

# Size Distribution and Trace Elements Contents of Coal Fly Ash from Pulverized Boilers

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## Abstract

Pulverized coal boilers, commonly used in the power and heat-generating industries, constitute one of the most important sources of fine particulate matter (PM) emitted to ambient air. The evidence on airborne PM and its public health impact is consistent in showing adverse health effects at exposures currently experienced by urban populations in both developed and developing countries [1]. The amount, size distribution, chemical composition, and harmfulness of coal fly ash depends on a number of factors such as coal type, composition, preparation method, boiler type and construction, combustion conditions, and the type and efficiency of the applied air pollution control devices. This paper summarizes and discusses the parameters affecting size distribution and trace element contents of fly ash particles emitted from the energetic combustion of hard coal in pulverized boilers equipped with electrostatic precipitators.

**Keywords:** coal fly ash, particulate matter, trace elements, coal combustion, pulverized boilers

## Introduction

According to current knowledge, atmospheric particulate matter (PM) – a complex mixture of solid and liquid particles of organic and inorganic substances suspended in the air – affects more people than any other pollutant [2]. In recent years research has centered on small particles and their compounds that can be detected by new sophisticated analytical techniques [3]. While adverse effects of PM on human health are now well established and accepted [4], major uncertainties and important gaps of knowledge related to PM source-specific compositions and health effects, as well as its total impact on public health, remain [2, 5]. Large number of epidemiological studies have demonstrated that exposure to PM is related to respiratory and cardiovascular diseases. Health effects range from modest temporary changes, through increased risk of symptoms requiring hospital admission and increased risk of death [6-9]. These adverse effects of PM follow both short- and long-term

exposures, and moreover there is little evidence to suggest a threshold below which no adverse health effects would be anticipated [1, 2].

The main components of PM mixture are organic matter, mineral dust, secondary inorganic aerosols (SIA, which include sulphates, nitrates, and ammonia) and water, as well as an unspecified part. Most current studies are focused especially on the so-called fine  $PM_{2.5}$  particles (with aerodynamic diameter smaller than  $2.5 \mu m$ ) and coarse  $PM_{2.5-10}$  particles (in the size range between  $2.5$  and  $10 \mu m$ ).  $PM_{2.5}$  is believed to be the most harmful, as when inhaled it can penetrate deep into the lungs. According to the results of the Clean Air for Europe (CAFE) research program [10], exposure to  $PM_{2.5}$  contributes to life-span shortening of Europeans by about nine months, while the latest studies show that  $PM_{2.5}$  air pollution causes around 450,000 premature deaths a year in the 27 EU countries, which corresponds to a total of almost 4.5 million years taken away from people's lives [11]. The atmospheric PM varies in size and composition and consists of a mixture of primary

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(emitted directly from anthropogenic and natural sources) and secondary (formed in the atmosphere from the reaction of primary pollutants) compounds. Solid fuel burning in the power industry is an important anthropogenic source of both primary particulates (commonly called fly ash) and gaseous precursors of secondary particles, such as SO<sub>2</sub> and NO<sub>x</sub>.

Currently around 40% of electricity worldwide, and around 90% in Poland, is generated from coal [12]. The forecasts predict that the next two decades will witness the installation of the same amount of power generation capacity as that installed over the whole 20<sup>th</sup> century [13]. For the last decade much effort to fulfil energy demand by renewable energy sources has been undertaken, but coal still is, and is likely to be for the foreseeable future, one of the most important electricity-producing fuels [14-16]. Therefore, all by-products produced during coal combustion are of major concern from the perspectives of human health and the environment as a whole.

Coal is a sedimentary rock, composed primarily of organic matter along with varying amounts of inorganic rock fragments and mineral matter, for example clays, shales, quartz, and calcite [17]. During high-temperature coal combustion and subsequent cooling of the flue gas, mineral matter undergoes chemical and structural modifications such as dehydration, dehydroxylation, decomposition, and the formation of new phases and vitrification [18]. Particles that are captured by flue gas as it exits the furnace are referred to as coal fly ash (CFA). CFA is a complex mixture with unique polycomponent, heterogeneous, and variable composition, containing intimately associated and finely dispersed solid, liquid, and gaseous components [17]. The overall mineralogical composition of CFA resembles that of siliceous rocks from which it was derived, with oxides of silicon, aluminum, iron, and calcium making up more than 90% of most fly ash. Other major and minor elements (sulfur, sodium, potassium, magnesium, titanium) make up an additional 8%, while trace elements (TEs) constituents account for less than 1% [19]. TEs originating from coal utilization that are believed to be of main concern from the human health perspective include As, Cd, Cr, Hg, Mn, Ni, and Pb [20, 21]. CFA is of key meaning from the air pollution point of view, because when emitted to ambient air it becomes basic primary PM.

The emission volume, size distribution, and chemical composition of primary particulates emitted into the atmosphere from the energy and transformation industries (sector 01 from SNAP 97 – Selected Nomenclature for Air Pollution), is influenced by a wide range of factors such as: coal type and parameters (granulation, chemical composition, mode of occurrence of chemical compounds), combustion process parameters (temperature, oxygen concentration), boiler type and construction and type and parameters of the applied air-pollution control devices (APCDs). The APCDs in large combustion plants (LCPs) usually consist of highly efficient de-dusting facilities such as electrostatic precipitators (ESPs) or fabric filters (FFs) and flue gas desulfurization (FGD) installations.

Both field and laboratory measurements as well as theoretical calculations have led to the conclusion that primary PM emitted from coal combustion is composed of three main constituents [22]:

- (1) un-burnt carbon from the incomplete combustion of coal
- (2) non-volatile mineral elements, a portion of which may directly escape the burning coal grain, and transfer into fly ash without phase change (solid-to-particles path)
- (3) volatile mineral elements that vaporize in the flame zone and nucleate, forming an ultrafine aerosol. It condenses in the post-flame zone when combustion gases cool rapidly, and the aerosol particles grow by coagulation (solid-vapor-particle path).

Studies analyzing the factors affecting final emission of CFA from electric power plants (EPPs) and thermoelectric power plants (TPPs) have been conducted since the 1970s, with the main focus on TEs emissions due to their harmfulness to humans. In Poland, Pacyna in his precursory work [23] as well as Mazur and Koniecznyński [24] and Koniecznyński et al. [25, 26] recently, studied the distribution of TEs in the combustion products of coal burned in EPPs and TPPs. Pacyna and co-authors published further a number of TEs emission inventories for both regional and global scales [27-29]. The European studies on the fate of TEs in the coal-fired power stations in general have been intensively conducted by Meij [30, 31] and Querol et al. [32, 33]. In the US, Tomeczek and Palugniok [34] studied kinetics of mineral matter transformation during coal combustion, while Senior and co-authors [35-37] conducted research on TEs distribution during coal combustion processes. The influence of electrostatic precipitators on particle size distributions was studied by Clack [38]. However, the majority of current studies examining associations between coal combustion and CFA/TEs emissions is conducted in China. Among others, Huang et al. [39] and Xiaowei et al. [40] investigated emissions from pulverized coal boilers, while Zhang et al. [41] studied the emissions of select toxic TEs from several bench-scale furnaces, and the retention of TEs by several typical sorbents and additives. Recently, Zhao et al. [42], developed the database of Chinese emission factors and compared it with widely used U.S. EPA AP-42 database [43].

In Japan, Zhang et al. [44] investigated the influence of combustion temperature on the formation of submicron particulate matter (PM<sub>1</sub>). Also in India, a study on twelve TEs emissions from coal-fired EPPs equipped with ESPs was conducted [45]. Recently, Bhangare et al. [46] analyzed coal and ash samples collected from five different TPPs across India in order to determine TEs distribution, enrichment, and partitioning behavior.

The Polish power and heat industry is almost exclusively based on coal combustion, with pulverized coal boilers and electrostatic precipitators being the most commonly used technologies for coal burning and flue gas de-dusting, respectively. Therefore, understanding the behaviour of coal grains, CFA particles, and TEs during coal combustion and flue gas cleaning is crucial for assessing the characteristics of primary PM emitted to ambient air. The aim of this

paper is to compare and analyze the factors influencing size distribution of CFAs emitted from EPPs and TPPs and its TEs contents. The focus is put on combustion processes typical for Polish industry.

### TEs Contents and Mode of Occurrence in Coal

Coal is a heterogeneous fuel comprising an organic part, highly calorific and mainly consisting of carbon with a small amount of mineral inclusions, and an inorganic part mainly consisting of mineral substances. So far about 84 elements have been identified in coal, including major, minor, and trace elements. TEs exist in coal in a variety of different modes of occurrence. They can be found either as main or trace components of discrete minerals or as adsorbed elements in the inorganic fraction, while in the organic fraction they occur as organometallic, chelate, or ion-exchange compounds [47]. In bituminous coals the following TEs are present: antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), fluorine (F), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), niobium (Nb), rubidium (Rb), selenium (Se), strontium (Sr), yttrium (Y), zinc (Zn), and zirconium (Zr), as well as radioactive elements such as radium (Ra), thallium (Th), and uranium (U). The contents of TEs in various coals exhibit a great variation, not only in the concentrations of different elements, but also in the range – typically >100-fold – of concentration exhibited by each element [36]. The present paper is focused on these TEs that are present in parent coal and its CFA in relatively large quantities (i.e. As, Cr, Pb, Mn, Ni, and Zn) or that occur in smaller quantities but are exceptionally harmful: Cd and Hg. Seven from among the abovementioned elements – As, Cd, Cr, Pb, Ni, Hg, and Mn – are among 35 air pollutants considered harmful to human health by WHO [20].

The comparison of selected TEs contents in different Polish bituminous coals is presented in Table 1.

Average concentration of TEs in Polish bituminous coals varies from a low value of around 0.1 ppm for Cd and Hg to the highest value for Mn (150-180 ppm). Data from [48] and [49] presented in Table 1 are quite similar because they are averaged over a number of mines. However, for individual power plants (coal mines) differences in TEs contents may be large, as it can be noticed for Miechowice and Łagisza EPPs for Zn. Among the investigated coals from the Upper Silesian Coal Basin [23, 48, 49], the one from the Wawel coalmine has the greatest Zn content of 238 ppm, plus high contents of Mn (492 ppm) and Pb (44 ppm). The highest level of Mn was found in coal from the Marcel coalmine (508 ppm), where high concentrations of Pb (47 ppm) and Zn (121 ppm) were measured. Bituminous coal from the Rudytłowy coalmine was found to have the highest concentration of Pb (54 ppm) and high content of Mn (321 ppm). In the Upper Silesian Basin, the largest concentration of Ni occurs in coals from the coalmines Kazimierz-Juliusz (47 ppm) and Chwałowice (39 ppm).

Table 1. The contents of the analyzed trace elements in Polish hard coals according to: Pacyna [23], Jezierska and Juda-Rezler [48], and Gabzdyl [49].

Trace element	Contents in Polish bituminous coals [ppm]			
	Miechowice Power Plant [23]	Łagisza Power Plant [23]	Upper Silesian Coal Basin [48]	Upper Silesian Coal Basin [49]
As	40.10	67.60	50.30	-
Cd	-	-	0.1	-
Cr	-	-	29.10	25.00
Hg	0.09	0.08	0.10	-
Mn	-	-	157.00	183.00
Ni	-	-	21.9	24.00
Pb	14.30	17.60	20.60	25.00
Zn	38.40	65.00	56.30	69.00

The largest Cr deposits were found in Krupiński coalmine (50 ppm). The average content of Cd in Polish coals is low, typically around 0.1 ppm.

For mercury, which constitutes a serious hazard to human health (due to its harmful impact on the central nervous system) more data is available. Trace amounts of Hg exist in coal in a wide range of contents, with the world average of 0.1 ppm [50]. Coal combustion in EPPs is a major stationary source of Hg emission worldwide [51]. The data shows that Hg content in coals from different coalmines varies significantly, and that the concentration of Hg in coal burnt in Polish EPPs differs in the order of magnitude, from 0.013 to 0.163 ppm (Table 2). The highest concentrations were recorded in the Lower Silesian Coal Basin, although no coal is mined there anymore. In the Upper Silesian Coal Basin the highest amount of Hg was recorded in Brzeszcze, Jaworzno, and the Siersza coalmines, as well as in the Halemba coalmine. In the latter, the maximum content of Hg amounts to 0.758 ppm, whereas the average values are comparable to the results obtained in Siersza and Jaworzno. A similar average level of 0.105 ppm was recorded in Bogdanka (Lublin Coal Basin). The average Hg concentration in coals from the Katowice Coal Holding (coalmines located in the central part of the Upper Silesian Coal Basin) amounts to 0.140 ppm. The highest values of 0.145-0.163 ppm were recorded in the Murcki, Mysłowice, and Wujek coalmines.

With respect to TEs concentrations in Polish bituminous coals, the contents of all analyzed elements fall in the worldwide concentration ranges given by Swaine [55], being for the majority of elements (with the exception of Cd and Hg) higher than the mean values of worldwide coals reported by Ketris and Yudovich [50] (Table 3 and Fig. 2). Average concentration of Cd in Polish coals is lower than the world average, while for Hg average concentration equals mean worldwide value.

Table 2. Average mercury content in hard coal from Polish mines according to: Bojakowska and Sokołowska [52], Smoliński [53], CLE Energopomiar, Wojnar and Wisz [54].

Coalmine	Average contents of Hg [ppm]	Coalmine	Average contents of Hg [ppm]	Coalmine	Average contents of Hg [ppm]
According to [52]		According to [53]		According to [54]	
Halemba	0.113	Wujek	0.163	1	0.064-0.100
Jaworzno	0.106	Mysłowice	0.151	2	0.097-0.141
Bogdanka (Lower Silesian Coal Basin)	0.105	Murcki	0.145	3	0.084-0.120
Brzeszcze	0.073	Staszica	0.113	4	0.053-0.092
Janina	0.066	Wesoła	0.113	5	0.100-0.105
Śląsk	0.049	Wieczorek	0.104	6	0.093-0.132
Jas-Mos	0.037			7	0.066-0.109
Marcel	0.029			8	0.054-0.124
Anna	0.020			9	0.056-0.090
Krupiński	0.013				

Table 3. Comparison of trace elements contents in coal from different countries.

Country, Author, Source	The contents of trace elements in coal [ppm]							
	As	Cd	Cr	Hg	Mn	Ni	Pb	Zn
World MIN, Swaine [55]	0.50	0.10	0.50	0.02	5.00	0.50	2.00	5.00
World MAX, Swaine [55]	80.00	3.00	60.00	1.00	300.00	50.00	80.00	300.00
World average, Ketris and Yudovich [50]	8.30	0.22	16.00	0.10	71.00	13.00	7.80	23.00
China, Huang et al. [39]		0.02	26.00	0.10	109.00		16.00	15.00
China, Dai et al. [56]	3.79	0.25	15.40	0.16		13.70	15.10	41.40
USA, Dai et al. [56]	24.00	0.47	15.00	0.17		14.00	11.00	53.00
India, Srinivasa et al. [45]	41.90	4.31	21.00	0.20	98.50	16.00	29.40	30.00
India, Bhangare et al. [46]	1.14	0.27	6.77	2.31	38.40	18.32	10.42	117.15
Canada, Goodarzi [57]	2.75	0.22	22.88	0.07			10.48	
Norway, Lewińska-Preis et al. [58]		0.12	1.39		16.00	1.96	2.69	4.73
United Kingdom, Spears and Tewalt [59]	31.30	0.05	14.80	0.17	30.10	40.00	23.50	8.44
Spain, Llorens et al. [60]	16.70	0.30	38.20	0.19	86.30	23.60	21.00	49.00
Poland, Pacyna [23]	53.85			0.09			15.95	51.7
Poland, Jezierska and Juda-Rezler [48]	50.30	0.10	29.10	0.10	157.00	21.90	20.60	56.30

There is high potential of significant reduction in the contents of TEs as early as at the stage of coal preparation, i.e. before combustion. The process of coal cleaning, frequently applied in coal mines as pre-combustion emission control technology, apart from increasing coal calorificity, leads to the reduction of the contents of mineral substances. Consequently, the concentration of TEs in fuel decreases as well. The extent of possible reduction depends on the mode

of occurrence of a given element in coal, which greatly influences its partitioning during coal cleaning as well as its fate during the process of combustion [36]. In order to reduce sulphur and ash contents in coal, two major minerals – pyrite and illite – are targeted for removal in coal cleaning processes; therefore, TEs associated with these minerals are removed as well. Many TEs (As, Cr, Mn, Ni, Se, etc.) are typically bound to these minerals [61], but

Table 4. The mode of occurrence of selected trace elements in hard coal from the eastern Upper Silesian Coal Basin (based on Mazur and Koniecznyński) [24].

Trace element	Mode of occurrence in Polish bituminous coals			
	Inorganic part		Organic part	
	[ppm]	[%]	[ppm]	[%]
Cd	7.0	92.0	0.6	8.0
Ni	135.3	83.0	28.5	17.0
Pb	209.1	97.0	6.6	3.0
Zn	258.5	91.0	27.1	9.0

numerous studies have shown that the presence of TEs in coal is highly heterogeneous, and can vary from the element being totally dispersed in the macerals (e.g. organic sulfur, carboxyl-bound Ca in lignite) to discrete mineral occurrences (e.g. pyrite, FeS<sub>2</sub>, quartz, SiO<sub>2</sub>, etc.) [61-63]. Knowledge of specific modes of occurrence of select TEs is still incomplete [37, 64, 65]. Moreover, this mode varies with coal rank, depositional environment, etc. [31]. The studies of Finkelman [64, 66] ranked the level-of-confidence (from one to ten) in the assignment of the likely occurrence mode for selected TEs. For example, Cr content is vastly variable, from highly organic to almost entirely inorganic, depending on the coal. According to the one of the recent works of Huggins and co-workers [61] As, Cr, V, Mn, Ni, and Se are typically associated with pyrite and/or illite. In the study of Illinois coal, V and Cr were found to

be predominantly inorganically associated with illite, with minor amounts (5-15% Cr, 20-30% V) associated organically in the macerals, whereas As and Se were strongly associated with pyrite. Arsenic association with pyrite was almost sole (90%), with only ~10% of As present as arsenate due to minor oxidation of the pyrite [61].

However, in the former x-ray absorption fine structure (XAFS) spectroscopy conducted by Huggins and co-workers [62, 63, 67, 68], certain lithophile trace elements (e.g. Ti, V, Cr, Zr, etc.) were found to have surprisingly high organic affinities in some bituminous coals, typically of highly volatile bituminous rank. These authors also found that Mn, Zn, As, and Br can be widely organically associated with certain coals.

In Canadian coal, As is dominated by arsenical pyrite and less toxic As<sup>+5</sup> in arsenate forms, while Cr is present as Cr<sup>+3</sup> in association primarily with illite [69]. The recent work of Riley and co-workers [65] reports the mode of occurrence of the wide range of TEs in six Australian coals.

The studies of Polish coal from the Eastern Upper Silesian Coal Basin (Table 4) show that Cd, Ni, Pb, and Zn are widely associated with the mineral part of coal [24], but for Ni the organic share (17%) is also substantial.

Due to different modes of occurrence of TEs in coal and various coal structures, the reduction of TEs during coal cleaning by physical separation techniques varies from 15 to 80% [24, 61, 70]. In the majority of Polish coals the contents of sulphur significantly decreases, along with the increase in the level of coal cleaning. This effect influences the behavior of some TEs, such as Hg and As, that have a high affinity for sulphur compounds. If most Hg in coal occurs in connection with sulphur, a considerable amount

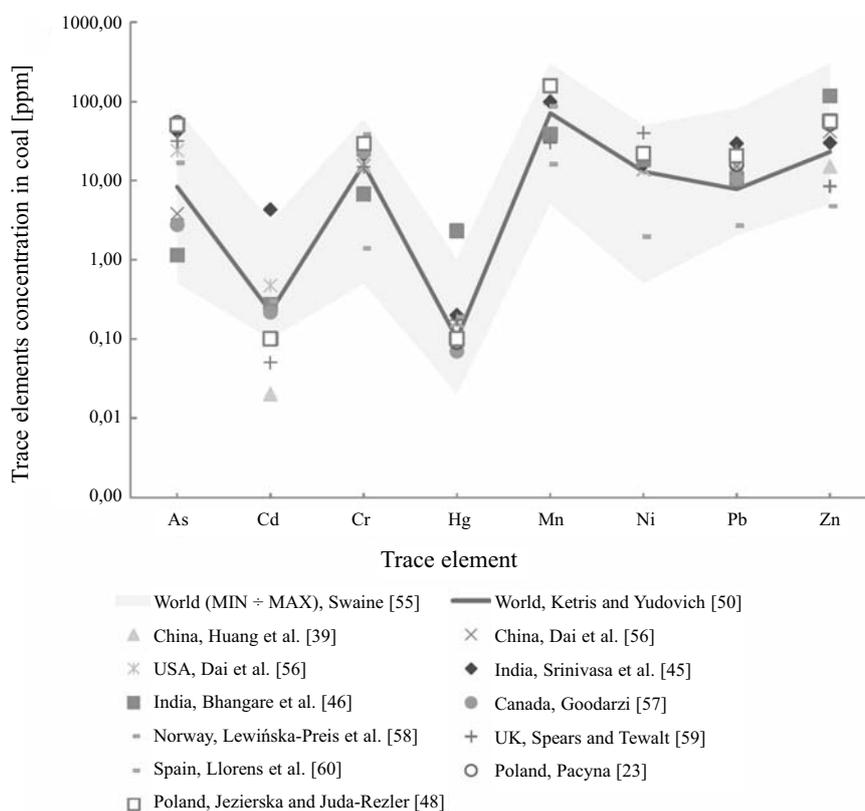


Fig. 1. Comparison of trace elements concentrations in coal from various countries.

of it can be eliminated at the stage of coal processing. The results differ depending on the size of coal grains. Even 65-70% of Hg compounds in Polish coal can occur in combination with sulphur – usually in pyrite. The remaining 30-35% occurs in the organic fraction. With the application of the flotation method in the process of cleaning, in the case of the finest fractions, it is possible to decrease the content of Hg to even 30-45%. Higher reduction can be obtained with the application of the chemical coal-cleaning process.

### Mineral Matter Transformations during Combustion

There are two main groups of mineral substances in coal [34, 71-73]:

1. Extraneous minerals: particles containing over 90% by weight of mineral substances separated from organic matter as a result of coal fragmentation before burning, usually sized from 40 to 70  $\mu\text{m}$  (organic particles are sized up to 100  $\mu\text{m}$ ).
2. Included mineral matter: closely linked to the organic particles of coal, which are not separated before combustion. Mineral matter contents usually account for less than 10% by weight (mostly 2-4% by weight) in organic particles. Organically-bound mineral matter or elements may be further divided into two subcategories:
  - included minerals,
  - organically-bound elements (cations).

During high-temperature processes such as combustion of coal, non-flammable mineral elements contained in raw fuel may entirely or partially:

- (1) remain in bottom ash
- (2) escape from coal grain and directly form a particle of fly ash
- (3) evaporate and condense on a fly ash particle
- (4) be retained in precipitators

These particles of fly ash that are not collected by dedusting and FGD installations are released into the ambient air with exhaust gases. Coal combustion products are therefore divided into two parts: bottom ash and CFA.

The difficulties with CFA and TE<sub>s</sub> emission estimations are caused by the transformations that mineral substances and TE<sub>s</sub> undergo during coal combustion. These processes are dependent on many factors, such as parent coal grain size distribution, the mode of occurrence of TE<sub>s</sub> in coal, furnace type and construction, and combustion conditions, as well as the interactions of different elements during and after combustion. In most cases the transformations of TE<sub>s</sub> and mineral substances depend on the distribution of inorganic compounds in coal. The majority of mineral substances occur as particles sized from 1 to 100  $\mu\text{m}$ . A considerable amount of research has focused on understanding how CFA forms and on its characteristics [19], but these matters are not fully recognized so far.

In the process of combustion CFA is predominantly created with the participation of the following mechanisms:

- (1) thermal decomposition of mineral matter
- (2) coalescence of mineral particles
- (3) direct fragmentation of mineral particles
- (4) evaporation and subsequent condensation of volatile mineral elements

As a result of the first three mechanisms fine particles are formed, and the last mechanism leads to the formation of submicron particles [34, 40, 44]. Larger particles of fly ash are of secondary importance, since they are eliminated to a high extent in APCDs such as ESP, thanks to which they have small impact on the final level of TE<sub>s</sub> emissions. However, they are important in the formation of a condensation layer and in the reactions of TE<sub>s</sub> vapors, so they influence TE<sub>s</sub> contents in CFA. Greater importance in the emission of TE<sub>s</sub> from fossil fuel burning is related to the formation of smaller particles, the sizes of which enable them to penetrate even through precipitators of relatively high efficiency.

Fig. 2 presents a simplified mechanism of mineral matter transformation in pulverized coal boilers, when both extraneous and organically-bound mineral substances are burned. During heating, coal grains liberate volatile substances, leaving unburned remains. They reach

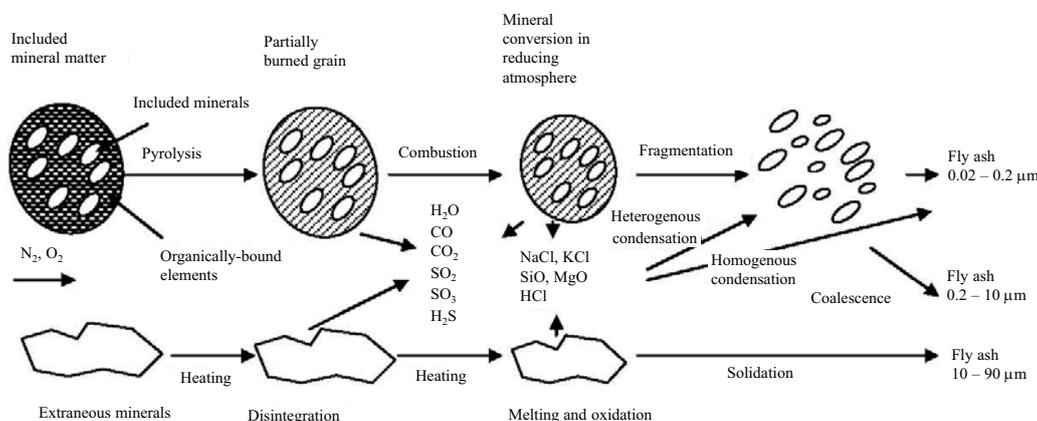


Fig. 2. The mechanism of the transformation of mineral matter during coal combustion in pulverized coal boiler, modified after Tomeczek and Palugniok [34].

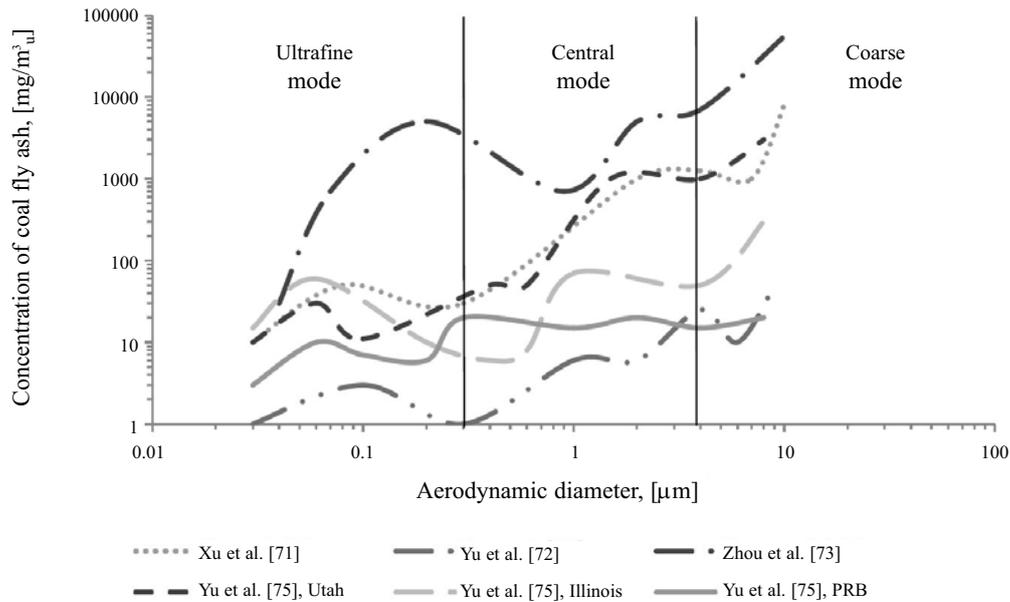


Fig. 3. Comparison of different tri-modal distributions of fly ash particles from the combustion of Chinese coals [71-73] and US coals from Utah, Illinois, and Powder River Basin (PRB) [75].

much higher temperatures than mineral particles, which contain not more than 10% of organic matter. Ultrafine mineral fly ash particles, sized less than  $0.1 \mu\text{m}$ , are formed from gradually disintegrating non-flammable remains. The decomposition of mineral matter and its solid phase remains leads to the production of gases that react and condense. Condensation and mineral constituents fragmentation cause the forming of CFA particles sized  $0.02\text{-}0.2 \mu\text{m}$ . The coalescence of small particles creates particles of average size  $0.2\text{-}10 \mu\text{m}$ . The largest particles ( $10\text{-}90 \mu\text{m}$ ) are generated from the disintegration of extraneous minerals [34].

According to many studies the particle size distribution (PSD) of fly ash produced during pulverized coal combustion is bimodal [22, 38, 40, 42, 44]. For example, Zhao et al. [42] studied the emission factors from eight Chinese coal-fired power plants. For all investigated boilers, these authors found the bimodal PSD in flue gases after fly ash collectors (with peaks of submicron and coarse modes at  $0.2\text{-}0.3$  and  $2\text{-}3 \mu\text{m}$ , respectively). Larger particles originating from extraneous minerals were concentrated to a diameter of around  $10 \mu\text{m}$ .

However, recent experimental and modeling studies reported an additional central particle mode between the commonly observed two modes of fly ash PSD [71-75]. According to Xu et al. [71], the ultrafine mode has a very small size distribution ( $< 0.2$  or  $< 0.3 \mu\text{m}$ ), coarse mode is larger than  $3$  or  $5 \mu\text{m}$ , and central mode is found in the size range of  $0.2\text{-}3 \mu\text{m}$  or  $0.3\text{-}5 \mu\text{m}$ . The formation of the ultrafine and the coarse modes are believed to be due to vaporization-condensation and mineral coalescence plus char fragmentation, respectively [72, 73], while central mode is attributed to heterogeneous condensation on fine residual ash particles [71]. Comparison of the recent results concerning tri-modal distribution of CFA particles is shown in Fig. 3.

### The Influence of Coal Grain Size and Combustion Conditions on the Formation of CFA

The grain size of burned coal influences the concentration and particle distribution of CFA. To study these relationships Ninomiya et al. [22] conducted a laboratory-scale experiment with a drop-tube furnace. The results show that when the diameter of coal grain decreases, fly ash concentration increases. When coal with grain size up to  $63 \mu\text{m}$  is burned, CFA concentration is about three times higher than in the case of coal with grain diameters between  $125$  and  $250 \mu\text{m}$  [22]. Fig. 4 shows the concentration of fly ash particles as measured in flue gases after combustion of three different Chinese coals with three different grain sizes each.

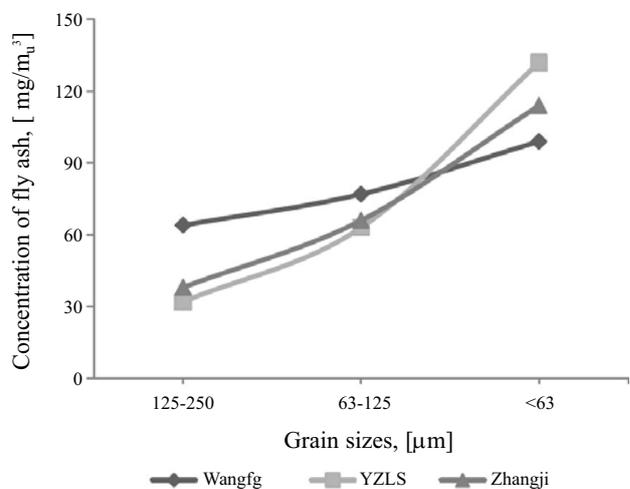


Fig. 4. Concentration of fly ash particles in flue gases from burning three different Chinese coals with three different grain sizes each, based on data from [22].

The research of Xiaowei et al. [40] demonstrated that during combustion of coal grains of 125-250  $\mu\text{m}$ , the fly ash PSD is bimodal with the maxima at around 4.0  $\mu\text{m}$  and 10.0  $\mu\text{m}$ . The share of particles smaller than 0.1  $\mu\text{m}$  is insignificant. Particles sized above 1.0  $\mu\text{m}$  comprise mainly non-flammable elements. These results show that mineral constituents are the main factor causing the formation of fly ash particles during combustion of coal grains of 125-250  $\mu\text{m}$ . For coal grains of 63-125  $\mu\text{m}$  similar results were obtained, while for smaller coal grains (< 63  $\mu\text{m}$ ) the resulting PSD differs significantly, especially for submicron particles. The bimodal distribution reaches maximum for 4.0  $\mu\text{m}$  and a smaller peak for 0.5  $\mu\text{m}$  particles. For the creation of 4.0  $\mu\text{m}$  diameter particles the transfer of minerals is important. In comparison with the two above-mentioned sizes, coal grains sized up to 63  $\mu\text{m}$  are richer in mineral inclusions that can be easily transferred to fly ash particles. On the other hand, a significant amount of  $\sim 0.5$   $\mu\text{m}$  particles means that other factors may also be involved in their formation [40].

The size distribution of CFA from EPPs and TPPs is to a large extent dependent also on combustion conditions. There is significant difference in fly ash PSD depending on combustion temperature and oxygen concentration [40, 44]. Xiaowei et al. [40] showed that when the content of oxygen amounts to 20% and the temperature rises from 1375 K to 1525 K, particle concentration rises insignificantly; however, when the temperature increases up to 1675 K, a significant concentration increase – more than three-fold for 0.1  $\mu\text{m}$  particles – is observed. There can be two reasons for the particle concentration increase along with the temperature. One is that higher temperature causes coal grain decomposition, which leads to the formation of a large number of small grains. Each fragment of the decomposed grain may or may not contain mineral substances. The second reason is that many mineral substances, especially those contained in < 10  $\mu\text{m}$  particles, can separate from burning grains and join fly ash without phase alternation (solid-to-particles path). The study of Zhang et al. [44] confirms the increased formation of submicron particles with the increase of coal combustion temperature.

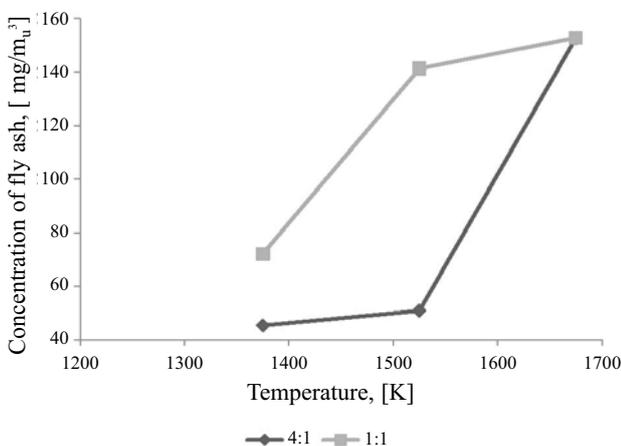


Fig. 5. The effect of reaction temperature and the  $\text{NO}_2$  to  $\text{O}_2$  ratio of on the formation of < 10  $\mu\text{m}$  particles, based on data from [40].

During the combustion of low-quality coal in low temperature, non-flammable oxides, MgO and CaO, are considered to be the compounds that dominate fine fly ash particles, whereas in the case of high-quality coal,  $\text{SiO}_2$  prevails.

The effect of the reaction temperature and the ratio of  $\text{NO}_2$  to  $\text{O}_2$  on the formation of CFA particles with diameter < 10  $\mu\text{m}$  is presented in Fig. 5. The results of the experiment show that when  $\text{O}_2$  concentration accounts for 50%, concentration of < 10  $\mu\text{m}$  particles in flue gases is much higher than when it is of 20% [40, 73]. Similar results have been obtained by Fix et al. [74], who studied the impact of excess air of 5%, 20%, and 35% on fly ash PSD. These authors showed that the low oxygen content is lowering the coal grain temperature and the mineral components do not melt and coalesce to form the larger particles; as a result, the finer sized fractions prevail [74].

### Trace Elements Enrichment

It is well known that TEs undergo enrichment along the pollution stream in combustion utilities. For the EPPs and TPPs, the enrichment factor expresses the elemental behaviour during coal combustion in the various streams of coal-fired plants [31, 45, 46]. In order to determine the concentration of each TE in combustion products (bottom ash, fly ash), the relative enrichment factor (RE) was introduced. RE is variously defined in the literature, one example of which can be the relative enrichment factor suggested by Cenni et al. [76]:

$$RE_{Cenni} = \frac{(C_{if} - C_{ib})}{C_{ib}} C_{if} \quad (1)$$

...where  $C_{if}$  stands for trace element  $i$  concentration in fly ash, and  $C_{ib}$  for trace element  $i$  concentration in bottom ash. An advantage of this factor is that it comprises only values from an ash sample, thanks to which there are no errors resulting from coal analysis.

The enrichment of elements in relation to their contents in raw coal was studied by Meij [30, 31], who measured concentrations and distributions of TEs in coal, bottom ash, pulverized-fuel ash (ash collected in the ESPs), and fly ash in coal-fired power plants in the Netherlands. This author developed a detailed classification of elements based on their occurrence and volatility, and defined RE as a ratio of combustion product concentration to fuel concentration [30]:

$$RE_{Meij} = \frac{C_{in}}{C_{ic}} (A_{ad})_c / 100 \quad (2)$$

...where  $C_{in}$  denotes trace element  $i$  concentration in various combustion products, and  $C_{ic}$  describes trace element  $i$  concentration in raw coal.  $(A_{ad})_c$  is the percentage content of ash in raw coal.

Table 5. Meij's [31] classification of elements based on their behaviour during combustion in boilers and with their relative enrichment (RE) factors.

Class	RE factor	Classified elements	Behavior in installation
I	~ 1	Al, Ca, Ce, Cs, Eu, Fe, Hf, K, La, Mg, Sc, Sm, Si, Sr, Th, and Ti	Not volatile
II a	> 4	Ba, Cr, Mn, Na, and Rb	Volatile in boiler, but complete condensation in ESP on the fly ash particles
II b	2 < - ≤ 4	Be, Co, Cu, Ni, P, U, V, and W	
II c	1.3 < - < 2	As, Cd, Ge, Mo, Pb, Sb, Tl, and Zn	
III	<< 1	B, Br, C, Cl, F, Hg, I, N, S, and Se	Very volatile: some to hardly any condensation on fly ash particles in ESP

Table 6. Enrichment factors of trace elements as obtained by Huang et al. [39] ( $RE_{Huang}$ ) for different conditions of combustion in a pulverized coal boiler with three-field electrostatic precipitator.

Sample origin	Sample number	Furnace temperature [K]	Excess air factor [-]	Relative enrichment factor $RE_{Huang}$ [-]					
				Cd	Cr	Hg	Mn	Pb	Zn
Bottom ash ( $RE_b$ )	01-01	1417	1.34	1.317	<b>0.656*</b>	0	<b>1.024</b>	<b>0.170</b>	<b>0.388</b>
	02-01	1437	1.37	<b>0.730</b>	0.519	0	0.942	0.351	0.524
	03-01	1412	1.47	1.591	0.584	0	0.883	0.347	0.888
	04-01	1363	1.48	0.931	0.564	0	0.831	0.470	0.525
	05-01	1306	1.47	1.048	0.578	0	0.820	0.393	0.489
Fly ash ( $RE_f$ )	01-02	1417	1.34	0.818	0.336	<b>0.363</b>	0.764	1.022	0.921
	02-02	1437	1.37	0.900	0.333	0.306	0.807	1.190	1.108
	03-02	1412	1.47	1.076	0.394	0.263	0.849	0.918	1.184
	04-02	1363	1.48	1.090	0.354	0.199	0.862	1.107	1.181
	05-02	1306	1.47	1.014	<b>0.299</b>	0.127	0.850	1.141	1.014
Fields 1 ( $RE_f$ )	01-03	1390	1.49	1.024	0.341	0.068	0.821	1.024	1.138
Fields 2 ( $RE_f$ )	02-03			1.895	0.534	0.190	0.596	1.692	1.444
Fields 3 ( $RE_f$ )	03-03			<b>2.807</b>	0.650	0.232	<b>0.552</b>	<b>1.818</b>	<b>1.984</b>

\* Minimum and maximum values are in bold

The Meij's classification presented in Table 5 is the most widely used classification of TEs. It was applied by e.g. Li et al. [77], Huang et al. [39], Bhangare et al. [46], Srinivasa et al. [45], and Goodarzi [57].

However, the enrichment factor defined by Meij considers only ash contents in raw coal, but it does not include its contents in fly and bottom ashes. Therefore, the following improvement was proposed by Huang et al. [39]:

$$RE_{Huang} = \frac{C_{in} (A_{ad})_c}{C_{ic} (A_{ad})_n} \quad (3)$$

...where  $(A_{ad})_n$  stands for ash concentration in various combustion products. The factor reflected by formula (3) describes TE enrichment in various products, normalized to the content of ash in fuel.

The value of  $RE_i = 1$  means that  $TE_i$  is not enriched nor impoverished in fly ash. If  $RE_i$  is larger or smaller than 1,  $TE_i$  is correspondingly enriched or impoverished.  $RE_{Huang}$  for selected trace metals are presented in Table 6 and Fig. 7.

Based on data from Table 6, it can be stated that the decrease in oxygen concentration (with a slight increase of temperature) increases the content of some TEs like Cr, Mn, and Zn in the ash, and Hg in the fly ash. For Cd, Pb, and Zn, large enrichment in the last fields of ESP is seen. From Fig. 7 it can also be noticed that the majority of TEs has a tendency to be deposited on smaller particles. The smaller the fly ash diameter, the bigger the TE enrichment. Only Mn is characterized by an opposite trend – the smaller the fly ash diameters, the smaller the enrichment factor. Between the first and the third zone of an ESP, particle diameter decreases and fly ash surface increases. Metals evaporate from coal during combustion and condense again

Table 7. Concentrations of trace elements in Polish hard coal and its combustion products according to Pacyna [23].

Trace element	Concentration [ppm]							
	Miechowice Power Plant				Łagisza Power Plant			
	Coal	Bottom ash	Fly ash before ESP	Fly ash after ESP	Coal	Bottom ash	Fly ash before ESP	Fly ash after ESP
As	40.10	56.00	206.10	498.00	67.60	82.10	259.50	548.20
Hg	0.09	0.09	0.02	0.00	0.08	0.09	0.01	0.00
Pb	14.30	20.90	56.60	280.00	17.60	30.80	67.50	380.00
Zn	38.40	74.00	201.00	470.00	65.00	99.00	248.00	520.00

in the post-combustion zone. Fly ash particles with diameter ranging from 0.01 to 0.1  $\mu\text{m}$  are formed mainly as a result of the evaporation and condensation of major elements such as C, Si, and Fe. The large surface of submicron particles can cause the deposition of a larger part of TEs on them, which leads to the enrichment of some elements [23, 39].

Polish research on TEs enrichment during coal combustion was carried out by Pacyna [23], Mazur and Koniecznyński [24], and Wojnar and Wisz [54]. The results obtained by Pacyna for the Miechowice and Łagisza EPPs are presented in Table 7, while those of Wojnar and Wisz in Table 8. Mazur and Koniecznyński conducted their research in the Jaworzno and Łagisza EPPs, as well as in Kraków TPP [24].

The results given in Tables 7 and 8 show that all analyzed TEs undergo significant enrichment along the pollution stream in combustion utilities of Polish EPPs. Among the combustion products, the highest concentrations of TEs are present in fly ash after ESP. For Hg, fly ash concentration amounts even to 1 ppm (Table 8).

Pacyna [23] divided the elements into two groups, depending on their boiling and melting temperatures, as well as the heat of evaporation. Until now, this is the widest

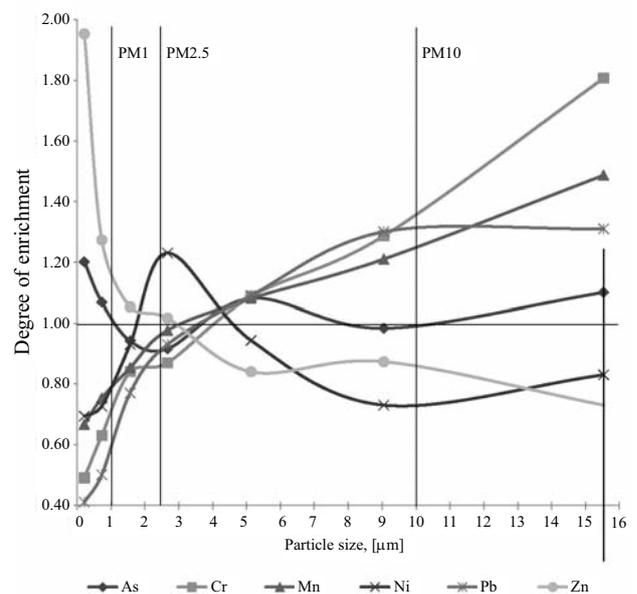


Fig. 7. The degree of enrichment of trace elements in different fractions of particulate matter emitted into the atmosphere, averaged for Jaworzno III, Kraków S.A. and Łagisza power plants (Pb only for Jaworzno III power plant). Authors' elaboration based on data from [24].

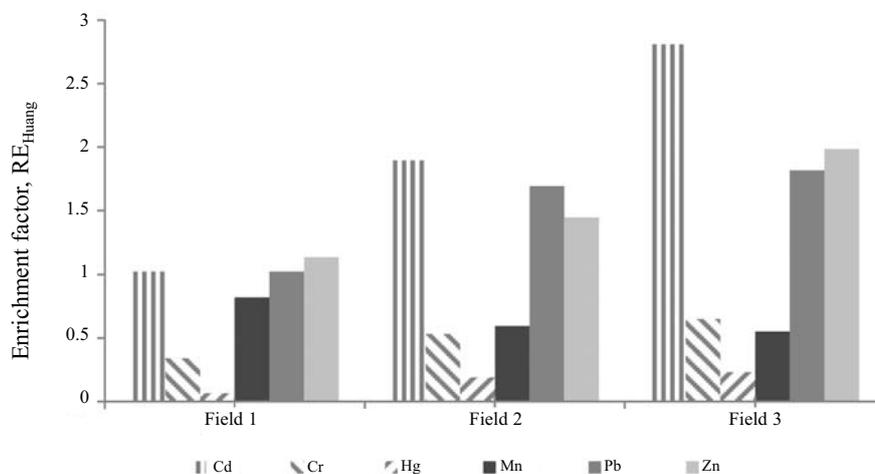


Fig. 6. Relationship between  $RE_{Huang}$  of trace elements in fly ash and order of fields of electrostatic precipitator, based on data from [39].

Table 8. Mercury concentrations in Polish hard coal and its combustion products based on measurements of CLE Energopomiar, according to Wojnar and Wisz [54].

Object	Concentration of Hg [ppm]		
	Coal	Bottom ash (dry mass)	Fly ash (dry mass)
1	0.064-0.100	0.009-0.016	0.126-0.265
2	0.097-0.141	0.006-0.010	0.445-1.000
3	0.084-0.120	0.002-0.005	0.372-0.468
4	0.053-0.092	0.002-0.011	0.187-0.476
5	0.100-0.105	0.004-0.005	0.374-0.486
6	0.093-0.132	0.002-0.005	0.224-0.229
7	0.066-0.109	0.005-0.017	0.318-0.554
8	0.054-0.124	0.004-0.011	0.229-0.539
9	0.056-0.090	0.013-0.030	0.378-0.710

TEs classification reported in Poland. This author concluded that [23]:

- (1) the more volatile the metal, the better it enriches
- (2) low-volatile metals are subject to little enrichment compared to highly volatile ones
- (3) the more non-metallic properties a metal has, the greater its enrichment along the pollutant stream (due to the ionic potential of non-metallic TEs)
- (4) the metals from the low volatile group (Na, Fe, Ca) are absorbed mainly by particles containing metals from the highly volatile group (As, Zn, Pb, Mo, Sb, Cu)
- (5) the most volatile metals (like Hg and Se) partially penetrate electrostatic precipitators in the gaseous state

While in the case of most TEs contained in coal the process of evaporation plays a significant role, for Hg the processes that have lead to condensation are more important. In combustion conditions Hg acquires a totally gaseous state: Hg<sup>0</sup>. The oxidation of elemental Hg in the gaseous state begins at a temperature of around 350 K. According to the measurements of Hg emissions from different boilers, 5-95% of gaseous Hg can occur in the oxidized form of Hg<sup>+</sup> [31].

Several authors have further studied the partitioning of TEs between different combustion products and classified these elements into three main groups [23, 31, 32, 39, 45, 46]:

- (1) very volatile TEs that remain in gaseous phase through the entire process (Hg is classified to this group by the majority of authors)
- (2) partially volatile TEs that are emitted mostly in fly ash while flue gas cools down
- (3) hardly volatile TEs that are equally distributed between bottom ash and fly ash

However, the classification criterion applied in these studies was not entirely the same, have nor all the elements been considered. Moreover, country-specific coal properties, as well as power plant characteristics, influence the results. For example, Pacyna [23] classified As and Zn (which correspond to [24] and [46]), as well as Pb and Cu (which is contradictory to both [24] and [46]) to group 2; while Mg (which is inconsistent with [46]) to group 3. Highly toxic elements, Cd and Cr, were not analyzed by Pacyna [23], but in other studies Cd was found to be volatile [39] or semi-volatile [46]. Cr is the most difficult to classify, as its mode of occurrence in coal is known with the least confidence [78]; as it was already discussed, it may be associated with both organic and mineral parts of coal. Although some authors classified Cr to group 3 [46], the

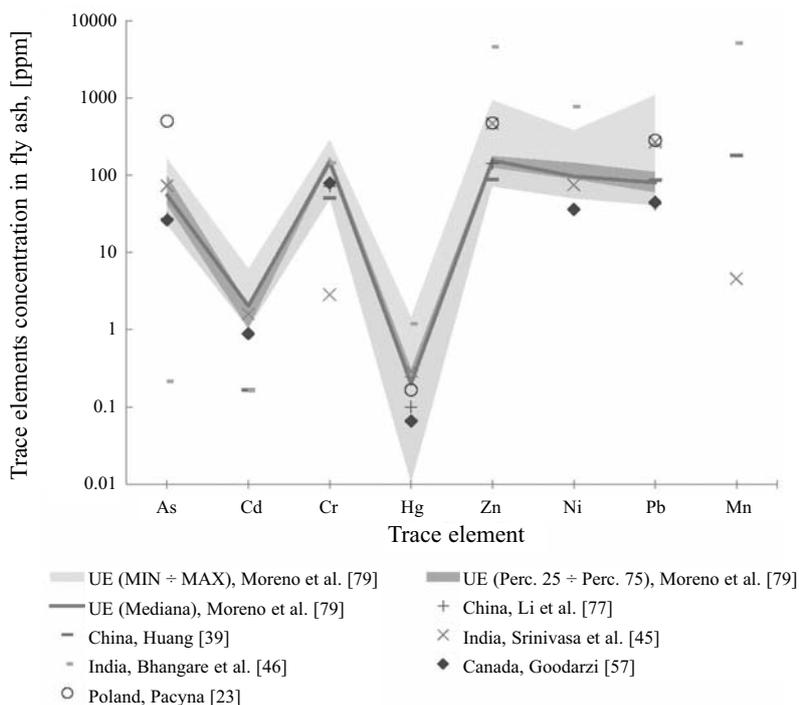


Fig. 8. Trace elements contents in fly ash after the electrostatic precipitator, according to different authors.

Table 9. Trace elements contents in fly ash after the electrostatic precipitator according to different authors.

Country, Author, source	Trace elements contents in fly ash after the electrostatic precipitator [ppm]							
	As	Cd	Cr	Hg	Mn	Ni	Pb	Zn
Europe, MIN, Moreno et al. [79]	22.00	1.00	47.00	0.01		49.00	40.00	70
Europe, Perc.25, Moreno et al. [79]	40.00	1.00	137.00	0.20		87.00	59.00	123
Europe, Median, Moreno et al. [79]	55.00	2.00	148.00	0.20		96.00	80.00	154
Europe, Perc.75, Moreno et al. [79]	97.00	2.00	172.00	0.30		144.00	109.00	175
Europe, MAX, Moreno et al. [79]	162.00	6.00	281.00	1.40		377.00	1075.00	924
China, Li et al. [77]	27.33		71.33	0.10			41.50	140
China, Huang et al. [39]		0.17	50.00	0.07	178		86.00	88
India, Srinivasa et al. [45]	72.30	1.57	2.80	0.29	4	73.90	266.10	465
India, Bhangare et al. [46]	0.22	0.16	143.86	1.18	5116	771.82	238.93	4598
Canada, Goodarzi [57]	25.81	0.87	78.34	0.07		35.68	44.28	
Poland, Pacyna [23]	498.00			0.17			280.00	470

more adequate solution was proposed by Huang et al. [39], who proposed classifying Cr to group 3, but only if most of it in coal is associated with minerals. In the case when most Cr is associated with organics, it should constitute a special group. In addition, TEs associated with sulphide minerals and organic matter were found to be more volatile compared to those in different chemical forms, like oxides [46].

Mazur and Koniecznyński examined TEs enrichment in selected particle fractions  $f$ , which is reflected by equation 4 [24]:

$$Sw_f = \frac{C_f}{C_{sr}} \quad (4)$$

...where  $Sw_f$  stands for the degree of TE enrichment in particle fraction  $f$ ,  $C_f$  for TE concentration in particle fraction  $f$ ,  $\mu\text{g/g}$ , and  $C_{sr}$  for average weighted concentration with weights reflecting mass percent share of individual fractions in the emitted fly ash  $\mu\text{g/g}$ . Herein we averaged  $Sw_f$  calculated by Mazur and Koniecznyński [24] for different Polish plants in order to obtain the pattern of enrichment of selected TEs in different fractions of emitted fly ash (Fig. 7).

From the results presented in Fig. 7 it can be concluded that As and Zn are enriched in the emitted submicron particulates, Ni in the fine ones, while Cr, Mn, and Pb in the coarse and bigger particulates. Concerning Mn, these results correspond to Huang et al. [39] and to Bhangare et al. [46].

Finally, it should be pointed out that the discrepancies in the classification of TEs described above are also present in the degree of enrichment assigned to them by different authors. For example, the majority of authors agree that Cd undergoes high enrichment in CFA [31, 32, 38, 45, 46], while Na is not enriched [23, 31, 32]. In the case of As and Pb, the results are dispersed; some authors report

high As [23, 31, 32] and Pb [23, 31, 32, 39, 46] enrichment, while others did not find it for As [24, 46] nor Pb [24, 45]. In addition, the enrichment of As was found to increase highly along with combustion temperature [35, 36]. Comparison of RE factors obtained by various authors is shown in Fig 8.

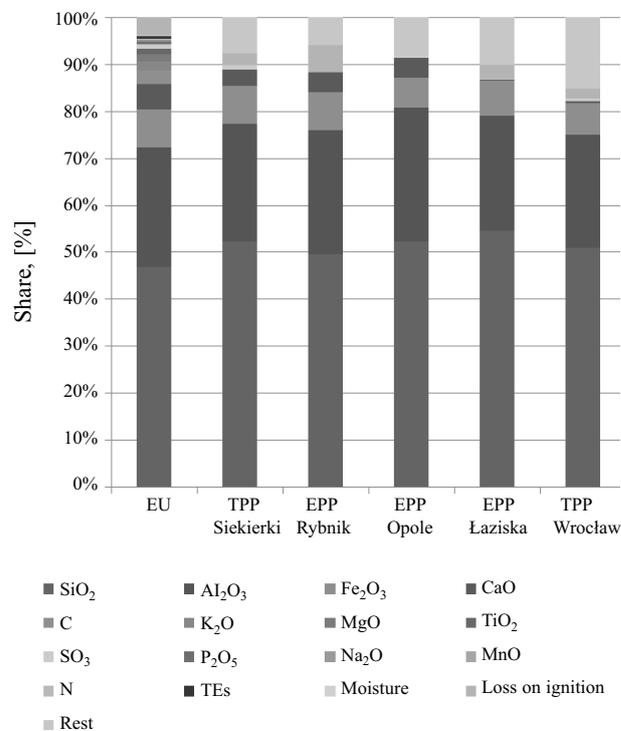


Fig. 9. The mineralogical and chemical composition of fly ash from coal combustion in energy and transformation industries. Data for Europe averaged for 23 sources by Moreno et al. [79], Polish sources based on Galos and Uliasz-Bocheńczyk [80] (missing components for Polish power plants included in the item – the rest).

### Composition of CFA Emitted to Ambient Air

CFA is composed mainly of amorphous or glassy aluminosilicates along with some crystalline compounds. Most of the CFA from pulverized coal boilers have pozzolanic properties and are characterized by [79]:

- (a)  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 70\%$
- (b)  $\text{SO}_3 < 5\%$
- (c) moisture content  $< 3\%$
- (d) loss on ignition (LOI)  $< 6\%$

The composition of the European and Polish CFA is shown in Fig. 9.

As Si and Al evaporate only to a small extent, they dominate elements in the emitted particulate fraction ranging from 1 to 10  $\mu\text{m}$  ( $\text{PM}_{1-10}$ ) [34, 40]. Among alkaline elements, the majority of K and Na is contained in  $\text{PM}_1$ . Similarly, most of P is contained in  $\text{PM}_1$  as well. Also, S is very important as it dominates  $\text{PM}_1$ , and its concentration substantially exceeds the contents of alkaline elements. This means that there is a possibility of formation of sulphates in  $\text{PM}_1$  (e.g.  $\text{Na}_2\text{SO}_4$ ) and aluminium silicates (e.g.  $\text{SiO}_2$ ,  $\text{Al}_6\text{Si}_2\text{O}_{13}$ , and  $\text{NaAlSi}_3\text{O}_8$ ) in  $\text{PM}_{1-10}$  during coal combustion [40, 81]. The central mode particles ( $\sim 4 \mu\text{m}$ ) are found to be enriched in As and Cd. As a result of vaporization of TEs at high temperatures and their condensation or adsorption on the surface of the particles at lower temperatures, the concentration of some elements such as As, Cd, Cr, Ni, Pb, and Zn significantly increases with decreasing particle size. By heterogeneous condensation, adsorption, or reaction, the surface layer of particles also is enriched in volatile elements compared to ash particle cores [71, 72].

Concerning the overall TEs amount, in the recent study by Bhangare et al. [46], conducted in India, the relative elemental abundance in emitted CFA was found to be in the order of  $\text{Fe} > \text{Mn} > \text{Zn} > \text{Cu} > \text{Cr} > \text{Ni} > \text{Mg} > \text{Pb} > \text{Li} >$

$\text{Co} > \text{Hg} > \text{Cd} > \text{As}$ . The order of median contents of TEs reported for European CFA by Moreno et al. [79] was similar, however As was showing greater, and Cd and Hg smaller concentrations:  $\text{Zn} > \text{Cr} > \text{Ni} > \text{Pb} > \text{As} > \text{Cd} > \text{Hg}$ .

Comparison of TE contents in CFA collected after dedusting in ESP as reported by various authors is given in Table 9 and illustrated in Fig. 10. From this data, it is clear that the reported concentrations of TEs vary considerably between elements and, according to different authors, for the same element. Concentrations of As in the European CFA ranges from 22 to 169 ppm, while median value equals 55 ppm [79]. The smallest As content is reported for India (0.22 ppm, [46]) and the larger one for Poland (498 ppm, [23]). The concentrations of Cd vary from 1 to 6 ppm in Europe, at the same time being quite small in China (0.17 ppm, [39]) and India (0.16 ppm, [46]). Cr concentration in Europe amounts to 47-281 ppm, whereas in India varies from 3 ppm [45] to 144 ppm [46]. The values for Hg range from 0.01 ppm (European minimum) to 1.4 ppm (European maximum). Ni and Zn are present in CFA in relatively high concentrations with 96 ppm (Ni) and 154 ppm (Zn) as European median values, and 772 ppm (Ni) and 4598 (Zn) as reported from India [46]. Finally, all reported Pb concentrations are in the range of European data and differ from 40 ppm to as much as 1075 ppm.

### Summary and Conclusions

The issue of coal fly ash formation and composition is complex because of the transformations that the mineral coal impurities undergo during high-temperature combustion and post-combustion processes. These transformations depend on various factors such as: the mode of occurrence of TEs in coal and their concentrations, coal grain size distribution, combustion conditions (temperature, content of oxygen) and their interactions during, as well as after com-

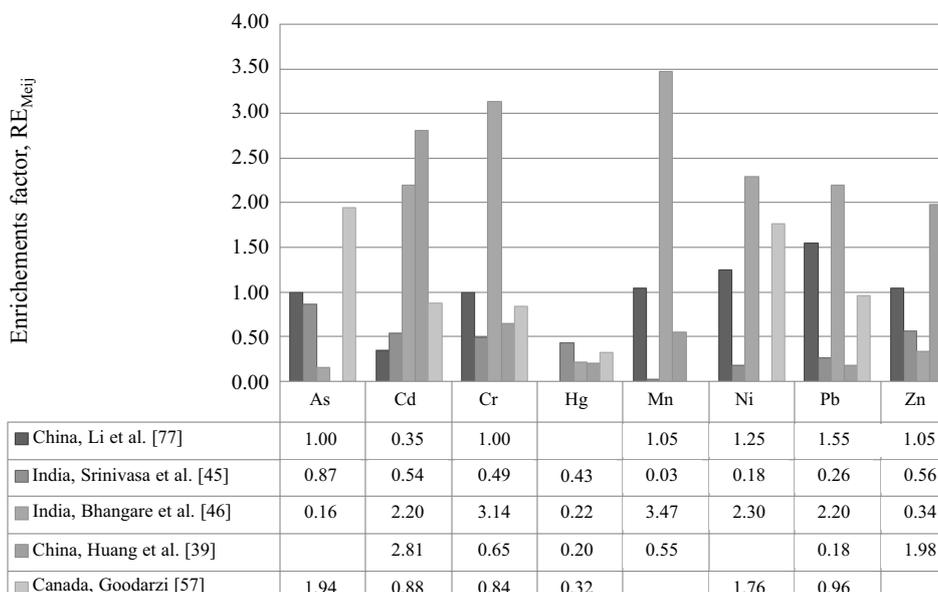


Fig. 10. Comparison of trace element enrichment factors in fly ash after the electrostatic precipitator,  $RE_{Meij}$ , according to different authors.

bustion. In this paper we compared and analyzed the experimental data concerning TE emissions from bituminous coal combustion in pulverized coal boilers for heat and electricity production purposes.

The results show that the particulate size distribution of CFA is bi- or tri-modal and influenced primarily by the temperature of combustion. High temperature causes more ultrafine (with diameter  $< 0.1 \mu\text{m}$ ) and medium (with diameter  $< 5 \mu\text{m}$ ) particles to be formed, and the excess air determines which fraction prevails. When the concentration of oxygen is high, medium fraction dominates. The majority of TEs have a tendency to deposit on smaller particles. Therefore, the smaller the diameter of fly ash, the higher the enrichment of trace elements. Volatile metals having non-metallic properties – As, Cu, Mo, Pb, Sb, and Zn – are usually more enriched along the pollution stream.

Based on the comparative analysis of the results obtained by different researchers, we can determine three groups of elements. The first group comprises Cr, Mn, and Pb, the majority of which is contained in the coarse fraction of emitted fly ash ( $\text{PM}_{2.5-10}$ ) and larger. The second group includes As and Zn, which are contained mainly in submicron  $\text{PM}_1$  particles and even ultrafine  $\text{PM}_{0.1}$  ones due to fly ash fragmentation. The third group contains Ni, the highest concentrations of which are observed in particles with diameters of  $2.5 \mu\text{m}$  and  $5 \mu\text{m}$ . Additionally, Hg is mainly present in the gaseous part of exhaust gases as a result of high combustion temperature. When the excess air factor increases, the increase in the enrichment factor of Cd, Cr, Mn, and Zn in CFA can be noticed, while the enrichment of Hg decreases.

Relatively high concentrations of Cr, Ni, Pb, and As in the European CFA emitted to ambient air from power plants are of great concern because of the underlying health risks of these trace elements. In addition, the elements enriched within very fine and ultrafine fractions of CFA are able to penetrate lungs and get into the blood circulation system, posing a serious threat to human health. We showed that As is typically accumulated in these fractions, which is especially dangerous, as this TE has been classified by the WHO as carcinogenic and is also known to cause chronic diseases and damage to the digestive system, as well as anaemia [20, 82]. Moreover, in the recent study of Juda-Rezler et al. [83], As was found to be a marker of industrial sources of PM.

Except for the above findings, it should be highlighted that our review of the literature clearly demonstrates that although the formation of the CFA, its PSD, and composition is fairly well understood, its dependence on the type of coal burned, combustion conditions, and the applied flue gas cleaning technology is so large that research should be undertaken for each specific coal rank, its depositional environment, and combustion facility.

Finally, it should be also pointed out that coal combustion for power and heat generation is a main source of Hg emissions in Poland (56% of total Hg emission) and a significant source of Ni emissions (20% of total Ni emissions) [84]. For other TEs analyzed herein, the combustion processes in industry (for As and Pb); in residential sector

(for Cd, Cr and Ni) or in both industry and residential sectors (Zn), dominate in total country emissions. Therefore, it seems essential to carry out research on the impact of coal parameters and conditions of combustion process on the volume, size, distribution and composition of CFA emitted from different sectors of the national economy. The results of such research would enable the application of the best solutions in order to reduce exposure of the population to the negative impacts of particulate matter and toxic trace elements therein.

### Acknowledgements

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