

Partitioning behavior of trace elements during pilot-scale fluidized bed combustion of high ash content lignite

Nevin Selçuk^{*}, Yusuf Gogebakan¹, Zuhâl Gogebakan²

Department of Chemical Engineering, Middle East Technical University, 06531 Ankara, Turkey

Received 3 April 2006; received in revised form 2 May 2006; accepted 3 May 2006

Available online 7 May 2006

Abstract

This study describes the partitioning of 20 trace elements (As, B, Ba, Cd, Co, Cr, Cu, Hg, Li, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Tl, V, Zn) and eight major and minor elements (Al, Ca, Fe, K, Mg, Na, Si, Ti) during the combustion of high ash content lignite. The experiments were carried out in the 0.3 MW_t Middle East Technical University (METU) atmospheric bubbling fluidized bed combustor (ABFBC) test rig with and without limestone addition. Inert bed material utilized in the experiments was bed ash obtained previously from the combustion of the same lignite without limestone addition in the same test rig. Concentrations of trace elements in coal, limestone, bottom ash, cyclone ash and filter ash were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). Partitioning of major and minor elements are influenced by the ash split between the bottom ash and fly ash and that the major proportion of most of the trace elements (As, Ba, Cr, Hg, Li, Mo, Ni, Sn, V, Zn) are recovered in fly ash. Limestone addition shifts the partitioning of Ba, Cr, Mo, Ni, Sn, V, Zn from bottom ash to fly ash.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Lignite; Major and minor elements; Trace elements; Partitioning; Bubbling fluidized bed combustion

1. Introduction

Applications of fluidized bed combustion technology developed for burning coal with high efficiency and within acceptable levels of gaseous pollutant emissions have been steadily increasing in both capacity and number over the past decade. However, gradual introduction of increasingly restrictive legislations on emissions from combustion sources and increasing public concern relating to the emissions of trace elements has been keeping the topic attractive for further research.

Extensive research on the trace elements and their partitioning behavior has been mostly carried out in pulverized coal combustion systems [1–12]. There are few studies on trace element behavior in fluidized bed coal combustion systems burning high quality coals [13–15] and investigations are mainly based on partitioning of trace elements especially when co-firing coals with different sustainable fuels [16–22]. Furthermore, whilst

these studies are performed in beds of sand, lignites under consideration have to be burned in their own ashes due to high ash content. Absence of data on partitioning behavior of trace elements in bubbling fluidized bed combustion of these lignites and recent trend in utilization of indigenous lignites in industry and utility boilers, necessitate the investigation of fluidized bed combustion characteristics of indigenous lignites with respect to trace element partitioning.

In an attempt to achieve this objective, a typical Turkish lignite with high ash content was burned in its own ash in the 0.3 MW_t Middle East Technical University (METU) atmospheric bubbling fluidized bed combustor (ABFBC) test rig with and without limestone addition and partitioning behavior of major and minor ash components and trace elements was determined.

2. Experimental

Combustion tests were carried out on the 0.3 MW_t ABFBC Test Rig located in the Chemical Engineering Department of Middle East Technical University. Fig. 1 shows the flow sheet of the test rig. As can be seen from the figure, the test rig basically consists of a forced draft (FD) fan, a wind box with an ash

^{*} Corresponding author. Tel.: +90 312 210 26 03; fax: +90 312 210 12 64.

E-mail addresses: selcuk@metu.edu.tr (N. Selçuk), yusufg@metu.edu.tr (Y. Gogebakan), zcoskun@metu.edu.tr (Z. Gogebakan).

¹ Tel.: +90 312 210 43 98; fax: +90 312 210 12 64.

² Tel.: +90 312 210 43 87; fax: +90 312 210 12 64.

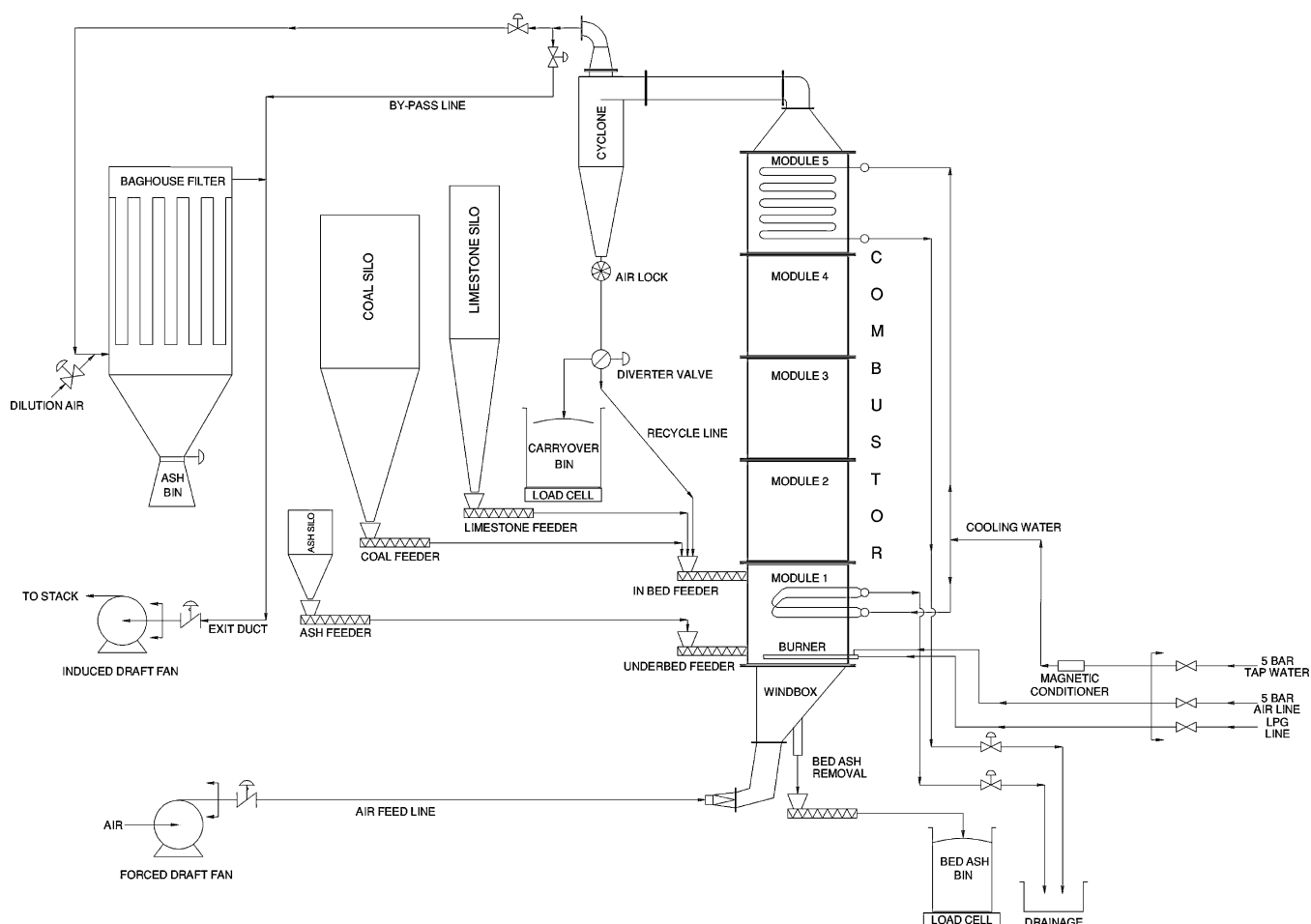


Fig. 1. METU 0.3 MW_t ABFBC test rig.

removal system, a modular combustor, a cyclone with a recycle leg, a bag house filter, an induced draft (ID) fan and a coal and limestone feeding system.

The main body of the test rig is the modular combustor formed by five modules of internal cross-section of 0.45 m × 0.45 m and 1 m height. Inner walls of the modules are refractory lined and insulated. The first and fifth modules from the bottom refer to bed and cooler, respectively, and the ones in between are the free-board modules. There exist two cooling surfaces in the modular combustor, one in the bed and the other in the cooler providing 0.35 and 4.3 m² of cooling surfaces, respectively. There are 14 ports for thermocouples and 10 ports for gas sampling probes along the combustor. Two ports for feeding coal/limestone mixture are provided in the bed module, one 0.22 m, the other 0.85 m above the distributor plate.

Crushed and sieved coal and limestone are stored in two separate silos and conveyed into the hoppers of feeders at controlled flow rates via pre-calibrated volumetric feeders placed under their respective silos. The coal/limestone mixture is continuously fed to the bed through water-cooled screw feeders.

Analytical system of the test rig consists of a bank of analyzers for O₂, CO, CO₂, SO₂ and NO/NO_x. In order to measure concentrations of O₂, CO, CO₂, SO₂, NO_x at the combustor exit at steady state, combustion gas is sampled from the exit

of the combustor and passed through gas conditioning system where the sample is filtered, dried and cooled. O₂ concentration is measured by means of Leeds and Northrup paramagnetic O₂ analyzer. CO and CO₂ are measured by Anarad AR-600 series infrared (IR) analyzer. SO₂ and NO_x are measured by Siemens Ultramat 6 non-dispersive infrared (NDIR) analyzer and Servomex 1491 chemiluminescence analyzer, respectively. After the measurement of species concentrations, sample gas is vented to the atmosphere.

The test rig is equipped with a data acquisition and control system namely Bailey INFI 90. Real time process data is monitored, manipulated, collected and analyzed with the aid of control software called Bailey LAN-90 Process Control View installed on an IBM compatible PC running under QNX operating system. The output signals from analyzers and process values such as temperatures, air and water flow rates, pressures and speed of screw conveyors are logged by means of a data acquisition and control system.

In order to investigate partitioning of trace elements during the fluidized bed combustion of a typical low calorific value and high ash content Turkish lignite, two runs; one without (Run 1) and the other with addition of limestone (Run 2) were carried out. Characteristics of the lignites burned in these runs are summarized in Tables 1–3. In all runs, the lignite was burned in its own

Table 1
Lignite characteristics

	Lignite 1	Lignite 2
Proximate analysis (wt.% as fired)		
Moisture	13.7	14.3
Ash	36.4	35.2
Volatile matter	32.7	31.5
Fixed carbon	17.2	19.0
HHV (MJ/kg)	13.2	12.7
d_{32} (mm)	1.26	0.86
ρ_p (kg/m ³)	1580	1580
Ultimate analysis (wt.% dry basis)		
Carbon	38.1	37.2
Hydrogen	3.2	2.9
Oxygen (by difference)	12.4	14.6
Nitrogen	1.4	1.3
Sulfur _{combustible}	2.7	2.9
Ash	42.2	41.1

Table 2
Ash analysis of lignites (wt.% dry basis)

	Lignite 1	Lignite 2
SiO ₂	41.4	49.4
Al ₂ O ₃	14.1	14.3
Fe ₂ O ₃	10.6	10.1
CaO	0.8	0.5
MgO	1.3	1.0
SO ₃	19.6	15.6
Na ₂ O	7.3	6.4
K ₂ O	1.5	1.6
TiO ₂	3.4	1.1

ash due to its high ash content (~42% on dry basis). Inert bed material utilized in both runs was bed ash obtained previously from combustion of the same lignite in the same test rig. Characteristics of limestone added are displayed in Tables 4 and 5.

Table 3
Trace element concentrations in lignites (mg/kg)

	Lignite 1	Lignite 2	Detection limit
As	162.33	132.00	>0.8067
B	<1.2667	<1.2667	>1.2667
Ba	65.00	41.00	>0.0300
Cd	1.12	0.71	>0.0633
Co	<0.0200	<0.0200	>0.0200
Cr	18.17	17.53	>0.0763
Cu	494.00	102.33	>0.1567
Hg	0.31	0.29	>0.1333
Li	1.65	2.33	>0.0667
Mn	197.00	142.33	>0.0133
Mo	<0.2400	11.89	>0.2400
Ni	47.00	41.40	>0.4133
P	1322.33	914.33	>0.6000
Pb	8.76	27.47	>2.1667
Sb	<0.9367	<0.9367	>0.9367
Se	<0.6733	<0.6733	>0.6733
Sn	322.17	83.63	>0.3333
Tl	<0.6600	<0.6600	>0.6600
V	108.00	94.33	>0.0800
Zn	17.10	16.66	>0.2100

Table 4
Characteristics of limestone (wt.% dry basis)

CaCO ₃	93.21
MgCO ₃	0.69
SiO ₂	4.72
Na ₂ O	0.10
K ₂ O	0.10
Al ₂ O ₃	0.69
Fe ₂ O ₃	0.49
d_{32} (mm)	0.32
ρ_p (kg/m ³)	2400

Table 5
Trace element concentrations in limestone (mg/kg)

	Limestone	Detection Limit
As	11.79	>0.8067
B	11.38	>1.2667
Ba	79.33	>0.0300
Cd	0.06	>0.0633
Co	<0.0200	>0.0200
Cr	7.87	>0.0763
Cu	16.00	>0.1567
Hg	0.33	>0.1333
Li	3.00	>0.0667
Mn	46.87	>0.0133
Mo	2.90	>0.2400
Ni	8.72	>0.4133
P	634.67	>0.6000
Pb	4.66	>2.1667
Sb	<0.9367	>0.9367
Se	<0.6733	>0.6733
Sn	38.23	>0.3333
Tl	<0.6600	>0.6600
V	5.56	>0.0800
Zn	7.03	>0.2100

Concentrations of trace elements in coal, limestone and ash were measured by Spectro Spectroflame Modula inductively coupled plasma optical emission spectrometer (ICP-OES) after digestion of each sample in nitric and hydrochloric acid.

Table 6 lists the operating conditions of the both runs. As can be seen from the table, first run is performed without whereas the second run with limestone addition with a Ca/S molar ratio of 3. Bed pressure drop was kept constant through-

Table 6
Operating conditions

	Run 1	Run 2
Coal flow rate (kg/h)	101	102
Limestone flow rate (kg/h)	0	25
Ca/S molar ratio	0	3
Bed drain flow rate (kg/h)	7	13
Carryover flow rate (kg/h)	24	34
Baghouse ash flow rate (kg/h)	1	1
Air flow rate (kmol/h)	22	19
Excess air (%)	43	30
Superficial velocity (m/s)	3.0	2.5
Average bed temperature (°C)	875	853
Average freeboard temperature (°C)	847	839

out the experiments. Feed point location was 0.85 m above the distributor plate for the runs under consideration.

3. Results and discussions

3.1. Recovery rates

Ash recovery rates for Run 1 and Run 2 were found to be 85 and 95%, respectively. Compared to the ash recovery rates reported in the literature [17,22] and considering the difficulty in closing the total solid mass balances over the fluidized bed combustors, the closure of the total ash balances is acceptable in both runs. However, deviation in the total mass balance from 100% was taken into account in order not to reflect the imbalance in the total mass balance to the species mass balances [17,22].

Fig. 2 shows the recovery rates of major and minor ash components for both runs. As can be seen from the figure, the closure is fairly good for most of the components. Recovery rates of trace elements are given in Fig. 3. The imbalances are observed in the species mass flow rates. These imbalances could result from analyzing very small quantity of sample from large quantities of highly heterogeneous matter, very low concentrations of elements under investigation, analytical errors and experimen-

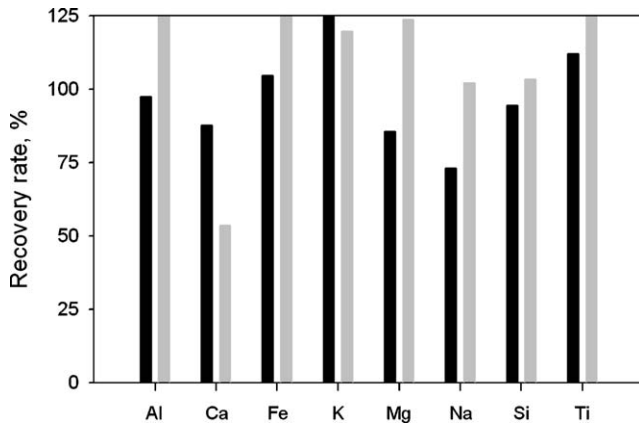


Fig. 2. Major and minor element recovery rates (Run 1: ■, Run 2: ▒).

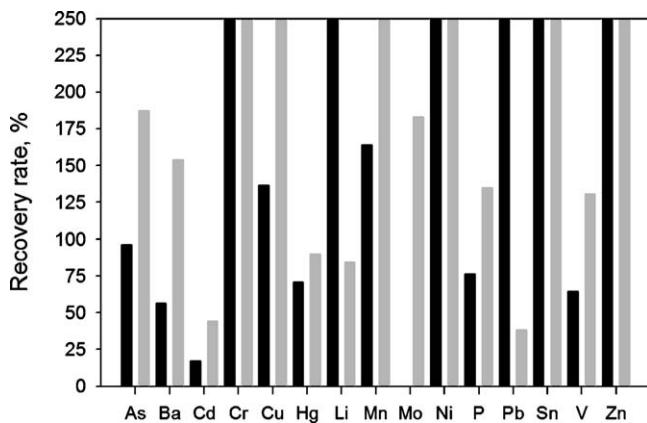


Fig. 3. Trace element recovery rates (Run 1: ■, Run 2: ▒).

Table 7
Major and minor element concentrations (wt.% dry basis)

	Run 1			Run 2		
	Bottom ash	Cyclone ash	Filter ash	Bottom ash	Cyclone ash	Filter ash
SiO ₂	47.84	46.52	28.37	35.46	41.75	27.41
Al ₂ O ₃	15.72	16.58	13.00	16.80	13.95	9.26
Fe ₂ O ₃	12.10	12.98	23.80	9.94	10.34	19.43
CaO	2.38	0.37	1.16	8.21	9.03	7.82
MgO	2.21	0.99	1.20	1.17	0.99	1.89
SO ₃	10.73	8.44	18.16	21.88	15.87	26.24
Na ₂ O	4.59	6.92	4.73	3.86	5.40	3.78
K ₂ O	2.02	2.28	1.52	1.82	1.38	1.82
TiO ₂	2.42	4.92	8.05	0.86	1.29	2.36

tal errors in preparing the samples for ICP-OES analysis or a combination of all [1].

3.2. Partitioning of major and minor elements

Major and minor element concentrations of bed, cyclone and filter ashes during the fluidized bed combustion of lignites with and without limestone addition are given in Table 7. As lignites utilized in the experiments have similar ash content and also have similar ash composition, order of magnitudes of major and minor species concentrations in bed, cyclone and filter ashes are close to each other for both runs except for CaO due to the addition of limestone in Run 2.

Fig. 4 displays the partitioning of major and minor ash components in bed, cyclone and filter ashes for the runs under consideration. As can be depicted from the figure, the partitioning of major and minor ash components follow the ash split between the bottom ash and fly ash except CaO. For the experiments and the test rig under consideration ash splits to fly ash were found as 79 and 73% for Run 1 and Run 2, respectively. Higher percentage in the former run is considered to be due to higher operational gas velocity. The difference in partitioning behavior of CaO stems from the addition of limestone in Run 2 which shifts the partitioning of CaO from bottom ash to fly ash.

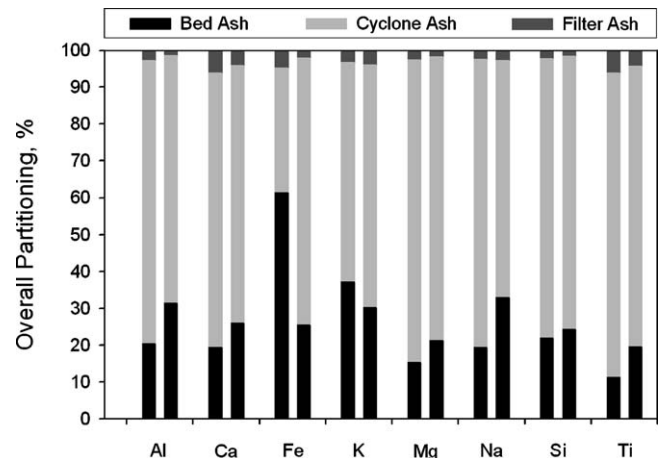


Fig. 4. Partitioning of major and minor elements (Run 1: left bar, Run 2: right bar).

Table 8
Relative enrichment factors of trace elements in bottom, cyclone and filter ashes

	Run 1			Run 2		
	Bottom ash	Cyclone ash	Filter ash	Bottom ash	Cyclone ash	Filter ash
As	0.47	0.38	2.88	0.49	0.45	6.79
Ba	0.43	0.23	0.48	0.84	0.76	3.58
Cr	2.12	2.49	11.82	0.63	3.12	8.05
Cu	1.44	0.50	0.09	3.39	0.21	0.22
Hg	0.39	0.34	0.37	0.30	0.44	0.40
Li	2.43	1.24	6.60	0.58	0.14	6.33
Mn	1.62	0.56	1.72	1.49	0.61	1.85
Mo	–	–	–	0.33	0.71	11.10
Ni	1.26	1.96	8.69	0.38	3.00	5.79
P	0.77	0.25	0.84	1.03	0.30	1.84
Pb	1.23	0.68	20.32	0.25	0.08	0.20
Sn	2.26	1.85	5.53	3.45	7.39	6.82
V	0.16	0.36	0.58	0.09	0.52	1.14
Zn	1.03	2.27	12.68	0.56	3.24	7.40

3.3. Partitioning of trace elements

Concentrations of B (<1.2667 mg/kg), Cd (<0.0633 mg/kg), Co (<0.0200 mg/kg), Sb (<0.9367 mg/kg), Se (<0.6733 mg/kg), Tl (<0.6600 mg/kg) could not be measured as their concentrations were below the detection limits of the instrument. To compare the trace element concentrations in bed, cyclone and filter ashes, relative enrichment factors were calculated. Relative enrichment factor (RE) is defined as [2];

$$RE = \frac{\text{element concentration in ash}}{\text{element concentration in coal}} \times \frac{\% \text{ ash content in coal}}{100}$$

The enrichment factors of trace elements in different streams are given in Table 8. Enrichment factors of As, Cr, Ni, Pb and Zn were found to be larger in fly ash compared to bottom ash. This finding was in agreement with those of [14,15,22]. As for Hg, the relative enrichment factor was lower than 1 and hence belongs to class III elements within the classification scheme given in [2]. The relative enrichment factors of As, Ba, V and P were found to be lower than 0.7 in both bottom and cyclone ashes and hence fall into class II elements which are enriched in fly ash [2].

Although, species mass balances over the fluidized bed combustor could not be closed, some light could be shed to the fate of trace elements in fluidized bed combustion of high ash content low quality lignites by investigating their partitioning behavior.

Fig. 5 illustrates the partitioning of trace elements in bed, cyclone and filter ashes for Run 1 and Run 2, respectively. Due to imbalances in the closure of species balances, calculation of trace element partitioning was related to the output of trace elements instead of input of trace elements.

As can be seen from the figure, Mn and P were almost equally distributed between bottom and fly ashes for both runs. Similar trend was also reported for Mn previously [17,18]. The major proportions of As, Cr, Ni, V, Zn were recovered in the cyclone ash for both runs. This finding complies with the data given in [22]. As can also be seen from the figure, Ba, Hg, Li, Sn and Mo were mostly recovered in fly ash.

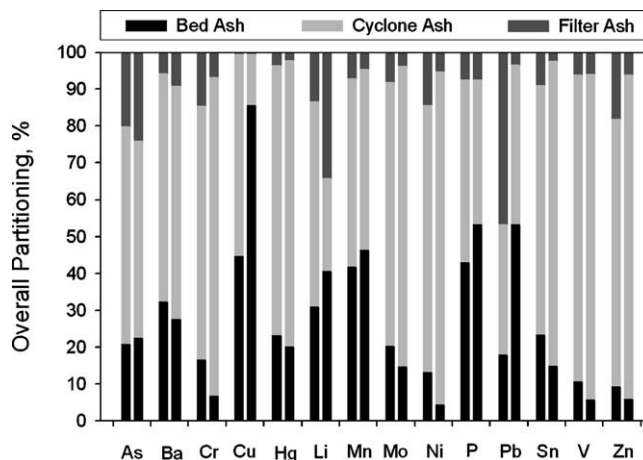


Fig. 5. Partitioning of trace elements (Run 1: left bar, Run 2: right bar).

For As and Hg, the capture of these elements in fly ash could be attributed to partial condensation of these high volatile species due to the low operating temperatures (~350 °C) both at the exit of the combustor due to presence of cooler and in the cyclone [20].

Cu was found to be almost equally distributed between bed and cyclone ashes in Run 1. In Run 2, on the other hand, Cu was mostly recovered in bed ash. Recovery of Cu in bed ash with limestone addition is in agreement with findings of [17].

Cr and Ni were mostly captured in fly ash [14,15,21,22]. The recovery of these low volatile elements in fly ash may be considered to be due to contaminations from the erosion of the alloyed steel in-bed cooling tube bundle and stainless steel gas sampling probes in the combustor.

Pb was mostly recovered in cyclone and filter ashes for Run 1. However, in Run 2, with the addition of limestone, partitioning of Pb was observed to shift towards bed ash. Similar trend was also reported in [17].

Sn and V were mainly found in fly ash rather than bottom ash. This trend was in agreement with that on a lignite-fired CFB power plant [15].

Comparisons between the trace element partitioning of the runs with and without limestone addition reveal that addition of limestone shifts the partitioning of Ba, Cr, Mo, Ni, Sn, V, Zn from bottom ash to fly ash. The reason behind the shift is explained as follows. When limestone is fed together with coal, number of very fine fly ash particles increase firstly due to the addition of limestone particles much finer than coal, secondly due to generation of even finer particles owing to decrepitation of limestone during calcination. This leads to increase in surface area of particles over which condensation of vaporized elements can take place. As Ba, Cr, Mo, Ni, Sn, V and Zn belong to Class II elements which vaporize and condense in cooler regions, addition of limestone shifts their partitioning from bottom to fly ash.

4. Conclusions

Partitioning of major and minor ash components and trace elements of a typical low calorific value and high ash con-

tent Turkish lignite during the fluidized bed combustion was investigated by performing two experiments in 0.3 MW_t METU ABFBC test rig; one without (Run 1) and the other with addition of limestone (Run 2). The following conclusions were reached under the observations of this study:

- Ash split between the bottom and fly ashes is the major parameter determining the distribution of major and minor ash components.
- Major proportions of As, Ba, Cr, Hg, Li, Mo, Ni, Sn, V, Zn are recovered in fly ash.
- Addition of limestone shifts the partitioning of Ba, Cr, Mo, Ni, Sn, V, Zn from bottom ash to fly ash.

References

- [1] J.A.R. Brown, Overview of trace element partitioning in flames and furnaces of utility coal-fired boilers, *Fuel Process. Technol.* 39 (1994) 139–157.
- [2] R. Meij, Trace element behavior in coal-fired power plants, *Fuel Process. Technol.* 39 (1994) 199–217.
- [3] X. Querol, J.L. Fernández-Turiel, A. López-Soler, Trace elements in coal and their behavior during combustion in a large power plant, *Fuel* 74 (1995) 331–343.
- [4] M.R. Martínez-Tarazona, D.A. Spears, The fate of trace elements and bulk minerals in pulverized coal combustion in a power plant, *Fuel Process. Technol.* 47 (1996) 79–92.
- [5] T. Yokoyama, K. Asakura, H. Matsuda, S. Ito, N. Noda, Mercury emissions from a coal-fired power plant in Japan, *Sci. Total Environ.* 259 (2000) 97–103.
- [6] W.J. Quick, R.M.A. Irons, Trace element partitioning during the firing of washed and untreated power station coals, *Fuel* 81 (2002) 665–672.
- [7] M. Thellefsen Nihelsen, H. Livbjerg, Formation and emission of fine particles from two-coal fired power plants, *Combust. Sci. Technol.* 174 (2002) 79–113.
- [8] A. Georgapoloulos, A. Filippidis, A. Kassoli-Fournaraki, Leachability of major and trace elements of fly ash from Ptolemais power station, northern Greece, *Energy Sour.* 24 (2002) 103–113.
- [9] R. Meij, B. Winkel, The emissions and environmental impact of PM₁₀ and trace elements from a modern coal-fired power plant equipped with ESP and wet FGD, *Fuel Process. Technol.* 85 (2004) 641–656.
- [10] M.S. Reddy, S. Basha, H.V. Joshi, B. Jha, Evaluation of the emission characteristics of trace metals from coal and fuel oil fired power plants and their fate during combustion, *J. Hazard. Mater.* 123 (2005) 242–249.
- [11] R. Yan, D. Gauthier, G. Flamant, Volatility and chemistry of trace elements in a coal combustor, *Fuel* 80 (2002) 2217–2226.
- [12] M. Xu, R. Yan, C. Zheng, Y. Qiao, J. Han, C. Sheng, Status of trace element emissions in a coal combustion process: a review, *Fuel Process. Technol.* 85 (2003) 215–237.
- [13] A.H. Clemens, L.F. Damiano, D. Gong, T.W. Matheson, Partitioning behavior of some toxic volatile elements during stoker and fluidized bed combustion of alkaline sub-bituminous coal, *Fuel* 78 (1999) 1379–1385.
- [14] I. Demir, R.E. Hughes, P.J. De Maris, Formation and use of coal combustion residues from three types of power plants burning Illinois coals, *Fuel* 80 (2001) 659–1673.
- [15] Z. Klika, L. Bartonova, D.A. Spears, Effect of boiler output on trace element partitioning during coal combustion in two fluidised-bed power stations, *Fuel* 80 (2001) 907–917.
- [16] H. Lopes, T. Trindade, I. Gulyurtlu, I. Cabrita, Characterisation of FBC ashes from co-combustion of coal with oily residues, *Fuel* 80 (2001) 785–793.
- [17] L.E. Ámand, H.M. Westberg, M. Karlsson, B. Leckner, B. Coda, M. Hocquel, R. Berger, K.R.G. Hein, X. Feng, M. Abul Milh, Co-combustion of dried sewage sludge and coal - The fate of heavy metals, in: D.W. Geiling (Ed.), *Proceedings of 16th International Conference on Fluidized Bed Combustion*, ASME, Reno, Nevada, USA, May 13–16, 2001, FBC01-108 in CD-ROM.
- [18] B. Coda, K. Sandelin, R. Backman, R. Berger, K.R.G. Hein, Trace element behavior when co-firing coal, straw, paper sludge under bubbling fluidized bed conditions, in: D.W. Geiling (Ed.), *Proceedings of 16th International Conference on Fluidized Bed Combustion*, ASME, Reno, Nevada, USA, May 13–16, 2001, FBC01-122 in CD-ROM.
- [19] M.Y. Tsai, K.T. Wu, C.C. Huang, H.T. Lee, Co-firing of paper mill sludge and coal in circulating fluidized bed boiler, *Waste Manage.* 22 (2002) 439–442.
- [20] I. Gulyurtlu, M.H. Lopes, P. Abelha, I. Cabrita, J.F.S. Oliveira, The study of partitioning of heavy metals during fluidized bed combustion of sewage sludge and coal, in: S. Pisupati (Ed.), *Proceedings of 17th International Conference on Fluidized Bed Combustion*, ASME, Jacksonville, Florida, USA, May 18–21, 2003, FBC2003-079 in CD-ROM.
- [21] N. Wolski, R. Berger, J. Maier, K.R.G. Hein, Bubbling fluidized bed co-combustion of different sustainable fuels - Trace element behavior, in: S. Pisupati (Ed.), *Proceedings of 17th International Conference on Fluidized Bed Combustion*, ASME, Jacksonville, Florida, USA, May 18–21, 2003, FBC2003-131 in CD-ROM.
- [22] L.E. Ámand, B. Leckner, Metal emissions from co-combustion of sewage sludge and coal/wood in fluidized bed, *Fuel* 83 (2004) 1803–1821.