

REMOVAL OF HEAVY METALS IN WASTE WATER BY USING COAL FLY  
ASH

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Approval of the Graduate School of Natural and Applied Sciences.

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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## **ABSTRACT**

### **REMOVAL OF HEAVY METALS IN WASTE WATER BY USING COAL FLY ASH**

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In this research, it is aimed to remove toxic heavy metals in waste water with the help of fly ash from Çayırhan thermal power plant. The chemical and physical properties (size distribution, specific surface area, porosity, chemical composition, etc.) of fly ash were determined. The experiments were carried out in synthetic waste water containing lead, zinc and copper metals at different concentrations with the addition of fly ash. The effects of metal concentration, agitation time, particle size, ash amount, and pH in the metal removal were examined. With the addition of even very small amount of fly ash, heavy metal removal from waste water was attained at up to 99%. Fly ash particle size has no significant effect on removal of heavy metal ions from solutions. Higher solution pH and longer treatment time were resulted better metal removal. The results also indicated that the main mechanism for metal removal was precipitation due to alkaline characteristics of fly ash and more than 90 % of metals in solutions were removed by precipitation. The pH ranges for maximum metal precipitation were 10-11, 8-10, and 10-11 for copper, zinc, and lead respectively. Very small percentages of adsorbed metal was released during the desorption test.

Keywords: Coal Fly Ash, Heavy Metals, Adsorption, Precipitation.

## ÖZ

### ATIK SULARDAKİ AĞIR METALLERİN UÇUCU KÜL KULLANILARAK UZAKLAŞTIRILMASI

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Bu çalışmada, Çayırhan Termik Santralinden temin edilen uçucu kül yardımıyla atık sulardaki zehirli ağır metallerin uzaklaştırılması amaçlanmıştır. Deneylere başlamadan önce santral külünün kimyasal ve fiziksel özellikleri belirlenmiştir ( tane boyu dağılımı, birim yüzey alanı, gözeneklilik, kimyasal içeriği gibi ). Deneyler sentetik olarak hazırlanan ve farklı konsantrasyonlarda kurşun, çinko ve bakır metal içeren atık sulara uçucu kül ilave edilmesiyle gerçekleştirilmiştir. Metal konsantrasyonunun, karıştırma süresinin, tane boyunun , kül miktarının ve pH gibi parametrelerin ağır metallerin sudan uzaklaştırılması üzerindeki etkileri araştırılmıştır. Çok az miktarda baca külü kullanılması durumunda dahi ağır metalin %99'lara varan oranda ortamdan uzaklaştırıldığı gözlemlenmiştir. Kömür külü tane boyutunun, atık sudan metal uzaklaştırılmasında önemli bir etkisi olmamıştır. Yüksek çözelti pH'sı ve uzun karıştırma süresi daha iyi metal uzaklaştırması sağlamıştır. Çökelme ve soğurulan metalin uçucu külden geri alınması deneyleri de yapılmıştır. Deneylerin sonunda metal uzaklaştırmadaki esas mekanizmanın uçucu külün bazik özelliğinden kaynaklanan çökelme olduğu, ve ağır metalin %90'nından fazlasının çökelme yoluyla ortamdan uzaklaştığı anlaşılmıştır. En fazla metalin çökeldiği pH aralıklarının ise bakır, çinko ve kurşun için sırasıyla 10-11, 8-10 ve 10-11 olduğu görülmüştür. .Soğurulan metalin geri

verilmesi ile ilgili deneylerde ise, soğurulan metalin çok az bir bölümü uçucu kül tarafından geri verilmiştir

Anahtar Kelimeler: Uçucu Kömür Külü, Ağır Metaller, Soğurulma, Çökelme.

*To My Family*

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# CHAPTER 1

## INTRODUCTION

### 1.1. General Remarks

Protecting the environment from hazardous pollutants associated with waste generation and disposal is a major concern in today's heavily industrialized world. Thus far, various technologies have been developed which transform hazardous wastes to non-toxic, or reduce the potential release of toxic species into the environment.

Industrial waste management is essential for sustainable ecological balance. Fly ash is the by-product of the coal combustion process for energy generation, and is recognized as an environmental pollutant. Because of environmental problem of fly ash a good deal of work and applications on the utilization of fly ash has been undertaken world over.

One of the utilization areas of fly ash is the adsorption of metallic ions at fluid/solid interface has been studied for several years, as well as the use of some so-called low cost sorbents. Moreover, fly ashes produced by coal combustion are considered in numerous studies aimed at their valorization. Different applications (cements, roads and backfill) already allow a recycling of an important part of fly ash production which, for instance, reached 450,000 tons in 1997 in France. The use of fly ashes for metallic ions removal from aqueous solution is today's concern and

some studies have showed that fly ashes might be beneficial for removal of heavy metals ions in waste waters (Rio, and Delebarre, 2003).

## **1.2. Objectives of the Thesis and Statement of the Problem**

In this study, the removal capacity of coal fly ash as low-cost adsorbent for heavy metal removal from contaminated water has been examined. Instead of using high-cost commercial adsorbent; such as, activated carbon, chitosan, zeolites, study has been focused on inexpensive materials, which is, coal fly ash and, have high adsorption capacity and are locally available.

## **1.3. Methodology of the Study**

In this research three metal salts were used as heavy metal source. Copper chloride, zinc chloride and lead chloride. From these metal salts synthetic waste waters were prepared. The working ppm levels were 10 ppm, 50 ppm and 100 ppm for each of these metals. Experiments were done in 200 ml beakers with 100 ml solutions, varying fly ash amounts and time values. The known starting values (10, 50, 100 ppm) of metal solutions were treated with 1, 2, 4, 8 grams of fly ash it means, solid/liquid (fly ash/metal solution) ratios were 0,01, 0,02, 0,04 and 0,08 respectively for different time values (5, 10, 30, 60 minutes).

Series precipitation experiments were carried out by changing the pH values of solutions. In adsorption experiments, the effects of time and fly ash amount on heavy metal removal were examined in natural pH values, whereas in precipitation experiments, the pH values of the solutions were changed by addition of NaOH.

Desorption stage of the experimental series is related with the metal retention capacity of the fly ash which is used in the adsorption experiments described above.

The treatment processes were carried out by magnetic stirrer for those particular time values. At the end of treatment, the final or equilibrium concentrations of filtrated solutions were measured by ATOMSPEK H1580 Analytical Instrument.

#### **1.4. Thesis Outline**

Following the introduction in Chapter I, a literature survey covering very broad concepts about Coal Fly Ash (CFA), Heavy Metals, Heavy Metals in Waste Waters and Industrial Waste Waters, Waste Waters and Industrial Waste Waters Treatment Techniques are given out in Chapter II.

Chapter III covers experimental, material characterization and methods employed for the removal of Cu, Zn, and Pb metals from waste waters. Materials and instrumentation used, and the experimental procedure are described.

Experimental results are discussed in Chapter IV.

Finally, Chapter V provides conclusions and recommendations about this study. Additional information associated with the thesis is given in the Appendices.

## **CHAPTER 2**

### **LITERATURE SURVEY**

#### **2.1 Coal Fly Ash (CFA)**

Coal is a major source of energy and its use is predicted to increase in order to meet the continuous demand for electric power generation. With the increase in the usage of coal, especially in industrialized areas, coal combustion waste products became very important for environmental pollution, especially due to their toxic trace element contents.

The solid wastes resulting from the combustion of coal are mainly fly ash, bottom ash and slag.

##### **2.1.1 Definition & Origin**

Fly ash is defined as “the finely divided residue resulting from the combustion of ground or powdered coal which is transported from the firebox through the boiler by flue gases; known in UK as pulverized fuel ash (pfa)”(Dermatas, and Meng, 2003) or fly ash can be described as, it is all particulate material that is carried in a gas stream with the stack gases. It is obtained as a partially inorganic, fine, solid, mineral residue left behind after a majority of combustibles in the coal are burned out and it is a solid, fine-grained material resulting from the combustion of pulverized coal in power station furnaces. The material is collected in mechanical

or electrostatic separators. The term fly ash is not applied to the residue extracted from the bottom of boilers.

Fly ashes may be sub-divided into two categories, according to their origin:

Class F: Fly ash normally produced by burning anthracite or bituminous coal.

Class C: Fly ash normally produced by burning lignite or sub-bituminous coal.

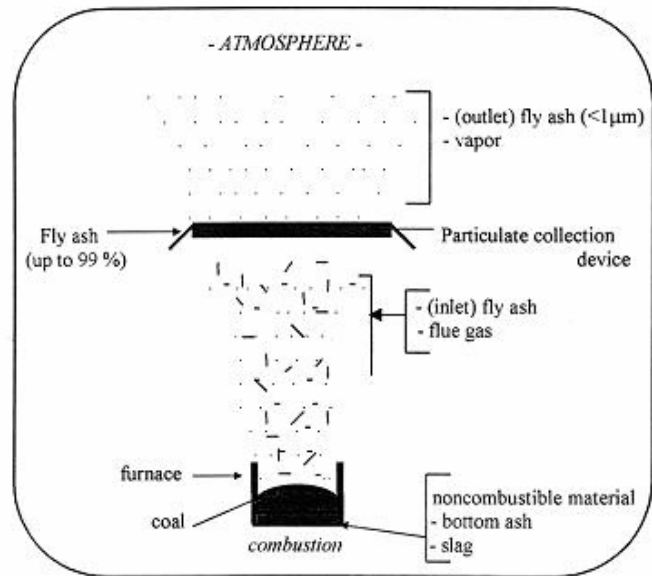
Class C fly ash possesses some cementitious properties. Some Class C fly ashes may have lime contents in excess of 10 % (Weshe, 1991).

### *Bottom Ash & Slag*

Bottom ash is the ash which is removed from a fixed grate by hand or which falls by gravity from the combustion zone. It is coarser and heavier than fly ash particles. Bottom ash forms when ash particles agglomerate to form aggregates similar to volcanic rock.

Slag is the material retained in the furnace. It is a kind of a solidified molten ash. Hence, the material is glassy and the larger pieces resemble obsidian. Compared to bottom ash, slag may have slightly higher bulk density and lower absorption capacity (Çanci, 1998). The formation of coal combustion products can be seen in Figure 1.





**Figure 1.** Sketch diagram indicating the formation of fly ash, bottom ash and slag (Çanci, 1998)

## 2.1.2 Composition of Fly Ash

### 2.1.2.1 Mineralogical Composition

Fly ash is one of the most abundant waste materials; its major components make it a potential agent for the adsorption of heavy metal contaminants in water and waste waters (Gupta, and Torres, 1998). The chemical and mineralogical composition of fly ashes depends upon the characteristics and composition of the coal burned in the power plant. Owing to the rapid cooling of the material, fly ashes are composed chiefly (50-90%) of mineral matter in the form of glassy particles. A small amount of ash occurs in the form of crystals. Unburned coal is collected with the fly ash as particles of carbon, which may constitute up to 16% of the total, depending on the rate and temperature of combustion, the ; degree of pulverization of the original coal, the fuel/air ratio, the nature of the coal being burned, etc.

The most important minerals found in fly ashes from bituminous coal are:

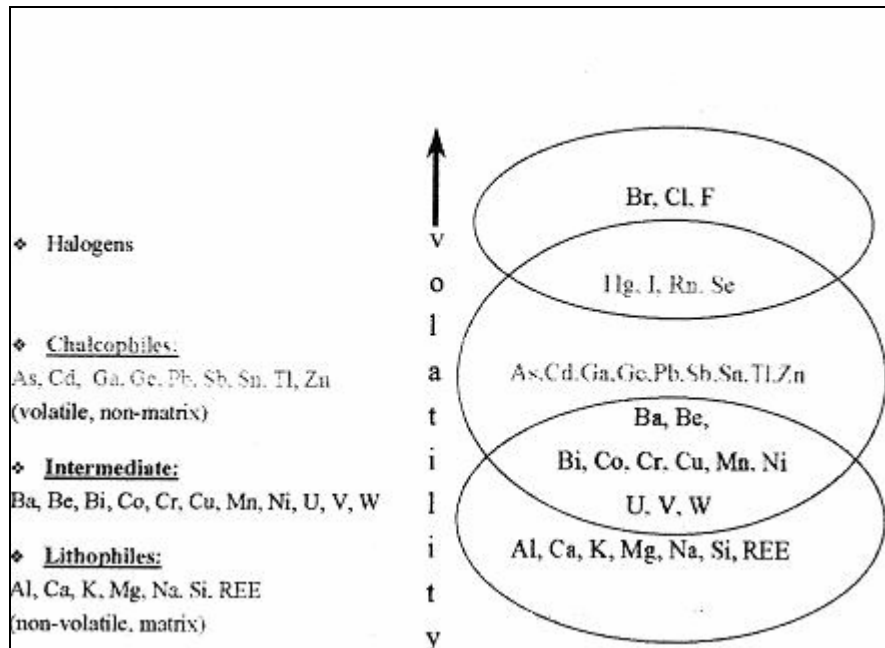
- Magnetite
- Hematite
- Quartz
- Mullite
- Free calcium oxide
- Magnesium oxide

Other minerals like goethite, pyrite, calcite, anhydrite and periclase range from trace amounts to 2.5 % (Weshe, 1991).

### **2.1.2.2 Chemical Composition of Fly Ash**

The elements in the fly ash are mainly lithophiles and chalcophiles. Lithophiles are the elements that are concentrated in aluminosilicates as oxide forms rather than in the metallic and sulfide phases. They are mainly, Al, Ca, K, Mg, Na, Si and the rare earth elements. Chalcophiles are the elements that are concentrated in the sulfide phases rather than in the metallic and silicate phases. They are mainly, As, Cd, Ga, Ge, Pb, Sb, Sn, Tl and Zn. Being nonvolatile, lithophiles form the matrix of fly ashes. Chalcophiles, on the other hand, are volatile elements and are associated with the non-matrix structure. They are concentrated at the surface of the fly ashes. Br, Cl and F are halogenes which remain mainly in the gas phase. Others, such as Ba, Be, Bi, Co, Cr, Cu, Mn, Ni, U, V and W, are intermediate, showing an equal distribution between the matrix and non-matrix structure (Figure 2).

The matrix of fly ash particles is principally composed of aluminum-silicon-oxygen compounds (non-volatile oxides of the major elements), with smaller amounts of Fe, Mg, Na, K, Ca, Th, Ti and the rare earth elements. This structure is commonly called the aluminosilicate matrix (Çancı, 1998).



**Figure 2.** Geochemical classification of the elements in fly ashes by their behavior during combustion and gasification.

### 2.1.3 Uses and Utilization Areas of CFA

In recent years, attempts have been increased to use fly ash as a raw material. However, the recycle of fly ash hardly exceeds 10 % in, most European countries. It is about 15 % in United States and much less in Turkey. Japan produced 8.43 million tons of fly ash and the utilization of coal fly ash is now 6.93 million tons in Japan (Nomura, 2004). United Kingdom, Russia, and USA utilize the 1 %, 4 %, 30 % of total produced coal fly ash, respectively (Tomanec, and Tanic, 2004). The annual production of United Kingdom, Australia, USA, Serbia, India, Russia and Israel are 10 million tons, 8 million tons, 45-50 million tons, 7 million tons, 50-60 million tons, 100 million tons and 1.5 million tons, respectively (Cohen, 2004). The main areas of application of fly ash can be summarized as follows:

### **2.1.3.1 Uses of CFA in Civil Engineering Works**

Fly ash can be used in the construction of road beds and pavements. It is mixed with sand or cement in percentages ranging from 10 to 70 - 80 %. It can also be used as an additive for concrete building blocks. The pozzolanic behaviour of fly ash makes it adequate for preparation of concrete and cement. However, to reduce a possible radiation exposure, fly ash would better be mixed with waste gypsum from power plants (Ege, 1993). Tütünlü studied the stability of Çayırhan Thermal Power Plant Fly Ash as an additive in manufacturing of building bricks. It was found that addition of fly ash up to 60 % at firing temperature of 950 °C has no significant harmful effect on the brick quality with regard to compressive strength, drying and firing shrinkage, water absorption, firing loss, plasticity water and weight per unit volume (Tütünlü, 2000).

### **2.1.3.2 Uses of CFA in Metallurgy and Valuable Metal Extraction**

Fly ash is a potential resource of metals which are available as premined and pulverized ore and it contains various kinds of elements (slagging, toxic, etc) according to which thermal power plant it comes. There are some examples of extraction processes of these elements, and processes are carried out with metallurgical and mineral processing techniques:

The SO<sub>2</sub> was used from flue gases as a reagent to recover uranium from coal ash and after solid-liquid separation and ion exchange process 90% of uranium in fly ash is recovered. At normally, gallium is recovered as a by-product in the aluminum and zinc industries. An alternative potential source of aluminum is fly ash, which has significant levels of Al<sub>2</sub>O<sub>3</sub> (Ege, 1993).

The recovery of valuable elements from fly ashes will increase the economic value of coal utilization by-products. Although studies showed that it is possible to

extract metals from fly ash, the acid and alkaline methods used have negative environmental implications. However, the totally different occurrence of elements in gasification fly ashes from that in combustion fly ashes will give more feasible extraction methods for some elements (Font, et. al, 2004).

There is some laboratory work carried out on two aspects of germanium recovery: the first being leaching of fly ash in order to dissolve the metal by sulphuric acid dilute solutions, which did not react significantly with the other constituents of fly ash and the second involving ion flotation of germanium from dilute aqueous solutions.

### **2.1.3.3 Uses of CFA in Agriculture**

Fly ash can be utilized as amendment for soils in order to regulate physical characteristics or pH. Besides, it may be beneficial to plant growth and improve agronomic properties of soil. Non-essential elements such as Cd, Co, F and V in the fly ash were shown to be non-deleterious to plants, while; Mo, B and Se would be potential hazards to soil environments. So, weathering (contact with water) of fly ash may be required depending on metal leachability characteristics of ash in order to reduce the availability of leaching elements (Ege, 1993).

Fly ash is being used extensively in soil amendment. Fly ash can improve the water holding capacity of soil being a source of essential plant nutrients, fly ash finds applications in agriculture (Sarkar, et. al, 2004).

Alkaline fly ash can be used in problematic soil as an amended material and also it acts as source of plant nutrition for crop production. Direct and residual effects of fly ash were assessed based on crop yield, nutrient uptake and changes in soil characteristics (Mitra, et. al, 2004).

#### **2.1.3.4 Uses of CFA in Ceramic Industry**

Fly ash based ceramic products show good mechanical properties like resistance and strength. To make soft porcelain as kitchen ceramics by using Seyitömer Thermal Power Plant fly ash; the ash containing 56.75 SiO<sub>2</sub> was added to plastic mud having a composition of 20-30 % quartz, 40-50 % kaolin and 30-40 % feldspar (Eşmeliler, 1996).

#### **2.1.3.5 Uses of CFA in Environmental Engineering**

Fly ash has, for many years, been considered a waste material, the production of which has continued to increase, hence, the motivation to look possible industrial applications. One of these is the potential use in waste water treatment. (Ayala, et. al, 1998). Numerous studies have been conducted in the application of fly ash in environmental pollution control issues. The adsorbent capacity of ash allows the removal of colour or soluble and suspended organic pollutants from wastewaters. Mixing sludge with fly ash may reduce the water content from 80 to 60% (Ege, 1993).

Fly ash contains reasonable amount of iron, calcium and sodium oxides and these could be used as adsorbent to reduce SO<sub>2</sub> and NO<sub>x</sub> emissions (LU, et. al, 1991).

#### **2.1.3.6 Uses of CFA in Reclamation of Damaged Areas**

In the mining industry it is a common practice to fill the mines, once the mineral is extracted. This is known as “Stowing”. In various mines of India, it has now become a common practice to use fly ash as stowing materials (Sarkar, et. al, 2004).

Fly ash has been proved to be suitable for exhausted mines fill, for reclaiming damaged areas. Large areas remain virtual wastelands due to damage from mining of coal. The acidic spoils are infertile and support only sparse vegetation, subjecting them to severe corrosion. Fly ash has been proved to be effective in reclaiming these areas. When mixed with bottom ash, fly ash was reported to be an acceptable final cover material for landfill operations (Ege, 1993).

In Table 1, 2 and Figure 3, the production and utilization of fly ash and coal combustion products can be seen

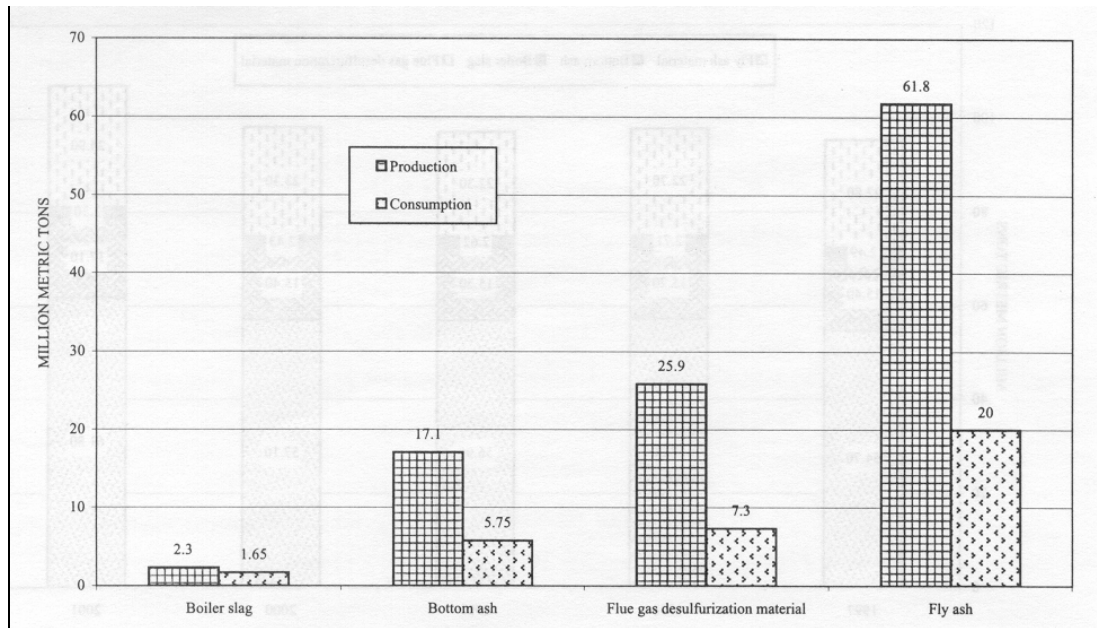
**Table 1.** Fly ash production and utilization in various countries. (Weshe, 1991).

Country	Production (10 <sup>6</sup> t/a)			Utilization (10 <sup>6</sup> t/a)			Utilization in % of Production		
	1977	1984	1986/87	1977	1984	1986/87	1977	1984	1986/87
Australia	5.4	3.5	5.2	0.58	0.25	0.56	11	7	11
Canada	2.6	3.3	3.2	0.71	0.8	1.1	27	24	34
China		35	41		7.2	9.5		21	23
Denmark		1	1.2		0.45	0.9		45	73
France	4.8	5.1	2.2	2.0	1.5	1.3	42	29	58
Germany		2.6	2.9		2.0	2.2		77	76
Hungary	5.0		4.1	0.43		1.1	9		26
India		19	39		0.5	1.2		3	3
Japan	2.0	3.7	3.3	0.45	0.5	0.96	23	14	29
Netherlands		0.5	0.74		0.3	0.72		60	97
South Africa		13	13		0.1	0.58		1	4
Spain	5.0		7.4	0.65		1.5	13		20
Sweden		0.1	0.14		0.02	0.08		20	57
UK	13.9	13.8	10.4	5.6	1.3	5.9	40	9	57
USA	61.0	47	38.3	9.1	5	8.0	13	11	18

**Table 2.** Consumption of coal combustion products in 2001 in the world  
(Kalyoncu, 2002)

	<b>Fly ash</b>	<b>Bottom ash</b>	<b>Boiler slag</b>	<b>FGD material</b>	<b>Total coal combustion products</b>
<b>Production (x10<sup>3</sup> ton)</b>					
<b>Consumption</b>					
Agriculture	20	20		100	140
Blasting grift		40	1,350		1,390
Cement clinker	940	710		440	2,090
Concrete-grout	11,200	710		440	12,400
Flowable fill	730	10			740
Mineral filler	100	10	10		120
Mining applications	740	110		130	980
Road base and subbase	930	550		40	1,520
Snow and ice control		770	20		790
Soil modification	670	100			770
Structural fills	2,910	1,050	10	170	4,140
Wallboard				5,650	5,650
Waste stabilization and solidification	1,310	60		40	1,410
Other	410	1,610	260	280	2,550
<b>Total</b>	<b>20,000</b>	<b>5,750</b>	<b>1,650</b>	<b>7,300</b>	<b>34,700</b>
Individual use %	32.30	33.70	71.70	28.20	XX
Cumulative use %	32.30	32.60	33.70	32.40	32.40
1/Data are rounded to no more than three significant digits; may not add to totals shown					
2/Includes categories I and II, dry and ponded, respectively					





**Figure 3.** Production and consumption of coal combustion products in the U.S. in 2001 (Kalyoncu, 2002)

### 2.1.3.7 Fly Ash Utilization in Turkey

The disposal of fly ash represent a significant problem for Turkey. In 1998, 14.5 million tons of ash was generated by power plants alone (not including industry and other coal utilization applications). By the year 2020, ash production is expected to reach 500 million tons per year with an additional 2-3 million tons of flue gas desulphurization (fgd) sludge or gypsum (Tütünlü, 2000). The waste water treatment has been occupied great importance for several years, in the agenda of environmentally leadership countries, but this subject has just been introduced to Turkey. But the fly ash utilization is improving day by day while production and utilization technologies of fly ash develop.

## **2.2 Heavy Metals**

The term heavy metal refers to any metallic element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), zinc (Zn), copper (Cu), selenium (Se) and lead (Pb).

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. They enter our bodies to a small extent via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can cause poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain.

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical compound in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things than their disintegration they are broken down (metabolized) or excreted.

Heavy metals can enter a water supply by industrial and consumer waste water, or even from acidic rain by breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater.

### **2.2.1 Copper (Cu)**

Copper is an essential element for all living organisms and one of the earliest known metals. Copper is lustrous, ductile, malleable, and a good conductor of heat. It may have been the first metal worked by ancient man 8000 years ago. Artifacts

hammered from copper that date back to 6000 BC have been found in the Near and Middle East (Berman, 1980).

The world's copper production is still rising. This basically means that more and more copper will contaminate the environment. Rivers are depositing sludge on their banks that is contaminated with copper, due to the disposal of copper-containing wastewater. Copper enters the air, mainly through release during the combustion of fossil fuels. Copper in air will remain there for an eminent period of time, before it settles when it starts to rain. It will than end up mainly in soils. As a result soils may also contain large quantities of copper after copper from the air has settled.

Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. A few examples of human activities that contribute to copper release have already been named (Berman, 1980). Other examples are mining, metal production, wood production and phosphate fertilizer production. Because copper released both naturally and through human activity is very widespread in the environment. Copper contamination is often found near mines, industrial settings, landfills and waste disposals.

When copper ends up in soil it strongly attaches to organic matter and minerals. As a result it does not travel very far after release and it hardly ever enters groundwater. In surface water copper can travel great distances, either suspended on sludge particles or as free ions.

Copper does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. On copper-rich soils only a limited number of plants has a chance of survival. That is why there is not much plant diversity near copper-disposing factories. Due to the effects upon plants copper is a serious threat to the productions of farmlands. Copper can seriously

influence the proceedings of certain farmlands, depending upon the acidity of the soil and the presence of organic matter. Despite of this, copper-containing fertilizers are still applied.

Copper can interrupt the activity in soils, as it negatively effects the activity of microorganisms and earthworms. The decomposition of organic matter may seriously slow down because of this.

When the soils of farmland are polluted with copper, animals will absorb concentrations that are damaging to their health. Mainly sheep suffer a great deal from copper poisoning, because the effects of copper are manifesting at fairly low concentrations. Chemical properties of copper can be seen in Table 3.

**Table 3.** Chemical properties of copper

Atomic number	29
Atomic mass	63.546 g.mol <sup>-1</sup>
Electronegativity	1.9
Density	8.9 g.cm <sup>-3</sup> at 20°C
Melting point	1083 °C
Boiling point	2595 °C
Vanderwaals radius	0.128 nm
Ionic radius	0.096 nm (+1) ; 0.069 nm (+3)
Isotopes	6
Electronic shell	[ Ar ] 3d <sup>10</sup> 4s <sup>1</sup>
Energy of first ionisation	743.5 kJ.mol <sup>-1</sup>
Energy of second ionisation	1946 kJ.mol <sup>-1</sup>
Standard potential	+ 0.522 V ( Cu <sup>+</sup> / Cu ) ; + 0.345 V (Cu <sup>2+</sup> / Cu )

### 2.2.2 Zinc (Zn)

Zinc metals mixed with copper were employed by the ancients in making brass. Oxides of zinc, obtained from furnace fumes by constructing dust chambers to collect the sublimate, were used for medical purposes about 2000 years before zinc metal itself became generally known (Berman, 1980).

Zinc occurs naturally in air, water and soil, but zinc concentrations are rising unnaturally, due to addition of zinc through human activities. Most zinc is added during industrial activities, such as mining, coal and waste combustion and steel processing.

The world's zinc production is still rising. This basically means that more and more zinc ends up in the environment.

Water is polluted with zinc, due to the presence of large quantities of zinc in the wastewater of industrial plants which is not purified satisfactorily. One of the consequences is that rivers are depositing zinc-polluted sludge on their banks. Zinc may also increase the acidity of waters in deposition zones.

Some fish can accumulate zinc in their bodies, when they live in zinc-contaminated waterways. When zinc enters the bodies of these fish, it is able to bio magnify up the food chain.

Large quantities of zinc can be found in soils. When the soils of farmland are polluted with zinc, animals will absorb concentrations that are damaging to their health. Water-soluble zinc that is located in soils can contaminate groundwater. Zinc cannot only be a threat to cattle, but also to plant species. Plants often have a zinc uptake that their systems cannot handle, due to the accumulation of zinc in soils.

On zinc-rich soils only a limited number of plants has a chance of survival. That is why there is not much plant diversity near zinc-disposing factories. Due to the effects upon plants zinc is a serious threat to the productions of farmlands. Despite of this zinc-containing manures are still applied.

Finally, zinc can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms. The breakdown of organic matter may

seriously slow down because of this. Chemical properties of zinc can be seen in Table 4.

**Table 4.** Chemical properties of zinc

Atomic number	30
Atomic mass	65.37 g.mol <sup>-1</sup>
Electronegativity	1.6
Density	7.11 g.cm <sup>-3</sup> at 20°C
Melting point	420 °C
Boiling point	907 °C
Vanderwaals radius	0.138 nm
Ionic radius	0.074 nm (+2)
Isotopes	10
Electronic shell	[ Ar ] 3d <sup>10</sup> 4s <sup>2</sup>
Energy of first ionisation	904.5 kJ.mol <sup>-1</sup>
Energy of second ionisation	1723 kJ.mol <sup>-1</sup>
Standard potential	- 0.763 V

### 2.2.3 Lead (Pb)

Lead, one of the seven metals of antiquity, has accompanied all civilizations since their beginnings. It was in use of before the time of the Hebrew exodus from Egypt.

Lead does not found in elemental state in nature but as its sulphide ore or galena. Discovery of metallic lead may have resulted from the accidental dropping of galena into campfire (Berman, 1980).

Because lead does not occurs naturally in the environment, most lead concentrations that are found in the environment are a result of human activities. Due to the application of lead in gasoline an unnatural lead-cycle has consisted. In car engines lead is burned, so that lead salts (chlorines, bromines, and oxides) will originate.

These lead salts enter the environment through the exhausts of cars. The larger particles will drop to the ground immediately and pollute soils or surface waters, the smaller particles will travel long distances through air and remain in the atmosphere. Part of this lead will fall back on earth when it is raining. This lead-cycle caused by human production is much more extended than the natural lead-cycle. It has caused lead pollution to be a worldwide issue.

Not only leaded gasoline causes lead concentrations in the environment to rise. Other human activities, such as fuel combustion, industrial processes and solid waste combustion, also contribute.

Lead can end up in water and soils through corrosion of leaded pipelines in a water transporting system and through corrosion of leaded paints. It cannot be broken down; it can only convert to other forms.

Lead accumulates in the bodies of water organisms and soil organisms. These will experience health effects from lead poisoning. Health effects on shellfish can take place even when only very small concentrations of lead are present. Body functions of phytoplankton can be disturbed when lead interferes. Phytoplankton is an important source of oxygen production in seas and many larger sea-animals eat it. That is why we now begin to wonder whether lead pollution can influence global balances.



Soil functions are disturbed by lead intervention, especially near highways and farmlands, where extreme concentrations may be present. Soil organisms than suffer from lead poisoning, too.

Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains ([www.lenntech.com](http://www.lenntech.com)). Chemical properties of lead can be seen in Table 5.

**Table 5.** Chemical properties of lead

Atomic number	82
Atomic mass	207.2 g.mol <sup>-1</sup>
Electronegativity	1.8
Density	11.34 g.cm <sup>-3</sup> at 20°C
Melting point	327 °C
Boiling point	1755 °C
Vanderwaals radius	0.154 nm
Ionic radius	0.132 nm (+2) ; 0.084 nm (+4)
Isotopes	13
Electronic shell	[ Xe ] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>
Energy of first ionisation	715.4 kJ.mol <sup>-1</sup>
Energy of second ionisation	1450.0 kJ.mol <sup>-1</sup>
Energy of third ionisation	3080.7 kJ.mol <sup>-1</sup>
Energy of fourth ionisation	4082.3 kJ.mol <sup>-1</sup>
Energy of fifth ionisation	6608 kJ.mol <sup>-1</sup>

### 2.3 Heavy Metals in Waste Waters and Industrial Waste Waters

Some physical or chemical operations result in excess amount of heavy metals in waste water. For example, the desulphurization treatment of fumes in power plants results in wastewater with high content of heavy metals. But, the main sources of heavy metals in waste waters are the mining operations and metal industries.

Heavy metals in concentrations above trace amounts are generally toxic to living organisms. Trace amounts ( $<0.05$  mg/L) of Zn, Cu and Pb are present in most natural waters. Zn and Cu may be present in higher levels in irrigation areas due to the use of galvanized iron, copper and brass in plumbing fixtures and for water storage. In irrigation areas, acceptable levels are 0.2 mg/L for  $\text{Cu}^{2+}$  and 2.0 mg/L for  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  (<http://www.humate.com>). On the other hand, different types of industries' waste water charging allowable limits according to the Ministry of Environment and Forestry can be seen in following tables (Table 6-12).

**Table 6.** The allowable standards for discharging of waste waters to waste water substructure foundations (Ministry of Environment and Forestry of Turkish Republic)

<b>Parameters</b>	<b>Concentration</b>	<b>In the Waste Water Substructure Foundations whose Sewer Systems Ends with Complete Cleaning</b>	<b>In the Waste Water Substructure Foundations whose Sewer Systems Ends with Deep Sea Charging</b>
Temperature(C°)	-	40	40
pH	-	6.5-10	6-10
Suspended Solid Matter	(mg/l)	500	350
Oil	(mg/l)	250	50
Tar and Petroleum Based Oils	(mg/l)	50	10
Chemical Oxygen Need	(mg/l)	4000	600
Sulphate(SO <sub>4</sub> <sup>-2</sup> )	(mg/l)	1000	1000
Total Sulphur(S)	(mg/l)	2	2
Phenol	(mg/l)	20	10
Free Chloride(Cl <sup>-2</sup> )	(mg/l)	5	5
Total Nitrogen(N) (mg/l)	(mg/l)	-	40
Total Phosphorus(P)	(mg/l)	-	10
Arsenic(A) (mg/l)	(mg/l)	3	10
Total Cyanide(CN)	(mg/l)	10	10
Total Lead(Pb) (mg/l)	(mg/l)	3	3
Total Cadmium(Cd)	(mg/l)	2	2
Total Chromate(Cr)	(mg/l)	5	5
Total Mercury(Hg)	(mg/l)	0.2	0.2
Total Copper(Cu)	(mg/l)	2	2
Total Nickel(Ni)	(mg/l)	5	5
Total Zinc(Zn)	(mg/l)	10	10
Total Tin(Sn)	(mg/l)	5	5
Total Silver(Ag)	(mg/l)	5	5

**Table 7.** The allowable standards for discharging of waste waters of mining industry (Ministry of Environment and Forestry of Turkish Republic)

<b>Parameters</b>	<b>Concentration</b>	<b>Composite Sample For 2 hours</b>	<b>Composite Sample For 24 hours</b>
pH	-	6-9	6-9
Suspended Solid Matter	(mg/l)	70	50
Chemical Oxygen Need	(mg/l)	80	60
Total Cyanide(CN)	(mg/l)	0.1	-
Lead(Pb)	(mg/l)	0.5	-
Cadmium(Cd)	(mg/l)	-	0.2
Total Chromate(Cr)	(mg/l)	2	1
Mercury(Hg)	(mg/l)	-	0.05
Free Sulphur(S)	(mg/l)	15	10
Copper(Cu)	(mg/l)	5	3
Iron(Fe)	(mg/l)	3	-
Zinc(Zn)	(mg/l)	3	-

**Table 8.** The allowable standards for discharging of waste waters of ceramic industry (Ministry of Environment and Forestry of Turkish Republic)

<b>Parameters</b>	<b>Concentration</b>	<b>Composite Sample For 2 hours</b>	<b>Composite Sample For 24 hours</b>
pH	-	6-9	6-9
Suspended Solid Matter	(mg/l)	100	-
Chemical Oxygen Need	(mg/l)	80	-
Lead(Pb)	(mg/l)	10	-
Cadmium(Cd)	(mg/l)	0.1	-
Zinc(Zn)	(mg/l)	3	-

**Table 9.** The allowable standards for discharging of waste waters of glass industry (Ministry of Environment and Forestry of Turkish Republic)

Parameters	Concentration	Instantaneous Sample	Composite Sample For 2 hours
pH	-	6-9	6-9
Chemical Oxygen Need	(mg/l)	-	160-260
Flor(F <sup>-</sup> )	(mg/l)	-	30
Nickel(Ni)	(mg/l)	-	3
Silver(Ag)	(mg/l)	-	1
Lead(Pb)	(mg/l)	-	1
Sulphate(SO <sub>4</sub> <sup>2-</sup> )	(mg/l)	-	3000

**Table 10.** The allowable standards for discharging of waste waters of chemical industry (Ministry of Environment and Forestry of Turkish Republic)

Parameters	Concentration	Composite Sample For 2 hours	Composite Sample For 24 hours
pH	-	6-9	6-9
Chemical Oxygen Need	(mg/l)	200	150
Lead(Pb)	(mg/l)	2	1
Cadmium(Cd)	(mg/l)	-	0.2
Zinc(Zn)	(mg/l)	4	3
Chromate(Cr <sup>+6</sup> )	(mg/l)	0.5	0.3
Total Chromate	(mg/l)	2	1
Iron(Fe)	(mg/l)	30	-
Total Cyanide(CN)	(mg/l)	2	1

**Table 11.** The allowable standards for discharging of waste waters of metal industry (Metal Preparing in General) (Ministry of Environment and Forestry of Turkish Republic)

Parameters	Concentration	Composite Sample For 2 hours	Composite Sample For 24 hours
pH	-	6-9	6-9
Suspended Solid Matter	(mg/l)	120	50
Oil	(mg/l)	20	10
Ammonium Nitrogen(NH <sub>4</sub> -N)	(mg/l)	100	-
Chemical Oxygen Need	(mg/l)	200	100
Nitrate Nitrogen(NO <sub>2</sub> -N)	(mg/l)	10	5
Active Chlorine	(mg/l)	0.5	-
Sulphur(S <sup>-2</sup> )	(mg/l)	2	-
Chromate(Cr <sup>+6</sup> )	(mg/l)	0.5	0.5
Aluminium(Al)	(mg/l)	3	2
Flor(F <sup>-</sup> )	(mg/l)	50	30
Iron(Fe)	(mg/l)	3	-
Total Cyanide(CN)	(mg/l)	0.5	0.1
Lead(Pb)	(mg/l)	2	1
Cadmium(Cd)	(mg/l)	0.5	0.1
Total Chromate(Cr)	(mg/l)	2	1
Mercury(Hg)	(mg/l)	0.05	0.01
Copper(Cu)	(mg/l)	3	1
Nickel(Ni)	(mg/l)	3	2
Zinc(Zn)	(mg/l)	5	3
Silver(Ag)	(mg/l)	0.1	-

**Table 12.** The allowable standards for discharging of waste waters of automotive industry (Ministry of Environment and Forestry of Turkish Republic)

Parameters	Concentration	Composite Sample For 2 hours	Composite Sample For 4 hours
pH	-	6-9	6-9
Suspended Solid Matter	(mg/l)	80	40
Oil	(mg/l)	20	10
Ammonium Nitrogen(NH <sub>4</sub> -N)	(mg/l)	100	-
Chemical Oxygen Need	(mg/l)	400	300
Nitrate Nitrogen(NO <sub>2</sub> -N)	(mg/l)	5	-
Free Cyanide(CN <sup>-</sup> )	(mg/l)	0.05	-
Chromate(Cr <sup>+6</sup> )	(mg/l)	0.05	-
Aluminium(Al)	(mg/l)	3	-
Flor(F <sup>-</sup> )	(mg/l)	5	-
Iron(Fe)	(mg/l)	3	-
Lead(Pb)	(mg/l)	0.3	-
Cadmium(Cd)	(mg/l)	0.05	-
Total Chromate(Cr)	(mg/l)	0.5	-
Mercury(Hg)	(mg/l)	0.005	-
Copper(Cu)	(mg/l)	0.3	-
Nickel(Ni)	(mg/l)	1	-
Zinc(Zn)	(mg/l)	2	-

## 2.4 Waste Waters and Industrial Waste Waters Treatment Techniques

Several methods, such as chemical precipitation, flotation, ion exchange, adsorption and biological treatment, are often used to remove the heavy metals from waste water. Fly ash is used based on its high adsorption and ion-exchange capacity of heavy metals.

## **2.4.1 Mechanism of Heavy Metal Removal by Fly Ash**

There are three main heavy metal removal mechanisms of fly ash from waste waters which are adsorption, ion-exchange and precipitation. Usually, the pH value of the fly ash solution is the most important parameter that determines the predominant mechanism. Adsorption and ion-exchange usually occurs between the limit levels of pH 4-8. At higher pH levels precipitation occurs.

### **2.4.1.1 Adsorption**

When aqueous metal ions come into contact with solid phases, the adsorbed substance usually decreases through its association with the solid phase. This uptake has generally been attributed to adsorption, ion exchange, and/or co-precipitation. The parameters which influence the process are specific surface area of fly ash, physical state of the adsorbent and the adsorbed substance, amorphous or crystalline, the metal concentration of solution, the quantity of the adsorbent in relation to that of the adsorbed substance (Nriagu, 1980).

The major components of the investigated fly ashes are alumina, silica, ferric oxide and calcium oxide. Each of these oxide components can be ideal as a metal absorbent. Moreover, the alkaline nature of these fly ashes makes them a good neutralizing agent (Bayat, 1997).

### **2.4.1.2 Ion Exchange**

Ion exchange is a process whereby ions adsorbed by electrostatic forces to charged functional groups on the surface of a solid are exchanged for ions of similar charge in a solution in which the solid is immersed. This process continues until the solution being treated exhausts the resin exchange capacity. When this point is reached, the resin must be regenerated by another chemical that replaces the ions given up in the ion exchange operation. Cation resins are generally regenerated

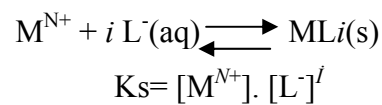


with acids; anion resins with bases. The end result is concentrated regenerent brine, which also must be treated. In some cases chemicals can be recovered from the brine.

Ion exchange is an attractive method for the removal of small amounts of impurities from dilute wastewaters or the concentration and recovery of expensive chemicals from segregated concentrated waste waters (Nriagu, 1980).

### 2.4.1.3 Precipitation

Precipitation is a standard method of treatment for most heavy metals, as the relatively insoluble hydroxide, at alkaline pH, or occasionally as the sulphide. Coprecipitation by addition of ferrous sulphate has also been suggested for strongly complexed copper wastewaters (Patterson, J). When considering metal solubility, simple equilibrium calculations have little real meaning. The simplest case:



suggests that the concentration of metal in solution is wholly dependent on the concentration of  $L^{-}$ . If  $L^{-}$  is hydroxide ion, the residual metal concentration is a function of the pH of the solution, and the metal concentration in solution decreases as the pH increases (Nriagu, 1980).

## **2.4.2 Other Removal Techniques**

### **2.4.2.1 Flotation**

Ion flotation technique is used in removal of heavy metal ions from waste waters. Ion flotation, as its name indicates, is a flotation-based technology for removing and concentrating ions from their mother solution. In this technique, an ionic surface-active reagent (collector), which can preferentially concentrate at the solution/ vapor interface, is added to the solution. The collector must have the opposite charge to the ions to be removed from the solution (the colligend). The colligend is then electrostatically adsorbed at the interface. As gas bubbles rise through the solution, the co-adsorbed colligend ions are removed from the mother solution along with the collector, and report to a foam phase that can be physically removed (Liu and Doyle, 2001).

Known flotation techniques are also used in the removal of heavy metals from waste waters. But mostly used flotation technique is froth flotation or dissolved air flotation (DAF) which is known name in industry. In this technique, air is dissolved into water, mixed with the waste stream and released from solution while in intimate contact with the contaminants. Air bubbles form, attach to the solids, increase their buoyancy and float the solids to the water's surface as in the case of ion flotation. A percentage of the clean effluent is recycled and super-saturated with air, mixed with the wastewater influent and injected into the DAF separation chamber (<http://www.panamenv.com>).

### **2.4.2.2 Evaporative Recovery**

Use of evaporative recovery has been practised nearly for 50 years. Unless a recovery process is a closed loop operation, however, the concentrated waste water

may still require final treatment for residual removal. Process modification for waste stream segregation and flow reduction is usually an integral part of the recovery process. Logic of the operation is based on the evaporation of waste stream which is washed continuously by distilled water in a closed circuit. After evaporation occurs final metal is taken. One disadvantage of evaporative recovery is the build-up of impurities in the plating bath, since both the impurities which are added with plating chemicals and those formed by decomposition of additives are returned quantitatively to the plating bath (Patterson, 1985).

#### **2.4.2.3 Coagulation**

Treatment of wastewater from a tetraethyl lead plant has been described in “An Integrated Plant for Tetraethyl Lead”(Patterson, 1985). The effluent was alkaline, and contained inorganic lead salts in solution and suspension, plus organic lead salts. The pH was adjusted 8-9, and inorganic lead precipitated by addition of lime. The precipitation was assisted by the addition of ferrous sulphate, which acted as a coagulating agent (Patterson, 1985).

#### **2.4.2.4 Biological treatment**

Biological treatment can successfully reduce levels of certain heavy metals by oxidizing/reducing metal contaminants via microorganism activity. During phytoremediation, the plants remove metals from contaminated soils and groundwater by absorption and concentration into the plant roots, or they can be used as a containment strategy by stabilizing the metals in the soils and limiting mobility (<http://www.humate.com>).

## CHAPTER 3

### EXPERIMENTAL, MATERIAL CHARACTERIZATION AND METHODS

#### 3.1 Chemical Analysis of the Sample

Fly ash which was taken from the Çayırhan Thermal Power Plant was the test material in this study. Chemical composition of the coal fly ash sample was determined by X-Ray Florescence Spectrometer method. XRF analysis was done in General Directorate of Mineral Research and Exploration. Table 13 shows the chemical analysis of the test sample. The heavy metal contents of the test sample were determined by optic spectrographic semi quantitative analysis method. Table 14 shows the heavy metal contents of the test sample.

**Table 13.** Chemical analysis of the sample (XRF)

<b>Na<sub>2</sub>O</b>	3.3 %	<b>Al<sub>2</sub>O<sub>3</sub></b>	12.2 %
<b>K<sub>2</sub>O</b>	1.6 %	<b>SiO<sub>2</sub></b>	50.3 %
<b>SO<sub>3</sub></b>	5.25 %	<b>TiO<sub>2</sub></b>	0.5 %
<b>MgO</b>	4.9 %	<b>P<sub>2</sub>O<sub>5</sub></b>	0.4 %
<b>CaO</b>	14.5 %	<b>Fe<sub>2</sub>O<sub>3</sub></b>	8.5 %

**Table 14.** Heavy metal contents of test sample

<b>Cu</b>	<b>Pb</b>	<b>Zn</b>	<b>Mn</b>
0.0025 %	0.0014 %	0.0032 %	0.2 %
<b>Cr</b>	<b>B</b>	<b>Ni</b>	
0.02 %	0.02 %	0.02 %	

## **3.2 Characterization of the Sample**

### **3.2.1 Specific Gravity Determination**

Specific gravity of the coal fly ash was determined with water pycnometer. First the dry pycnometer was weighed ( $P_1$ ). Then the sample was introduced in to the pycnometer and weighed ( $P_2$ ). As a next step the pycnometer was filled with distilled water and again weighed ( $P_3$ ). The last weighing was ( $P_4$ ) which is filling of empty pycnometer with distilled water. Finally, the specific gravity of the coal fly ash was calculated by using below equation.

$$\text{Specific Gravity} = \frac{(P_2 - P_1)}{(P_2 + P_4) - (P_1 + P_3)}$$

This procedure was repeated 4 times (Table 15). And the arithmetic average of the 4 measurements (1.97) was taken as specific gravity of the sample.

**Table 15.** Results of specific gravity measurement

Test Number	Specific Gravity
1.	1.94
2.	1.96
3.	1.98
4.	1.99
AVERAGE	1.97

### 3.2.2 Size Analysis

#### 3.2.2.1 By Screening

Screen analyses of the CFA were both done with dry and wet screening. Tyler mesh series were used. Dry and wet screen results are given in Table 16 and Table 17 respectively.

**Table 16.** Dry screening of CFA

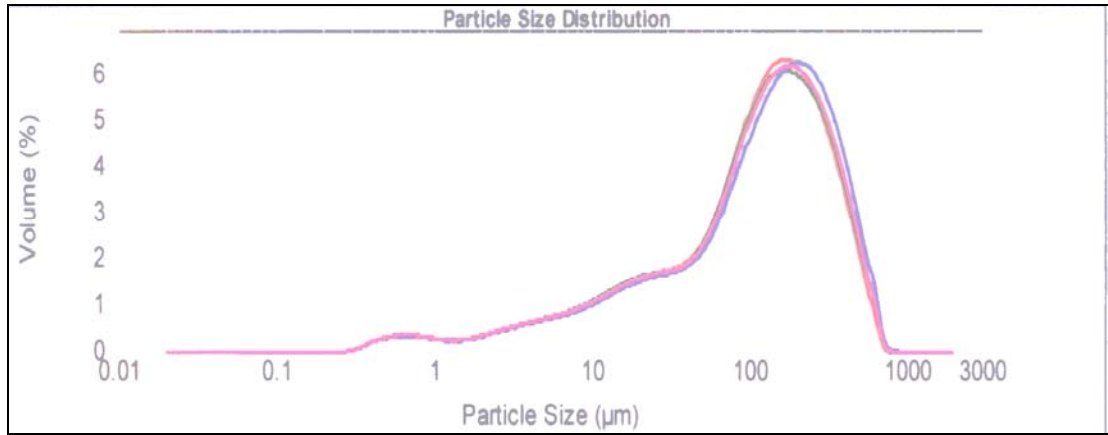
Micron	Weight %	Cumulative Retained %
+105	57,07	57,07
-105+74	13,56	70,63
-74+53	20,13	90,76
-53+44	2,38	93,14
-44+37	3,72	96,86
-37	3,14	

**Table 17.** Wet screening of CFA

<b>Micron</b>	<b>Weight %</b>	<b>Cumulative Retained %</b>
+105	51,24	51,24
-105+74	15,60	66,84
-74+53	3,94	70,78
-53+44	1,97	72,75
-44+37	2,97	75,72
-37	24,28	

### **3.2.2.2 Laser Size Analysis**

Analysis was done by Mastersizer 2000 Version 5.1 device. Laser size analysis of the CFA was done in Central Laboratory at METU. It was seen that the d (50) value is about 100  $\mu\text{m}$  for dry and wet screen analysis, whereas it was found as 124.663  $\mu\text{m}$  from the laser size analysis results. Surface and volume mean diameters are found 14.165  $\mu\text{m}$  and 159.199  $\mu\text{m}$  respectively. Particle size distribution of Laser Size Analysis can be seen in Figure 4 and volumetric under size % values of Laser Size Analysis can be seen in Table 18.



**Figure 4.** Sketch diagram of particle distribution of laser size analysis

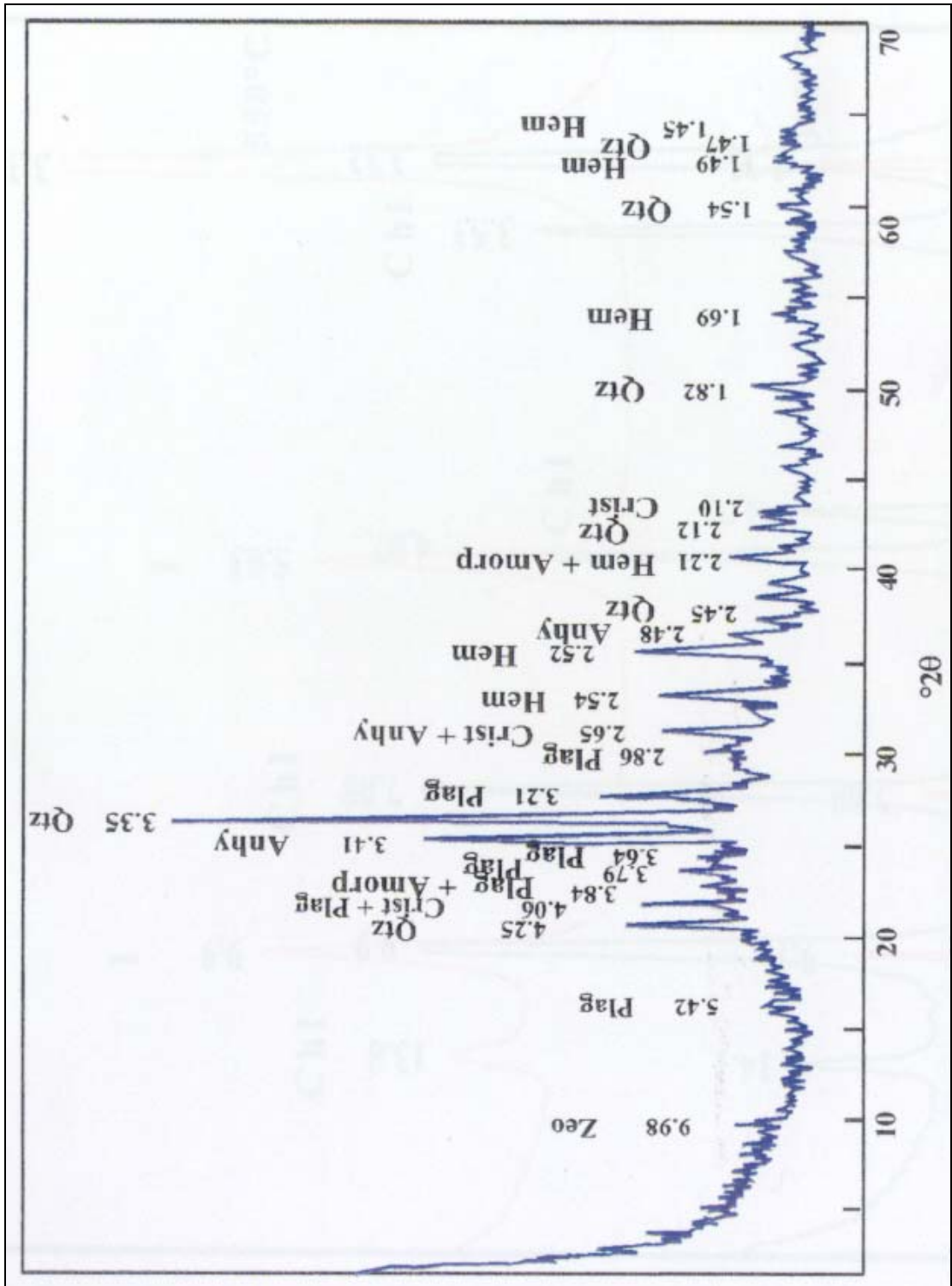
**Table 18.** Volumetric under size % values of laser size analysis

Size (µm)	Vol. U.Size %	Size (µm)	Vol. U.Size %	Size (µm)	Vol. U.Size %	Size (µm)	Vol. U.Size %	Size (µm)	Vol. U.Size %	Size (µm)	Vol. U.Size %
0.020	0.00	0.142	0.00	1.002	2.02	7.096	8.05	50.238	26.73	355.656	89.32
0.022	0.00	0.159	0.00	1.125	2.22	7.962	8.70	56.368	28.53	399.052	92.43
0.025	0.00	0.178	0.00	1.262	2.40	8.934	9.39	63.246	30.58	447.744	95.05
0.028	0.00	0.200	0.00	1.416	2.58	10.024	10.15	70.963	32.97	502.377	97.13
0.032	0.00	0.224	0.00	1.589	2.76	11.247	10.96	79.621	35.72	563.677	98.65
0.036	0.00	0.252	0.00	1.783	2.96	12.619	11.84	89.337	38.86	632.456	99.63
0.040	0.00	0.283	0.00	2.000	3.19	14.159	12.80	100.237	42.39	709.627	99.99
0.045	0.00	0.317	0.01	2.244	3.45	15.887	13.83	112.468	46.27	796.224	100
0.050	0.00	0.356	0.07	2.518	3.75	17.825	14.92	126.191	50.46	893.367	100
0.056	0.00	0.399	0.18	2.825	4.09	20.000	16.07	141.589	54.86	1002.374	100
0.063	0.00	0.448	0.35	3.170	4.47	22.440	17.26	158.866	59.42	1124.683	100
0.071	0.00	0.502	0.56	3.557	4.88	25.179	18.49	178.250	64.05	1261.915	100
0.080	0.00	0.564	0.79	3.991	5.33	28.251	19.75	200.000	68.68	1415.892	100
0.089	0.00	0.632	1.05	4.477	5.81	31.698	21.02	224.404	73.24	1588.656	100
0.100	0.00	0.710	1.31	5.024	6.32	35.566	22.33	257.785	77.66	1782.502	100
0.112	0.00	0.796	1.56	5.637	6.87	39.905	23.69	282.508	81.86	2000.000	100



### **3.2.3 X-Ray Diffractometry (XRD) Analysis**

X-ray diffractometry analysis of the test sample was done in General Directorate of Mineral Research and Exploration. The peaks of diffraction were recorded and plotted against a horizontal scale in degrees of  $2\theta$ . The XRD results of the CFA sample showed that quartz, plagioclase, anhydrite, hematite, cristobalite, amorphous silicate and zeolite the main constituents (CFA). XRD pattern of the CFA is given in Figure 5.



**Figure 5.** X-Ray diffraction pattern of fly ash

### 3.2.4 Scanning Electron Microscopy (SEM)

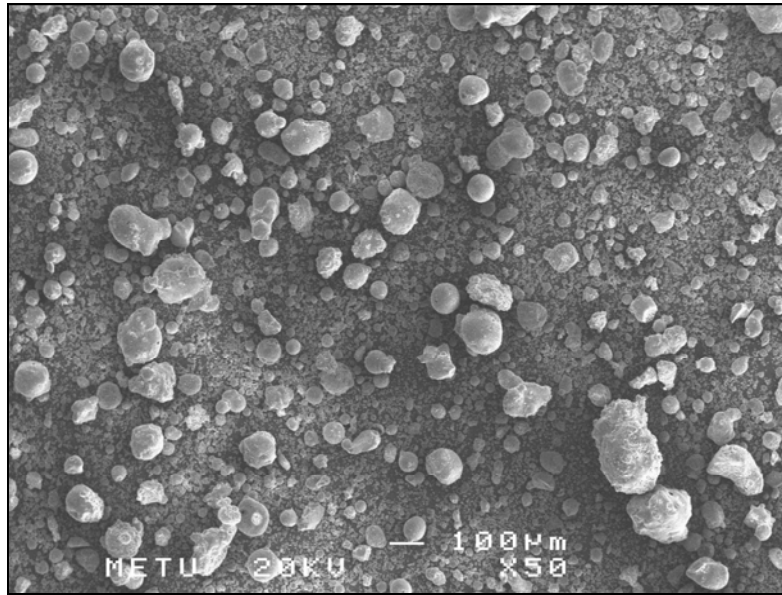
Morphological properties of coal fly ash were determined by the Scanning Electron Microscopy (SEM-JEOL JSM 6400) in the laboratory of Materials and Metallurgical Engineering Department at METU. Fly ash particles mainly contain small, glass-like particles of spherical shape and irregularly shaped particles.

Fly ash particles are morphologically heterogeneous, showing a wide variation of particles shapes densities. Differences in morphology can be generally correlated to the differences in the coal used. Spherical particles make up most of the fly ash particles, especially in finer fractions. These are glassy and mostly transparent, indicating complete melting of silicate minerals.

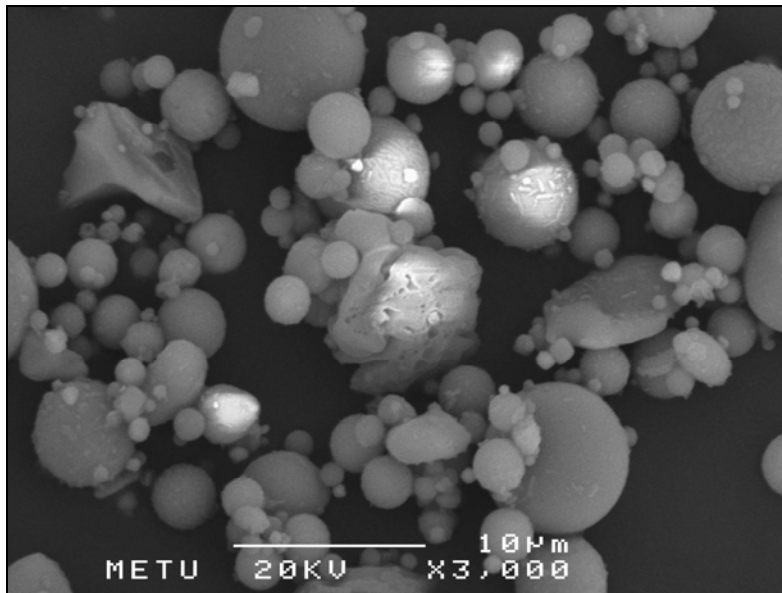
Generally, besides some amorphous and crystalline parts, non-opaque cenosphere (hollow) and plerosphere (filled with micro spheres) dominate the morphology in finer size fractions of fly ash particles. The crystals present in ash particles may be acicular, elongated or irregularly shaped. Generally, larger particles show a greater irregularity compared to smaller ones.

Opaque amorphous particles predominantly arise from coal components that were not combusted completely. Complete opaque spheres are mostly magnetite or other iron oxides, alone or in combination with silicates. Non-opaque particles are mostly silicates derived from clays and siltstones associated with the coal.

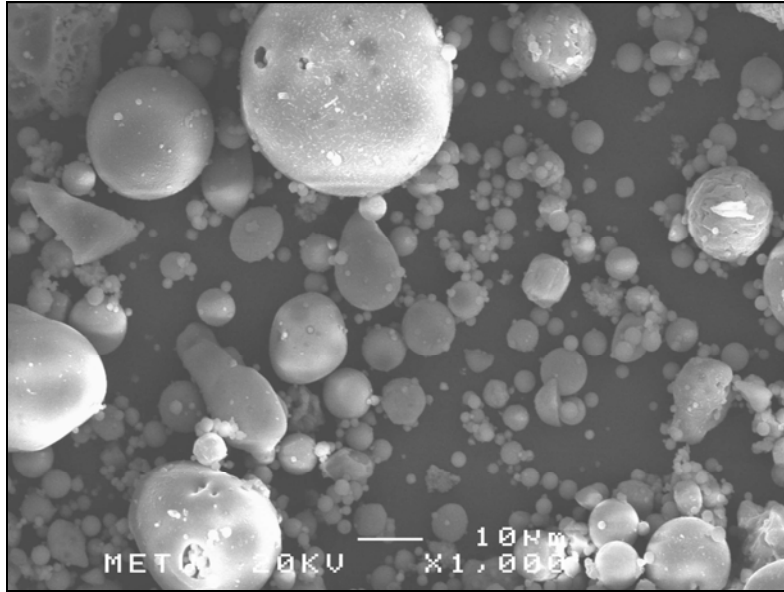
Results of the XRD analysis shows that the more than half of the fly ash composition is occupied by silica, so non-opaque sphere particles in fly ash are the silica particles. Complete opaque spheres are mostly aluminum and iron oxide compounds. Elemental analysis of the plerospheres type of particles of Figure 8 is given in Table 19 and Figure 11.



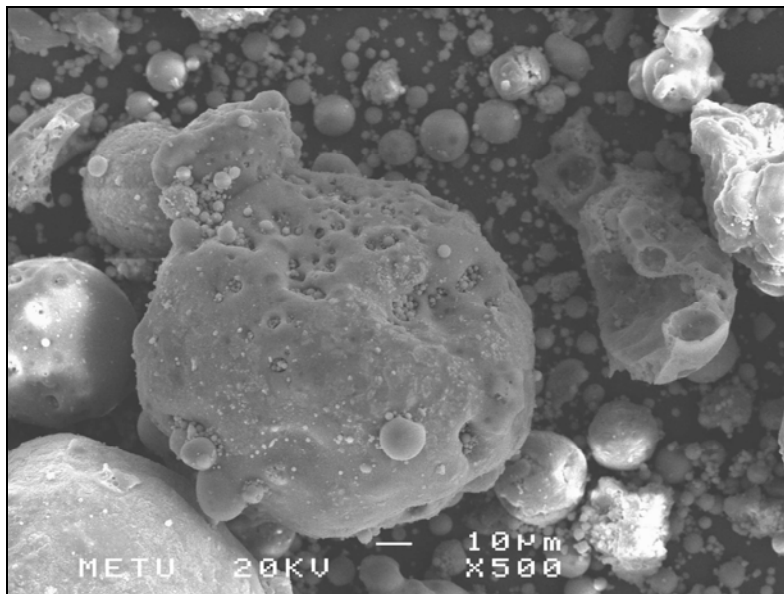
**Figure 6.** General view of fly ash particles



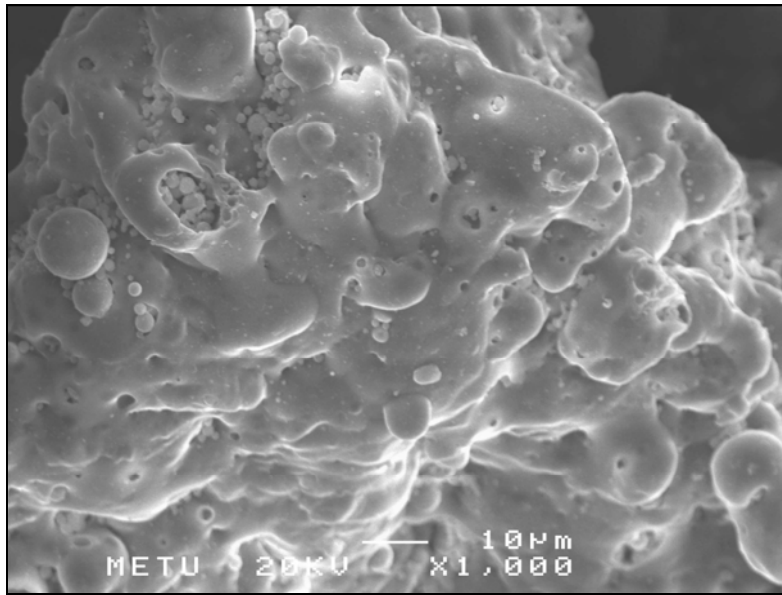
**Figure 7.** General view of fly ash particles



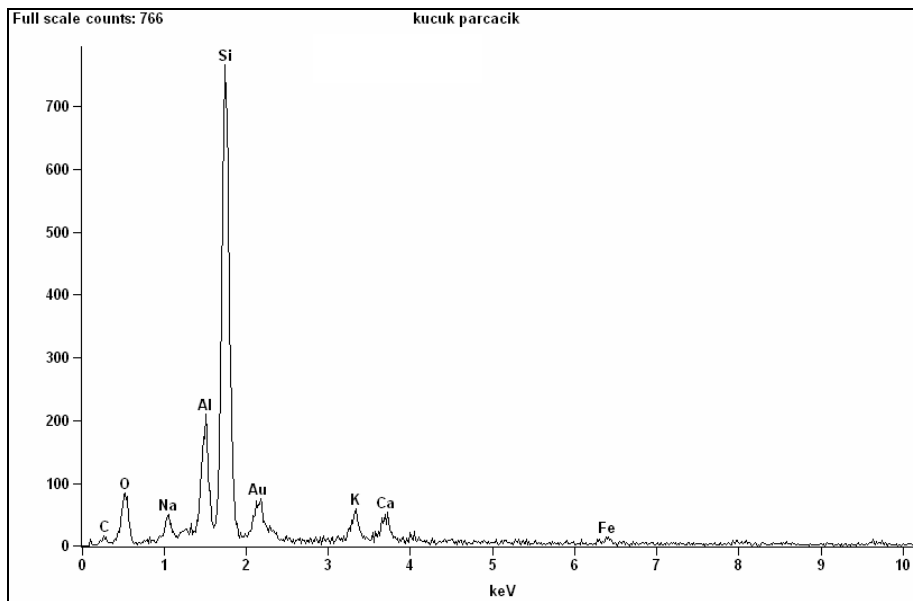
**Figure 8.** Spherical, glass like particles



**Figure 9.** Non-opaque, spongy, hollow spherical particle



**Figure 10.** Non-opaque, spongy particle



**Figure 11.** Elemental analysis of glass like particle

**Table 19.** Elemental analysis of glass like particle

<b>Element</b>	<b>Weight Content. %</b>	<b>Atomic Content. %</b>	<b>Compound Content. %</b>	<b>Formula</b>
O	48.34	62.76	0.00	
Na	3.46	3.13	4.67	Na <sub>2</sub> O
Al	7.12	5.48	13.45	Al <sub>2</sub> O <sub>3</sub>
Si	33.75	24.96	72.20	SiO <sub>2</sub>
K	3.17	1.68	3.81	K <sub>2</sub> O
Ca	2.94	1.52	4.11	CaO
Fe	1.23	0.46	1.76	Fe <sub>2</sub> O <sub>3</sub>

### 3.2.5 Porosity Measurement

Porosity measurement of the CFA was done in Central Laboratory at METU. Because of the powder composition of the fly ash only the pore size distribution of micro pores and total porosity values can be obtained. The macro pore values could not be examined. In other word, the pore size distribution of particles smaller than 100,000 Å (10 µm) were obtained. Total porosity value is 15.0532 % by volume.

The operation of mercury porosimeters depends on the physical principle that a non-reactive, non-wetting liquid will not penetrate fine pores until sufficient pressure is applied to force its entry. The relationship between the applied pressure and the pore diameter is given by the Laplace equation:

$$D = (-4\gamma \cos\theta) / P$$

Where P is applied pressure, D is pore diameter,  $\gamma$  is surface tension of mercury (480 dyne/cm), and  $\theta$  is the contact angle between mercury and pore wall (usually 140°). The mercury intrusion data is useful for generation of pore size/volume distributions. The pore size distribution is given in Figure 12.





**Figure 12.** Specific volume vs. pore size histogram

### 3.2.6 Specific Surface Area Measurement (BET)

The specific surface areas of different sizes of coal fly ash were determined by single point BET nitrogen adsorption method with the equipment of Micromeritics Flowsorb II 2300. The aim of specific surface area measurement was to determine the surface areas and surface area changes with respect to the different size fraction of coal fly ash sample. Measurements were done in three size fractions: +300  $\mu\text{m}$ , -300+212  $\mu\text{m}$  and -75+53  $\mu\text{m}$ , respectively. It is commonly known that the specific surface area, increases as the particle size decreases. But this is not the case for the coal fly ash sample. The greatest specific surface area was measured in the +300  $\mu\text{m}$  size fraction. The reason for the decreasing of specific surface with the decreasing of particle size in this case would be the lack of porosity in smaller size fractions. Specific surface areas of three sizes of fly ash samples were given in Table 20.

**Table 20** The specific surface area adsorption results of coal fly ash

Sample		Adsorption Value ( $\text{m}^2$ )	Sample Weight (gr)	Specific Surface Area ( $\text{m}^2/\text{g}$ )
Size Fraction	Geometric Mean			
+ 300 micron	300 micron	1.77	0.8437	2.0979
-300+212 micron	250 micron	0.58	1.0608	0.5467
-75+53 micron	63 micron	0.25	0.6445	0.3879

### **3.3 Methods**

#### **3.3.1 Adsorption Experiments**

In this research three metal salts were used as heavy metal source: copper chloride ( $\text{CuCl}_2$ ), zinc chloride ( $\text{ZnCl}_2$ ) and lead chloride ( $\text{PbCl}_2$ ). From these metal salts synthetic solutions were prepared. The working ppm levels were 10 ppm, 50 ppm and 100 ppm for each of these metals. Experiments were carried out in 200 ml beakers with 100 ml metal solutions, varying fly ash amounts and time values. The prepared solutions were treated with 1 g, 2 g, 4 g, and 8 g of fly ash, that is, solid/liquid (fly ash/metal solution) ratios were 1 %, 2%, 4 %, and 8 % respectively for different treatment durations (5 min, 10 min, 30 min, 60 min). The treatment processes were carried out by magnetic stirrer for those particular durations. At the end of this period, the final or equilibrium concentrations of filtrated solutions were measured by ATOMSPEK H1580 Analytical Instrument.

#### **3.3.2 Precipitation Experiments**

Precipitation experiments were carried out by changing the pH values of solutions, to evaluate the metal precipitation at the pH values during the metal removal with fly ash tests. In adsorption experiments, the effects of time and fly ash amount on heavy metal removal were observed in natural pH values, whereas in the precipitation experiments, the pH values of the solutions were changed by addition of NaOH. It is known that particular metals have different stability zones in different pH values; hence, it was aimed to observe the dramatic decrease in total dissolved metal concentrations by precipitation by changing (increasing) the pH of the waste water solutions, in the absence of fly ash. The copper, zinc and lead chloride solutions with initial concentration of 10 ppm, 50 ppm, and 100 ppm were treated with the addition of NaOH. Then the solutions were filtered and the final or

equilibrium concentrations of filtrates were measured by ATOMSPEK H1580. Initial (natural) pH values of solutions are presented in Table 21.

**Table 21** Initial (natural) pH values of solutions

ppm Values	pH		
	Cu <sup>++</sup>	Zn <sup>++</sup>	Pb <sup>++</sup>
10	6	6.3	6.4
50	5.7	6	5.7
100	5.5	5.9	5.6

**Table 22.** Different pH values studied

Metal ion	pH values		
	10 ppm	50 ppm	100 ppm
Cu <sup>++</sup>	6	5.7	5.5
	8.2	6.9	5.8
	9.8	10.4	6.2
	10.7	11.3	9.9
	11.7	11.7	11.9
Zn <sup>++</sup>	6.3	6	5.9
	8.4	7.3	8
	9.5	9	10.6
	9.9	11.4	11.6
	11.5	11.8	11.8
Pb <sup>++</sup>	6.4	5.7	5.6
	9.9	9.8	9.1
	10.3	10.3	10.1
	10.8	11	10.8
	11.2	11.7	11.2

The initial pH values were changed by addition of NaOH for precipitation experiments, and examined pH values are given in Table 22.

### **3.3.3 Desorption Experiments**

The desorption (metal release) stage of the experimental series is related with the metal retention capacity of the fly ash which is used in the adsorption experiments described above. Desorption experiments were carried out only at the level of 100 ppm which is naturally the most acidic pH level of the studied ppm levels in adsorption experiments. Experiments were carried out in two stages; the first of which is the metal removal from 100 ppm (Cu, Zn, Pb) metal containing solutions with 2 gr of fly ash. After filtration and drying of fly ash, the second stage whereby 2 grams of fly ash (used in adsorption) was treated, that is, agitated for 10 hours and subjected to metal analysis periodically at 2<sup>nd</sup>, 6<sup>th</sup> and 10<sup>th</sup> hours, in 100 ml double distilled water.

## CHAPTER 4

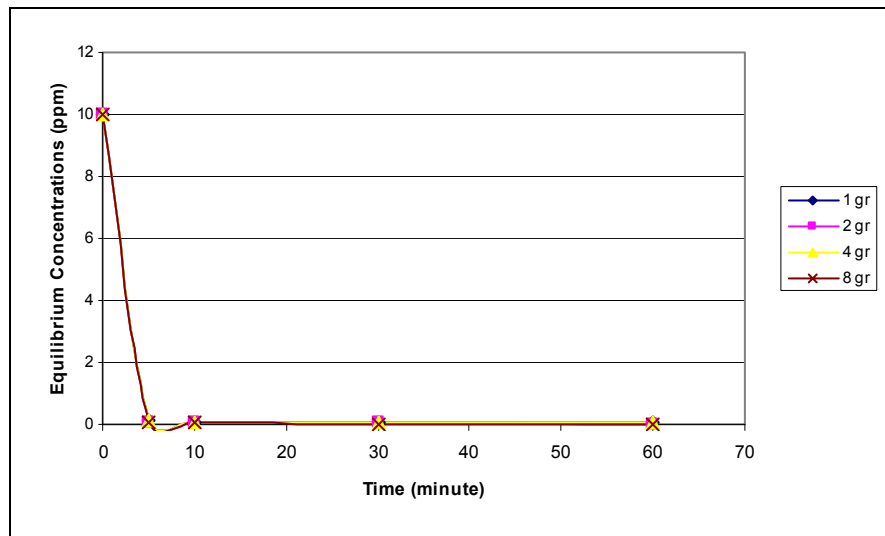
### RESULTS AND DISCUSSION

#### 4.1 Effect of Time on Metal Removal

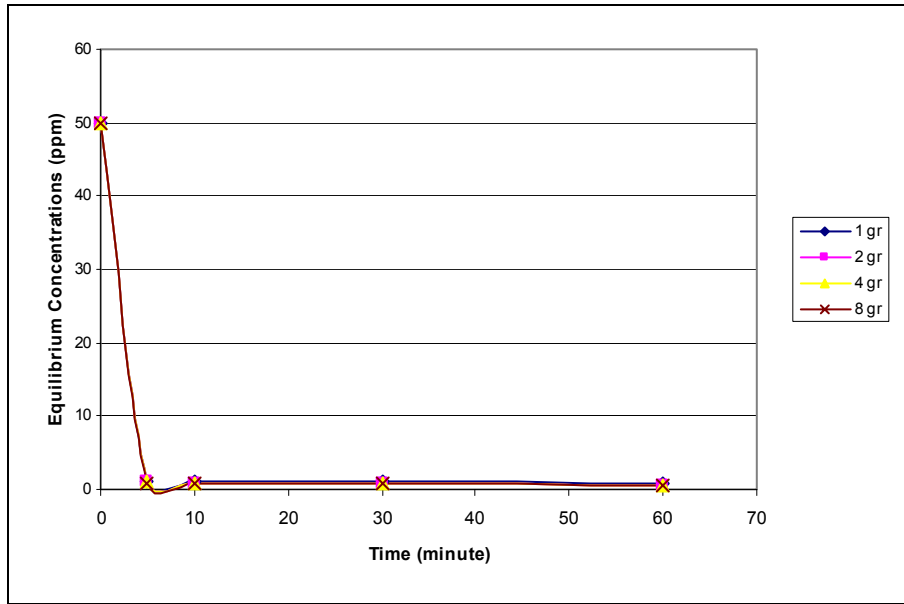
In general, in all three concentrations levels (10, 50, and 100 ppm) of metals (copper, zinc, and lead), there is a decrease in total metal ion concentration with time. However, the noticeable or sharp decrease in metal ions occurs within the first 7.5 minutes. After that there is a gradual decrease in metal ions. Copper metals show better removal characteristics compared to the other metals. At the same ppm levels; namely, 10 ppm copper and 10 ppm zinc and lead, 50 ppm copper 50 ppm zinc and lead, 100 ppm copper and 100 ppm zinc and lead, copper concentration was well decreased in compared to the other two metals (zinc and lead). Because of the basic character of the ppm levels there is also precipitation in addition to the adsorption mechanism.

It is obviously seen in Figures 13-21 that time has positive effects on the removal of copper ions for all levels of fly ash addition (1, 2, 4, 8 gr) studied. At low concentration level (10 ppm) copper metal removal occurred in first 7 minutes after that minutes there is no significant change in metal concentrations (Figure 13). And also, at concentration level of 50 ppm copper, the metal removal process occurred in first 7 minutes (Figure 14).

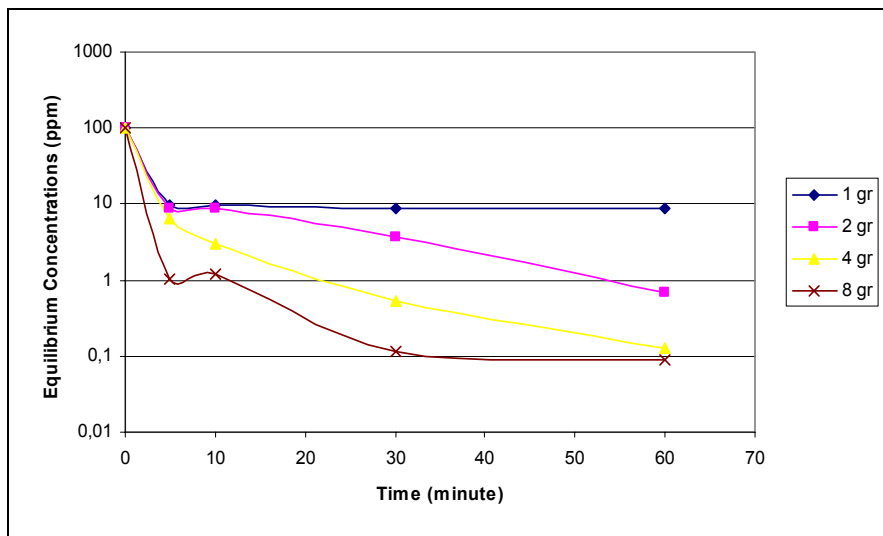
100 ppm copper solution level also showed the expected result in which the reduction of metal ions is in good proportion with time and added fly ash amount (Figure 15).



**Figure 13.** Effect of time on the equilibrium concentration of initially 10 ppm copper solution



**Figure 14.** Effect of time on the equilibrium concentration of initially 50 ppm copper solution

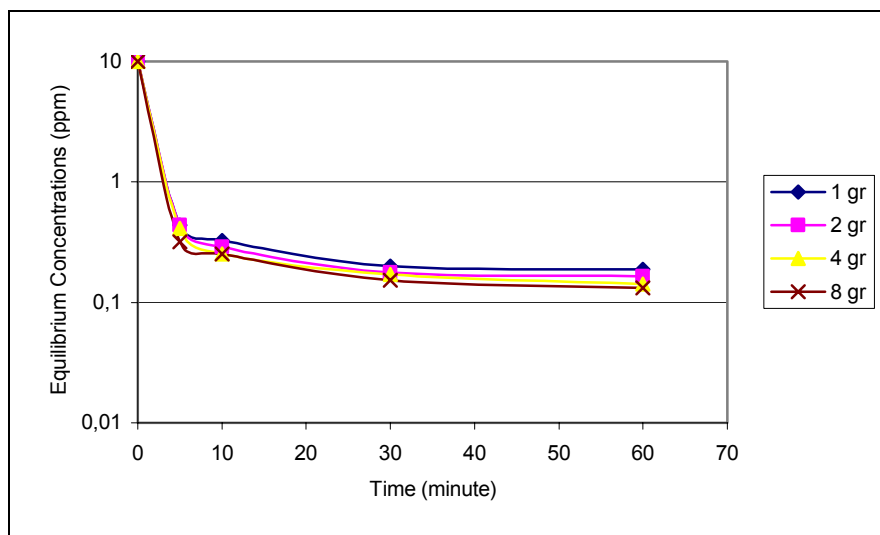


**Figure 15.** Effect of time on the equilibrium concentration of initially 100 ppm copper solution

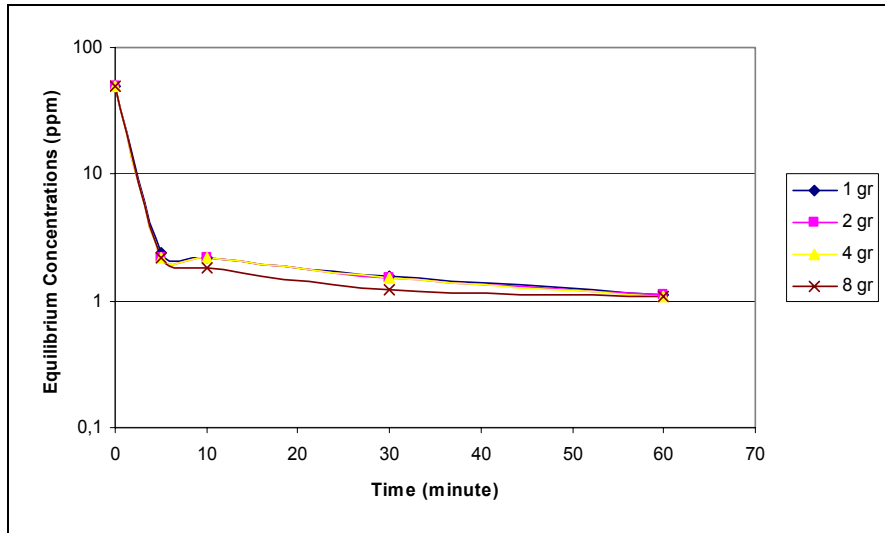


As in the case of copper metal, for zinc and lead, time has positive effects on the removal of zinc and lead metallic ions for all gram levels (1, 2, 4, 8 g) studied.

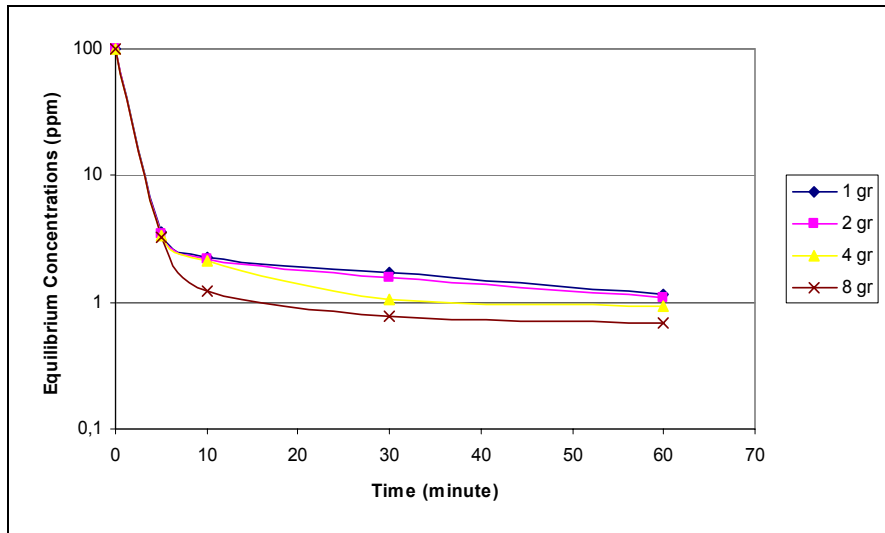
In the studied levels of 10, 50 and 100 ppm the expected results were obtained. There is direct decreasing of zinc and lead metal ion concentrations with time and fly ash amount. The reduction of metal ions is proportional to time and added fly ash amount. 8, 4, 2 and 1 g of fly ash amounts show the adsorption in decreasing order (Figures 16-21).



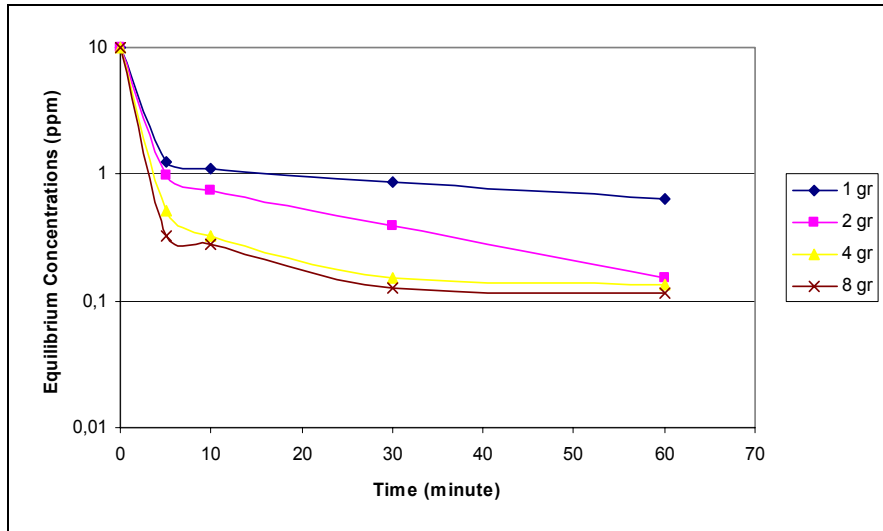
**Figure 16.** Effect of time on the equilibrium concentration of initially 10 ppm zinc solution



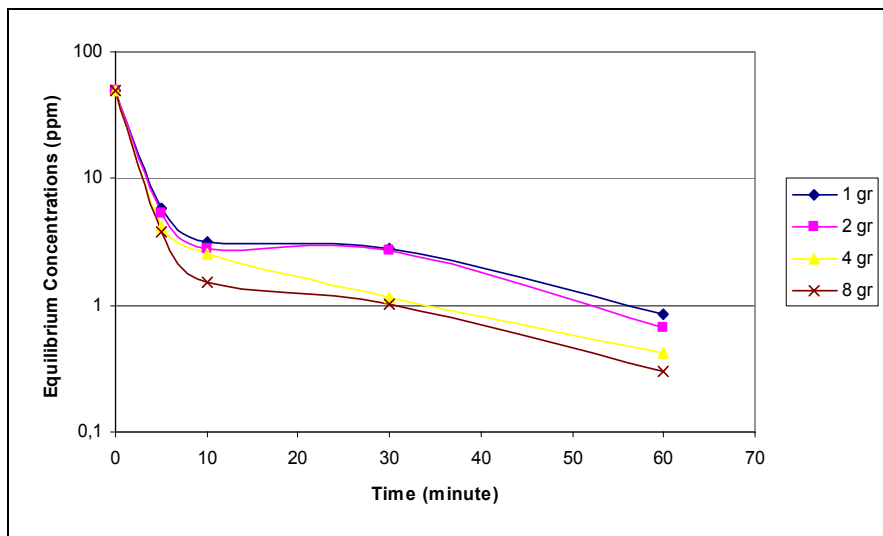
**Figure 17.** Effect of time on the equilibrium concentration of initially 50 ppm zinc solution



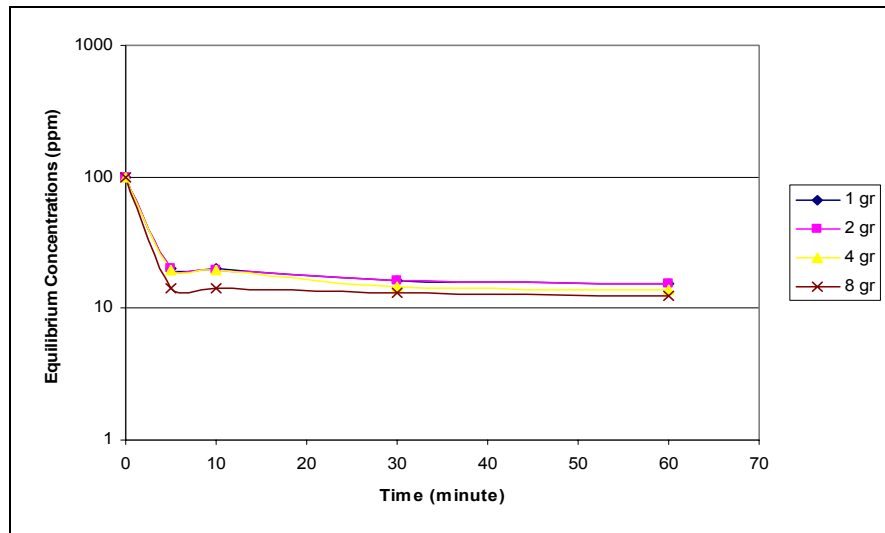
**Figure 18.** Effect of time on the equilibrium concentration of initially 100 ppm zinc solution



**Figure 19.** Effect of time on the equilibrium concentration of initially 10 ppm lead solution



**Figure 20.** Effect of time on the equilibrium concentration of initially 50 ppm lead solution

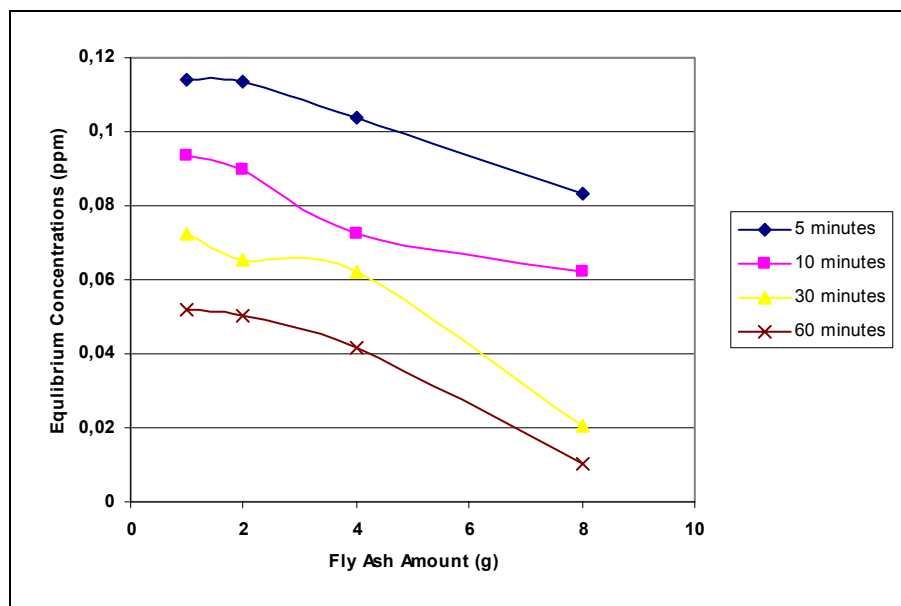


**Figure 21.** Effect of time on the equilibrium concentration of initially 100 ppm lead solution

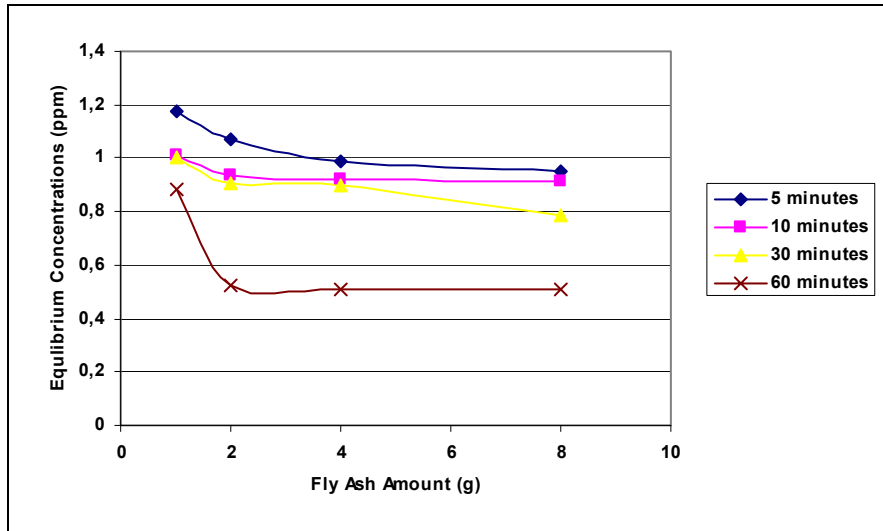
#### 4.2 Effect of Fly Ash Amount on Metal Removal

The effect of fly ash amount and effect of time on metal removal should be considered together. In effects of time on the experiments' arguments, the effect of fly ash amount was also examined. The resulting figures (Figures 22-30) of particular fly ash amount levels (1, 2, 4, 8 gr) shows metal removal from solutions in these studied fly ash amount levels. In general, fly ash amount has positive effects on removal of metallic ions from synthetic waste water solutions. Fly ash amount is inversely proportional with the metal concentrations in the solutions. While the fly ash amounts increases the initial metal concentrations of synthetic waste water decreases. Furthermore it was seen that 10 minutes' agitation showed the lowest removal of metals from waste water, whereas; 60 minutes agitation showed the best removal in total metal concentrations in all agitation levels for all three metals.

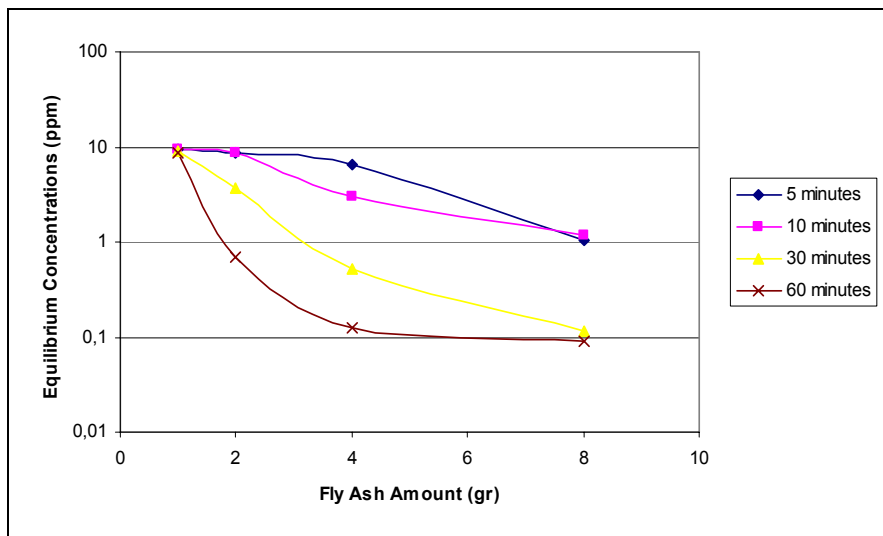
At 10, 50 and 100 ppm concentrations of copper that were studied, there is a decrease of metallic ions concentrations with the added fly ash amount. From the figures 22, 23 and 24 the decrease in initial metal concentration levels (10, 50, and 100 ppm copper) can be seen.



**Figure 22.** Effect of fly ash amount on the equilibrium concentration of initially 10 ppm copper solution

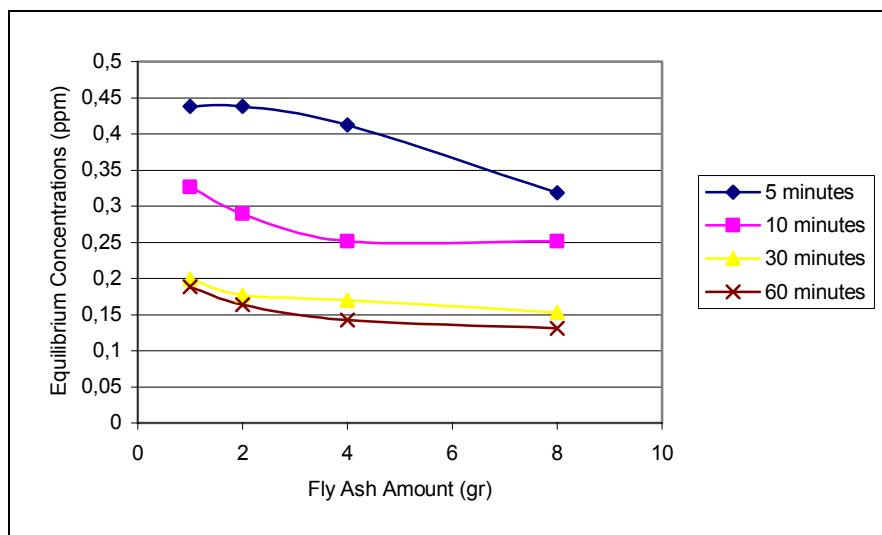


**Figure 23.** Effect of fly ash amount on the equilibrium concentration of initially 50 ppm copper solution

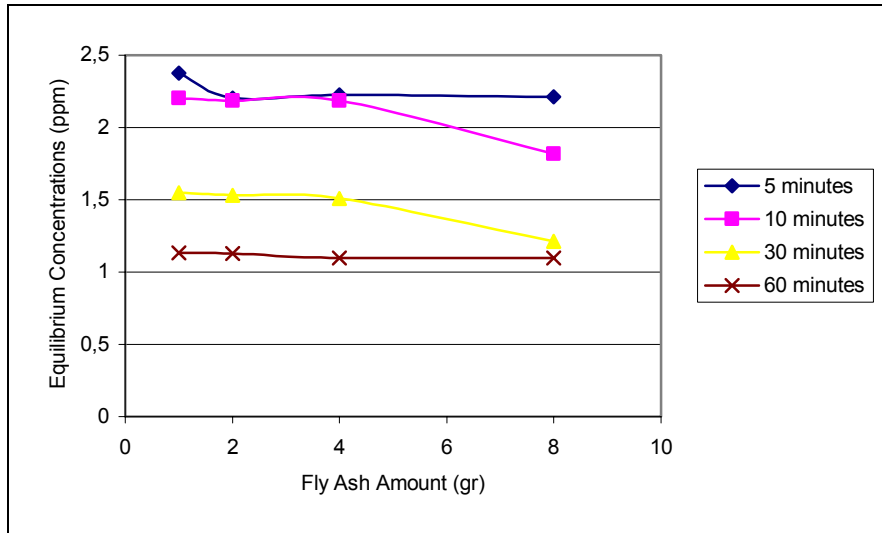


**Figure 24.** Effect of fly ash amount on the equilibrium concentration of initially 100 ppm copper solution

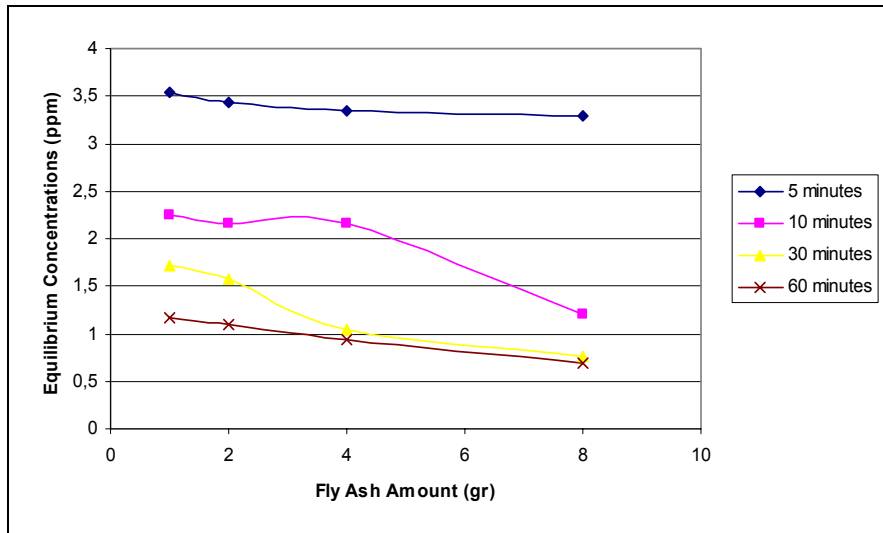
In Figures 25-30 pertaining to the zinc and lead experiments there is a decrease in equilibrium concentrations of zinc and lead ions in all three ppm levels (10, 50, and 100 ppm), whereby while the fly ash amount increases, the metal concentration of waste water' decreases.



**Figure 25.** Effect of fly ash amount on the equilibrium concentration of initially 10 ppm zinc solution

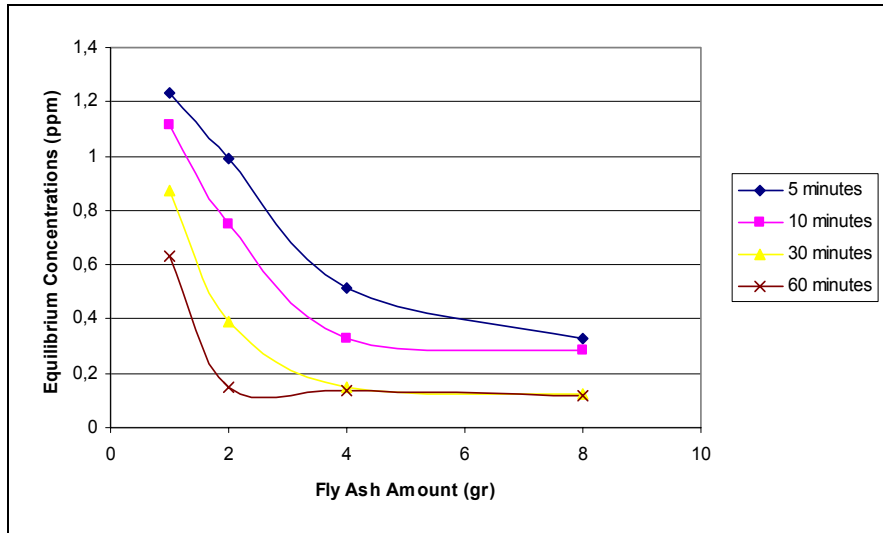


**Figure 26.** Effect of fly ash amount on the equilibrium concentration of initially 50 ppm zinc solution

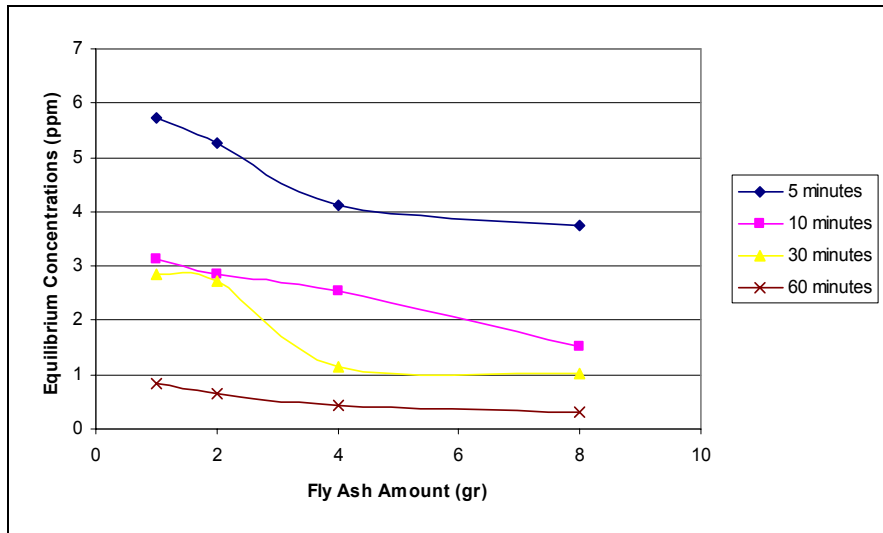


**Figure 27.** Effect of fly ash amount on the equilibrium concentration of initially 100 ppm zinc solution

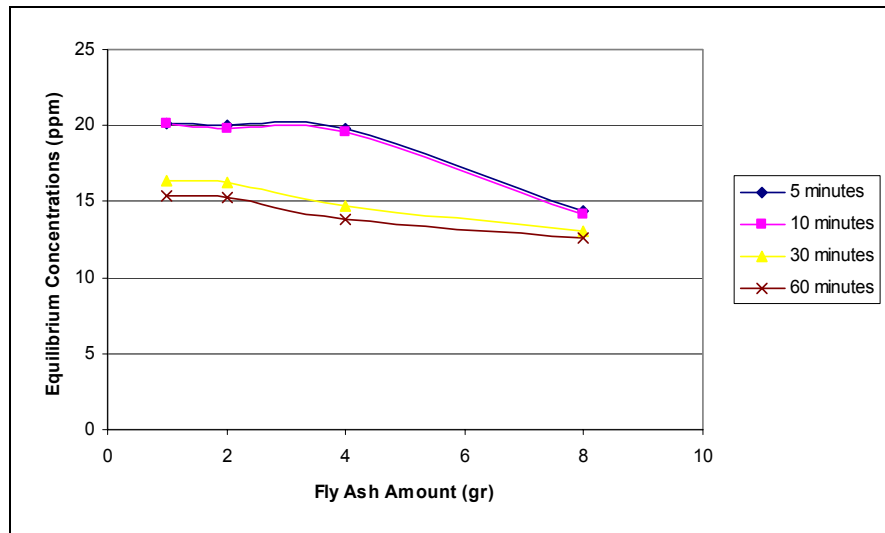




**Figure 28.** Effect of fly ash amount on the equilibrium concentration of initially 10 ppm lead solution



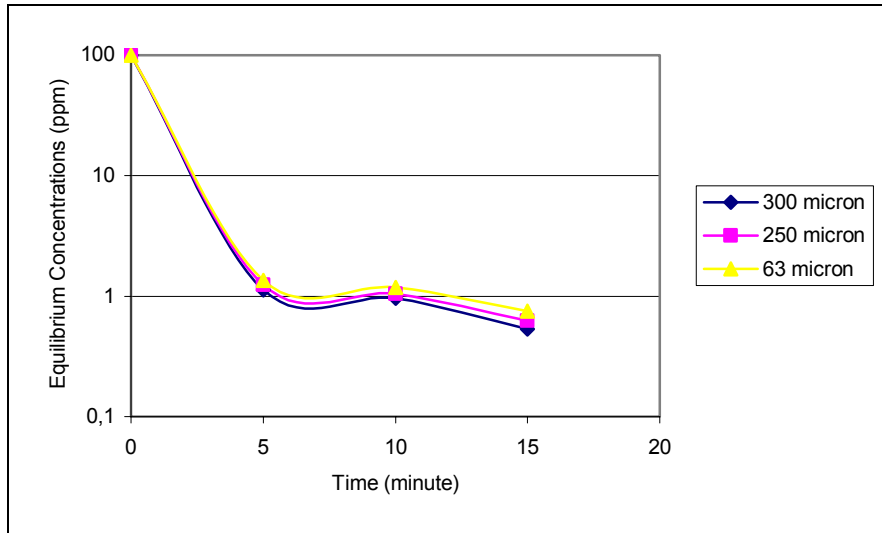
**Figure 29.** Effect of fly ash amount on the equilibrium concentration of initially 50 ppm lead solution



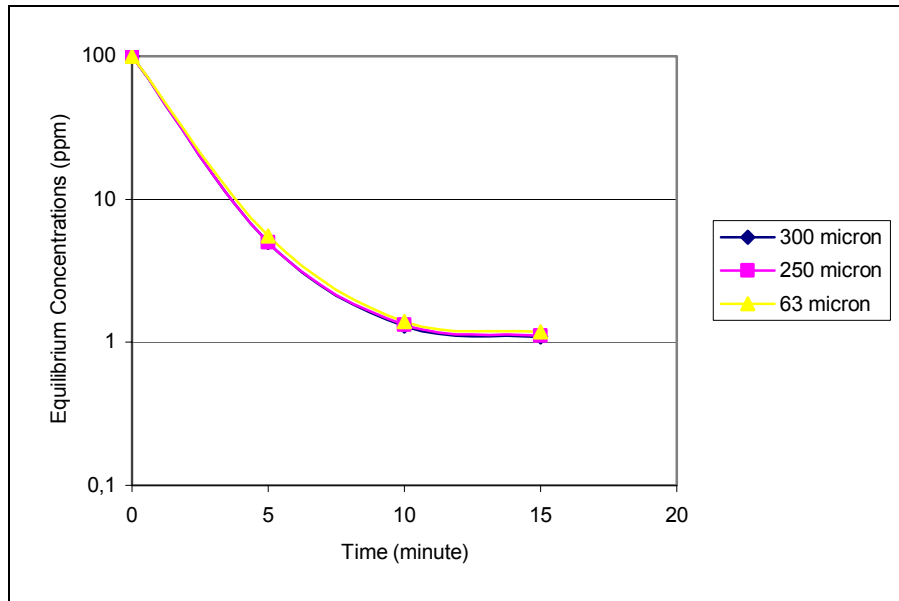
**Figure 30.** Effect of fly ash amount on the equilibrium concentration of initially 100 ppm lead solution

### 4.3 Effect of Particle Size on Metal Removal

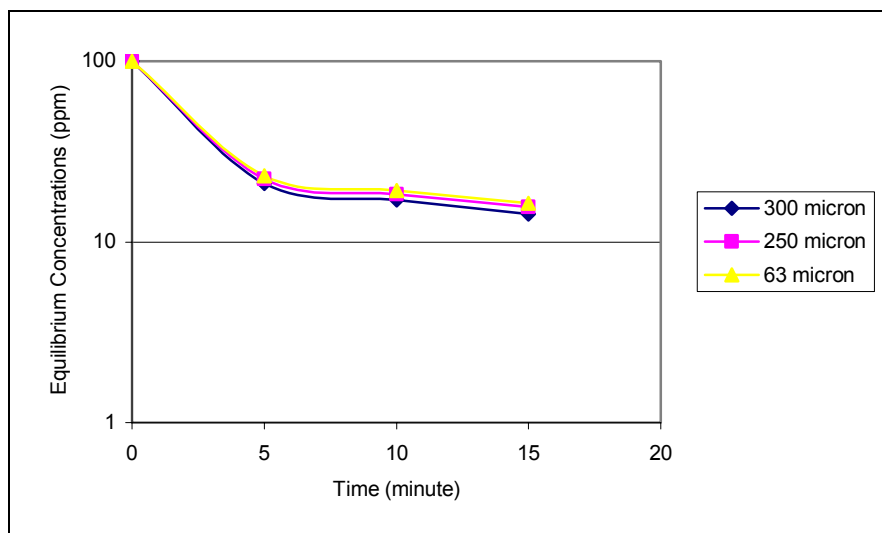
Experiences dictate that there is no significant effect of particle size of fly ash on the removal of heavy metal ions from synthetic waste waters. The decrease in metal ions concentration at the first 5 minutes of treatment was very sharp. Figures 31-33 show the effect of particle size on the removal of metallic ions for copper, zinc, and lead, respectively.



**Figure 31.** Effect of particle size on the removal of copper ions from 100 ppm copper solution after 15 minutes' treatment with 8 gr fly ash



**Figure 32.** Effect of particle size on the removal of zinc ions from 100 ppm zinc solution after 15 minutes' treatment with 8 gr fly ash

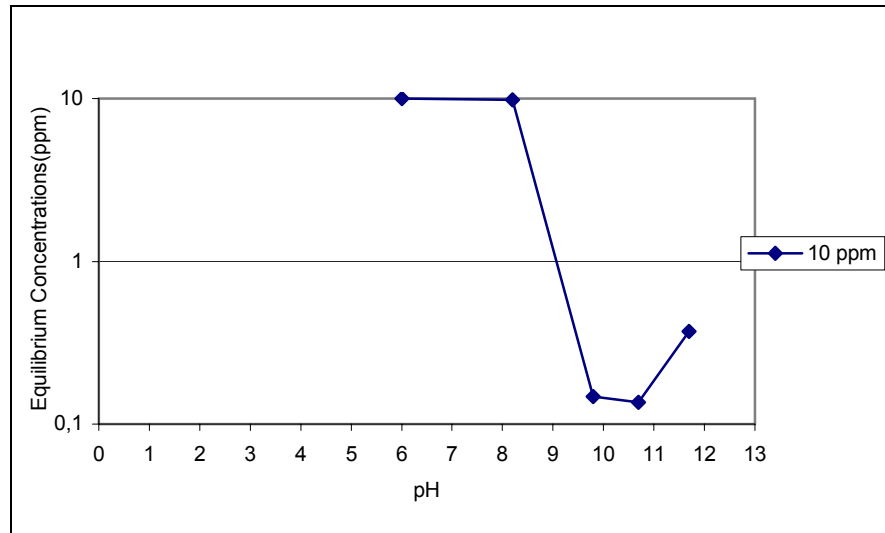


**Figure 33.** Effect of particle size on the removal of lead ions from 100 ppm lead solution after 15 minutes' treatment with 8 gr fly ash

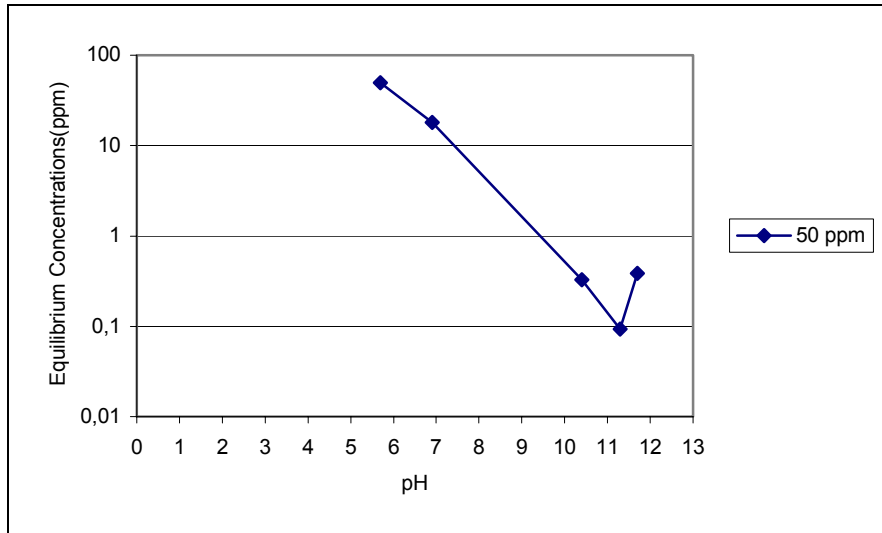
#### 4.4 Effect of pH on Metal Removal

Fly ash has an alkaline property and it provides for the precipitation of metallic ions. At alkaline pH levels, metal ions tend to precipitate and for this reason, the effect of the adsorption mechanism is clearly seen in acidic pH values. In this study natural pH levels of 10, 50, and 100 ppm Cu, Zn and Pb solutions after 1, 2, 4, and 8 gr fly ash treatment for 15 minutes were measured (Table 23). In addition to this, precipitation tests were also carried out to check studied metals' (Cu, Zn, Pb) stability zones and to compare adsorption and precipitation characteristics. The initial pH values (Table 21) of solutions, were changed by addition of NaOH and solutions were agitated for 15 minutes after addition of NaOH, nearly the all metal ions removal were occurred. It is understood that for all ppm levels and metals in general, copper shows a tendency to precipitate between pH 8-11, zinc between pH 9.5-11, and lead between pH 10-11. Between these pH ranges (Table 23), Cu, Zn, and Pb metal are in the form of Me-OH and they results in the reduction of total

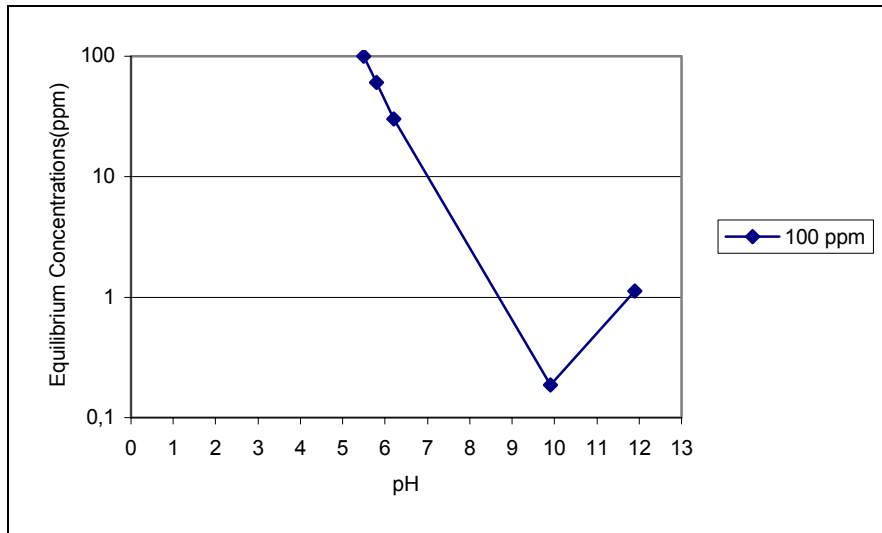
dissolved metal ions in solutions. The results of precipitation tests are given in Figures 34-42.



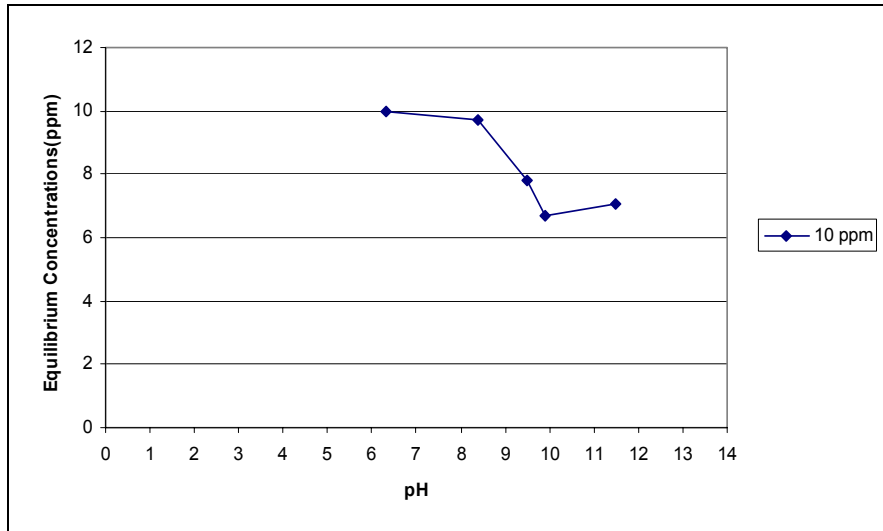
**Figure 34.** Effect of pH on the equilibrium concentration of initially 10 ppm copper solution



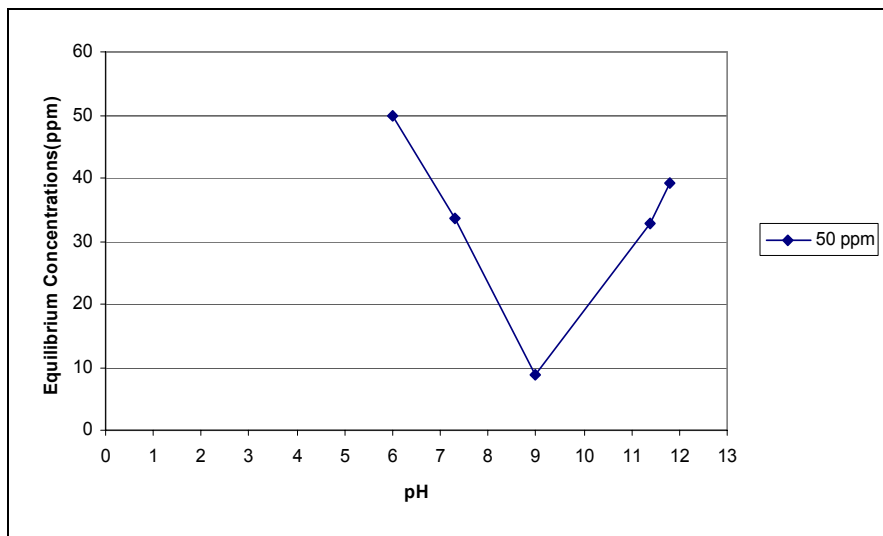
**Figure 35.** Effect of pH on the equilibrium concentration of initially 50 ppm copper solution



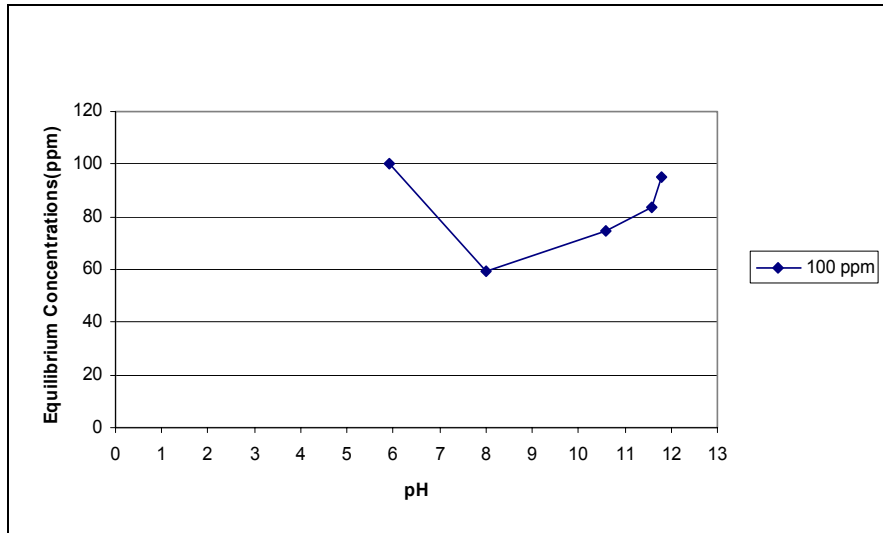
**Figure 36.** Effect of pH on the equilibrium concentration of initially 100 ppm copper solution



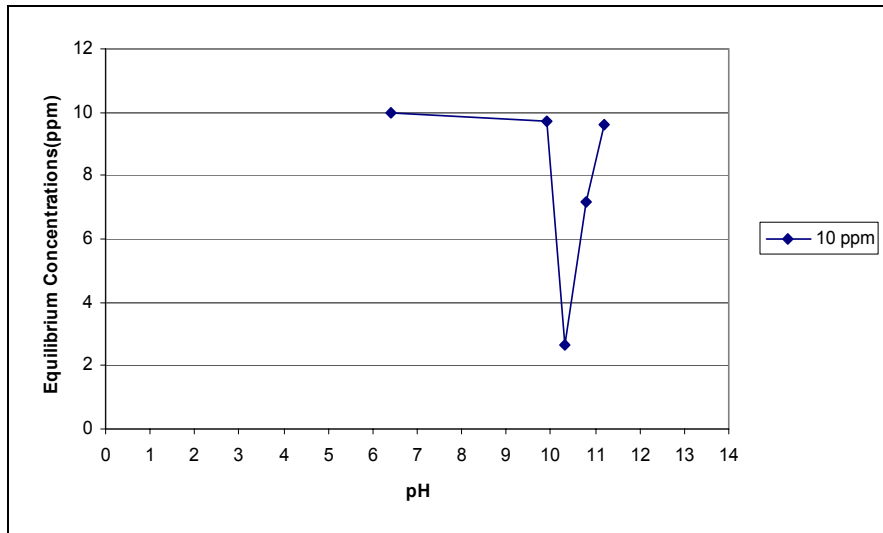
**Figure 37.** Effect of pH on the equilibrium concentration of initially 10 ppm zinc solution



**Figure 38.** Effect of pH on the equilibrium concentration of initially 50 ppm zinc solution

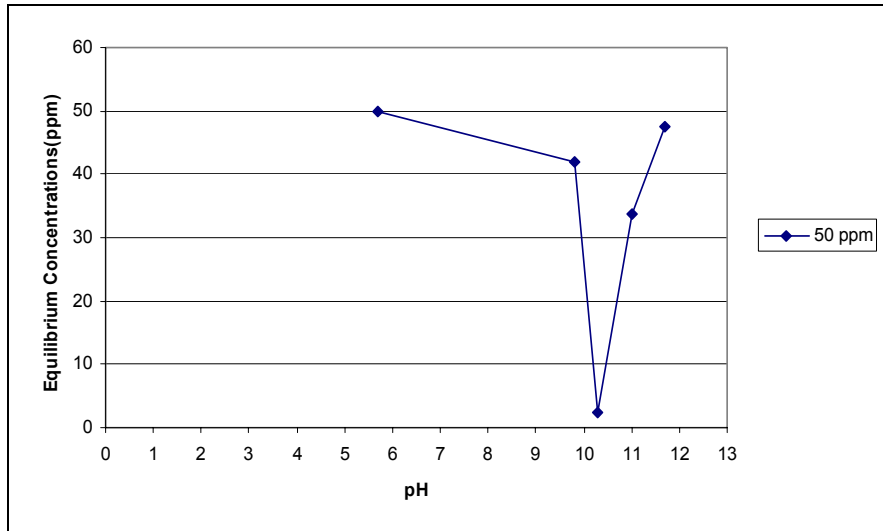


**Figure 39.** Effect of pH on the equilibrium concentration of initially 100 ppm zinc solution

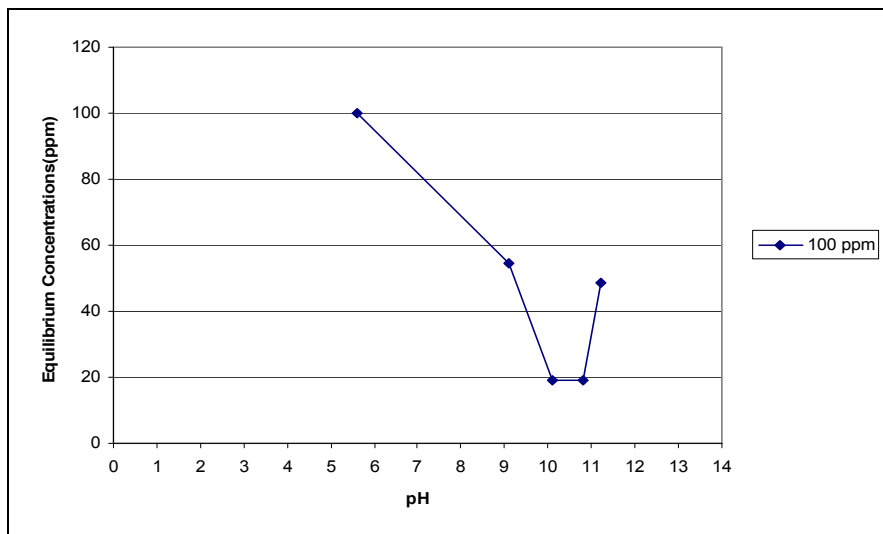


**Figure 40.** Effect of pH on the equilibrium concentration of initially 10 ppm lead solution





**Figure 41.** Effect of pH on the equilibrium concentration of initially 50 ppm lead solution



**Figure 42.** Effect of pH on the equilibrium concentration of initially 100 ppm lead solution

**Table 23.** pH ranges of solutions after treatment with different amounts of fly ash

pH range of measured ppm levels of Copper solution after treatments	
ppm levels	pH
10 ppm	10,5-11,5*
50 ppm	8,5-9,5*
100 ppm	6,5-7,5
pH range of measured ppm levels of Zinc solution after treatments	
ppm levels	pH
10 ppm	10,5-11,5
50 ppm	8-9*
100 ppm	6,3-7,3
pH range of measured ppm levels of Lead solution after treatments	
ppm levels	pH
10 ppm	10,5-11,5
50 ppm	8-9
100 ppm	6,5-7

- = there is a possibility of precipitation of metal ions (or decreasing the concentration of total dissolved metal ions in solution) in addition to adsorption by fly ash.
- Treatment duration is 15 minutes

#### **4.5 Effect of Time and Fly Ash Amount on the pH of Distilled Water**

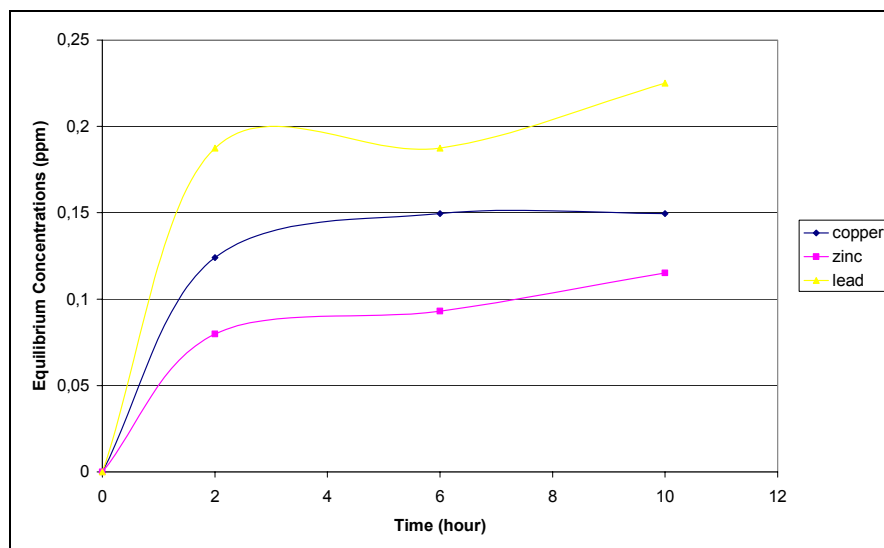
The effect of agitation time and fly ash amount on the double distilled water show the alkaline property of the fly ash. With the increasing of agitation time (treatment of distilled water with fly ash only) the pH of the distilled water also increase Table 24 show the variances of pH of distilled water with ash amount and agitation time.

**Table 24.** Effect of time& ash amount to the pH of distilled water

<b>Time(minutes)</b>	<b>Fly Ash Amount(gr)</b>			
	<b>1</b>	<b>2</b>	<b>4</b>	<b>8</b>
<b>0</b>	6.6	6.6	6.6	6.6
<b>5</b>	10.7	11	11.2	11.5
<b>10</b>	10.9	11.2	11.4	11.5
<b>30</b>	11	11.3	11.5	11.6
<b>60</b>	11	11.3	11.5	11.6

#### **4.6 Results of Desorption Experiments**

In the desorption experiments it was observed that the fly ash containing the metal lead released the adsorbed metal more than the other metals. When considering all three metals, it can be said that desorption of heavy metal ions nearly negligible at natural pH of the fly ash added distilled water. The results demonstrated that, heavy metal removal involves stable adsorption and complexation of the metal cations on the reactive surfaces of fly ash. The studied lead ppm level in desorption experiment was 100 ppm, at this high ppm level, a maximum metal release of 0.225 ppm, at the end of the 10-hours agitation is acceptable. The very small percentages of adsorbed metal released during the desorption tests indicated that the metal sequestered in fly ash remains stable over time. Figure 43 show the results of metal release experiments.



**Figure 43.** Result of metal release (desorption) experiments

#### 4.7 Metal Removal test on a Mixture solution

A final test was carried on combined solutions of lead, copper, and zinc metal ions prepared using the soluble salts of these metals. Combined solution was prepared containing 100 ppm of each metal.

In order to elucidate the mechanism of metal removal with fly ash two different procedures described below were followed.

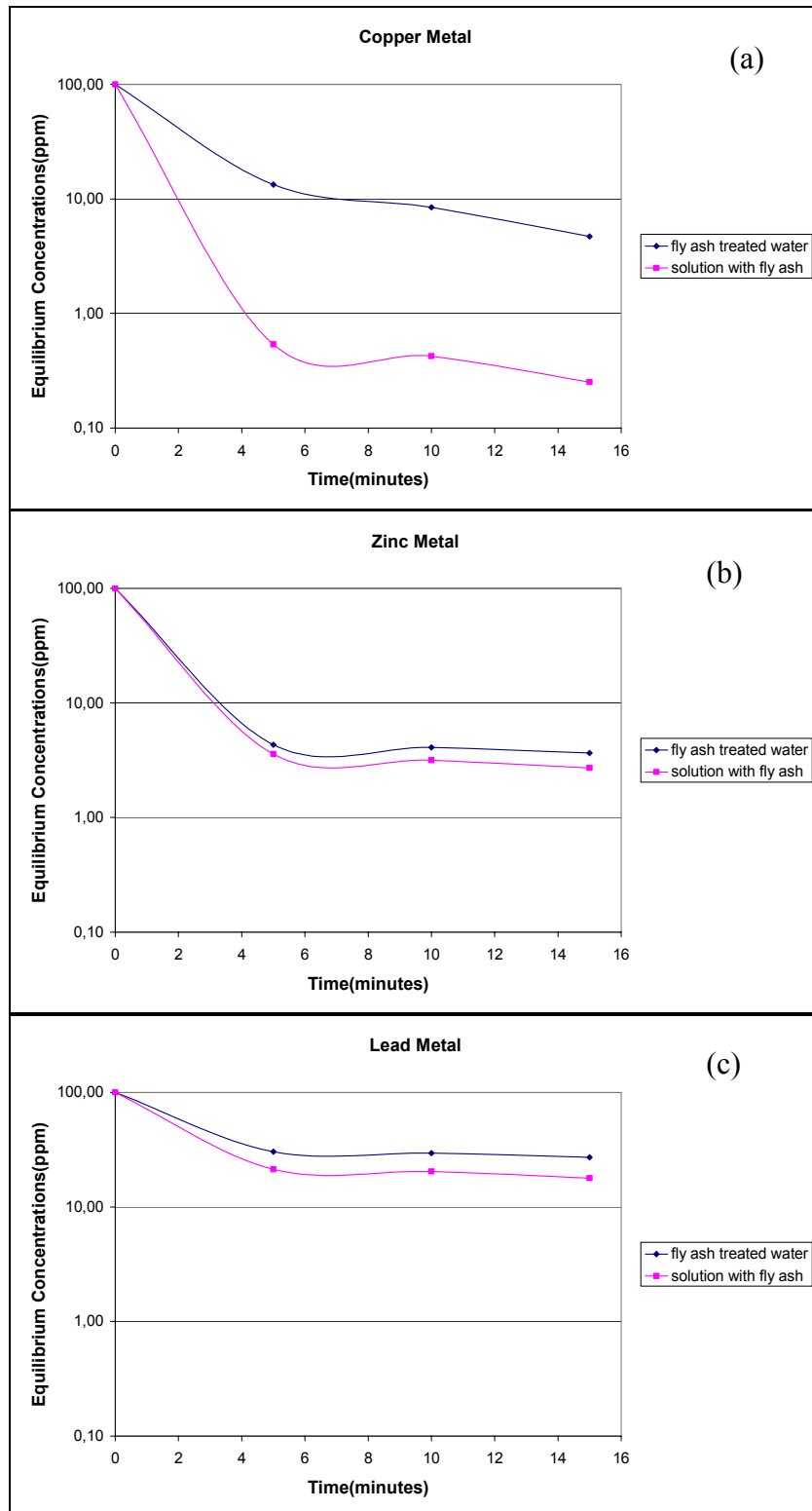
- I. To understand the role of precipitation in metal removal, a fly ash treated water was prepared. For this purpose 80 grams of fly ash was added to a liter of distilled water and agitated for predetermined time intervals of 5, 10, and 15 minutes. The mixture was filtered and a proper amount of metal salts were added into filtrate to obtain 100 ppm concentration for each metal. The metal ions added solution were left to stand for 15 minutes, then

filtered using a filter paper and chemical analysis were performed on the filtrate.

- II. To understand the role of adsorption in metal removal, 8 grams of fly ash added to combined solutions of 100 ppm lead, zinc, and copper. The solution was mixed for 5, 10, and 15 minutes using a magnetic stirrer. After filtration a chemical determination of lead, zinc, and copper ions were performed on the filtrate.

The equilibrium concentrations of all filtrates are plotted in figure 44.

The results of the experimental tests for solutions containing a mixture metals indicated that the dominant mechanism in metal removal was precipitation due to alkaline characteristics of fly ash. The rest of metal removal process is due to adsorptive properties of fly ash. The pores of zeolite content and some particles give fly ash a very high internal surface area available for adsorption. The finding also indicates that fly ash has greater amenability of copper and zinc to removal compared to lead metal. Results confirmed that metal removal from the single metal solution is higher than the metal removal the mixture of metal solutions.



**Figure 44** Equilibrium concentrations of combined solution

## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

Heavy metal removal studies were conducted to investigate to investigate the adsorption capacity of coal fly ash under different conditions and the following conclusions can be drawn from this study.

- Metal adsorption is a very quick process. Although time has positive effects on removal of heavy metals, a sharp decrease in metal concentrations occurs within the first 7.5 minutes.
- The removal of heavy metal ions increases with increasing pH and copper is the most sensitive metal for changing pH among the studied metal ions. At higher pH ranges considerable amount of metal is precipitated in the form of Me-OH and results in reduction of total dissolved metal ions in solution.
- Amount of fly ash has positive effect on removal of heavy metal ions from waste water.
- Although fly ash particle size has no significant effect on removal of heavy metal ions from solutions, the coarser fraction of fly ash exhibited higher metal removal efficiencies than finer fractions. This may be explained by the fact that coarse fractions contain significant amount alumina silicate compounds and porous particles contained therein.

- The results demonstrated that, desorption of heavy metal ions from fly ash nearly negligible at natural pH.
- Çayırhan Thermal power plant's fly ash is able to remove copper, zinc and lead to a level of which are in allowable standards of the Ministry of Environment and Forestry of Turkish Republic.
- From the literature it is understood that, modification of fly ash seems to increase its adsorption capacity. A research related with modification of fly ash is recommended.



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## **APPENDIX A**

### **EXPERIMENTAL PROCEDURE OF ATOMSPEK H1580 ANALYTICAL INSTRUMENT FOR ADSORPTION MEASUREMENTS**

#### **PART 1**

##### **1. General Considerations in Flame Analysis**

The operating range of the Atomspek is from 0-1 Absorbance Unit (A); above 1A readings become uncertain due to noise, and around 1.2A the instrument indicates an over-range reading. The concentrations of solutions required to produce absorption readings within this range depend on the oscillator strength of the particular resonance line chosen, and the number of free atoms present in the flame. As most elements are found to have several resonance lines of different oscillator strengths in the wavelength range 192-854 nm, this first factor allows the operator to select an appropriate line for any particular analysis. The second factor depends on the nature of the element being determined, the temperature and character of the flame employed, the matrix, and the efficiency of the nebuliser.

##### **2. Flame Types**

Much of the early work in AAS was performed with flames using coal gas or propane as the fuel, but more recently it has become standard practice to use Acetylene ( $C_2H_2$ ), together with compressed Air or Nitrous Oxide ( $N_2O$ ) as the oxidant gas. The Air/ $C_2H_2$  flame has a maximum temperature of about 2300°C, while the  $N_2O/C_2H_2$  flame is hotter (up to 2600 °C) and has somewhat different chemical properties. A third type of flame for specific applications uses an

Argon/Hydrogen gas mixture, and draws the oxygen needed for combustion from the surrounding air. It is sometimes referred to as the "Argon/Hydrogen/Entrained Air" flame.

### **3. Sensitivity, Detection Limit, and Working Range**

These three terms are very commonly encountered in AAS. The first two can be rigidly defined as follows:

"Sensitivity is the minimum concentration, in solution, of the element to be determined which will produce a change, compared to pure solvent, of 0.0044 Absorbance Units, that is, 1% absorption, in the optical transmission of the atomic vapour at the wavelength of the resonance radiation".

"Limit of Detection is the minimum amount of an element which can be detected with a 95% certainty. This is that quantity of the element which gives a reading equal to twice the standard deviation of a series of at least ten determinations at or near the blank level."

There is no agreed definition of Working Range, but throughout the manual of Atomspek H1580 this is taken to be from 10 to 200 times the sensitivity. This should give readings from approximately 0.044 to 0.880 A.

### **4. Solution Preparation**

#### **(a) Standards**

The normal chemical supply companies market stock standard solutions which are specially prepared for use in AAS. These are solutions of the pure element in a dilute acid medium, usually molar HCl, HNO<sub>3</sub>, or HClO<sub>4</sub>, and are referred to as "aqueous standards". The stock solutions generally contain one gram of the element per litre of solution, i.e. one milligram per millilitre, equivalent to 1000µg/ml or

1000 ppm. At this concentration level and stabilised with acid, the stock solutions should keep for a considerable period of time.

If a suitable standard is not available, or if the user prefers to make up stock solutions in his own laboratory, the following general points should be noted:

(i) All materials used should be of the purest grade, conforming to normal analytical requirements as a minimum standard. If possible, spectroscopic grade materials should be used.

(ii) Solvents should be of the purest grade. Water should be glass distilled and/or deionised to remove impurities.

(iii) All chemical and volumetric apparatus should be carefully cleaned before use, ensuring that all solid deposits and traces of oil or grease are removed.

(iv) Aqueous standard solutions should be stored in acid-washed polythene containers at an element concentration of 1000  $\mu\text{g/ml}$  or greater. All bottles should be clearly labelled.

(v) All weighings and dilutions should be as accurate as possible, as any error will be reflected in the analytical results subsequently obtained.

(vi) Care should be taken in the handling of the acids and other chemicals used in the preparation of stock standard solutions.

#### (b) Samples

While the Applications Laboratory staff can usually provide a method for dissolving a particular sample matrix, it is acknowledged that the user will have more expert knowledge of the chemistry of his own samples, and may wish to employ existing methods of sample dissolution. We would, however, like to emphasise the following general points :



(i) It is normal practice to prepare solutions at levels from 0.1% to 2% i.e. from 0.1g to 2g dissolved in a volume of 100 mls. Higher concentrations of solid can lead to blockage of the nebuliser and burner.

(ii) The minimum quantity of reagents should be used to dissolve the sample.

(iii) Avoid the use of reagents likely to increase or decrease the viscosity of the sample solution, e.g.  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , methanol, etc. If these reagents cannot be avoided, it is necessary to add an equivalent amount to the standards, or use the method of additions.

(iv) Undissolved solid particles should be removed (by filtering or centrifuging) to avoid blockage of the nebuliser.

(v) Saturated solutions should be avoided as crystallisation may occur in the nebuliser, causing a blockage.

## **5. Setting up the Instrument**

The operator should determine the optimum settings for the determination of each element as follows :

a) Set the fuel flow to give approximately the right flame stoichiometry as directed (Part 2).

b) Optimise the burner height setting to give the maximum reading for an aqueous standard solution, i.e. for best sensitivity. Note the setting.

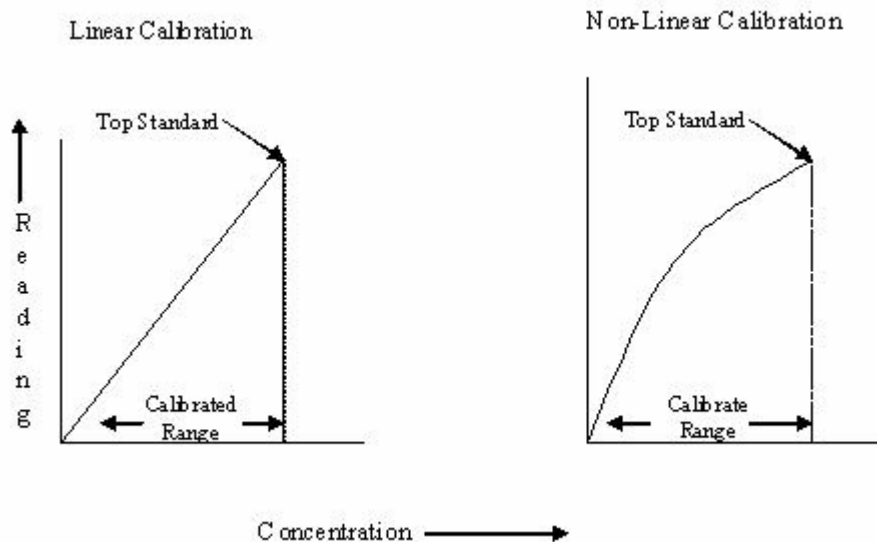
c) Adjust the fuel flow rate to give the maximum reading for the aqueous standard solution, and note the setting.

d) Remember that changing the burner height and/or the fuel flow setting may lead to a change in the baseline, and this should be reset to zero before taking the reading of aqueous standards.

e) The optimum burner height and fuel flow settings for each element should not vary from day to day, so that once these values have been found for a particular element, they can be reset immediately each time that element is to be analysed.

## 6. An Introduction to Analytical Measurements

In all analyses using the Atomic Absorption and Flame Emission techniques, sample solutions of unknown concentration are analysed against standard solutions of known concentration. The readings are obtained when the solutions are aspirated into the required flame. All readings are measured relative to a fixed baseline, obtained by aspirating pure water or a reagent/matrix blank solution. To simplify the calculation of results this baseline may be set to zero. The readings may be obtained using either the Atomic Absorption or the Flame Emission technique. Examples of typical calibration curves are shown below :



For a linear plot the Atomspek may be set up to give direct digital readout in concentration units; for a non-linear plot, curvature correction may be applied for the same effect. This facility is not available with Flame Emission, or when using Automatic Background Correction, and in these cases a calibration graph should be drawn from the observed readings. Alternatively, the programmable Calculator System (A6029) can be used to calculate the results direct from the Atomspek readings. Whichever method is employed to convert the observed sample readings into concentration results, any values outside the calibrated range must be regarded as suspect; the sample should be diluted down or a more concentrated standard prepared.

## **PART 2**

### (a) Stock Standard Solutions

The methods of preparation given should be carried out with great care. If the pure element or the recommended salt is not available, use any pure compound which can be weighed out accurately and dissolved in water or acid

### (b) Instrument Settings

#### (i) Wavelength

The wavelength given is the principal resonance line, that is, the most sensitive available line (lowest characteristic concentration). In a few cases, another line has been found to give a better limit of detection, e.g. when the principal line is only emitted weakly by the lamp.

#### (ii) Lamp Current

The value given is the optimum for current Rank Hilger 2000 Series Hollow Cathode Lamps. Usually, the value is around  $1/2 - 3/4$  of the maximum current on the lamp label. This maximum current rating must not be exceeded.

### (iii) Slit Width

The recommended setting gives the best compromise between sensitivity, linearity, and signal to noise ratio. To improve sensitivity and linearity, a narrower slit width may be used, but a poorer signal to noise ratio may result. To improve the limit of detection, use a wider slit setting. All values refer to the Atomspek H1550, H1551, and H1580 models (having a grating monochromator of reciprocal dispersion 2.6 nm/mm).

### (iv) Flame Type

This is the type of flame giving the best sensitivity.

### (v) Fuel Flow and Burner Height Settings

These spaces have been left blank for the operator to note the optimum values for his own instrument. It is most important to optimise and maintain these settings in order to achieve good analytical results.

### (c) Observed Performance

Space has been allowed here for the operator to note the performance achieved with the optimum operational settings, i.e:

5 ppm → 0.32A, sensitivity = 0.07 ppm

### (d) Lamp Spectrum

The spectrum shown is that obtained from the current Rank Hilger 2000 Series Hollow Cathode Lamp close to the principal resonance line, recorded on a very high resolution Monospek D400 monochromator. Lamps from other manufacturers may give slightly different spectra for some elements because of the use of different materials in the construction of the lamp.

### PART 3

#### Instrument Settings and Typical Performance for Studied Elements

**Table 25.** Instrument settings and typical performance for studied elements for copper

<b>Property</b>	<b>Suggested by Manufacturer</b>	<b>Experimental Settings</b>
Wavelength	324.8 nm	324.8 nm
Lamp Current	4 mA	6 mA
Slit Width	239 $\mu\text{m}$	239 $\mu\text{m}$
Flame Type	Air/C <sub>2</sub> H <sub>2</sub>	Air/C <sub>2</sub> H <sub>2</sub>
Burner Height	4 mm	8 mm
<b>Typical Performance</b>		
Sensitivity	0.03 $\mu\text{g/ml}$	-
Working Range	0.5-10 $\mu\text{g/ml}$	-

**Table 26.** Instrument settings and typical performance for studied elements for zinc

<b>Property</b>	<b>Suggested by Manufacturer</b>	<b>Experimental Settings</b>
Wavelength	213.9 nm	324.8 nm
Lamp Current	5 mA	6 mA
Slit Width	239 $\mu\text{m}$	239 $\mu\text{m}$
Flame Type	Air/C <sub>2</sub> H <sub>2</sub>	Air/C <sub>2</sub> H <sub>2</sub>
Burner Height	4 mm	8 mm
<b>Typical Performance</b>		
Sensitivity	0.005 $\mu\text{g/ml}$	-
Working Range	0.1-2 $\mu\text{g/ml}$	-

**Table 27.** Instrument settings and typical performance for studied elements for lead

<b>Property</b>	<b>Suggested by Manufacturer</b>	<b>Experimental Settings</b>
Wavelength	217.0 nm	324.8 nm
Lamp Current	6 mA	8 mA
Slit Width	239 $\mu\text{m}$	239 $\mu\text{m}$
Flame Type	Air/C <sub>2</sub> H <sub>2</sub>	Air/C <sub>2</sub> H <sub>2</sub>
Burner Height	4 mm	8 mm
<b>Typical Performance</b>		
Sensitivity	0.06 $\mu\text{g/ml}$	-
Working Range	1-20 $\mu\text{g/ml}$	-

## APPENDIX B

### EFFECT OF TIME ON METAL REMOVAL EXPERIMENTS DATA

**Table 28.** Figure 13 data (effect of time to the equilibrium concentration of initially 10 ppm copper solution)

X-axis (time- minute)	Y-axis (equilibrium concentration-ppm)			
	1 gr fly ash	2 gr fly ash	4 gr fly ash	8 gr fly ash
0	10	10	10	10
5	0,11414	0,1133	0,103763	0,083011
10	0,093387	0,08978	0,072634	0,062258
30	0,072634	0,06544	0,062258	0,020753
60	0,051882	0,050145	0,041505	0,010376

**Table 29.** Figure 14 data (effect of time to the equilibrium concentration of initially 50 ppm copper solution)

X-axis (time- minute)	Y-axis (equilibrium concentration-ppm)			
	1 gr fly ash	2 gr fly ash	4 gr fly ash	8 gr fly ash
0	50	50	50	50
5	1,1725	1,0687	0,9871	0,9512
10	1,0112	0,9382	0,9214	0,9154
30	1,0012	0,90456	0,8971	0,7891
60	0,8821	0,5261	0,5124	0,5122

**Table 30.** Figure 15 data (effect of time to the equilibrium concentration of initially 100 ppm copper solution)

<b>X-axis (time- minute)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>			
	<b>1 gr fly ash</b>	<b>2 gr fly ash</b>	<b>4 gr fly ash</b>	<b>8 gr fly ash</b>
<b>0</b>	100	100	100	100
<b>5</b>	9,545064	8,591849	6,433089	1,044037
<b>10</b>	9,506157	8,552942	2,970088	1,172048
<b>30</b>	8,980916	3,757689	0,012918	0,115702
<b>60</b>	8,737749	0,693785	0,51875	0,090909

**Table 31.** Figure 16. data (effect of time to the equilibrium concentration of initially 10 ppm zinc solution)

<b>X-axis (time- minute)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>			
	<b>1 gr fly ash</b>	<b>2 gr fly ash</b>	<b>4 gr fly ash</b>	<b>8 gr fly ash</b>
<b>0</b>	10	10	10	10
<b>5</b>	0,438204	0,438204	0,412098	0,318863
<b>10</b>	0,326322	0,289028	0,251734	0,251734
<b>30</b>	0,199523	0,177146	0,169687	0,15347
<b>60</b>	0,18889	0,16345	0,1428	0,1314



**Table 32.** Figure 17 data (effect of time to the equilibrium concentration of initially 50 ppm zinc solution)

X-axis (time- minute)	Y-axis (equilibrium concentration-ppm)			
	1 gr fly ash	2 gr fly ash	4 gr fly ash	8 gr fly ash
0	50	50	50	50
5	2,373982	2,201329	2,223849	2,212589
10	2,205082	2,186315	2,186315	1,818489
30	1,548249	1,529482	1,510716	1,210449
60	1,131629	1,127876	1,097849	1,097849

**Table 33.** Figure 18 data (effect of time to the equilibrium concentration of initially 100 ppm zinc solution)

X-axis (time- minute)	Y-axis (equilibrium concentration-ppm)			
	1 gr fly ash	2 gr fly ash	4 gr fly ash	8 gr fly ash
0	100	100	100	100
5	3,536889	3,435572	3,33886	3,288201
10	2,247398	2,164502	2,155292	1,2112
30	1,717786	1,579626	1,040803	0,764484
60	1,160542	1,096067	0,934881	0,681588

**Table 34.** Figure 19 data (effect of time to the equilibrium concentration of initially 10 ppm lead solution)

<b>X-axis (time- minute)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>			
	<b>1 gr fly ash</b>	<b>2 gr fly ash</b>	<b>4 gr fly ash</b>	<b>8 gr fly ash</b>
<b>0</b>	10	10	10	10
<b>5</b>	1,233899	0,993138	0,511617	0,326472
<b>10</b>	1,113519	0,752378	0,331046	0,283889
<b>30</b>	0,872758	0,391236	0,150476	0,1254
<b>60</b>	0,631997	0,150476	0,13457	0,11547

**Table 35.** Figure 20 data (effect of time to the equilibrium concentration of initially 50 ppm lead solution)

<b>X-axis (time- minute)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>			
	<b>1 gr fly ash</b>	<b>2 gr fly ash</b>	<b>4 gr fly ash</b>	<b>8 gr fly ash</b>
<b>0</b>	50	50	50	50
<b>5</b>	5,74261	5,259022	4,1105	3,747809
<b>10</b>	3,143323	2,841081	2,538838	1,511213
<b>30</b>	2,841081	2,720184	1,148522	1,027625
<b>60</b>	0,846279	0,664934	0,42314	0,302243

**Table 36.** Figure 21 data (effect of time to the equilibrium concentration of initially 100 ppm lead solution)

<b>X-axis (time- minute)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>			
	<b>1 gr fly ash</b>	<b>2 gr fly ash</b>	<b>4 gr fly ash</b>	<b>8 gr fly ash</b>
<b>0</b>	100	100	100	100
<b>5</b>	20,09174	20,04396	19,80506	14,35807
<b>10</b>	20,09174	19,75727	19,61393	14,11916
<b>30</b>	16,36485	16,26929	14,74031	13,02021
<b>60</b>	15,40924	15,31368	13,88026	12,63797

## APPENDIX C

### EFFECT OF FLY ASH AMOUNT ON METAL REMOVAL EXPERIMENTS DATA

**Table 37.** Figure 22 data (effect of fly ash amount to the equilibrium concentration of initially 10 ppm copper solution)

<b>X-axis (fly ash amount- gram)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>			
	<b>5 minutes</b>	<b>10 minutes</b>	<b>30 minutes</b>	<b>60 minutes</b>
<b>1</b>	0,11414	0,093387	0,072634	0,051882
<b>2</b>	0,1133	0,08978	0,06544	0,050145
<b>4</b>	0,103763	0,072634	0,062258	0,041505
<b>8</b>	0,083011	0,062258	0,020753	0,010376

**Table 38.** Figure 23 data (effect of fly ash amount to the equilibrium concentration of initially 50 ppm copper solution)

<b>X-axis</b>	<b>Y-axis (equilibrium concentration-ppm)</b>			
	<b>5 minutes</b>	<b>10 minutes</b>	<b>30 minutes</b>	<b>60 minutes</b>
<b>1</b>	1,1725	1,0112	1,0012	0,8821
<b>2</b>	1,0687	0,9382	0,90456	0,5261
<b>4</b>	0,9871	0,9214	0,8971	0,5124
<b>8</b>	0,9512	0,9154	0,7891	0,5122

**Table 39.** Figure 24 data (effect of fly ash amount to the equilibrium concentration of initially 100 ppm copper solution)

<b>X-axis (fly ash amount- gram)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>			
	<b>5 minutes</b>	<b>10 minutes</b>	<b>30 minutes</b>	<b>60 minutes</b>
<b>1</b>	9,545064	9,506157	8,980916	8,737749
<b>2</b>	8,591849	8,552942	3,757689	0,693785
<b>4</b>	6,433089	2,970088	0,012918	0,51875
<b>8</b>	1,044037	1,172048	0,115702	0,090909

**Table 40.** Figure 25 data (effect of fly ash amount to the equilibrium concentration of initially 10 ppm zinc solution)

<b>X-axis (fly ash amount- gram)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>			
	<b>5 minutes</b>	<b>10 minutes</b>	<b>30 minutes</b>	<b>60 minutes</b>
<b>1</b>	0,438204	0,326322	0,199523	0,18889
<b>2</b>	0,438204	0,289028	0,177146	0,16345
<b>4</b>	0,412098	0,251734	0,169687	0,1428
<b>8</b>	0,318863	0,251734	0,15347	0,1314

**Table 41.** Figure 26 data (effect of fly ash amount to the equilibrium concentration of initially 50 ppm zinc solution)

<b>X-axis (fly ash amount- gram)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>			
	<b>5 minutes</b>	<b>10 minutes</b>	<b>30 minutes</b>	<b>60 minutes</b>
<b>1</b>	2,373982	2,205082	1,548249	1,131629
<b>2</b>	2,201329	2,186315	1,529482	1,127876
<b>4</b>	2,223849	2,186315	1,510716	1,097849
<b>8</b>	2,212589	1,818489	1,210449	1,097849

**Table 42.** Figure 27 data (effect of fly ash amount to the equilibrium concentration of initially 100 ppm zinc solution)

<b>X-axis (fly ash amount- gram)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>			
	<b>5 minutes</b>	<b>10 minutes</b>	<b>30 minutes</b>	<b>60 minutes</b>
<b>1</b>	3,536889	2,247398	1,717786	1,160542
<b>2</b>	3,435572	2,164502	1,579626	1,096067
<b>4</b>	3,33886	2,155292	1,040803	0,934881
<b>8</b>	3,288201	1,2112	0,764484	0,681588

**Table 43.** Figure 28 data (effect of fly ash amount to the equilibrium concentration of initially 10 ppm lead solution)

<b>X-axis (fly ash amount- gram)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>			
	<b>5 minutes</b>	<b>10 minutes</b>	<b>30 minutes</b>	<b>60 minutes</b>
<b>1</b>	1,233899	1,113519	0,872758	0,631997
<b>2</b>	0,993138	0,752378	0,391236	0,150476
<b>4</b>	0,511617	0,331046	0,150476	0,13457
<b>8</b>	0,326472	0,283889	0,1254	0,11547

**Table 44.** Figure 29 data (effect of fly ash amount to the equilibrium concentration of initially 50 ppm lead solution)

<b>X-axis (fly ash amount- gram)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>			
	<b>5 minutes</b>	<b>10 minutes</b>	<b>30 minutes</b>	<b>60 minutes</b>
<b>1</b>	5,74261	3,143323	2,841081	0,846279
<b>2</b>	5,259022	2,841081	2,720184	0,664934
<b>4</b>	4,1105	2,538838	1,148522	0,42314
<b>8</b>	3,747809	1,511213	1,027625	0,302243

**Table 45.** Figure 30 data (effect of fly ash amount to the equilibrium concentration of initially 100 ppm lead solution)

<b>X-axis (fly ash amount- gram)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>			
	<b>5 minutes</b>	<b>10 minutes</b>	<b>30 minutes</b>	<b>60 minutes</b>
<b>1</b>	20,09174	20,09174	16,36485	15,40924
<b>2</b>	20,04396	19,75727	16,26929	15,31368
<b>4</b>	19,80506	19,61393	14,74031	13,88026
<b>8</b>	14,35807	14,11916	13,02021	12,63797



## APPENDIX D

### PRECIPITATION AND DESORPTION EXPERIMENTS DATA

**Table 46.** Figure 34 data (effect of pH to the equilibrium concentration of initially 10 ppm copper solution)

<b>X-axis (pH values)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>
6	10
8,2	9,777182
9,8	0,147491
10,7	0,135776
11,7	0,370075

**Table 47.** Figure 35 data (effect of pH to the equilibrium concentration of initially 50 ppm copper solution)

<b>X-axis (pH values)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>
5,7	50
6,9	17,95844
10,4	0,327433
11,3	0,093134
11,7	0,386008

**Table 48.** Figure 36 data (effect of pH to the equilibrium concentration of initially 100 ppm copper solution)

<b>X-axis (pH values)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>
5,5	100
5,8	60,28397
6,2	30,05939
9,9	0,186268
11,9	1,123464

**Table 49.** Figure 37 data (effect of pH to the equilibrium concentration of initially 10 ppm zinc solution)

<b>X-axis (pH values)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>
6,3	10
8,4	9,717952
9,5	7,819914
9,9	6,681092
11,5	7,060699

**Table 50.** Figure38 data (effect of pH to the equilibrium concentration of initially 50 ppm zinc solution)

<b>X-axis (pH values)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>
6	50
7,3	33,69016
9	8,730972
11,4	32,74115
11,8	39,09957

**Table 51.** Figure 39 data (effect of pH to the equilibrium concentration of initially 100 ppm zinc solution)

<b>X-axis (pH values)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>
5,9	100
8	59,21877
10,6	74,40307
11,6	83,89325
11,8	95,28148

**Table 52.** Figure 40 data (effect of pH to the equilibrium concentration of initially 10 ppm lead solution)

<b>X-axis (pH values)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>
6,4	10
9,9	9,733919
10,3	2,654705
10,8	7,170756
11,2	9,611864

**Table 53.** Figure 41 data (effect of pH to the equilibrium concentration of initially 50 ppm lead solution)

<b>X-axis (pH values)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>
5,7	50
9,8	41,95655
10,3	2,288539
11	33,83986
11,7	47,44904

**Table 54.** Figure 42 data (effect of pH to the equilibrium concentration of initially 100 ppm lead solution)

<b>X-axis (pH values)</b>	<b>Y-axis (equilibrium concentration-ppm)</b>
5,6	100
9,1	54,77237
10,1	18,9491
10,8	19,25424
11,2	48,6696

**Table 55** Figure 43 data (result of metal release (desorption) experiments)

X-axis (time - hour)	Y-axis (equilibrium concentration-ppm)		
	Copper	Zinc	Lead
0	0	0	0
2	0,125	0,087	0,193
6	0,153	0,097	0,195
10	0,155	0,118	0,227

**Table 56** Figure 44 data (Equilibrium concentrations of combined solution)

X-axis (time - minutes)	Y-axis (equilibrium concentration-ppm)	
	Copper	
	Solution with fly ash	Fly ash treated solution
0	100	100
5	0,538068 ppm	13,30628 ppm
10	0,423555 ppm	8,439473 ppm
15	0,251786 ppm	4,717797 ppm
	Zinc	
	Solution with fly ash	Fly ash treated solution
0	100	100
5	3,587719 ppm	4,318713 ppm
10	3,154971 ppm	4,084795 ppm
15	2,710526 ppm	3,646199 ppm
	Lead	
	Solution with fly ash	Fly ash treated solution
0	100	100
5	21,33096 ppm	30,30158 ppm
10	20,4339 ppm	29,53908 ppm
15	17,83242 ppm	27,07216 ppm