GEOCHEMICAL ASSESSMENT OF ENVIRONMENTAL EFFECTS OF FLY ASH FROM SEYİTÖMER (KÜTAHYA) THERMAL POWER PLANT

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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

GEOCHEMICAL ASSESSMENT OF ENVIRONMENTAL EFFECTS OF FLY ASH FROM SEYİTÖMER (KÜTAHYA) THERMAL POWER PLANT

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This thesis includes the geochemical analysis of fly ash samples from the disposal sites, bottom ash and slag samples from the boiler units, and soil samples collected from the vicinity of Seyitömer (Kütahya) Thermal Power Plant, which consumes 20 000 tons of coal, producing 8000 tons of solid wastes per day. Geochemical studies include Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, Pb, Zn, Cd, Cu and Co analyses through the use of atomic absorption spectrophotometry. During the study, scanning electron microscopy (SEM) was also used for the determination of some morphological features and mineral phases in the fly ash particles.

The results of the geochemical analyses were assessed in terms of the potential of leaching of trace elements and the tendency of the fly ash particles to contaminate the environment, as this possible contamination could lead to health, environmental and land-use problems. The results revealed that relative concentrations of major and trace elements in coal combustion solid waste products and soil samples show variation due to both the elemental behaviors of solid waste products and soil, and some external factors like basement lithologies. It is found out that major and trace element behaviors also vary with particle size of fly ash samples. The elemental concentrations in soil samples, when compared with the maximum allowable concentration values for agriculture for different countries, are found to exceed the limits for Co and Pb concentrations, while Cd, Cu and Zn concentrations do not exceed the given values.

By the use of SEM analyses, four major types of fly ash morphology could be identified, which are mainly, plerospheres, cenospheres, particles containing crystals and irregularly shaped particles. Hematite and anhydrite were observed in the fly ash sample, while anhydrite was also found in the slag sample.

Key Words: Fly Ash, Thermal Power Plant, Environment, Geochemistry,
Seyitömer, Kütahya

ÖZET

SEYİTÖMER (KÜTAHYA) TERMİK ELEKTRİK SANTRALINDAKİ UÇUCU KÜLLERİN ÇEVRESEL ETKİLERİNİN JEOKİMYASAL DEĞERLENDİRMESİ

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Bu tez, günde 20 000 ton kömür kullanılarak, 8000 ton kül üreten Seyitömer (Kütahya) Termik Elektrik Santralına ait döküm alanlarından alınan uçucu küllerin, ısı birimlerinden toplanan taban küllerinin ve cürufun, ve santral civarındaki toprak örneklerinin jeokimyasal analizlerini kapsamaktadır. Jeokimyasal çalışmalar, atomik absorpsiyon spektrofotometresi kullanılarak yapılan Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, Pb, Zn, Cd, Cu ve Co analizlerini içerir. Çalışma esnasında, uçucu küllerin morfolojisi ve birtakım mineral fazlarının da belirlenebilmesi için, taramalı elektron mikroskobundan (SEM) yararlanılmıştır.

Jeokimyasal analiz sonuçları, olası bir kirlilik, sağlık, çevre ve alan kullanım problemlerine yol açabileceğinden, iz elementlerin yıkanma potansiyelleri ve uçucu küllerin çevreyi kirletme eğilimleri açısından değerlendirilmiştir. Sonuçlara göre katı atık ve toprak örneklerindeki ana ve eser element derişimleri, elementlerin farklı katı atıklar ve topraktaki davranışlarına ve temel litolojisi gibi birtakım faktörlere göre değişmektedir. Ayrıca ana ve eser element derişimlerinin uçucu küllerin tane boyu ile de değiştiği saptanmıştır. Toprak örneklerinin element derişimleri farklı ülkelerin tarım amaçlı olarak belirlenen üst limitleri ile karşılaştırıldığında, Cd, Cu ve Zn derişimlerinin verilen değerlerin altında kaldığı, Co ve Pb derişimlerinin ise, bu değerleri aştıkları bulunmuştur.

SEM analizleri kullanılarak, plerosfer, senosfer, kristalli parçacıklar ve düzensiz şekillenmiş parçacıklar olmak üzere, dört çeşit uçucu kül morfolojisi belirlenmiştir. Uçucu kül örneğinde, hematit ve anhidrit gözlenirken, cüruf örneğinde de anhidrit bulunmuştur.

Anahtar Kelimeler: Uçucu Kül, Termik Santral, Çevre, Jeokimya, Seyitömer, Kütahya

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CHAPTER 1

INTRODUCTION

1.1. Purpose and Scope

This study is concerned with the geochemical assessment of environmental effects of fly ash produced from Seyitömer (Kütahya) thermal power plant which consumes low quality lignite reserves of Seyitömer basin. Fly ash particles emitted from coal-fired power plants show an enrichment of several toxic trace elements (Natusch et. al, 1973; Davison et. al, 1974; Kaakinen et. al, 1975; Klein et. al, 1975; Campbell et. al, 1978; Wangen et. al, 1978; Hansen and Fisher, 1980; Hulett et.al, 1980). Therefore, the aim of this study is to find out the behavior of major and hazardous trace elements during coal combustion and solid waste disposal, as these elements are the potential pollutants of the environment.

The objectives of this study are to determine, i) the relative concentrations of major and trace elements in coal combustion solid waste products, namely fly ash, bottom ash and slag, and in soil samples in the vicinity of the plant, ii) the possible relationship between the elemental concentrations and distance away from the disposal site for fly ash and soil samples, iii) the elemental concentrations with respect to certain size fractions of fly ash samples, iv) the major mineralogical and morphological features of fly ash, and v) the range of the concentrations for soil samples of this study compared to the maximum allowable agricultural limits for different countries.

1.2. Geographic Setting

Seyitömer Thermal Power Plant is located, in the northern part of the innerwest Anatolia, 28 kilometres northwest of Kütahya city (Figure 1.1). It is included in the Kütahya i23c3 quadrangle of the 1/25000 scaled topographic map of Turkey.

The study covers nearly a 24 square kilometre area. Transport to the study area is by the use of Eskişehir-Afyon main road. Besides this road, the villages nearby have good quality stabilized roads. Main villages next to the plant are Kınık, Ayvalı, Bozcahüyük and Turgutlar (Figure 1.1)

Typical climatic characteristics of the innerwest Anatolia are seen in the area. Winter seasons are cold and rainy/snowy, while summers are hot and arid.

Agriculture has an important role in the area. Therefore, the rivers of the area that become active in rainy seasons are also very important. Porsuk River, which supplies Eskişehir City its drinking water, is fed from some of those rivers in the study area.

1.3. Methods of Study

This study is carried out in mainly four stages as literature survey, field studies, laboratory studies and data interpretation.

1.3.1. Literature Survey

The literature survey includes the compilation of i) the studies regarding solid waste disposals, ii) information about Seyitömer Thermal Power Plant and iii) the previous studies related to the geology of the study area.

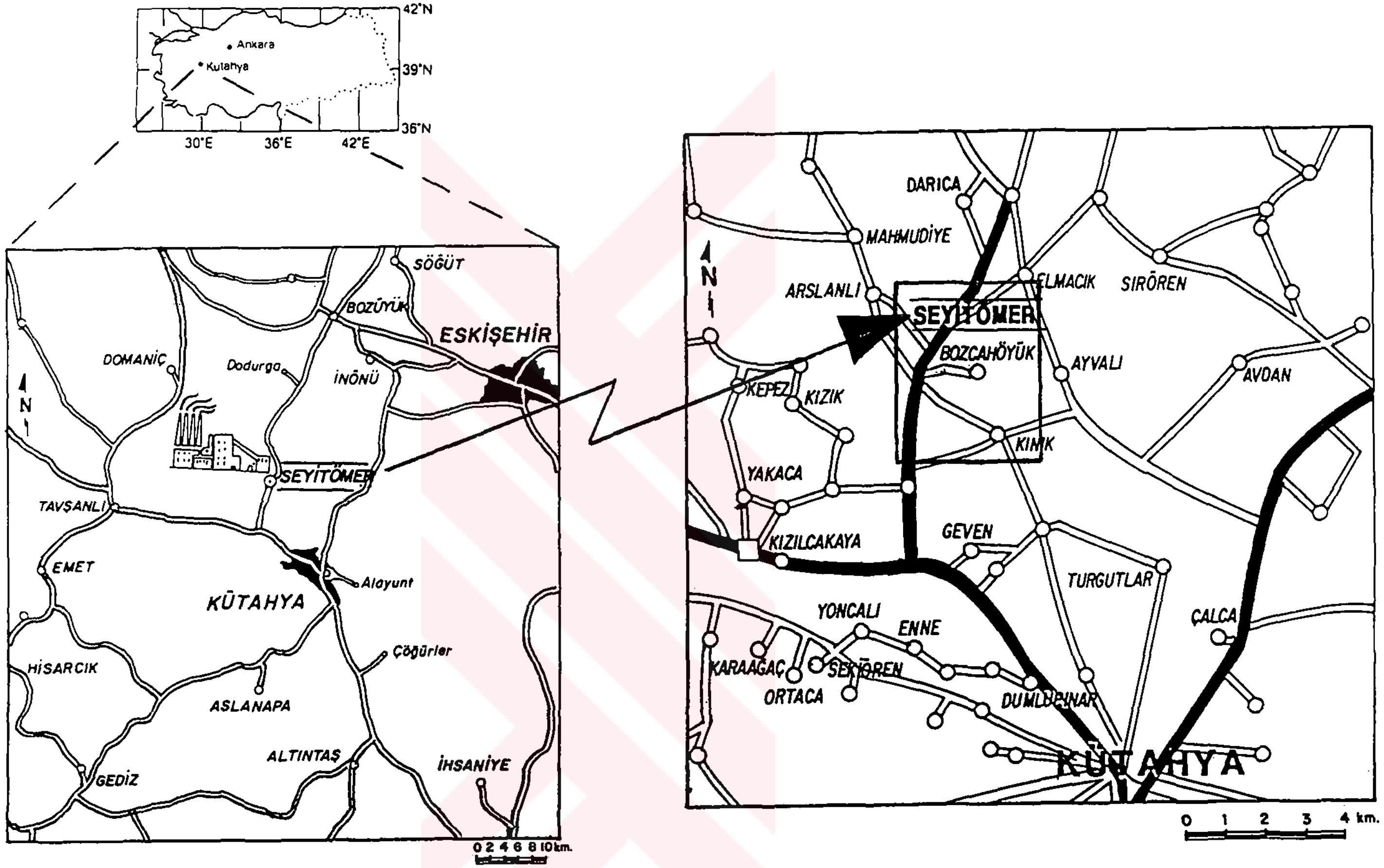


Figure 1.1. Location map of Seyitömer Thermal Power Plant

1.3.2. Field Studies

Field studies consist of reconnaissance in the vicinity of the Seyitömer Thermal Power Plant and sampling. The study area covers nearly 24 square kilometers, including the plant, related facilities, disposal sites and some of the nearby villages (Figure 1.1). The field work was carried out during summer months (July-August), 1996. Samples of coal combustion waste products, namely fly ash, bottom ash and slag, and samples of soil from the vicinity of the plant were collected for this study. During sampling period, as indicated by the meteorological data of the area, average rain fall was at its minimum compared to the other months of the year, while average temperature was at its maximum (Figure 1.2). Therefore, the sampling period was the driest and the hottest period in the year 1996, leading a decrease in river flows, enhancing the blowing of the fine fly ash particles.

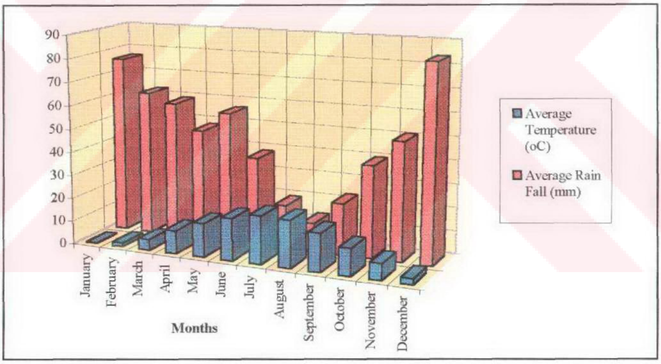


Figure 1.2. Graph illustrating average temperature (^{o}C) and average rain fall (mm) vs months (1996) in the study area

1.3.3. Laboratory Studies

Laboratory studies include sample preparations and analysis, comprising geochemical, morphological and mineralogical analyses.

Geochemical analyses were carried out on fly ash, bottom ash, slag and soil samples and included the determination of Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, Pb, Zn, Cd, Cu and Co contents through the use of Atomic Absorption Spectrophotometry (AAS, Rank Hilger/1551).

To get a general idea, morphological and mineralogical analyses were carried out on one fly ash and one slag sample through the use of Scanning Electron Microscopy (SEM - JEOL JSM/840-A) with Energy Dispersive X-Ray Spectrometer (EDX - TRACOR TN-5502).

1.3.4. Data Interpretation

The data produced from the analyses of fly ash, bottom ash, slag and soil samples were interpreted in terms of the investigation of distribution of the elemental concentrations in solid waste products, and the potential of those samples to contaminate the environment and damage human health.

For this purpose, the relative elemental concentrations in fly ash, bottom ash, slag and soil samples, the elemental concentrations with respect to certain size fractions of fly ash samples, the possible relationship between the elemental concentrations and distance away from the disposal site for fly ash and soil samples, and the major morphological features and mineralogy of fly ash and slag samples were investigated. Besides, the range of the elemental concentrations for soil samples of this study were compared to the maximum allowable limits of agriculture for different countries.

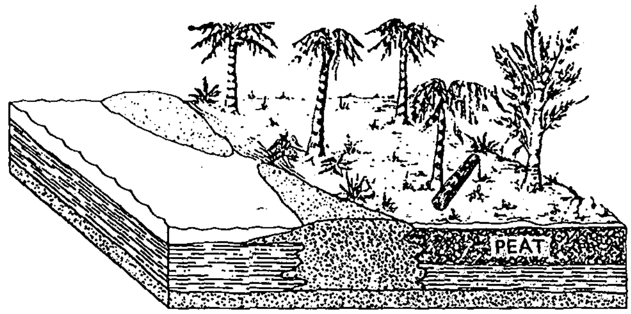
1.4. Background

1.4.1. Geology of Coal

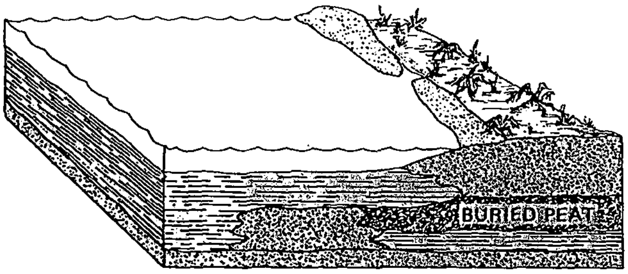
Coal is a sedimentary rock that forms from the compaction of plant material, which has not completely decayed. Rapid plant growth and deposition in water with low oxygen content are needed, therefore shallow swamps or bogs in a temperate or tropical climate are likely environments of deposition. The plant fossils in coal beds include leaves, stems, tree trunks, and stumps with roots often extending into the underlying shales, therefore most coal were formed in-situ where the plants grew. Coal is essentially the altered residue of plants that flourished in ancient freshwater or brackish water swamps, typically found in estuaries, coastal lagoons and low-lying coastal plains or deltas (Keller, 1992).

Coal forming processes (Figure 1.3) first require the development of a swamp rich in plants, which are partially decomposed in an oxygen deficient environment. Partial decay of the abundant plant material uses up any oxygen in the swamp water, so the decay stops and the remaining organic material is preserved forming a thick layer of peat. These swamps and accumulations of peat may then be inundated by a prolonged rise of sea level (a relative rise as the land may be sinking) and covered by sediments such as sand, silt, clay and carbonate-rich material. Burial by sediment compresses the plant material, gradually driving out any water or other volatile compounds. As more and more sediment is deposited, water and organic gases (volatiles) are squeezed out and the percentage of carbon increases in the compressed peat. As this process continues, the peat is eventually transformed to coal. The color of coal changes from brown to black as the amount of carbon in it increases (Keller, 1992).

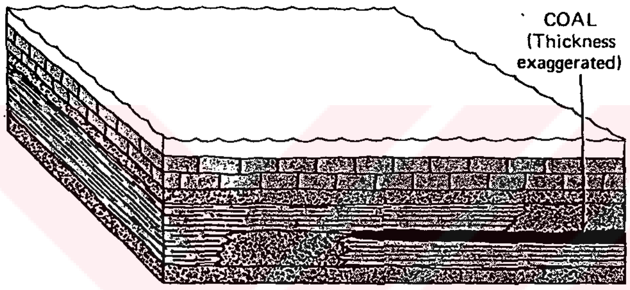
The major components of coal can be listed as, organic matter, inorganic matter (minerals and elements), water, oil and gas. Factors affecting coal chemistry are mainly, ash yield, water chemistry (Eh, pH, salinity), geology (source rocks, volcanism) and climate (Finkelman, 1996).



(a) *Coal swamp forms.*



(b) *Rise in sea level buries swamp in sediment.*



(c) *Compression of peat forms coal.*

Figure 1.3. The processes by which buried plant debris (peat) is transformed into coal (Keller, 1992).

Coal is commonly classified according to rank and sulfur content. The rank is generally based on the percentage of carbon. Table 1.1 shows the common ranks of coal. Peat, a mat of unconsolidated plant material, is not coal but represents the initial stage of coal development. When dry, it can be burned as a fuel. With compaction, it can change to lignite (brown coal), which may still contain visible pieces of wood. Lignite is soft and often crumbles as it dries in air. It is subject to spontaneous combustion as it oxidizes in air, and this somewhat limits its use as a fuel. Heat content is minimum in lignite, which has a high moisture content. Subbituminous coal and bituminous coal are black and often banded with layers of different plant material. They are dusty to handle, ignite readily and burn with a smoky flame. Anthracite is actually a metamorphic rock, generally formed only under the regional compression associated with folding. It is hard to ignite but is dust-free and smokeless.

Table 1.1. Ranks of Coal (Keller, 1992)

	Color	**Water Content (%)**	**Other Volatiles (%)**	**Fixed Carbon (%)**	**Approximate Heat Value (kcal/kg)**
Peat	brown	75	10	15	varies
Lignite	brown-brownish black	45	25	30	3889
Subbituminous Coal	black	25	35	40	5556
Bituminous Coal	black	5-15	20-30	50-75	6667-8333
Anthracite	black	5	5	90	7778

Figure 1.4 shows that heat content is maximum in bituminous coal which has relatively few volatiles (oxygen, hydrogen and nitrogen) and low moisture content.

Coal quality is defined by the compositional and the physical properties of coal that enhance or restrict its use. It is also an important factor in environmental considerations affecting human health by air toxics, liquid and solid wastes. Coal that is consumed in thermal power plants, when of low quality with high sulfur content, leads to the production of sulfur dioxide and high amounts of ash and therefore leads to air pollution.

The sulfur content of coal may be generally classified as low (0-1%), medium (1.1-3%) or high (>3%). The location of coal reserves has environmental significance, because, with all other factors equal, the use of low sulfur coal as a fuel for power plants causes less air pollution. Therefore to avoid air pollution, thermal power plants on the highly populated areas have to treat coal to lower its sulfur content before burning or capture the sulfur after burning by a process such as scrubbing (Keller, 1992).

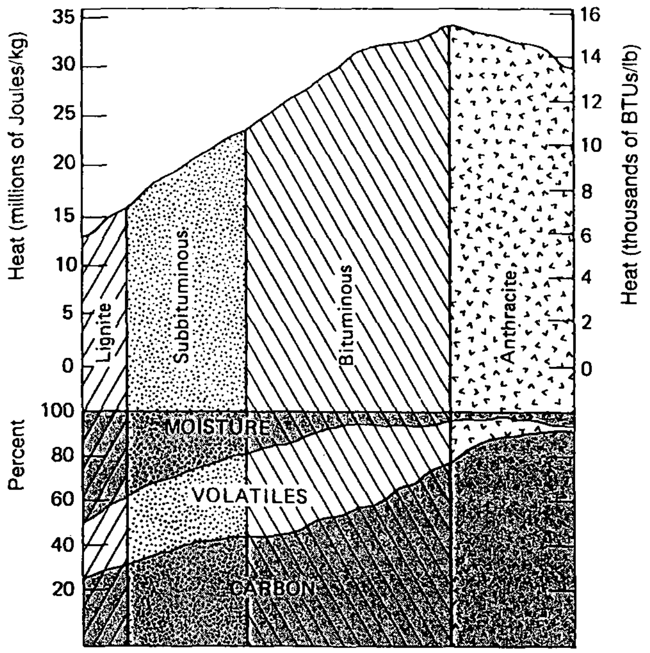


Figure 1.4. Generalized classification of different types of coal based upon their relative content (%) of moisture, volatiles and carbon with heat values (Keller, 1992)

Extracting and using coal creates environmental problems. The presence of an underground mine usually lowers local water table as ground water is pumped out of the mine. The drainage out of the mines tends to be highly acidic, polluting surface streams and water supplies. When coal is burned, ash and sulfur gases can pollute air, surface and water resources, hence, precautions are required to prevent environmental pollution.

1.4.2. Coal Combustion Solid Waste Products

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 (Abel and Rancitelli, 1975; Block and Dams, 1975; Bolton et al., 1975; Dudas, 1981; Ondov et al., 1975; Piperno, 1975)

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

Fly ash is all particulate material that is carried in a gas stream with the stack gases. It is obtained as an inorganic, fine, solid, mineral residue left behind after a majority of combustibles in the coal are burned out. Fly ash particles have a diameter range varying between 0.5-200 μm and make up 10-85% of the total ash produced (Fisher et. al, 1978).

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 (Bertine and Goldberg, 1971).

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 (Bertine and Goldberg, 1971).

Flue Gas Desulfurization Sludge (FGD) is the liquid waste product of coal combustion (Bertine and Goldberg, 1971).

Although the proportions of the solid wastes resulting from coal combustion show variation with the ash content of the coal, the plant design and the particle collection devices employed, fly ash generally comprises more than 50% of all the solid waste products (Finkelman, 1996).

When coal is burned, a portion of the non-combustible material is retained in the furnace as either slag or bottom ash, while the rest leaves as fly ash in the flue gas and the volatilized elements. As fly ash is small enough to be carried in the flue gas, a further fractionation occurs when the flue gas passes the particulate control devices. These devices may remove up to 99% of the larger fly ash particles, but they are less efficient in collecting the smaller (<1μm) particles and vapor (Klein et. al, 1975).

The smaller and more respirable particles, together with the vapor, pass through the collectors and are emitted to the environment through the stack system (Norton et. al, 1988). Owing to their high specific surface, fly ash particles have a greater tendency to adsorb those toxic trace elements than the coal or the collected solid wastes (Andren et. al, 1975) (Figure 1.5).

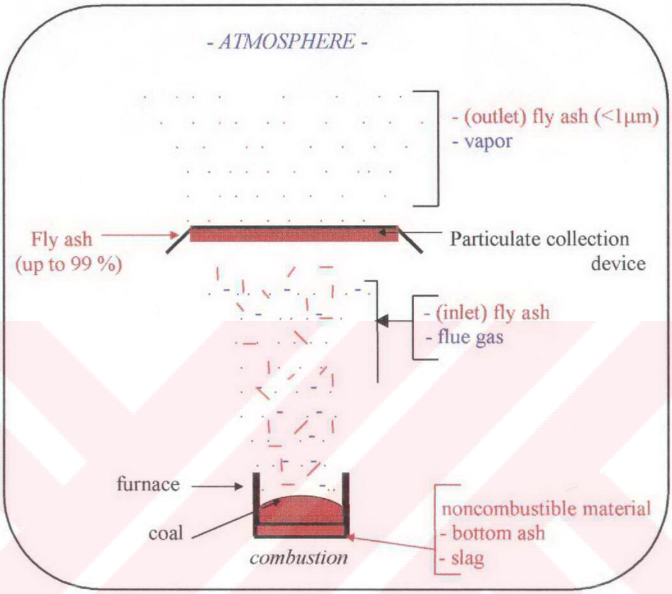


Figure 1.5. Sketch diagram indicating the formation of fly ash, bottom ash and slag

1.4.3. Environmental Effects of Coal Combustion and Related Solid Waste Products

Environmental pollution has become a subject of considerable interest especially in industrialized countries. The waste disposals resulting from the use of fossil fuel energy resources, such as coal and petroleum, are the main causes of environmental pollution.

Industries cause environmental pollution by three ways:

a. Solid Wastes: Getting rid of the solid waste products of different processes by disposing them to nearby areas.
b. Stack Gases: Escape of stack gas emissions to atmosphere resulting from the absence of filtration and purification.
c. Discharged Waters: Disposal of waters that were used for different purposes without making the necessary purification.

Liquid, gas and solid waste products cause air (atmospheric), water, soil pollution, aesthetic destruction and thermal pollution (Figure 1.6).

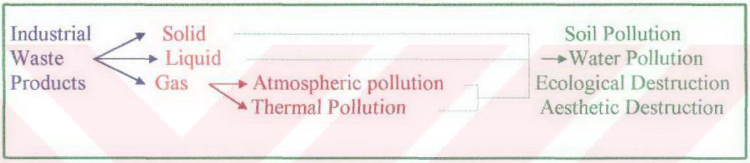


Figure 1.6. Pollution types caused by industrial waste products

Regardless of how it is used, coal always generates some process wastes that, if freely discharged or carelessly disposed of, would cause serious environmental pollution and attendant ecological damage (Figure 1.7) and, in some instances, even pose major health hazards. Therefore, it is important to know the fate of potentially toxic trace elements at coal-fired power plants for the total assessment of associated health risks.

Assessment of the environmental impact of coal and its combustion residues requires detailed information regarding the leachability of potentially hazardous components under a wide variety of site-specific applications and disposal conditions.

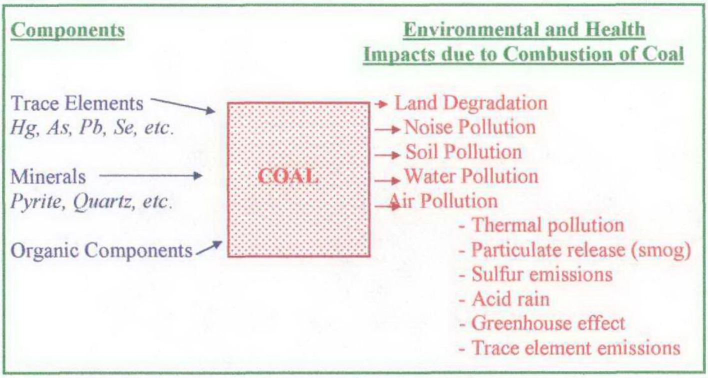


Figure 1.7. Environmental and health impacts due to combustion of coal (modified from Finkelman, 1996)

Factors affecting exposure and risk at coal combustion waste sites (Finkelman, 1996) are mainly, distance to surface water and groundwater flow, hydraulic measurements (depth to groundwater, hydraulic conductivity, net recharge and groundwater hardness), population characteristics of waste disposal sites (proximity of site to human populations and proximity to public drinking water systems) and ecological characteristics.

By combustion of coal, the trace elements in coal are transferred to slag, coal ash and gases, which are discharged to the environment by wet or dry deposition. Being of clay origin, heat treated and aided by properties like porosity and high specific surface, the fly ash particles emitted from coal-fired power plants are well suited for adsorption purposes in aqueous and gas media and they show an enrichment of several toxic trace elements (Zouboulis and Tzimou-Tsitouridou, 1990). Coal combustion can mobilize these elements by introducing them to atmospheric, terrestrial and aquatic environments (Bertine and Goldberg, 1971). If leached, followed by underground transportation of the contaminants, these trace elements may contaminate soils, as well as surface water and groundwater. Therefore, these elements may become a hazard to the environment because of their contribution to the formation of toxic compounds if the ash is not utilized or disposed of properly. This possible contamination of waters and soils could lead to health, environmental and land-use problems (Lee, 1982; Gehrs et al., 1979).

Impacts on the terrestrial environment include disruption of land, aquifers and natural drainage contours, soil erosion, flooding, subsidence of land surfaces. Impacts on the aquatic environment include disruption of surface and underground aquatic systems, and thermal, particulate and chemical contamination of waters. Impacts on the atmospheric environment include deterioration of air quality by particulate and gaseous emissions, and modification of the climate.

The various impacts on air, land and water can result in damage to plant and animal species and to their habitats, as well as modification or elimination of ecosystems, damage to property or food resources and modification of the aesthetic environment (Gehrs et al., 1979).

Along with the other anthropogenic sources, coal combustion makes a contribution to the trace element load in the atmosphere. In recent decades, the problem of acid rain has gained more and more attention; today it is considered one of the major environmental problems facing industrialized society. Acid rain encompasses both wet and dry acidic deposits that often occur near where major emission of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) are blown to atmospheric environment from the stacks of the thermal power plant (Billings and Matson, 1972). As a result of scattering of the fine fly ash particles from stack to atmosphere, dust cover is resulted on soils and plants. This cover is then converted to a hard cover by rain, which destructs the materials and destroy the plant tissues. Today, electrofilters are used all over the world to keep those fly ash particles away from spreading to atmosphere from stacks of the plants. If those electrofilters are used efficiently, the concentration levels of the toxic trace elements can be kept below the maximum allowable limits.

Fly ash contains an appreciable amount of soluble compounds (Arslan and Boybay, 1994). Soluble forms of the elements are generally regarded as having more adverse affects than those tied up as insoluble-oxides or in glassy structures (Henry and Knapp, 1980). Soils and sediments are effective sinks for most trace elements. The trace elements in fly ash may permeate soil horizons even up to meters (Ravi Chander, 1994), while being uniformly mixed within the top 1-2 cm of soil mass (Wangen and Williams, 1978). In order to clarify potential surface water and groundwater pollution caused by fly ash disposal, it is necessary to study the interaction of the fly ash leachate with soils and water resources (Abel and Rancitelli, 1975; Theis and Richter, 1979). In the case of dissolved ions, these interactions take the form of precipitation of a discrete solid phase or adsorption onto particle surfaces (Theis and Richter, 1979).

Assessment of potential, environmental and toxicological effects of particulate material from coal combustion, together with design of emission control strategies requires detailed physical, chemical and morphological characterization of the fly ash particles, as the variabilities play an important role in long term leaching of trace elements from the ashes after disposal (Lee, 1982; Denoyer et al., 1983).

The morphological, physical, and chemical properties of fly ash depend on a variety of factors (Gay and Frigge, 1989; Goldberg et al., 1981), including, composition of coal burned, coal processing and combustion technologies (operating conditions), pollution control systems, fly ash collection mechanism applied and particle size distribution of fly ash.

As a result, since industrial use of coal expands and coal fired thermal power plants grew in size and complexity as well as in number, much attention should be given to operating procedures that mitigated health effects, and the procedures should be improved to provide means for keeping coal operations as environmentally ‘clean’ as contemporary pollutant standards require. Careful disposal is necessary to minimize the release of potentially hazardous leachates, as they contain many toxic trace elements.

CHAPTER 2

GEOLOGY OF THE SEYİTÖMER REGION

Seyitömer Basin is located at the Northeast Aegean Region, in the borders of Kütahya City. The basin is aligned in northeast – southwest direction. Seyitömer Village, located at 20 km north-northwest of Kütahya City, is at the middle of the basin. Figure 2.1 shows the general geology of the area in the vicinity of the Seyitömer Village. The basement in the area is comprised by Paleozoic aged metamorphics and Mesozoic aged ophiolitic rocks. Neogene (Miocene – Pliocene) aged sedimentary sequences overlie the basement units and are unconformably overlain by Quaternary Alluvium. Figure 2.2 shows the generalized sketch columnar section of the region.

In the Seyitömer Basin, the Neogene aged sequence has been divided into two as Old Neogene (Miocene) and Young Neogene (Pliocene) (Lebküchner, 1959). The Old Neogene units were called as Beke and Tunçbilek Formations by Baş (1986), and as Seyitömer Formation by Sarıyıldız (1987). Young Neogene units were called as Saruhanlar, Çokköy and Emet Formations by Baş (1986).

Middle-Upper Miocene aged Seyitömer Formation (Sarıyıldız, 1987) unconformably overlies the basement which contains serpentinites, radiolarites, crystalline limestone, gabbros, diorites and amphibolites. Seyitömer Formation begins with conglomerates and sandstone with a thickness of 50-100 m. Blue-green claystone and mudstone, which are mainly observed in the regions where the basement is serpentinite, overlies those clastics. In the Seyitömer Region, they have an average thickness of 15-30 m. Main Lignite Seam with an average thickness of 20 m (0-37 m) overlies those units. Claystone-bituminous marl-limestone layers, having a thickness of 20-80 m, observed on top of the Main Seam, can be considered as the upper part of the Main Seam. This upper part is overlain by the Upper Lignite Seam Zone of clayey lignite - claystone alternations with 6-25 m thickness. 20-40 m thick marl, diatomitic claystone, silicified limestone and clayey limestone occupies the upper part of the Upper Lignite Seam Zone. This part is rich in diatomites in Seyitömer and Arslanlı Regions.

Young Neogene Units (Lebküchner, 1959) begins with 10-25 m thick sandstone, limestone, marl layers, ends with the key beds of tuff and tuff-sandstone-marl alternations. On top the key beds of tuff, partially silicified limestone, marl and tuff with up to 100 m thickness can be observed. They are covered with Quaternary alluvium (Figure 2.1)

The Neogene aged units in the basin forms some folded structures with WNW-ESE trending axes. Those units were faulted by NE-SE trending faults.

Quaternary alluvium unconformably overlies the Seyitömer Formation at the western part of the basin (Sarıyıldız, 1987). The formation consists of terrace and channal fill deposits of weakly cemented or uncemented conglomerate and sandstone, with a thickness up to 75 m (Baş, 1986; Sarıyıldız, 1987).

Main Seam has a thickness of 23 m in the middle of the basin, near Arslanlı-Seyitömer Region. Seam thickness decreases towards Kükürt and İshakçılar at west, Kıranşıh, Güzelyakup, Mahmudiye and Darıca (0.25-0.50 m) at north, Dereyalak at northeast, Elmacık-Ayvalı (4-7 m) at east, Sırören (0.05-0.50 m) and Porsuk Valley at southeast.

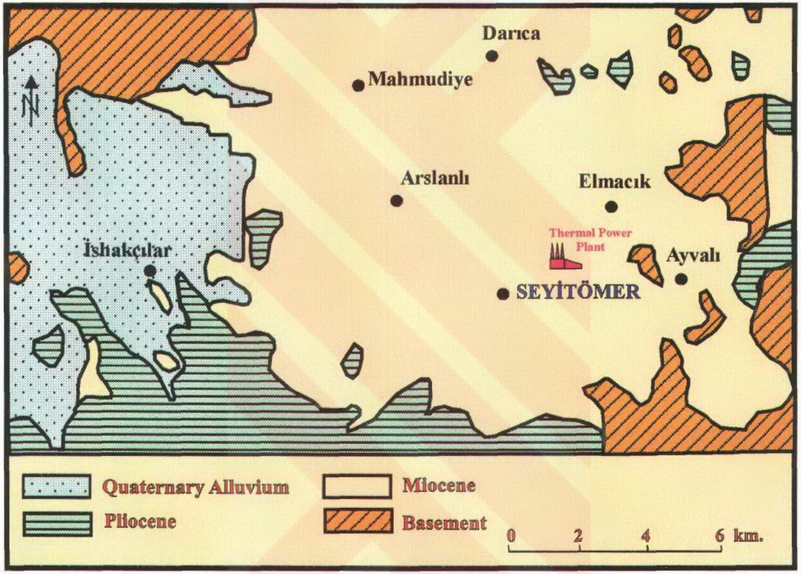


Figure 2.1. Sketch geological map of the Seyitömer area (Nakoman, 1968)

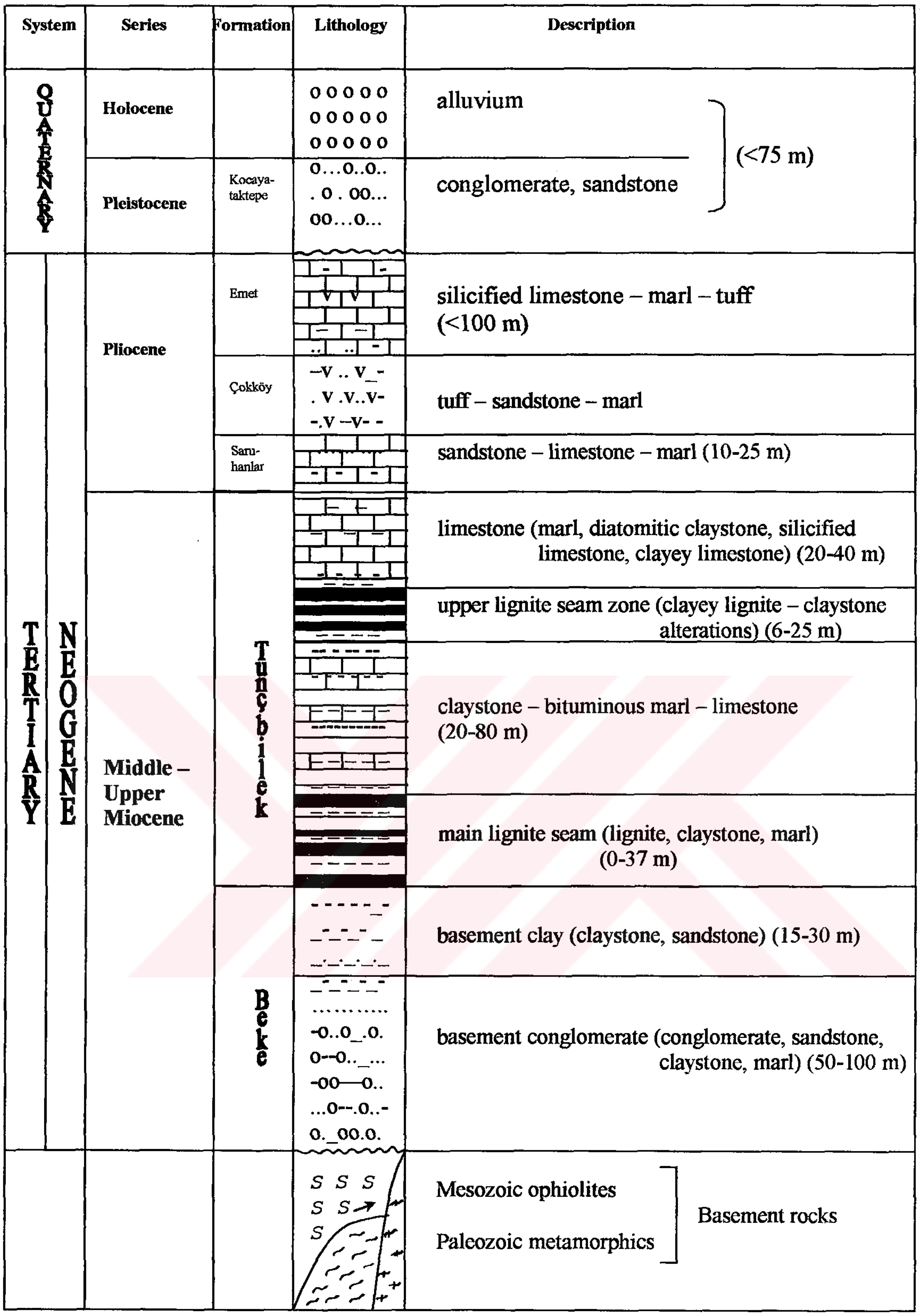


Figure 2.2. Generalized sketch columnar section of Seyitömer Region (Baş, 1986) (not to scale)

CHAPTER 3

SEYİTÖMER THERMAL POWER PLANT

3.1.Historical Background

Studies about establishment of a thermal power plant in the Seyitömer Basin were first started in 1960s by EİEİ (Turkish Electricity Department) and in 1966, a pre-project concerning the general plans and feasibility reports of Seyitömer Lignite Basin was prepared. Following this, tests and feasibility studies, related with the grinding and burning of 203 million tons of lignite and 140 million tons of bituminous schist, were started. In December 1968, first unit with 150 MW energy capacity and in February 1969, second unit with 150 MW energy capacity were put in operation by French Stein Industrie (SI) and Italian Gruppo Industrie Electro Mecaniche Per Impianti All'entero (GIE), respectively. Third unit was put in operation in 1974-1978 period with 150 MW energy capacity, and forth unit in 1984-1989 period, with 150 MW energy capacity. After the construction of Unit IV, wastewater clearance unit was established in 1990 to prevent water pollution. (Personal communication, Ms. Ayşegül Bahayetmez) The power plant is currently operated by TEAŞ (Turkish Electricity Generation and Transmission Corporation).

3.2. Structure of the Plant

The Seyitömer Thermal Power Plant is about 1130 meters above sea level. It consumes low quality lignite produced from the Seyitömer Basin. Coal that is necessary for electricity production is mined by TKİ (Turkish Coal Enterprises)/Seyitömer Lignite Operations, and it is used after crushing in the plant. The lignite has a calorific heat value of 1750 +/- 100 kcal/kg, an ash amount of 35 %, a sulfur content of 1.36 % and a humidity value of 40 % (TKİ, 1973). Due to the classification scheme given in table 1.1, Seyitömer lignite has a lower calorific heat value than what has been found as an approximate value for lignites. The sulfur content of the Seyitömer coals, being 1.36 %, is classified as a medium sulfur content.

In the plant, there are four boiler units, each producing 150 MW energy, with a total of 600 MW (4x150=600) energy capacity (Figure 3.1), having 3.6 billion kwh total annual production. Therefore, 4.6 % of Turkey's energy production is from this plant.

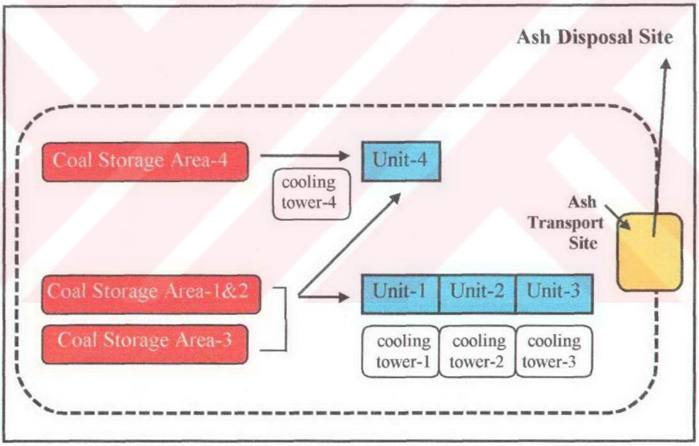


Figure 3.1. Schematic figure showing boiler units and the disposal site in Seyitömer Thermal Power Plant

In Seyitömer Thermal Power Plant, in each boiler, 260 tons/h of lignite and marl burn, producing 500 tons/h of vapor. For each unit, 500 tons/h water is necessary. This water is taken from the Enne Dam located 13 km away from the plant, which is constructed on the Felet stream at 1.9.1972 by DSİ (State Hydraulic Works). As the water contains some toxic materials, it is cleaned by adding chlorine, lime and aluminum sulfate. Therefore, its organic matter content is decreased.

In Seyitömer Plant, 20 000 tons of coal is burned and 6000-8000 tons of fly ash is produced per day, which means, 30-40% of the coal burned becomes ash. In the annual basis, 5 000 000 tons of coal is burned and 1.5-2 million tons of it is ash. The ash hill in the disposal site (Figure 3.2, 3.3) is about 100 meters high, containing approximately 30 million tons of ash.

Figure 3.2. Photograph of the solid waste disposal site of Seyitömer Thermal Power Plant

Figure 3.3. Photograph of the ash hills in the disposal site

In each boiler unit, there are two electrofilters, which are necessary for preventing larger fly ash particles to spread to the atmospheric environment. While blowing with the stack gases, the ash from the coal is kept by the electrofilters, which work with 98 % efficiency. The rest 2% leaves the stack and enter the atmospheric environment. Especially in hot and dry weather, the fly ash particles that escape from the stacks, together with the blow offs from the disposal site, produce a great amount of ash blowing in the air (Figure 3.4). The ash particles kept by electrostatic filters are sent to ash silos by a pneumatic system.

The slag of the coal burned is kept by a system located below the boiler that is full of water, which behaves also as a cooling system there. Those slag pieces are then sent to slag silos by the help of conveyor belts.

Figure 3.4. Photograph of the blow offs from the ash disposal

Ash taken from the ash silos are damped and combined with slag taken from the slag silos. Figure 3.5 illustrates the generalized scheme of the plant indicating the boiler units and ash-slag flow through the plant. The solid wastes produced are then transferred to the ash disposal site (Figure 3.6), 3 kilometers away from the plant (NE), by the use of conveyor belts (Figure 3.7), having 450 tons/hr capacity. The conveyor belts end at Yumaklı Hill ('Yumaklı Tepe') and the waste products are disposed off towards the south of the Hill (Figure 3.8). The disposal activity is continuous, resulting in 500 tons/hr ash disposed of on land.

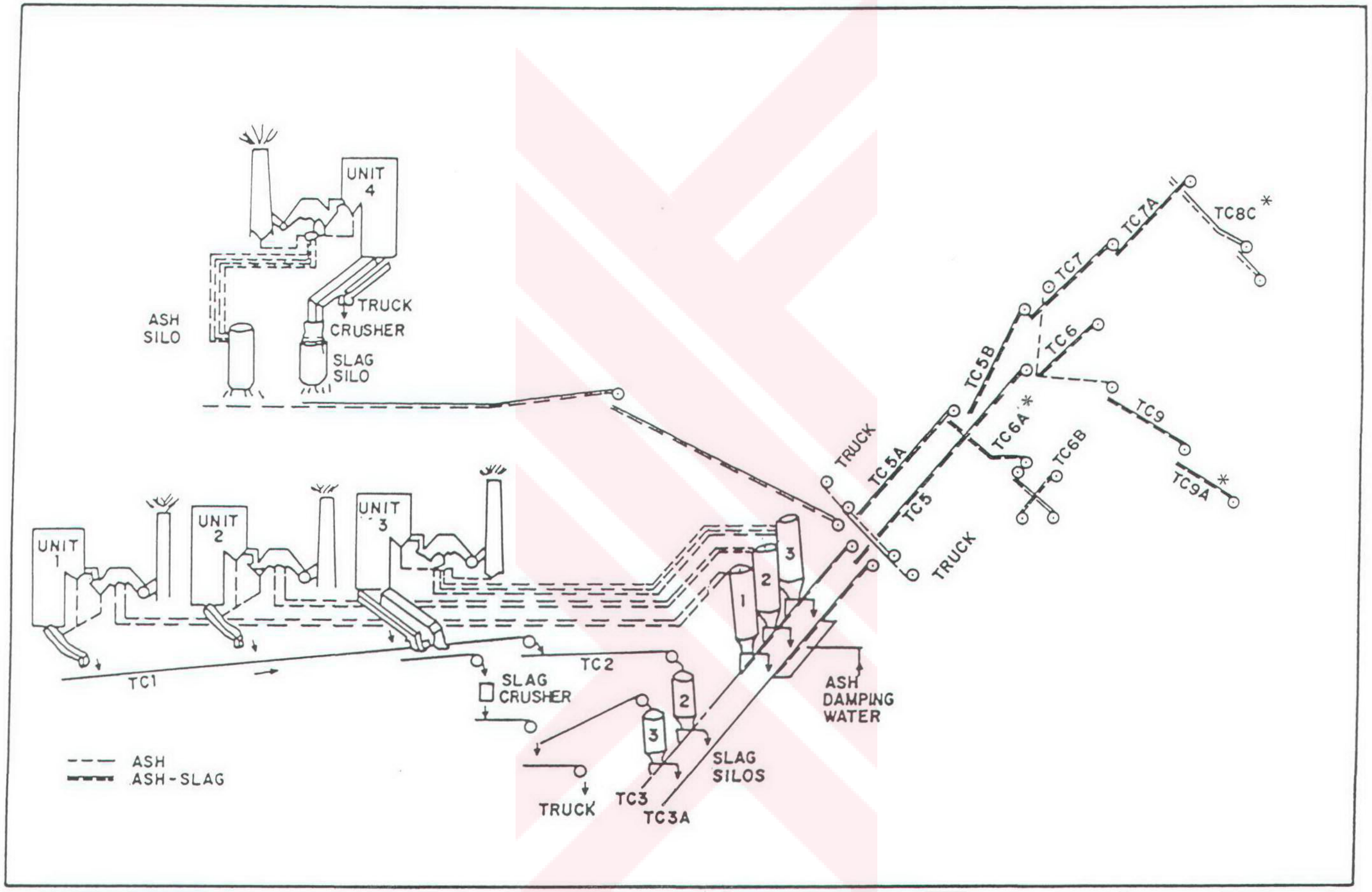


Figure 3.5. Generalized ash-slag flow chart illustrating the transportation of the solid wastes and the disposal sites (*: disposal sites, TC-8C, TC-9A and TC-6A, from which the samples were collected)

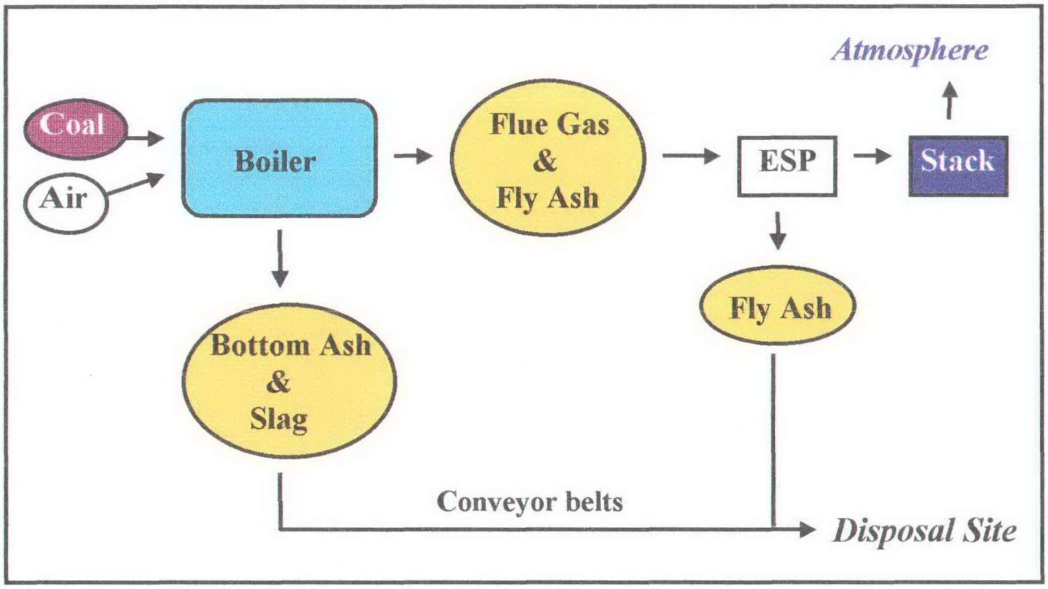


Figure 3.6. Schematic diagram illustrating flow through Seyitömer Thermal Power Plant (ESP: Electrostatic Precipitator)

Figure 3.7. Photograph of conveyor belts for solid waste transportation from plant to the disposal site

(a)

(b)

Figure 3.8. Photographs of the end of conveyor belts at the disposal sites, TC-6A (a) and TC-8C (b)

In Seyitömer Thermal Power Plant, for the purpose of protecting the environment, ash disposals are covered with a thin layer of soil cover (Figure 3.9). The area is also revegetated and planted with trees and plants of Koringa type. Fly ash particles produced from the combustion of coal are still in use in cement industry.

Figure 3.9. Photograph of the soil cover (<10 cm) on the disposed ash

CHAPTER 4

GEOCHEMISTRY

4.1. Geochemistry of Coal Combustion Solid Waste Products: Review

The elements in the fly ash are mainly lithophiles and chalcophiles (Klein et. al, 1975). 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 (Klein and Russel, 1973) (Figure 4.1).

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 (Hulett and Weinberger, 1980; Hansen and Fisher, 1980).

The aluminosilicates are not decomposed and volatilized by combustion, rather, they melt and coalesce to form the slag and fly ash on which the volatile elements condense. These non-volatile elements show little preferential partitioning between slag, bottom ash and fly ash particles (Klein et al., 1975). The concentrations of these elements, which form the aluminosilicate matrix, are almost independent of the particle size.

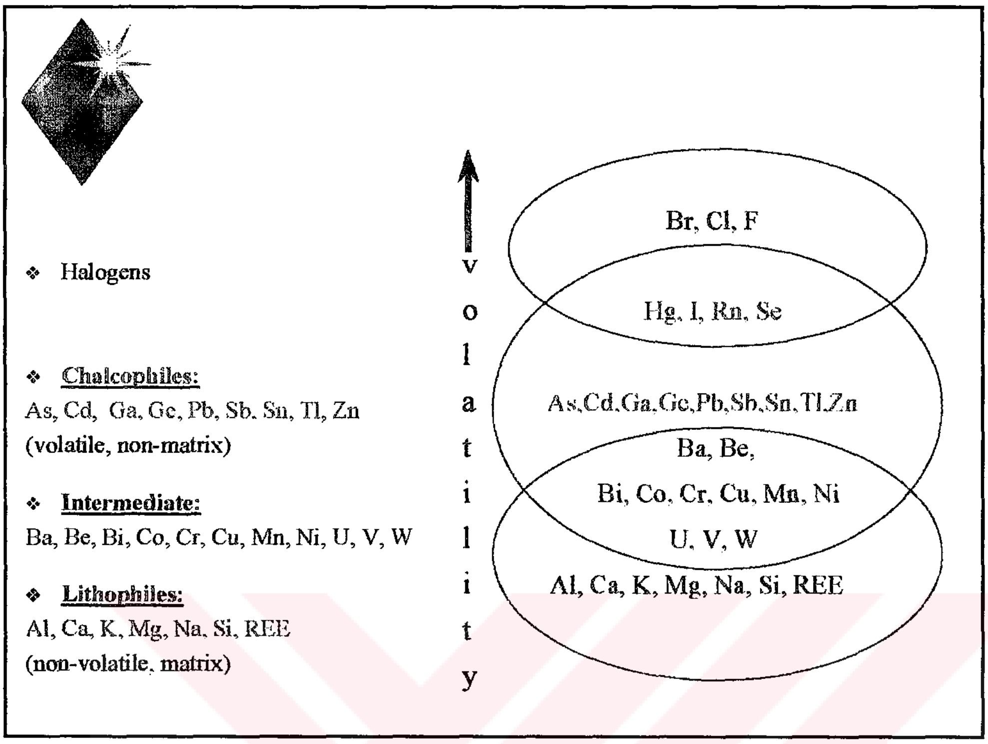


Figure 4.1. Geochemical classification of the elements in fly ashes by their behavior during combustion and gasification (modified from Finkelman, 1996).

The elements that form the aluminosilicate matrix built up the bulk of fly ash structure; while, being volatile, most toxic trace elements are mainly concentrated at the surface of those fly ash particles, forming the non-matrix structure and they show an inverse relationship between the size of fly ash particles and the concentration of the trace elements.

Br, Cl, F, Hg, I, Rn and Se are mostly lost during volatilization (Abel and Rancitelli, 1975; Anderson and Smith, 1977; Block and Dams, 1975; Kaakinen et al., 1975; Klein et al., 1975; Klein and Russel, 1973). Most Br, Cl, F, Hg, some I, Rn and Se are discharged to the atmosphere as gases. These elements, being very volatile, mostly remain in the gas phase during their passage through the power plant, although they may in part be associated with the fly ash particles.

The elements that are volatile or form volatile oxides at the temperature of combustion (1300 - 1600°C), namely chalcophiles, such as, As, Cd, Ga, Ge, Mo, Pb, Sb, Se, Sn, Tl and Zn tend to show completely non-matrix behavior, being present at the surface of fly ash particles.

During the initial stages of combustion, the conditions in a coal particle and within its immediate vicinity are reducing. Under these conditions, the chemical bonding between chalcophile elements and sulfur in sulfide mineral inclusions is broken and these metallic elements form volatile species.

The size of the emitted fly ash particles is of particular interest, as it is these particles which can pass through the collection devices and efficiently deposit in the pulmonary region of the lungs (Davison et al., 1974). If the specific surface of fly ash particles is directly proportional to the composition of an element and if particle sphericity is assumed, elemental concentrations are inversely proportional with particle size, and it is often assumed that the element is located at the surface of that particle (Block and Dams, 1976; Campbell et al., 1978; Coles et al., 1979; Furuya et al., 1987; Hansen and Fisher, 1980; Klein et al., 1975; Norton et al., 1986; Norton et al., 1988). Fine particles have greater specific surface to adsorb volatile toxic compounds and elements. Therefore, they are more enriched in the trace elements (Taylor et al., 1982; Weissman et al., 1983). The larger fractions are diluted as bulk of them is of matrix material. Hence, they reflect the matrix composition mainly, being primarily composed of the non-volatile elements. These fractions are quite heterogeneous since they reflect the chemistry of the individual mineral inclusions and are composed primarily of material not volatilized during combustion.

After combustion, as the flue gas cools, the volatile species presumably condense and accumulate onto the surface of the fly ash particles, forming a surface coating (Coles et al., 1979). Therefore, their concentration directly correlates with the surface to volume ratio of the particles. The composition of this surface coating results in the deterioration of the aqueous solutions (Theis and Wirth, 1977). Therefore, they are considered detrimental to the environment. The elements that are enriched on the smaller particles usually have boiling points comparable to or less than the temperature of the combustion zone. Hence, metal compounds (e.g. pyritic compounds) are reduced to the elemental forms before volatilization. These elements, initially volatilized and dispersed in the flue gas stream, may then be oxidized to form less volatile species which may then condense or be adsorbed on the fly ash as the temperature of the flue gas drops. Therefore, the amount of trace elements remaining at the surface of fly ash particles is also related with the vapor pressure of the particular trace element being considered.

The slag is removed directly and quickly from the combustion zone, while the fly ash remains in contact with the cooling flue gas. Since the slag is in contact with the flue gas for a short time and at a high temperature, the volatile elements have no opportunity to condense on the slag. They do, however, preferentially condense or become adsorbed on the finer fly ash particles as the flue gas cools, since such particles have a larger surface area to volume ratio. Therefore, condensation of the volatile elements on the slag is minimal. These elements are more concentrated in coal ash compared to slag, and more concentrated in fly ash (ash discharged through the stack) than in bottom ash (ash collected by the precipitator) (Klein et al., 1975; Norton et al., 1988).

Many elements show an equal distribution between matrix and non-matrix structure. These elements, that exhibit an intermediate behavior between the two structures, are mainly, Ba, Be, Co, Cr, Cu, Mn, Ni, U and V. They also show an intermediate partitioning behavior (Hansen et al., 1984; Klein et al., 1975).

4.2. Methods of Study

4.2.1. Sampling

Samples of coal combustion waste products, namely fly ash, bottom ash and slag, and samples of soil were collected for this study. Twenty fly ash samples were collected, of which sixteen samples were from the ash disposal site (TC-8C, TC-9A and TC-6A) and four samples were away from the ash disposal site over a distance of 200 meters. Three bottom ash and three slag samples were taken from the boiler units (No:1, No:2 and No:4). Samples from Unit 3 could not be obtained as it was not in operation during the sampling period. Eight soil samples were taken away from the disposal site, over a distance of 3 kilometers from the ash hill to Kınık Village, with increasing intervals towards south which was the wind direction at the time of sample collection; one soil sample was taken from the northern side of the ash disposal, opposite to the wind direction (Figure 4.2).

4.2.2. Analysis Techniques

Solid waste products and soil samples were analyzed for a total of 11 elements, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, Pb, Zn, Cd, Cu and Co, by Atomic Absorption Spectrophotometry (AAS, Rank-Hilger/1551) at the laboratories of the Geological Engineering Department of Middle East Technical University in Ankara.

4.2.2.1. Principles of Atomic Absorption Spectrophotometry (AAS) Technique

Atomic Absorption Spectrophotometry technique is based upon the observation that atoms of an element can absorb electromagnetic radiation. This occurs when the element is atomized and the wavelength of light absorbed is specific to each element. Therefore, Atomic Absorption Spectrophotometry comprises an atomizing device, a light source and a detector. A lowering of response in the detector during the atomization of a sample in a beam of light, as a consequence of atomic absorption, can be calibrated and is sensitive at ppm level. The sample is prepared in solution and aspirated by a nebulizer and atomized in an acetylene-air or acetylene-nitrous oxide flame (Rollinson, 1993).

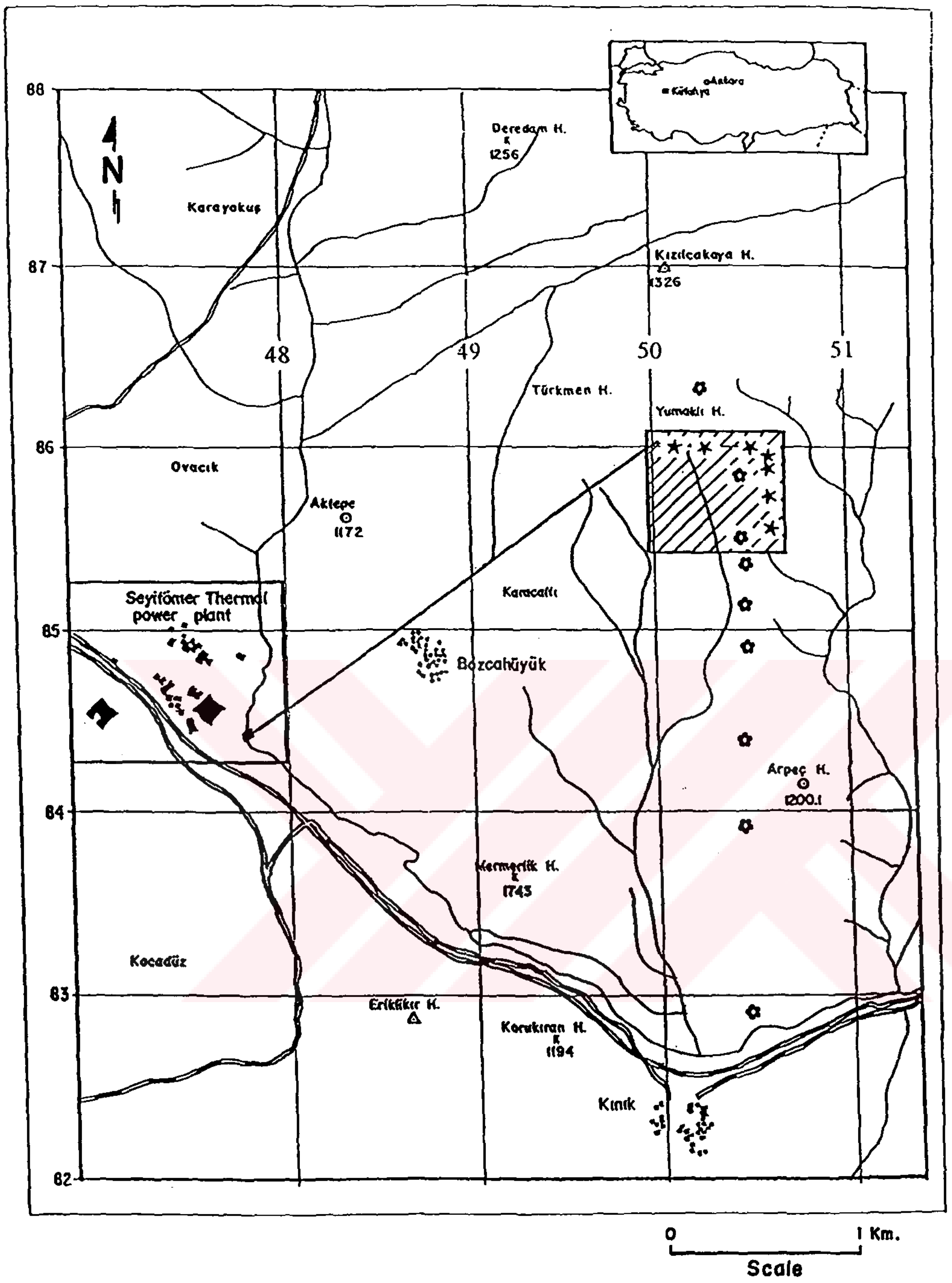


Figure 4.2. Schematic map of the study area illustrating the sampling locations

★: Ash Samples ✿: Soil Samples

4.2.2.2. Sample Preparation

Prior to analyses by Atomic Absorption Spectrophotometry (AAS), the solid waste products (fly ash, bottom ash and slag) and soil samples were first dried at room temperature and then taken into solution (solution B - Appendix).

For the analysis of matrix elements, mainly the rock standard G-2 was used, while for the analysis of other elements, the elemental standards were used. For precision measurements, replicate analyses were performed on samples from each sample type (fly ash, bottom ash, slag and soil samples). Average concentration values of the replicate analyses were used for the geochemical interpretations.

For the determination of the relationship between size and chemical composition of fly ash particles, size fractionation of fly ash samples from two ash disposal sites, TC-8C and TC-9A, was performed at the geochemistry laboratory of the Research Center of Turkish Petroleum Corporation in Ankara. Those fly ash samples were separated into three size fractions, which were <10 µm, 10-38 µm and 38-180 µm, by wet sieving method using isopropyl alcohol in order to prevent the solubility of the elements in water. Isopropyl alcohol (2-propanol) has a density of 0.9790, therefore less dense than water. Fly ash samples, from disposal sites TC-8C and TC-9A, were centrifuged in the isopropyl alcohol for 2 minutes at 2500 rpm to differentiate 180-38 and 10-38 µm fractions. To obtain the fraction <10 µm, fly ash samples were centrifuged for 5 minutes at 3500 rpm. Centrifugation was applied for the purpose of increasing the gravitational force and hence the rate of particle sedimentation, which becomes important in the separation of clay size particles. Then these fractionated samples were oven dried and analyzed by AAS to assess the relationship between size and chemical composition of fly ash particles, as they are those smaller particles, which can easily pass through the respiratory system, owing greater concentrations of toxic trace elements at the surface.

4.3. Results and Discussion

In this study, concentrations of five toxic trace elements (Cd, Pb, Co, Cu, Zn) and of six major oxides (Al_2O_3, CaO, Na_2O, K_2O, MgO, Fe_2O_3) were determined on the coal combustion solid waste products and soil samples.

Results of the geochemical analyses of eleven elements for the collected samples are listed in Tables 4.1, 4.2 and 4.3. The results of the replicate analyses for precision measurements are given in Table 4.4.

Table 4.1. Chemical Analysis of the samples of solid waste products

Elements Samples Type	No	Cd (ppm)	Pb (ppm)	Zn (ppm)	Cu (ppm)	Co (ppm)	Fe_2O_3 (%)	MgO (%)	Na_2O (%)	K_2O (%)	CaO (%)	Al_2O_3 (%)
*fly ash	1	<5	90	107	56	86	3.88	2.54	0.54	1.28	2.25	5.51
*fly ash	2	<5	119	126	86	57	3.94	5.17	0.55	0.38	2.62	5.54
*fly ash	3	<5	195	110	71	86	4.03	2.63	0.46	1.21	2.15	5.13
*fly ash	4	<5	135	97	56	65	3.78	2.8	0.45	1.05	1.85	4.53
*fly ash	5	<5	269	125	67	72	3.78	2.25	0.5	0.96	1.31	4.83
*fly ash	6	<5	90	90	64	50	3.80	2.42	0.52	0.99	1.32	5.22
*fly ash	7	<5	239	113	67	57	3.80	2.25	0.48	0.96	1.78	4.8
*fly ash	8	<5	74	96	67	50	3.78	2.3	0.5	0.93	1.82	5.07
*fly ash	9	<5	164	92	64	36	3.85	2.16	0.5	1.00	1.57	5.06
*fly ash	10	<5	195	119	67	72	3.78	2.3	0.5	0.94	1.54	4.89
*fly ash	11	<5	119	126	67	50	3.95	2.66	0.49	0.69	1.19	5.27
*fly ash	12	<5	224	110	67	65	3.94	2.21	0.51	1.24	1.32	5.54
*fly ash	13	<5	135	114	71	72	3.95	2.18	0.47	1.12	1.25	5.27
*fly ash	14	<5	119	89	67	93	3.96	2.63	0.51	1.08	1.13	5.96
*fly ash	15	<5	90	112	71	72	3.92	2.18	0.48	1.03	1.43	5.33
*fly ash	16	<5	74	95	71	65	3.53	2.66	0.51	1.08	1.56	5.93
**bottom ash	17	<5	119	91	67	57	4.05	2.14	0.62	1.13	1.65	7.17
**bottom ash	18	<5	165	113	67	65	4.06	2.25	0.57	1.30	1.63	6.31
**bottom ash	19	<5	164	162	64	72	4.08	2.28	0.58	1.58	1.68	6.19
***slag	20	<5	74	135	60	65	4.17	2.06	0.41	0.95	1.19	5.07
***slag	21	<5	119	139	112	72	3.85	3.54	0.48	0.77	1.19	5.24
***slag	22	<5	135	105	86	57	3.97	2.66	0.42	0.63	2.17	4.92

* Sample no 1-4 are from disposal site TC-6A
Sample no 5-10 are from disposal site TC-9A
Sample no 11-16 are from disposal site TC-8C
** Sample no 17 is from Boiler Unit 1
Sample no 18 is from Boiler Unit 2
Sample no 19 is from Boiler Unit 4
*** Sample no 20 is from Boiler Unit 1
Sample no 21 is from Boiler Unit 2
Sample no 22 is from Boiler Unit 4

Table 4.2. Elemental concentrations of fly ash samples with increasing distance away from the ash disposal site

Distance	***Concentration***										
(m)	***Ppm***					*%*					
	Cd	**Co**	**Cu**	**Zn**	**Pb**	**Na_2O**	**K_2O**	**Fe_2O_3**	**MgO**	**CaO**	**Al_2O_3**
0	<5	79	71	138	135	0.58	1.43	4.06	3.04	1.90	6.22
25	<5	57	67	132	119	0.58	1.47	4.09	2.97	1.90	6.22
100	<5	50	67	137	164	0.55	1.41	4.03	2.33	1.82	5.99
200	<5	65	71	119	179	0.54	1.33	4.03	2.40	1.77	5.66

Table 4.3. Elemental concentrations of soil samples with increasing distance away from the ash disposal site (opp: represents the sample at the north of disposal site, opposite of wind direction)

Distance	***Concentration***										
(m)	***ppm***					*%*					
	Cd	**Co**	**Cu**	**Pb**	**Zn**	**Na_2O**	**K_2O**	**Fe_2O_3**	**MgO**	**CaO**	**Al_2O_3**
100	<5	278	15	395	82	0.50	0.82	3.28	3.91	4.23	9.60
380	<5	193	41	395	60	0.38	0.46	3.20	5.62	16.99	7.26
500	<5	171	5	277	93	0.43	0.69	3.22	4.39	5.41	8.18
750	<5	246	56	356	80	0.45	0.85	3.24	4.50	0.78	8.53
1000	<5	332	92	436	89	0.45	0.86	3.31	2.41	11.06	9.66
1500	<5	225	41	475	68	0.43	0.81	3.20	4.00	10.78	9.10
2000	<5	353	46	475	83	0.40	0.89	3.26	3.60	7.11	10.19
3000	<5	235	15	356	91	0.46	1.16	3.13	7.50	5.90	7.17
opp	<5	107	21	436	118	0.33	0.73	3.15	2.35	6.69	7.73

Table 4.4. Results of the replicate analysis for precision measurements

Elements Samples Type	Measur.No	Cd (ppm)	Pb (ppm)	Zn (ppm)	Cu (ppm)	Co (ppm)	Fe_2O_3 (%)	MgO (%)	Na_2O (%)	K_2O (%)	CaO (%)	Al_2O_3 (%)
Fly Ash Sample No: 1	1	<5	60	109	56	100	3.88	2.49	0.55	1.29	2.26	5.49
	2	<5	149	109	56	79	3.87	2.56	0.54	1.29	2.26	5.52
	3	<5	60	103	56	79	3.88	2.56	0.54	1.27	2.24	5.52
	Average	<5	90	107	56	86	3.88	2.54	0.54	1.28	2.25	5.51
Bottom Ash Sample No: 17	1	<5	104	94	67	57	4.04	2.14	0.63	1.14	1.65	7.17
	2	<5	104	88	67	79	4.04	2.14	0.62	1.13	1.65	7.16
	3	<5	149	91	67	36	4.05	2.14	0.62	1.12	1.66	7.17
	Average	<5	119	91	67	57	4.05	2.14	0.62	0.13	1.65	7.17
Slag Sample No: 20	1	<5	104	134	56	57	4.16	2.06	0.41	0.96	1.19	5.06
	2	<5	60	137	67	57	4.17	2.06	0.41	0.95	1.20	5.07
	3	<5	60	134	56	79	4.17	2.06	0.42	0.94	1.18	5.08
	Average	<5	74	135	60	65	4.17	2.06	0.41	0.95	1.19	5.07
Soil Sample No: 26	1	<5	356	87	72	257	3.24	4.46	0.45	0.85	5.52	8.7
	2	<5	356	70	56	225	3.24	4.52	0.45	0.85	5.49	8.4
	3	<5	356	82	41	257	3.25	4.52	0.44	0.84	5.54	8.4
	Average	<5	356	80	56	246	3.24	4.5	0.45	0.85	5.52	8.53

As a first approximation to the evaluation of the results, concentration plots of the collected samples for each element were prepared in order to get a general idea on the relative elemental concentrations of each sample type (Figure 4.3, 4.4).

It appears from figure 4.3 that, except Pb, there is almost no trend between the elemental concentrations for slag, bottom ash and fly ash samples. Pb, on the other hand, shows an enrichment on fly ash particles, when compared with other solid wastes, and on bottom ash, when compared with slag. Concerning the soil samples, Pb and Co concentrations are much higher, whereas Cu and Zn concentrations are lower than those of solid waste products.

Being a volatile element at the temperature of combustion, Pb condenses and is adsorbed on the solid waste products. Since condensation and adsorption are surface phenomena, the concentration of the condensed elements is strongly dependent on the surface area to volume ratio of the adsorbing particles and a decrease in particle size leads to an increase in the concentration (Block and Dams, 1976; Campbell et al., 1978; Coles et al., 1979; Furuya et al., 1987; Hansen and Fisher, 1980; Klein et al., 1975 and Norton et al., 1986). Therefore, the observed behavior of Pb in solid waste products (i.e. increase in Pb concentration from slag through bottom ash to fly ash) reflects the inverse relationship between particle size and concentration of volatile elements.

Although Zn, Cu and Co are also volatilized at the temperature of combustion, the same partitioning behavior as Pb could not be observed in solid waste products. This is mainly due to the intermediate character of these elements, being equally distributed between the surface and matrix of these solid waste products. The considerably high Pb and Co concentrations in soil samples (above those of solid waste products) can be attributed to the effects of background values originating from the basement lithologies in Seyitömer Basin, or less probably, high Pb concentration may be due to Pb in the exhaust gases of the tractors working in the area for agricultural purposes, as there is a stabilized road passing through the sampling site. The Cu and Zn concentrations in soil samples suggest either effects of the background values or the leaching of the elements (by surface waters) from solid waste products and their subsequent introduction to the soils, as Cu and Zn are the elements that can change into soluble phase easily, while Pb and Co are

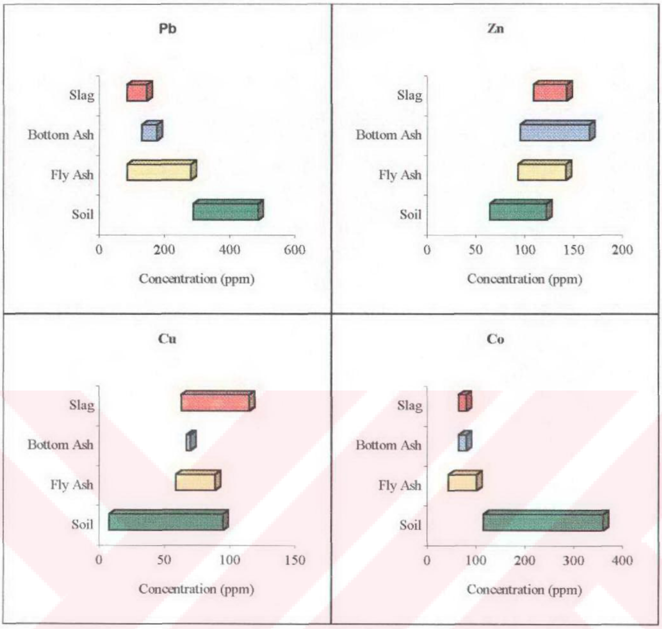


Figure 4.3. Trace element concentrations (ppm) of soil, fly ash, bottom ash and slag samples

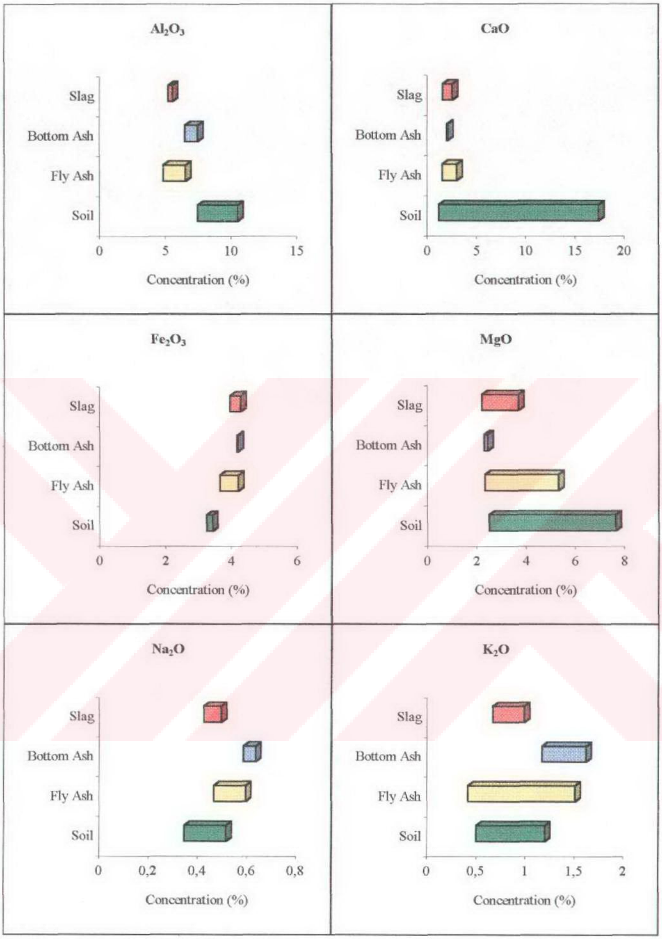


Figure 4.4. Major element concentrations (%) of soil, fly ash, bottom ash and slag samples

relatively insoluble elements. Therefore the leaching of Pb and Co from coal combustion solid waste products is not expected.

Regarding the major elements (Figure 4.4), no preferential partitioning is observed between the solid waste products. Since these elements are not volatilized in the combustion zone, but rather melt and form the matrix structure of slag, bottom ash and fly ash, they remain in the matrix, showing no preferential partitioning between these waste products. Fe_2O_3, Na_2O and K_2O concentrations of soil samples are similar to those of solid waste products. MgO, Al_2O_3 and especially CaO concentrations, on the other hand, are above those recorded from the solid waste products. Therefore, these major element contents of soil samples are likely to be related to the mineral (and hence the chemical) composition of the soil itself, reflecting the basement lithologies.

As another approach to the geochemical assessment of environmental effects of coal combustion solid waste products, fly ash and soil samples that are collected away from the disposal site were analyzed to find out the distribution of the major and trace elements with increasing distance. The results of these analyses are given in Tables 4.2 and 4.3.

For fly ash samples, regarding the trace elements, Pb concentration shows an increase with distance away from the disposal site (Figure 4.5). This may be attributed either to the case that, in finer fly ash particles, which are carried for longer distances, greater concentrations are reached, or to the exhaust gases of the tractors passing nearby the area. Another possibility for the reason of high Pb concentration with distance may be the probable mixing of soil and fly ash in the sampling site. As the soil Pb concentrations are relatively high with respect to the solid waste products, it might have increased the Pb concentration of fly ash samples. The same trend as Pb, can not be observed for the other trace elements. This may be due to their intermediate character.

From figure 4.6, it is observed that, except Al_2O_3 and MgO, the major element concentrations of fly ash samples show no trend with distance. Al_2O_3 and MgO concentrations show a slightly decreasing trend with increasing distance. This decrease in Al_2O_3 and MgO contents, may suggest a possible leaching of these elements from the long-distance travelled fly ash particles, or they may represent the background data.

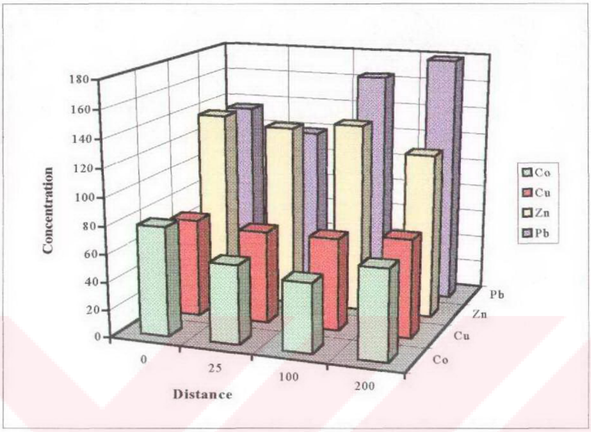


Figure 4.5. Graph illustrating the relationship between distance (m) and trace element concentrations (ppm) of fly ash samples

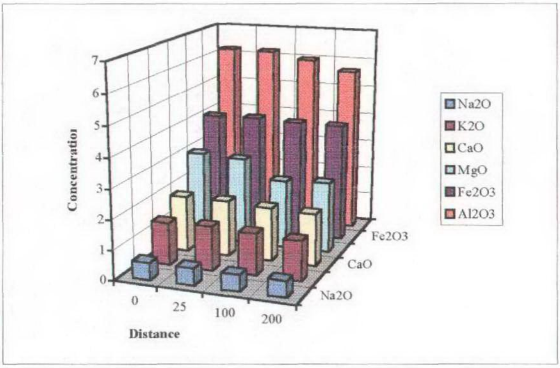


Figure 4.6. Graph illustrating the relationship between distance (m) and major element concentrations (%) of fly ash samples

For soil samples, for both major and trace elements, data show fluctuations (Figure 4.7, 4.8). Therefore, no trend is obtained with distance away from the ash disposal site. This may be because the distance, over which the soil samples were collected, was limited with rural areas which makes bulk soil sample collection difficult. Therefore, there is a possibility in some soil samples to be mixed with a small amount of fly ash. Also, the data may be representing the background values.

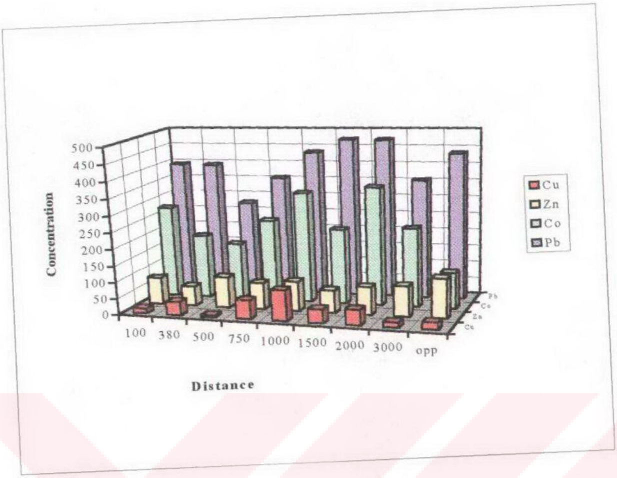


Figure 4.7. Graph illustrating the relationship between distance (m) and trace element concentrations (ppm) of soil samples

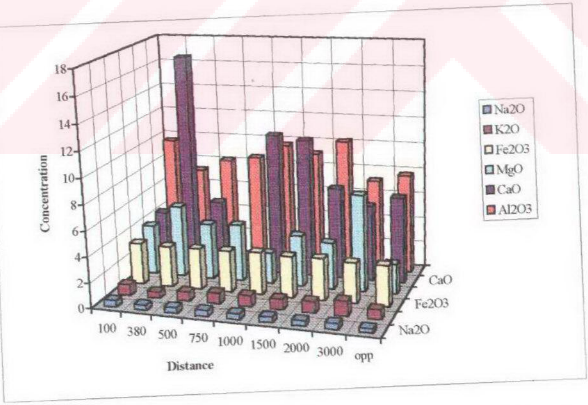


Figure 4.8. Graph illustrating the relationship between distance (m) and major element concentrations (%) of soil samples

As a further evaluation of the relationship between the elemental concentrations and particle size, fly ash samples from two disposal sites were size-fractionated. Each fraction was analyzed for major and trace elements, the results of which are summarized in Table 4.5.

Table 4.5. Composition of fly ash samples as a function of particle size at disposal sites TC-8C and TC-9A

Disposal Site	**TC-8C**			**TC-9A**		
Elements	***Particle Size (μm)***			***Particle Size (μm)***		
	38-180	**10-38**	**<10**	**38-180**	**10-38**	**<10**
Ppm						
Pb	150	209	344	119	135	195
Zn	117	180	240	119	176	289
Cu	90	127	199	90	131	165
Co	50	100	136	79	100	115
%						
Fe_2O_3	4.02	4.04	4.13	4.00	4.11	4.07
MgO	2.78	2.92	3.01	2.68	2.73	2.78
Na_2O	0.57	0.56	0.52	0.57	0.56	0.56
K_2O	1.02	1.30	1.37	0.97	1.17	1.32
CaO	1.69	1.76	1.83	1.63	1.86	2.39
Al_2O_3	5.93	5.42	6.25	5.75	5.60	5.19

Concentration profiles of fly ash samples, from two disposal sites, TC-8C and TC-9A, as a function of particle size are shown in Figures 4.9 and 4.10. For elements volatilized during combustion (examples include Pb, Zn, Cu and Co), concentrations decrease with increasing particle size (Figure 4.9), because of larger surface area-to-volume ratio of the smaller particles. This trend is not expected for the major elements as they are non-volatile and present primarily in the matrix of fly ashes. Indeed, the major element concentrations show different behaviors with increasing particle size (Figure 4.10). Al_2O_3 and Fe_2O_3 concentrations showed irregular trends, while Na_2O concentration almost decrease with decreasing particle size. On the other hand, CaO, MgO and K_2O concentrations increase with decreasing particle size, probably indicating partial volatilization of these elements (Markowski and Filby, 1985; Campbell et al., 1978).

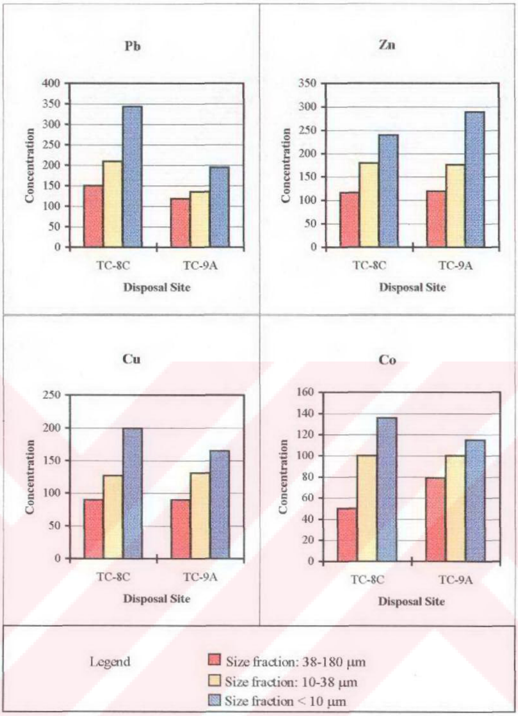


Figure 4.9. Trace element composition (ppm) of fly ash as a function of particle size (μm)

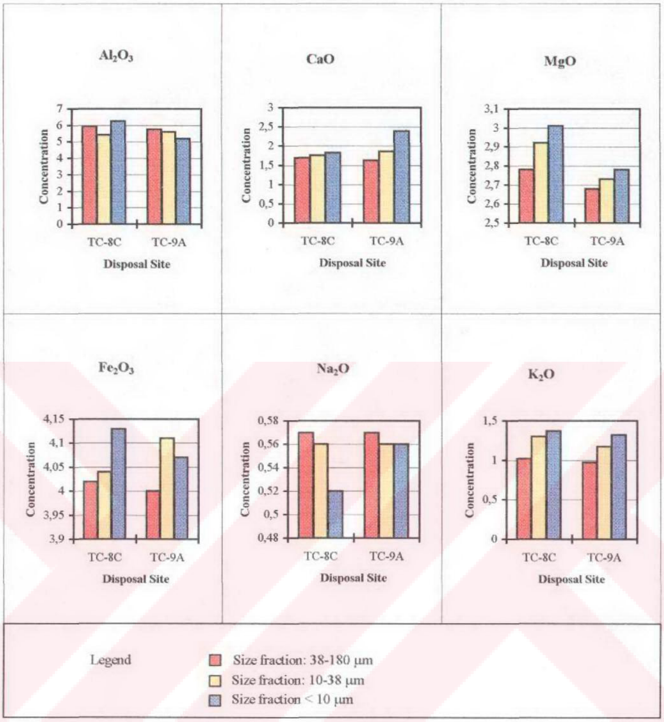


Figure 4.10. Major element composition (%) of fly ash as a function of particle size (μm)

Therefore, as the toxic trace element concentrations of the finer fly ash particles is greater than larger ones, and as finer particles can be directly inhaled, serious dangers to ecosystems and public health can develop if certain trace constituents of fly ash (which are generally complexed with organic matter in the coal and only isolated by combustion) are set free to enter a biological cycle.

As a final evaluation, the results of the geochemical analyses of soil samples are compared with the maximum allowable concentration limits for agricultural soils (Kabata-Pendias, 1995), put forward by several countries (Table 4.6). The comparison reveals that, Pb and Co concentrations, showing a range between 277-475 ppm and 107-353 ppm, respectively, exceed the limits of many countries, while the other elements, Cd, Cu and Zn are below these limits.

Table 4.6. Proposals for maximum allowable concentrations (MAC) of trace elements considered as toxic in agricultural soils for different countries (Kabata-Pendias, 1995) and the value ranges obtained from this study

Element *(ppm)*	Austria	Canada	Poland	Japan	G.Britain	This Study
Cd	5	8	3		3	<5
Co	50	25	50	50		107-353
Cu	100	100	100	125	100	5-92
Pb	100	200	100	400	100	277-475
Zn	300	400	300	250	300	60-118

The higher Pb and Co concentrations in soil samples may be due to the basement lithologies in the area, and the exhaust gases might have been effective in the high Pb concentrations, as discussed before.

CHAPTER 5

MORPHOLOGY AND MINERALOGY

5.1. Morphology of Coal Combustion Solid Waste Products: Review

Characterization of fly ash emissions is important for the development of technology for both reducing fly ash emissions and dealing with medical and environmental problems associated with fly ash release.

The morphology of fly ash particles is mostly studied by scanning electron microscopy. Coal fly ash particles are morphologically heterogeneous, showing a wide variation of particle shapes and densities (Campbell et al., 1978; Hansen et al., 1984). Differences in morphology (the impurity content) can be generally correlated to the differences in the coal used (Lichtman and Markowski, 1985). Spherical particles make up most of the fly ash particles, especially in the finer fractions. These spheres are glassy and mostly transparent, indicating complete melting of silicate minerals (Henry and Knapp, 1980; Theis and Wirth, 1977; Lichtman and Markowski, 1985; Hock and Lichtman, 1982; Shure et al., 1985).

Generally, besides some amorphous and crystalline parts, non-opaque cenospheres (hollow) and plerospheres (filled with micro-spheres) dominate the morphology in finer size fractions of fly ash particles (Fisher et al., 1979). The crystals present in ash particles may be acicular, elongated or irregularly shaped. Generally, larger particles show a greater irregularity compared to smaller ones (Schure et al., 1985).

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.

Shape characteristics of the particles depend on their exposure conditions (time and temperature) in the combustion chamber. Amorphous particles with little rounding had limited exposure to high temperatures. These particles are probably similar to precombustion particles and may be derived from coal, silicates, or both. Amorphous particles with rounded edges and vesicles are probably coal and silicates exposed to higher temperatures or longer residence times in the combustion zone.

The color of fly ash particles is generally a shade of gray. Degree of coloring depends on the amount and size of the associated particles of carbon (Zouboulis and Tzimou-Tsitouridou, 1990). Spheres may range in color from water-white through yellow and orange to deep red or brown to opaque, probably because of varying iron oxide contents within the glass or on the surface of the particles (Fisher et al., 1978). Fly ashes produced at different power plants or at one plant with different coal sources may have different colors.

5.2. Mineralogy of Coal and Coal Combustion Solid Waste Products: Review

The minerals in coal are very important, as they affect the technological, economical and environmental impact of coal. There are more than a hundred minerals observed in coal, but only a small portion are commonly present at percent level.

The major minerals in coal are, Quartz (SiO_2), Clay Minerals (Illite - K, Al, Si; Kaolinite - Si, Al; Mixed-layer clays), Carbonates (Calcite - $CaCO_3$; Siderite - Fe, $MnCO_3$) and Pyrite (FeS_2).

The accessory minerals in coal are, Galena (PbS), Sphalerite (ZnS), Clausthalite (PbSe), Chalcopyrite ($CuFeS_2$), Crandallite Group (Ca, Ba, Sr, Al, P), Monazite (REE, P), Apatite (Ca, P), Barite ($BaSO_4$), Rutile (TiO_2), Zircon ($ZrSiO_4$), Feldspars (Ca, Na, K, Al, Si), Zeolites (Ca, Na, K, Al, SiO_2), Ankerite (Fe, Mg, Ca) and Micas (K, Fe, Mg, Ti, Al, Si) (Finkelman, 1996).

By combustion, due to the effects of heating, minerals in the coal undergo some reactions (Holcombe et al., 1985), which are mainly (Finkelman, 1996), dehydration, degassing, oxidation, volatilization, lattice destruction and phase transformation. The thermal transformation of major inorganic phases during coal combustion are given in Figure 5.1. Iron oxides, feldspars and anhydrite do not undergo phase changes during combustion (Finkelman, 1996).

Generally, fly ash particles are separated into three phases (Hulett et al., 1980; Roy et al., 1984) as, Glass Phase (amorphous phase), Mullite-Quartz Phases (crystalline phases) and Magnetic Spinel Phase (in which trace elements exist to a large extend as solid solutions).

The oxides of major elements may be present in both amorphous and crystalline phases. The crystalline phases containing the two most abundant compounds in the ash, the oxides of Al and Si, are quartz (SiO_2) and mullite ($3Al_2O_3.2SiO_2$) phases. Mullite is a product of thermal breakdown of clay minerals.

Minerals in Coal	*Transformation products in fly ashes*
- Phyllosilicates	Glass, Mullite ($Al_6Si_{12}O_{13}$), Quartz (SiO_2)
- Quartz	Glass, Quartz (SiO_2)
- Pyrite (FeS_2) Siderite ($FeCO_3$) Iron Sulfates	Hematite (Fe_2O_3), Magnetite (Fe_3O_4)
- Calcite ($CaCO_3$)	Lime (CaO)
- Dolomite ($CaMg(CO_3)_2$	Lime (CaO), Periclase (MgO)
- Gypsum $CaSO_4.2H_20$	Anhydrite ($CaSO_4$)
- Ankerite ($CaMg_xFe_{(1-x)}(CO_3)_2$)	Calcium Ferrite ($CaFe_2O_4$) Periclase (MgO)

Figure 5.1. Diagram indicating the thermal transformations of major inorganic phases during combustion of coal (Finkelman, 1996).

The nonmagnetic aluminosilicate components, the glass phases, contain most of the potentially toxic trace elements. Most of the trace elements of high concentration in the mullite-quartz phase have valances of either +3 or +4, they are probably contained in the mullite crystalline lattice as isomorphic substitutions for Al and Si. Their ionic radii are sufficiently small to allow this.

Na, Mg, K and Ca are mainly contained in the glass phase, which is silicon rich. Alkali rare earth, and many transition elements are more concentrated in the glass phase than in the mullite-quartz phase. The aluminosilicate matrix of fly ash can contain as much as 30-40 % mullite and quartz, but most of it is glass (Hulett and Weinberger, 1980).

Depending on the coal sources, Fe may also be a major component, occurring both as separate matrix of magnetic spinels and as oxides in a dissolved form in the aluminosilicate matrix (Hulett et al., 1980). Major magnetic spinel species are magnetite and hematite (Goldberg et al., 1981; Van Der Hook and Comans, 1995). The first row transition elements, Co, Cr, Cu, Mn, Ni and Zn show a substantial enrichment in the magnetic spinel phase, probably in the form of substituted spinels.

5.3. Methods of Study

Morphological features of fly ash, slag and coal samples were determined by the use of Scanning Electron Microscopy (SEM - JEOL JSM 840-A) and Energy Dispersive X-Ray Spectrometer (EDX-TRACOR TN-5502) at the laboratories of Sedimentology and Reservoir Geology Unit at the Research Center of Turkish Petroleum Corporation in Ankara.

5.3.1. Principles of Scanning Electron Microscopy (SEM) Technique

The interaction of the primary electron beam with the sample produces various forms of radiation such as secondary electrons (SEM Micrograph) and characteristic x-rays (EDX Spectrum).

Instead of using light, the SEM image is formed by an internally generated electron beam. The electrons are accelerated through the column, magnified and focused through a series of electromagnetic lenses into a finely focused beam, which bombards the sample. As the electron beam traverses the sample, the secondary electrons emitted are collected by a secondary electron detector mounted in the SEM sample chamber and processed by the electronics console into the familiar SEM image. This image is either displayed on TV screen or photographed with an attached camera. By this way, elemental analysis of a sample is also possible by the use of the characteristic x-rays generated as the electron beam scans the sample. Each element in the sample produces x-rays with characteristic energies and wavelengths. These x-rays can be analyzed using either an energy sensitive detector in an energy dispersive system (EDX), or by dispersing the x-rays according to wavelength using the crystal detector of a wavelength dispersive system (WDX) (Welton, 1984). In this study, the EDX (TRACOR TN-5502) system was used as an attachment to SEM, by applying point, linear and areal analysis. Photographs were also taken from the image where necessary.

5.3.2. Sample Preparation

The sample was attached to a SEM specimen plug with epoxy or silpaste and dried overnight in a low-temperature drying oven. A thin line of silpaint was added to provide an electrical ground from the sample to the plug. The sample was then coated with a conductive metal, namely gold. This coating is required to obtain a clear image of an insulating material (such as a rock sample), but is so thin that it does not hinder the identification of specific minerals. After preparation, samples were put inside the electron microscope sample chamber for identification and became ready for SEM analysis.

5.4. Results

In this study, the fly ash sample was found to be generally heterogeneous, showing a wide variation in particle shapes. Fly ash consists of many small (0.01-200 μm diameter), glass-like particles of a nearly spherical character (Figure 5.2).

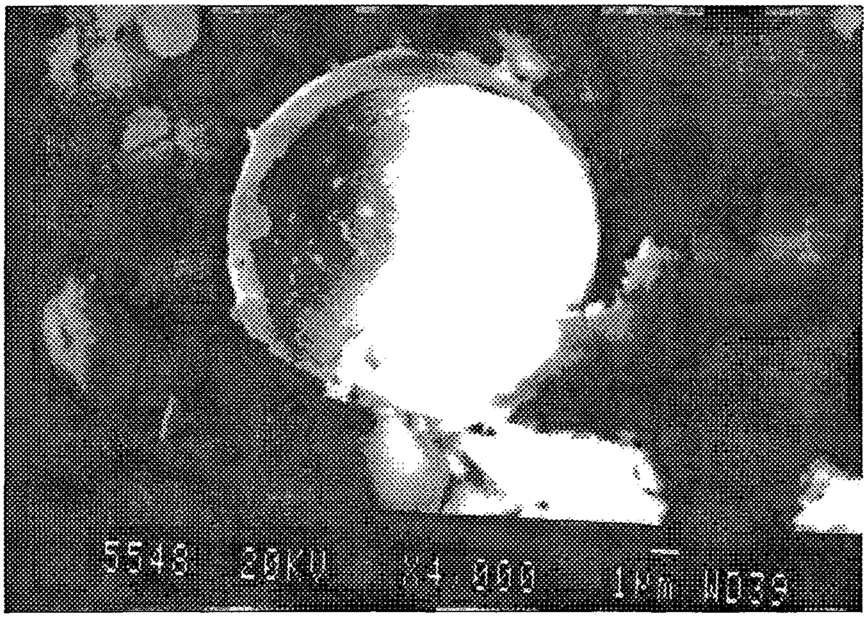
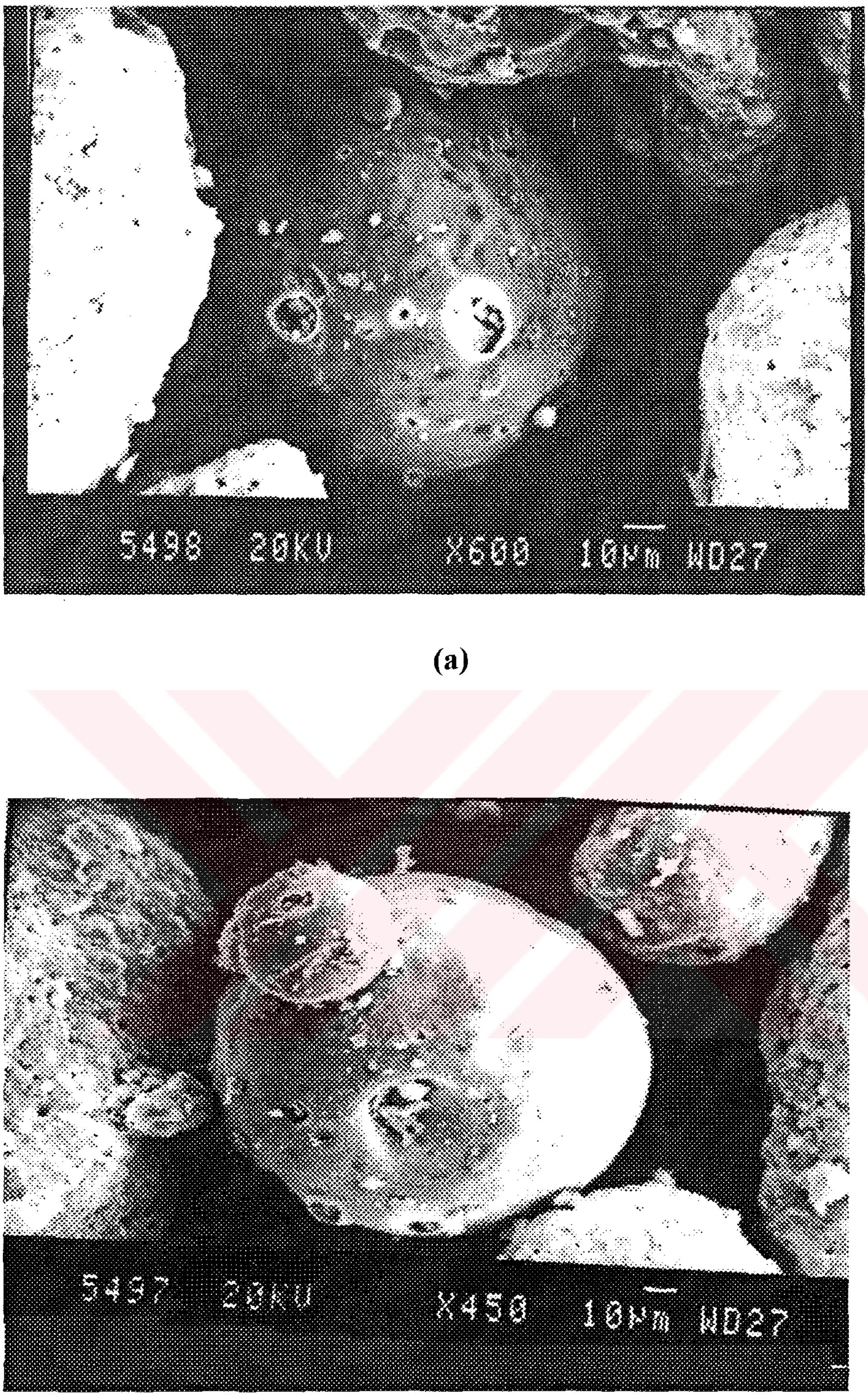


Figure 5.2. Scanning Electron Micrograph of a glass-like fly ash particle with spherical character

Four types of particle morphology could be identified: i) Plerospheres (spherical particles packed with other spheres) (Figure 5.3), ii) Cenospheres (opaque, spongy, hollow spherical particles) (Figure 5.4), iii) Spherical particles containing crystals and iv) Irregularly shaped solid particles (Figure 5.5).

Apart from morphological identifications, to have a general idea about the mineralogical and chemical composition, the resultant SEM micrographs and EDX spectra were compared with the ones included in the SEM Petrology Atlas (Welton, 1984), which consists of SEM micrographs and EDX spectra for most of the common minerals found in sedimentary rocks.



(a)

(b)

Figure 5.3. (a-b) Scanning Electron Micrographs of plerospheres

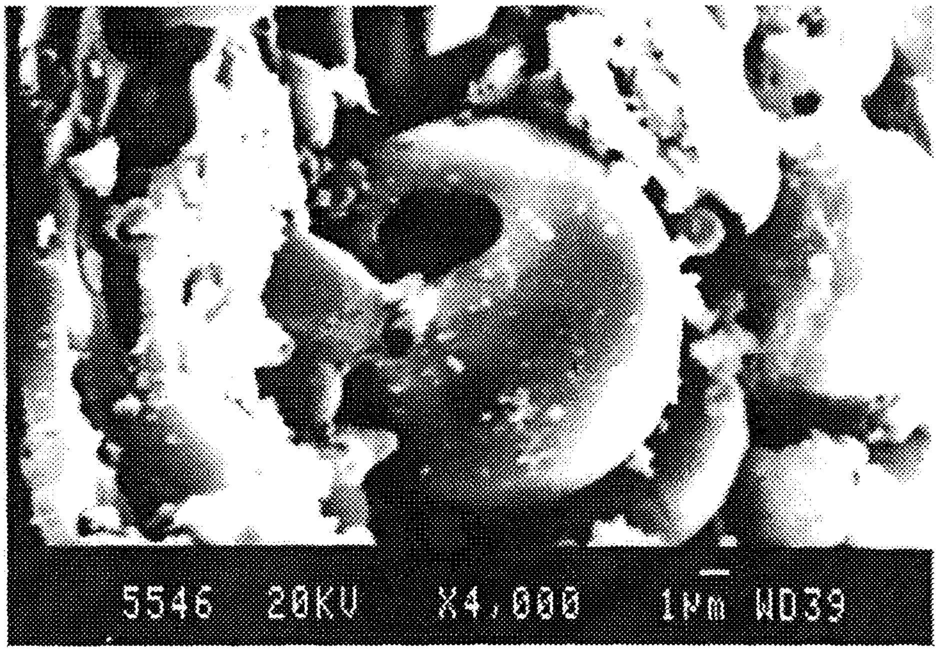


Figure 5.4. Scanning Electron Micrograph of a cenosphere

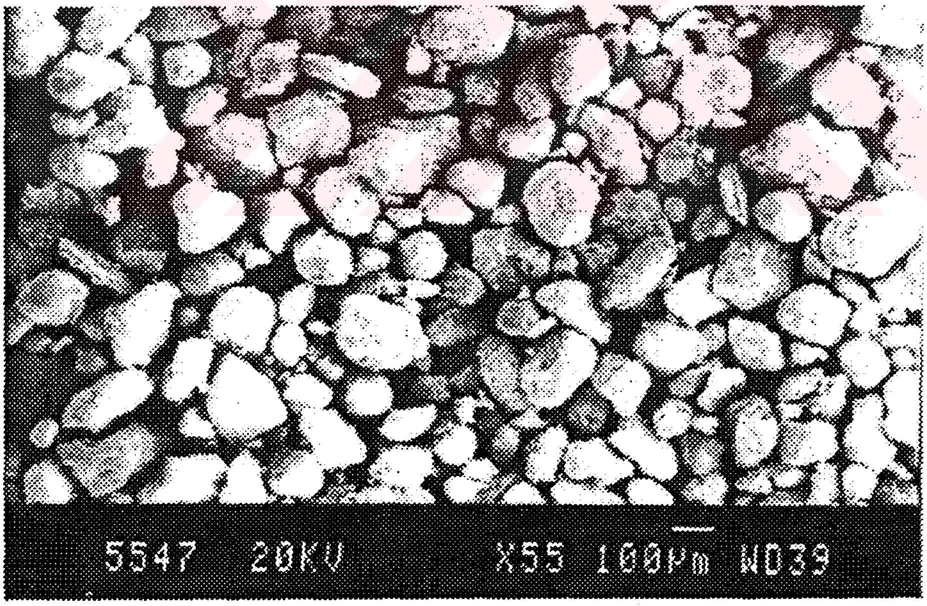


Figure 5.5. Scanning Electron Micrograph of irregularly shaped particles

As revealed by these spectra, the fly ash particles consist essentially of an aluminosilicate matrix (Al and Si peaks in the spectrum in Figure 5.6). Main identifiable minerals on this Al-Si matrix of fly ash include, Anhydrite (Figure 5.7, 5.8) and Hematite (Figure 5.9, 5.10).

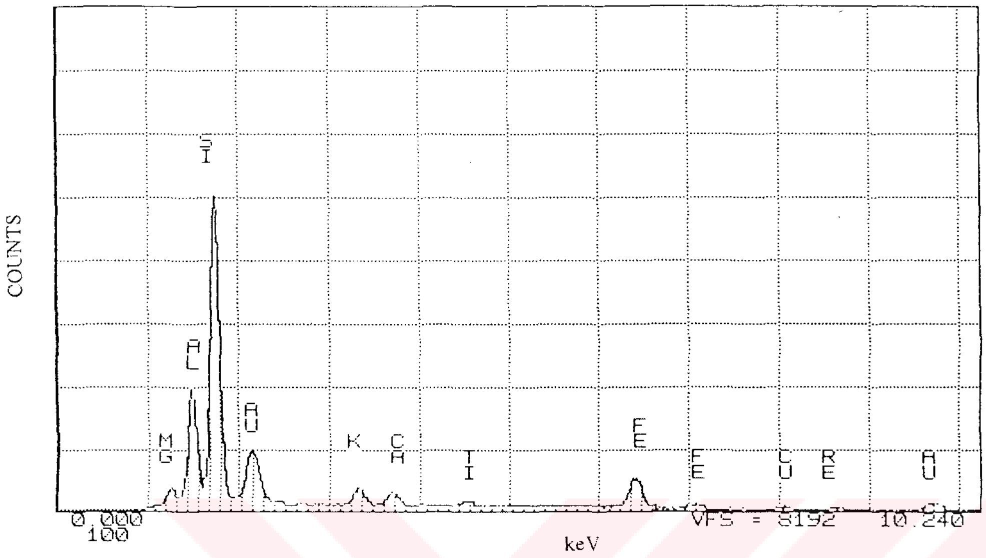


Figure 5.6. Energy Dispersive X-Ray Spectrum of the general chemical composition of fly ash defining an Al-Si matrix

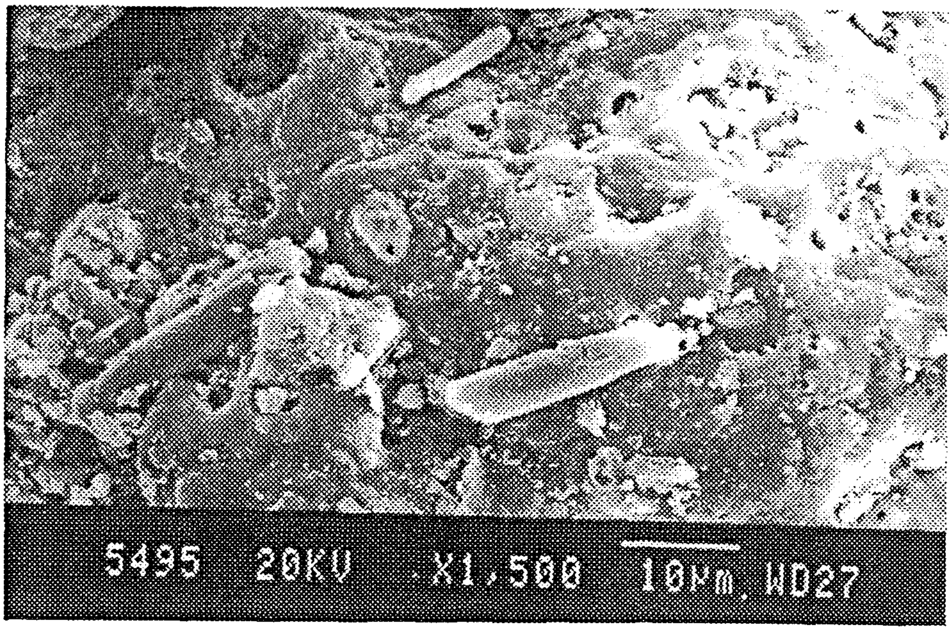


Figure 5.7. Scanning Electron Micrograph of Anhydrite from the fly ash sample

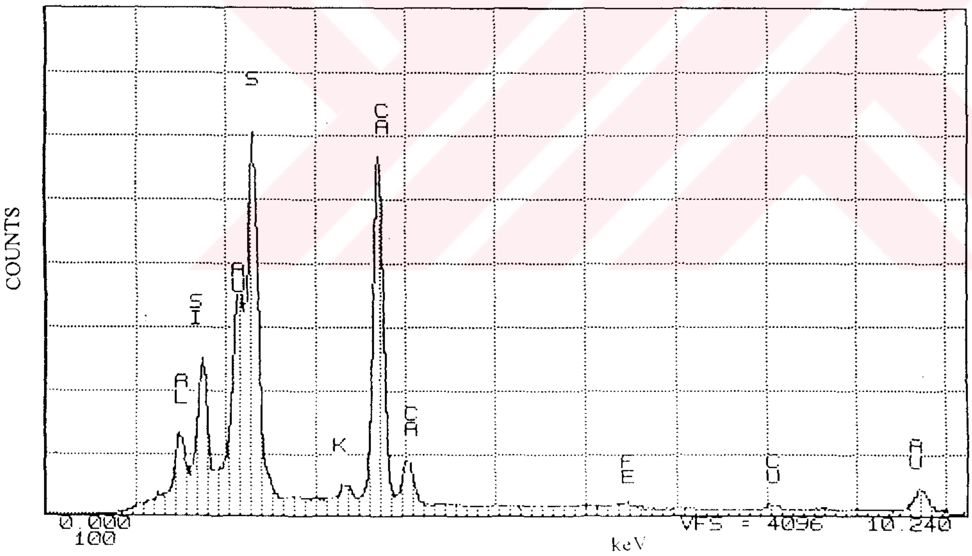


Figure 5.8. Energy Dispersive X-Ray Spectrum of the elemental composition of Anhydrite from fly ash

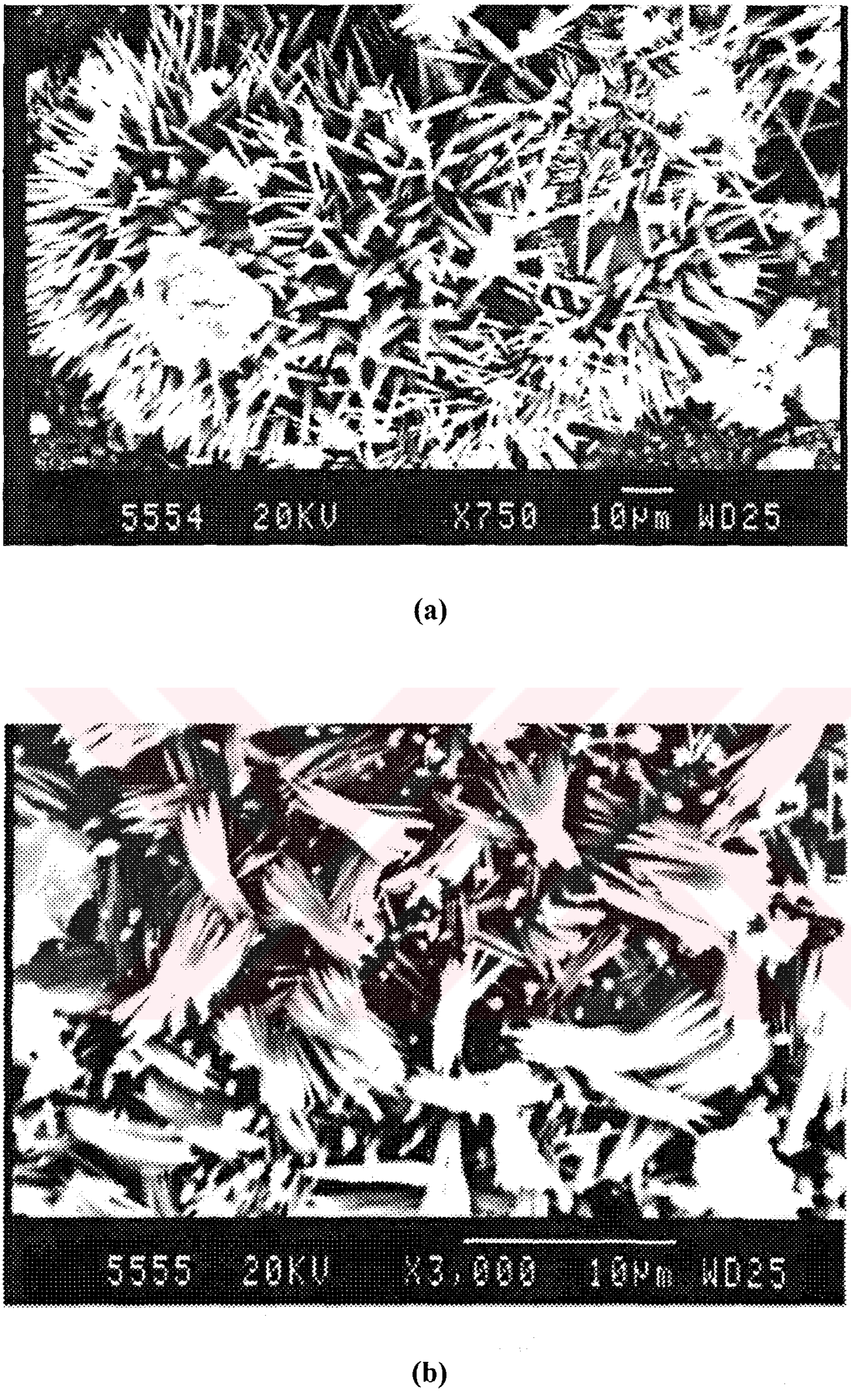


Figure 5.9. (a-b) Scanning Electron Micrographs of Hematite from fly ash

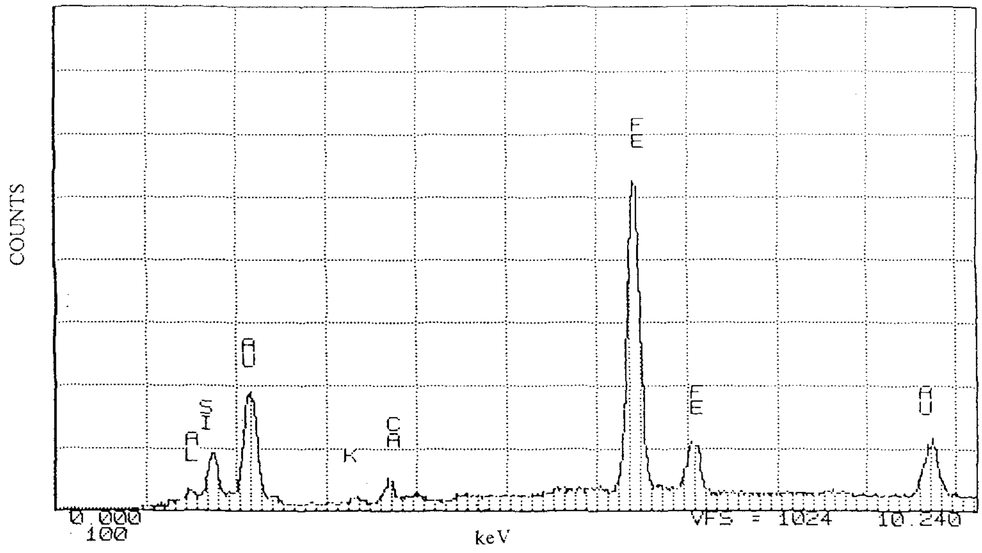


Figure 5.10. Energy Dispersive X-Ray Spectrum of the elemental composition of Hematite from fly ash

From the slag sample, majority is of Al-Si material (Figure 5.11), while anhydrite crystals can perfectly be identified (Figure 5.12, 5.13). Even though a complex morphology was obtained from this slag sample, some of the gasification/cooling structures were also detected (Figure 5.14).

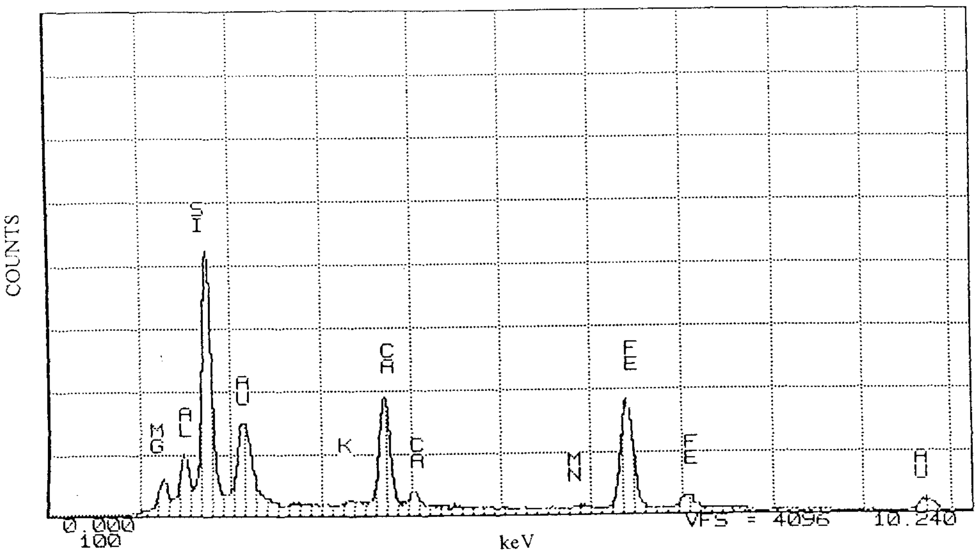


Figure 5.11. Energy Dispersive X-Ray Spectrum of the general chemical composition of slag sample, defining an Al-Si matrix

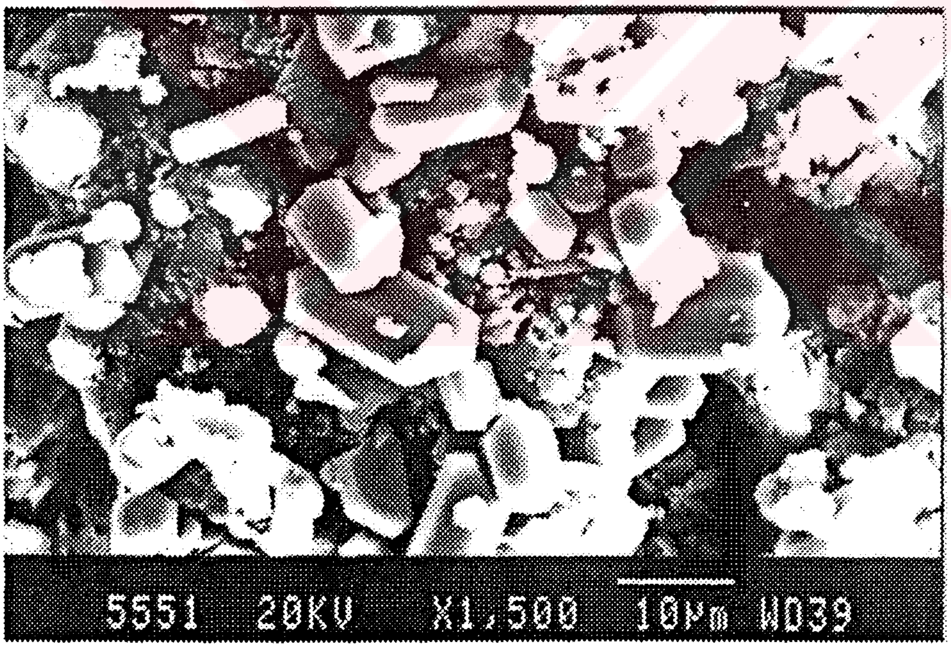


Figure 5.12. Scanning Electron Micrograph of Anhydrite from the slag sample

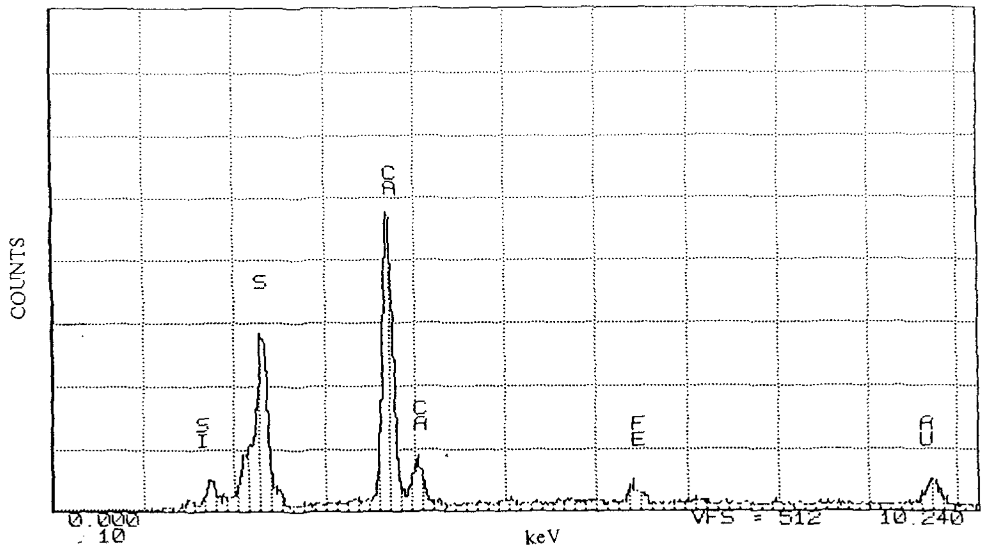


Figure 5.13. Energy Dispersive X-Ray Spectrum of the elemental composition of Anhydrite from slag sample

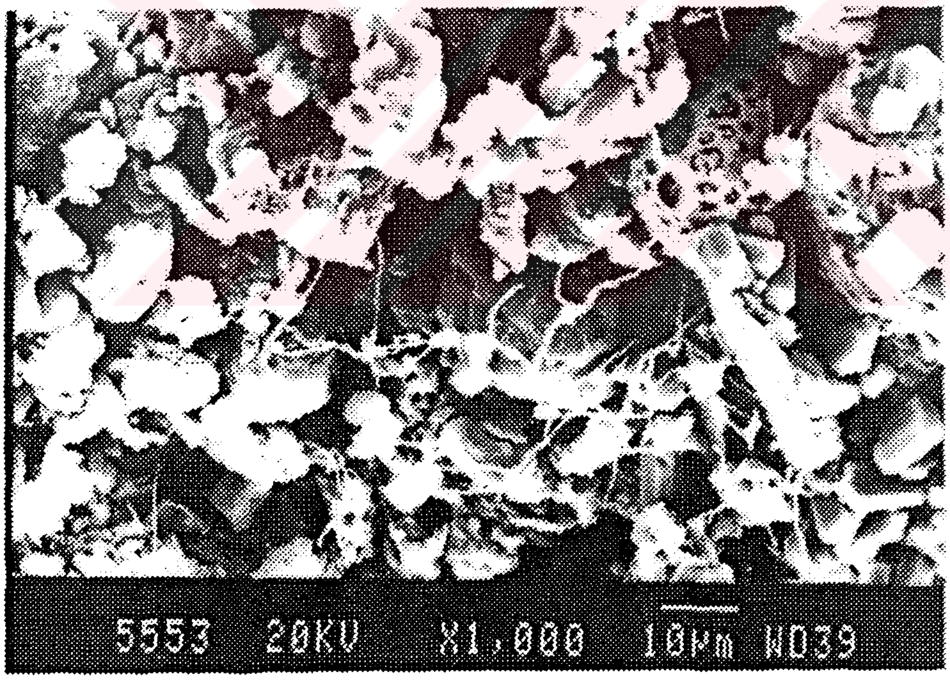


Figure 5.14. Scanning Electron Micrograph of some gasification/cooling structures from the slag sample

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The conclusions derived from this study are as follows:

1a. The volatile toxic trace element concentrations (as exemplified by Pb) show an increase from slag to bottom ash and from bottom ash to fly ash, as fly ash (being the finest coal combustion solid waste product) has the largest surface area to volume ratio. On the other hand, Co, Cu and Zn, having an intermediate volatility character, do not show the same trend as Pb.

1b. The considerably high Pb and Co concentrations in soil samples can be attributed to the basement lithologies, as these elements are not easily get soluble. High Pb concentration may also result from the exhaust gases of the tractors working in the area for agricultural purposes. Cu and Zn concentrations in soil samples may result from either the background values or the leaching from the solid waste products by surface waters.

2a. Major element concentrations do not show a preferential partitioning behavior between coal combustion solid waste products as they are mainly found in the matrix structure, rather than at the surface of the particles.

2b. The major element concentrations of soil samples are most likely to represent the basement lithologies in the Seyitömer region. Less probably, there might have been some leaching from the solid waste products to soil by surface waters.

3a. For fly ash samples, considering the trace elements, Pb concentration shows an increase with distance away from the disposal site, which may result from the fining of fly ash particle size with distance, having a greater surface area to volume ratio. To a less extent, the exhaust gases from the tractors, or the possible mixing of soil and fly ash might have caused this increase in Pb concentration with increasing distance. Co, Cu and Zn do not show the same trend as Pb, probably, due to their intermediate character.

3b. For fly ash samples, considering the major elements, Al_2O_3 and MgO concentrations show a slightly decreasing trend with increasing distance, which may result from the leaching of these elements from finer fly ash particles, or the data may represent the background values.

3c. For soil samples, regarding both the trace and major elements, no specific trend is observed with increasing distance away from the ash disposal site, which may be due to insufficient distance (for representative sampling) limited by the rural areas surrounding the disposal site, or the data may represent the background values. There is also a possibility of the samples to be mixed with ash.

4a. For fly ash samples, concentrations of the volatile elements (Pb) and some others of intermediate character (Co, Cu, Zn) show an inverse relationship with particle size. With decreasing particle size, there is an increase in concentration due to the greater specific surface of finer fly ash particles. Therefore, as finer particles can be directly inhaled, serious dangers to ecosystems and public health can develop.

4b. Being non-volatile and present at the matrix structure, major elements in fly ash samples, showed irregular trends. The increase in CaO, MgO and K_2O concentrations with decreasing particle size probably indicate partial volatilization of these elements.

5. Elemental concentrations in soil samples, when compared with the 'Maximum Allowable Concentration' values for agriculture for different countries, exceed the limits for Pb and Co concentrations, while Cd, Cu, and Zn concentrations do not exceed the given values. The high Pb and Co concentrations reflect, probably, the effects of the basement lithologies in the area. High Pb concentration may also result from the exhaust gases of the tractors passing through the area.

6. The morphology of the fly ash sample is found to be heterogeneous, consisting of four major types, namely, plerospheres, cenospheres, spherical particles containing crystals and irregularly shaped solid particles.

7. The SEM-EDX analysis reveals an Al-Si matrix for both fly ash and slag. Anhydrite could clearly been identified on both fly ash and slag samples, while Hematite was observed on the fly ash sample studied.

8. For further studies in the area, it is highly recommended to study the trace element content of the basement lithologies, coal and the nearby water resources for a more proper assessment of the environmental effects of coal combustion waste products.

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APPENDIX

PREPARATION OF SOLUTION B

Solution B

Reagents:

1. Solution (B) Acid Mixture

400 ml. HF was transferred to a 1 liter polyethylene bottle. The polyethylene bottle was kept in the cold water bath and 165 ml. of H_2SO_4 was added, mixed and allowed to cool. Then, 40 ml. of concentrated HNO_3 was added and mixed.

2. $HClO_4$ - HNO_3 Mixture

100 ml. of $HClO_4$ and 100 ml. of concentrated HNO_3 were mixed and stored in a 200 ml. glass-stoppered pyrex bottle.

3. Hydrazine - Sulfate Solution

0.2 gram hydrazine - sulfate ($NH_2.NH_2.H_2SO_4$) was dissolved in 100 ml. of distilled water. This solution was prepared freshly for each analysis.

Procedure:

- 0.2 gram of each sample were put in special teflon beakers.
- 15 ml. of the Solution (B) acid mixture was added to each teflon beaker and mixed in the fume cup to wet the sample powder.
- The teflon beakers were placed on a hot plate (or sand bath) to be heated for about

4-5 hours until SO_3 fumes were observed.

- About 4 drops of $HClO_4$ - HNO_3 mixture were added to each beaker and the beakers were placed on the hot plate again for heating purposes. Each beaker was heated until strong fumes were observed. If any color caused by organic matter remains, then this step was repeated.
- The beakers were removed from the hot plate, allowed to cool for a few minutes. After they were cooled and dried, about 40 ml. of distilled water, 5 ml. of concentrated HNO_3 and 1 ml. of hydrazine - sulfate solution were added to the beakers.
- The beakers were placed on the hot plate and heated till boiling occurs.
- The solutions were cooled down to room temperature, transferred to 200 ml. volumetric flasks and then diluted to volume.
- The solutions were transferred to polyethylene bottles and preserved as stock for determining elements which do not require a special dissolution technique.