ANALYSIS OF TRACE ELEMENTS IN POWER PLANT AND INDUSTRIAL INCINERATOR FLY ASHES BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA)

Wadeeah M. Al-Areqi*, Amran Ab. Majid, and Sukiman Sarmani

Programme of Nuclear Science, School of Chemical Sciences & Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor

**Corresponding author: walareqi@yahoo.com*

Abstract

An elemental analysis of fly ash samples from Selangor & Perak coal-fired power plants and an industrial incinerator from Negeri Sembilan were carried out using instrumental neutron activation analysis (INAA). All samples were irradiated at the Malaysian Nuclear Agency laboratory PUSPATI Reactor for 6 hours and later counted at the Nuclear Science Program, UKM using an HPGe detector with a relative efficiency of 10% and resolution of 1.8 KeV (FWHM) at 1.33 MeV. International Atomic Energy Agency (IAEA) coal fly ash 1633a reference material (SRM) was used as a standard for quantitative analysis. A total of 11 elements (i.e. As, Ba, Ca, Ce, Cr, Co, Fe, Hf, Sc, Th and U) were determined in all three types of fly ashes. The concentration range of environmentally concern elements, As and Cr in the Selangor coal-fired power plant samples are 11.17 - 23.24 and 160.28 - 867.97 $\mu g.g^{-1}$ respectively. The concentration range of radioactive elements U and Th are 4.79 - 10.29 and 14.6 - 61.29 $\mu g.g^{-1}$ respectively, and the concentration range of Co, Hf, Fe, Sc, Ba, Ce, Ca are 11.88-83.61, 3.24 - 10.48, 30338 - 53885, 16.62 - 28.48, 178.97 - 8491, 127.41 - 217.2 and 10447 -20647 $\mu g.g^{-1}$ respectively. The concentration range of As, Cr, U, Th in the Perak samples were found to be 22.16 - 48.38, 44.37 - 74.78, 4.18 - 6.85, 8.71 - 11.43 $\mu g.g^{-1}$ respectively, whereas the concentration range of Co, Fe, Sc, Ba, Ce and Ca are 23.21 -29.66, 54621 - 71099, 30.9 - 31.77, 100.34 - 116.61 and 11533 - 16423 $\mu g.g^{-1}$ respectively. Differences exist in the elemental concentrations of both power plant fly ash samples due to the different feed coal and combustion temperature used. The concentration of Cr, Th and Ce in the Selangor fly ash samples was generally higher compared to the samples obtained from the Perak power plant. This study also shows that only As and Ca were detected in the Negeri Sembilan samples with the concentration ranging from 36.66 - 98.67 and 31709.10 – 45606 $\mu g.g^{-1}$ for As and Ca respectively. The results indicated that the concentration of As and Ca in the industrial incinerator fly ashes are higher compared to the concentration of the same elements in the two power plants. The variations of elemental existence and concentration in the industrial incinerator and power plant fly ashes samples depend on the differences in compositions and characteristics of the feed sources and combustion temperature.

Keywords: trace elements, power plant and industrial incinerator fly ashes, INAA

Introduction

Recently, fly ash has become a field worthy of study in several countries because of the greater appreciation to its environmental effects and its potential use and disposal. Power plant and industrial incinerator by-products (bottom and fly ash) emitted into the environment represents a significant source of potential toxic elements that causes air pollution and water and soil contaminations. Determination of minor and major elements qualitatively and quantitatively is usually the first step taken towards subsequent evaluation of the associated environmental and biological risks.

Fly ash is a predominantly inorganic residue obtained from pulverized coal power plants and municipal solid waste (MSW) incinerators which are the two primary sources of fly ash [1].

Coal fired fly ash comprises of micron sized, translucent spherical particles which consist primarily of alumina, silica, iron oxides, with unburnt carbon contributing only a small fraction of the total ash content. It may also contain traces of hazardous elements such as arsenic, lead, barium, and mercury [1,2], whereas, MSW ashes are mainly composed of metal oxides such as Al_2O_3, SiO_2 , Na_2O,K_2O, MgO, CaO, and Fe_2O_3 and contain some heavy metals and dioxins [3]. Characteristics and composition of bottom ash and fly ash differ depending on the sources of the feed coal or solid wastes and the method of combustion [1].In general, bottom ash and fly ash constitute up to 25 and 75% respectively, of the total ash which is enriched in most elements that are found in coal or MSW except for

the most volatile elements, such as Hg [2, 4]. Marrero and Fardy [5, 6] reported that higher enrichment factors were obtained for As, V, Sb, Sc, Se, Pb, Th and U, with some of these elements classified as the greatest concern for environmental quality and the last two are radioactive.

Much of the research into fly ash focuses on the measurement of trace element concentrations [2,4,5,6,7,8,9,10,11] and the effects of leaching by employing various methods such as X-ray fluorescent [9], atomic absorption [9], inductively coupled plasma-optical emission spectroscopy [2,4], inductively coupled plasma mass spectroscopy[9, 4], laser ionization mass spectroscopy as well as instrumental neutron activation analysis .Various researchers have studied trace elements occurrence and their concentration in fly ash by instrumental neutron activation analysis [5,6,7,10,11]. Fardy [6] for example, has determined forty elements by INAA in a wide range of Australian coal and fly ash. Moreover, up to 45 elements were routinely evaluated in different coal bottom and fly ashes as well as city waste bottom and fly ashes by Orvini using INAA [7].

The analytical technique used in this work, neutron activation analysis (NAA) has provided simultaneous assaying of the majority of elements in representative mass of sample with high sensitivity, accuracy and reliability. In Malaysia, wastes from incineration plants and coal fired power plants are poorly characterized, thus the aim of this study is to determine the concentration of traces elements in fly ash samples from 3 difference locations and to determine the possible impact of these elements to the environment.

Materials and methods

Sampling and sample preparation

Fly ash samples analyzed in this study were collected from three different locations i.e. from Selangor & Perak coal power plants and an industrial incinerator in Negeri Sembilan. Sampling was done in twice for every location. Since all samples were already in a fine form, no further sample preparation was necessary. For analysis, 0.1 g of each sample and standard reference material (coal fly ash 1633a) were placed in high-purity polyethylene irradiation vials. All samples and standards were prepared in triplicates.

Irradiation and counting

Samples and SRM were irradiated together for 6 hours in the rotary rack (RR) facility of the TRIGA Mark 11 reactor at the Malaysian Nuclear Agency. The normal operating power of the reactor is 750 KW with a thermal flux of about $10^{12} cm^{-2} s^{-2}$. Irradiated samples were counted using an HPGe detector with a relative efficiency of 10 % and resolution of 1.8 KeV (FWHM) at 1.33 MeV and the analysis of photo peaks were carried out using Genie-2000 software (Canberra Inc). Irradiation, cooling, and counting times were optimized, depending on the half-lives of the analyzed elements. In this study, in order to determine long-lived and medium-lived radionuclides, 6 hours irradiation time was used. After a cooling period of 2-3 days, the irradiated samples were counted for 3600 s to evaluate the medium half lived radionuclides such as As, Np and the same samples were counted again after cooling time of 2-3 weeks for 3600 s to determine the long-lived radionuclides. The concentration of an element in the sample was determined by comparing the radioactivity of element in the sample and standard using the following equation:

$$C_{sp} = W_{sd}. A_{sp}. C_{sd} / W_{sp} . A_{sd}$$

where

C_{sp} = concentration of element in the sample (ppm).
C_{sd} = concentration of element in the standard (ppm).
W_{sp}= weight of the sample (g).
W_{sd} = weight of the standard (g).
A_{sp} = activity of element in the sample (cps).
A_{sd} = activity of element in the standard (cps)

Result and discussions

A total of 11 trace and major elements i.e. As, Cr, U, Th, Co, Hf, Fe, Sc, Ba, Ce, and Ca were determined in the Selangor and Perak coal-fired power plants. Table 1 presents the trace elemental concentration in fly ash samples obtained from the Selangor and Perak power-fired plants.

Table 1: Elemental concentration (ppm) of fly ash samples from Selangor & Perak coal-fired power plants by INAA.

Element	Nuclide utilized	Perak p.p. P1 (ppm)	Perak p.p. P2 (ppm)	Selangor p.p. S1 (ppm)	Selangor p.p. S2 (ppm)	Selangor p.p. S3 (ppm)	World coal [5]	World fly ash [2]
As	As-76	22.16 ± 1.37	48.38 ± 4.30	19.04 ± 8.24	11.17 ± 1.21	23.24 ± 0.00	0.5 – 80	5 – 70
Ba	Ba-131	ND	934.11 ± 77.5	2155 ± 144.17	178.97 ± 309	8491± 10309	20 - 1000	1000-5000
Ca	Sc-47	1.15 ± 0.07%	1.64 ± 0.2%	2.06 ± 0.28%	1.04 ± 0.12%	1.85 ± 0.06%	0.04-1.8%	1 - 6%
Ce	Ce-141	116.61± 2.62	100.34 ± 4.86	136.65 ± 11.24	217.2± 45.21	127.41± 1.56	9 - 56	120 - 460
Cr	Cr-51	44.37 ± 0.20	74.78 ± 16.30	867.97 ± 73.72	262.14± 3.23	160.28± 3.96	0.5 - 60	110 - 2900
Co	Co-60	29.66 ± 2.22	23.21 ± 4.62	11.88 ± 0.54	14.52± 16.63	83.61 ± 7.52	0.5 – 30	35 - 55
Fe	Fe-59	5.46 ± 0.63%	7.1 ± 0.6%	5.4 ± 0.2%	3.65 ± 0.6%	0.09 - 3%	6 - 10%	
Hf	Hf-181	ND	ND	4.09 ± 0.36	3.03 ± 0.2%	10.48 ± 0.28	0.62 - 5.6	6 - 10
Sc	Sc-46	31.77 ± 3.4	30.9 ± 1.66	36.94 ± 3.19	3.24 ± 2.84	16.62± 19.15	0.2 - 1.4	25 - 50
Th	Pa-233	11.43 ± 1.45	8.71 ± 1.01	14.6 ± 1.08	28.48 ± 0.82	61.29 ± 0.69	0.5 - 10	15 - 80
U	Np-239	6.85 ± 0.39	4.18 ± 0.30	6.75 ±1.66	21.3 ± 16.31	4.79 ± 0.58	0.5 - 10	11 - 25
					10.29 ± 0.08			

* ND: Note Detected

Table 2: Elemental concentration (ppm) of fly ash samples from Negeri Sembilan industrial incinerator by INAA

Element	Nuclide utilized	Negeri Sembilan incinerator K1 (ppm)	K2 (ppm)	K3 (ppm)	K4 (ppm)	Other waste fly ash [2] (ppm)
As	As-76	40.98 ± 1.37	98.67 ± 6.94	74.27 ± 2.42	36.66 ± 2.7	60 – 230
Ca	Sc-47	3.17 ± 0.79%	4.56 ± 0.68%	3.84 ± 0.10%	3.58 ± 0.32%	5 - 10%

The concentration range of environmentally concerning As and Cr in the Selangor coal-fired power plant are 11.17 - 23.24 and 160.28 - 867.97 $\mu g.g^{-1}$ respectively. The range of the concentration of radioactive elements U and Th are 4.79 - 10.29 $\mu g.g^{-1}$ and 14.6 - 61.29 $\mu g.g^{-1}$ respectively, while the concentration range of the remaining elements, Co, Hf, Fe, Sc, Ba, Ce, Ca are 11.88 - 83.61, 3.24 - 10.48, 30338 - 53885, 16.62 - 28.48, 178.97 - 8491, 127.41 - 217.2 and 10447 - 20647 $\mu g.g^{-1}$ respectively. Those results were compared to the elemental concentration ranges of the Perak coal-fired power plant, which ranged at 22.16 - 48.38, 44.37 - 74.78, 4.18 - 6.85, 8.71 - 11.43 $\mu g.g^{-1}$ for As, Cr, U and Th respectively, whereas the range of concentration of Co, Fe, Sc, Ba, Ce and Ca were 23.21 - 29.66, 54621 - 71099, 30.9 - 31.77, 100.34 - 116.61 and 11533 - 16423 $\mu g.g^{-1}$ respectively.

The elemental concentrations of coal-fired power plant fly ashes from Selangor differ to the samples obtained from Perak because of the different feed coal and combustion temperatures used. The concentration of Cr, Th and Ce from the Selangor fly ash samples was generally higher compared to the samples obtained from the Perak power plant. At the same time, some elements were present in almost equal concentrations in both locations, especially the element U. For some elements such as Fe and Ca, were expected to be higher concentrations because normally these elements were already high in most of coal [12]. This study also shows that As and Ca were only detected in the Negeri Sembilan fly ash samples with the concentration range of 36.66 - 98.67 and 31709.10 - 45606 $\mu g.g^{-1}$ for As and Ca respectively. These results indicate that the concentration of As and Ca from the industrial incinerator fly ashes are higher than the concentration of the same elements in fly ashes the two coal-fired power plants. The variations of elemental concentration and existence in industrial incinerator and power plant fly ashes samples depend on the differences in compositions and characteristics of feed sources and combustion temperature.

On the other hand, these results indicate that trace elements contents of the Selangor, Perak and Negeri Sembilan fly ashes are significantly lower and are within the ranges found in world fly ash levels [2, 5]. For instance, the concentration of As, Cr, U and Th in all fly ash samples in this study are within the ranges for world fly ash [2].

Conclusion

Fly ash contains varying amounts of numerous enriched major and minor elements i.e. As, Ba, Ca, Ce, Cr, Co, Fe, Hf, Sc, Th and U. The differences in compositions and characteristics of the feed sources and combustion temperature result in the variations of elemental existence and concentration in the industrial incinerator and power plant fly ashes. Despite all elemental concentration in Selangor, Perak and Negeri Sembilan fly ashes are within the ranges of world fly ash, the impact of particulate elements on the environment and human health is very important. The results of the impact of elemental emission from the power plant on the environment [4] indicate that all the concentration of elements of environmental concern emitted from the power plant are lower than the health guidelines of issue by USEPA (2001). Therefore a through and accurate measurement is required to study the impact of fly ashes from coal-fired power plant especially in the case accidental release. We recommended more accurate measurements of trace elements emitted from power plant and industrial incinerator to determine the long-term environmental effects.

References

1. Literature review of fly ash. 2003. University of Pretoria etd- Landman, A A.
2. Goodarzi F. 2006. Characteristics and composition of fly ash form Canadian coal- fired power plants. *Fuel 85*: 1418-1427.
3. Hwang H. & Ro C. 2006. Single- particle characterization of municipal solid waste (MSW) ash particles using low-Z particle electron probe X-ray microanalysis. *Atmospheric Environment 40*: 2873-2881.
4. Goodarzi F. 2005. Assessment of elements 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.

5. Marrero J., Polla G., Rebagliati R. J., Pla R., Gomez D. & Smichowski P. 2007. Characterization and determination of 28 elements in fly ashes collected in thermal power plant in Argentina using different instrumental techniques. *Spectrochimica Acta Part B* 62: 101-108
6. Fardy J. J., McOrist G. D. & FarrarY.J. 1989. Neutron activation analysis and radioactivity measurements of Australian coals and fly ashes. *Journal of Radioanalytical and Nuclear Chemistry 133*(2): 217-226.
7. Orvini E. & Pirico R. 1995. Mass Balance Evaluation in Power Plants Using Neutron Activation Analysis. *Microchemical Journal 51*: 159-165.
8. Steinnes E. & Rowe J. J. 1976. Instrumental activation analysis of coal and fly ash with thermal and epithermal neutrons and short-lived nuclides. *Analytica Chimica Acta 87*: 451-462.
9. Spears D. A. & Martinez-Tarrazona M. R. 2004. Trace elements in combustion residues from a UK power station. *Fuel 83*: 2265-2270.
10. Rowe J. J. & Steinnes E. 1977. Determination of 30 elements in coal and fly ash by thermal and epithermal neutron activation analysis. *Talanta 24*: 433-439.
11. Duong P., Thanh V., Dien P. & Binh N. 1995. Application of nuclear activation analysis (NAA) and low-level gamma counting to determine the radionuclide and trace element-pollutant releases from coal-fired power plants in Vietnam. *The Science of the total Environment 173/174*: 339-344.
12. White S. C. & Case E. D. 1990. Characterization of fly ash from coal-fired power plants. *Journal of Materials Science* 25: 5215-5219