung cancer, Kidney and Liver damage, Respiratory problem and skin rashes, etc. All these information are summarized in the Table1.1

Table 1.1 Health Effects of Heavy Metals of Fly Ash

Heavy Metals	**Health Effects**
Zinc	Loss of appetite , nausea, Anemia, Respiratory Disorder, Skin Irritation
Iron	Choroiditis , Conjunctivitis , Siderosis
Calcium	Kidney stones, Scierosis of Kidney, Osteoporosis
Cadmium	Diarrhea, Lung Damage, Kidney Damage, Psychological disorder
Cobalt	Lung Effect, Asthma, Pneumonia, Vision problem, Thyroid damage
Nickel	Lung cancer, Larnyx Cancer, lung embolism, Birth defect
Copper	Liver damage, Kidney Damage, Stomachaches, Dizziness
Lead	Miscarriage, Brain damage, Disruption of nervous system, Behavioural disruption
Manganese	Fatness, Skeleton disorder, Birth defects, Neurological Symptoms
Chromium	Respiratory Disorder, Lung Cancer, Kidney damage

CHAPTER 2 LITERATURE REVIEW

Various studies on leaching characteristics on fly ash, Leaching study were carried out by many researchers in the past. Chapter reviews the previous published literatures, which lays foundation and basis for further work in this investigation. This helps to give a better understanding about the topic and also acts as a guideline for this thesis. The major focus of the following study is relates to rheological characteristics, Leaching testing on fly ash and its applications in various areas. This section deals with literature review on leaching testing of Fly Ash. The leaching study on fly ash and their characterization has received attention in recent years because of widespread application in industry and academic interest. The focus of investigations has mostly been on extraction of heavy metals from fly ash by various procedures.

Ahn et al. (2006) were analyzed the municipal incineration Bottom ash for the investigation of leaching properties of Cu and lead and for the stabilization of both elements. They concluded that by the interaction with carbon dioxide with bottom ash both the elements were more stabilized by carbonation reaction the pH quickly dropped and heavy metal depends on pH extraction solution.

Akar et al. (2012) were analyzed the alkaline ash samples . During physical and chemical characterization of fly ash sample they determined the particle size is the most important factor influencing the reaction in leaching of fly ash because fine particle size have large active surface area.Ca was found as the most mobile element while Mn and Fe had the lowest mobility. Concentration of Cr in some fraction exceeded the non-hazardous material limit so it should be carefully monitored. The results showed that CaO dominates in the Yenikoy fly ash sample which directly affects the mobility of trace elements by determining the pH of the leaching medium.

Baba et al. (2004) determined when the low quality lignite is burned, its fly and bottom ashes contain several toxic elements, such as Lead (Pb), Zinc (Zn), Cadmium (Cd), Nickel (Ni) and Cobalt (Co), which can leach out and contaminate soils as well as surface water and groundwater During there study they have clear that HF is the only acid which can dissolve silicate lattices completely. It was also determined that percentages of SiO_2, Al_2O_3, and CaO in fly ashes were generally higher when compared with bottom ashes. During the study they are adopting the three different extraction procedure were adapted EP, TCLP and ASTM. They have concluded that the extraction results were pH dependent. From the testing result they have found that both fly ash and bottom ashes as "toxic waste". From ASTM procedure classifies the ashes as non "toxic wastes" So ASTM Procedure cannot be used to predict the Subsurface contamination.

Baba et al. (2010) were studied about the leaching characteristics of fluidized bed combustion. They were conducted the toxicity test for their study. Their result showed the pH value, temperature, quality of lime stone were the most significant factor for the leaching properties. concentration of toxic element was higher on higher temperature range and when $pH<5$. At $pH=5$ there was no detection of heavy metal presence in fly ash from fluidized bed thermal power plant. Concentration of As and S is most leachates than the heavy metal in ash.

Cetin et al. (2012) were studied about on the leaching behavior of brown coal ash. The main targeted metal in their study was Mg. after 60 min. of leaching 53.4% at 100°C were leached. But at room temperature its leaching rates were very low near about 38.3%.they concluded that at 100°c Mu leaching rates was very high but there is no significant effect in the leaching rates at 150°c.

Cheng et al. (2012) were studied about extraction of aluminum with high acid pressure leaching method of fly ash. They concluded in their study that extraction efficiency of aluminum depends upon increases with the reducing size of coal fly ash. Optimum size for coal fly ash for extraction of aluminum is 74 mm., temperature range180°, experiment timing 4hrs. They prove that pressure acid leaching method for extracting aluminum is better. It also reduces the residue and safe the environment from contamination.

Guven et al. (2011) compared different acid digestion procedures. Four acid digestion procedures were allied to certified samples to offer a proper method for determination of Cr, Cu, Pb and Zn in soils and sediments. EPA's Acid Digestion Procedure 3050B and three low pressure microwave heating programmed modified in this study were tested by using two standard reference materials; Estuarine Sediment-1646a and San Joaquin Soil-2709. Short digestion time, less acid consumption, and high extraction efficiency were noted as the advantages of microwave digestion procedures. According to the results, San Joaquin Soil was efficiently extracted with the second microwave heating programmed named as P2 (84.4% Cr, 96.9%Cu, 102.3% Pb, 90.1% Zn) where Estuarine Sediment gave the most accurate results (99.8% Cr, 103.9% Cu, 97.4% Pb, 96.3% Zn) with the third microwave extraction procedure (P3).

Georgakopoulos et al. (2002) determined trace and major elements in experimental leachates of fly ash from the Ptolemais coal-fired power plant (Northern Greece). Experimental leaching was carried out using one stage and column leaching procedures. These leaching experiments allowed for the characterization of the relative mass leached and the element behavior as function of time. Relative mass leached was generally low. Only Sr and Mo were lost during the first five pore volumes of the leaching. The foremost transformations were relatively fast, implying mainly Ca and S reactions and an important lowering of pH values.

Jiao et al. (2013) were studying on two Australian bituminous coals fly ash. During their testing they had adopted the Japanese Industrial Standard for the leaching test. After testing they concluded that Leaching performance of Arsenic (As) from fly ash is largely depending upon finally pH of leachates. CaO in fly ash generates high pH leachates during leaching. Cao content in parent coal affect the retention of Arsenic in fly ash. Acidic leachates favors the leaching of arsenic from fly ash where as alkaline leachates prevent the leaching of Arsenic.

Lokeshappa et al. (2012) were studied about the heavy metal extraction of ash by different leaching methods. According to their study when ash was directly dump in open and without lived ash pond it is a serious environment threat. They have also concluded the concentration of Arsenic, Chromium was found increase in the old ash dump instead of earliest ash formed in case of class F ash.

Luis et al. (2002) were studied about the leaching characteristics of Greek thermal power plants ash and investigate about the heavy trace element in fly ash. They had used synthetic groundwater leaching procedure. According to their study S, Ca, Br all are most mobile element. The moderate mobility elements i.e. Cd, Cr, Zn etc. can represent a potential hazard to environment. Due to this moderation mobility these elements are highly effect to the groundwater.

Neupane et al. (2013) were testing the acidic and alkaline fly ash samples then concluded that during the leaching test the trace element concentration in (mg/kg) i.e. Al, Ca, Fe, Si are present significantly in fly ash. In acidic fly ash samples trace element As, Co, Cr, Ni, Zn, were significantly richer than the alkaline fly ash The leaching tests performed in this study indicate that the major long-term environmental challenge for the management of coal fly ash is to control the potential leakage of leachates from fly ash disposal facilities into the environment. Once the leachates plume from a fly ash disposal facility reaches groundwater or surface water, it could potentially contaminate drinking water supplies. In particular, the older unlined fly ash disposal facilities pose a greater contamination risk than the lined disposal facilities. Therefore, development of economical and efficient methods for containing the hazardous trace elements within the fly ash disposal facility sites is needed.

Popovic et al. (2009) were studied about the leaching characteristics of coal dump ash by verifying pH values. According to their study the environment threat of most recently deposited fly was too much greater than the older deposited dump coal ash because it had already lost its pollution potential .They have also concluded that rate of extraction of heavy element or metals are directly proportional to the acidity of extraction. Among the other elements chromium is significant elements during leaching analyzing.

Popovic et al. (2011) were studied about major tracing element in fly ash by using the sequential extraction procedure. According to their study they declare that during coal combustion cadmium is distributed in extractable fraction in bottom ash as compare to fly ash. Lead presence also found higher in bottom ash sample as compare to fly ash. According to their study they concluded that cadmium is not present in filtered fly ash. During and after transportation absorbed and ion exchangeable forms are partially leached. Al, Fe, Zn concentration present in absorbed form instead of ion exchangeable form in filtered fly ash. On the other hand Cu, Cr, Mg, Si, K were in both of the fractions forms.

Popovic et al. (2011) studied the leaching characteristics of trace and major elements of six composite samples of filter fly, bottom and dump coal ash from “Obilic” power plant. The samples were subjected to the sequential extraction procedure. Alumina silicates (associated with potassium, nickel, copper, and zinc) and mixed oxides of iron and manganese (associated with magnesium, chromium, and nickel) were dissolved in the third phase of extraction. Cadmium was not extracted from coal filter fly ash samples, while lead was present only in the fifth, environmentally non-significant form. Manganese was not extracted from the first and second, easily extractable phases, of filter fly ash and it cannot pollute the environment, under regular circumstances, during and immediately after transport of the ash to the dump.

Popovic et al. (2013) were studied about trace and major element in filter lignite fly ash. The concentration of Arsenic leached from coal as it was not affected by the enhancement in the ionic strength of surrounding water. Leaching of Si, Cu, Ni, Fe, Mg were highly influenced by ionic strength of water. While other elements like K, Lead, Cadmium, Al, Cr, Mn were not influenced by ionic strength of water when it was contacted with fly ash.

Prasad et al. (2008) were using laboratory leaching test method for analyzing the potential effect of heavy metal in fly ash of a thermal power plant. They were using the pH range. According to their study releasing of heavy metal depends upon the pH of ash. As the pH increased gradually the dissolution of metal from ash surface decreased. For defining the limits of ion migration in groundwater it is mandatory to know about the chemical nature of ash and hydrological characteristic of disposal site.

Palumbo et al. (2005) were studied about the toxicity metals in fly ash by verifying the pH value of solvent (3.7-12.4).They were using their methods for leaching. During their testing they had cleared that little toxicity potential present in fly ash sample when the PH value is at lower side. But when the pH value of leachates is 12.4 then toxicity was eliminated.

Sarenbo et al. (2009) were studied about the reactivity and leaching of wood ash pallets. In their study the release of inorganic contents and reactivity from wood ash pallets dehydrated was investigate at room temperature by using flue gas and hot air. According to them flue gas treated pallets were lower reactive as compared to hot air treated pallets in tests of pH value. Factor that effect the leaching of inorganic contents are particle size test duration temperature, L/S ratio. The release of Ca is suppressed when pH exceeds 12.

Sarode et al. (2010) were studied about the leaching ability of heavy metals from thermal power plant ash. According to their results utilization of fly ash in brick making and cement industries is totally safe from environmental point of view as per their leaching experiment results. According to them water samples having same permissible limits those were located near ash pond as well as near surrounding village.

Singh et al. (2012) were studied about leaching characteristics of fly ash. During their investigation they declared that Ni, Cr having higher leachability in extraction solution as compare to aqueous, buffer solution. Cu leachability was increased with time in aqueous solution and extraction solution. Leachability of Cd increased with time aqueous and buffer solution. By this extraction fluid (pH~7), buffer solution (~10-11). In their investigation they concluded that released of heavy metal in fly ash is totlly depends upon the pH solution and duration of experiment.

Snigdha et al. (2006) were analyzed the fly ash samples for the presence of Cr, Mn, Pb, n, Cu, Ni and Co and detectable levels of all were found in both fly ash and bottom ash. The concentrations of Cr and Zn were highest while Co concentration was less. In fly ash samples Cr and Zn were most abundant elements as compare to bottom ash. Elements having lower mass can be carried and precipitated with the fly ash (Cu, Zn) while elements having higher mass may settle rapidly after combustion and be enriched in bottom ash (Co). Certain studies reveal that for most of the elements present in coal ash, a significant fraction, ranging from 8% in case of nickel to 17% in case of chromium, is able to leach. To leaching of heavy metals is possible to control by providing the ash pond lining . For better management practices increased utilization and proper practice need to be undertaken to minimize the adverse environmental impact.

Steenari et al. (1999) studied chemical characteristics of fly ash samples from combustion of three fuels: coal, peat and wood chips. The ash materials were collected in the 12 MW CFB at Chalmers University of Technology during full load combustion with similar standard combustion parameters. The samples were characterized in terms of chemical composition, mineralogy and leaching behavior. The special characteristics of the mineral matter in each fuel were reflected in the leaching results. Upon reaction with moderate amounts of water secondary mineral phases such as ettringite and calcite, were formed. These compounds were shown to affect the leaching rates for calcium and sulfate as well as the pH of the leachates. The leaching of calcium is significantly reduced when the ash material is hydrated and agglomerated before leaching. This effect is due to the hydration of CaO and the subsequent carbonation of $Ca(OH_2)$ to $CaCO_3$.Manganese, zinc and cadmium were present at higher levels in wood ash than in the higher grade fuel ashes.

Tsiridis et al. (2006) were analyzed the fly ash sample for the toxicity evaluation. According to their study compound contained in fly ash easily be transferred to liquid with the effective leaching procedure. Heavy metals concentration was higher in the TCLP test results. The starting pH value of leaching medium is significantly affected the transfer rate of these elements to the liquid phase . pH of leaching media solution is the most significant factor for the extraction of heavy metal toxicity results of TCLP test was affected by acetic acid when it was used as an extraction medium.

Ugurlu et al. (2004) investigated the leaching behavior of fly ashes disposed in Kemerkoy Power Plant (Turkey) fly-ash-holding pond. The studies were conducted with fly ashes from the electrostatic precipitators (fresh fly ash) and from the fly ash pond (pre-leached fly ash). The fly ashes were alkaline in nature and pH range was between 11.9 to 12.2. The pre-leached fly ash exhibited lower EC values (7,400 µS) than the fresh fly ash (10,300 µS). In contrast to Fe and Pb, the elements such as Cr, Cd, Cu and Co did not leach from the fly ash. The Ca and Mn concentrations decreased with increasing temperature whereas, Na and K concentrations increased. The results showed that the most important effects of fly ash leaching were pH, Na, Ca, K, Fe, Mg, Mn and Pb. The EC values decreased after each extraction. In the both flyash samples Ca, Na, K, Mn, Fe, S and Pb showed maximum leachability, whereas, Cd, Mg, Cu, Cr, Zn and Co showed minimum leachability. The leaching of heavy metals was low for the studied fly ash due to high pH.

Zhang et al. (2008) were studied about the effects of different parameter such as L/S ratio, leaching time, pH etc. on heavy metal extractions from municipal solid waste bottom ash. According to them when the L/S ratio was high then the extraction rate of heavy metal was rapidly decreased due to dilution. Heavy metal leaching result highly effected by leachates pH. Leaching concentration were partly depends upon the absorption reaction.

CHAPTER 3 LEACHING & TESTING PROCEDURE

Leaching is the process of extracting heavy metals from a solid by dissolving these solids in a liquid, either through the industrial process or naturally. Through this process organic and inorganic contaminants are released in solid form into the water phase under the influence of desorption processes, mineral dissolution, as affected by pH range, dissolved organic matter and micro biological activity. The process itself is unique and applicable universally, as any material or heavy metal/tracing element exposed to contact with water will leach out from its surface or its interior depending on the porosity of the material considered. It is necessary to analyze the leaching behavior of the fly ash for the prevention of its effects to the environment as well as for the aquatic environment where ash is majorly disposed off in water.

While transporting, disposal and storage of fly ash, the residues from coal combustion Undergo a process called leaching due to rainfall or by weathering, by which an undesirable components get leached of into ground water, surface water, in soil, creating pollution. These leached out components in higher concentration than drinking water can cause contamination in drinking standards (**Ugurlu et al. 2004)**

Leaching process correlate with many industrial application mainly which are concerned with the chemical processing there is large number of commercial work exists related to leaching such as extraction of sugar from sugar beets by using hot water and separation of metal from ore with the help of acids etc.

3.1 FACTORS EFFECTING LEACHABILITY

3.1.1 Temperature is adjusted to optimize solubility and mass transfer.

3.1.2 Liquid-to-solid contact is essential for the extraction to take place and maximize contact area per unit volume reduces equipment size.

3.1.3 Solvent selection plays an important role in solubility as well as the separation steps that follow leaching. Nearly all leaching equipment employs some type of agitation to aid in mass transfer and to ensure proper mixing.

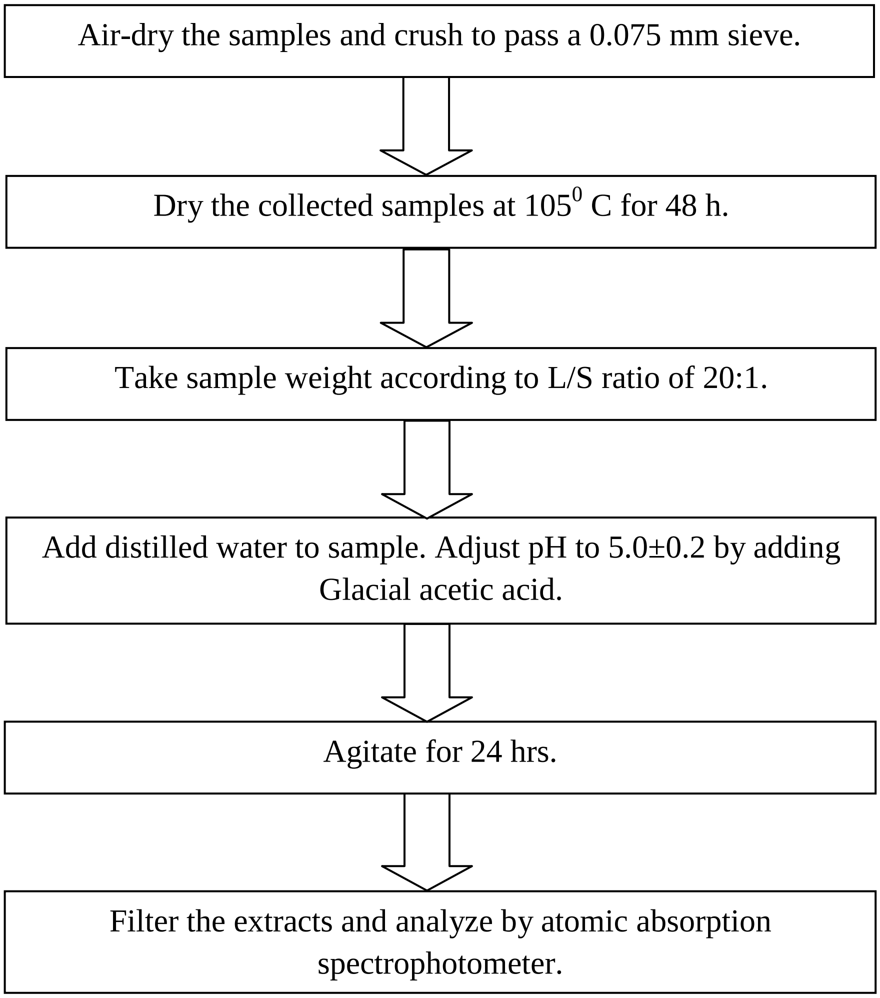
3.2 TOXICITY TESTING (Ugurlu et al., 2004 , Akar et al., 2012)

After the Resource Conservation and Recovery Act (RCRA) of 1976, the US Environmental Protection Agency (US EPA) developed specific criteria for two different fly ash extraction procedures, called EP and Toxicity Characteristic Leaching Procedure (TCLP) (US EPA Method1311). However, independent of the US EPA, the US ASTM (American Society of Testing and Materials) has developed a procedure, Method D-3987, in which distilled water is used as the extracting medium. It should be stated, however, that a number of other procedures have been developed and applied by other regulatory agencies; however, this is beyond the scope of this study. Mostly the three procedures were employed to compare analyses of the bottom and fly ashes of the thermal power plants and to evaluate their effectiveness in predicting subsurface contamination due to leaching.

3.2.1. Extraction Procedure (EP)

The EP method was developed to classify a solid waste as hazardous, based on eight specific organic and inorganic constituents designated in the US Federal Register (1980). According to the pertinent US legislation, a solid waste exhibits the characteristic of ‘EP toxicity’ if the extract from EP or any other approved test of a similar kind contains any of the listed contaminants at a concentration equal to or greater than the specified value. The EP procedure (US EPA (1980)) was replaced by the TCLP for determining the characteristics of toxicity. The EP procedure involves adding an appropriate quantity of water to a representative sample of the residue, then the sample is agitated and pH is adjusted to 5.0 ± 0.2 by adding acetic acid.

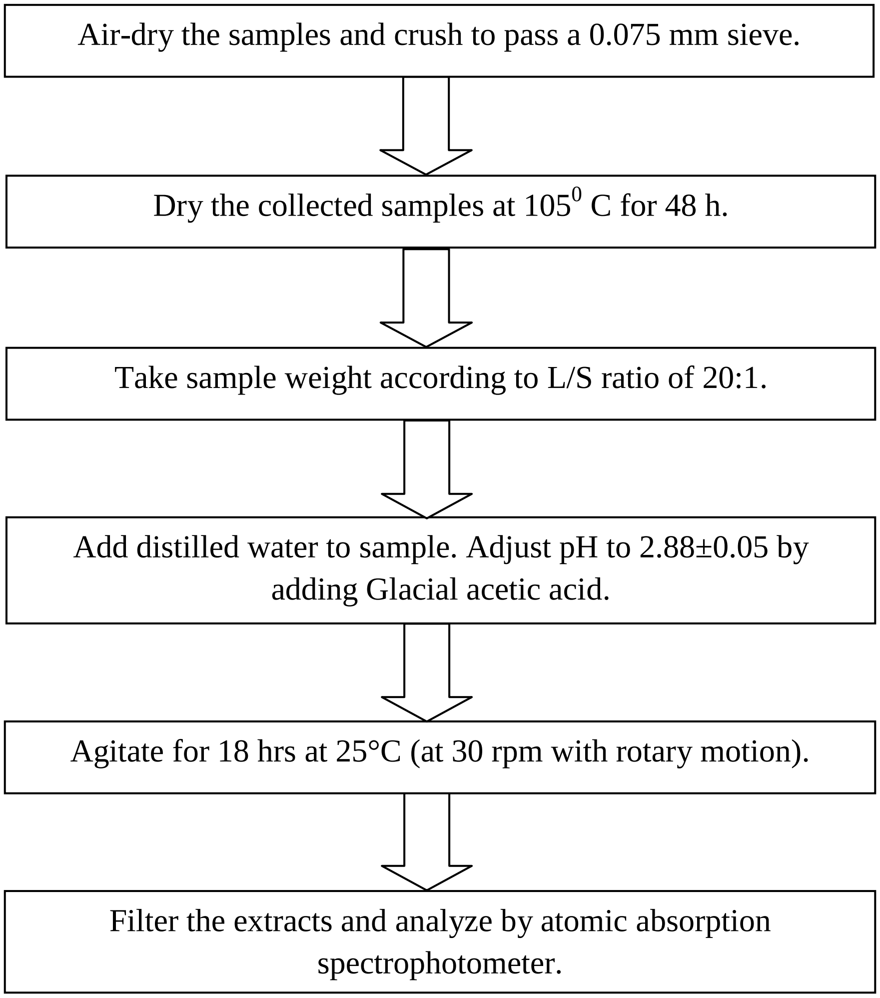
Flow Chart 3.1: EP 3050B) Method



3.2.2. Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP procedure is commonly used by regulatory agencies as a supplement to the EP toxicity testing method for identification and classification of hazardous wastes (US Federal Register, 1980). The test conditions for the TCLP method are somewhat milder than those of EP. The TCLP waste classification is based on a much more extensive list of organic and inorganic compounds and covers a broader range of waste types in comparison with EP. TCLP is more aggressive than EP towards leaching of silver, arsenic, and chromium from the waste tested, while EP is more aggressive towards leaching of barium. Selenium is equally well leached by both TCLP and EP.

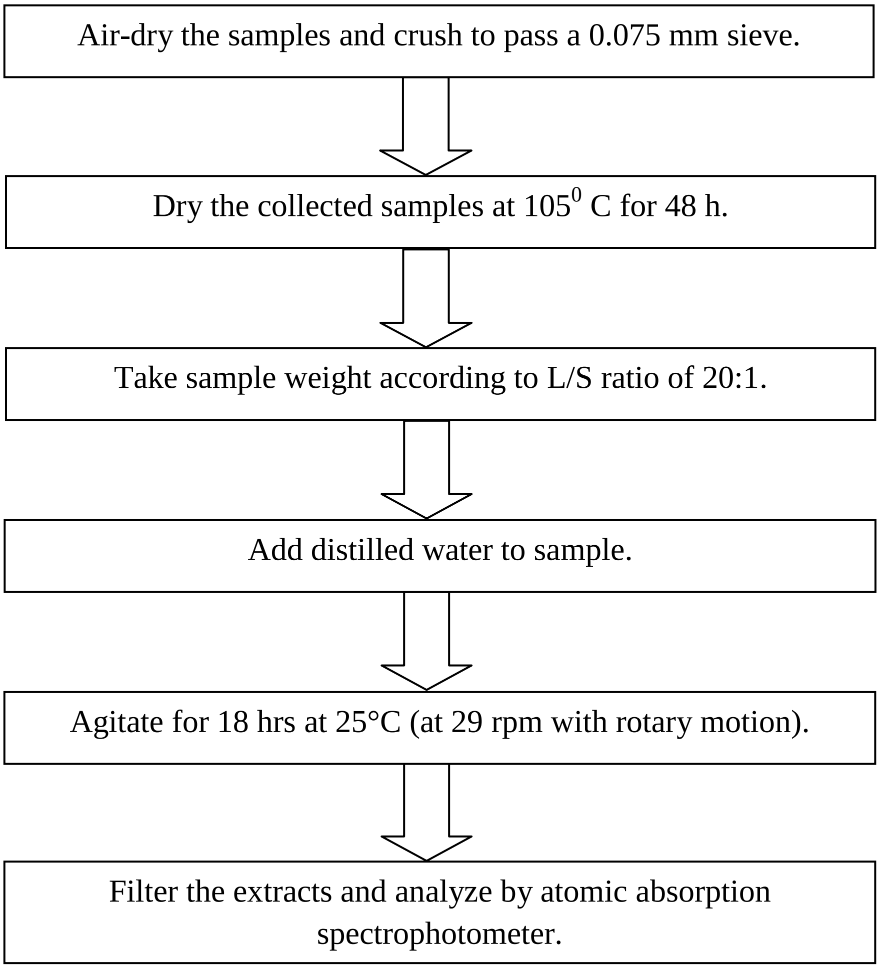
Flow Chart 3.2: TCLP (1311) Method



3.2.3 ASTM (American Society for testing and material)

The ASTM Method D-3987 extraction procedure is based on an extended extraction with distilled water. This method is useful to evaluate the leaching potential of a material being exposed to normal precipitation.

Flow Chart 3.3: ASTM (D-3987) Method



CHAPTER 4 EXTRACTION APPARATUS DESIGN

According to standard procedures most of the standard leaching tests require very low rpm and rotary motion of the sample and leaching solution like Toxicity Characteristic Leaching Procedure (TCLP 1311) , ASTM D-3987. According to standard method the figure of the rotary apparatus is as follow

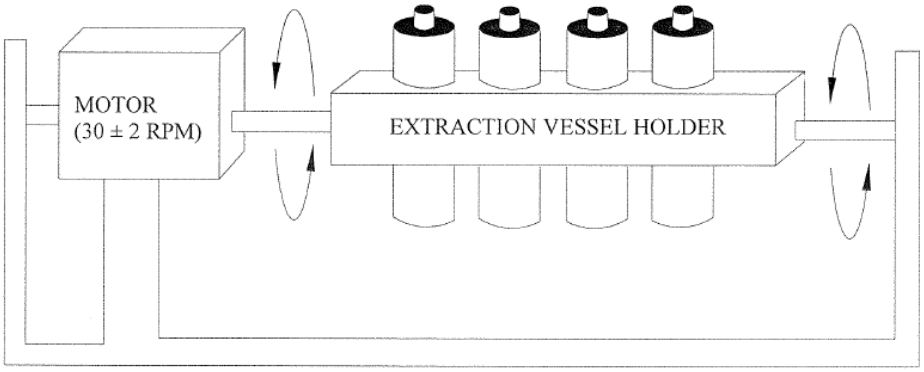


Figure 4.1: Rotary Agitation Apparatus **(Singh et al., 2012)**

After study about the requirement of the TCLP method we had decided for the in house fabrication of TCLP Equipment then afterward we had prepared Schematic drawing for the Rotary Agitation Apparatus. Then the material was procured from market then further work was done for the fabrication of equipment as described in paragraph 4.1.

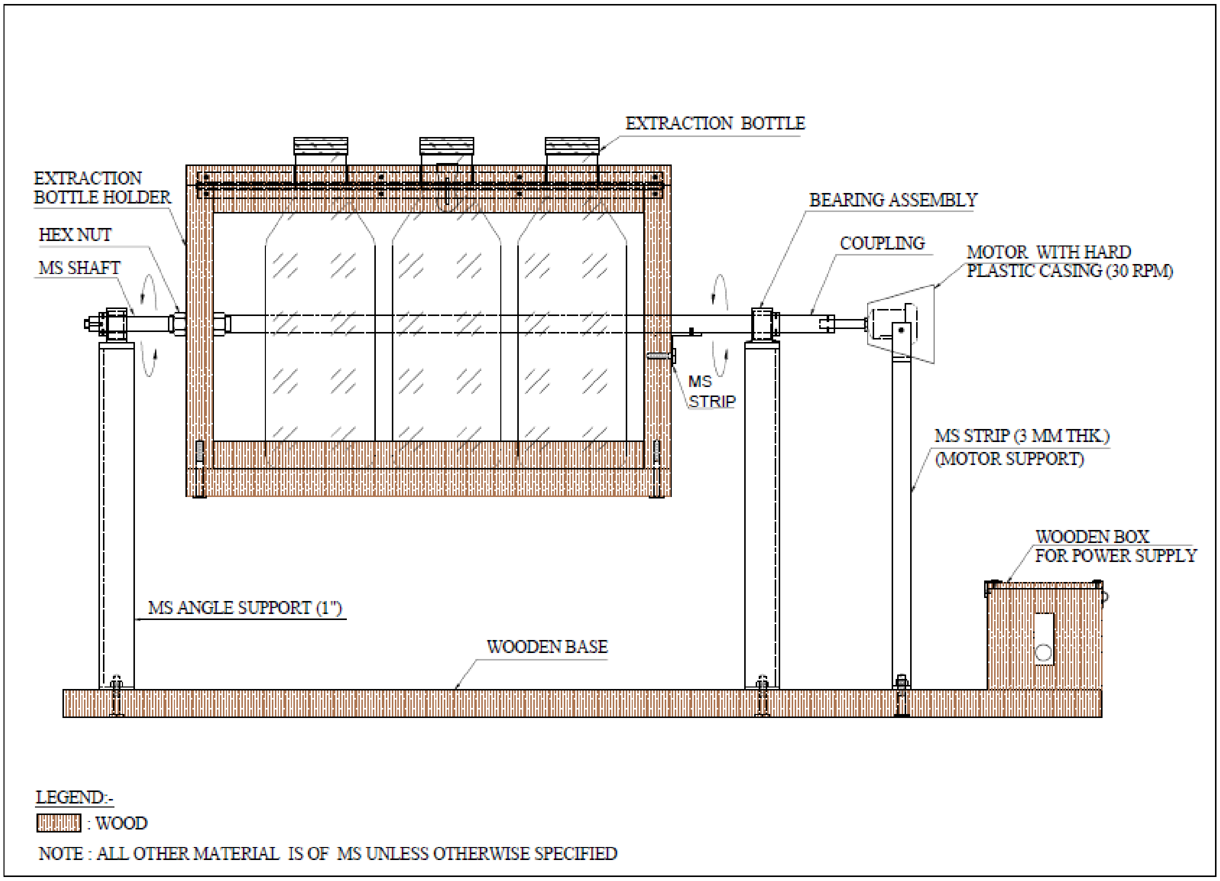


Figure 4.2: Schematic Drawing Of Rotary Extraction Agitation Apparatus

4.1 Steps For The Fabrication of Rotary Agitation Apparatus

4.1.1 Procure all the required items from the market. i.e. wooded board, M.S. shaft, Bearing assembly, Motor 30 rpm, 12V adapter.

4.1.2 Initially Wooden board cut for the base of equipment so that the alignment between the motor shaft and between main shaft which is fixed with the bearing casing should be properly aligned.

4.1.3 Fabricate the Extraction bottle holder (Size: 280mm x 240mm x 160mm) according to the Extraction bottle size.

4.1.4 Fabricate the ms angle support for holding the bearing assembly according to the extraction bottle holder size and bearing assembly size.

4.1.5 Then fabricate the MS strip support for the motor casing support.

4.1.6 Fabricate the Wooden box for the power supply through the adaptor to the motor.

4.1.7 Then using the lathe machine for the turning of ms shaft.

4.1.8 After completion of all the operation assemble all the parts according to the schematic drawing.

4.1.9 Finally the rotary agitation apparatus is ready for the operation.

Figure 4.3: Front View Picture of Rotary Equipment

Figure 4.4: Top View Picture of Rotary Equipment

Figure 4.5: Side View Picture of Rotary Equipment

CHAPTER 5 MATERIAL & METHODS

Three Samples were collected from JTL Industries, Boparai Steel Rolling Mill, Laxami Steel Limited (Mandi Gobindgarh) located in Punjab named as Sample 1, Sample2 , Sample 3 respectively. The samples were dried and sieved (75 µm) before laboratory analysis. and TCLP (1311) , ASTM (D-3987) method was applied for the leaching. To understand the short term leaching effect these methods was carried out.

5.1 TCLP-1311 Method

The test was performed by using liquid to solid ratio 20:1 at pH 2.9 , 10 gm of fly ash was taken in extraction bottle and 200 ml extraction fluid (Glacial Acetic Acid Solution) was added then agitated continuously at 30 rpm for 18 hrs. at 25°C . Then filtrate samples were used for AAS (Atomic Absorption Spectrophotometer)

5.2 ASTM (D-3987) Method

The test was performed by using liquid to solid ratio 20:1, 10 gm of fly ash was taken in extraction bottle & then 200 ml extraction fluid (Deionized Water) was added & agitated continuously at 29 rpm for 18 hrs. at 25°C . Then filtrate samples were used for AAS (Atomic Absorption Spectrophotometer, Make: GBC).

Morphology of fresh and leached fly ash samples was studied using Scanning electron Microscopy (SEM), JEOL-6510 LV, attached with Energy Dispersive Spectroscopy (EDS-Oxford Instrument)

Mineralogy of fly ash samples was studied by X-ray Diffractometer (Make: Phillips)

CHAPTER 6 RESULTS & DISCUSSION

During this study the samples were analyzed by SEM/EDS, XRD, and AAS. Brief information about these testing is as follows

6.1 Scanning Electron Microscope (SEM) / Energy Dispersive Microscope (EDS)

SEM/EDS method is used for the imaging of various types of materials, chemical analysis and surface analysis.SEM equipment is equipped with an EDS. This method provide analytical result of fine or minute particles and also use for the chemical analysis results. By this method we can detect approximate 90 elements with low atomic number.

Figure 6.1: SEM Machine (Make: JEOL)

6.2 XRD (X-ray Diffraction)

During XRD measurement a sample is placed on the Goniometer which rotates gradually during bombard with X-rays during bombard a regular spaced spot of diffraction pattern is produce. The 2D images are taken at different rotations and convert them in to 3D model of density of electron density with the crystal with the use of Fourier transforms (mathematical method) combine with data of chemical for the known sample.

Figure 6.2: X-Ray Diffractometer (Make: PHILIPS)

6.3 Atomic Absorption Spectrophotometer (AAS)

During the AAS the light energy of specific wavelength absorbed by ground state atom after it enters in the excited state. The absorbed amount of light is increased with the number of atoms present in the light path. The right selection of wave length and good source of light allow determining the individual element.

Figure 6.3: Atomic Absorption Spectrophotometer (Make: GBC)

6.4 Result

6.4.1 Morphology

The SEM/EDS Machine (Model: SEM-JSM-6510 LV, Make: JEOL) was used to find the elemental and the morphological composition of rolling mill ash samples. The Scanning Electron Micrograph (SEM) of rolling mill ash samples shows the presence of solid spherical shape particles so called cenospheres. In all the micrographs, the pre leached fly ash spherical shaped particles having smooth surfaces as compared to the post leached ash spherical cenospheres as shown in the Figure 6.4 to 6.9. The EDS spectrum also indicates the presence of high carbon and oxygen content. From the EDS spectrum we can conclude that the elements like Zn, Cu were traced in significant amount in the postleached samples as compared to preleached samples.

6.4.2 Mineralogy

The X-Ray Diffractometer (Make: PHILIPS) was used to determine the predominant phases in the ash samples with the qualitative evaluation. The unknown substances were identified by comparing the pattern of their diffraction data against a database archived in the powder Diffraction file .The diffractogram figure: 6.15 to 6.17 , Pattern table:6.4 to 6.7 shows the highest percentage of quartz among all the samples as compare to other compound. The presence of irregular background and large humps showed the presence of glassy particles in the ash. As compare to all samples results the highest amount of quartz present in the sample 1. On the other side the aluminum and silicon significantly present in the sample 2.

6.4.3 Concentration of Heavy Metals In Leachates & Aqueous Solution

The Atomic Absorption Spectrophotometer (Make: GBC) was used to determine the exact concentration (mg/kg) of heavy metal present in the leachates and (mg/l) in aqueous solution. As per the results (Table: 6.6 and Table 6.7) of AAS the element Fe, Ca is present in the higher amount in all of samples. According to environment point of view both of these elements are not critical but it effect the human health as already described in the Table1.1. Among the other heavy elements those are hazardous for the environment as per figures 6.24 Pb, Cd is present in the greater extent and cadmium is present in least one but very close to the permissible limit. As per comparison of aqueous solution of TCLP samples the Concentration of Pb, Fe above the limits of WHO as described in Table 6.8. By comparing the results of both TCLP leachates samples & ASTM leachates samples as per the figure 6.21- figure 6.23 we can easily say that TCLP-1311 is more effective for the extraction of heavy metals as compare to the ASTM (D-3987) method.

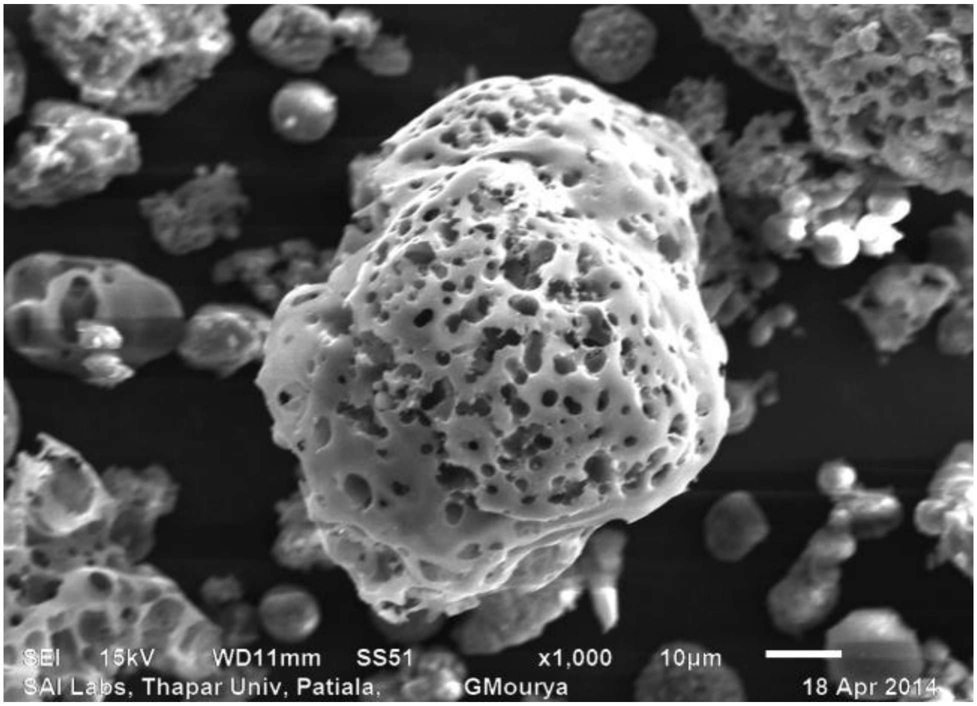


Figure 6.4 SEM of Sample 1 (Before Leaching)

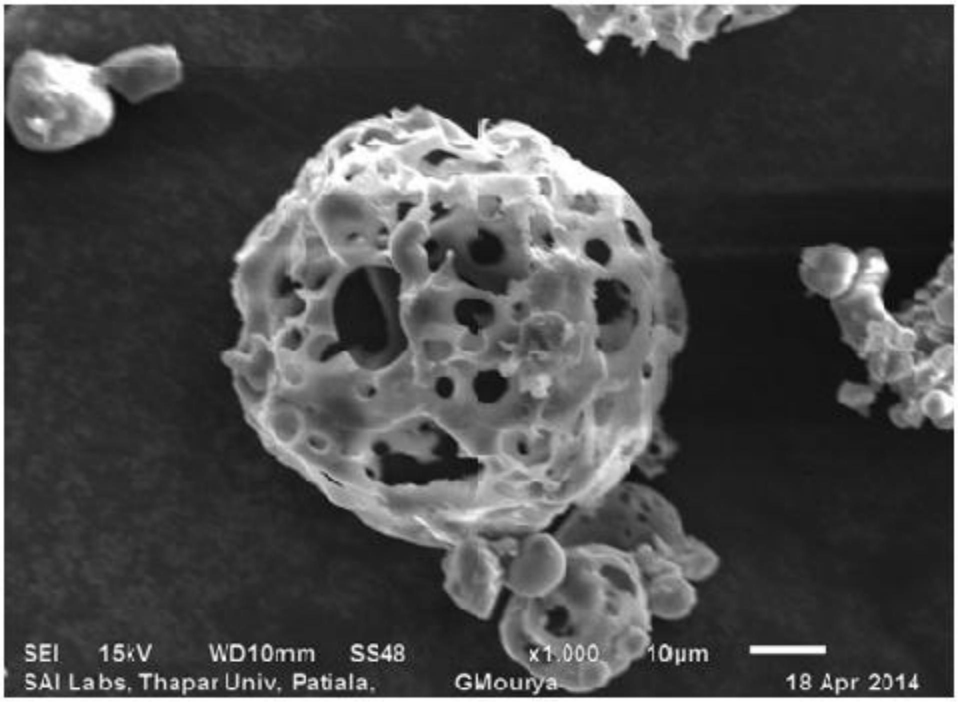


Figure 6.5: SEM of Sample 1 (After Leaching)

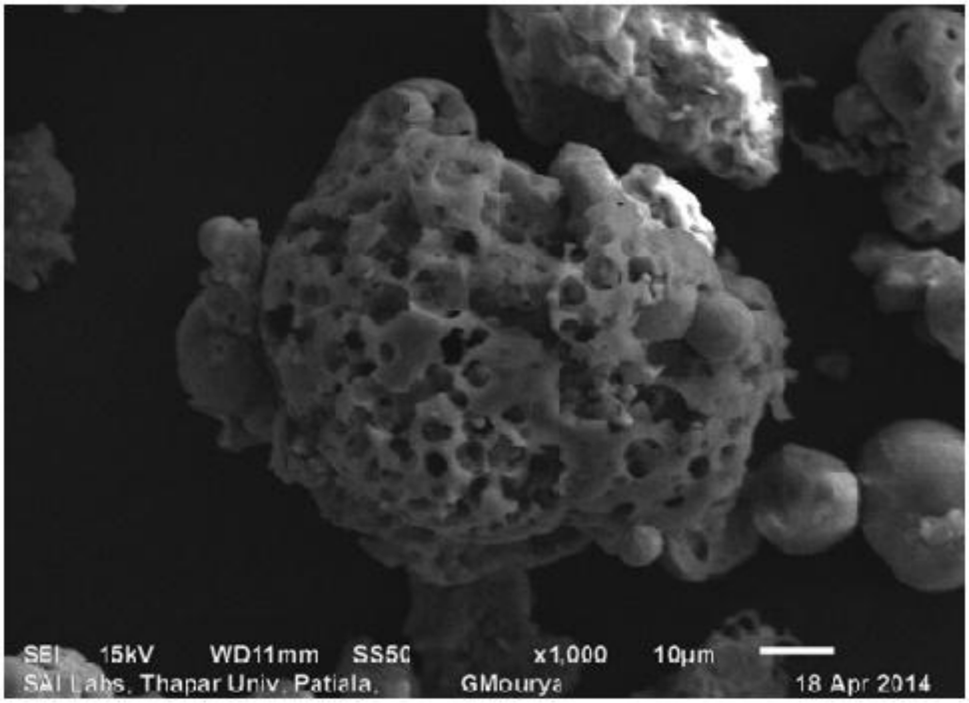


Figure 6.6: SEM of Sample 2 (Before Leaching)

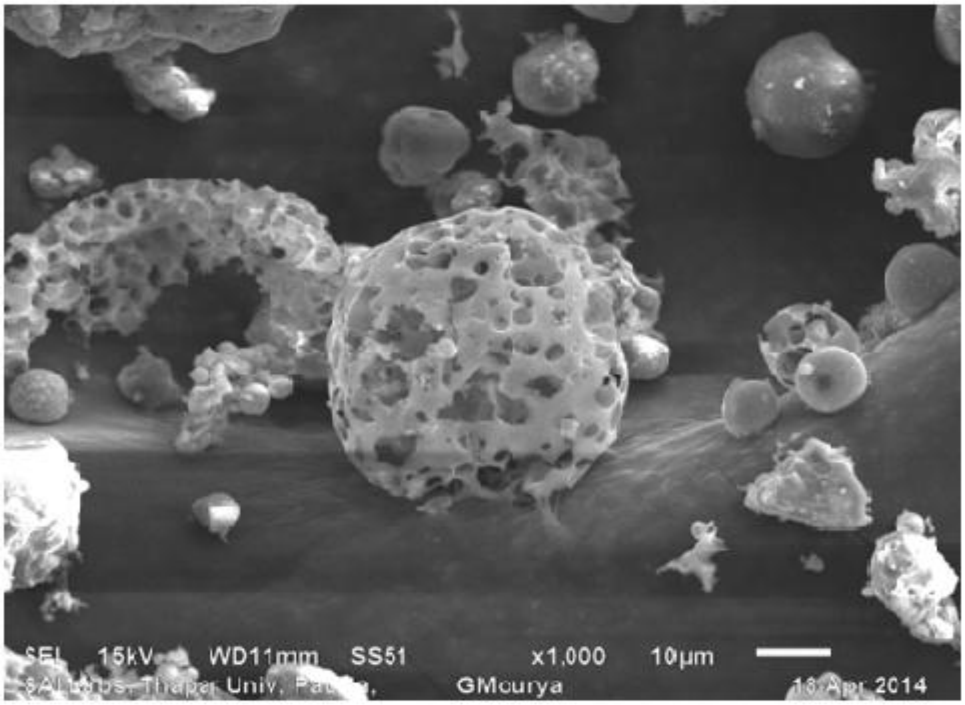


Figure 6.7: SEM of Sample 2 (After Leaching)

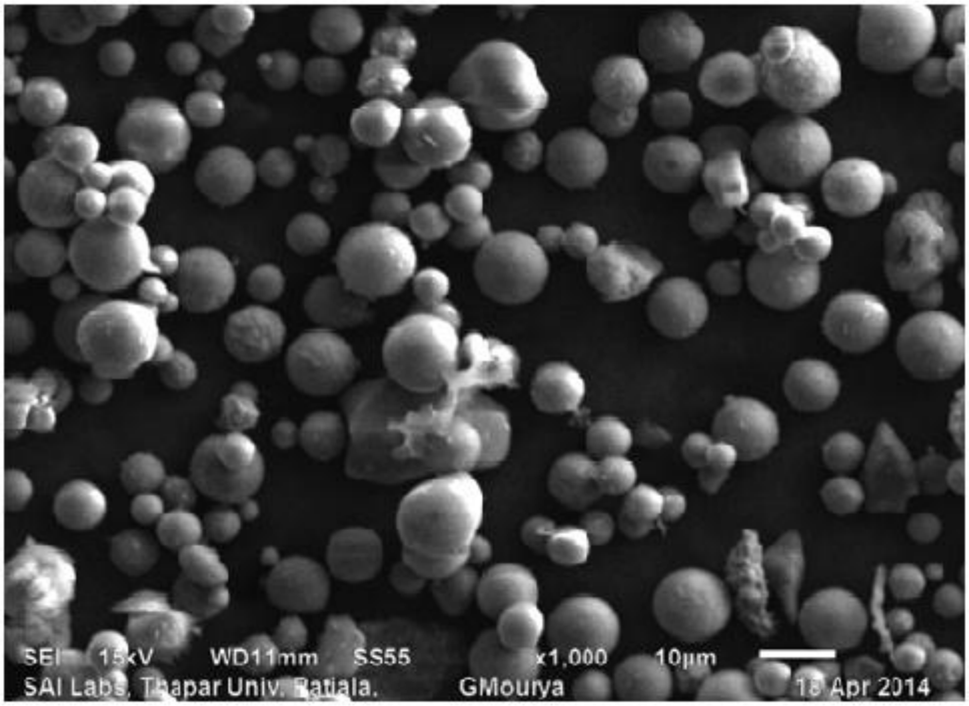


Figure 6.8: SEM of Sample 3 (Before Leaching)

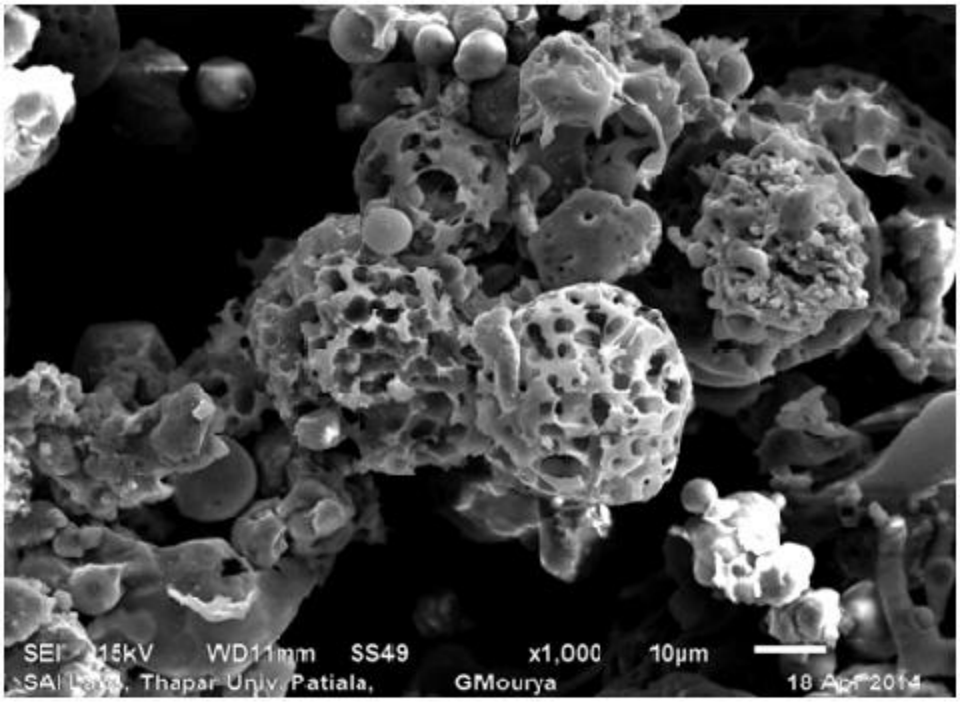


Figure 6.9: SEM of Sample 3 (After Leaching)

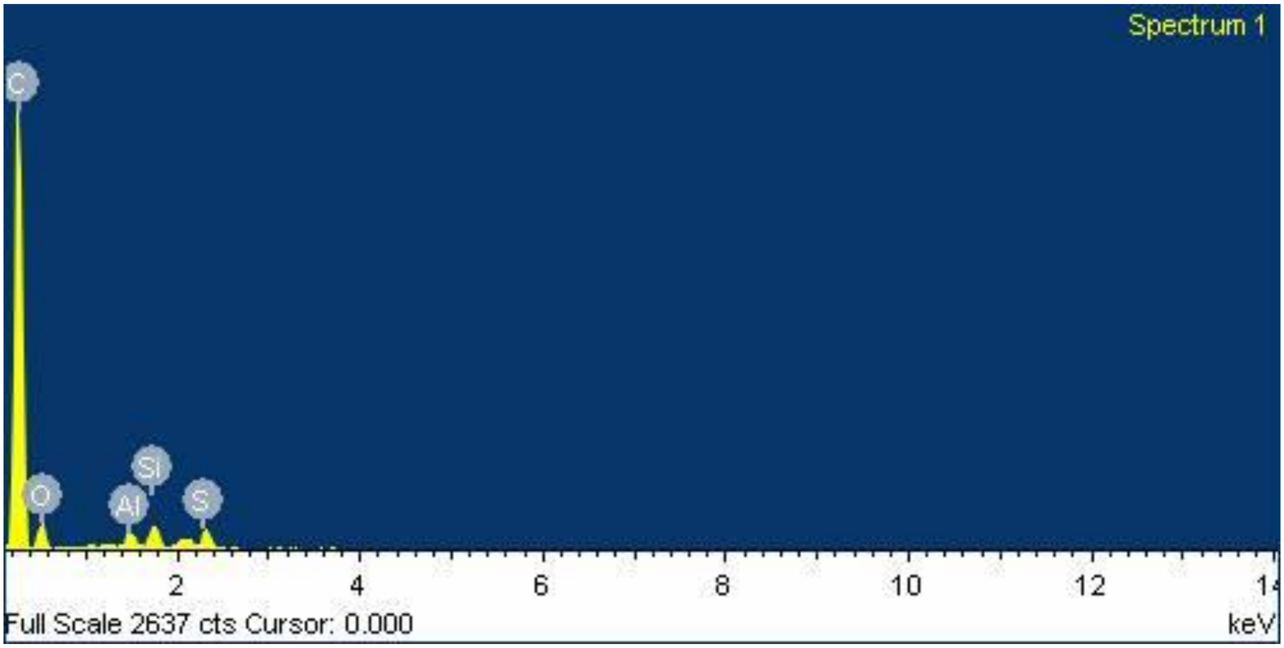


Figure 6.10: EDS Spectrum of Sample 1 (Before Leaching)

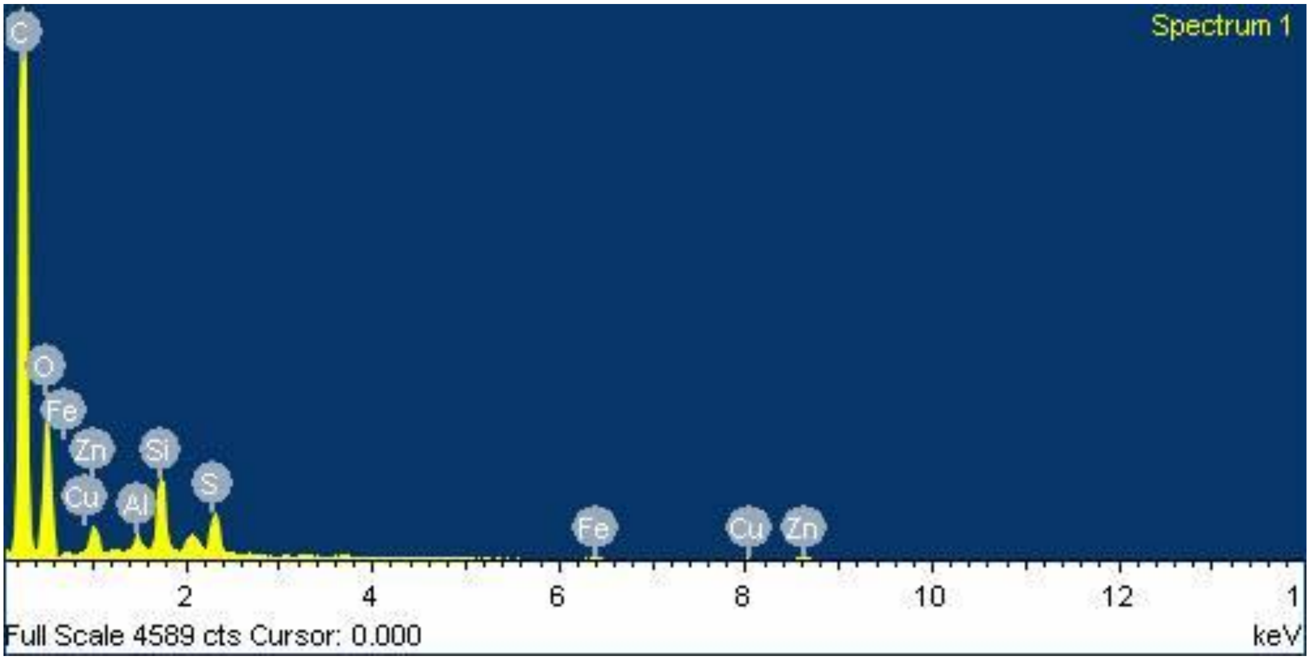


Figure 6.11: EDS Spectrum of Sample 1 (After Leaching)

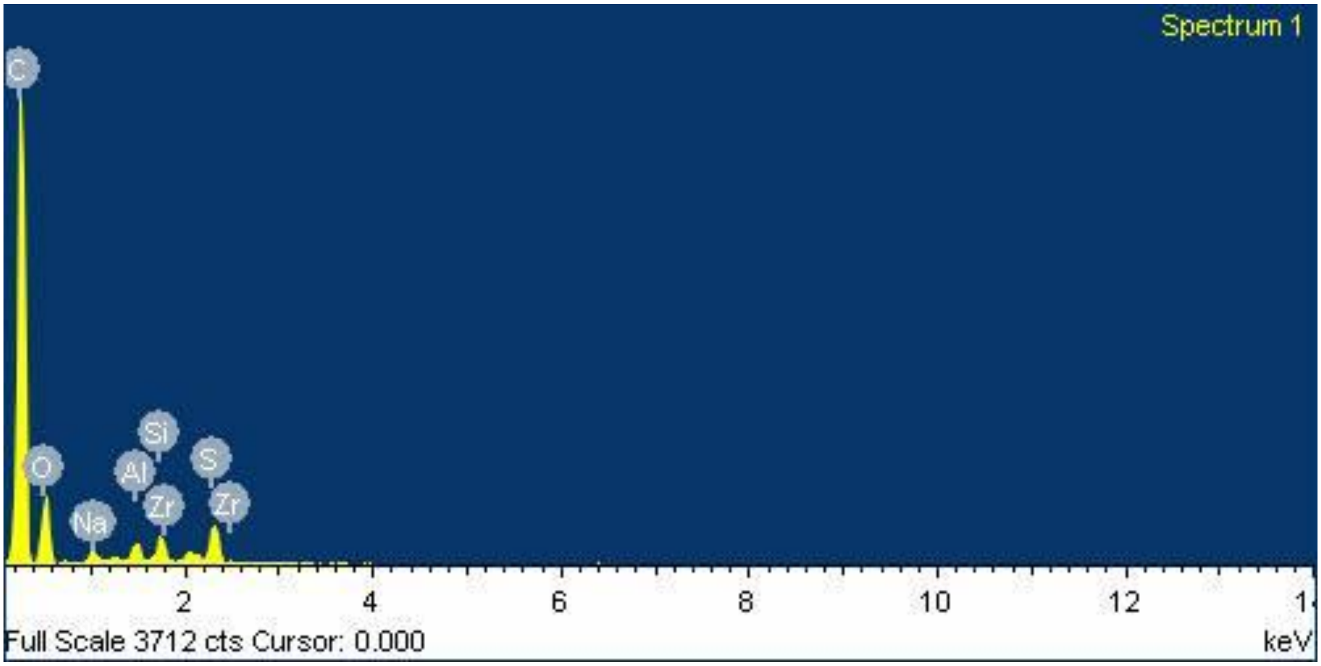


Figure 6.12: EDS Spectrum of Sample 2 (Before Leaching)

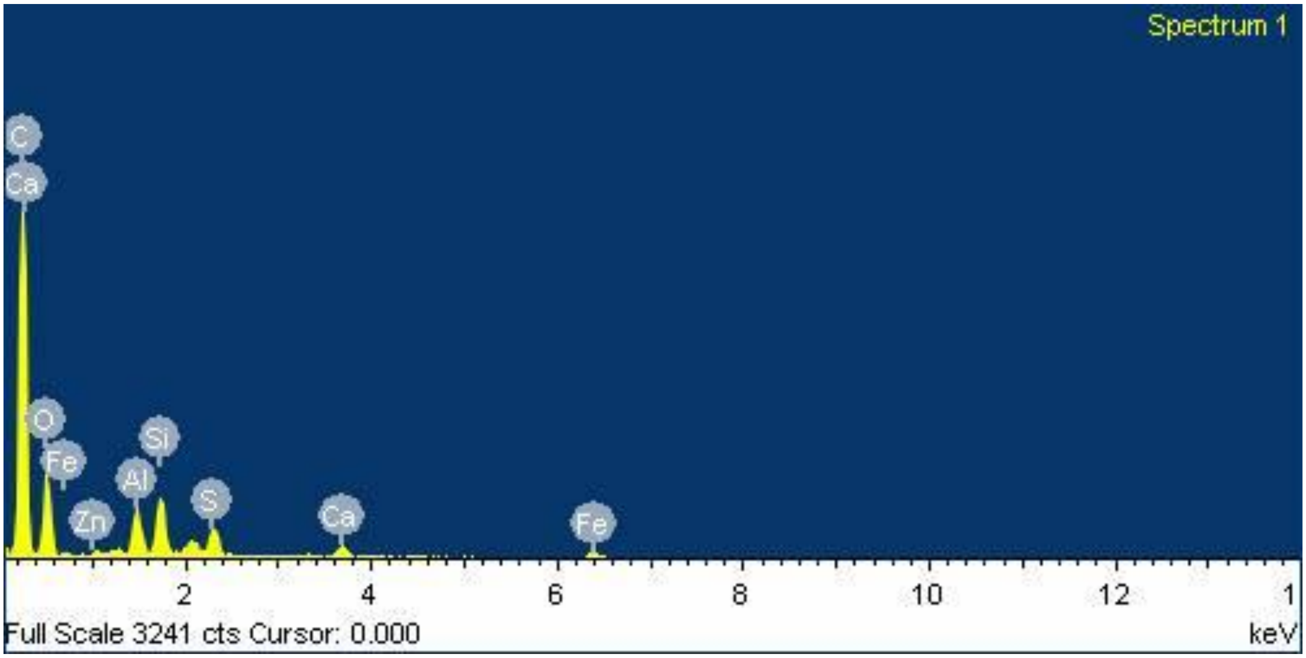


Figure 6.13: EDS Spectrum of Sample 2 (After Leaching)

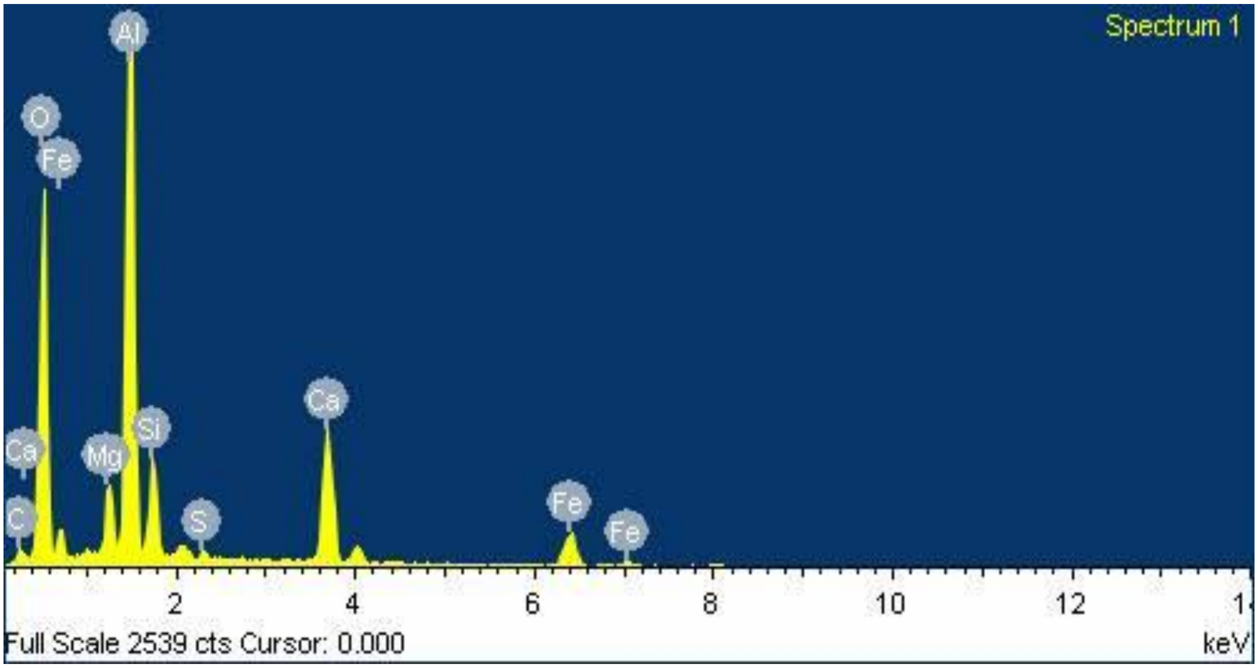


Figure 6.14: EDS Spectrum of Sample 3 (Before Leaching)

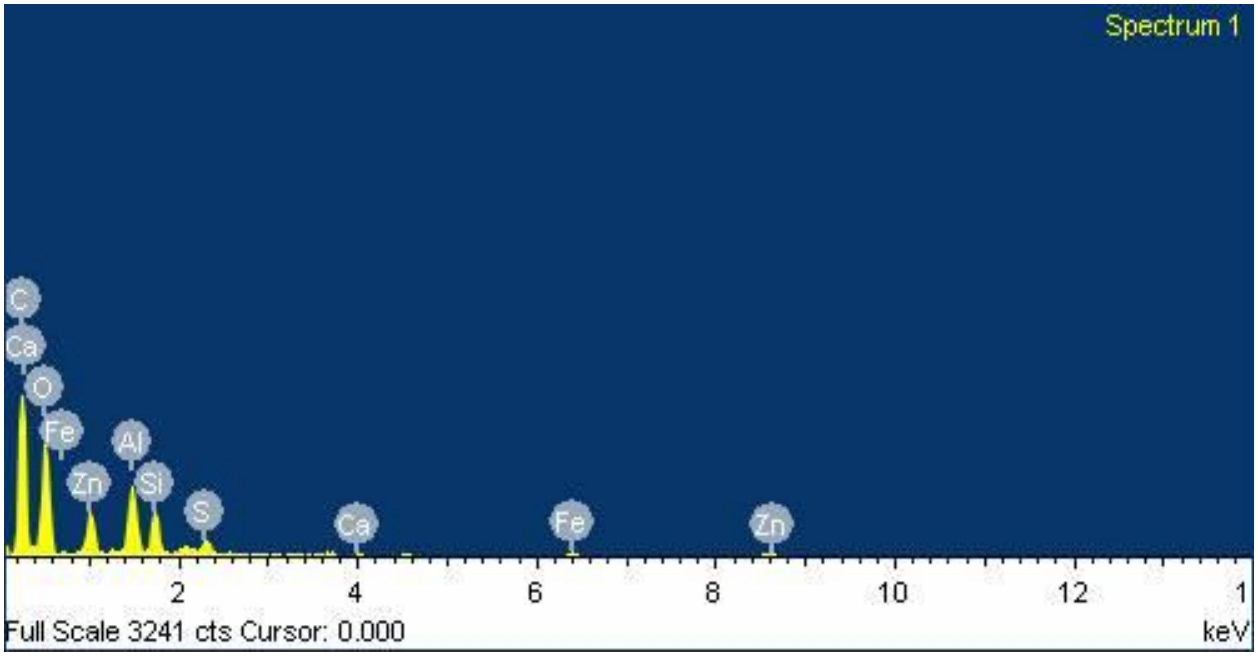


Figure 6.15: EDS Spectrum of Sample 3 (After Leaching)

Table 6.1: Elemental Composition for Spectrum of Three Samples (Before Leaching)

Sample	**1**		**2**		**3**	
Elements	**Weight%**	**Atomic%**	**Weight%**	**Atomic%**	**Weight%**	**Atomic%**
C	81.85	86.59	70.67	77.67	6.02	9.64
O	15.35	12.19	24.97	20.6	54.86	66.01
Mg	-	-	-	-	2.86	2.27
Al	0.66	0.31	0.65	0.32	19.04	13.59
Si	1.05	0.48	0.82	0.38	4.25	2.91
S	1.09	0.43	1.6	0.66	0.4	0.24
Ca	-	-	-	-	7.41	3.56
Fe	-	-	-	-	5.17	1.78
Na	-	-	0.44	0.25	-	-
Zr	-	-	0.86	0.12	-	-
Totals	100	100	100	100	100	100

Table 6.2: Elemental Composition for Spectrum of Three Samples (After Leaching)

Sample	**1**		**2**		**3**	
Element	**Weight%**	**Atomic%**	**Weight%**	**Atomic%**	**Weight%**	**Atomic%**
C	63.71	71.54	63.8	72.35	48.82	58.49
O	31.61	26.65	29.04	24.72	41.64	37.45
Al	0.34	0.17	1.63	0.82	3.47	1.85
Si	1.81	0.87	2.05	0.99	2.13	1.09
S	1.15	0.49	1.19	0.51	0.77	0.34
Fe	0.22	0.05	1.04	0.25	0.94	0.24
Cu	0.3	0.06	-	-	-	-
Zn	0.86	0.18	0.55	0.12	1.99	0.44
Ca	-	-	0.7	0.24	0.24	0.09
Totals	100	100	100	100	100	100

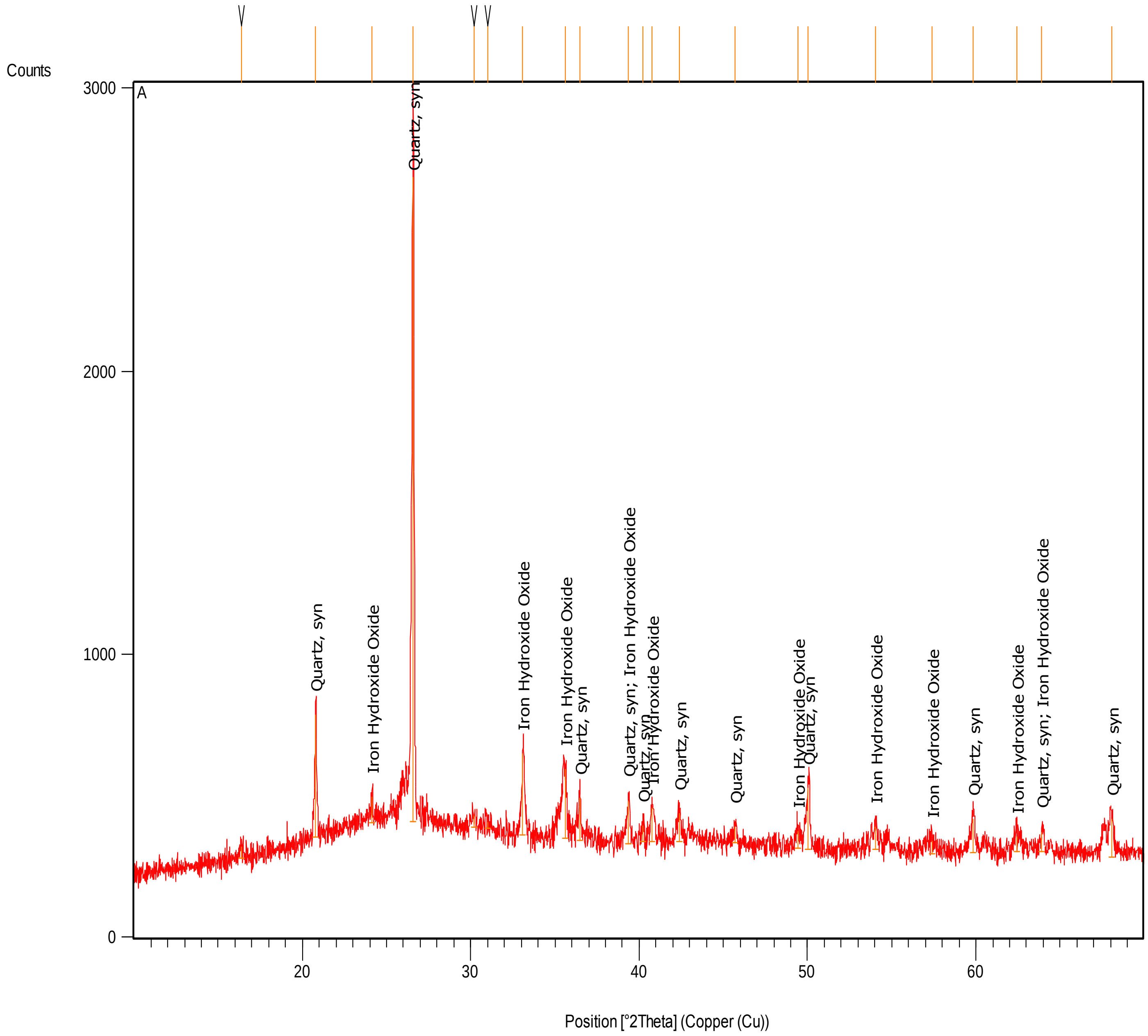


Figure 6.16: X-ray Diffractogram of Sample 1

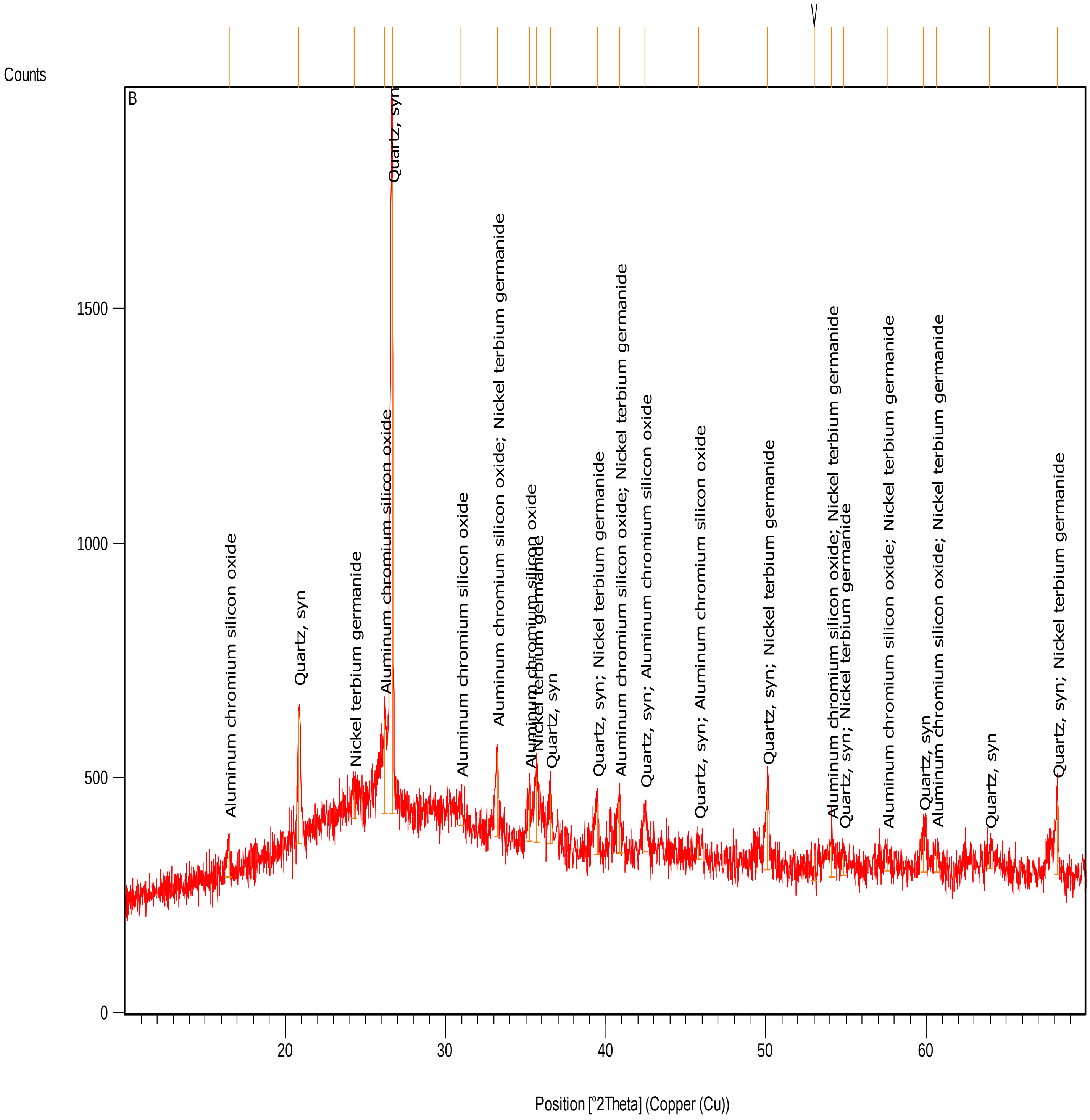


Figure 6.17: X-ray Diffractogram of Sample 2

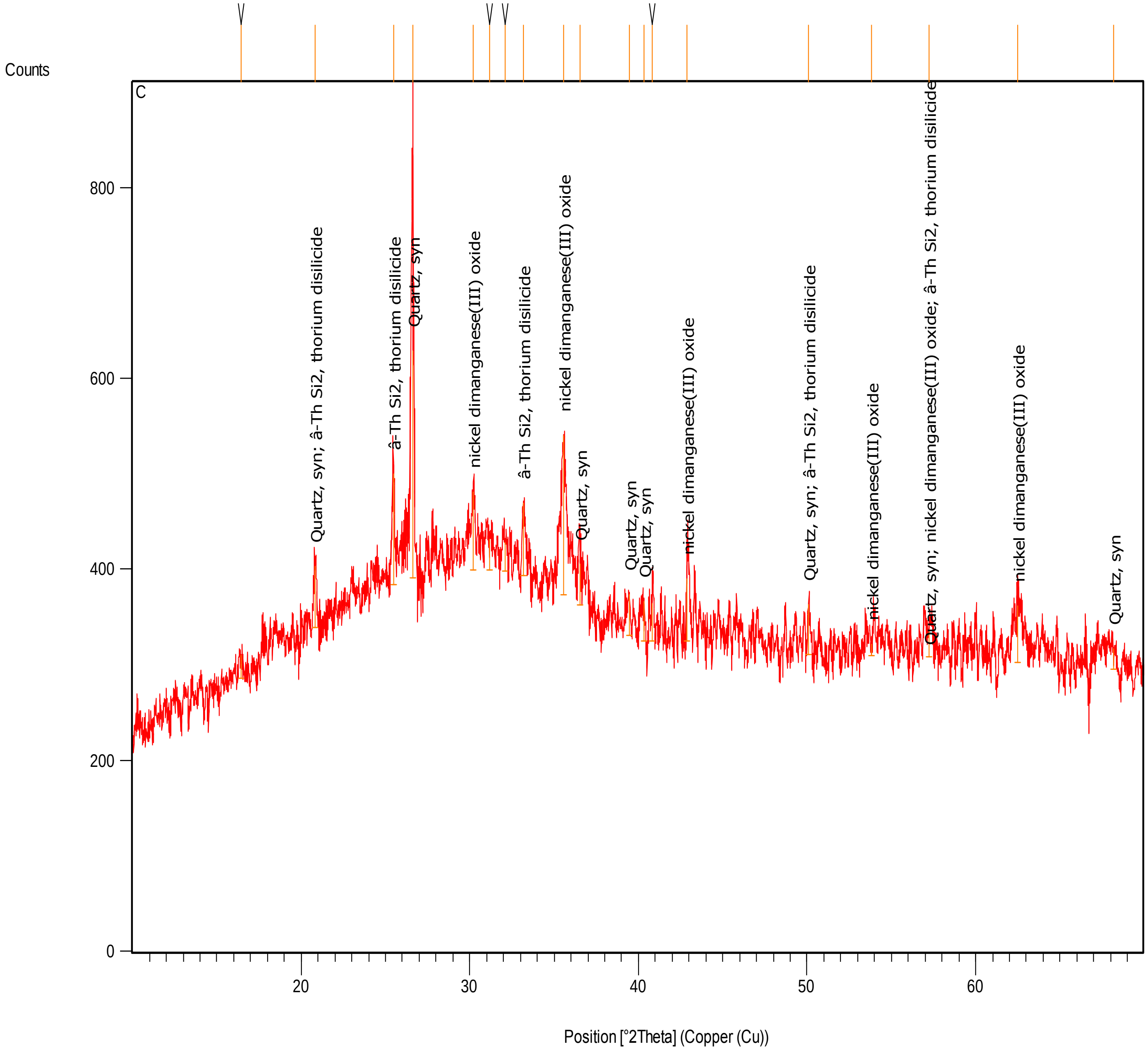


Figure 6.18: X-ray Diffractogram of Sample 3

Table 6.3: XRD Pattern List of Sample 1

Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula	Semi Quant [%]
01-083-0539	66	Quartz, syn	-0.017	0.987	SiO_2	87
01-076-0182	47	Iron Hydroxide Oxide	-0.053	0.129	$Fe_{1.833}(OH)_{0.5}O_{2.5}$	13

Table 6.4: XRD Pattern List of Sample 2

Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula	Semi Quant [%]
01-085-0797	55	Quartz, syn	0.009	1	SiO_2	62
01-074-4147	29	Aluminum chromium silicon oxide	0.083	0.115	$(Al_{1.52}Cr_{0.48})Al_{2.56}Si_{1.44}O_{9.87}$	35
01-073-8569	14	Nickel terbium germanide	0.034	0.093	$NiTbGe$	3

Table 6.5: XRD Pattern List of Sample 3

Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula	Semi Quant [%]
01-085-0798	38	Quartz, syn	-0.014	1.007	SiO_2	76
01-070-9039	27	nickel dimanganese(III) oxide	0.294	0.268	$NiMn_2O_4$	21
01-074-0889	13	â-$ThSi_2$, thorium disilicide	-0.288	0.202	$ThSi_2$	3

Table 6.6: Concentration of Heavy Metals in TCLP Leachates Samples (mg/kg)

Parameters	TCLP Samples			Waste acceptance criteria, mg/kg (Akar et al., 2012)
	1	2	3	
Fe	2869	2920.8	2879	
Ca	1534	1680	1634.53	
Zn	28.63	35.28	26.34	50
Cd	2.52	2.46	1.98	1
Ni	11.59	11.8	10.6	10
Cu	13.63	10.32	9.76	50
Pb	21	19.65	21.8	10
Mn	26	32.4	24.6	
Cr	11.37	12	9.62	10

Table 6.7: Concentration of Heavy Metals in ASTM Leachates Samples (mg/kg)

Parameters	ASTM Samples (mg/kg)			Waste acceptance criteria, mg/kg (Akar et al., 2012)
	1	2	3	
Fe	2748	2838	2714.9	
Ca	1466	1522.28	1535.96	
Zn	26.91	33.73	24.76	50
Cd	2.02	2.12	1.62	1
Ni	11.08	10.81	10.13	10
Cu	13.03	9.49	9.17	50
Pb	18	16.9	19.95	10
Mn	22.8	27.86	23.12	
Cr	9.87	11.04	9.02	10

Table 6.8: Concentration of Heavy Metals in TCLP Aqueous Solution Samples (mg/l)

Element (mg/l)	**TCLP Sample 1**	**TCLP Sample 2**	**TCLP Sample 3**	**WHO Limits for Drinking Water (mg/l) (Sarode et al. , 2010)**
Zn	2.3	1.92	2.72	3
Cd	0.18	0.31	0.02	0
Ni	0.08	0.05	0.01	0.02
Cu	0.32	0.28	0.19	2
Pb	0.59	0.42	0.38	0.01
Mn	0.04	0.07	0.65	0.1
Fe	28.42	24.28	32.6	0.3

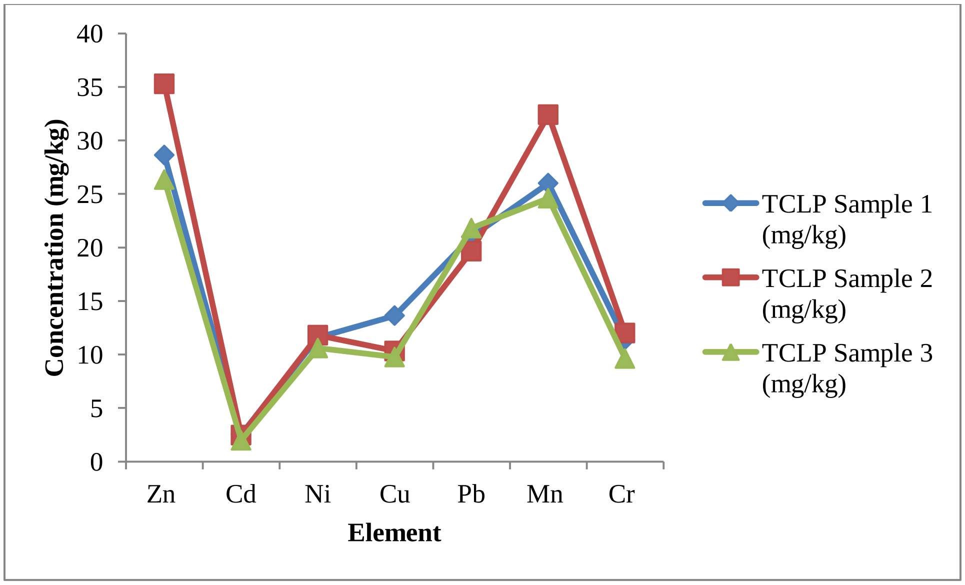


Figure 6.19: Concentration of Heavy in TCLP Samples

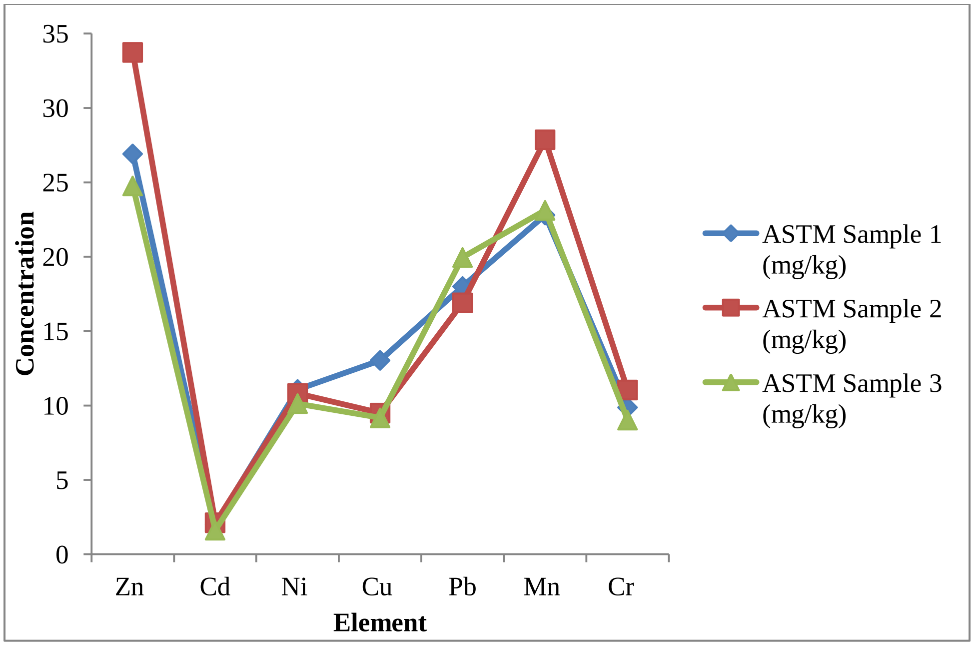


Figure 6.20: Concentration of Heavy in ASTM Samples

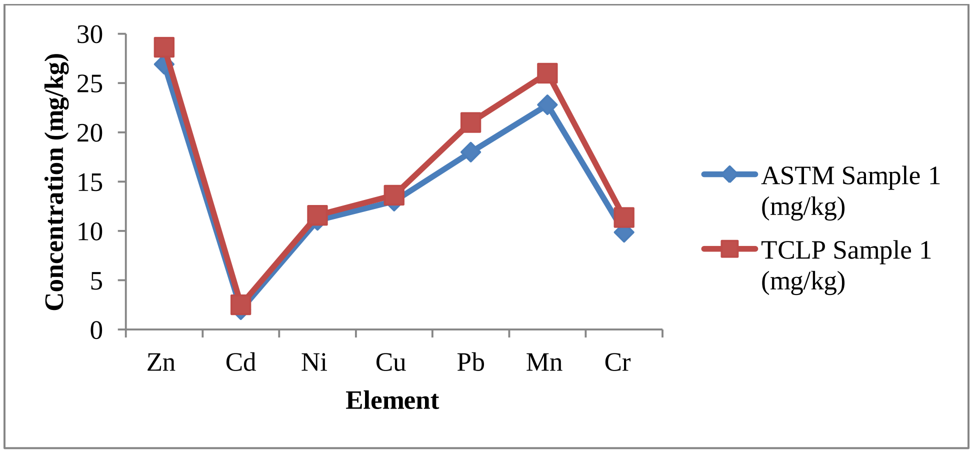


Figure 6.21: Comparison of Heavy Metals in ASTM and TCLP Sample 1

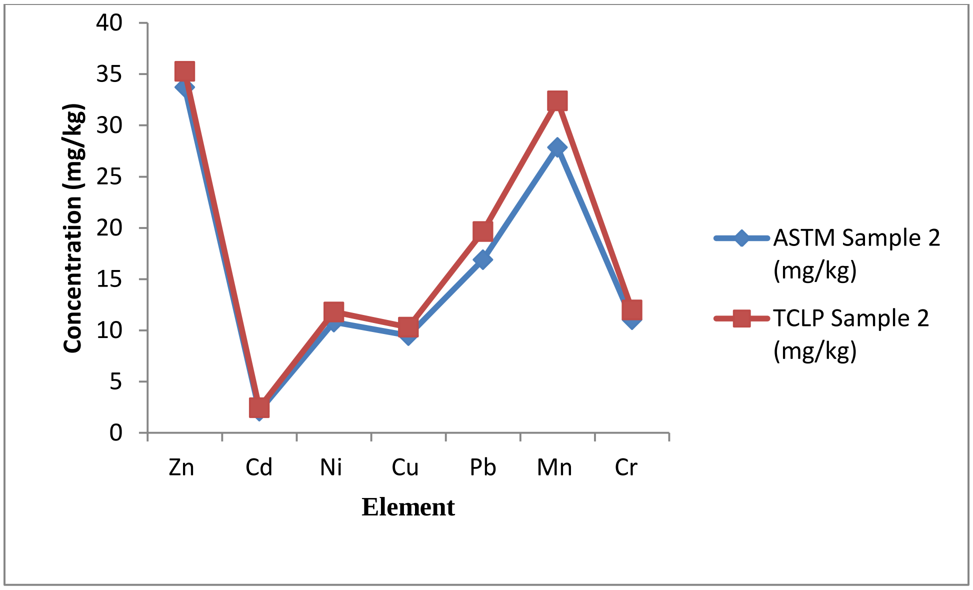


Figure 6.22: Comparison of Heavy Metals in ASTM and TCLP Sample 2

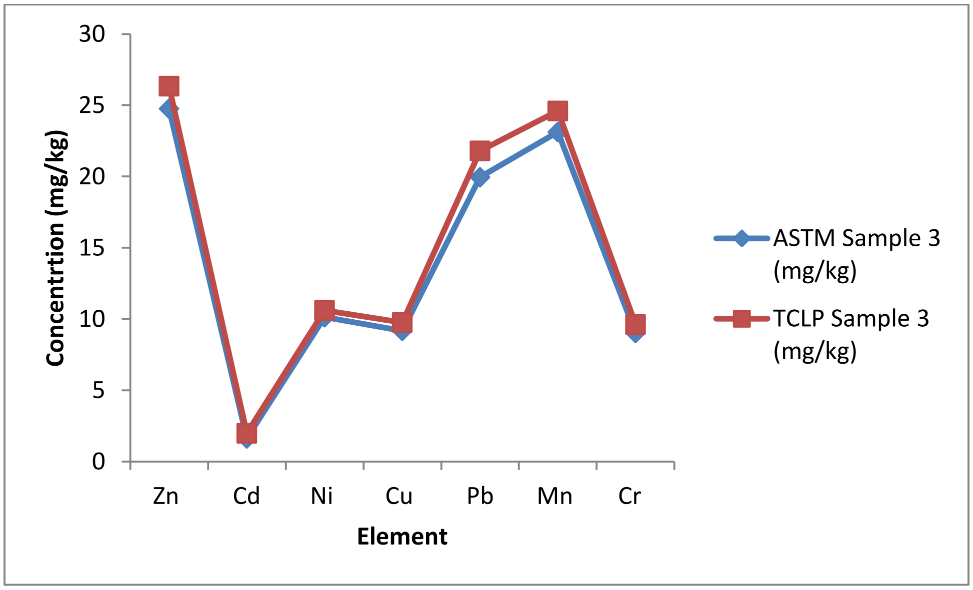


Figure 6.23: Comparison of Heavy Metals in ASTM and TCLP Sample 3

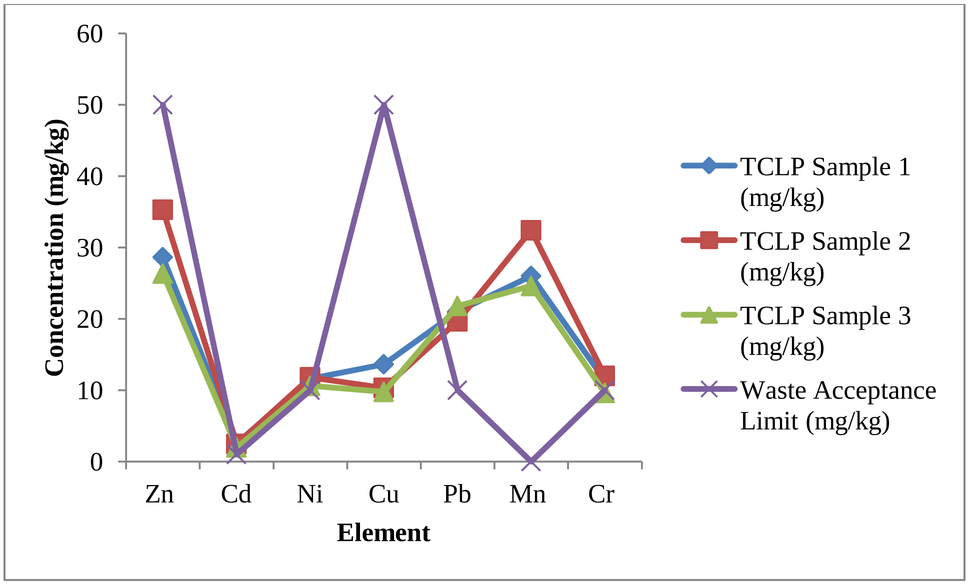


Figure 6.24: Comparison of Heavy Metals in TCLP Samples and Permissible Limit

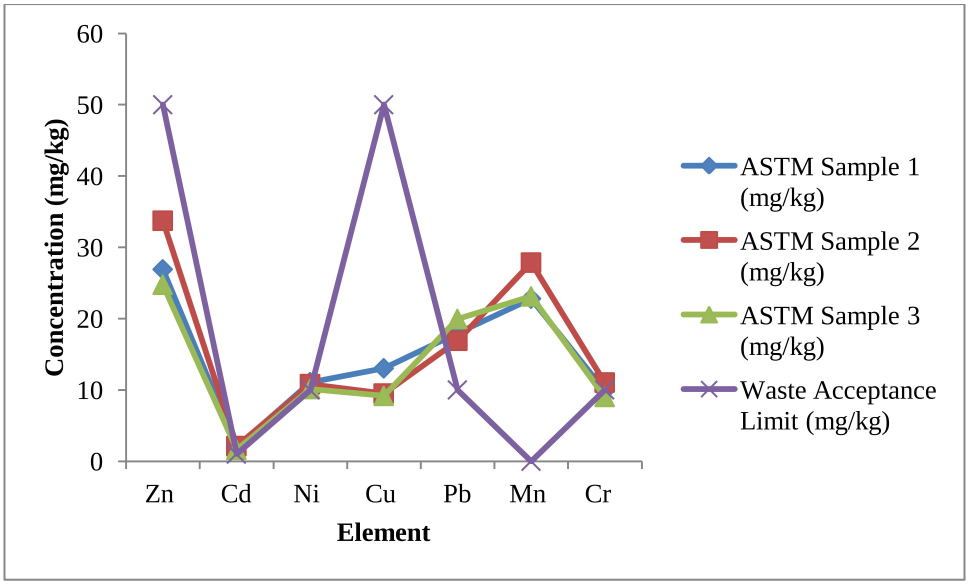


Figure 6.25: Comparison of Heavy Metals in ASTM Samples and Permissible Limit

CHAPTER 7 CONCLUSIONS & FUTURE SCOPE

During this study we observed that the fine particles released to the atmosphere by storage of ash gives the threat to the animal and human health. The finest particle due to their very small size having the sticky tendency like combine with other element those are potentially toxic. The elements those are available in the rolling mill ash have the ability to leach. By the experimental result of this study we can easily conclude that the structure of the ash particles is totally impacted when leaching process occur. The extraction of heavy elements is totally depending upon the pH value of the leaching solution, experimental time. The two test i.e. TCLP-1311 and ASTM (D-3987) methods were performed for the exact concentration analyze of heavy metals in the Rolling mill Ash samples. As per the AAS result it is proves that the TCLP method is more significant as compare to ASTM method. The heavy metal present in the Rolling mill ash is within the permissible limit as per waste acceptance criteria. By the results we can conclude that Lead, Cadmium, Iron as found above the permissible limit in most of the samples.

FUTURE SCOPE

This study has been carried out for the short term leaching effect of Rolling mill ash samples. So the other long test such as Sequential leaching test can also be performed for the detection of heavy metal present in rolling mill ash samples & the results can be compared with the previous results. There is so much research work has been done for the utilization of fly ash produced by power station but very less work has been carried for the utilization of industrial ash it may have the better adhesive property as compare to other. It is also necessary for checking the contamination of underground water by comparing the toxicity of various water samples collected from nearest industrial area, Town ship area etc. so that the industrial environmental effect can also be detected.

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