

THE OCCURRENCE OF TRACE ELEMENTS IN FLUE GASES FROM
CIRCULATING FLUIDIZED BED BOILERSJAN KONIECZYŃSKI¹, KATARZYNA STEC²

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Abstract: The emission of dust from coal fired furnaces introduces a lot of contamination into the environment, including dangerous metal compounds, which occur as trace elements in hard and brown coal. After the coal is burnt, they are contained in the grains of respirable dust, which creates health hazard. The results of investigations into the distribution of several trace elements in granular composition of ash emitted from CFB boilers used in coal-fired heat and power station are presented. The research material was taken by means of a cascade impactor, enabling a different granulometric fraction to be separated from a stream of dust that penetrated the electrofilter. The ICP-AES method (inductively coupled plasma atomic emission spectroscopy) was used to determine trace elements after prior mineralization of samples by microwave method. The Authors presented the results of measurements and analyses, determining the ranges of trace elements' occurrence in dust, characterizing the distribution in PM₁, PM_{2,5} and PM₁₀ granulometric fractions and determining the emission factors.

INTRODUCTION

The achievements in the protection of air against contamination cannot make us blind to the fact that the hazard caused by the emission of relatively small amounts of substances which, due to particularly dangerous properties, create hazard to people's health still exists. These include heavy metals. When introduced into the air from natural and anthropogenic sources, they are subject to wet or dry deposition. Their harmful effect on the biological functions in the human organism, into which they penetrate chiefly by respiratory tracts, but also via the alimentary system while participating in particular links of food chain, is enhanced by the heavy metals' ability to move between particular components of the environment. The air emission is one of the main reasons for the presence of heavy metals in soil, waters and plants. These substances include trace elements and their com-



pounds. In the USA, twelve of them have been identified as hazardous air pollutants: Sb, As, Be, Cd, Cu, Cr, Co, Pb, Mn, Hg, Ni and Se. These elements, most frequently in a form of different compounds, are emitted into the atmosphere from various types of furnaces and boilers which burn coal [11]. On a global scale a reduced emission of heavy metals is being observed [28], which chiefly results from the progress in flue gas dedusting and the use of cleaner technologies.

In Poland, an inventory of contamination emission is taken, which serves the needs of national statistics and, as National Reference Center, serves European institutions such as EEA, EMER or IPCC. Table 1 presents data on the annual emission of heavy metals in Poland. It has to be added that the emission varies depending on the region – most sources of the discussed emissions are located in the Upper Silesian and Lower Silesian Provinces [10].

Table 1. Total emission of heavy metals in Poland according to the types of activity in 2006 [Mg]

Specification	As	Cr	Zn	Cd	Cu	Ni	Pb	Hg
Professional powerhouses and CHP plants	2.8	3.5	26.1	0.2	8.9	7.3	10.7	8.3
District heat generating plants	1.4	1.9	55.1	2.2	0.7	7.5	13.6	0.8
Municipal heat generating plants	1.0	1.4	41.5	1.6	6.0	5.4	10.4	0.2
Housing and services	13.1	15.6	465.2	20.1	68.9	66.2	115.9	1.0
Combustion processes in boilers, turbines and engines in the industry	1.1	1.4	42.0	1.7	6.0	7.4	10.4	0.5
Production processes	1.0	9.3	171.4	2.6	18.3	6.8	90.1	1.4
Road transport	0.0	2.0	0.0	0.3	2.9	4.9	17.5	0.0
Waste burning	0.0	0.0	0.9	0.1	0.1	0.0	1.4	0.1
Total	46.3	46.8	1303.2	42.2	344.7	177.5	524.2	21.3

Combustion of fuels is one of the main sources of heavy metals' emission, though the previously mentioned progress in flue gas dedusting, involving the use of electrofilters or bag filters, reduces the emission in large combustion plants. It also has to be emphasized that flue gas desulphurization installations (FDG) which are commonly used in these plants ensure an effective second stage flue gas dedusting and contribute to a further drop in metal emission. The interest in air pollution due to coal burning is justified in such countries as Poland because of a particularly high – reaching 62% – contribution of this fuel in the current use of power resources [10]. The combustion of coal in different furnaces causes the emission of ca 270 000 Mg/a, which accounts for 61% of dust emission from all the sources in Poland, amounting to 443 000 Mg/a [10]. The above mentioned interest is justified especially that on a global scale the position of hard and brown coals is strong and has a rising tendency. This results from the analyses forecasting an increased use of coal – from 6.3 billion Mg in 2010 to 9.6 billion of Mg in 2030 [36].



TRACE ELEMENTS IN COAL, THE EMISSION OF TRACE ELEMENTS IN PROCESSES INVOLVING THE USE OF COAL

Trace elements originate from Carboniferous era plants which gave rise to coal beds. With regard to quantity, the concentration of trace elements in coals from various basins and beds is very differentiated. Recent investigations of coal from less known regions: China, North Korea, revealed a general similarity of all coals in the world: a considerable enrichment in ash of potentially dangerous elements and most of them being bound with inorganic matter [31, 44]. Their amount and composition is considerably influenced by the enrichment processes in later geological eras [35]. It has been found that some trace elements occur in coal beds in higher concentrations than those in the earth crust. The degree of trace elements' accumulation in coal ashes is characterized by an enrichment coefficient expressed by the ratio of trace element concentration in coal ash to its average concentration in the earth crust.

The content of trace elements in hard and brown coals has been thoroughly examined. In their earlier studies the Authors investigated the composition of coals used in Polish power industry [33] and coke plants [43]. Table 2 presents the ranges of concentrations of selected trace elements in the ash from 35 power coal samples from many Upper Silesian mines. The ranges have been reduced so as to present the analyses of 80% of ash samples included in the investigations.

Table 2. Ranges of concentrations of the selected
trace elements in power ashes of Upper Silesian coals
[ppm]

Element	Content
Ag	0–2
As	0–36
Ba	373–3737
Cd	0–9
Co	44–173
Cr	82–306
Cu	98–466
Mn	136–1586
Mo	4–16
Ni	40–364
Pb	50–200
Rb	74–119
Sb	0–3
Sn	0–4
Sr	659–2960
V	182–597
Zn	117–3242



After the coal is burnt, the mineral substance contained in it forms slag and flue ash. The latter is composed of different size grains, of the diameter ranging from submicrons to 100 μm , which are lifted from the furnace with a flue gas stream. The character of flue ash granulometric composition is bimodal [41]. The factors influencing the formations of flue ash particles are still the subject of investigations [3]. Flue ash is chiefly composed of: oxides of calcium, silicon, iron, aluminium, magnesium, sodium and potassium as well as numerous secondary or trace components. They include the compounds of chlorine and fluorine, as well as compounds of trace elements: antimony, arsenic, barium, beryllium, boron, bromine, chromium, tin, zinc, cadmium, cobalt, manganese, copper, molybdenum, nickel, lead, mercury, selenium, thallium, vanadium and others. In coal they are chiefly bounded with mineral matter, and partly with organic matter in a form of metal-organic compounds, organic acid salts and others.

Depending on the behavior in the process of coal combustion, the elements which form mineral matter fall into the category of non-volatile (I), including aluminium, calcium, potassium, magnesium, silicon, iron, titanium, thorium and others; volatile elements which condense on ash particles (II), including, among others, barium, chromium, manganese, sodium, beryllium, cobalt, copper, nickel, phosphorus, vanadium, arsenic, cadmium, molybdenum, lead, antimony, thallium, zinc; and volatile elements which escape in a form of vapors (III) – these include: boron, bromine, chlorine, fluorine, mercury, iodine and selenium. The elements belonging to I group are those which do not evaporate during combustion, their concentration is similar in all solid products of combustion. The remaining elements evaporate in the boiler. Vapors of some of them, after the waste gas has been cooled, condensate mainly on the finest particles of flue ash, whose specific surface area is the biggest [23]. The elements which condensate inside the installation are included in group II. The elements which are emitted in a form of vapors belong to group III [35].

The composition and quantity of trace element compounds released into the atmosphere with flue gas depend on coal burnt [22]. The enrichment of fine particles through the condensation of trace components [8, 15–17, 25], which has been confirmed in many studies, may be limited by competitive reactions on the surface of bigger grains [32]. The flue ash produced in the combustion of biofuels is marked by differences in the manner of enriching the flue ash granular fractions [4, 5]. Despite the observed deviations, general tendencies in the distribution of trace elements in three streams have been determined, chiefly for solid waste (ash and slag), and partly for waste emitted into the air (particulate matter and gases or vapors) [20]. Investigations into the process of pyrolysis of Upper Silesian coke coals have provided information on the behavior of trace elements [43]. In the process of pyrolysis, trace elements were released with volatile products of pyrolysis. The degree of release was differentiated: the highest for mercury, cadmium and lead, medium – for selenium, arsenic, nickel and manganese, and the lowest – for beryllium.

FLUE GASES DEDUSTING, TOTAL AND FRACTIONAL EFFICIENCY

The characteristic feature of all dust collecting devices is fractional efficiency, specific for a given type of device, which drops with the decreasing size of dust grains. Even in the case of the highest technically possible total collection efficiency, the fractional collection efficiency of a dust fraction with grain size lower than 0.4 μm does not exceed 95%.

The electrofilters achieving very high total collection efficiency display a minimum efficiency when collecting grains whose diameter ranges from 0.1 to 2 μm [40]. This results from the limited electric charging capacity in the case of dust particles of this size. In consequence, the mass contribution of $\text{PM}_{2.5}$ in the emitted dust is increased, even by 50%. The efficiency of capturing many trace elements (occurring in the solid phase) is close to the total efficiency of dust collection. Some elements (manganese, beryllium, chromium) are slightly enriched; a bit higher enrichment was observed in the case of antimony, lead, nickel and selenium, while the highest – in the case of arsenic and cadmium [35]. More trace elements were found in the flue dust collected in a bag filter than in the one collected by an electrofilter [9]. Although the collection efficiency has a major effect on the size of trace elements emission, in the case of arsenic the effect of waste gas temperature has a strong influence [12].

A relative drop in the collection efficiency of fine dust fractions is not so high in the case of bag filters. However, even when PTFE membranes are used, the efficiency of filtration drops as the size of grain decreases [1].

The common use of flue gas desulphurization installation has also contributed to the reduced dust emission. A flue gas desulphurization (FGD) installation, most frequently by wet lime method placed behind the electrofilter, is at the same time the second stage of dust collection, the general efficiency of which reaches 80%. Behind the FGD the mass contribution of submicron fraction increases to 50%; however, this concerns the residual flue dust emission, which accounts for maximum 0.05% of the total amount of ash produced in the coal combustion process. Nevertheless, trace elements deposited on fine dust particles penetrate and are released into the atmosphere air [27]. The emission rates for elements characterized by low volatility depend directly on the efficiency of flue gases dedusting and cleaning [39]. The evaluation of the impact exerted by power plants using hard or brown coal is greatly dependent on the emission of $\text{PM}_{2.5}$ dust due to the presence of dangerous substances in dust grains: PAHs, dioxins and heavy metals, and because of this dust capability to penetrate into the human organism through respiratory tracts. The presence of respirable dust in the air poses a health hazard. It is estimated that in the USA 15 000 premature infants die for this reason every year [19]. As regards power and heat boilers, it may be said that the use of an effective electrofilter and wet desulphurization process reduces the threat caused by the emission of trace elements [26, 34]. As trace elements accumulate in the products of dust removal and flue gas desulphurization, more attention has been recently paid to the effects of the washing out of toxic elements, including trace elements from the transported [30], deposited and utilized ashes, both fresh and old, obtained at different temperatures of coal combustion [6]. These investigations help get to know the manner of binding trace elements to organic and mineral coal matter [7, 38].

Compared to hand-fired furnaces, furnaces equipped with mechanical stocker and pulverized coal boilers, the emission of pollutants from fluidized bed boilers is not thoroughly investigated, and these boilers have a great prospect of being widely used for the combustion of coal, sludge, muds and waste fuels in industry boilers, power plants or power and heat plants. Combustion in a fluidized bed has evolved, starting with the technology of atmospheric fluidized bed combustion (AFBC), through pressurized fluidized bed combustion (PFBC), and finishing with combustion in a multi-solid fluidized bed (MSFB). Also combustion of coal and waste fuels in a fluidized bed with internal

circulation of granular material – Twin Interchanging Fluidized Bed, or with heat exchangers placed in the fluidized bed – Internally CFB has been mastered. Combustion in a circulating fluidized bed with the participation of an alkaline additive, a relatively low temperature of combustion and the use of high-efficient dedusting devices allows the ecological requirements to be satisfactorily fulfilled [18]. There are only few papers on trace elements in fly ash from CFB boilers. The newest one concerns leaching characteristics of metals in fly ash [42].

SELECTION OF PLANTS, CHARACTERISTICS OF CFB BOILERS AND FUEL BURNT

The presented investigations into the emission of selected trace elements have been carried out in four heat plants equipped with circulating fluidized bed (CFB) boilers, where an additive of limestone has been used to remove sulphur dioxide from waste gas. These are modern, well maintained plants which work in a combined system and play an important role in heat production in the Silesian province, inhabited by ca 5 million people in the south-western part of Poland.

Tables 3 and 4 present technical parameters of the examined CFB boilers and coal burnt. Plant I is Elektrociepłownia Tychy SA (EC Tychy), Plant II – Elektrociepłownia Chorzów Elcho Sp. z o.o. (EC Elcho), Plant III – Południowy Koncern Energetyczny SA Elektrownia Jaworzno III (Elektrownia II) and Plant IV – Południowy Koncern Energetyczny SA Elektrociepłownia Katowice (EC Katowice).

Table 3. Technical parameters of the tested boilers

Boiler parameters	Plant I	Plant II	Plant III	Plant IV
Type of boiler	CFB Aker Kvaerner ASA	2 × CFB Foster Wheeler	2 × CFB Foster Wheeler	CFB Foster Wheeler
Boiler power output	40 MW _e , 70 MW _t	274 MW _t	180 MW _t	135 MW _e , 200 MW _t
Type of boiler	CFB Cymic	CFB Compact	CFB Compact	CFB
Fuel consumption	25.0 Mg/h	56.1 Mg/h	33.7 Mg/h	68.3 Mg/h
Efficiency	88.5%	90.7%	91%	92%
Nominal steam efficiency:	135 Mg/h	404 Mg/h	260 Mg/h	483 Mg/h
Year of start-up	2000	2003	1999	1999
Mean stream of flue gas volume during investigations	157730 m ³ _n /h	420340 m ³ _n /h	261610 m ³ _n /h	556650 m ³ _n /h
Mean concentration of dust in the emitted flue gas	26.5 mg/m ³ _n	21.9 mg/m ³ _n	12.0 mg/m ³ _n	26.4 mg/m ³ _n
Density of dust (trapped in the electrofilter)	2555 kg/m ³	2646 kg/m ³	2701 kg/m ³	2757 kg/m ³

Table 4. Parameters of fuel burnt in the tested boilers

Fuel parameters	Unit	Plant I	Plant II	Plant III		Plant IV	
				coal	sludge ^a	coal	sludge ^a
Calorific value	kJ/kg	19915	19775	18942	9000	19454	9053
Humidity content	%	10.51	14.90	20.90	42.00	13.80	40.70
Sulphur content	%	0.92	1.22	1.26	0.80	1.17	0.73
Ash content	%	24.78	14.90	15.67	28.00	19.70	26.10
Volatile matter	%	28.91	25.08	23.26	no data	27.00	no data

^a a mixture of coal and post-flotation coal sludge, the contribution of sludge corresponded to 30% of the chemical energy introduced with the fuel into the boiler

METHODS

Measurement of the emitted dust granulometric composition and dust sampling

The emitted dust granulometric composition was measured by determining the mass of dust collected in particular stages of cascade impactor, introduced into the flue gas channel behind the device for flue gas removal. A six-stage impactor Andersen Mark III with a backup filter arresting the finest dust grains was applied. The masses of separated grain fractions (6 + 1) were calculated into mass contributions and size composition was determined. The cut-off diameter at 50% efficiency of separation depends on the stream, density and temperature of waste gas aspirated through the impactor.

In order to average the results for each plant and to enable a comparison of the granulometric composition of dust measured in particular plants, the results of all measurements were referred to the same unified fraction size ranges. For the needs of this work, four such fraction intervals: < 1; 1–2.5; 2.5–10 and > 10 μm were adopted. The cumulative values and fractions were calculated by interpolation method for those particular ranges.

Determination of trace elements in dust

Before determining the content of trace elements by ICP AES method, the samples of flue dust were digested in a one-station mineralizer with focused micro-wave energy. The samples of the tested ashes were placed in a vessel and 15 cm^3 of concentrated suprapure HNO_3 was added [24]. After the reaction vessel was closed, the microwave system worked for 60 minutes at 600 W. The process temperature was 483 K (with an admissible 10% measurement error), the pressure in the vessel was 15 bar. When the digestion process was completed and the inside of the reaction vessel reached the ambient temperature, the vessel was opened and the samples placed on a quantitative microporous filter paper. The filtrate was collected into a measurement flask, after supplementing it with deionised water to reach the volume of 50 cm^3 . The analytes were determined by means of ICP AES with optical detection. The residue on the filter paper consisted of filter paper remains with deposited dust. During the sample analysis by ICP AES method a glass Mainhard atomizer was used and optimized measurement parameters were applied [14]. The glass Mainhard atomizer is the most commonly used type of concentric atomizer. In this atomizer a sample is placed right into the centre of an argon stream, which enables achieving high measurement stability and sensitivity of determination [13].

Apart from the selection of appropriate atomizer, the major problem in the process of optimizing the parameters of emission spectrometer's work is to establish the optimal velocity of carrier and spraying gas flow. These parameters should be set so as to obtain a maximum ratio of peak intensity of the determined element to the intensity of the sample background for each analyzed element [37]. The emission lines were selected according to the Polish Standard (PN-EN ISO 11885, 2001) [29]. The spectrometer was calibrated using the certified multi-element solutions produced by Merck company. Concentrations used for calibrations reached 1 ppm, 5 ppm, 10 ppm and 15 ppm.

RESULTS

Concentrations of the selected trace elements in dust

In the process of measuring the granulometric composition of the emitted dust by means of a cascade impactor, 84 samples of dust were obtained for investigations into trace elements' content. The measurements consisted of three series, each containing 7 granular fractions from each of the four tested plants. The mass of single samples was small, ranging from a fraction to several mg. In order to ensure the required concentration of analytes in the mineralization solution, the samples containing grains with approximate diameters – 1 μm , 1–2.5 μm and > 2.5 μm were mineralized together.

The concentration of the examined trace elements in granular fractions of the emitted dust has a very wide range. Table 5 presents the full range of the measured concentrations [ppm] and the range limited to values found in 80% of the examined samples.

Table 5. Full and reduced range of the examined trace elements' concentrations in dust samples

Element	Full range			Reduced range	
	average	max	min	min	max
Be	16	176	1	2	52
Cd	4	64	0	0	12
Co	8	82	0	0	24
Cr	2872	205432	0	8	1175
Cu	706	14627	0	0	1033
Hg	68	618	0	0	205
Mn	1834	116615	0	35	1518
Mo	30	748	0	0	98
Ni	1917	86271	0	9	1996
Pb	14495	514038	5	28	1213
Sb	435	14763	0	0	944
Se	251	2366	0	8	693
Tl	343	7555	0	2	838
V	243	3636	0	0	538
W	54	1993	0	0	114
Zn	1566	18462	0	34	2961

Table 6 presents concentrations of selected trace elements in real granular fractions taken at the tested plants as well as the calculated enrichment coefficient (R_j) for particular elements, determined from the ratio of concentration in the fraction containing the smallest and in the fraction containing the largest grains, according to the following formula:

$$R_j = \frac{C_{j \min}}{C_{j \max}} \quad (1)$$

where:

$C_{j \min}$ – concentration of j^{th} trace element in the fraction containing the smallest grains,
 $C_{j \max}$ – concentration of j^{th} trace element in the fraction containing the largest grains.

The content and contributions of selected trace elements in dust fractions

On the basis of the determined trace elements’ concentrations in particular dust fractions separated by means of an impactor and unified fractions, the content (Tab. 7) and cumulated mass contributions (M_j) of trace elements in unified $PM_{1,}$ $PM_{2,5}$ and PM granular fractions contained in the emitted dust (Tab. 8) were determined.

The presented values have been calculated in the following way:

$$D_{ji} = C_{ji} \cdot f_i \quad (2)$$

where:

D_{ji} – content of j^{th} trace element bound to the i^{th} fraction in the emitted dust [mg/g],
 C_{ji} – concentration j^{th} of trace element in the i^{th} fraction [mg/g],
 f_i – fraction contribution.

$$D = \sum_{i=1}^n D_{ji} \quad (3)$$

where:

D – content of j^{th} trace element in the emitted dust [mg/g].

$$M_{ji} = \frac{D_{ji}}{D} \quad (4)$$

M_{ji} – cumulated mass contribution of j^{th} trace element in the i^{th} fraction of the emitted dust.

Emission factors (EF) of selected trace elements

The obtained results were used to calculate the emission factors for particular trace elements. To this end the emission factors of $EF_{PM1,}$ $EF_{PM2,5}$ and EF_{PM} in 1 kg of the emitted dust in relation to 1 Mg of the burned fuel (Tab. 9), determined as a result of measurements taken in the tested plants [18] were used. Basing on the dust emission factors and the content of the examined trace elements in relevant unified granular fractions of the dust, the emission factors EF_j for particular trace elements were calculated, both for $PM_{1,}$ $PM_{2,5}$ and PM fractions. The obtained results have been given in Table 10.

Table 6. Concentrations of selected trace elements in real granular fractions (μm) emitted from a CFB boiler in the examined plants [ppm] and enrichment coefficient

Element	EC Tychy				EC Elcho				EC Jaworzno II				EC Katowice			
	< 1.26	1.26–2.53	> 2.53	R_j	< 1.40	1.40–2.80	> 2.80	R_j	< 0.68	0.68–3.30	> 3.30	R_j	< 1.46	1.46–2.90	> 2.90	R_j
Zn	2880.96	2867.93	1352.73	2.13	3479.98	3040.92	3273.17	1.06	1666.57	2452.47	1340.78	1.24	1465.37	1190.43	3539.98	0.41
Cd	15.39	3.10	1.04	14.79	21.18	4.05	13.01	1.63	6.72	5.57	57.46	0.12	3.74	21.03	1.66	2.26
Pb	813.71	891.38	520.28	1.56	1462.60	1135.28	888.74	1.65	456.96	613.12	328.36	1.39	488.46	595.21	786.66	0.62
Co	7.48	11.24	5.72	1.31	6.30	7.10	7.37	0.86	6.18	6.13	2.24	2.76	4.88	1.63	8.49	0.58
Mn	2137.63	2344.73	1097.79	1.95	2443.55	1709.00	2009.42	1.22	999.94	1479.84	889.30	1.12	1057.37	1357.09	2088.79	0.51
Cr	461.83	821.62	1546.96	0.30	524.52	545.34	444.37	1.18	263.43	236.89	205.22	1.28	264.34	1305.50	279.47	0.95
Cu	382.66	507.70	360.73	1.06	345.48	391.27	351.16	0.98	327.94	278.69	845.51	0.39	175.27	484.11	399.54	0.44
Mo	105.56	4.26	84.98	1.24	882.60	273.68	58.53	15.08	29.57	44.59	30.10	0.98	31.61	43.65	178.03	0.18
Se	15.39	15.50	6.94	2.22	20.17	8.11	10.84	1.86	24.19	5.57	8.21	2.95	14.37	27.78	12.42	1.16
Sb	2529.09	1085.16	953.84	2.65	3303.46	1885.37	2276.05	1.45	725.76	1700.01	875.61	0.83	488.46	309.51	2587.70	0.19
W	105.56	108.52	32.95	3.20	239.56	133.80	2297.72	0.10	102.14	78.03	24.63	4.15	135.04	226.18	175.96	0.77
Hg	351.87	213.16	190.77	1.84	302.61	93.26	563.59	0.54	564.48	178.36	125.87	4.48	212.62	111.11	248.42	0.86
Tl	1869.33	1007.65	1855.66	1.01	504.34	587.91	541.92	0.93	209.66	275.90	175.12	1.20	238.48	1150.75	289.82	0.82
Be	48.38	93.01	31.22	1.55	55.48	180.43	43.35	1.28	59.14	50.16	60.20	0.98	57.47	55.55	51.75	1.11

Table 7. Content of selected trace elements in μg which are present in unified granular fractions contained in 1 g of dust emitted from a CFB boiler in the examined plants

	EC Tychy			EC ELCHO			EC Jaworzno			EC Katowice		
	PM ₁	PM _{2.5}	PM	PM ₁	PM _{2.5}	PM	PM ₁	PM _{2.5}	PM	PM ₁	PM _{2.5}	PM
Zn	604.43	1828.46	2320.04	592.3	1840.0	3213.1	92.0	709.3	1638.6	51.0	344.8	2887.9
Cd	3.23	4.55	4.93	3.6	5.3	10.7	0.4	1.8	41.6	0.1	5.3	6.5
Pb	170.72	551.16	740.23	248.9	714.7	1087.6	25.2	179.5	407.1	17.0	163.9	729.0
Co	1.57	6.37	8.45	1.1	4.0	7.1	0.3	1.9	3.4	0.2	0.6	6.7
Mn	448.47	1449.2	1848.13	415.9	1117.1	1960.0	55.2	427.7	1044.1	36.8	371.7	1872.3
Cr	96.89	447.56	1009.73	89.3	313.0	499.4	14.5	74.2	216.4	9.2	331.4	532.7
Cu	80.28	296.97	428.06	58.8	219.3	366.6	18.1	88.3	674.3	6.1	125.6	412.6
Mo	22.15	23.97	54.85	150.2	262.5	287.1	1.6	12.9	33.7	1.1	11.9	139.8
Se	3.23	9.85	12.37	3.4	6.8	11.3	1.3	2.7	8.4	0.5	7.4	16.3
Sb	530.6	993.75	1340.38	562.3	1335.8	2290.6	40.1	468.0	1074.8	17	93.4	1952.4
W	22.15	68.46	80.44	40.8	95.7	1059.6	5.6	25.3	42.3	4.7	60.5	186.9
Hg	73.82	164.8	234.13	51.5	89.8	326.2	31.2	76.1	163.3	7.4	34.8	213.3
Tl	392.18	822.25	1496.59	85.8	327.1	554.4	11.6	81.1	202.4	8.3	292.3	500.5
Be	10.15	49.85	61.2	9.4	83.5	101.7	3.3	15.9	57.6	2	15.7	52.9

Table 8. Cumulated mass contributions of the selected trace elements to unified granular fractions of the dust emitted from the examined boilers

Element	EC Tychy		EC Elcho		EC Jaworzno II		EC Katowice	
	PM ₁	PM _{2.5}						
Zn	0.261	0.788	0.184	0.573	0.056	0.433	0.018	0.119
Cd	0.655	0.923	0.336	0.495	0.010	0.043	0.015	0.815
Pb	0.231	0.745	0.229	0.657	0.062	0.441	0.023	0.225
Co	0.186	0.754	0.155	0.563	0.088	0.559	0.030	0.090
Mn	0.243	0.784	0.212	0.570	0.053	0.410	0.020	0.199
Cr	0.096	0.443	0.179	0.627	0.067	0.343	0.017	0.622
Cu	0.188	0.694	0.160	0.598	0.027	0.131	0.015	0.304
Mo	0.597	0.906	0.605	0.698	0.039	0.205	0.008	0.141
Se	0.789	0.944	0.453	0.524	0.067	0.262	0.002	0.144
Sb	0.425	0.837	0.497	0.757	0.054	0.327	0.022	0.226
W	0.404	0.437	0.523	0.914	0.047	0.383	0.008	0.085
Hg	0.261	0.796	0.301	0.602	0.155	0.321	0.031	0.454
Tl	0.396	0.741	0.245	0.583	0.037	0.435	0.009	0.048
Be	0.275	0.851	0.039	0.090	0.132	0.598	0.025	0.324

Table 9. EF_{PM1}, EF_{PM2.5} and EF_{PM} dust emission factors for the examined CFB boilers

Plant	Emission factors [kg/Mg]		
	EF _{PM}	EF _{PM1}	EF _{PM2.5}
EC Tychy	0.167	0.035	0.107
EC Elcho	0.164	0.028	0.095
EC Jaworzno II	0.093	0.005	0.029
EC Katowice	0.215	0.007	0.061

$$EF_{jPMi} = EF_{PMi} D_j \quad (5)$$

where:

EF_{jPMi} – emission factor of j^{th} trace element in the i^{th} granular fraction of dust [mg/g], [mg/Mg],

EF_{PMi} – emission factor of the i^{th} dust granular fraction [kg/Mg]

D_{ji} – content of j^{th} trace element bound to the i^{th} fraction in the emitted dust [mg/g], [mg/kg].

DISCUSSION

With a particular regard to dangerous substances it might be said that the concentration of beryllium (in ppm) ranges from 2 to 52, for cadmium it reaches 12, cobalt – 24, chromium – from 8 to 1175, mercury – 205, lead – from 28 to 1213, antimony – 944, and selenium – from 8 to 693 (Tab. 5, reduced range) The measured concentrations' level does not depart from the one established in previous investigations into the ashes of Upper Silesian power coals [33]. An attempt to evaluate the degree of fine dust fractions'

Table 10. Emission factors of selected trace elements in unified granular fractions in mg per 1 Mg of burnt coal from a CFB boiler in the examined plants

Element	EC Tychy			EC Elcho			EC Jaworzno II			EC Katowice		
	EF _{jPM1}	EF _{jPM2.5}	EF _{jPM}	EF _{jPM1}	EF _{jPM2.5}	EF _{jPM}	EF _{jPM2.5}	EF _{jPM}				
Zn	21.2	195.6	387.4	16.6	174.8	526.9	0.5	20.6	152.4	0.4	21.0	620.9
Cd	0.1	0.5	0.8	0.1	0.5	1.8	0.0	0.1	3.9	0.0	0.3	1.4
Pb	6.0	59.0	123.6	7.0	67.9	178.4	0.1	5.2	37.9	0.1	10.0	156.7
Co	0.1	0.7	1.4	0.0	0.4	1.2	0.0	0.1	0.3	0.0	0.0	1.4
Mn	15.7	155.1	308.6	11.6	106.1	321.4	0.3	12.4	97.1	0.3	22.7	402.5
Cr	3.4	47.9	168.6	2.5	29.7	81.9	0.1	2.2	20.1	0.1	20.2	114.4
Cu	2.8	31.8	71.5	1.6	20.8	60.1	0.1	2.6	62.7	0.0	7.7	88.7
Mo	0.8	2.6	9.2	4.2	24.9	47.1	0.0	0.4	3.1	0.0	0.7	30.1
Se	0.1	1.1	2.1	0.1	0.6	1.9	0.0	0.1	0.8	0.0	0.4	3.5
Sb	18.6	106.3	223.8	15.7	126.9	375.7	0.2	13.6	100.0	0.1	5.7	419.8
W	0.8	7.3	13.4	1.1	9.1	173.8	0.0	0.7	3.9	0.0	3.7	40.2
Hg	2.6	17.6	39.1	1.4	8.5	53.5	0.2	2.2	15.2	0.1	2.1	45.9
Tl	13.7	88.0	249.9	2.4	31.1	90.9	0.1	2.3	18.8	0.1	17.8	107.6
Be	0.4	5.3	10.2	0.3	7.9	16.7	0.0	0.5	5.4	0.0	1.0	11.4

enrichment did not bring clear-cut results. Contrary to pulverized-fuel boilers, no enrichment of fine dust grains can be observed (Tab. 6). For the examined elements belonging to the second group according to Swain's classification [35], the enrichment coefficient (R_i) was not found to be higher than one in all 4 tested plants. The value of 1 in 3 of the examined plants was exceeded in the case of beryllium, cadmium, manganese, lead and zinc. It should be emphasized that significant differences were observed in the process of coal combustion in PC and CFB boilers, i.e. the temperature of combustion (1600 K and 1100 K respectively), the time of fuel grain retention (seconds and minutes), dust grain reaction (neutral/acid and alkaline), dust grain porosity (low and high). In the process of CFB combustion, an intense abrasion of dust grain, and in consequence renewing of grain surface was observed. The flue dust from CFB does not contain glassy phases characteristic of high-temperature processes; but there is gypsum, calcium and quartz as well as iron and magnesium oxides [2]. Reactions causing the redistribution of trace elements may occur on the renewed surface of dust grains due to continuous collisions and abrasion [32]. Co-burning of coal and coal sludge used in plants III and IV may also contribute to the changes in the manner of trace elements' accumulation, which was observed in the case of co-burning with biomass [4]. From the point of view of environmental threat, the size of the examined trace elements' contribution in granular fractions contained in the emitted dust is more important. In the opinion of the Authors, some interesting information is contained in Table 8. The presented values of contributions result from the processing of data on the content of the examined elements in unified granular fractions. The general observation is the difference in contributions calculated for coal-fired plants and plants fired

with coal with addition of coal sludges. This difference cannot be clearly interpreted due to the low number of investigated examples. However, it should be emphasized that coal sludges containing much bigger amounts of mineral matter are a source of trace elements which are bound to this mineral matter and occur in inorganic compounds. In coal-fired boilers the contribution of $PM_{2.5}$ fraction in the emission of the examined trace elements ranges from 0.443 to 0.944, and the contribution of PM_1 fraction ranges from 0.096 to 0.789. Particularly high is the contribution of PM_1 fraction in the emission of selenium, antimony, tungsten and thallium, and $PM_{2.5}$ fraction in the emission of cadmium, cobalt, copper, mercury, manganese, molybdenum, lead, antimony, selenium, thallium and zinc. It should be noted that dangerous elements introduced into the air, namely, cadmium, cobalt, chromium, mercury, lead, antimony and selenium are present mainly in the respirable fraction. The size of these elements' contributions is influenced by the previously mentioned processes of dust grain enrichment with trace elements due to condensation of vapors of these elements' compounds or vapors of a given element. The fractional efficiency of dedusting devices is also significant. Electrofilters which achieve a very high total dedusting efficiency show minimum efficiency when removing the grains with diameters ranging from 0.1 to 2 μm [40]. In consequence, as observed in the case of two coal-fired boilers, the mass fraction of $PM_{2.5}$ in the emitted dust increases to 64% [18]. A relative drop in the efficiency of fine dust fraction extraction is not so high in the case of bag filters. For this reason more trace elements were found in the flue ash collected in the bag filter compared to flue ash captured in the electrofilter [9]. One might then expect further progress in the reduction of dust emission from CFB boilers by using bag filters. This will allow achieving a dedusting efficiency comparable to that obtained for PC boilers equipped with FGD system by wet lime method, which is the second stage of dedusting. This does not eliminate completely the emission of submicron fraction which is accompanied by some amounts of trace elements [27], but it greatly reduced the threat [26, 34].

In order to evaluate the scale of the risk for the population due to emission of dust containing dangerous substances, the emission factors for selected trace elements from the examined plants were calculated (Tab. 10). Similarly to the previous observation regarding the contributions in granular fractions, a significant difference in the values of emission factors for coal-fired boilers and boilers fired with coal and coal sludge may be observed, with a similar efficiency of dust removal from the four examined plants. In the first group of plants the emission factors for the selected elements containing PM_1 range from a fraction to 21 mg/Mg, and for those containing $PM_{2.5}$ – from a fraction to nearly 200 mg/Mg. In the second group of plants the emission factors for the selected elements with PM_1 do not exceed a fraction of mg/Mg, and with $PM_{2.5}$ they range from a fraction to nearly 23 mg/Mg. The emission factors of chromium, lead and antimony in the respirable dust reaching the respective values of 30, 68 and 127 mg/Mg should be considered high. The example of mercury, whose average TSP emission factor reaches 38 mg/Mg for all the plants, is noteworthy. It proves that the emission of mercury even from modern power plants is high. The examined plants located within the area of ca 1000 km², burning ca 10⁶ Mg of coal annually, emit ca 40 kg of mercury in a solid phase. As the degree of binding mercury to the solid phase in a fluidized bed boiler is estimated to reach ca 50% [21], in the considered case the total emission of mercury may be evaluated as 80–100 kg/a. The example of mercury is important considering the fact that in 2020 a 50% reduction of mercury emission is planned to be achieved, as compared to 2000.

The results of investigations may contribute to updating the inventory of trace elements' emission in Poland and Europe by specifying the dust emission factors, taking into account the real granular composition of the emitted dust. They will also facilitate a more accurate evaluation of the influence that the power plants exerts on the environment, including the effects of washing out toxic trace elements from the ashes transported for utilization or storage [6, 30].

CONCLUSIONS

Although the flue gas emitted from CFB boilers is removed by means of effective electrofilters, it contains dust grains, in which compounds of numerous trace elements, including elements considered as dangerous i.e. beryllium, cadmium, cobalt, chromium, mercury, lead, antimony and selenium, are present. The range of these elements' concentrations does not differ from the one observed in the case of dust emitted from PC boilers. The examination of dust granular composition and the analysis of granular fractions, separated by means of a cascade impactor, revealed that the phenomenon of fine grains' enrichment with some trace elements takes place also in CFB boilers. The investigations and analyses showed that a significant, or even a prevailing part of the emitted trace elements' mass are released into the atmosphere with the respirable fraction of $PM_{2.5}$ dust, which poses a potential threat to people's health. The calculated emission factors for the investigated trace elements, expressed in mg per a ton of fuel burnt, are not very high, but they prove that modern CFB boilers, equipped with effective electrofilters cannot be omitted in the inventory of emission of trace elements, including heavy metals. The results of investigations will enable to accurately specify the size of global emission and will help evaluate the influence exerted by power plants on the environment and the selection of technical methods of reducing the harmful effect of these plants.

Further investigations are needed to obtain more information on the behavior of trace elements contained in fuel in the process of combustion in a CFB boiler and their distribution in the products of combustion.

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WYSTĘPOWANIE METALI W SPALINACH Z KOTŁÓW Z CYRKULACYJNYM ZŁOŻEM FLUIDALNYM

Emisja pyłu ze źródeł energetycznych powoduje wprowadzenie do środowiska wielu zanieczyszczeń, w tym związków niebezpiecznych metali, występujących jako pierwiastki śladowe w węglu kamiennym i brunatnym. Po spaleniu węgla znajdują się one w ziarnach pyłu respirabilnego, co stwarza zagrożenie dla zdrowia ludzi. Przedstawiono wyniki badań nad dystrybucją wybranych kilkunastu pierwiastków śladowych we frakcjach ziarnowych popiołu lotnego emitowanego z kotłów z cyrkulacyjnym złożem fluidalnym stosowanych w elektrociepłowniach opalanych węglem. Materiał badawczy został pobrany za pomocą impaktora kaskadowego umożliwiającego wydzielenie ze strumienia spalin odpylonych w elektrofiltrze frakcji pyłu o różnej wielkości ziarna. Do oznaczenia pierwiastków śladowych wykorzystano metodę atomowej emisyjnej spektrometrii o wzbudzeniu plazmowym ICP-AES po uprzedniej mineralizacji próbek metodą mikrofalową. Przedstawiono wyniki pomiarów i analiz, określając zakresy występowania pierwiastków śladowych w popiele lotnym, charakteryzując dystrybucję we frakcjach ziarnowych PM_{10} , $PM_{2,5}$ i PM_{10} i wyznaczając wskaźniki emisji.