Physicochem. Probl. Miner. Process. 47(2011) 51-60

www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems of Mineral Processing

ISSN 1643-1049

Received February 23, 2011; reviewed; accepted April 11, 2011

Partitioning of major and trace elements of a Turkish lignite with size and density

Gulhan OZBAYOGLU

Atilim University, Faculty of Engineering, İncek/Gölbaşi, Ankara, Turkey, gulhan@atilim.edu.tr

Abstract. This research was devoted to determine the concentration and distribution of major and trace elements in a Turkish lignite and to investigate the partitioning behaviour of them in various size and density fractions to estimate the possibility of removal of trace elements by conventional coal cleaning. Three size fractions which were used in industrial coal cleaning processes were chosen. Each size fraction was separated into various density fractions by float and sink tests, which were evaluated for major and trace elements. These tests showed that by applying the same size and density fractions of industrial coal cleaning processes, more than 70% of Mo, Nb, Nd, W, Hg and Zr could be removed, which were approximately equal to the result achieved for ash removal.

keywords: physical coal cleaning, lignite, trace elements, partitioning of trace elements

1. Introduction

Coal is the world's most abundant fossil fuel which is mainly used to generate electricity. Coal contributes about 40% of world's electricity generation. Turkey has 11.6 Pg (petagrams, billion tons) of lignite reserves. The production is around 84 Tg (teragrams, million tons of which 40% of the country's lignite production is washed. Lignite accounts for 20% of country's electricity generation. The quality and properties of the coal used in power plants determines its environmental effect. During combustion, coal-fired plants emissions may cause serious environmental and health risks. Trace elements in coal are important as they are potentially hazardous to human health and ecosystems. Around 25 trace elements are considered to be of environmental interest (Swaine, 2000, Spears et al. 1999). Elements As, B, Cd, Hg, Mo, Pb, Se and S are in the group of major concern in the classification of trace elements by level of concern introduced by the US National Research Council (Clarke and Sloss, 1992). Elements of moderate concern include Cr, Cu, Ni, V, Zn, and fluorine while Ba, Co, Mn, Sb, Sr, Li, Na, Ge, and Br are in the group of minor concern. Every trace element may be associated, to some extent, with the inorganic or organic matters of coal (Liu et al., 2004). The major elements which constitute the mineral matter of coal are shown by their oxides in the chemical analysis. They consist of SiO_2, Al_2O_3, Fe_2O_3 and CaO and little amounts of P_2O_5, Na_2O, K_2O and TiO_2 at which many valuable and/or hazardous trace elements are concentrated.

Most of the trace elements in coal are associated with three major minerals: pyrite, kaolinite and illite. The inorganic matters in coal, including trace elements, are not uniformly distributed, either in particle size or density fractions. Besides, they behave differently in physical separation and in combustion. Each trace element is different in its modes of occurrence and concentration (Song et al. 2007; Spears et al.1999; Solari et al. 1989; Gluskoter et al. 1977). If these inorganic matters can be removed from the coal, their associated trace elements should follow. The beneficial aspect of conventional coal cleaning is that, in addition to bulk ash removal, much of the trace element content, notably those associated with sulfide and other minerals, can be removed. Although, there is a general relationship between overall ash and trace elements removal, for individual trace element, the removal percentage is specific to the coal and to the cleaning process used (CAER, 1996; DeVito et al., 1994; Akers, 1995; Swaine, 1998; Conaway, 2001). The partitioning of trace elements has been investigated under the conditions of different coal ranks and coal preparation types (heavy medium, jigging and froth flotation). It was reported that the partitioning behaviour of trace elements are mainly controlled by their modes of occurrence, the distribution forms of its carrier minerals and the cleaning technique types. Tang et al. (2009) supposed that the migration and distribution of the 15 toxic trace elements during coal washing might be controlled by clay minerals and pyrite. The trace elements associated with fine minerals (Pb, U, and Be) and organic constituents (Br) could not be reduced by physical coal cleaning nor can they be enriched in the cleaned coal (Wenfeng et al. 2006).

The objective of this study was i) to determine the concentration and distribution of trace and major elements in a Turkish lignite, ii) to determine the partitioning behaviour of trace elements in coal by size and density used in existing coal preparation plant.

2. Materials and method

The Tertiary age Soma lignite (R_{max} 0.435), which is located in the western part of Turkey, was used in this study. The representative sample was analyzed to determine its ash, moisture, volatile matter, fixed carbon and total sulfur contents as well as its major and trace element contents. XRF and ICP-OES techniques were used in the analyses of major and trace elements. Size and density effects on the partition of major and trace elements were examined by conducting screen analysis on the representative run of mine sample and float-sink tests on three size fractions, namely +50 mm, (-50+18) mm, -18 mm which were chosen in accordance with the sizes normally used in industrial coal preparation plants. Each size fraction was separated in a laboratory vessel to generate sp. gr. levels between 1.3 to 1.9 by the use of $ZnCl_2$. The sink of each size fraction was evaluated for major and trace elements.

3. Results and discussions

3.1. Chemical composition of the sample

Representative sample of Soma lignite consisted of 40.65% ash, 39.97% volatile matter, 0.63% total sulfur and 12.97 MJ/kg heating value on dry basis. Major and trace element contents of the sample are shown in Table 1. Analytical errors were estimated at ≤ 5% for both proximate analysis and major/trace elements. As seen in Table 1, CaO, SiO_2, Al_2O_3 and Fe_2O_3 are the dominant major compounds which are followed by Na_2O, K_2O and MgO. Among the trace elements examined in raw coal, Co, Nb, Ag, Sb and Ce levels are above US coals and Ni, Se, Br, Zr, Mo, Cd, and La levels are below US coals levels (Xu et al., 2004). Trace elements in ten Turkish coal fired power plants showed that the concentration of As, Co Cu, Ga, Mn, Li, Sc, Sn, Ta, Tl and some rare earth elements in coals exceed the currently available ranges for most world coals (Karayigit et al., 2000).

Table 1. Major and trace element contents of representative sample of Soma lignite

Major Elements	%	Trace Elements	ppm	Trace Elements	ppm
Na_2O	1.05	Co	4.19	La	2.00
MgO	0.83	Ni	14.21	Ce	2.00
Al_2O_3	8.25	Se	1.02	Nd	33.61
SiO_2	10.33	Zr	35.50	W	0.74
P_2O_5	0.19	Nb	2.63	Hg	0.79
SO_3	1.61	Mo	0.59	Bi	0.87
K_2O	0.91	Ag	1.68		
CaO	16.03	Cd	2.00		
TiO_2	0.12	Sn	12.93		
MnO	0.02	Sb	4.64		
Fe_2O_3	3.24	Cs	4.00		

3.2. Mineralogical composition

The XRD investigation of the representative sample showed that the minerals in the coal are quartz, carbonate minerals, gypsum, smectite, clay minerals and feldspar. The clay minerals were represented mainly by kaolinite and to a lesser extends illite. As is known, clay minerals and feldspar are transformed into aluminosilicate during combustion. Carbonate minerals were calcite, dolomite and siderite. This agrees with the findings of Karayiğit et al. (2000), who reported a considerable amount of siderite occurrences in Soma coals. During combustion, carbonate minerals are converted into oxides and formed Ca-Mg silicates.

Al_2O_3 was mainly due to the occurrences of kaolinite and feldspar. SiO_2 mostly originated from quartz, as well as feldspar and clay minerals. Dolomite was the main source of MgO, while CaO was derived from calcite, dolomite and siderite.

Screen analysis evaluated for major and trace element contents and distributions are shown in Table 2 and 3.

Table 2. Major elements contents and distributions in screen fractions

Major Elements	Screen Fractions					
	(+50 mm) Weight %:21.59		(-50+18)mm Weight %:26.71		(-18 mm) Weight %:51.70	
	%	%Distrib	%	%Distrib	%	%Distrib
Na_2O	1.14	23.53	1.02	26.05	1.02	50.42
MgO	0.74	19.28	0.84	27.08	0.86	53.64
Al_2O_3	3.15	8.24	7.70	24.94	10.66	66.82
SiO_2	4.22	8.82	10.12	26.15	13.00	65.03
P_2O_5	0.16	18.27	0.21	29.71	0.19	52.01
K_2O	0.29	6.89	0.94	27.65	1.15	65.46
CaO	19.46	26.21	18.74	31.22	13.20	42.57
TiO_2	0.06	10.51	0.16	34.77	0.13	54.72
MnO	0.03	29.41	0.02	23.98	0.02	46.61
Fe_2O_3	3.62	24.09	2.91	23.96	3.26	51.95
SO_3	1.64	21.97	1.38	22.87	1.72	55.16

As indicated in Table 2, major elements in screen fractions showed that the contents of Na_2O, CaO, MnO, and Fe_2O_3 decreased with the decrease in particle size while Al_2O_3, SiO_2 and K_2O contents increased 3-fold in the finest size of screen fractions when contrasted with the coarse size.

When trace elements are concerned, their partition was observed in screen fractions as shown in Table 3. As is seen, most of the trace elements contents and distributions increased with the fineness of the size fractions. Especially, the increase in contents of Nb and Zr are 5- and 3-fold, respectively in the finest fraction than in coarse fraction. It can be observed that more than 60% of Co, Ni, Se, Zr, Nb, Ag and Nd distribution are found in the finest fraction. On the other hand, distributions of Sb and W are more or less uniform in three size fractions. As stated before, the size fractions are the same with the existing coal preparation plant. If the top size of coal were decreased to liberate inorganic materials, more removal of trace elements in the sinks would be achieved.

In order to determine the density effect on the partition of major and trace elements, float-sink tests were carried out on each screen fraction. The sink products obtained at 1.90 specific gravity of float and sink test of each screen fraction were evaluated in terms of removal of major and trace elements. The results are shown in Table 4 and 5.

When major elements' contents of screen fractions and their +1.90 sp. gr. sink products were compared, it was found that Na_2O, Al_2O_3, P_2O_5, K_2O, SO_3 and Fe_2O_3 contents decreased in the sink products while CaO, SiO_2, MgO, TiO_2 and MnO contents increased. Most of the calcite and dolomite were concentrated in the sink.

Table 3. Trace elements contents and distributions in screen fractions

Trace Elements	Screen Fractions					
	(+50 mm) Weight %:21.59		(-50+18) mm Weight %:26.71		(-18 mm) Weight %:51.70	
	ppm	%Distr	ppm	%Distr	ppm	%Distr
Co	3.0	15.46	3.0	19.13	5.3	65.41
Ni	7.6	11.55	12.6	23.69	17.8	64.77
Se	0.9	18.89	0.8	20.78	1.2	60.33
Zr	14.3	8.70	33.3	25.05	45.5	66.25
Nb	0.7	5.74	2.7	27.42	3.4	66.83
Mo	1.0	36.82	1.0	45.55	0.2	17.63
Ag	0.5	6.44	2.0	31.87	2.0	61.69
Cd	2.0	21.59	2.0	26.71	2.0	51.70
Sn	11.7	19.54	16.1	33.27	11.8	47.19
Sb	6.2	28.77	6.6	37.89	3.0	33.34
Cs	4.0	21.59	4.0	26.71	4.0	51.70
La	2.0	21.59	2.0	26.71	2.0	51.70
Ce	2.0	21.59	2.0	26.71	2.0	51.70
Nd	21.2	13.62	30.9	24.55	40.2	61.83
W	1.0	29.12	1.0	35.54	0.5	34.86
Hg	1.0	27.22	1.0	33.67	0.6	39.11
Bi	1.0	24.92	0.5	15.41	1.0	59.67

Table 4. Major elements distributions in (+1.90) sink products of float–sink tests of screen fractions.

Major Elements	+1.90 sp. gr. sink products of screen fractions					
	(+50mm) Weight % 13.73*		(-50+18) mm Weight % 13.60*		(-18 mm) Weight % 18.00*	
	%	% Distrib.	%	% Distrib.	%	% Distrib.
Na_2O	0.65	8.54	0.83	10.79	0.74	12.74
MgO	1.16	19.22	1.14	18.70	1.00	21.72
Al_2O_3	5.36	8.92	4.98	8.21	5.86	12.79
SiO_2	13.88	18.44	13.81	18.17	15.38	26.79
P_2O_5	0.14	12.77	0.14	12.64	0.14	16.77
K_2O	0.66	9.98	0.62	9.28	0.71	14.07
CaO	33.06	28.31	31.69	26.88	18.88	32.43
TiO_2	0.23	25.73	0.22	24.35	0.22	32.25
MnO	0.05	31.22	0.04	24.43	0.04	32.58
Fe_2O_3	2.63	11.13	2.32	9.72	2.45	13.59
SO_3	0.48	4.09	0.43	4.05	0.53	5.92

*) These weights are given according to the original feed

As seen in the table above, Ni, Se, Zr, Nb, and Nd concentrations (grades) are more in sink products of float and sink tests of different size fractions than original trace elements contents of screen sizes. These trace elements showed the affinity to the inorganic matter. On the other hand, Sb, Co and Bi grades decreased in the sink products, especially in the fine sizes. From the literature survey, no direct evidence was found to support any particular mode of occurrence of antimony in coal. Swaine (1990) asserted that antimony is apparently organically bound in coal which is in good aggrement with our findings. However, Finkelman (1994) indicated that antimony may be found in solid solution in pyrite.

Ogala et al. (2009), Conaway (2001) and Swaine (1990) assert that antimony and beryllium are organically bound in the coal. In most of U.S. coals, arsenic and antimony are mainly associated with mineral matter, especially with pyrite and sphalerite, respectively (Finkelman, 1994). In Chines coal, elements of Br and Ba show a strong affinity to the organic matter, while Cs, Cd, Pb, Zn and Hg are partly associated with organic matter and the other trace elements are mainly associated with the mineral matter (Wang, 2004). Australian coals contain substantially lower key environmental elements selenium, arsenic and mercury than those most of the international coals (Acarp, 1996). The majority of cobalt and nickel are organically bound, but some associations with mineral matter cannot be excluded (Swaine, 1990; Gluskoter et al., 1977).

When sink is removed at 1.80 sp. gr., the major and trace elements rejections from the sink products of float and sink tests of different size fractions are compared with the sink of 1.90 sp. gr in Table 6 and 7, respectively.

Table 5. Trace elements distributions of +1.90 sp. gr. sink products of float and sink tests of screen fractions

Trace Elements	Screen Fractions					
	+1.90 of (+50 mm) Weight % 13.73		+1.90 of (-50+18)mm Weight % 13.60		+1.90 of (-18 mm) Weight % 18.00	
	ppm	%Distr	ppm	%Distr	ppm	%Distr
Co	3.1	10.06	3.1	9.97	3.11	13.19
Ni	16.5	15.94	16.1	15.42	13.4	17.03
Se	1.3	17.36	1.1	14.55	1.1	19.25
Zr	52.9	20.44	47.5	18.17	49.7	25.22
Nb	3.4	17.85	3.4	17.32	4.3	29.15
Mo	1.0	23.41	0.4	9.28	1.0	30.70
Ag	2.0	13.73	2.0	13.60	2.0	18.00
Cd	2.0	13.73	2.0	13.60	2.0	18.00
Sn	14.1	14.98	15.8	16.65	12.1	16.89
Sb	3.0	8.88	4.7	13.65	3.0	11.64
Cs	4.0	13.73	4.0	13.60	4.0	18.00
La	2.0	13.73	2.0	13.60	2.0	18.00
Ce	2.0	13.73	2.0	13.60	2.0	18.00
Nd	50.3	20.55	42.7	17.28	46.9	25.11
W	1.0	19.07	1.0	18.89	1.0	25.00
Hg	1.0	17.31	1.0	17.15	1.0	22.69
Bi	0.3	4.75	1.0	15.70	1.0	20.78

Trace element removals at 1.90 sp. gr. varied from the lowest percentage of 33.22 for Co to the highest of 64.32% for Nb. For 1.80 sp. gr. the lowest and highest trace element removals were 37.42% for Co and 75.52% for Nd. Trace element rejections above 50% at 1.90 sp. gr. were for Se, Zr, Nb, Mo, Nd, W and Hg. However, at 1.80 sp. gr. most of the trace elements, excluding Bi, Sb and Co, could be removed at a level of above 50%. Wang(2004) found that by physical coal cleaning processes, more than 60% of As and Hg were, and more than 30% of Sb, S, Pb and Cd were removed.

Table 6. Summary of total removal of major elements at +1.90 and +1.80 sp gr. fractions of float and sink tests

Major Elements	Removal in +1.90 sink fraction,%	Removal in +1.80 sink fraction,%
Na_2O	32.07	40.62
MgO	59.64	64.70
Al_2O_3	29.92	35.97
SiO_2	63.40	74.75
P_2O_5	42.18	36.91
K_2O	33.33	39.19
CaO	87.62	93.09
TiO_2	82.33	97.06
MnO	88.23	96.38
Fe_2O_3	34.44	38.92
SO_3	14.06	16.94

Table 7. Summary of total removal of trace elements at +1.90 and +1.80 sp. gr. fractions of float and sink tests

Trace Elements	Removal in +1.90 sink fraction,%	Removal in +1.80 sink fraction,%
Co	33.22	37.42
Ni	48.39	55.18
Se	51.16	56.57
Zr	63.83	73.60
Nb	64.32	75.35
Mo	63.39	72.74
Ag	45.33	51.06
Cd	45.33	51.06
Sn	48.52	54.12
Sb	34.17	37.84
Cs	45.33	63.97
La	45.33	52.26
Ce	45.33	51.06
Nd	62.94	75.52
W	62.96	70.72
Hg	57.15	70.36
Bi	41.23	46.84

4. CONCLUSIONS

The degree of removal of trace elements depends on the mode of occurrence, and on the degree of liberation of the trace element bearing mineral and the specific gravity (density) of the medium. Based on float and sink tests, it was found that more than 70% of Mo, Nb, Nd, W, Hg and Zr could be removed at 1.80 sp. gr. which were approximately equal to the result achieved for ash (77.78%), showing a high degree of removal due to their association with inorganic matter. From 37 to 50% of Co, Sb and Bi could be rejected, showing a relatively low degree of removal as they show strong association with organic matter. Hence, it will be more difficult for them to be removed by physical coal cleaning method. From 50 to 70% of Se, Ag, Cd, Sn, La, Ce and Ni were removed due to their partial association with the organic matter. As higher trace element rejections can be achieved by removing the maximum possible amount of ash, the trace element removals at + 1.8 sp.gr. are higher than +1.9 sp.gr as the ash removals from the sink fractions were 77.78% against 69.57% at 1.90 sp.gr. The ash contents of cleaned coals were reduced to 18.42% at 1.8 sp.gr and 22.58% at +1.9 sp.gr.

Acknowledgements

The author would like to acknowledge to Dr. Selahaddin Anaç for his permission to perform chemical analyses at the TKI-Soma laboratories.

References

ACARP REPORT, (1996) Trace elements in Coal, Issue No.3, http://www.acarp.com.au/Newsletters/tracelelements.html

AKERS, D.J.(1995) *The redistribution of trace elements during beneficiation of coal, in D.J.Swaine, F.Goodarzi (eds), Environmental Aspects of Trace Elements in Coal, Kluwer Academic Publishing, Netherlands, 93–110*

CLARKE, L.B. and SLOSS, L.L. (1992) *Trace elements-Emissions during coal combustion and gasification, IEA Report IEACR/49,IEA Coal Research, London*

CONAWAY, S.M.(2001), *Characterizing trace element association in the Pittsburgh No.8, Illinois No.6 and Coalburg coal seams, M.Sc Thesis, Virginia Polytechnic Institute and State University, U.S.A.*

DEVITO M.S. ROSENDALE, L.W. and CONRAD, V.B.(1994) *Comparison of trace element contents of raw and clean commercial coals, Fuel Processing Technology, 39, 87–106*

FINKELMAN, R.B.(1994), *Modes of occurrence of potentially hazardous elements in coal: levels of confidence, Fuel Processing Technology, vol.39, Issues 1–3, 21–34*

GLUSKOTER, H.J. RUCH, R.R. MILLER, W.G. CAHILL, R.A. DREHER, G.B. and KUHN, J.K.(1977), *Illinois State Geological Survey, Circular 499*

KARAYİĞİT, A.I. GAYER, R.A. QUEROL, X. and 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*

LIU,G., VASSILEV, S.V., GAO, L., ZHENG, L., PENG, Z., (2004), *Mineral and chemical composition and trace element contents in coals and coal ashes from*

Huaibei coal field, Energy Conversion and Management, Vol.46, Issue 13-14, 2001-2009

SOLARI, J.A.FIEDLER, H. SCHNEIDER, C.L.(1989) *Modelling of the distribution of trace elements in coal, Fuel 68, 536–539*

SONG, D.YONG, Q. ZHANG, J. WANG, W.and ZHENG,C., (2007), *Concentration and distribution of trace metals in some coals from Northern China, International Journal of Coal Geology, 69, 179-191*

SPEARS, D.A. MANZARANES-PAPYANOPOULOS, L.I. and BOOTH, C.A.(1999), *The distribution and origin of trace elements in a UK coal; the importance of pyrite, Fuel 78, 1671–1677*

SWAINE, D.J.(1990), *Trace elements in coal, Butterworth, London, 278*

SWAINE, D. (2000), *Why trace elements are important, Fuel Processing Technology, 65–66, 21–33*

SWAINE, D.J.(1998) *Trace elements during the mining, and beneficiation of coal, Coal Preparation 19, 3–6, 177–193*

TANG, Y. CHANG, C. ZHANG, Y. LI, W.(2009), *Migration and distribution of fifteen toxic elements during the coal washing of the Kailuan Coalfield, Hebei Province, China, Energy, Exploration and Exploitation, Vol.27, No: 2, 143–152*

WANG, W.F.(2004), *Modes of occurrence and cleaning potential of trace elements in coals from the northern Ordos Basin and Shanxi Province, China, Acta Geologica Sinica-English edition 78, 960–969*

WENFENG, W.YONG, Q. CHONGTAO, W. ZHUANGFU, L. YINHAI, G. YANMING, Z. (2006), *Partitioning of elements and macerals during preparation of Antaibao coal, International Journal of Coal Geology, 68, 223–232*

XU, M.YAN, R. ZHENG, C. QIAO, Y. HAN, J. SHENG, C.(2004), *Status of trace element emission in a coal combustion process: a review, Fuel Processing Technology, vol.85, Issue 2–3, 215–237*