geologica **acta**

Element behaviour during combustion in coal-fired Orhaneli power plant, Bursa-Turkey

S. ESENLIK [1] **A.I. KARAYIGIT** [1] **Y. BULUT** [1] **X. QUEROL** [2] **A. ALASTUEY** [2] **and O. FONT** [2]

[1] **Department of Geological Engineering, Hacettepe University,**
Beytepe, 06532 Ankara, Turkey. Esenlik E-mail: esenlik@hacettepe.edu.tr   Karayigit E-mail:aik@hacettepe.edu.tr
Bulut E-mail: ybulut@hacettepe.edu.tr

[2] **Institute of Earth Sciences "Jaume Almera", CSIC**
C/Lluís Solé i Sabarís s/n, 08028 Barcelona, Spain. Querol E-mail:xavier.querol@ija.csic.es Alastuey E-mail:aalastuey@ija.csic.es
Font E-mail: ofont@ija.csic.es

---| **A B S T R A C T** |---

This study focuses on element behaviour during combustion in the Orhaneli thermal power plant (a 210 MW unit, Bursa-Turkey). A total of 51 samples, feed coals (FCs), fly ashes (FAs) and bottom ashes (BAs), which were systematically collected over an eight-week period, have been analysed for major, minor and trace elements (Al, Ca, Fe, K, Mg, Na, S, As, B, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Ga, Ge, Hf, Hg, Li, Mn, Mo, Nb, Ni, P, Pb, Rb, Sb, Sc, Se, Sn, Sr, Ta, Th, Ti, Tl, U, V, W, Y, Zn, Zr and REEs). This study shows that FCs on an air-dried basis have high moisture (av. 9%), high volatile matter (av. 33%), very high ash yield (av. 53%), relatively high sulfur content (av. 2.14%) and low gross calorific value (av. 1775 kcal/kg). Proximate analyses of combustion residues imply that BAs have higher contents of unburned carbonaceous matter than FAs. Mean values of trace element concentrations in FCs fall within the ranges of most world coals, except for Cr, Cs, Ni and U which occur in concentrations slightly higher than those determined for most of world coals. Some elements such as S, Hg, As, B, Bi, Cd, Cs, Ge, K, Pb, Rb, Sb, Se, Sn, Tl, and Zn are indicating enrichments in FAs. The remaining elements investigated in this study have no clear segregation between FAs and BAs. The mass balance calculations point to Ca content of feed coal controlling the partitioning of elements in this power plant, producing a high removal efficiency for highly volatile elements such as Hg, B and Se, and a high retention of As, Bi, Cd, Cs, Ge, Pb, Rb, Sb, Sn, Tl and Zn in FAs. However, the high enrichment in trace elements of FAs can increase the hazardous potential of this coal by-product.

KEYWORDS | Trace elements. Feed coal. Fly ash. Bottom ash. Orhaneli-Turkey.

INTRODUCTION

Turkish coal reserves are estimated to be in the order of 8.3 Gt of lignite and 1.4 Gt of bituminous coal, and total annual lignite production in 2003 is about 46.2 Mt, of which 76% was consumed for power generation (Energy Report, 2004). The total power generation capacity from coal in Turkey is about 8445 megawatt (MW), 95%

of which is generated from lignite-subbituminous and 5% from bituminous coals (Energy Report, 2004). Coal combustion in power plants is considered a significant source of potentially hazardous air pollutants (HAPs), including As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, Se, Tl, and radionuclides (Th, U) (Finkelman, 1994; Finkelman and Gross, 1999). The behaviour of trace elements during coal combustion has previously been investigated and several studies on partitioning of elements among fly ash, slag/bottom ash and gas phase have been carried out (Clarke and Sloss, 1992; Meij, 1992; Querol et al., 1995; Clemens et al., 1999; Li et al., 2005).

The Bursa-Orhaneli lignite field is located in the western Anatolia, which was developed in a lacustrine depositional environment during the Miocene (Fig. 1). This field has been mined by Turkish Coal Enterprises (T.K.I.) since 1979 with open-pit mining methods. There is a mineable lignite seam with 4.7 m average thickness. This lignite field has a coal potential of 67 Mt, and producing run-of-mine coals of approximate 1.4 Mt per year are consumed in a coal-fired power plant in Orhaneli with a 210 MW capacity (Esenlik, 2005). The combustion residues were disposed of in landfills near the power plant, but up to 10 % were used as aggregates in the building industry.

The geology of the Orhaneli coal basin has been described and illustrated in detail by some previous authors such as Ozkocak (1969), Memikoglu et al. (1976), Emre (1986), Gokmen et al. (1993), Tanriverdi (2001). The metamorphic schist and recrystallized limestones of Palaeozoic age and Late Cretaceous aged serpentinites form the basement of the coalfield (Fig. 1). A coal-bearing sequence of Late Miocene age uncomformably overlies the basement rocks. This sequence includes conglomerate-sandstone-claystone, lignite-claystone-siltstone and marl-tuffite. The volcanic-pyroclastic rocks of Pliocene age consist of tuff-tuffite and andesite-basalt, which are widespread in the coalfield. The sequence ends with Quaternary aged unconsolidated pebble-sand-clay, alluvium and talus deposits.

The preliminary studies (Karayigit et al., 2000) have shown that some Turkish coals have higher trace element contents than most world coals (see compilation by Swaine, 1990). It is possible that these high trace element concentrations are due to the active plate tectonic setting
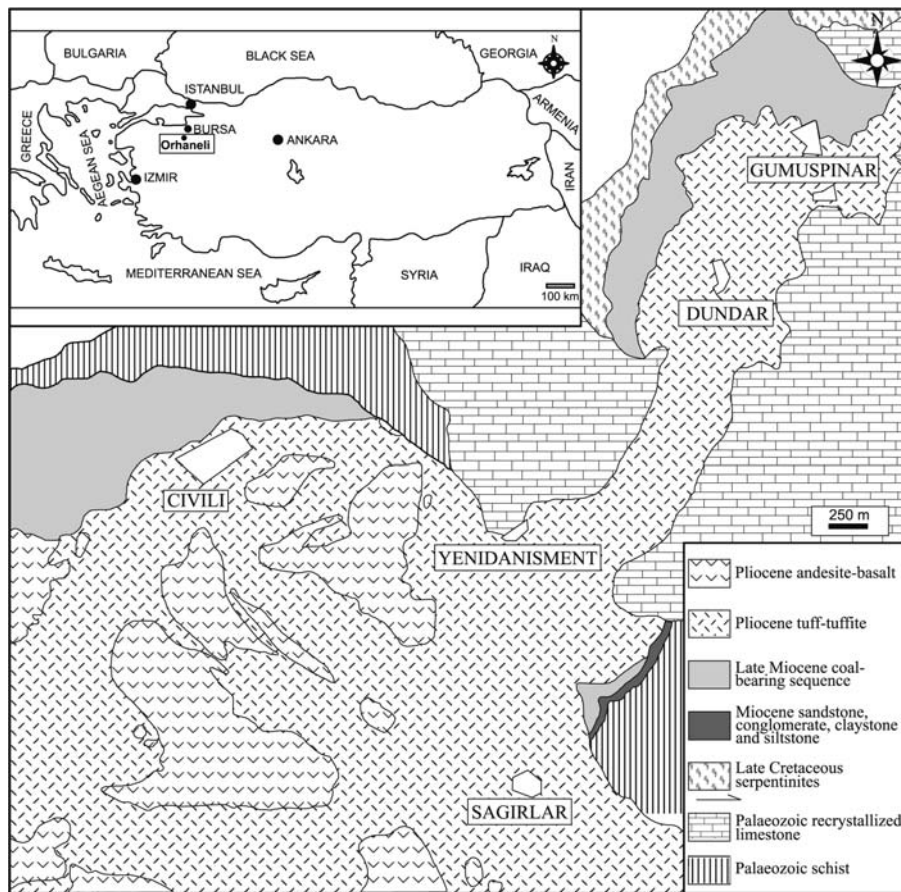

FIGURE 1 | **Location and simplified geological map of the Orhaneli coalfield (modified from Gökmen et al., 1993).**

of the Anatolian plate prior to, during and following coal formation, and volcanic input. In Turkish literature very little is currently known about the trace element concentrations in feed coals (FCs) and combustion residues (fly ashes (FAs) and bottom ashes (BAs)), as well as about combustion behaviour of elements in coal-fired power plants, and, subsequently, the fate of these elements in the environment for Turkish power plants. The present study focuses on determination of elemental contents of FCs, FAs and BAs, and mass balance calculations of major and especially trace elements in the Orhaneli power plant for better evaluation of elements in feed coals and combustion residues.

MATERIAL AND METHODS

A total of 51 samples (FCs, FAs and BAs), which were systematically collected over an eight-week period, were evaluated in this study. FCs (5-10 kg) were sampled from the feed coal conveyor system after the boiler mills, and then crushed, blended and split to obtain 0.5-1 kg sub-samples for analysis. BAs were obtained from the boilers via the boiler doors. The ash conveyor system for BAs was stopped to allow collection of a mixed, representative sample. FAs were sampled from the pre-emission control device sampling point by allowing the ash to fall onto a sampling sheet. After cooling the ash was sampled, mixed and then split for analysis. This sampling strategy is thought to give a good probability the sampled FA and BA represent the combustion products of the sampled FC.

Standard proximate analyses of 51 samples were carried out according to procedures of the American Society for Testing and Materials (ASTM, 1991). Mineralogical characterisation of the selected powder FCs, FAs and BAs was performed by X-ray diffraction spectrometry (XRD) with CuK· radiation and a 3-70° 2Θ (Fig. 2). Major, minor and trace elements of 24 samples (8 FCs, 8 BAs and 8 FAs) selected from 51 samples (due to limited analytical facilities) were analysed in an air-dried basis using inductively coupled plasma - atomic emission spectrometry (ICP-AES) and inductively coupled plasma - mass spectrometry (ICP-MS). Mercury analysis of bulk samples on an air-dried basis was only run on 6 samples (2 FCs, 2 FAs and 2 BAs) with a LECO AMA-254 atomic absorption spectrometer. For major, minor and trace elements, except for Hg, the samples were previously digest-
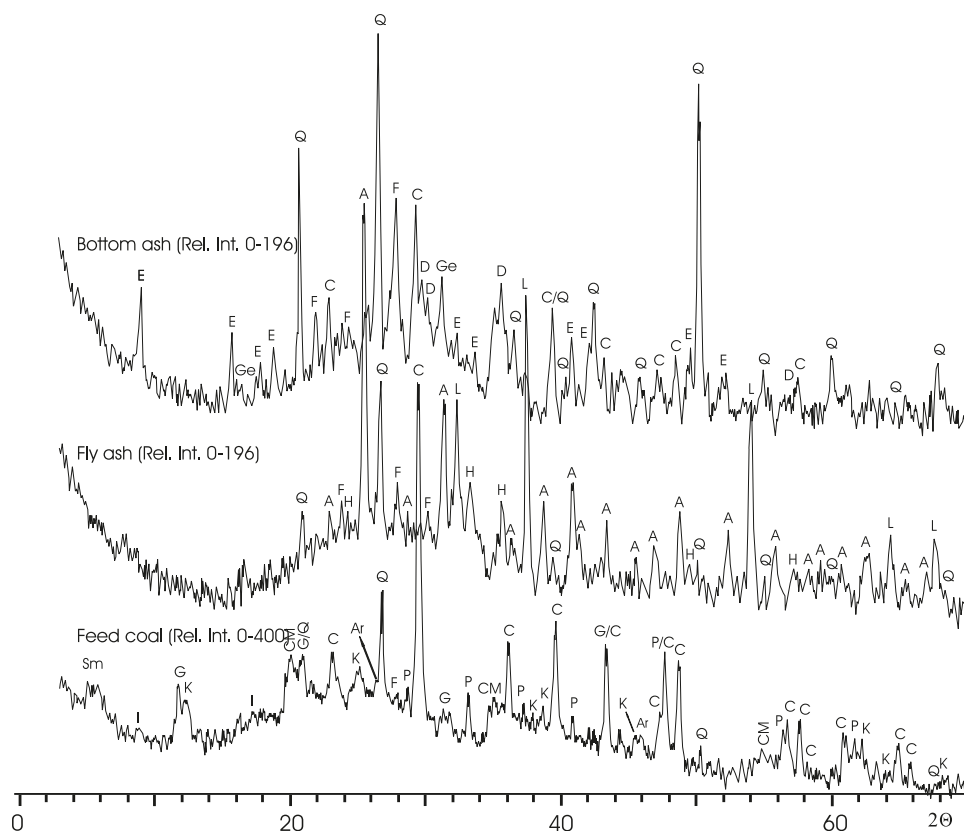

FIGURE 2 | Selected XRD traces of feed coal, fly ash and bottom ash from Orhaneli thermal power plant. Abbreviations: CM: Clay Minerals; Sm: Smectite; I: Illite; K: Kaolinite; Q: Quartz; C: Calcite; Ar: Aragonite; F: Feldspar; P: Pyrite; G: Gypsum; A: Anhydrite; L: Lime; E: Ettringite; D: Diopside; Ge: Gehlenite; H: Hematite.

ed using a two-stage extraction procedure devised to retain volatile elements (such as As and B) during the analysis. A detailed description of the digestion procedure has been given earlier (Querol et al., 1997). Digestion of international reference materials (SARM 19 and NBS 1633b) and blanks were prepared using the same procedure. Analytical errors were estimated at < 5% for most of the elements.

In this study, the balance factor (BF) and total enrichment factor (EF_t) or mass balance of major, minor and trace elements in FCs, FAs and BAs were calculated to elucidate the behaviour of major, minor and trace elements in coal combustion. Such calculations, as noted by some authors such as Clarke (1991), Meij (1992), Querol et al. (1995), Vassilev et al. (2001), and Vassilev et al. (2005), Karayigit et al. (in press) reveal elements that have the susceptibility to liberate into the atmosphere. The balance factor was calculated using the formula (1) given by Egorov et al. (1979), in which C_{FA} is the element content in FA (ash basis); C_{BA} is the element content in BA (ash basis); C_{FCA} is the element content in FC (ash basis); K_1 (0.8) and K_2 (0.2) are the coefficients showing the ratio between FA and BA produced from Orhaneli power plant, respectively. Furthermore, to quantify the partitioning among flue gas, fly ash and bottom ash, Al-normalised enrichment factors for major, minor and trace elements in fly ash/feed coal (EF_{FA}) and bottom ash/feed coal (EF_{BA}) have been calculated considering Al as a non volatile element during combustion. $[C]_s$ and $[C]_{FC}$ are the contents of element X in the fly ash or bottom ash and in the feed coal, respectively. $[Al]_s$ and $[Al]_{FC}$ are the corresponding aluminium contents (2). Using this normalisation system, elements enriched in fly ash will yield an enrichment factor (EF_{FA}) >1. Low-volatile elements will not be enriched in fly ash, and will yield enrichment factors (EF_{BA}) ≥1. Low EFs for both fly ash and bottom ash point to volatilisation processes with very minor condensation from flue gas. The EF_t, calculated with the formula given below (3) (Gordon and Zoller, 1973; Querol et al., 1995), is obtained from the adjusted EFs with the fly ash and bottom ash production (4:1) and allows determination of the volatile fraction of each element present in the raw gas. Thus, a EF_t value <1 points to a partial gaseous phase in the raw gas for a given element. In addition, the ratios of EF_{FA} to EF_{BA} were calculated in this study, which show elements enriched in FA or BA. During BF, EF and EF_t calculations mean, minimum, maximum values of elemental concentrations of FCs, FAs and BAs and their analytical errors have been taken into consideration, for better evaluation.

$$\text{Balance Factor (BF)} = ((C_{FA}*K_1+C_{BA}*K_2-C_{FCA})\,/C_{FCA})*100 \quad (1)$$

$$\text{Enrichment Factor (EF)} = ([C]_s/([Al]_s)/([C]_{FC}/([Al]_{FC}) \quad (2)$$

$$\text{Total Enrichment Factor (EF}_t) = (EF_{FA}*\,K_1)+(EF_{BA}*\,K_2) \quad (3)$$

Pearson correlation coefficients were calculated to determine relationships between concentrations of elements and ash yields. The significance levels for correlation coefficients used in this study are 99% and 95%, which indicates that there is either 1% or 5% probability that the relation between the variables found in the sample set is not valid.

RESULTS AND DISCUSSIONS

Proximate Analysis and Mineralogy

Table 1 summarises the results of proximate analyses of FCs, FAs and BAs. The feed coal samples on an air-dried basis have a moisture content ranging from 6 to 17% (av. 9%), high volatile matter content (av. 33%), very high ash yield (av. 53%), relatively high sulfur content (av. 2.14%) and low gross calorific value (av. 1775 kcal/kg). Esenlik (2005) indicated that coals from the Orhaneli lignite field have a mean random huminite reflectance of 0.29%, and they are dominated by huminite group macerals. Selected microphotographs from FCs as well as FAs are presented in Figs. 3 and 4.

TABLE 1 | **Results of proximate analysis of feed coals, fly ashes and bottom ashes from thr Orhaneli thermal power plant. Abbreviation: as-rec:as received basis.**

Analysis	Range	Mean
Feed Coal (air-dried)		
% Moisture (as-rec)	21.6 – 32.0	26.1
% Moisture	5.7 – 17.4	9.3
% Volatile Matter	25.3 – 36.4	33.2
% Ash	29.7 – 64.9	52.7
% Fixed Carbon	0 – 20.8	4.9
% Total Sulphur	1.5 – 3.1	2.1
Gross Calorific Value, kcal/kg	998 – 3846	1775
Fly Ash (as-determined)		
% Moisture	0 – 0.1	0
% Volatile Matter	0.3 – 1.2	0.5
% Ash	98.8 – 99.8	99.5
% Fixed Carbon	0	0
% Total Sulphur	0.8 – 3.5	1.8
Bottom Ash (air-dried)		
% Moisture (as-rec)	33.8 – 54.7	46.0
% Moisture	1.4 – 3.9	2.5
% Volatile Matter	2.8 – 7.7	5.4
% Ash	88.8 – 95.8	92.1
% Fixed Carbon	0	0
% Total Sulphur	0.4 – 0.9	0.6

The BA on an as-received basis contains a high moisture content (av. 46%) due to wet quenching in the combustion boiler (Table 1). After air-drying, the FC and BA lose their surface moisture. The content of volatile matter of combustion residues imply that BAs have higher contents of unburned carbonaceous matter than FAs The mean values of the total sulphur content in FAs and BAs are 1.76 and 0.60%, respectively.

This study shows that the detectable minerals in FCs are calcite, quartz, clay minerals (smectite, illite, kaolinite), aragonite, pyrite, feldspar and gypsum (see Figure 3B and 3C for carbonates and pyrites). Aragonite and some calcites are mainly related to fossil shells identified in FCs. Gypsum presumably forms as a secondary weathering product from sulphides and calcium carbonate. The combustion residues are made up in a high proportion of an amorphous aluminium-silicate glass as evidenced from the high XRD background hump. The detectable minerals in the combustion residues include quartz, anhydrite, feldspar, lime, hematite, calcite, ettringite, gehlenite, and diopside. This study indicates that calcite, ettringite, gehlenite, diopside are higher and the anhydrite and lime contents are lower in the BA than in the FA samples.

Some minerals such as anhydrite, lime, hematite, diopside and gehlenite are formed during combustion from the syngenetic and epigenetic minerals in the feed coal. Quartz, feldspar and calcite may be of both primary and, rarely, secondary origin in the combustion residues, as explained in detail by Vasilev and Vassileva (1996).

Elemental Concentrations

Major and minor element data in conjunction with the mineralogical data may be used to establish the element-mineral associations for FCs from the power plants. Although the element associations may vary from one coal to another, a correlation analysis would demonstrate the general trends. Elements that do not correlate with the ash yields probably have different modes of occurrence in the coals (Karayigit et al., 2000). Range and mean values of original concentrations of major, minor and trace elements in FCs, FAs and BAs from Orhaneli thermal power plant are summarised in Table 2. In this study, a statistically positive correlation (at the 95% and 99% confidence levels) between the element and the ash yield has only been established for Mg and Fe (r=0.90), Al (r=0.83), K (r=0.81) and Ti (r=0.82). The other major and minor ele-

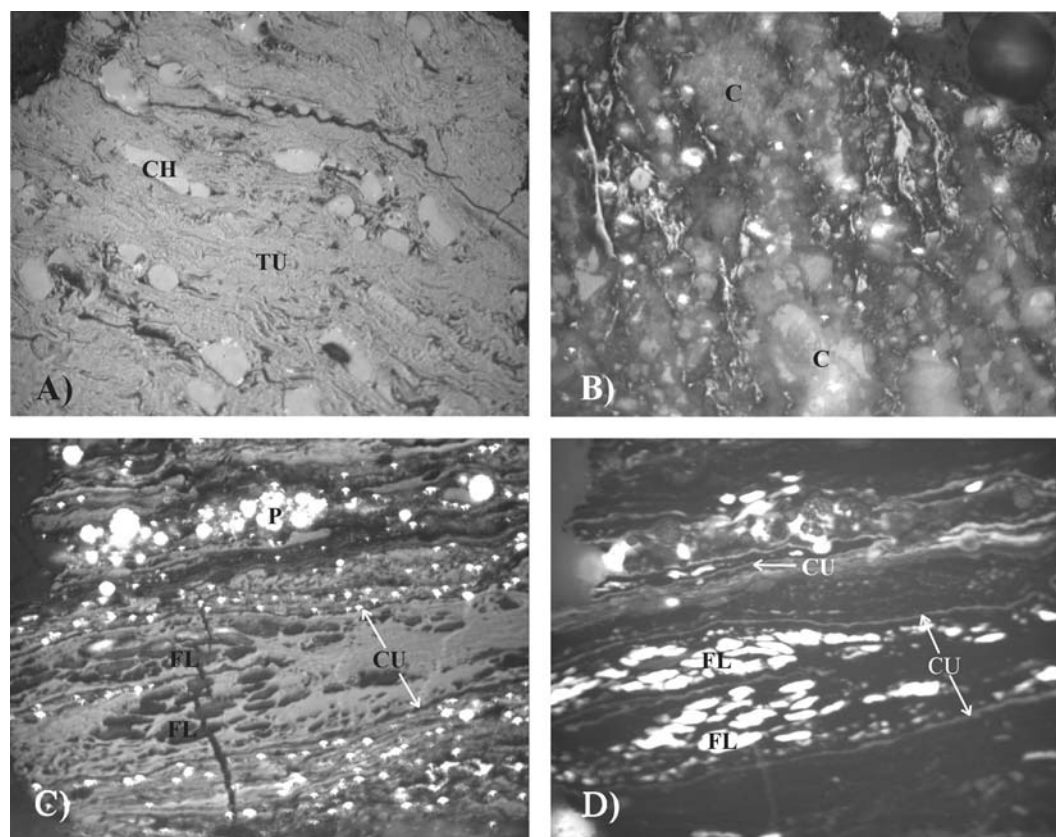FIGURE 3 | **Selected micrographs of the feed coals from the Orhaneli thermal power plant. Photo dimensions are 270x340?m. A) Corpohuminites (CH) within textoulminites (TU). B) Syngenetic carbonate minerals (C) and small huminite group macerals (attrinite). C) Good appearance of fluorinites, cutinites and pyrites in the feed coal (P: pyrite; CU: cutinite; FL: fluorinite). D) Fluorescence appearance of the same area of Figure 3C.**

ments (Ca, S and Na) have no significant correlation coefficients. The elements that have correlations with ash yields in FCs can be related to clay minerals, feldspars, quartz and pyrite. In the light of XRD and SEM studies calcium can be related to calcite, aragonite, gypsum, clay minerals, feldspar and organic matter; sulfur to gypsum, pyrite and organic matter; sodium to clay minerals and feldspar. However, further analytical work is needed to resolve the modes of occurrence of the major and minor elements.

The results from this study imply that original analytical data analysed in FCs are characterised by high concentrations of trace elements such as Cr, Cs, Ni and U (Table 2). These elements occur in concentrations close to or even higher than the maximum Swaine's content for most world coals. Mn and Th occur in concentrations

close to the maximum Swaine's values, while Be, Cd, Ge, P, Sn and Y showed concentrations close to the minimum Swaine's content. Although it is acknowledged that trace element analyses published subsequent to 1990 will modify the ranges in Swaine (1990), these data remain the best compilation currently available. The high Cr and Ni contents, as inferred by Karayigit et al. (2000), are to be expected because of the basement ophiolitic rocks having mineable chromite ores.

Trace element associations with coal ash have been widely reported and information obtained on the degree of organic/inorganic association (Finkelmann, 1994; Goodarzi, 1988; Mukhopadhyay et al., 1998; Spears and Zheng, 1999). The concentration values of most trace elements in FCs have very significant positive correlation coefficients (at the 95% and 99% confidence levels) with ash
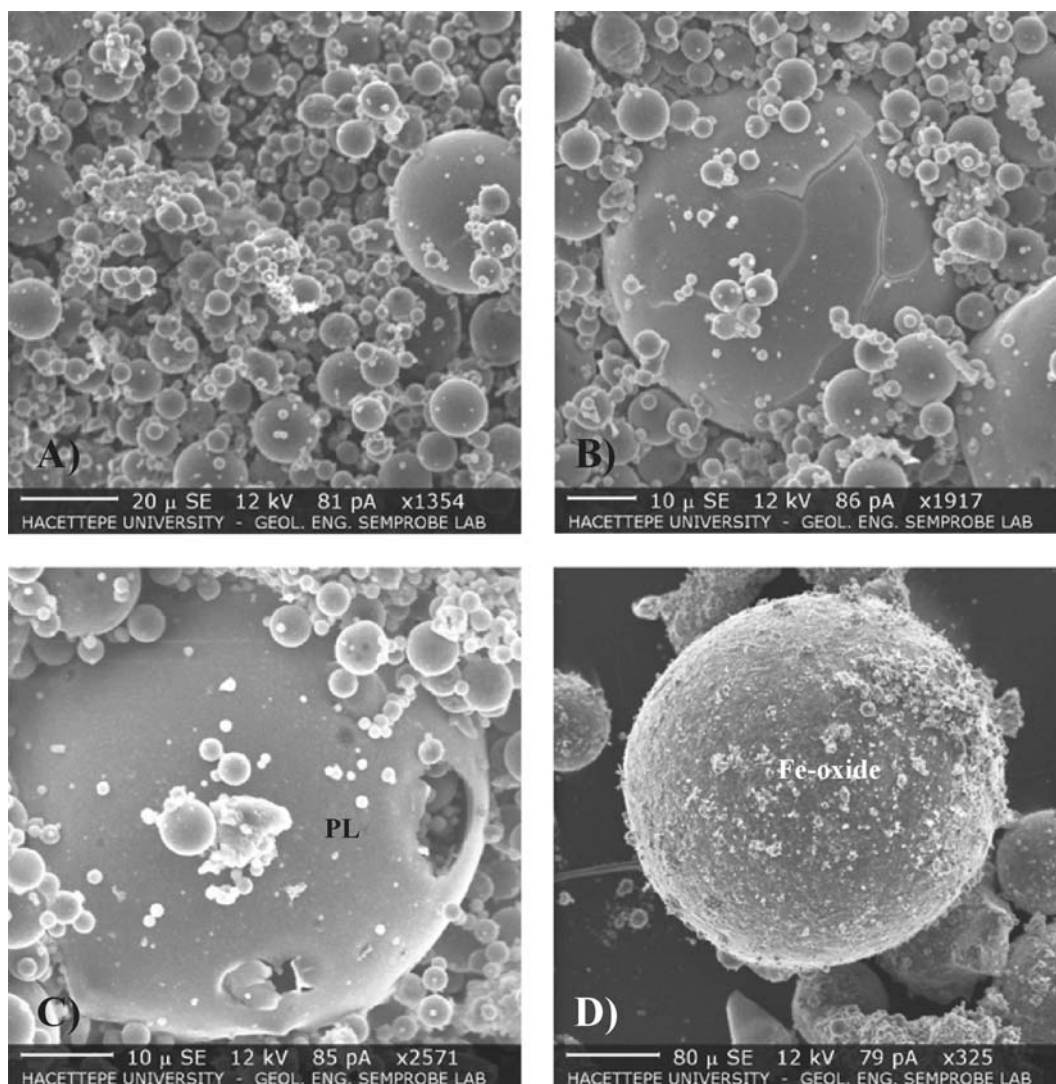

FIGURE 4 | **Selected scanning electron micrographs of the fly ashes from the Orhaneli thermal power plant. A and B) general view of the fine fly ash particles. C) spheres-within sphere structure of the fly ash particle (PL: Plerosphere). D) Fe-oxide particle in the fly ash.**

TABLE 2 | **Elemental concentrations of the feed coals, fly ashes and bottom ahes from the Orhaneli thermal power plant (ppm, unless indicated otherwise). Abbreviation: bdl: below detection limit.**

Analysis	Feed coal (FC)			Fly ash (FA)		Bottom ash (BA)	
	Range	Mean	World coals, Swaine (1990)	Range	Mean	Range	Mean
% Al	2.6 - 7.1	4.4	-	7.7 - 11.0	9.0	5.7 - 10.2	7.9
% Ca	5.0 - 12.7	8.5	-	9.2 - 18.9	14.2	8.0 - 15.2	12.2
% Fe	1.5 - 2.9	2.2	-	4.6 - 5.5	4.9	3.9 - 4.8	4.5
% K	0.3 - 1.1	0.6	-	1.1 - 1.6	1.3	0.5 - 1.4	0.9
% Mg	0.5 - 0.9	0.7	-	1.4 - 1.8	1.6	1.3 - 2.4	1.9
% Na	0.1 - 0.4	0.2	-	0.2 - 1.1	0.5	0.1 - 0.9	0.5
% S	1.5 - 3.0	2.2	-	0.6 - 2.9	1.4	0.3 - 0.6	0.4
% Ti	0.1 - 0.2	0.1	-	0.2 - 0.3	0.3	0.2 - 0.4	0.3
P	195.5 - 392.4	319.8	10 - 3000	591.1 - 775.8	688.2	569.7 - 725.8	662.6
As	24.7 - 36.2	30.5	0.5 - 80	47.3 - 259.0	156.8	17.9 - 37.8	29.5
B	28.3 - 206.2	107.6	5 - 400	167.8 - 1246.3	648.4	163.9 - 605.0	361.3
Ba	263.5 - 571.4	463	20 - 1000	708.3 - 1156.1	872.9	554.0 - 963.0	737.4
Be	0.7 - 2.1	1.3	0.1 - 15	3.2 - 4.8	3.7	2.1 - 4.2	3.3
Bi	0.1 - 0.4	0.3	2 - 20	0.7 - 1.8	1.1	0.1 - 0.2	0.1
Cd	0.1 - 0.5	0.3	0.1 - 3	0.6 - 1.4	1.0	0.1 - 0.3	0.2
Co	6.1 - 16.4	11	0.5 - 30	21.4 - 29.9	24.9	20.1 - 26.5	23.0
Cr	31.6 - 85.6	66.6	0.5 - 60	153.0 - 267.5	203.2	92.2 - 206.5	181.1
Cs	4.1 - 11.3	8	0.5 - 5	16.8 - 24.3	19.8	5.0 - 15.2	12.1
Cu	14.9 - 37.4	25.4	0.5 - 50	54.1 - 67.8	60.7	39.5 - 53.6	48.0
Ga	5.9 - 15.8	10	1 - 20	20.3 - 33.2	25.9	13.5 - 23.6	16.4
Ge	0.8 - 2.6	1.1	0.5 - 50	2.7 - 9.3	5.9	0.3 - 2.4	1.5
Hf	0.6 - 1.8	1.2	0.4 - 5	2.1 - 3.5	2.7	1.5 - 3.0	2.6
Hg	0.5 - 1.0	0.8	0.02 - 1	1.1 - 2.0	1.6	< 0.1	0
Li	17.4 - 53.0	36.3	1 - 80	65.5 - 92.4	78.9	40.5 - 74.7	61.9
Mn	189.6 - 405.7	263.4	5 - 300	614.5 - 718.1	662.0	543.3 - 675.8	603.6
Mo	0.5 - 1.9	1.2	0.1 - 10	4.5 - 23.8	15.7	4.5 - 7.9	6.4
Nb	3.0 - 7.0	5	1 - 20	5.3 - 11.4	8.0	1.2 - 11.3	6.9
Ni	57.5 - 185.7	137.2	0.5 - 50	247.9 - 467.6	335.1	254.4 - 421.6	330.2
Pb	13.8 - 40.3	24.3	2 - 80	53.9 - 97.4	72.6	13.8 - 39.7	22.8
Rb	19.5 - 71.1	39	2 - 50	80.2 - 111.0	89.4	26.0 - 99.6	60.7
Sb	1.3 - 3.1	2	0.1 - 10	3.3 - 11.5	7.4	0.6 - 3.8	2.0
Sc	2.6 - 8.7	4.2	1 - 10	9.1 - 14.0	11.2	7.7 - 13.5	10.0
Se	bdl - 3.9	< 4.0	0.2 - 10	bdl - 10.2	< 6.2	bdl - 5.1	< 2.6
Sn	0.2 - 2.6	1.2	1 - 10	1.8 - 6.5	3.6	0 - 1.8	0.7
Sr	212.2 - 413.9	320	15 - 500	382.9 - 784.0	608.5	373.3 - 846.1	598.4
Ta	0.3 - 1.0	0.7	0.1 - 1	0.2 - 0.7	0.4	0.1 - 0.8	0.3
Th	3.8 - 11.1	7.3	0.5 - 10	13.3 - 17.9	15.9	9.0 - 16.6	13.9
Tl	0.4 - 1.0	0.6	< 0.2 - 1	1.8 - 3.3	2.5	0.2 - 1.2	0.6
U	7.8 - 14.8	11.9	0.5 - 10	25.9 - 46.7	38.5	26.6 - 48.2	38.7
V	33.1 - 72.1	49.3	2 - 100	122.5 - 153.7	139.4	94.1 - 145.5	123.4
W	1.4 - 2.5	2.1	0.5 - 5	4.5 - 8.2	6.0	1.1 - 5.6	3.6
Y	5.0 - 14.1	8.4	2 - 50	16.8 - 22.5	19.0	14.4 - 21.6	17.8
Zn	45.3 - 101.0	67.3	5 - 300	119.7 - 208.4	159.1	57.9 - 96.8	68.0
Zr	19.0 - 55.7	41.6	5 - 200	85.4 - 143.5	105.6	61.8 - 121.0	99.9
La	9.3 - 28.7	16.9	1 - 40	31.1 - 44.2	36.0	24.0 - 40.9	31.7
Ce	17.8 - 54.8	32.1	2 - 70	59.3 - 83.1	68.4	46.0 - 77.6	59.2
Pr	2.0 - 6.4	3.7	1 - 10	6.7 - 9.6	7.9	5.3 - 9.0	6.8
Nd	8.0 - 25.3	14.7	3 - 30	27.2 - 39.4	31.5	21.4 - 36.4	27.4
Sm	1.1 - 3.7	2.1	0.5 - 6	4.0 - 5.6	4.5	3.1 - 5.2	4.0
Eu	0.3 - 0.9	0.5	0.1 - 2	1.0 - 1.4	1.2	0.8 - 1.3	1.0
Gd	1.3 - 4.1	2.4	0.4 - 4	4.4 - 6.2	5.1	3.5 - 5.9	4.5
Tb	0.2 - 0.5	0.3	0.1 - 1	0.6 - 0.8	0.7	0.5 - 0.8	0.6
Dy	1.0 - 2.9	1.7	0.5 - 4	3.2 - 4.5	3.8	2.7 - 4.3	3.4
Ho	0.2 - 0.5	0.3	0.1 - 2	0.6 - 0.8	0.7	0.5 - 0.8	0.6
Er	0.5 - 1.3	0.8	0.5 - 3	1.5 - 2.1	1.8	1.3 - 2.1	1.7
Tm	0.1 - 0.2	0.1	0.5 - 3	0.3 - 0.4	0.3	0.2 - 0.4	0.3
Yb	0.5 - 1.3	0.8	0.3 - 3	1.5 - 2.1	1.8	1.4 - 2.0	1.7
Lu	0.1 - 0.2	0.1	0.03 - 1	0.3 - 0.4	0.3	0.2 - 0.3	0.3

yields on an air-dried basis, evidencing a main association with inorganic constituents in FCs. The elements showing significant correlations are: Be, Bi, Cd, Co, Cr, Cs, Cu, Ga, Li, Mn, Ni, P, Pb, Rb, REEs, Se, Th, Tl, V, Y, Zn and Zr. shows significant negative correlation coefficient (r=-0.80) suggesting a main organic association for this element. This study also indicates that the remaining trace elements analysed show no significant correlation coefficients with the ash yields. These elements are: As, B, Ba, Hf, Mo, Nb, Sb, Sc, Sn, Sr, Ta, U and W. Organic, inorganic, sulphide or sulphate associations for these elements are possible.

As expected from the trace element content in the FCs, fly ashes are characterised by high contents of Cr, Ni, Mo and U when compared with the range for 23 European fly ashes (Moreno et al., 2004). Furthermore As, B and Hg also occur in higher concentrations than the highest content determined for European fly ashes. This fact is probably due to the high Ca content of FCs, which may favour a high retention of these elements in FAs during coal combustion by sorption processes between gaseous As, B and Hg species and CaO (Querol et al., 1995; Clemens et al., 1999; Meij and Winkel, 2003). The high anhydrite and lime contents in FAs detected by XRD supports this fact (Fig. 2).

The comparison between FAs and BAs using their ratios of EF_{FA} to EF_{BA} show the following features (Table 3; this table, as noted earlier, was prepared using mean, minimum, maximum values of elemental concentrations of FCs, FAs and BAs and their analytical errors):

In Orhaneli thermal power plant, Hg is highly enriched in FAs with respect to BAs, showing EF_{FA}/EF_{BA} ratio of 679 (Table 3). As, B, Bi, Cd, Cs, Ge, K, Pb, Rb, S, Sb, Se, Sn, Tl and Zn are indicating enrichments in FAs (EF_{FA}/EF_{BA} concentration ratios ranging from 1.2 to 9) relative to BAs (Table 3). Only Cr and U are clearly enriched in BAs, showing EF_{FA}/EF_{BA} ratios of 0.7 and 0.6, respectively. The remaining elements investigated in this study have no clear segregation between FAs and BAs, which their EF_{FA}/EF_{BA} concentration ratios ranging between 0.8 and 1.2. Similar results are obtained in the Soma thermal power plant (Karayigit et al., in press).

Mass Balance Calculations

Mass balance calculations (Table 3) demonstrate that total enrichment factor (EF_t) of elements show positive linear correlations (r=0.997) with balance factor (BF), indicating that both methods seem to be very useful in order to elucidate the behaviour of major and trace elements in coal combustion. The results of mass balance (Table 3) have revealed S and Hg as the only elements showing significant proportions in gas phase, with mean balance factors equal to 70 and 16%-20%, respectively, at the fly ash removal temperatures. However, these proportions in the gas phase are lower than those reported for S and particularly for Hg, with an average of >50% in gas phase, in several partitioning studies in coal combustion (Clarke, 1991; Meij, 1992; Meij and Winkel, 2003; Querol et al., 1995; Li et al., 2005). As stated above the high Ca content of the feed coal accounts for the very high Ca content in the FAs (9-18%). This high occurrence of lime (CaO) and anhydrite ($CaSO_4$) in FAs accounts for the high S and also Hg retention in this combustion by-product. As indicated by Goodarzi et al. (2006), the reactive char particles in the fly ash may be also responsible for the capture of mercury. It is known that the most common retention mechanism of S in fly ashes is the reaction between CaO and SO_2 to form $CaSO_4$ (Querol et al., 1995; Clemens et al., 1999). Ca-bearing species are also highly effective to retain Hg. High Ca levels can reduce the effect of high Cl contents on the volatile behaviour of Hg, promoting the adsorption of $HgCl_2$ in fly ash particles (Gullit et al., 1999; Meij and Winkel, 2003, in press). The high lime and anhydrite contents of FAs can also explain the complete retention in fly ash of B and Se elements, which are commonly volatile, as well as the high proportions (90-99%) of As, Bi, Cd, Cs, Ge, Pb, Rb, Sb, Sn, Tl and Zn retained in FAs. Although using the mean values for mass balance a complete retention in fly ash were determined for As and Cd, a small proportion of these elements (10 and 20%, respectively) could be in gas phase at fly ash removal temperatures in the Orhaneli power plant, given the accumulated error in the mass balance calculation,

Statistically positive correlations of S with Se (r=0.81), As (r=0.79), Sb (r=0.76) and Ge (r=0.75) at the 95% confidence level evidence a main sulphate affinity for these elements in FAs suggesting that the retention of most of these elements, such as As and Se, can occur by similar reactions than that to form $CaSO_4$ (Querol et al., 1995; Clemens et al., 1999).

Some principle factors for the element behaviour (partitioning, volatilisation, condensation, capture and retention) in a coal-fired power plant have been discussed earlier (Vassilev et al., 2001). The modes of element occurrence in FCs, FAs and BAs are the fundamental guide for the volatilisation behaviour of elements during combustion.

However, the results of mass balance evidence that other parameters, mainly the Ca content in the feed coal, can exert much more control on the partitioning of elements in coal combustion power plants than the mode of occurrence of trace elements in coal. Then, the high Ca content of feed coal in Orhaneli thermal power plant pro-

TABLE 3 | **Results of mass balance calculations from the Orhaneli thermal power plant. Abbreviations: BF: Balance factos; EF$_{FA}$: Enrichment factor in fly ash; EF$_{BA}$: Enrichment factor in bottom ash; EF$_t$: Total enrichment factor.**

Elements	Feed coal ash (FCA)	Fly Ash (FA)	Bottom Ash (BA)	BF	EF$_{FA}$	EF$_{BA}$	EF$_{FA}$/EF$_{BA}$	EF$_t$
% Al	8.2	9.0	7.9	7.0	1.0	1.0	1.0	1.0
% Ca	13.4	14	12	3.2	1.0	0.9	1.0	1.0
% Fe	4.5	4.9	4.5	6.9	1.0	1.0	1.0	1.0
% K	1.1	1.2	0.9	5.7	1.0	0.8	1.2	1.0
% Mg	1.7	1.6	1.9	1.3	0.9	1.2	0.8	1.0
% Na	0.5	0.5	0.5	11.5	1.0	1.0	1.0	1.0
% S	4.1	1.4	0.4	-69.6	0.3	0.1	2.9	0.3
As	41.5	47	29	5.3	1.0	0.7	1.4	1.0
B	528.8	648	361	11.8	1.1	0.7	1.6	1.0
Ba	831.0	873	737	1.8	1.0	0.9	1.0	1.0
Be	3.0	3.2	3.3	6.2	1.0	1.1	0.8	1.0
Bi	0.8	1.1	0.1	12.2	1.2	0.1	8.9	1.0
Cd	0.8	1.0	0.2	5.7	1.1	0.3	4.4	1.0
Co	22.7	25	23	8.2	1.0	1.1	0.9	1.0
Cr	156.8	153	181	1.2	0.9	1.2	0.7	1.0
Cs	16.2	19.8	12.1	12.1	1.1	0.8	1.4	1.0
Cu	51.9	61	48	12.1	1.1	1.0	1.1	1.0
Ga	19.0	20	16	2.8	1.0	0.9	1.1	1.0
Ge	1.9	2.7	0.3	14.1	1.3	0.1	8.6	1.0
Hf	2.5	2.7	2.6	8.0	1.0	1.1	0.9	1.0
Hg	1.5	1.5	0.0	-15.7	1.0	0.0	679	0.8
Li	68.5	79	62	10.2	1.1	0.9	1.1	1.0
Mn	632.7	662	604	2.8	1.0	1.0	1.0	1.0
Mo	4.5	4.7	4.5	4.4	1.0	1.0	0.9	1.0
Nb	7.0	8.0	6.9	11.9	1.0	1.0	1.0	1.0
Ni	328.6	335	330	1.7	0.9	1.0	0.9	1.0
P	613.8	688	663	11.3	1.0	1.1	0.9	1.0
Pb	76.1	97	40	12.8	1.2	0.5	2.2	1.0
Rb	75.5	89	61	10.8	1.1	0.8	1.3	1.0
Sb	5.9	7.4	2.0	6.9	1.1	0.4	3.2	1.0
Sc	8.3	9.1	10.0	11.4	1.0	1.3	0.8	1.0
Se	4.9	6.2	2.6	11.1	1.1	0.5	2.1	1.0
Sn	2.7	3.6	0.7	10.5	1.2	0.3	4.3	1.0
Sr	588.2	608	598	3.1	0.9	1.1	0.9	1.0
Ta	0.6	0.7	0.7	7.9	1.0	1.2	0.8	1.0
Th	13.9	15.9	13.9	11.8	1.0	1.0	1.0	1.0
Ti	2730.4	2941	2692	5.9	1.0	1.0	1.0	1.0
Tl	1.9	2.5	0.6	14.0	1.2	0.3	4.0	1.0
U	27.9	25.9	38.7	2.2	0.8	1.4	0.6	1.0
V	133.1	139.4	123.4	2.3	1.0	1.0	1.0	1.0
W	4.0	4.5	3.6	7.3	1.0	0.9	1.1	1.0
Y	16.8	19.0	17.8	11.7	1.0	1.1	0.9	1.0
Zn	127.1	159.1	68.0	10.9	1.1	0.6	2.1	1.0
Zr	102.4	106	100	2.0	0.9	1.0	0.9	1.0
La	31.9	36	32	10.0	1.0	1.0	1.0	1.0
Ce	60.7	68	59	9.7	1.0	1.0	1.0	1.0
Pr	6.9	7.9	6.8	10.1	1.0	1.0	1.0	1.0
Nd	27.7	32	27	10.8	1.0	1.0	1.0	1.0
Sm	4.0	4.5	4.0	11.7	1.0	1.0	1.0	1.0
Eu	1.0	1.2	1.0	11.5	1.0	1.1	1.0	1.0
Gd	4.5	5.1	4.5	12.1	1.0	1.1	1.0	1.0
Tb	0.6	0.7	0.6	12.2	1.0	1.1	1.0	1.0
Dy	3.3	3.8	3.4	11.6	1.0	1.1	1.0	1.0
Ho	0.7	0.7	0.6	1.8	0.9	1.0	0.9	1.0
Er	1.7	1.8	1.7	6.8	1.0	1.0	0.9	1.0
Tm	0.3	0.3	0.3	7.0	1.0	1.1	0.9	1.0
Yb	1.6	1.8	1.7	11.3	1.0	1.1	0.9	1.0
Lu	0.3	0.3	0.3	5.5	1.0	1.1	0.9	1.0

duces a high removal efficiency for highly volatile elements such as S, Hg, B and Se being retained in FAs. The significant influence of Ca in the behaviour of elements is especially noticeable in the case of B. As stated above, B is mainly organically bound in FCs. This fact results in a high and easy volatilisation of B during combustion with low condensation of B species. This fact accounts for the usual relatively high proportions of B remaining in gaseous phase at fly ash removal temperatures (Clarke, 1991; Meij, 1992; Meij and Winkel, 2003; Querol et al., 1995; Li et al., 2005). In the Orhaneli thermal power plant B volatilises from coal during combustion but due to the high Ca content. Ca reacts with this element, being incorporated in the Ca silicates framework structure and condensing as oxide on the lime surface (Clemens et al., 1999). Usually, the high B retention in fly ashes occurs when this element is bound to inorganic constituents of coal, mainly tourmalines (Querol et al., 1995; Boyd, 2002).

CONCLUSIONS

This study has indicated that the feed coals show enrichments in Cr, Cs, Ni and U, which exceed the ranges of most world coals. Fly ashes are characterised by high contents of Cr, Ni, Mo, U, As, B and Hg when compared with the range of EU fly ashes. Hg is highly enriched in FAs with respect BAs, showing EF_{FA}/EF_{BA} ratio of 679. S, As, B, Bi, Cd, Cs, Ge, K, Pb, Rb, Sb, Se, Sn, Tl and Zn are indicating enrichments in FAs (EF_{FA}/EF_{BA} concentration ratios from 1.2 to 9). Only Cr and U are clearly enriched in BAs, showing EF_{FA}/EF_{BA} ratios of 0.7 and 0.6, respectively.

The results of mass balance have revealed S and Hg as the only elements showing significant proportions in gas phase, with mean values of the mass balance factor equal to 70 and 16%-20%, respectively, at the fly ash removal temperatures. These low proportions of S and Hg in the gas phase are due to the high occurrence of lime (CaO) and anhydrite ($CaSO_4$) in FAs which account for the high S and also Hg retention in FAs. The latter can be adsorbed by Ca-bearing species. The high lime and anhydrite content of FAs can also explain the complete retention in fly ash of B and Se as well as the high proportions of As, Bi, Cd, Cs, Ge, Pb, Rb, Sb, Sn, Tl and Zn retained in FAs. Se, As, Sb and Ge show mainly a sulphate affinity in FAs suggesting that the retention of these elements occur by similar reactions to those that form $CaSO_4$.

Therefore, the high Ca content of feed coal in the Orhaneli thermal power plant is the main parameter controlling the partitioning of elements in this power plant, producing a high removal efficiency for highly volatile elements such as S, Hg, B and Se, and a high retention of As, Bi, Cd, Cs, Ge, Pb, Rb, Sb, Sn, Tl and Zn in FAs.

However, the high enrichment in trace elements of FAs can increase the hazardous potential of this coal by-product.

REFERENCES

American Society for Testing and Materials, 1991. Annual book of ASTM standards. Section 5: Petroleum Products, Lubricants, and Fossil Fuels. 5.05: Gaseous Fuels: Coal and Coke.

Boyd, R.J., 2002. The partitioning behaviour of boron from tourmaline during ashing of coal. International Journal of Coal Geology, 53, 43-54.

Clarke, L., 1991. The Behaviour of Trace Elements during Coal Combustion and Gasification: An Overview. Managing Hazardous Air Pollutants: State of the Art, 150 pp.

Clarke, L.B., Sloss, L.L., 1992. Trace elements emissions from coal combustion and gasification. International Energy Agency Coal Research, IEACR, 49, 111 pp.

Clemens, A.H., Damiano, L.F., Gong, D., Matheson, T.W., 1999. Partitioning of some toxic volatile elements during stoker and fluidised bed combustion of alkaline sub-bituminous coal. Fuel, 78, 1379-1385.

Egorov, A., Laktionova, N., Popinako, N., Novosselova, I., 1979. Behaviour of some trace elements in coal during burning at TPS. Toploenergetika 2, 22-25, (in Russian).

Emre, H., 1986. Geology and petrology of Orhaneli ophiolite. Doctoral thesis. Istanbul University, 165 pp., (in Turkish).

Energy Report, 2004. Turkey Energy Statistics. World Energy Council, Turkish National Committee, Ankara.

Esenlik, S., 2005. Mineralogy, petrography and elemental contents of feed coals and combustion residues from Orhaneli thermal power plant, Bursa - Turkey. MSc thesis. Hacettepe University, 121 pp., (in Turkish).

Finkelman, R.B., 1994. Modes of occurrence of potentially hazardous elements in coal: Level of confidence. Fuel Processing Technology, 39, 21-34.

Finkelman, R.B., Gross, P.M.K., 1999. The types of data needed for assessing the environmental and human health impacts of coal. International Journal of Coal Geology, 40, 91-101.

Gokmen, V., Memikoglu, O., Dagli, M., Oz, D., Tuncali, E., 1993. Turkish Lignite Inventory. Ankara, Turkey, MTA Publication, 356 pp., (in Turkish).

Goodarzi, F., 1988. Elemental distribution in coal seams at the Fording coal mine, British Columbia, Canada. Chemical Geology, 68, 129-154.

Goodarzi, F., Reyes, J, Schulz, J., Hollman, D., Rose, D., 2006. Parameters influencing the variation in mercury emissions from an Alberta power plant burning high inertinite coal over thirty-eight weeks period. International Journal of Coal Geology, 65, 26-34.

Gordon, G.E., Zoller, W.H., 1973. Normalization and interpretation of atmospheric trace element concentration patterns. 1st Annual National Science Foundation (NSF) Trace Contaminants Conference. Oak Ridge National Laboratory, Oak Ridge, Tennessee, Proceedings, CONF-730802, 314-325.

Gullit, B.K., Ghorishi, B., Huggins, F.E., 1999. Mercury chloride capture by alkaliner sorbents. Proceedings of the Air and Waste Management Association 93rd Annual Meeting, Salt Lake City, Utah, Paper 259.

Karayigit, A.I., Gayer, R.A., Querol, X., Onacak, T., 2000. Contents of major and trace elements in feed coals from Turkish coal-fired power plants. International Journal of Coal Geology, 44, 169-184.

Karayigit, A.I., Bulut, Y., Karayigit, G., Querol, X., Alastuey, A., Vassilev, S., Vassileva, C., in press. Mass balance of major and trace elements in coal-fired Soma power plant, Manisa-Turkey. Energy Sources.

Li, Z., Clemens, A.H., Moore, T.A., Gong, D., Weaver, S.D., Eby, N., 2005. Partitioning behaviour of trace elements in a stoker-fired combustion unit: An example using bituminous coals from the Greymouth coalfield (Cretaceous), New Zealand. International Journal of Coal Geology, 63, 1-2, 98-116.

Meij, R., 1992. Elemental Analysis of Coal and its By-Products. International conference proceedings, Kentucky, USA, 1991, p. 299.

Meij, R., Winkel, H., 2003. Mercury emissions from coal-fired power station, firing bituminous coal, as a function of plant parameters, coal composition and co-combustion. International Conference on Air quality IV (Mercury, Trace elements and particulate Matter), Arlington, VA, USA, Proceedings,

Meij, R., Winkel, H., in press. Mercury emissions from coal-fired power stations: The current state of the art in the Netherlands. Science of the Total Environment.

Memikoglu, O., Engin, O., Has, F., Isiganer, T., 1976. Bursa Orhaneli coalfield feasibility research. MTA report, 19 pp., (in Turkish).

Moreno, N., Querol, X., Lopez-Soler, A., Andrés, J.M., Janssen, M., Nugteren, H., Towler, M., Stanton, K., 2004. Determining suitability of fly ash for silica extraction and zeolitite synthesis. Journal of Chemical Technology and Biotechnology, 79, 1009-1018.

Mukhopadhyay, P.K., Goodarzi, F., Crandlemire, A.L., Gillis, K.S., MacNeil, D.J., Smith, W.D., 1998. Comparison of coal composition and elemental distribution in selected seams of the Sydney and Stellarton Basins, Nova Scotia, Eastern Canada. International Journal of Coal Geology, 37, 113-141.

Ozkocak, O., 1969. Étude Géologique Du Massif Ultrabasique d'Orhaneli Et De Sa Proche Bordure (Bursa-Turquie). Doctoral thesis. Université de Paris,

Querol, X., Fernandez-Turiel, J.L., Lopez-Soler, A., 1995. Trace elements in coal and their behaviour during combustion in a large power station. Fuel, 74, 331-343.

Querol, X., Whateley, M.K.G., Fernández-Turiel, J.L., Tuncali, E., 1997. Geological controls on the mineralogy and geochemistry of the Beypazari lignite, central Anatolia, Turkey. International Journal of Coal Geology, 33, 255-271.

Spears, D.A., Zheng, Y., 1999. Geochemistry and origin of elements in some UK coals. International Journal of Coal Geology, 38, 161-179.

Swaine, D., 1990. Trace elements in coal. London, Butherworths, 296 pp.

Tanriverdi, H., 2001. Planning TKI Orhaneli open pit lignite field. MSc thesis. Istanbul University, 159 pp., (in Turkish).

Vassilev, S.V., Vassileva, C.G., 1996. Mineralogy of combustion wastes from coal-fired power stations. Fuel Processing Technology, 47, 261-280.

Vassilev, S., Eskenazy, G., Vassileva, C., 2001. Behaviour of elements and minerals during preparation and combustion of the Pernik coal, Bulgaria. Fuel Processing Technology, 72, 103-129.

Vassilev, S., Vassileva, C., Karayigit, A.I., Bulut, Y., Alastuey, A., Querol, X., 2005. Phase-mineral and chemical composition of composite samples from feed coals, bottom ashes and fly ashes at the Soma power station, Turkey. International Journal of Coal Geology, 61, 35-63