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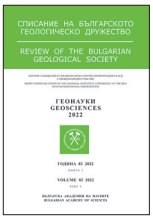

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Cadmium concentrations in coals and fly ashes from coal fired thermoelectric power plants in Bulgaria

Съдържание на кадмий във въглища и пепели от български топлоелектрически централи в България

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Abstract. The goal of the present study is to present new data regarding concentration and distribution of Cd in feed coals and fly ashes from seven Bulgarian coal fired thermoelectric power plans (TPPs). The study was performed on feed coals and fly ashes collected from Maritza East 2, Maritza East 3, Maritza 3, Republika, Bobov Dol, Varna and Russe TPPs. Bulk fly ash from Maritza East 2 and Maritza East 3 TPPs were obtained and fly ashes from each row of electrostatic precipitators (ESPs) of Maritza 3, Republika, Bobov Dol, Varna and Russe TPPs were also collected. Feed coals from bunkers were sampled at each TPPs. The Cd was determined by using ICP-MS. The present investigation shows that the concentration of Cd in studied coal and fly ashes from almost all TPPs is around the average or lower than Cd content in comparison with Clark values. The exceptions are the fly ashes from the 2-nd and 3-rd row of ESPs from Maritza 3 TPP, where up to 2.5 times higher Cd content was registered. This study shows that Cd concentration in fly ashes gradually increases from the 1st to 3rd and 5th-row of ESP from almost all sampled thermoelectric power plants, whence the conclusion that Cd content increases significantly and is mainly concentrated in the finest fly ash particles.

Keywords: cadmium, coal, fly ash, thermoelectric power plants.

Introduction

During the industrial coal combustion in thermoelectric power plants (TPPs), some part of Cd is released into the environment and another part is associated with solid waste products. The harmful effects of Cd on the environment and human health are well known and due to this reason it is important to determine the concentration and distribution of Cd in coals and their solid waste production, as well as to study the behavior of Cd during combustion process.

The aim of the present study is to present new data regarding concentration, distribution and mode of occurrence of Cd in feed coals and fly ashes from seven Bulgarian coal fired TPPs.

Material and methods

The study was performed on feed coals and fly ashes collected from seven Bulgarian TPPs – Maritza East 2, Maritza East 3, Maritza 3, Republika, Bobov Dol, Varna and Russe. Bulk fly ash from Maritza East 2 and Maritza East 3 TPPs were obtained. Fly ash samples from each row of electrostatic precipitators (ESPs) of Maritza 3, Republika, Bobov Dol, Varna and Russe TPPs were also collected. Feed coals from bunkers were sampled at each TPPs.

The chemical characteristics of coal and FAs were performed according ISO standards. The total sulphur and sulphur forms are determined by using Eschka and ASTM methods, respectively. The Cd was determined by using ICP-MS.

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Table 1. Cadmium concentration, enrichment/depletion factor (EDF), proximate (A, ash yield and W, moisture) and sulphur forms analysis in feed coals and fly ashes from seven Bulgarian thermoelectric power plants (TPP)

Samples Feed coal / Fly Ash (FA)	Cd analysis		Proximate analysis (d), %		Sulphur analysis (a), wt %			
	Cd content, ppm	EDF [a]	A	W	S_{py}	S_{sulph}	S_{org}	S_{total}
Maritza East 2 TPP								
Lignite	0.29	1.2	26.5	23.4	2.1	1.1	0.7	3.9
Bulk FA	1.01	0.8	97.8	0.9	1.0	0.8	0.1	1.9
Maritza East 3 TPP								
Lignite	0.22	0.9	26.5	23.8	2.7	1.2	1.0	4.9
Bulk FA	0.81	0.7	94.0	3.6	0.5	0.6	0.1	1.2
Maritza 3 TPP								
Lignite	0.14	0.6	23.0	13.5	1.9	0.4	1.9	4.2
ESP 1st-row	1.22	1.0	77.9	1.1	2.9	2.6	–	5.5
ESP 2nd-row	1.73	1.4	67.3	3.4	3.7	3.9	–	7.6
ESP 3rd-row	3.01	2.5	93.8	2.0	4.9	5.3	–	10.2
Republika TPP								
Subbituminous coal	0.29	1.2	57.9	6.0	0.8	0.3	0.1	1.2
ESP 1st-row	0.19	0.2	98.6	0.3	0.1	0.2	0.4	0.7
ESP 2nd-row	0.49	0.4	98.8	0.4	0.2	0.2	0.5	0.9
ESP 3rd-row	0.69	0.6	99.1	0.3	0.2	0.2	0.2	0.6
Bobov Dol TPP								
Coal mixture [b]	0.27	1.1	35.8	20.3	0.9	0.2	0.8	1.9
ESP 1st-row	0.36	0.3	99.0	0.1	0.5	0.4	0.2	1.1
ESP 2nd-row	0.38	0.3	99.0	0.1	0.5	0.6	0.1	1.2
ESP 3rd-row	0.54	0.5	99.1	0.1	1.0	0.8	0.0	1.8
Varna TPP								
Bituminous coal	0.19	1.0	15.8	2.3	0.7	0.4	0.4	1.5
ESP 1st-row	0.25	0.2	78.9	0.1	0.2	0.2	0.3	0.7
ESP 2nd-row	0.55	0.5	80.1	0.2	0.4	0.3	0.1	0.8
ESP 3rd-row	0.70	0.6	73.4	0.3	0.1	0.5	0.1	0.7
ESP 4th-row	0.87	0.7	72.4	0.4	0.3	0.3	–	0.6
ESP 5th-row	0.92	0.8	68.4	0.4	0.2	0.2	0.2	0.6
Russe TPP								
Bituminous coal	0.16	0.8	18.1	0.9	0.1	0.6	0.2	0.9
ESP 1st-row	0.74	0.6	82.4	0.2	0.2	0.2	–	0.4
ESP 2nd-row	0.79	0.7	85.1	0.2	0.1	0.2	–	0.4
ESP 3rd-row	0.53	0.4	37.7	0.3	0.3	0.3	–	0.6

[a] EDF – enrichment/depletion factor (a ratio of the mean Cd content in coal samples vs. the Clarke value for Cd in world coals); enrichment/depletion factor (a ratio of the mean element content in FA samples to the Clarke value for Cd in world coal ashes); [b], mixture between subbituminous coal and lignite; A, ash; W, moisture; py, pyrite; sulph, sulphate; org, organic; (a, analytical basis; d, dry basis)

The Clark value for Cd in low-rank coal is 0.24 ppm, in bituminous coal is 0.20 ppm and in coal FAs is 1.2 ppm (Ketris, Yudovich, 2009)

Results and discussion

The data concerning the main characteristics of feed coals and fly ashes including Cd content, cadmium enrichment/depletion factor (EDF), ash and moisture content and sulphur forms are given in Table 1. The Clark value for Cd in low-rank coal is 0.24 ppm, in bituminous coal is 0.20 ppm and in coal FAs is 1.2 ppm (Ketris, Yudovich, 2009). EDF is a coefficient that is calculated as a ratio between the Cd content of the coal / FA samples to the Clark value for Cd in the world coals / FA.

Cd content in feed coals. Cadmium in coals from TPPs vary from 0.14 to 0.29 ppm, where the

highest content was observed in the coal burned in Maritsa East 2 and Republika TPPs (0.29 ppm). It should be noted that, in general, the Cd content of coal from all TPPs is around the average world coal content (Clark value).

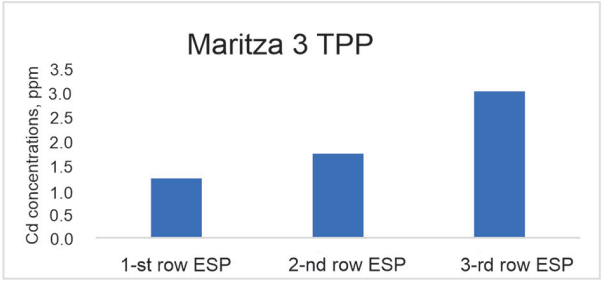
The main mode of occurrence of Cd in coal is mineral matter. Cadmium is mainly associated with sulfide minerals and 60% to 80% of Cd in coal associated with the mineral sphalerite (Finkelman at al., 2019). Another small part of cadmium is present in other less common sulfide minerals such as greenockite for or example (Hower et al., 2018).

Cd content in fly ashes. Cd in the fly ashes in studied TPPs varies from 0.19 to 3.01 ppm. The low content of Cd in fly ashes from almost all TPPs was observed, except for the ashes from Maritsa 3 TPP, where Cd varies from 1.22 to 3.01 ppm.

The distribution of cadmium in fly ash particles captured by different rows of electrostatic precipitators (ESP) from studied TPPs is presented in Figure 1. It is characteristic of the different rows of ESPs that they capture FA particles with different sizes. For example, the first electromagnetic plate (1st-row ESP) captures the largest, and the last (3rd-row or 5th-row ESP respectively) captures the finest FA particles. Taking into consideration the mentioned above, the present study shows that Cd concentration gradually increases from the 1st to 3rd and 5th-row of ESP for FAs from almost all sampled thermoelectric power plants. The only exception is the fly ashes captured from Ruse thermal power plant, where the maximum content of Cd is found in fly ashes captured from 2nd row of ESP which is probably due to the predominance of the sulfate sulfur, which is non-volatile. This trend is clearly reflected in Fig. 1. The conclusion that can be made is that Cd content increases significantly and is mainly concentrated in the finest fly ash particles.

Conclusion

Generally, it can be concluded that the concentration of Cd in studied coal and fly ashes from almost all TPPs is around the average or lower than Cd content in comparison with world Clark values. The exceptions are the fly ashes from the 2nd and 3rd row of ESPs from Maritza 3 TPP, where up to 2.5 times higher Cd content was registered. The present study shows that Cd concentration in fly ashes gradually increases from the 1st to 3rd and 5th-row of ESP from almost all sampled thermoelectric power plants, whence the conclusion that Cd content increases significantly and is mainly concentrated in the finest fly ash particles.



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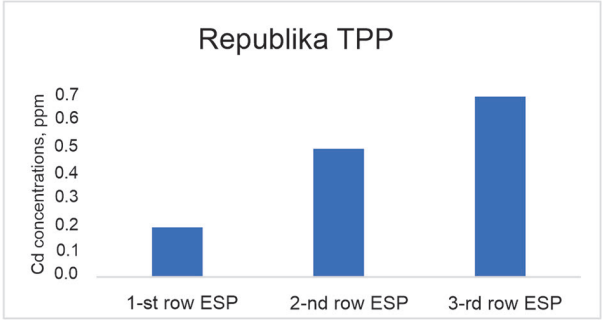

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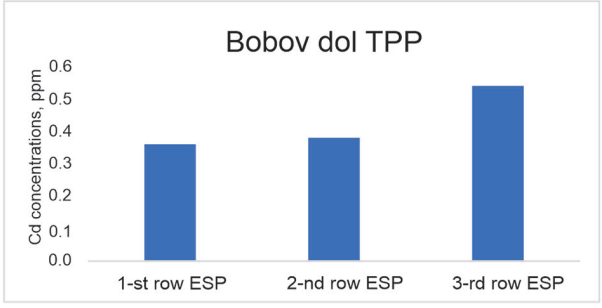

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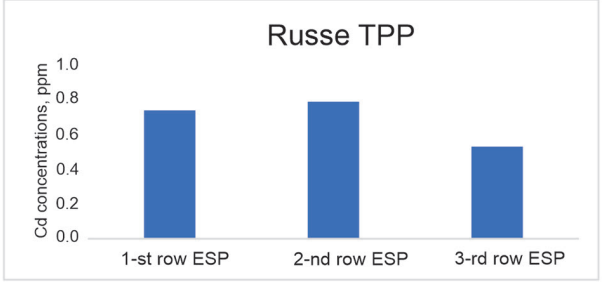

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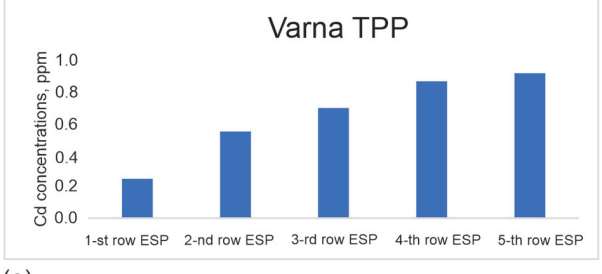

(e)

Fig. 1. Cadmium content in fly ashes (FAs) from different rows of electrostatic precipitators (ESPs) in thermoelectric power plants (TPPs)

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