Journal of Himalayan Earth Sciences Volume 49, No. 1, 2016 pp.50-57

Removal of trace elements from Thar coal to minimize its hazardous effect on the environment

Zafar Khan[1*] and Saqiba Bibi[2]
[1]National Centre of Excellence in Physical Chemistry, University of Peshawar
[2]Higher Education Department, Khyber Pakhtunkhwa, Government Girls Degree College Panjpir, Swabi
*Corresponding author E-mail: onlymardan@yahoo.com

Abstract

Four lignite coal samples from Thar coal fields Pakistan were selected for the trace elemental analyses studies. The data was obtained with the use of X-ray Fluorescence (XRF) Spectrometer. It was observed that (Aluminum, Arsenic, Barium, Bromine, Calcium, Cerium, Cobalt, Chromium, Cesium, Copper, Iron, Gallium, Hafnium, Lanthanum, Manganese, Molybdenum, Niobium, Neodymium, Nickel, Lead, Rubidium, Antimony, Scandium, Selenium, Silicon, Tin, Strontium, Samarium, Tantalum, Titanium, Uranium, Vanadium, Tungsten, Ytterbium, Zink and Zirconium) elements were present in all the coal samples under investigation. These trace metals are found to have an adverse effect on the health of the living organisms intact with coal utilization. Some of these elements such as Arsenic, Barium, Beryllium, Chromium, Cobalt, Copper, Lead, Molybdenum, Nickel, Selenium, Uranium, Vanadium and Zinc are extremely harmful to human health, if released to the environment during coal combustion. Therefore, the coal samples were being demineralized with washing the coal samples with standard solution of 2N HCl. The demineralized coal samples were then subjected in the same way to (XRF) Spectrometer for elemental analyses. The elements identified in raw samples were compared with the elements identified in the respective demineralized samples. It was found that demineralization caused better effect, in terms of metals removal from coal.

Keywords: Acid washing; Hazardous effect; Pakistani coal; Thar lignite; Trace elements; X-ray Fluorescence (XRF) Spectrometer.

1. Introduction

Coal is a major alternative naturally occurring energy source and is abundantly available as fossil fuel throughout the world. Coal is a black or brown solid combustible substance used as fuel from centuries which is formed under the earth crust from the decay of plants material (Damste et al., 1992) due to the very high pressure and temperature and due to the absorption of moisture from soil. Pakistan has plentiful supplies of coal. The estimated deposits of it are 186 billion tons. Thar has the largest reserve of coal in Pakistan, which alone has 175 billion tons coal reserves. To fulfill the world energy demand in future, one should utilize all the available energy resources including solid fuel such as coal (Izquierdo and Querol, 2012). It has been reported in the literature that at present 30.1% primary energy and 40% electrical energy is produced from coal world, whereas 70% steel production also rely on coal (Feng et al., 2015). The production of total world coal was 7822.7 metric tons (Mt), according to the 2013 survey. The regional share to this total can be easily obtained from the International Energy Agency and the BP Statistical Review of World Energy (Key World Energy Statistics, 2014; Statistical Review of World Energy, 2014).

Coal is a heterogeneous substance consists of organic and inorganic minerals components (Ahmad et al., 2009). The organic components of coal determine its rank and the appropriateness for its use as renewable energy (Saeed et al., 2010). The inorganic mineral elements present in coal acts as catalysts during coal conversion processes such as liquefaction, gasification and pyrolysis (Tian et al., 2002). Thus, they have beneficial role for the useful utilization of coal at this regard. On the contrary, heavier and trace mineral elements can have a deep adverse effects on the health of people using coal in houses and offices or dwelling close to coal reserves, coal mines, and coal-combustion plants. These trace metals are found to have a very harmful effect on the health of the living organisms intact with coal utilization. Some of these elements like Arsenic, Barium, Beryllium, Cadmium, Chromium, Cobalt, Copper, Lead, Molybdenum, Nickel, Selenium, Uranium, Vanadium and Zinc are extremely harmful to human health, if released to the environment during coal combustion and coal thermochemical processes (Franco et al., 2009; Swaine, 2000; Wang et al., 2010). The harmful mineral matter emissions during burning process have thoroughly studied recently (Zhang et al., 2008; Kizilshtein and Kholodkov, 1999; Goodarzi, 2006; Johnson et al., 2008; Gibbs et al., 2008;

Goodarzi et al., 2008; Yudovich and Ketris, 2005; Wang et al., 2008).

Severe health problems in Asia are being reported from the emission of these elements, such as arsenic and selenium to the environment during coal burning and utilization. In the developing countries the health problems are severe, where the coal is being used in homes for heating and cooking purposes. The peoples of such localities are mostly suffering from arsenism and fluorosis (Finkelman, 1999). The brick makers and brick furnaces owners burn the coals as such, without knowing their qualities, thus putting the public in great trouble, dwelling in the vicinity of that furnaces, for being effected from coal dust as well as from the harmful health hazard effects of environment being polluted with harmful health hazardous trace elements. Prior to coal utilization, knowledge about the coal quality can help to reduce the health problems, such as knowledge about the concentration and distribution of toxic metal in coal may help the coal to be avoided to use as such. Trace elements are being reported to be incorporated in the surrounding by natural and anthropogenic sources (Andriono, 1986). Knowledge about the elemental composition for the reduction of harmful effect of the environment and also for the effective utilization of coal is very important (Liu et al., 2001). The role of the trace metals is dependent upon the types (Sekine et al., 2008; Iwashita et al., 2004) and combustion parameters of coal. Reducing atmosphere and elevated combustion temperature enhances the release of trace elements (Guo et al., 2004).

The work presented in this manuscript is taken into consideration of the elemental composition of Thar coal, as the people are not eager to use Pakistani coal for power production due to high concentration of ash and the release of deleterious chemicals and hazardous gases. Due to the shortage of electricity and petroleum, there are golden chances for the locally available coal utilization especially in energy production but due to the lake of worthy of reliance or trustful information about quality of coal, the coal deposits are not fully utilized. The present work is therefore an attempt to explore the quality of Thar coal, which is a huge reserve of coal in Pakistan, to analyze its toxic metals, to cease or reduce its release into the environment with the help of acid treatment and finally to attract the users for its full utilization.

2. Experimental

2.1. Chemicals and reagents used

Analytical grade reagents (Merck) and standard hydrocarbon gases were supplied by Matheson Company, Germany.

2.2. Coal sample and its preparation

The representative raw coal (RC) samples were accumulated from Tharparkar coalfield, Sindh, Pakistan supplied by Sindh Coal Authority, Karachi, which were tightly closed in polyethylene bags. The as received coal samples were opened, crushed and sieved to a size of 106 µm, warmed to make them dry at 100 °C for 2 h in an oven, then chilled to room temperature (300 K) in a desiccators, and then stocked in a petri dish for further studies.

2.3. Demineralization of coal sample

Demineralization of coal was performed in a vat. A definite portion (1 g) of each of the prepared coal was slurred in 50 ml of 2M hydrochloric acid. The contents were kept in contact for three weeks at room temperature (27 ^{o}C), and filtered. The residual coal was washed several times with de-ionized water in order to remove last traces of the acid. The demineralized residual coal retained on the filter paper was subjected to dry in an oven at 100 °C for 2 hours and then utilized for trace elemental analyses.

2. 4. Trace elemental investigations

The trace elemental investigations of all the Thar coal samples were explored at National Centre of Excellence in Geology, University of Peshawar. The elemental investigations were pursued by employing X-ray fluorescence (XRF) spectrometer, Company Model No. PANalytical XRF Spectrometer PANalytical B. V. Lelyweg 1. 7602 EA, Almelo, the Netherland.

3. Results and discussion

Comparisons of the results of trace elemental analyses of the virgin and acid washed (demineralized) coal sample was made utilizing X-ray fluorescence (XRF) analyzer technique. Four coal samples collected from the Tharparkar coal deposits, marked as Thar 31-2, Thar 11-2, Thar 7-4 and Thar 3-2-3 were examined for the elemental analyses. The elements identified in Thar 31-2 coal sample, were Aluminum, Arsenic, Barium, Bromine, Calcium, Cerium, Cobalt, Chromium, Cesium, Copper, Iron, Hafnium, Lanthanum, Manganese, Molybdenum, Niobium, Neodymium, Nickel, Rubidium, Antimony, Scandium, Selenium, Tin, Strontium, Samarium, Tantalum, Titanium, Uranium, Vanadium, Tungsten, Yttrium, Zink and Zirconium. The elements identified in case of Thar 11-2 coal sample, were Arsenic, Barium, Bromine, Calcium, Cerium, Cobalt, Chromium, Cesium, Copper, Iron, Hafnium, Lanthanum, Manganese, Molybdenum, Niobium, Neodymium, Nickel, Lead, Rubidium, Antimony, Scandium, Selenium, Strontium, Titanium, Uranium, Vanadium, Tungsten, Yttrium, Ytterbium, Zink and Zirconium. The elements identified in Thar 7-4 coal sample, were Aluminum, Arsenic, Barium, Bromine, Calcium, Cerium, Cobalt, Chromium, Copper, Iron, Gallium, Hafnium, Lanthanum, Manganese, Molybdenum, Niobium, Neodymium, Nickel, Lead, Rubidium, Antimony, Scandium, Selenium, Silicon, Tin, Strontium, Samarium, Titanium, Uranium, Vanadium, Tungsten, Yttrium, Zink and Zirconium. The elements identified in case of Thar 3-2-3 coal sample, were Aluminum, Arsenic, Barium, Bromine, Calcium, Cobalt, Chromium, Copper, Iron, Gallium, Hafnium, Lanthanum, Manganese, Molybdenum, Niobium, Neodymium, Nickel, Rubidium, Antimony, Scandium, Selenium, Silicon, Tin, Strontium, Titanium, Uranium, Vanadium, Ytterbium, Yttrium, Zink and Zirconium. It has been observed that almost all the Thar coal samples contained the same trace elemental composition with some minor differences. For example, Al is absent in Thar 11-2 coal sample where as it is present in relative higher concentration in Thar 7-4 coal sample. Ytterbium is present in Thar 11-2 and Thar 3-2-3 while absent in Thar 31-2 and Thar 7-4. Similarly, Tantalum is present only in Thar 31-2 sample whereas it is absent in the rest of the coal samples. The reason for the similarity of the entire coal samples of Tharparkar under investigations for the elemental composition may be due to the fact that these samples belong to the same region and due to the same morphological, geological and atmospheric changes during coalification; the coal samples attained the same mineral compositions. The original (RC) were then slurred in 2M hydrochloric acid and made them demineralize and the existence of trace mineral elements before and after demineralization of raw samples were determined with the application of X-ray fluorescence (XRF) spectrometer. The elements identified in the raw coal samples were matched with the elements identified in its demineralized counterpart. The comparison of the results are given are given in Tables 1-4.

Table 1. Comparison of elemental analysis of raw and demineralized Thar 31-2 coal sample.

Elements	Values of Trace Elements in Thar 31 -2 Coal		Units
	Raw sample	Sample demineralized with 2N HCl	
Al	0.21	0.10	%
As	1.0	0.9	ppm
Ba	15.6	6.4	ppm
Br	3.4	2.8	ppm
Ca	3.7	0.1	%
Ce	4.9	LLD	ppm
Co	1.7	1.0	ppm
Cr	3.5	2.8	ppm
Cs	9.8	8.3	ppm
Cu	7.7	5.4	ppm
Fe	2.24	1.19	%
Hf	3.4	LLD	ppm
La	14.7	4.8	ppm
Mn	161.1	7.2	ppm
Mo	0.3	0.2	ppm
Nb	0.6	0.5	ppm
Nd	2.5	2.4	ppm
Ni	7.8	6.5	ppm
Pb	0.1	0.1	ppm
Sb	1.4	1.3	ppm
Sc	3.9	1.4	ppm
Se	14.2	11.6	ppm
Sn	3.8	2.8	ppm
Sr	343.5	10.4	ppm
Sm	2.8	LLD	ppm
Ta	1.7	LLD	ppm
Ti	0.1	LLD	%
U	3.5	1.4	ppm
V	6.1	1.6	ppm
W	2.0	1.9	ppm
Y	5.9	0.8	ppm
Zn	8.6	0.5	ppm
Zr	19.3	13.3	ppm

Table 2. Comparison of elemental analysis of raw and demineralized Thar 11-2 coal sample.

Elements	Values of Trace Elements in Thar 11 -2 Coal		Units
	Raw sample	Sample demineralized with 2N HCl	
As	1.3	0.2	ppm
Ba	33.8	9.6	ppm
Br	10.1	7.8	ppm
Ca	0.4	0.2	%
Ce	6.6	4.2	ppm
Co	5.3	4.1	ppm
Cr	291.8	12.3	ppm
Cs	8.6	LLD	ppm
Cu	10.7	2.9	ppm
Fe	0.3	0.2	%
Hf	6.8	1.3	ppm
La	10.7	7.6	ppm
Mn	0.2	0.1	ppm
Mo	1.7	1.1	ppm
Nb	1.5	0.9	ppm
Nd	4.6	3.4	ppm
Ni	18.5	8.8	ppm
Pb	1.2	0.8	ppm
Rb	1.4	0.6	ppm
Sb	1.8	0.6	ppm
Sc	0.3	0.2	ppm
Se	10.3	9.5	ppm
Sr	337.6	14	ppm
Ti	7.3	3.8	%
U	3.3	2.6	ppm
V	8.0	6.6	ppm
W	2.2	1.0	ppm
Y	5.9	1.7	ppm
Yb	1.6	LLD	ppm
Zn	0.8	LLD	ppm
Zr	39.7	23.0	ppm

Table 3. Comparison of elemental analysis of raw and demineralized Thar 7-4 coal sample.

Elements	Values of Trace Elements in Thar 7 -4 Coal		Units
	Raw sample	Sample demineralized with 2N HCl	
Al	3.3	3.0	%
As	1.1	0.6	ppm
Ba	28.2	20.5	ppm
Br	2.9	1.8	ppm
Ca	4.4	0.3	%
Ce	11.4	4.7	ppm
Co	4.8	2.5	ppm
Cr	19.8	17.8	ppm
Cu	23.3	17.3	ppm
Fe	1.4	0.7	%
Ga	7.3	4.9	ppm
Hf	0.4	LLD	ppm
La	13.5	12.0	ppm
Mn	155.4	11.6	ppm
Mo	1.5	1.3	ppm
Nb	3.7	3.1	Ppm
Nd	9.4	8.2	ppm
Ni	10.3	8.1	ppm
Pb	1.4	0.9	ppm
Rb	1.9	1.7	ppm
Sb	3.2	1.4	ppm
Sc	8.5	1.1	ppm
Se	3.7	2.9	ppm
Si	1.2	1,1	%
Sm	0.9	LLD	ppm
Sn	7.7	3.5	ppm
Sr	221.7	15.5	ppm
Ti	0.4	0.3	%
U	1.2	0.8	ppm
V	43.9	14.4	ppm
W	0.5	0.2	ppm
Y	17.5	4.6	ppm
Zn	7.7	6.0	ppm
Zr	47.9	36.2	ppm

Table 4. Comparison of elemental analysis of raw and demineralized Thar 3-2-3 coal sample.

Elements	Values of Trace Elements in Thar 3 -2-3 Coal		Units
	Raw sample	Sample demineralized with 2N HCl	
Al	0.5	0.4	%
As	1.5	1.4	ppm
Ba	17.6	17	ppm
Br	2.8	1.7	ppm
Ca	3.8	0.6	%
Co	0.5	0.3	ppm
Cr	12.1	9.2	ppm
Cu	10.6	8.3	ppm
Fe	2.0	1.3	%
Ga	0.4	0.3	ppm
Hf	2.5	1.1	ppm
La	11.1	9.4	ppm
Mn	228	24.8	ppm
Mo	5.9	0.7	ppm
Nb	2.4	2.2	ppm
Nd	5.1	4.8	ppm
Ni	3.4	2.7	ppm
Rb	0.7	LLD	ppm
Sb	3.4	3.3	ppm
Sc	1.8	1.3	ppm
Se	14.2	11.1	ppm
Si	1.8	LLD	%
Sn	3.7	2.4	ppm
Sr	211.9	27.9	ppm
Ti	0.2	0,1	%
U	2.2	LLD	ppm
V	8.3	4.6	ppm
Y	2.7	1.8	ppm
Yb	1.0	LLD	ppm
Zn	40.5	1.7	ppm
Zr	27.0	23.4	ppm

By matching the residues of each and every mineral element found in the virgin as well as in its demineralized form coal, it was observed that demineralization induced to remove the trace mineral elements, reduced in weight % and in ppm of almost each inorganic element. Among the elements determined, Ca, Hf, Mn, Sr, Sm, Ta, Ti, U, Y, Yb and Zn were found to remove in high concentration.

From the whole discussion here, we came to the conclusion that demineralization of raw coal removed substantial amount of inorganic mineral elements from raw coal sample. Present determinations are in conformity with the results presented earlier (Ahmad et al., 2009).

4. Conclusions

The coal is an important, easily available source of world energy, which can be directly used as heating sources in homes and for burning source for the cooking purposes. The coal is a complicated substance owing to its heterogeneous nature but, however, the study about its structure is very important for its effective utilization, due to its global copious nature. From the close examination of the structure of coal, it has been observed that the coal consists of organic and inorganic constituents. From the study of the organic portion, the nature, such as rank and type of coal is elucidated and also determines the appropriateness of the coal for its use as renewable energy, whereas, the study of the inorganic matter, provide the idea of the type of major and trace elements present in the coal.

The presence of some of the toxic mineral elements, which are released to the environment during coal conversion processes, such as liquefaction, gasification and combustion, causes a severe threat to human lives. A deep knowledge about the quality of coal is needed, which may help to reduce or minimize the health problems associated with coal utilization. Knowledge about the quantity and distribution of these undesirable and hazardous elements can help to avoid the direct use of these coal reserves, for being presence of toxic elements. The strength of the toxic mineral elements must be reduced or abolished by washing with acid solutions or applying different analytical techniques. Characterization and quality of coal can provide help to the biomedical researchers to protect the health of the people from the harmful effect of the toxic minerals in coal.

References

Ahmad, T., Awan, I.A., Nisar, J., Ahmad, I., 2009. Influence of inherent minerals and pyrolysis temperature on the yield of pyrolysates of some Pakistani coals. Energy Conservation and Management, 50, 1163-1171.

Ahmad, T., Nisar, J., Awan, I.A., Ahmad, I., 2009. Effect of solid additives on pyrolysis behavior of Makerwal coal. Journal of Chemical Society of Pakistan, 31, 11-14.

Damste, J.S.S., de las Heras, F.X.C., de-Leeuw, J.W., 1992. Molecular analysis of Sulphur-rich brown coals by flash pyrolysis-gas chromatography-mass spectrometry, The Type 111-S kerogen. Journal of Chromatography, 607, 361-376.

Feng, X., Zhang, N., Gong, L., Xue, F., Zheng, X., 2015. Application of a backfilling method in coal mining to realize an ecologically sensitive, “Black Gold” Industry. Energies, 8, 3628- 3639.

Finkelman, R.B., 1999. Trace elements in coal, environmental and health significance, Biological Trace Element Research, 67, 197-204.

Franco, A., Diaz, A.R., 2009. The future challenges for, clean coal technologies, joining efficiency increase and pollutant emission control. Energy, 34, 348-354.

Gibbs, B.M., Thompson, D., Argent, B.B., 2008. Mobilisation of trace elements from as-supplied and additionally cleaned coal, predictions for Ba, Be, Cd, Co, Mo, Nb, Sb, V and W. Fuel, 87, 1217-1229.

Goodarzi, F., 2006. Assessment of elemental content of milled coal, combustion residues, and stack emitted materials: possible environmental effects for a Canadian pulverized coal-fired power plant. International Journal of Coal Geology, 65, 17-25.

Goodarzi, F., Huggins, F.E., Sanei, H., 2008. Assessment of elements, speciation of As, Cr, Ni and emitted Hg for a Canadian power plant burning bituminous coal. International Journal of Coal Geology, 74, 1-12.

Guo, R., Yang, J., Liu, Z., 2004. Behavior of trace elements during pyrolysis of coal in a simulated drop-tube reactor. Fuel, 83, 639-643.

Iwashita, A., Tanamachi, S., Nakajima, T., Takanashi, H., Ohki, A., 2004. Removal of mercury from coal by mild pyrolysis and leaching behavior of mercury. Fuel, 83, 631-638.

Izquierdo, M., Querol, X., 2012. Leaching behaviour of elements from coal combustion fly ash. International Journal of Coal Geology, 94, 54-66.

Johnson, M.L., Lai, H-Y., Wortman, D., 2008.

Preventing mercury emissions from coal-fired power plants using environmentally preferable coal purchasing practices. Journal of Cleaner Production, 16, 716-721.

Kizilshtein, L.Y., Kholodkov, Y.I., 1999. Ecologically hazardous elements in coals of the Donets Basin. International Journal of Coal Geology, 40, 189-197.

Liu, G., Peng, Z., Yang, P., Gui, H., Wang, G., 2001. Characteristics of coal ashes in Yanzhou mining district and distribution of trace elements in them. Chinese Journal of Geochemistry, 20, 357-367.

Saeed, K., Ishaq, M., Ahmad, I., Shakirullah, M., Haider, S., 2010. Acidic surface functional groups and mineral elements in Lakhra coal, Sindh, Pakistan. Journal of Chemical Society of Pakistan, 32, 162-167.

Sekine, Y., Sakajiri, K., Kikuchi, E., Matsukata, M., 2008. Release behavior of trace elements from coal during high-temperature processing. Powder Technology, 180, 210-215.

Statistical Review of World Energy, 2014. Accessed on 20 March 2015.

Swaine, D.J., 2000. Why trace elements are important. Fuel Processing Technology, 65-66, 21-33.

Tian, F.J., Li, B.Q., Chen, Y., Li, C.Z., 2002. Formation of NOx precursors during the pyrolysis of coal and biomass, Part V. Pyrolysis of sewage sludge. Fuel, 81, 2203-2208.

Wang, J., Yaada, O., Nakazato, T., Zhang, Z-G., Suzuki, Y., Sakanishi, K., 2008. Statistical analysis of the concentrations of trace elements in a wide diversity of coals and its implications for understanding elemental modes of occurrence. Fuel, 87, 2211-2222.

Wang, W., Qin, Y., Wang, J., Li, J., Weiss, D.J., 2010. A preliminary method for determining acceptable trace element levels in coal. Energy, 35, 70-76.

Yudovich, Y.E., Ketris, M.P., 2005. Arsenic in coal, a review. International Journal of Coal Geology, 61, 141-196.

Zhang, L., Zhuo, Y., Chen, L., Xu, X., Chen, C., 2008. Mercury emissions from six coal-fired power plants in China. Fuel Processing Technology, 89, 1033-1040.