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Arsenic in feed coals and fly ashes from Bulgarian coal fired thermoelectric power plants

Арсен във въглища и пепели от български топлоелектрически централи

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Introduction

During the industrial combustion of solid fuels in thermoelectric power plants (TPPs), a huge amount of arsenic is released into the environment, which is emitted into the atmosphere or associated with solid waste by-products associated with fly ash and bottom ash. The harmful effects of arsenic on the environment and human health are well known and it is important to establish the concentration, distribution and mode of occurrence of arsenic in coal and solid waste products, as well as to study the behavior and transformations of As during the combustion process. The goal of this study is to present new data regarding As content in feed coals and fly ashes from seven coal fired TPPs. To determine the As content, a new analytical methodology was used, much more precise and accurate than the conventional one, proposed by Li et al. (2014). It includes pre-treatment of the samples and subsequent determination of As by using ICP-MS.

Sampling and analytical procedures

The study was performed on feed coals and fly ashes (FAs) from the following TPPs Maritza East 2, Maritza East 3, Maritza 3, Republika, Bobov Dol, Varna and Russe. Bulk fly ashes from Maritza East 2 and Maritza East 3 TPPs and fly ash samples from each row of electrostatic precipitators (ESPs) of Maritza 3, Republika, Bobov Dol, Varna and Russe were obtained. Feed coals from bunkers were also collected at each TPPs. The chemical characteristics of coal and ash samples including proximate and ultimate analysis were performed according ASTM methods. Arsenic in the coal and FAs was determined by ICP-MS in the University of Mining and Technology in Beijing. In order to determine As amount 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 (Li et al., 2014) in order to avoid the spectral interference of the Ar-based polyatomic ions.

Results and discussions

The data concerning the main characteristics of feed coals including As content, ash content, moisture, volatile matter, fixed carbon and sulphur forms are given in Table 1. The fly ash parameters including As concentration, proximate, ultimate and sulphur forms analysis are present in Table 2.

Arsenic content in feed coals. The As concentration in studied feed coals varies from 1.40 to 22.97 ppm. The arsenic Clarke value for worldwide coals is 7.6 ppm for low-rank and 9 ppm for bituminous coal. The enrichment/depletion factors (EDF), defined as ratio of the As content in each coal sample to the Clarke value were calculated. EDF shows that As is 3 times higher in feed coal from Bobov Dol TPP and about 2 and more than 2 times higher in coals from Varna, Maritza East 3, Maritza East 2 and Republika TPPs. The As in feed coal from Russe TPP is significantly lower than usual. A strong positive correlation between As and pyrite sulfur content in feed coal from all

Table 1. Arsenic concentration, proximate and sulphur forms analysis of feed coal from TPPs

TPPs	Feed coal; coal rank	As content, ppm	EDF[a]	Proximate analysis (d), %		Sulphur analysis (a), wt %			
				A	W	S_{py}	S_{sulph}	S_{org}	S_{total}
Maritza East 2	lignite	**15.83**	**2.08**	26.5	23.4	2.1	1.1	0.7	3.9
Maritza East 3	lignite	**17.56**	**2.31**	26.5	23.8	2.7	1.2	1.0	4.9
Maritza 3	lignite	**11.71**	**1.54**	23.0	13.5	1.9	0.4	1.9	4.2
Republika	subbituminous	**16.38**	**2.16**	57.9	6.0	0.8	0.3	0.1	1.2
Bobov Dol	mixture[b]	**22.97**	**3.02**	35.8	20.3	0.9	0.2	0.8	1.9
Varna	bituminous	**17.81**	**1.98**	15.8	2.3	0.7	0.4	0.4	1.5
Russe	bituminous	**1.40**	0.16	18.1	0.9	0.1	0.6	0.2	0.9

[a] EDF, enrichment/depletion factor (a ratio of the mean As content in coal samples vs. the Clarke value for As in world coals; the Clarke value of As in world coals is from Ketris and Yudovich, 2009).
[b] Mixture between subbituminous coal and lignite.
A, ash; W, moisture; py, pyrite; sulph, sulphate; org, organic; a, analytical basis; d, dry basis.
Clark value for As in worldwide coals is 7.6 ppm for low-rank and 9 ppm for bituminous coal.

Table 2. Arsenic concentration, main characteristics and sulphur forms of fly ashes from TPPs

Sample		As analysis		Proximate analysis (d), wt%		Forms of sulfur (a), wt%			
TPPs	EPS row	As, ppm	EDF[a]	A (d)	W (ar)	S_{py}	S_{sulph}	S_{org}	S_{total}
Maritza East 2	bulk sample	**56.48**	**1.20**	97.8	0.9	1.0	0.8	0.1	1.9
Maritza East 3	bulk sample	**25.49**	**0.54**	94.0	3.6	0.5	0.6	0.1	1.2
Maritza 3	1st-row	**56.84**	**1.21**	77.9	1.1	2.9	2.6	–	5.5
	2nd-row	**150.11**	**3.19**	67.3	3.4	3.7	3.9	–	7.6
	3rd–row	**222.09**	**4.73**	93.8	2.0	4.9	5.3	–	10.2
Republika	1st–row	**7.50**	0.16	98.6	0.3	0.1	0.2	0.4	0.7
	2nd–row	**28.17**	0.60	98.8	0.4	0.2	0.2	0.5	0.9
	3rd–row	**44.99**	0.96	99.1	0.3	0.2	0.2	0.2	0.6
Bobov Dol	1st–row	**26.76**	0.57	99.0	0.1	0.5	0.4	0.2	1.1
	2nd–row	**38.77**	0.82	99.0	0.1	0.5	0.6	0.1	1.2
	3rd–row	**57.20**	**1.22**	99.1	0.1	1.0	0.8	0.0	1.8
Varna	1st–row	**6.58**	0.14	78.9	0.1	0.2	0.2	0.3	0.7
	2nd–row	**51.25**	**1.09**	80.1	0.2	0.4	0.3	0.1	0.8
	3rd–row	**75.32**	**1.60**	73.4	0.3	0.1	0.5	0.1	0.7
	4th–row	**101.45**	**2.16**	72.4	0.4	0.3	0.3	–	0.6
	5th–row	**113.07**	**2.41**	68.4	0.4	0.2	0.2	0.2	0.6
Russe	1st–row	**6.70**	0.14	82.4	0.2	0.2	0.2	–	0.4
	2nd–row	**7.05**	0.15	85.1	0.2	0.1	0.2	–	0.4
	3rd–row	**5.44**	0.12	37.7	0.3	0.3	0.3	–	0.6

[a] EDF, enrichment/depletion factor (ratio of the mean element content in FA samples to the Clarke value for As in world coal ashes; As Clarke value after Ketris and Yudovich, 2009).
d, dry basis; a, analytical basis; ar, as-received basis; W, moisture; C, carbon; H, hydrogen; N, nitrogen; O, oxygen; py, pyrite; sulph, sulphate; org, organic.
Clark value for As in worldwide coal ashes is 47 ppm.

studied TPPs except Bobov Dol TPP was observed. This suggests that a significant proportion of As is associated with pyrite in coal. Such close relationship between As and pyrite has been observed and described by many authors around the world (Finkelman et al., 2019). The rest of the As is probably related to the organic compounds in the coal matter but in lesser extent (Yudovich, Ketris, 2005). As is primarily associated with Fe-sulphides minerals, especially pyrite in which As is mainly present in ani-

onic form in substitution for S, and in some cases, in cationic form in substitution for Fe (Dai et al., 2020). In some cases As can be organically associated especially in low-rank coals, therefore As can be also connected with the organic coal matter (Dai et al., 2020). Some experiments show that pyrite largely hosts As in bituminous coals and about 30 % As occurs in the organic matter in low-rank coals (Finkelman et al., 2019).

Arsenic content in fly ashes. During coal combustion in TPPs, main part if As evaporates to gaseous phase. In the widely used pulverized combustion like Maritza 3, Republika, Bobov Dol, Varna and Russe TPPs, most of the organic and pyrite associated As, and some As-bearing micromineral phases convert in a gaseous phase and only a minor part of As remains in bottom ash. The main part of the escaping As is captured by fly ash. The great amount of As was captured by the fly ashes which is collected by electrostatic precipitators (97–99%) and due to this reason the As atmospheric emissions (solid-phase and gaseous) is rather minor. The As content in studied fly ashes varies from 5.44 to 222.09 ppm. The arsenic Clarke value for worldwide coal ash is 47 ppm. The enrichment/depletion factors (EDF), defined as ratio of the As content in each fly ash sample to the Clarke value were calculated. The highest As concentration is found in the FAs from Maritza 3 TPP, where the As content is 1.2 to 4.7 times higher than the Clarke value. Increased amount of arsenic (up to 2.4 times) in the ashes obtained during coal burning in TPP Varna was also observed. The arsenic in fly ash from Maritza East 2 TPP is 1.2 times higher than Clarke value. The As concentration in the FA samples from Maritza East 3, Republika, Bobov Dol, and Russe TPPs is lower than the average value. It can be observed that As in FAs from almost all sampled TPPs increases from the first to each subsequent row of electrostatic precipitators. It means that As concentration is highest in the finest FA particles. According Yudovich and Ketris (2005) the sorption of As in the fly ash is controlled by the combustion rate. If particulate coal is very rapidly fired, kinetics limitations on the As sorption exist, and As capture appears as physisorption, with strong relation to particulate size (the finer fly ash particles, the higher As concentration). If the coal fires more slowly, the equilibrium thermodynamics shows a chemisorption process and there is no strong relation of As content in fly ash to the fraction size).

Conclusions

The concentration of As in feed coals and in fly ashes from seven Bulgarian TPPs was investigated. The As content in studied coals varies from 1.40 to 22.97 ppm. The data for As are compared with Clarke value for worldwide coals. Three times higher and 2 and more than 2 times higher As in coals combusted in Bobov Dol, Maritza East 3, Maritza East 2, Republika and Varna TPPs have been determined. The As content in FAs varies from 5.44 to 222.09 ppm. The highest As concentration is found in the FAs from Maritza 3 TPP, where the As content is 1.2 to 4.7 times higher than the Clarke value. Increased amount of As (up to 2.4 times) in the ashes obtained from Varna TPP was also observed. Arsenic in the FA samples from Maritza East 3, Republika, Bobov Dol, and Russe TPPs is lower than the average value. Strong connection between As and finest FA particles was determined.

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