

## LEACHING CHARACTERISTICS OF WASTES FROM KEMERKÖY (MUĞLA-TURKEY) POWER PLANT

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### ABSTRACT

A main problem related to coal ash disposal is the heavy metal content of the residue. In this regard, experimental results of numerous studies have indicated that toxic trace metals may leach when fly ash and bottom ash contacts with water.

In this study, fly ash and bottom ash samples obtained from Kemerköy thermal power plant, located on the south-western coast of Turkey, were subjected to toxicity tests such as the extraction procedures (EP) and toxicity characteristic leaching procedures (TCLP) of the U.S. Environmental Protection Agency (U.S. EPA), the so-called Method A extraction procedure of the American Society of Testing and Material (ASTM). When Pb and Cd concentrations, analysed according to EP and TCLP, were considered, Kemerköy fly and bottom ash can be classified as a hazardous waste under the principles of the Federal Resource Conservation and Recovery Act (RCRA).

Based on the geochemical analyses carried out, it was also determined that several toxic trace elements, such as Pb, Zn, Cd, Cu and Co were enriched at the fly and bottom ash of Kemerköy thermal power plant.

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**KEY WORDS:** Bottom ash, fly ash, leaching, power plant.

### INTRODUCTION

Coal is a major source of energy and its consumption in Turkey is predicted to increase in the future in order to meet the continuous demand for electric power generation. There are several coal burnt thermal power plants. Kemerköy thermal power plant, located 54 km south of Milas (Muğla), (Fig. 1), is one of them, with 4,100 TWh power production capacity. In this plant, 15,000 tons of coal is burned and 6,000 tons of fly and bottom ashes are produced daily.

Coal combustion waste has become a very important environmental problem due to their leach-

able toxic trace element contents. When these elements leach, they cause serious atmospheric and subsurface contamination. Fly ash and bottom ash from coal fired thermal power plants are known to contain several toxic elements, such as Pb, Zn, Cd and Cu (Gehrs *et al.*, 1979).

The solid waste produced from Kemerköy thermal power plant is then transported to a karstic and fractured dolomitic and cherty limestone disposal site. Thus, the amount of the toxic elements has to be known in order to take appropriate measurements to prevent underground water contamination due to water flow through the fractures in the



Figure 1. Location of the Study Area

formation. In this manner, the objective of this study is to set up laboratory scale test to determine the concentration of major and trace elements and leaching properties of Kemerköy thermal power plant waste products, namely fly ash and bottom ash, in the vicinity of the plant.

### GEOLOGY AND HYDROLOGY

Within the catchment area of the Kemerköy plain, lithological units from Mesozoic to Quaternary age crop out. Mesozoic units consist of Upper Triassic-Liyas dolomitic limestone and Lower Kretase cherty limestone in which the waste is disposed. These are overlain unconformably by Neogene. Neogen units are composed of clay limestone, marl limestone, conglomerate and weathered andesite. Quaternary deposits consist of alluvium.

Dolomitic and cherty limestone covers most parts of the study area. Fresh rock colour is gray to darkish gray. These units are thin to medium bedded, partly massive and densely jointed. The joints are filled with secondary quartz and calcite crystals. Limestone is the most extensive rock unit in this area and is densely fractured, porous and

partly karstified.

The catchment area of the aquifer is in the limestone and alluvium of the Kemerköy plain. The alluvium consists of loose, interlayered clay, silt, sand and gravel. The thickness of the alluvium is about 40-50 m.

The groundwater level varies between 2 and 7 m below the surface. Average water level change was 1 m between dry and wet seasons.

### GEOCHEMISTRY

It is known that fly ash particles emitted from coal fired power plants show an enrichment of several toxic trace elements (Burcu *et al.*, 1997; Campbell *et al.*, 1978; Davison *et al.*, 1974; Hansen and Fisher, 1980; Hulett *et al.*, 1980; Kaakinen *et al.*, 1975; Wangen and Williams, 1978). In this study, atomic absorption spectrophotometry techniques were used for the chemical analyses of the coal, fly ash and bottom ash. Major components were:  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{MnO}$ ,  $\text{SO}_3$ ; and trace elements were: Ba, Cd, Cu, Cr, Co, Ni, Pb, Sb and Zn. The concentrations of major and minor elements determined in collected samples are listed in Tables 1 and 2

Table 1. Major Elemental Concentrations of the Collected Samples from Kemerköy Thermal Power Plant

Major Element (%)	Coal	Bottom Ash	Fly Ash
SiO <sub>2</sub>	8.16-12.60	14.51-30.30	18.00-31.51
Al <sub>2</sub> O <sub>3</sub>	3.01-5.12	2.65-12.84	10.63-13.00
Fe <sub>2</sub> O <sub>3</sub>	1.20-2.81	3.51- 8.01	3.50-7.89
MgO	1.00-1.52	1.10-3.02	0.11-3.21
CaO	15.75-19.73	31.91-39.90	32.92-48.01
Na <sub>2</sub> O	0.18-0.31	0.42-1.15	0.18-0.60
K <sub>2</sub> O	0.51-0.96	0.25-2.52	0.31-2.43
TiO <sub>2</sub>	0.31-0.53	0.32-1.22	0.33-1.05
MnO	0.03-0.06	0.03-0.01	0.04-0.15
SO <sub>3</sub>	2.12-7.25	5.14-18.30	6.01-22.12

Table 2. Minor Elemental Concentrations of the Collected Samples from Kemerköy Thermal Power Plant

Minor Element (mg kg <sup>-1</sup> )	Coal	Bottom Ash	Fly Ash
Ba	55-89	73-115	69-117
Cd	<5	<5	<5
Cu	13-57	80-120	100-141
Cr	21-62	193-232	213-251
Co	2-4	3-6	5-10
Ni	50-91	186-225	287-326
Pb	24-65	28-67	43-84
Sb	<5	<5	<5
Zn	42-81	123-162	251-293

respectively. From the tables, it is seen that there is almost an overlap between the elemental concentrations for fly ash, bottom ash and coal samples.

### TOXICITY TESTING

Under the auspices of the Resource Conservation And Recovery Act (RCRA) of 1976, the U.S. Environmental Protection Agency (U.S. EPA) have developed specific criteria for two different extraction procedures, namely, the EP and TCLP. A number of other toxicity tests are also applied by regulatory agencies throughout the world. In this study, a third standardized extraction procedure developed by the ASTM, in which distilled water is used as the extracting medium, was also applied for the characterization of the Kemerköy fly ash and bottom ash samples.

In general, due to the short duration of extraction, laboratory toxicity tests may yield unsatisfactory results. For this reason, short-term toxicity tests are intended to be rather conservative (U.S. EPA, 1987). A summary of test conditions for the three selected extraction procedures are given in

Table 3. As shown in Table 3, the medium of extraction is buffered at an acidic pH value of about 5.0 for the EP and TCLP tests. In terms of simulating long-term geochemical behaviour in natural circumstances, such test conditions are generally accepted to be too aggressive (U.S. EPA, 1987), whereas water extraction, as in the case of the ASTM procedure, seems to be more adequate (U.S. EPA, 1987).

### Extraction Procedure (EP)

The EP method was developed to classify a solid waste as hazardous, based on 14 specific organic and inorganic constituents designated in the Federal Register (1980). According to the pertinent U.S. legislation, a solid waste exhibits the characteristic of "EP toxicity" if the extract from EP or any other approved test of a similar kind contains any of the listed contaminants at a concentration equal to or greater than the specified value (Table 4).

In summary, the EP was performed by adding an appropriate quantity of water to a representative sample of the residue. Then, pH was measured

Table 3. Comparison of Toxicity Tests (Egemen and Yurteri, 1996; Inyang, 1992; U.S. EPA, 1987).

Criteria	Tests	Test conditions	Relevance to field situation
Liquid: solid ratio	EP	20:1	Adequate
	TCLP	20:1	Adequate
	ASTM	4:1	Overestimation
Extraction medium	EP	0.5N acetic acid	Aggressive
	TCLP	Acetic acid	Aggressive
	ASTM	Distilled water	Adequate
Extraction time	EP	24h	Underestimation
	TCLP	18h	Underestimation
	ASTM	48h	Underestimation
pH control	EP	5.0±0.2	Aggressive
	TCLP	4.93 or 2.88	Aggressive
	ASTM	None	Adequate
Agitation methods	EP	Tumbler	Aggressive
	TCLP	Tumbler	Aggressive
	ASTM	Tumbler	Aggressive
Temperature control	EP	20-40 °C	Adequate
	TCLP	19-25 °C	Adequate
	ASTM	19-25 °C	Adequate
Number of extractions	EP	1	Underestimation
	TCLP	1	Underestimation
	ASTM	1	Underestimation

Table 4. Maximum Concentration Of Contaminants For Characteristic EP Toxicity (Finkelman, 1996).

U.S.EPA hazardous Waste number	Contaminant	Maximum Concentration (mg l <sup>-1</sup> )
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0

upon agitation. When the pH of the solution was higher than 5.0, it was adjusted to  $5.0 \pm 0.2$  by adding 0.5 N acetic acid. Continuous pH monitoring and adjustment was carried out throughout the test to eliminate any impurities coming from pH variations. The test conditions were set to be compatible with previous similar studies (Egemen and Yurteri, 1996; Inyang, 1992; U.S. EPA, 1987).

#### Toxicity Characteristic Leaching Procedure (TCLP)

Another commonly used extraction procedure

with regulatory significance is the TCLP, which was also developed by EPA as a supplement to the EP toxicity testing method for identification and classification of hazardous wastes (Federal Register, 1980). As can be seen in Table 3, the test conditions for the TCLP method are somewhat milder than those of EP. In comparison to EP, however, the TCLP waste classification is based on a much more extensive list of organic and inorganic compounds and covers a broader range of waste types.

#### ASTM Extraction Procedure

The Kemerköy ash samples were also subjected to Method A extraction procedure of the ASTM, which is based on extended extraction with distilled water. The analytical measurements obtained from the ASTM extracts are expected to emulate field conditions better than the more aggressive EP and TCLP methods (Egemen and Yurteri, 1996; Eisenberg *et al.*, 1986; Inyang, 1992).

#### EXPERIMENTAL METHODS

Fly ash and bottom ash samples acquired from Kemerköy were dried at 105 °C for 48 h and then desiccator-cooled. All glassware, plastic ware and

teflon ware were soaked in 20% nitric acid for 24h and rinsed with deionized water prior to use.

For determining the initial composition of raw Kemerköy fly ash and bottom ash, dried ash samples were completely dissolved in Beckmann digestion bombs by using nitric (HNO<sub>3</sub>) and hydrofluoric acids (HF). The metal concentrations measured in digested samples were reported as total concentration in raw ash.

To obtain EP and TCLP extracts, 5g of fly ash was agitated in sealed wide-mouth glass jars containing 100 ml of extracting medium for the specified time periods of 24 and 18 h, respectively. In this case of EP, the pH of the medium was adjusted to 5.0 using 0.5 N acetic acid. For TCLP, pH adjustment was with 0.1 N acetate buffer containing 64.3 ml of 1.0 N sodium hydroxide (NaOH) and 5.7 ml acetic acid in 1 liter of water. Under this condition, the final pH of the solution was buffered at  $4.93 \pm 0.02$ . The ASTM extractions were performed with 25 g of fly ash and bottom ash sample placed in 100 ml of distilled and deionized water. Extraction time was 48 h on a shaker platform at 70 one-inch strokes min<sup>-1</sup> similar to studies performed by Egemen and Yurteri (1996) and Eisenberg *et al.*, (1986).

The laboratory temperature was controlled between 19-25 °C during all extraction procedures. After the required period for agitation had elapsed, all extracts were stirred with a glass rod and filtered through 0.45 µm filter paper. The filtrates were acidified by concentrated HNO<sub>3</sub> addition. More alkaline ASTM extracts needed approximately 1 or 2 ml of HNO<sub>3</sub> per 100 ml, while about 0.2 ml was sufficient for the other

extracts initially buffered at an acidic pH. All extractions were carried out as triplicate runs.

The analyses of selected metal ions in digested raw ash samples and extracts were conducted according to standard techniques (APHA, 1989). All metals were analysed by atomic absorption spectrophotometry.

## RESULTS AND DISCUSSION

The concentration ranges of selected elements measured in different Kemerköy ash extracts are presented in Tables 5 and 6.

A comparison of the results listed in Table 5 and 6 reveals that ASTM procedure resulted in lower dissolved metal concentrations in comparison to EP and TCLP methods. These results demonstrate that pH is an important parameter affecting the leaching rate of metals from ash deposits. Studies indicate that lower pH values increase the leaching rate of inorganic constituents of fly and bottom ash. In this regard, ash deposited in the deeper layers of landfills and bottom of the ash ponds may continue to leach when the surrounding environment is changed to low pH conditions.

In ASTM extraction method, the measured Cd and Pb concentrations were found to be considerably below the specified characteristic EP toxicity levels of 1.0 and 5.0 mg l<sup>-1</sup> (see Table 4). But in other extractions (TCLP, EP), the measured Cd and Pb concentrations were found to be considerably above the specified characteristic EP toxicity levels of 1.0 and 5.0 mg l<sup>-1</sup> (see Table 4). Fly ash and bottom ash has been declared as "special waste" by the U.S. Environmental Protection Agency, in concordance with the Federal

Table 5. Composition of Kemerköy Fly Ash Extracts (mg l<sup>-1</sup> except pH).

Parameter	EP	TCLP	ASTM
Al	47.01-78.25	35.04-44.12	5.76-11.80
Cd	1.75-2.03	0.75-1.00	0.003-0.008
Cu	0.15-0.25	1.01-1.75	0.05-0.07
Cr	7.04-8.75	4.25-9.08	3.61-3.84
Fe	5.25-5.75	8.75-11.25	0.56-0.68
Mn	3.25-3.50	0.11-0.32	0.01-0.04
Ni	2.24-6.55	6.25-8.75	0.4-0.6
Sb	20.10-30.05	44.72-78.75	2.96-4.02
Pb	20.25-22.04	20.75-22.50	2.51-3.03
Zn	0.25-0.48	2.25-2.50	0.26-0.38
Final pH	5	5	9.76-10.8

Table 6. Composition of Kemerköy Bottom Ash Extracts (mg l<sup>-1</sup> except pH).

Parameter	EP	TCLP	ASTM
Al	80.12-156.25	30.04-41.03	9.02-10.64
Cd	1.05-1.50	0.025-0.50	0.002-0.007
Cu	0.17-0.45	0.50-1.01	0.04-0.07
Cr	3.51-5.25	0.98-1.03	0.11-0.16
Fe	24.21-42.64	6.75-7.50	0.49-0.67
Mn	15.04-20.25	0.14-0.22	0.02-0.03
Ni	2.51-3.46	5.15-6.75	0.4-0.6
Sb	13.23-24.07	32.17-48.25	2.02-3.01
Pb	14.25-18.12	20.75-22.50	2.45-3.16
Zn	0.82-1.52	1.25-4.75	0.28-0.32
Final pH	5	5	10.00-10.30

Resource Conservation and Recovery Act (RCRA) (Deborah and Ernest, 1981). This designation requires that coal ash disposal ponds should be sealed to prevent downward percolation of leachate and that groundwater monitoring systems should be installed at the site. In this regard, Kemerköy fly ash and bottom ash can be classified as a hazardous waste under the principles of RCRA. However, other toxic elements, such as As and Se, were not determined due to instrumental difficulties.

The results of analyses on major elements show that SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, TiO<sub>2</sub>, MnO and SO<sub>3</sub> content of bottom and fly ash was higher than that of the coal (see Table 1). It was also determined that percentages of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, MnO and SO<sub>3</sub> in fly ash were higher, when compared with bottom ash. Other major elements have approximately the same values. According to these results, when major element contents are considered, coal, bottom and fly ash can be ranked as follows.

Fly ash > bottom ash > coal

As a first approximation to the evaluation of Ba, Cd, Cu, Cr, Co, Ni, Pb, Sb and Zn, listed in Table 2, the concentration of most of these toxic trace

elements shows an enrichment on fly ash particles, when compared with coal and bottom ash, and on bottom ash when compared with coal.

The results of chemical and extraction analyses have shown that the heavy metal content of fly ash was higher than that of bottom ash. Since both fly ash and bottom ash are stored on densely fractured, porous and partly karstified limestone in power plant area, another problem that can be encountered is the quick spreading of the heavy metals present in the ash. The region, in which the waste is disposed, is touristically attractive and drinking water is supplied from groundwater. For this reason, appropriate measurements should be taken in order to prevent atmospheric and subsurface contamination during transportation and disposal of the ashes. Otherwise, contamination of the area could lead to serious health, groundwater pollution and land use problems in the future.

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