

Investigation of Geochemical and Leaching Characteristics of Solid Wastes from Yeniköy (Muğla-Turkey) Power Plant

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Abstract

The use of lignite in power generation has led to increasing environmental problems associated not only with gaseous emissions but also with the disposal of ash residues. In particular, the use of low quality coals with high ash content results in huge quantities of both fly and bottom ash to be disposed of.

An important problem related to coal ash disposal is the heavy metal content of the residue. In this regard, experimental results of numerous studies indicate that toxic trace metals may leach when fly ash and bottom ash come into contact with water.

In this study, fly ash and bottom ash samples obtained from Yeniköy thermal power plant, located on the south-western coast of Turkey, were subjected to toxicity tests, namely, the extraction (EP) and toxicity characteristic leaching (TCLP) procedures of the U.S. Environmental Protection Agency (USEPA) and the Method A extraction procedure of the American Society of Testing and Material (ASTM).

Key Words: Bottom ash; fly ash; leachate; solid waste; thermal power plants.

Yeniköy (Muğla-Türkiye) Termik Santralı Katı Atıklarının Jeokimyasal ve Özütlenme Özelliklerinin İncelenmesi

Özet

Linyitle çalışan termik santraller; sadece gas emisyonları nedeniyle değil, kül atıkları ile de önemli çevresel problemler oluşturmaktadırlar. Özellikle düşük kaliteli kömürlerin kullanılması ile yüksek oranda uçucu ve taban külleri atık olarak oluşmaktadır.

Kömür küllerinin depolanmasındaki ana problem atıkların ağır metal içerikleridir. Bu bakımdan, birçok deneysel çalışmanın sonucunda uçucu ve taban küllerinin suyla temasında toksik iz metaller özütlenmiştir.

Bu çalışmada, Türkiye'nin güneybatı kıyısında yer alan Yeniköy termik santrallinden alınan uçucu ve taban küllerinin toksisitesi; USEPA prosedürüne göre çözündürme yöntemi (EP), toksik karakteristik özütlenme yöntemi (TCLP) ile ASTM yöntemlerine göre ölçülmüştür. EP ve TCLP analiz sonuçlarına göre yöre atıklarının kurşun ve kadmiyum konsantrasyonları yüksektir. USEPA prensiplerine göre, yöredeki linyit atıkları tehlikeli atık sınıfına girmektedir.

Anahtar Sözcükler: Taban külü; uçucu kül; özütleme; katı atık; termik santral

Introduction

Coal is a major source of energy in Turkey and its consumption is predicted to increase in the future in order to meet the continuous demand for electric power generation. With the increase in the use of coal, especially in industrialised areas, coal combustion waste products have become significant sources of environmental pollution due to their leachable toxic trace element contents.

Fly ash and bottom ash from coal-fired thermal power plants are known to contain several toxic elements, such as lead (Pb), zinc (Zn), cadmium (Cd), nickel (Ni) and cobalt (Co), which can leach out from the ash and contaminate soils as well as surface water and groundwater (Baba, 2000; Deborah and Ernest, 1981; Gehrs et al, 1979).

Coal combustion can mobilise these trace elements by introducing them to the terrestrial, aquatic and atmospheric environment, and if leached, these elements cause the contamination of soils, 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 utilised or disposed of properly. This contamination could lead to health, environmental and land-use problems (Gehrs et al., 1979).

In the Yeniköy plant, 12,000 tons of coal is burnt and approximately 4,500 tons of fly and bottom ash is produced per day. The solid wastes produced are then transported to the disposal site by conveyor belts, nearly 1.5 km in length. Since the plant has to deal with thousands of tons of fly ash and bottom ash per day, the safe disposal of solid ash is a serious problem.

In this study, currently used toxicity tests were conducted on various fly ash and bottom ash samples obtained from the two units of the original 420 MW energy capacity Yeniköy thermal power plant, which consumes low-quality lignite reserves of the Hüsamilar-Sekköy-Ekizköy-Karacahisar Basin. The annual production capacity of this power plant is 2,700,000,000 KWh. Yeniköy Thermal Power Plant is located about 85 km from Muğla and 30 km from Milas, in south-western Anatolia (Figure 1).



Figure 1. Location Map of Study Area

The objective of this study is to determine the concentration of major and trace elements in coal combustion solid products, namely fly ash and bottom ash, in the vicinity of the plant. The study focuses specifically on the results of laboratory-scale toxicity testing procedures carried out to determine the general leaching properties of Yeniköy thermal power plant fly ash and bottom ash.

Geology and Hydrology

Within the catchment area of the Yeniköy Plain, lithological units consisting of sedimentary and metamorphic rocks, whose ages range from Paleozoic to Quaternary, crop out (Figure 2). The basement rocks surrounding this area are represented by metamorphic schist and marble. Metamorphic rocks crop out at the north-western part of the study area.

At the site, the top cover soil layer consists of the Neogene formation. The Neogene formations are solidified as a result of the tectonic movements in the surroundings, attaining a lithological characteristic. Among these series, the most widely encountered are breccias with calcite gravels and calcareous or clayey calcareous cementing agents, and conglomerates. As

a result of deposition in a lake environment and tectonic movements in the surrounding area, pinkish-white tuff formations with occasional calcite gravels are formed. The quaternary deposits consist of alluvium. The ash disposal site is located on alluvium and limestone.

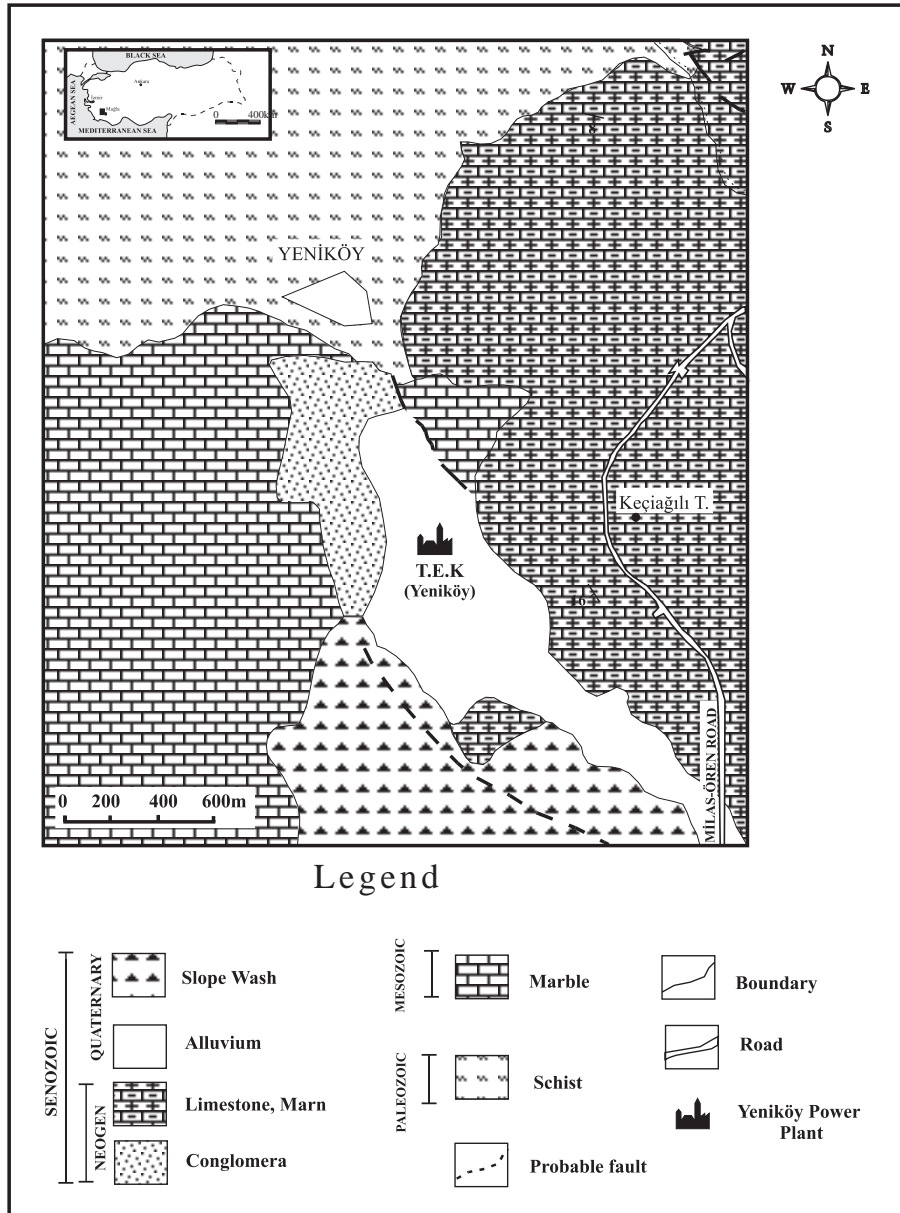


Figure 2. Geological Map of Study Area (YLI, 1997).

The climatic characteristics of the Mediterranean Region, with hot and dry summers and warm and rainy winters, prevail throughout the study area.

The groundwater is observed at 5.0 to 15.0 m depth from the ground surface. The catchment area of the aquifer is in marble, limestone and alluvium. The al-

luvium consists of loose, interlayered clay, silt, sand and gravel. The average water level change is about 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; Kaakine et al., 1975; Wangen et al., 1978). In this study, atomic absorption spectrophotometric techniques were used for the geochemical analyses of the coal, fly ash and bot-

tom ash obtained from the aforementioned power plant. The major components determined were SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO , Na_2O , K_2O , TiO_2 , MnO , and the trace elements were Ba, Cd, Cu, Cr, Co, Ni, Pb, Sb and Zn.

As the first step of the evaluation of the results, the concentrations of nine major and minor elements for the collected samples are listed in Table 1 and Table 2 in order to give a general idea of the relative metal concentrations of each sample type. It appears from these tables that there is almost an overlap between the elemental concentrations for fly ash, bottom ash and coal samples.

Table 1. Major elemental concentrations of the collected solid waste samples from Yeniköy Thermal Power Plant.

Major Element (%)	Coal	Bottom Ash	Fly Ash
SiO_2	5.39-9.41	10.80-38.50	14.80-38.50
Al_2O_3	1.36-4.36	2.51-14.71	3.43-17.32
Fe_2O_3	0.08-2.2	0.5- 8.09	0.86-11.75
MgO	0.05-3.5	1.15-4.61	0.53-9.13
CaO	21.38-30.45	23.31-45.13	22.31-54.13
Na_2O	0.01-0.18	0.15-0.62	0.25-1.23
K_2O	0.37-0.77	0.10-3.60	0.41-4.89
TiO_2	0.03-0.43	0.18-1.32	0.23-1.68
MnO	0.06-0.94	0.14-0.18	0.15-0.21

Table 2. Metal concentrations of the collected solid waste samples from Yeniköy Thermal Power Plant (mg metal extracted/kg of fly ash).

Metal (mg/kg)	Coal	Bottom Ash	Fly Ash
Ba	53-98	62-109	67-109
Cd	<5	<5	<5
Cu	9-49	18-121	58-141
Cr	4-44	47-194	174-252
Co	3-5	3-7	8-12
Ni	18-58	30-293	69-306
Pb	0.8-25	5-33.4	20.3-82
Sb	<5	<5	<5
Zn	30-70	33-226	49-270

Toxicity Testing

Under the auspices of the Resource Conservation and Recovery Act (RCRA) of 1976, the U.S. Environmental Protection Agency (USEPA) has developed specific sets of criteria for two different fly ash extraction procedures, namely, EP and TCLP.

A number of other toxicity tests are also employed by regulatory agencies throughout the world. In this study, a third standardised extraction procedure developed by the American Society of Testing and Materials (ASTM), in which distilled water is used as the extracting medium, was also used for the characterisation of the Yeniköy 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 (USEPA, 1987). A summary of test conditions for the three selected extraction procedures is 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 considered too aggressive (USEPA, 1987), whereas water extraction, as in the case of the ASTM procedure, seems to be more appropriate (Inyang, 1992; USEPA, 1987).

Table 3. Comparison of toxicity tests (Egemen, E. & Yurteri, C. 1996; Inyang, 1992; USEPA, 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

Extraction procedure (EP)

The EP method was developed to classify a solid waste as hazardous, based on 8 specific organic and inorganic constituents designated in the Federal Register (1980). According to US legislation, a solid waste exhibits the characteristic of EP toxicity if the extract from EP or any other approved test of a similar kind contains any of the listed contaminants at a concentration equal to or greater than the specified value (Table 4) (Finkelman, 1996).

Table 4. Maximum concentration of contaminants for characteristic EP toxicity (Finkelman, 1996).

USEPA hazardous Waste number	Contaminant	Maximum Concentration (mg l ⁻¹)
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

In summary, the EP is performed by adding an appropriate quantity of water to a representative sample of the residue. Then, pH is measured upon agitation. If the pH of the solution is higher than 5.0, it is adjusted to 5.0 ± 0.2 by adding 0.5N acetic acid.

Toxicity characteristic leaching procedure (TCLP)

Another commonly used extraction procedure with regulatory significance is the TCLP, which was also developed by the 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 Yeniköy 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 Yeniköy were dried at 105°C for 48 h and then desiccator-cooled. All glassware, plastic and Teflon were soaked in 20% nitric acid for 24 h and rinsed with deionised water prior to use.

For determining the initial composition of raw Yeniköy fly ash and bottom ash, dried ash samples were completely dissolved in Beckmann digestion bombs by using nitric (HNO₃) and hydrofluoric acid (HF) solutions. Generally speaking, HNO₃ is primarily used for dissolving the non-matrix constituents, whereas HF dissolves both matrix and non-matrix elements. In particular, HF is the only acid which can dissolve silicate lattices completely (Egemen and Yurteri, 1996).

The extractions have been performed as de-

scribed in ASTM, EP and TCLP. 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 Yeniköy ash extracts are shown in Tables 5 and 6. These results indicate that pH is an important parameter affecting the leaching rate of metals from ash deposits. Although less water is used for leaching in the ASTM method, concentrations of metals were lower than the other methods since 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 the bottom of ash ponds may continue to leach when the pH value drops in the surrounding environment. The lowering of pH should be considered, especially in areas exposed to acid rain.

Table 5. Composition of Yeniköy fly ash extracts (mg per litre extract except pH)

Parameter	EP	TCLP	ASTM	Maximum Concentration	Comments
Al ⁺	32.01-79.25	29.05-33.47	8.75-25.00		
Cd ⁺⁺	1.55-2.23	0.025-0.12	0.003-0.08	1.0	Toxic (EP)
Cu ⁺⁺	1.0-2.73	1.01-1.75	0.04-0.18		
Cr (total)	15.04-27.69	13.55-17.20	5.44-9.84	5.0	Toxic (EP, TCLP, ASTM)
Fe ⁺⁺	5.45-10.75	3.15-5.54	0.76-4.76		
Mn ⁺⁺	3.25-3.50	0.13-0.15	0.021-0.032		
Ni ⁺⁺	8.24-15.43	6.25-7.75	0.5-0.8		
Sb ⁺⁺	23.4-35.5	29.54-33.95	0.48-4.2		
Pb ⁺⁺	15.25-22.75	15.25-20.00	2.63-2.98	5.0	Toxic (EP, TCLP)
Zn ⁺⁺	0.25-3.50	1.25-1.95	0.32-0.48		
Final pH	5	5	9.90-10.1		

In the 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 ppm (see Table 4). But in other extractions (TCLP, EP), the measured Cd and Pb concentrations were found to be considerably above EP toxicity levels (see Table 4). Fly ash and bottom ash have been declared special wastes by the U.S. Environmental Protection Agency, in concordance with the Federal Resource Conservation and Recovery Act (RCRA) (Deborah et al., 1981). This designation

requires that coal ash disposal ponds be sealed to prevent the downward percolation of leachate and that groundwater monitoring systems be installed at the site. In this regard, Yeniköy fly ash and bottom ash can be classified as hazardous wastes under the principles of RCRA and the Regulation for the Control of Hazardous Waste (Official Gazette, 1995). Owing to instrumental difficulties, it was not possible to obtain reliable measurements of other relevant contaminants such as As and Se.

Table 6. Composition of Yeniköy bottom ash extracts (mg per litre extract except pH)

Parameter	EP	TCLP	ASTM	Maximum Concentration	Comments
Al ⁺	78.16-203.2	29.22-33.25	9.14-14.64		
Cd ⁺⁺	1.15-1.75	0.025-0.48	0.004-0.074	1.0	Toxic (EP)
Cu ⁺⁺	0.15-0.97	0.45-0.98	0.06-0.08		
Cr ⁺⁺	1.48-3.78	0.96-1.01	0.14-0.18	5.0	Nontoxic
Fe ⁺⁺	19.25-36.25	2.65-8.50	0.36-1.62		
Mn ⁺⁺	13.04-28.32	0.15-2.58	0.02-0.03		
Ni ⁺⁺	2.48-4.12	5.35-6.55	0.25-0.58		
Sb ⁺⁺	13.23-24.07	11.25-15.75	0.48-2.64		
Pb ⁺⁺	17.25-24.13	16.25-20.18	2.32-3.05	5.0	Toxic (EP, TCLP)
Zn ⁺⁺	0.94-3.52	1.25-7.75	0.28-0.40		
Final pH	5	5	9.38-9.62		

The results of analyses show that the SiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O, TiO₂ and MnO contents of bottom and fly ash are higher than those of coal (see Table 1). It was also determined that percentages of SiO₂, Al₂O₃, CaO and MnO in fly ash were higher than in bottom ash. Other major elements have approximately the same values. According to these results, when major element contents are considered, coal, bottom ash and fly ash can be ranked as follows: fly ash > bottom ash > coal.

Results of the geochemical analyses of Ba, Cd, Cu, Cr, Co, Ni, Pb, Sb and Zn for the collected samples are listed in Table 2. The concentration of most of the 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 geochemical and extraction analyses have shown that the heavy metal content of fly ash is higher than that of bottom ash. Since both fly ash and bottom ash are stored on densely fractured, porous, and partly karstified limestone in that

area, another problem that may be encountered is the quick spread of the heavy metals contained in the ash. As this area is important for tourism and the drinking water is supplied from groundwater, the necessary mitigation measures must be taken in consideration of the geological formation of the area. Otherwise, contamination of the area could lead to serious health, groundwater pollution and land use problems in the future.

When the compositions of the Yeniköy fly ash extracts and bottom ash extracts are compared with the EP toxicity criteria, it is observed that fly ash extracts are toxic due to the cadmium, chromium and lead contents, and the bottom ash extracts are toxic due to cadmium and lead contents. Thus, both wastes are considered toxic and hazardous. These wastes should be disposed according to the Control of Hazardous Waste Regulation and Removal of Solid Waste Regulation, which were promulgated on August 27, 1995 and March 14, 1991 in the Official Gazette respectively since lead and cadmium concentrations exceed the required limits for surface disposal on land.

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