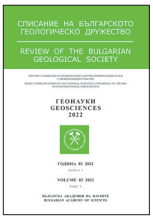
СПИСАНИЕ НА БЪЛГАРСКОТО ГЕОЛОГИЧЕСКО ДРУЖЕСТВО,
год. 83, кн. 3, 2022, с. 105–108

REVIEW OF THE BULGARIAN GEOLOGICAL SOCIETY,
vol. 83, part 3, 2022, p. 105–108



Национална конференция с международно участие „ГЕОНАУКИ 2022“
National Conference with International Participation “GEOSCIENCES 2022”

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

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

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Abstract. The study present new data regarding concentration and distribution of Se in feed coals and fly ashes from seven Bulgarian coal fired thermoelectric power plant (TPPs). The investigation was performed on feed coals and fly ashes from the following 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 and fly ash samples from each row of electrostatic precipitators (ESPs) from Republika, Bobov Dol, Varna and Russe TPPs were collected. Feed coals were also sampled from each TPPs. In order to determine Se concentration more precisely the samples were pre-treated before applying ICP-MS. As a result of the conducted research, the following regularities were established. Elevated amount of Se has been found in the lignite burned in Maritza East 2 and 3 TPPs, while in the bituminous coal burned in Varna and Russe TPPs Se is within the average and below average Se content. The low content of Se in fly ashes from almost all TPPs was observed, except Maritsa 3 TPP, where Se is from 4 to 7 times higher than Clarke value. It was found that the highest concentration of Se is in the finest fly ash fraction.

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

Introduction

During the industrial coal combustion in thermoelectric power plants (TPPs), some part of Se is released into the environment and another part is associated with solid waste - fly and bottom ashes. The negative effects of Se on the environment and human health are well known and due to it is important to establish the concentration, distribution and mode of occurrence of Se in coals and solid waste production, as well as to study the behavior of Se during combustion process. The study was performed on feed coals and fly ashes from seven Bulgarian TPPs – Maritza East 2, Maritza East 3, Maritza 3, Republika, Bobov Dol, Varna and Russe. Bulk fly ash or fly ash samples from each row of electrostatic precipitators (ESPs) from Republika, Bobov Dol, Varna and Russe TPPs were obtained. Feed coals were also collected from bunkers at each TPPs.

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

Material and methods

In order to determine Se concentration more precisely the samples were pre-treated before applying ICP-MS. Pre-treatment procedure includes using ultra-microwave system in order to digest the solid coal and ash samples into liquid. As was determined by ICP-MS with collision cell technique in order to avoid the spectral interference of the Ar-based polyatomic ions following technics published by Li et al. (2014).

https://doi.org/10.52215/rev.bgs.2022.83.3.105

Results and discussion

The data concerning the main characteristics of feed coals and fly ashes including Se content, selenium enrichment/depletion factor (EDF), ash and moisture content and sulphur forms are given in Table 1. The Clark value for Se in low-rank coal is 1 ppm, in bituminous coal is 1.6 ppm and in coal FAs is 8.8 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.

Se content in feed coals. The concentration of Se in coals from TPPs vary from 1.03 to 3.60 ppm, where the highest being in the lignite burned in Maritsa East 2 and 3 TPPs (3.60 and 2.50 ppm) and the calculated enrichment/depletion factor (EDF) of Se shows that the content of Se in them is 3.6 and 2.5 times higher than Clark value for Se in world low-grade coals. The content of Se in the bituminous coal burned in TPP Varna (coal from the Donetsk basin) and in TPP Ruse (coal from the Kuznetsk basin) is lower (2.28 and 1.03 ppm), as the EDF value for them shows that the Se con-

Table 1. Selenium 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)	Se analysis		Proximate analysis (d), %		Sulphur analysis (a), wt %			
	Se content, ppm	EDF [a]	A	W	S_{py}	S_{sulph}	S_{org}	S_{total}
Maritza East 2 TPP								
Lignite	3.60	3.6	26.5	23.4	2.1	1.1	0.7	3.9
Bulk FA	5.73	0.7	97.8	0.9	1.0	0.8	0.1	1.9
Maritza East 3 TPP								
Lignite	2.50	2.5	26.5	23.8	2.7	1.2	1.0	4.9
Bulk FA	4.32	0.5	94.0	3.6	0.5	0.6	0.1	1.2
Maritza 3 TPP								
Lignite	1.98	2.0	23.0	13.5	1.9	0.4	1.9	4.2
ESP 1st-row	37.96	4.3	77.9	1.1	2.9	2.6	-	5.5
ESP 2nd-row	40.20	4.6	67.3	3.4	3.7	3.9	-	7.6
ESP 3rd-row	65.75	7.5	93.8	2.0	4.9	5.3	-	10.2
Republika TPP								
Subbituminous coal	1.04	1.0	57.9	6.0	0.8	0.3	0.1	1.2
ESP 1st-row	1.23	0.1	98.6	0.3	0.1	0.2	0.4	0.7
ESP 2nd-row	2.41	0.3	98.8	0.4	0.2	0.2	0.5	0.9
ESP 3rd-row	3.31	0.4	99.1	0.3	0.2	0.2	0.2	0.6
Bobov Dol TPP								
Coal mixture [b]	1.10	1.1	35.8	20.3	0.9	0.2	0.8	1.9
ESP 1st-row	2.03	0.2	99.0	0.1	0.5	0.4	0.2	1.1
ESP 2nd-row	1.73	0.2	99.0	0.1	0.5	0.6	0.1	1.2
ESP 3rd-row	2.55	0.3	99.1	0.1	1.0	0.8	0.0	1.8
Varna TPP								
Bituminous coal	2.28	1.4	15.8	2.3	0.7	0.4	0.4	1.5
ESP 1st-row	2.45	0.3	78.9	0.1	0.2	0.2	0.3	0.7
ESP 2nd-row	3.95	0.5	80.1	0.2	0.4	0.3	0.1	0.8
ESP 3rd-row	6.64	0.8	73.4	0.3	0.1	0.5	0.1	0.7
ESP 4th-row	11.02	1.3	72.4	0.4	0.3	0.3	-	0.6
ESP 5th-row	12.59	1.4	68.4	0.4	0.2	0.2	0.2	0.6
Russe TPP								
Bituminous coal	1.03	0.6	18.1	0.9	0.1	0.6	0.2	0.9
ESP 1st-row	3.19	0.4	82.4	0.2	0.2	0.2	-	0.4
ESP 2nd-row	2.47	0.3	85.1	0.2	0.1	0.2	-	0.4
ESP 3rd-row	3.90	0.4	37.7	0.3	0.3	0.3	-	0.6

[a], EDF – enrichment/depletion factor (a ratio of the mean Se content in coal samples vs. the Clarke value for Se in world coals); enrichment/depletion factor (a ratio of the mean element content in FA samples to the Clarke value for Se 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 Se in low-rank coal is 1 ppm, in bituminous coal is 1.6 ppm and in coal FAs is 8.8 ppm (Ketris, Yudovich, 2009).

tent is around and below Clarke value for bituminous coal.

Selenium is present in both organic and inorganic coal matter. In most coals, sulfide minerals are likely the primary host of Se. When Se present in pyrite its usually substitute S in pyrite structure (Kolker, 2012). Another part of Se is connected with selenides in coal. Clausthalite is very common accessory mineral in coal and is a host for Se (Finkelman et al., 2019). Other selenides reported in coal include some rare Se-bearing minerals like ferroselite, krutaite, eskebornite and tiemannite (Dai et al., 2015; Finkelman, 2003).

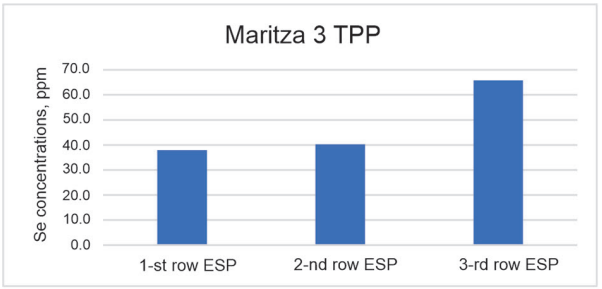
Se content in fly ashes. Se in the fly ashes from studied TPPs varies from 1.23 to 65.75 ppm. The low content of Se in fly ashes from almost all TPPs was observed, except for the ashes from Maritsa 3 TPP, where Se varies from 37.96 to 65.75 ppm and these values are 4.3 to 7.5 times higher than Clark value.

The distribution of Se 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 investigation represent that Se amount increases from the 1st to 3rd and 5th-row of ESP for FAs from almost all sampled thermoelectric power plants. This trend is clearly shown in Figure 1. The conclusion that can be made is that Se concentration increases significantly and is mainly concentrated in the finest fly ash particles.

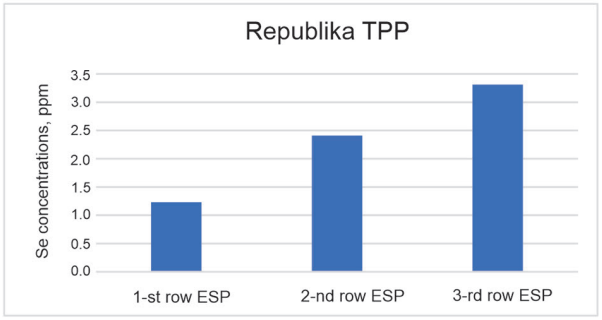
Conclusion

It can be concluded that increased Se content is found in the lignite burned in Maritza East 2 and 3 TPPs, while in the bituminous coal burned in Varna and Russe TPPs Se is within the average and below average Se content. The low content of Se in fly ashes from almost all TPPs was observed, except Maritsa 3 TPP, where Se is from 4 to 7 times higher than Clarke value. The present investigation represent that Se amount increases from the 1st to 3rd and 5th-row of ESP for FAs from almost all sampled thermoelectric power plants. The conclusion is that Se concentration increases significantly and is mainly concentrated in the finest fly ash particles.

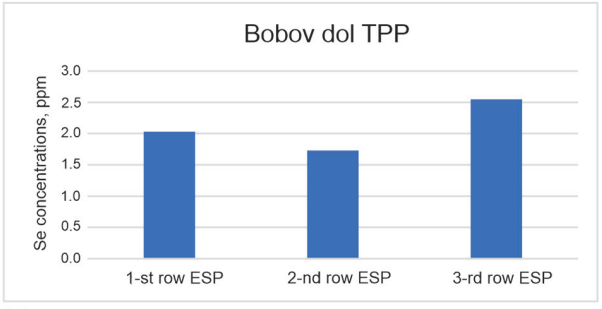
Acknowledgements: This research was supported by the Bulgarian National Science Fund in the frame of the project КП-06-Н34/2019. Many thanks to prof. Shifeng Dai for the opportunity to conduct



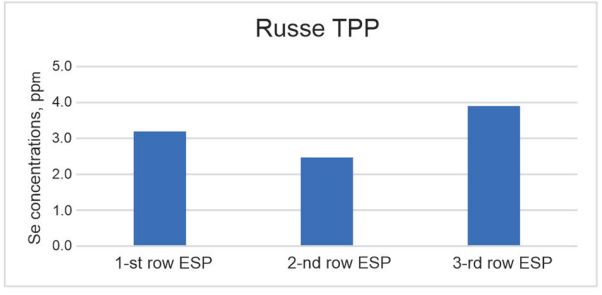
(a)



(b)



(c)



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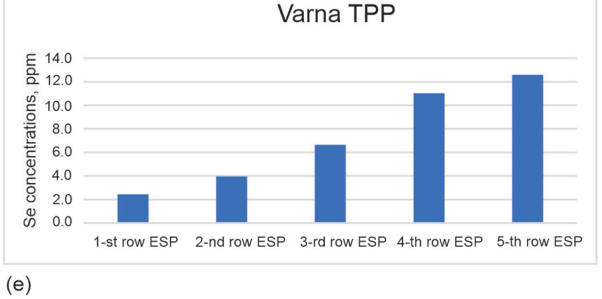

(e)

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

Se analysis in the University of Mining and Technology in Beijing, China.

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