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Characterisation of Fly Ash from the Kangal Power Plant, Eastern Turkey

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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 is about 65 Mt, of which 81 % is consumed for power generation [1]. The total power generation capacity from coal in Turkey is about 6400 megawatt (MW), 95 % of which is generated from lignite and 5 % from bituminous coal. The Kangal lignite basin, which is one of the most productive lignite basins in eastern Anatolia-Turkey, includes two thick lignite seams containing abundant gastropoda shells in the Lower Pliocene Kalburcayiri Formation. The seams are currently exploited in an open-cast mine in the Kalburcayiri field and supply feed coal to a power plant, which has two boiler units (I and II) each with 150 MW capacity and also one newly-installed boiler unit (III) with 150 MW capacity. The average thickness of each of the two seams in this mine is about 10 m, and they are separated by about 20 m of tuffaceous sedimentary rocks [2]. The former two units of this power plant consume approximately 3.600.000 ton/yr in lignites.

Figure 1. Location of the coal-fired Kangal power plant within other Turkish power plants.

The Departments of Earth Sciences of Hacettepe University and Cardiff University are studying the feed coals and combustion residues from the Kangal Power Plant under academic projects supported by the British Council of Turkey and the Scientific and Technical Research Council of Turkey (TUBITAK). This preliminary investigation involves a systematic study of the characterisation of fly ashes from the Kangal Power Plant by looking at the proximate analysis, mineralogy and element compositions.

SAMPLING AND ANALYTICAL METHODS

The Kangal power plant in this study utilises lignites, which have high moisture (av. 47.9% as-rec.), high ash yield (av. 47.9%), high sulfur content (av. 3.52%), and low calorific value (av. 2559 kcal/kg) on an air-dried basis (unpublished data from Karayigit). In order to evaluate characterisation of fly ashes, a total of 25 samples were systematically collected once a week in November 1999 to May 2000 from the pre-emission control device sampling point of two boiler units (I and II) of the Kangal power plant by allowing the ash to fall onto a sampling sheet. After cooling the ash was mixed and split for analysis. The samples were analysed by proximate analysis, X-ray powder diffraction (XRD), inductively coupled plasma-mass spectrometry (ICP-MS), and scanning electron microscopy with energy-dispersive X-ray microanalysis (SEM-EDX).

Standard proximate analyses of the fly ashes were carried out according to procedures of the American Society for Testing and Materials [3]. Mineral phases in all the fly ash samples were determined using an XRD with Cu Kα radiation (0.05^0 2θ step size and a $3\text{-}70^0$ 2θ range). SEM-EDX analyses were used to identify mineral phases hosting specific trace elements and were performed on carbon-coated 5 polished briquettes. The elemental composition of the fly ashes was studied using inductively coupled plasma-mass spectrometry (ICP-MS). For analysis by ICP-MS, approximately 200 mg of ash, accurately weighed, was digested, using concentrated HF, aqua regia and 5 M HCl. Five-ml of sample solution was analysed quantitatively for a wide range of trace elements on a Perkin Elmer Elan 5000 ICP-MS. Detection limits in the ash are approximately < 50 ppb for La, Th, U and Cs; 10-50 ppb Be and Tl; 250-500 ppb Ba, Pb, Ti, Mn, Co, W and Mo; 0.1-1 ppm Cu; 2.5 ppm Zn and As [4-5].

RESULTS AND DISCUSSION

The proximate analysis of the fly ash samples, as we expected, shows that they are high ash (av. 97.4%), low volatile matter (av. 2.2%), and high total sulfur (av. 3.82%). Selected examples of X-ray diffraction traces of feed coal, fly ash and bottom ash, and SEM microphotographs of minerals and amorphous components in the fly ashes are given in Figures 2-4. The minerals identified by XRD in the Kangal lignites were abundant calcite, minor quantities of quartz, clay minerals, feldspar, pyrite, opal-CT, gypsum and traces of aragonite. The high content of calcite is related to the abundance of fossil gastropod shells (made up of calcite and aragonite) in the feed coals [2]. The XRD peak intensities (count values) of the fly ash samples are very low, suggesting that non-crystalline amorphous (glass) phases are the main constituents of the combustion residues. SEM-EDX study imples that typical amorphous components include FeCaAl-silicate with traces of Ti, K and Mg. The crystalline constituents in the fly ashes include the minerals anhydrite, feldspar, quartz, lime, hematite, opal-CT, calcite and gehlenite. In addition, micron-sized minerals Fe-sulfur (FeS), rutile, ilmenite, ilmenite with Mn traces, REE-

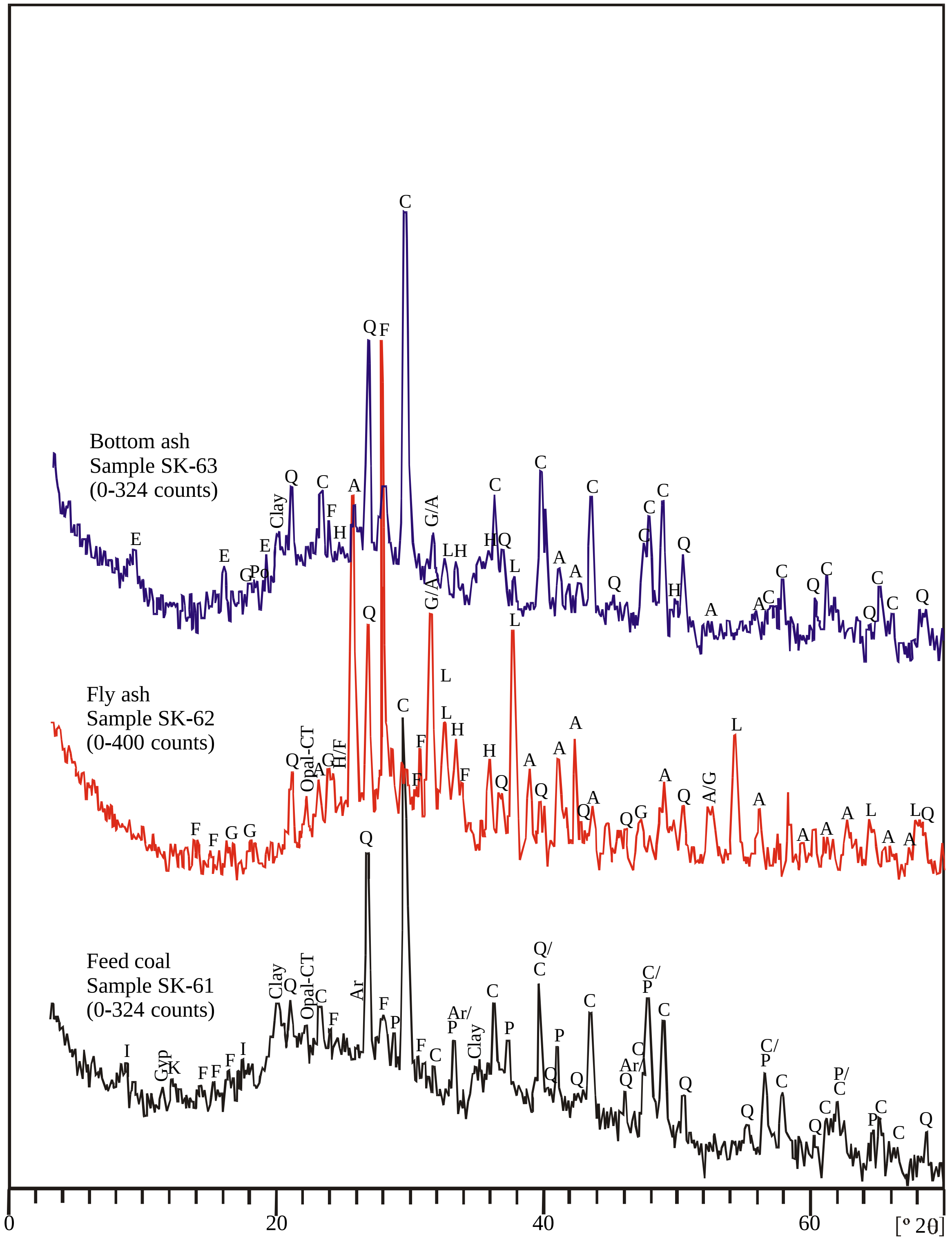

Figure 2. Selected examples of X-ray diffraction traces of feed coal, fly ash and bottom ash from the Kangal power plant, Turkey (unpublished data from Karayigit). Abbreviations: Q=quartz, C=calcite, Ar=aragonite, F=feldspar, I=illite, K=kaolinite, Clay=clay min., P=pyrite, Gyp=gypsum, A=anhydrite, L=lime, H=hematite, E=ettringite, G=gehlenite, Po=portlandite.

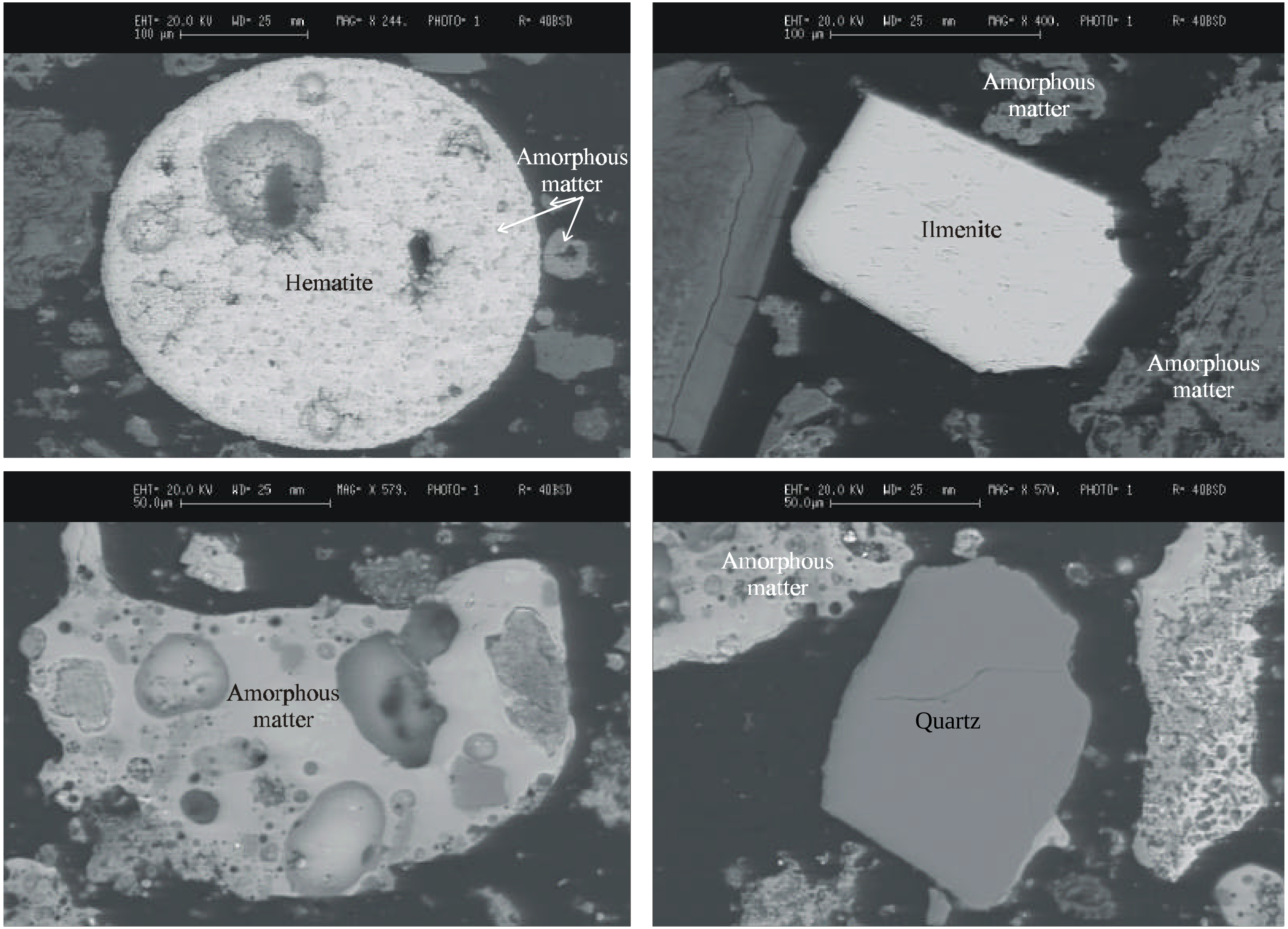

Figure 3. Selected SEM images of fly ash from the Kangal power plant, Turkey.

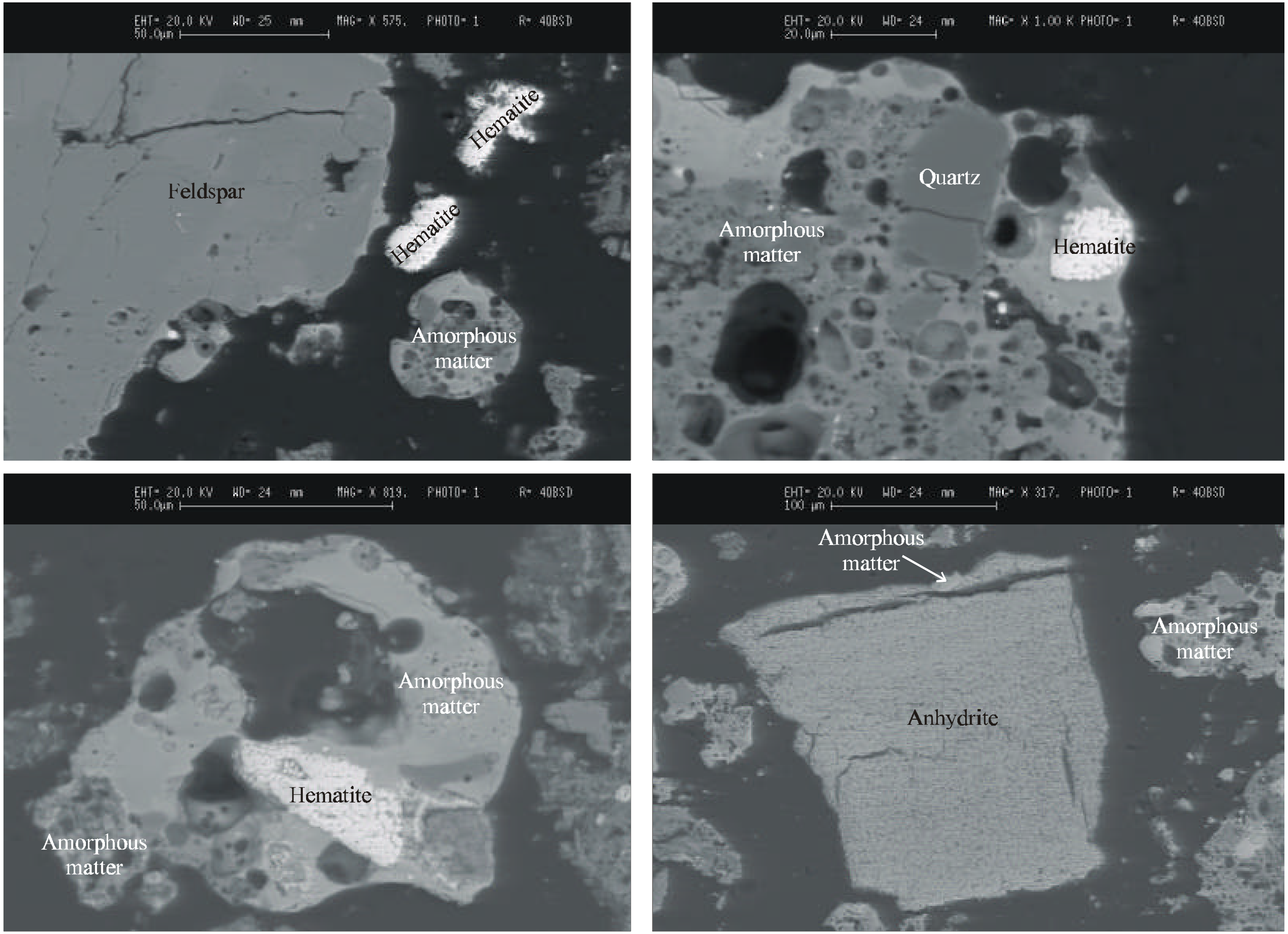

Figure 4. Selected SEM images of fly ash from the Kangal power plant, Turkey. Note that hematite originated from pyrite framboids.

phosphate, apatite, barite, barite with Ca traces, Ca-REE-phosphate, Ca-REE-phosphate with Th and U traces, FeCaAl-silicate, and pyrite in unburnt coal were identified by SEM-EDX.

The distribution of trace elements in the run-of-mine coal (feed coal) and/or combustion residues and the characterisation of fly ashes have been discussed extensively in literature [e.g. 6-17]. During combustion of coal in a conventional utility boiler glasses and neoformed high-temperature minerals comprised of aluminosilicates and oxides of iron are produced. These phases incorporate other elements in minor and trace quantities that are possibly partitioned within them. The products of coal combustion are all major sources of potentially Hazardous Air Pollutants (HAPs) elements, which include As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, Se, and radionuclides (e.g., Th, U) [11].

Table 1 summarises the elemental contents of the Kangal fly ashes, together with means for the Cayirhan fly ashes from Turkey. The later burns zeolite-bearing coals of upper Miocene age and was investigated by [17] in detail. The mean values of some element concenrations of the Kangal fly ash samples are relatively higher in Ca, As, Cs, Li, Mo, Rb, Sr, Tl, U, and Zn than in the fly ashes from the Cayirhan power plant (630 MW) that burns zeolite-bearing coals of Upper Miocene age. The previous study, Karayigit et al., in press. implies that enrichments of Zn and especially Mo and U, on a whole-coal dry basis, were also identified for the worked lignite seams to the Kangal feed coal.

IMPLICATIONS FOR ASH UTILISATION

As noted [4], approximately 18 Mt of solid residues were generated by Turkish power plants in 2000. Most of these were disposed of in landfills, but up to 1 % were used as aggregates in the building industry etc. This study has shown that the fly ashes may contain unusually high concentrations of As, Mo, U and Zn. The previous study shows that the concentrations of Zn, Mo and U in the worked seams to feed coals were significantly higher than global means for coals and thus the use of the enriched fly ash should be treated with caution.

Future work will endeavour to investigate mode of occurrence of elements in samples showing anomalous mass balance and/or fly ash to bottom ash ratios. The detection of feed coals and ashes with unusually high environmentally sensitive element concentrations and the recognition of the mineral phases in which they occur should allow management strategies to be developed.

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Table 1 summarises the element concentrations of the Kangal fly ashes, together with means for the Cayirhan fly ashes. Element concentrations are reported on µg/g, unless indicated otherwise (Cayirhan data from [17])

Elements	Cayirhan fly ash		Kangal fly ash	
	Mean	Stdev	Mean	Stdev
Mg %	3.0	0.10	1.6	0.2
Ca %	10.4	0.90	22.3	2.4
Ti %	0.3	0.03	0.4	0.03
P %	0.2	0.02	0.1	0.01
As	94	28	143	33
Ba	607	50	717	396
Bi	0.9	0.1	0.4	0.2
Co	20	1.3	15	1.0
Cs	6.7	0.5	47	3.4
Cu	49	3.5	45	7.7
Ga	13	1.3	16	1.3
Ge	6.2	1.9	1.2	0.7
Li	24	1.7	77	5.3
Mn	586	41	334	39
Mo	11	1.8	218	27
Nb	22	1.3	15	1.2
Pb	53	6.5	48	17
Rb	49	4.1	75	5.8
Sc	10	1.3	14	2.2
Sr	416	14	1448	133
Ta	1.8	0.3	1.6	0.7
Th	18	1.1	9.2	0.5
Tl	1.0	0.2	8.8	1.3
U	17	1.7	82	9.8
W	18	7.2	3.7	0.7
Y	17	0.8	18	1.5
Zn	80	15	282	45
Zr	317	23	103	7.6
La	27	0.9	25	1.9
Ce	53	1.6	48	3.4
Pr	6.2	0.2	5.5	0.4
Nd	23	0.8	20	1.6
Sm	4.8	0.2	3.9	0.3
Eu	1.3	0.1	1.1	0.1
Gd	4.9	0.2	3.9	0.3
Tb	0.8	0.04	0.6	0.05
Dy	4.5	0.2	3.3	0.3
Ho	0.9	0.04	0.6	0.1
Er	2.6	0.2	1.8	0.2
Tm	0.4	0.03	0.3	0.02
Yb	2.6	0.1	1.7	0.1
Lu	0.4	0.02	0.3	0.02

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