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Assessment of coal and ash environmental impact with the use of gamma- and X-ray spectrometry

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Gamma-ray spectrometry (GS), energy dispersive X-ray fluorescence (EDXRF) analysis methods and wavelength dispersive X-ray fluorescence (WDXRF) were applied for the studies of some coal components, e.g., sulphur, light and heavy metal element concentrations and naturally occurring radioactive isotope contents. Hundred fifty coal samples originating mostly from eight different coal mines from Upper Silesian Coal Basin and 150 samples of ash obtained from these coal samples in laboratory by total combustion at final temperature of 820 °C, were analyzed. Such comparitive analyses can be helpful in selection of most suitable kind of coal for burning in electrical power and heat plants to minimize the enviromental pollution.

Introduction

The combustion of coal for energy production and house heating has been the serious source of natural environment pollution. Gases and microscopic particles are emitted to the atmosphere and huge amounts of solid wastes in the form of ash and slag are produced.

Coal contains practically all the elements of periodic table in various concentrations. The concentration ranges of elements in typical coal can be found in Reference 1–5. Most of coal the deposits contain also the naturally occurring radioactive isotopes such as ^{238}U, ^{235}U and ^{232}Th, with the decay products of their series and ^{40}K isotope. The most important radioactive contaminants are some daughters of ^{238}U and ^{232}Th series. Radioactive isotopes and toxic elements pollute the environment mainly through deposition of fly ashes and their penetration to soil and water near waste dumps.

In order to determine the influence of large scale coal combustion on environmental pollution, the analysis of elemental composition of coals and resulting solid and gaseous wastes is necessary. It is expected that the environment contamination should be minimized. One way is to select a supplier of coal having the lowest concentration of pollutants. This can be done by comparing the chemical analysis results of coal and resulting ash from different coal mines. The following criteria for coal selection should be taken into account: (1) low ash content, resulting in decrease of solid waste amount, (2) low content of toxic elements (for example S and Pb) and naturally occurring radioactive isotopes, and (3) low content of toxic elements and radioactivity in ashes, enabling their use as secondary raw materials (for example in building industry).

The aim of the presented work was to show the usefulness of gamma-ray spectrometry and X-ray fluorescence analysis for the assessment of coal quality to minimize its impact in the environment. The results obtained enable us to select the coal for combustion in electric power and heat producing stations which is the most beneficial from the environment protection point of view.

Experimental

Methods of analysis

Gamma-spectrometry (GS): A gamma-ray spectrometer with Ge(Li) ORTEC detector with active volume of 36 cm^3, resolution of 4 keV, and relative detection efficiency of 5.4% for the 1.33 MeV line was used. The detector was placed inside a 10 cm thick lead housing, lined with cadmium and electrolytic copper layers. Measurement time ranged from 12 to 24 hours. The following gamma-ray intensities were calculated from the spectra: 351.9 keV (^{214}Pb), 609.3 keV (^{214}Bi), and 1764.4 keV (^{214}Bi) for the ^{226}Ra isotope, 583.3 keV (^{208}Tl), 911.2 keV (^{228}Ac), and 2614 keV (^{208}Tl) for ^{232}Th isotope, and 1460 keV for the ^{40}K, respectively. The GANAAS computer programme, developed by the IAEA in Vienna, was used for spectra evaluation. Summation of counts in an energy range of the spectrum from 410 keV to 2810 keV, gives a number proportional to the total activity of naturally occurring radioactive isotopes present in the coal and ash samples. Further, this number referred to as the total counts number, N_T, was taken for the determination of ash content in coal samples.[6]

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Energy dispersive X-ray fluorescence (EDXRF): Characteristic radiation of elements was excited using a KEVEX low power X-ray tube with a Rh anode, a beryllium lateral window and a maximum power of 50 W (1 mA maximum anode current, 50 kV maximum voltage). The X-ray radiation induced in a sample was measured by the Si(Li) ORTEC detector with a diameter of 4 mm, a 4.21 mm active layer thickness and 154 eV resolution for the Mn K_α line. A multichannel amplitude analyser, of SWAN type, installed in an IBM PC/AT computer was used for spectrum accumulation. The X-ray spectrum analysis and processing of results were carried out using the AXIL-QXAS programmes developed by the IAEA. For sulphur determination, the S K_α radiation was excited with a radioisotope ^{55}Fe source. A bottom of sample container was from mylar foil of 6 μm thickness. The time of spectrum accumulation in all these measurements was 1000 seconds.

Wavelength dispersive X-ray fluorescence (WDXRF): A PW 1480 Philips spectrometer with a Rh anode tube was used. The UniQuant® software package was used for measurements and evaluation of results. It was calibrated with a set of standards delivered with it. All elements with $Z \geq 9$ (fluorine) can be determined based on K or L series line intensity measurements. Three crystals are used: LiF 220 for K lines from Ba to V, Ge 111 for K lines from Ti to P and TlAP for K lines from Si to F. The time of measurement for one sample is about 20 minutes.

Preparation of samples

Preparation of coal and ash: All coal samples were delivered by the Heat and Power Station “Siekierki” in Warsaw. The coal sample of approximately 3 kg of weight was first crushed to the grain size less than 10 mm, dried at temperature of 40 °C and then ground in a ball mill to the grain size below 0.2 mm. This was enough for GS measurement. The samples for XRF analysis were additionally ground to the grain size of less than 100 μm.

Samples of ash were prepared by burning 1 to 2 kg of coal in a laboratory muffle furnace to obtain 150 to 200 g of ash. The burning of coal was performed in 2 stages: first, the volatile components were removed and eventually burnt at temperature range from 250 to 450 °C and then the resulting semi-coke was burnt at 800 to 820 °C. The ash obtained in this way does not contain unburnt coal and it retains very finely grained fractions. It differs in this respect from ash produced in power stations due to burning of coal at temperature in the range from 1300 to 1600 °C.

Samples for measurements

GS: Coal and ash amounting from 150 to 225 g were placed in a cylindrical container of 70 mm diameter and 60 mm height at the top of Ge(Li) detector. In all measurements the thickness of coal or ash layer was constant. It was compacted by hand with a piston to the same height. Based on the mass of material a sample density correction was introduced.

EDXRF: A plastic container of 40 mm internal diameter with a bottom of 10 μm mylar foil was filled with uniform layer of coal or ash.

WDXRF: Two grams of coal or ash as a disk of 28 mm diameter was pressed into a boric acid pellet in an evacuated die under a pressure of 230 MPa.

Calibration of the spectrometer

GS: A Soil-6 reference material of 79.92 Bq/kg activity, distributed by IAEA, was used for ^{238}U (^{226}Ra) calibration. An analytical purity K_2SO_4 reagent served as a standard for ^{40}K. A 7-A NBL reference material, containing 8.52% Th and 0.30% U in radioactive equilibrium with decay products, blended at our laboratory with pure SiO_2 in mass ratios of 1:28 and 1:85 was used as a standard for both ^{232}Th and ^{238}U measurement.

EDXRF: A set of reference materials consisting of soils (SO-1, SO-3, SO-4), rocks (SY-2, MGR-1), lake and marine sediments (SL-1-IAEA, SD-M-2/TM), ashes (BCR-176, CTA-FFA-1) and coals (5 RMs for sulphur in coal from Central Mining Institute, Katowice, Poland) was used. Common calibration curves were obtained for all elements both in coal and ash using the scattered radiation intensity for matrix effects correction.

WDXRP: A set of standards consisting of pure element or compound disks delivered with UniQuant was used. The following NIST reference materials were analyzed as test samples: 1632b bituminous coal, 2689 and 2690 coal fly ash. The agrement of the obtained concentrations with the certified ones for main components was within ±5%.

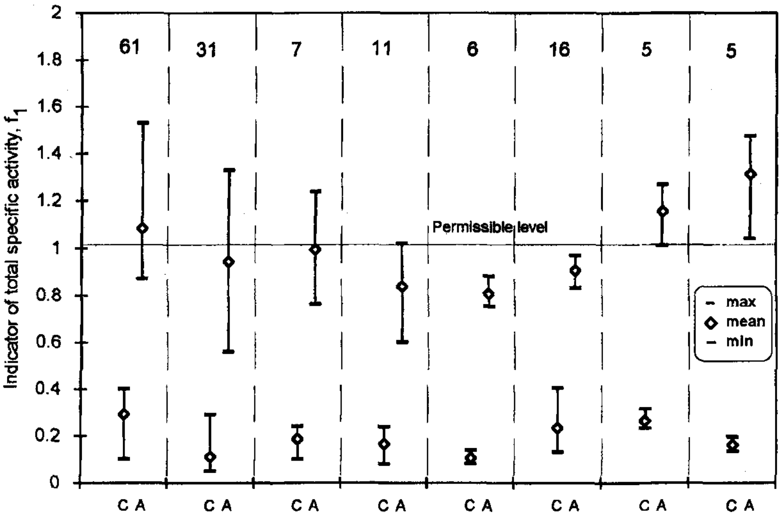

Fig. 1. F1 mean indices and their ranges for coal, C and ash, A, from 8 coal mines

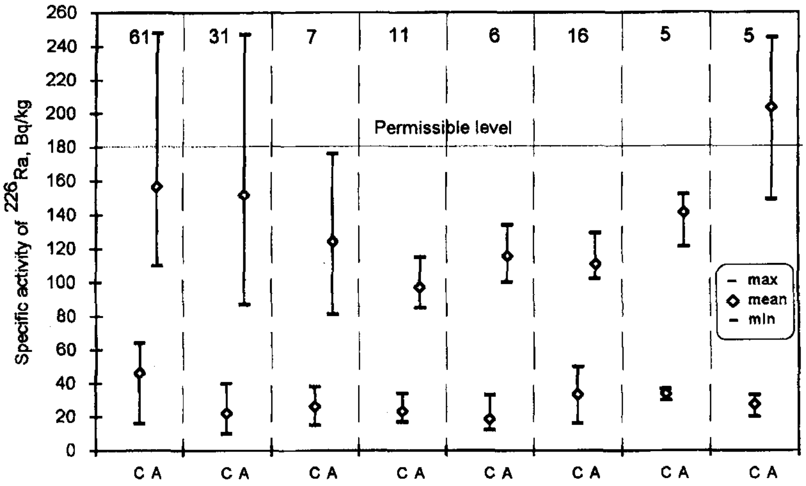

Fig. 2. Mean values and ranges of ^{226}Ra specific activity for coal, C and ash, A, from 8 coal mines

Results and discussion

Gamma-spectrometry measurements

The specific radioactivity of ash is very important parameter for its utilization in the construction industry. According to the Polish regulations,[7] based on international practices[8] the radioactivity of material to be used for construction purposes must satisfy two conditions expressed as radiation hazard indices

$$f_1 = 0.00027\ S_K + 0.0027\ S_{Ra} + 0.0043\ S_{Th} \le 1,$$

and $$f_2 = S_{Ra} \le 185\ \text{Bq/kg}$$

where S_K, S_{Ra} and S_{Th} are the specific activities of ^{40}K, ^{226}Ra, and ^{232}Th isotopes, in Bq/kg, respectively.

Figure 1 shows the indices for coals (C) and corresponding ashes (A) originating from 8 different mines in Upper Silesia region. Figure 2 presents the f_2 indices which are the ^{226}Ra specific activity values for the same coals and ashes as in Fig. 1. In both Figures the mean values (squares) and a range of indices are shown. The number of samples in each group and a permissible level are also given. As can be seen in Fig. 1 three mean values of ash specific activity are above the permissible level and the rest five are very close to it. Only one mean value of ^{226}Ra specific activity is above the permissible level, other two are very close to it.

EDXRF analysis

Concentration of 15 elements: S, K, Ca, Ti, Cr, Fe, Ni, Cu, Zn, Br, Sr, Zr, Rb and Pb was measured in all 150 samples of coal and ash. The detection limits for elements from Ti to Pb were about 10 ppm, for S about 0.05%, for K and Ca about 50 ppm. Only a short discussion concerning the two most common pollutants is given below. In Fig. 3 the mean values and the ranges of sulphur concentration are given for coal and ash from the same 8 mines as in Figs 1 and 2. Figure 4 presents the similar results for Pb concentration. The sulphur content in coal from all 8 mines is close to 0.5% and the range of change is from 0.15 to 0.85% (see Table 1). The mean concentrations, standard deviations and concentration ranges of major, minor and trace elements for all 150 coals and ashes are given in Tables 1 and 2. Also, the concentration of radioactive elements is indicated. Besides, in Table 1 the respective mean concentration of elements in US coals and the mean world values are also shown. In ash the concentration of S changes in the range from 0.16 to 4.87% with the mean value of 1.31% (Table 2). For 2 mines the mean value is in the range 2.5 to 3% with a very large spread of results. On the other hand for 3 mines the average content of S in coal and ash differs only slightly.

Table 1. Element and radioisotope concentrations in coal samples, elemental concentrations in US coals and a world mean coal composition

Constituent	This work			US coals^2		World mean^2
	Mean	Standard deviation	Range	Mean	Range	
Major and minor constituents, %						
Na (n=67)	0.098	0.042	0.018 – 0.21	0.06	0 – 0.20	0.02
Mg (n=67)	0.168	0.051	0.052 – 0.33	0.12	0.1 – 0.25	0.02
Al (n=67)	2.00	0.77	0.27 – 3.76	1.4	0.43 – 3.04	1.0
Si (n=67)	2.96	1.20	0.33 – 5.95	2.6	0.58 – 6.09	2.8
P (n=67)	0.026	0.019	0.0028 – 0.08	–	0.0005 – 0.143	0.05
S	0.53	0.15	0.18 – 0.85	2.0	–	2.0
K	0.24	0.15	0.01 – 0.58	0.18	0.02 – 0.43	0.01
Ca	0.35	0.10	0.08 – 0.78	0.54	0.05 – 2.67	1.0
Ti	0.127	0.081	0.03 – 0.81	0.08	0.002 – 0.32	0.05
Fe	0.77	0.27	0.25 – 2.1	1.6	0.32 – 4.32	1.0
Ash	20.9	8.2	5.5 – 35.7	11.0	4.1 – 25.0	–
Trace constituents, ppm						
Cr	28	12	5 – 63	15	0 – 610	10
Mn	121	71	20 – 660	100	0 – 181	50
Ni	44	15	<6 – 94	15	0.4 – 104	15
Cu	26	6	13 – 50	19	1.8 – 185	15
Zn	38	20	13 – 156	39	0 – 5600	50
Br	41	18	9 – 105	2.6	4 – 52	–
Rb	27	13	<6 – 56	2.9	–	100
Sr	198	60	68 – 495	100	–	500
Zr	48	22	<7 – 130	30	8 – 133	–
Pb	27	12	<8 – 61	16	4 – 218	25
Th	5.1	2.2	<1.2 – 11.8	1.9	–	–
U	2.7	1.0	0.9 – 5.1	1.6	<10 – 218	1.0
Radioactive constituents, Bq/kg						
^{40}K	131	75	2 – 317	–	–	–
^{226}Ra	34	13	10 – 64	–	–	–
^{232}Th	20	9	4 – 48	–	–	–

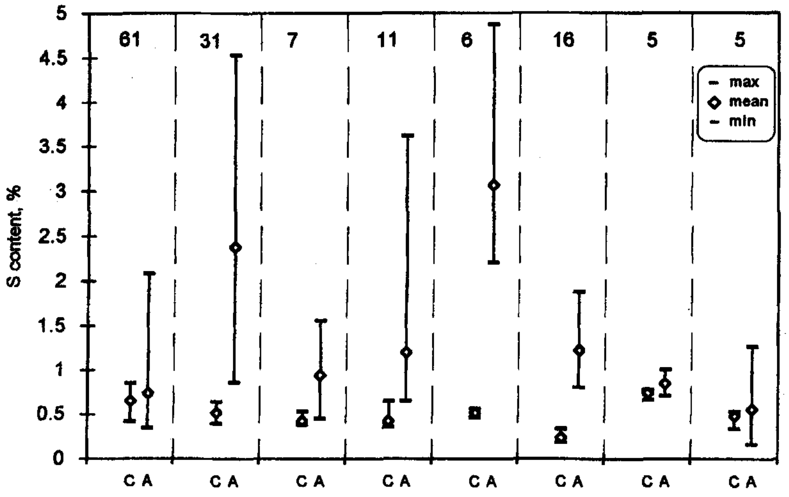

Fig. 3. Mean values and ranges of S content for coal, C and ash, A, from 8 coal mines

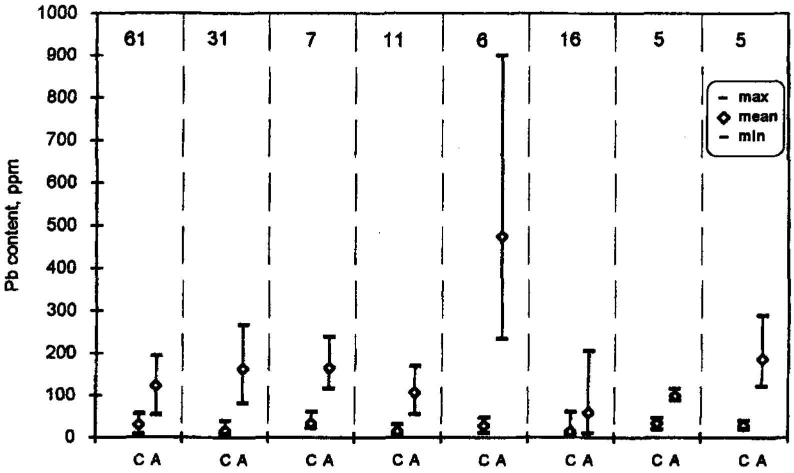

Fig. 4. Mean values and ranges of Pb content for coal, C and ash, A, from 8 coal mines

The concentration of lead in coal ranges from below 10 to 61 ppm with the average of 27 ppm (Table 1). Its concentration is increased to the average of 145 ppm in ash with the range from 10 to 900 ppm. This large spread is due mainly to one mine where the maximum Pb concentration in ash was 900 ppm with the average value of more than 400 ppm. It is worth noting that the average value for lead in coal from this mine is 29 ppm, with a very small spread. This would indicate that the distribution of lead is rather inhomogenous.

Table 2. Element and radioisotope concentrations in ash samples

Constituent	Element and radioisotope contents Mean	Standard deviation	Range
Major and minor constituents, %			
Na (n=67)	0.73	0.30	0.16 - 1.57
Mg (n=67)	1.65	0.81	0.40 - 4.82
Al (n=67)	14.24	2.06	8.36 - 18.92
Si (n=67)	22.35	3.38	11.64 - 26.97
P (n=67)	0.22	0.15	0.043 - 0.70
S	1.31	0.94	0.16 - 4.87
K	1.69	0.47	0.52 - 2.51
Ca	2.96	2.13	0.58 - 10.30
Ti	0.70	0.14	0.39 - 1.15
Fe	4.96	2.32	1.25 - 16.67
Trace constituents, ppm			
Cr	253	153	65 - 831
Mn	777	478	71 - 3054
Ni	264	101	88 - 620
Cu	109	40	40 - 259
Zn	240	230	54 - 2073
Br	17	11	5 - 103
Rb	132	47	21 - 214
Sr	760	518	126 - 3422
Zr	187	45	119 - 381
Pb	145	101	10 - 900
Th	25.5	5.2	12.8 - 44.2
U	11.4	3.0	6.5 - 20
Radioactive constituents, Bq/kg			
^{40}K	640	176	203 - 999
^{226}Ra	141	37	81 - 248
^{232}Th	102	20	52 - 179

WDXRF analysis

Beside the elements determined by EDXRF the following elements were analyzed by this method: Na, Mg, Al, Si and P. The agreement of results for the elements measured with both XRF techniques was completely satisfactory. The mean concentrations, standard deviations and concentration ranges for 67 coal samples and corresponding ash samples are included in Tables 1 and 2, respectively. Silicon and aluminum are the main inorganic components of coal and ash. The sulphur concentration agreed well with EDXRF results. The big advantage of WDXRF is that all interesting elements can be measured in one run. It should also be noted that UniQuant is a semiquantitative package and the measurement time for a single element does not exceed 10 seconds. Hence, the detection limits are not lower than 10 ppm for individual elements. However, for elements of special interest the time of measurement can be increased and the detection limit lowered to a few ppm.

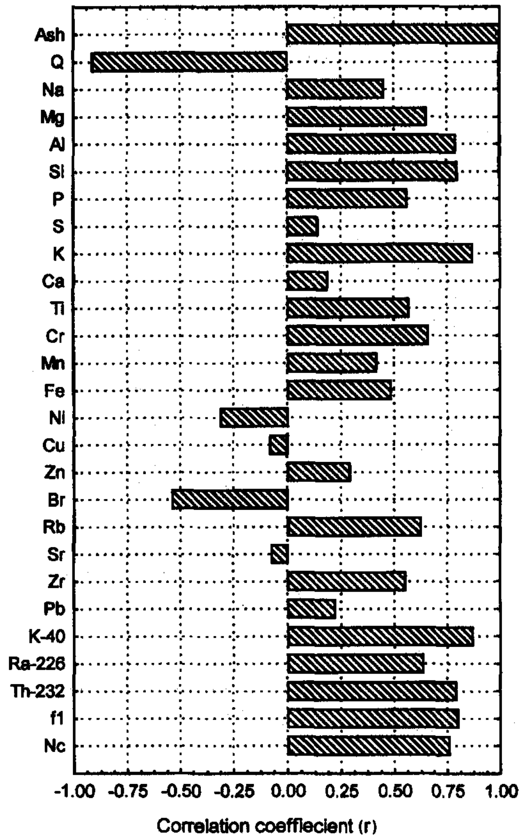

Fig. 5. Correlation coefficients, r, between ash content and the following variables for coals, element concentrations, radioactivity of elements, total gamma counts N_T and calorific value, Q

Conclusions

As can be seen from Tables 1 and 2, all elements contained in coal except Br are enriched in ash. The enrichment coefficient for the mean concentrations are betwen 5 and 8. However, it should be noted that the coefficient of variation (relative standard deviation) of the mean element concentration can vary within 50% relative. Therefore, it should be avoided to use the mean values for the assessment of environmental risk of coal combustion and resulting ash from a particular mine.

It should be mentioned that the mean ash content in all 150 coal samples is 20.9% with the standard deviation ±8.2%. It is almost twice of the mean ash content in American coal which is 11%. In consequence the combustion of this coal creates an increased burden for the environment.

Figure 5 shows the correlation coefficients between ash content, determined by combustion and concentration of all elements measured with XRF and gamma-ray spectrometry, total radioactivity, N_T and calorific value, Q. Rather low values of r for S (0.15), Ca (0.20) and Fe (0.48) have been observed. The highest value of r (0.78) is both for K concentration and ^{40}K radioactivity. Close to it are values for Al and Si, the main ash components.

References

1. L. B. CLARKE, L. L. SLOSS, Trace Elements-Emissions from Coal Combustion and Gasification, IEACR/49, London, UK, IEA Coal Research, July 1992.
2. V. VALKOVIĆ, Trace Elements in Coal, CRC Press, Boca Raton, Florida 1983.
3. O. VALKOVIĆ, M. JAKSIĆ, A. CARIDI, E. CEREDA, A. M. I. HAQUE, R. CHERUBINI, G. MOSCHINI, E. MENAPACE, A. MARKOWICZ, M. MAKAREWICZ, V. VALKOVIĆ, Nucl. Instr. Meth., B69 (1992) 479.
4. D. A. TILLMAN, Trace Metals in Combustion Systems, Academic Press, San Diego, New York, 1994.
5. E. SABBIONI, L. GOETZ, A. SPRINGERAND, R. PIETRA, Sci. Total Environ., 29 (1983) 213.
6. J. KIERZEK, B. MAŁOŻEWSKA-BUĆKO, Nukleonika, 41 (1996) 89.
7. Guidelines for Natural Radioactivity Measurements in Building Materials, No.234, Institute of Building Technology, Warszawa 1980 (in Polish).
8. M. S. EL-TAHAWY, R. H. HIGGY, Appl. Radiation Isotopes, 46 (1995) 1401.