Mercury concentrations in Maritsa East coal, coal lithotypes, clay partings and combustion wastes, Bulgaria

Концентрации на живак в източномаришки въглища, въглищни литотипи, глини и отпадъци от изгаряне, България

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Introduction

Mercury is a major hazardous element that naturally occurs in coal, and during combustion in coal-fired thermal power plants (TPP) gets into hard wastes and gas emissions. This study presents Hg contents, mode of occurrence and trends of concentration in the Maritsa East coal, clay partings and combustion wastes.

Materials and methods

The samples studied are: 1) representative coal technological samples (MME-02/21 and MME-04/46) provided by Mini Maritsa Iztok EAD; 2) briquette coal (BC) and clays (blue, yellow and black), collected from Troyanovo-3 deposit; 3) coal (fuel for burning) (P4F); combustion waste products (WP), collected from the lagoon pond (P1–P3); combustion waste products (fly and bottom ash) from boiler 8 (P5–P8), collected from TPP Maritsa East 2. In order to determine the Hg enrichment in different fractions separated, the following separation procedures were applied: 1) fine fraction (<0.063 mm); 2) non-magnetic and magnetic fractions (slightly and highly magnetic). The methods applied are: 1) X-ray diffraction (XRD) (phase composition); 2) scanning electron microscopy combined with microprobe analysis (SEM-EDS); 3) inductively coupled plasma mass spectrometry (ICP-MS) (major elements); 4) laser ablation combined with ICP-MS (LA-ICP-MS) (trace elements); and 5) cold vapor flow injection mercury system (Hg) (CV-FIMS).

Results and discussion

In order to establish a coefficient of enrichment (CE), the concentrations of Hg in coal, coal lithotypes and combustion wastes were compared to clarkes for brown coal (100 ppb) and ashes of brown coal (620 ppb) (Ketris, Yudovich, 2009), respectively, while Hg contents in clays were compared to clarkes for clays and shales (68 ppb) (Grigoriev, 2009). Concentrations of Hg in coal (fuel for burning in TPPs) from Maritsa East basin, are up to 2.6 times higher than clark value (Table 1). Higher concentrations of Hg were determined in briquette coal (BC), especially in its fine fraction (BC/f) (5.5 and 17.5 times, respectively). Both fine fractions of coal (P4F/f) and briquette coal (BC/f) exhibit much higher Hg contents, at least two times higher Fe, S and ash yield (A^d) contents than the original samples (Table 1). This indicates direct relation of Hg with pyrite content in coal and briquette coal. The content of pyrite determined by XRD is as follows (wt.%): P4F 2.2; P4F/f 3.0; BC 30.7; BC/f 45.0. Among coal lithotypes, fusain has the highest Hg content. This can be explained with its behavior as physical sorbent (Eskenazy, 2006). The increased carbon content in fusain during coalification (Taylor et al., 1998) may assist in entrapping Hg^0 (Mimna et al. 2016). Mercury is determined in all clay samples, but its concentration in black clays varies in wide range (CE=1.0–6.4), probably due to the 6% total carbon, framboidal pyrite and varying content of clay minerals (illite, kaolinite and montmorillonite). Major phases in combustion wastes are quartz, anorthite, feldspar, hematite, magnetite, gypsum, anhydrite, glass and char in differing contents in the various samples/fractions. Direct relation of Hg to particular phase in the waste products is hard to establish. Generally, fly ash (P5FA and P6FA) contains more Hg than bottom ash (P7BA), 376 ppb, 781 ppb and 66 ppb, respectively. However, the contents of Hg in samples/fractions from the lagoon pond, where the waste contain mixed fly ash, bottom ash and neoformed phases, resulting of flue gas desulfurization (gypsum), vary from 213 to 629 ppb. It can

Table 1. Concentrations of Hg, Fe, S, ash yield (A^d) and coefficient of enrichment (CE)

Sample No.	Hg, ppb	Fe %	S %	A^d %	CE
Coal and coal lithotypes (CV-FIMS)					
MME-04/46*	204	n.d.	7.99	30.10	2.0
MME-02/21*	258	n.d.	3.78	28.00	2.6
P4F	230	3.08	5.70	34.66	2.3
Fusain	200	n.d.	n.d.	n.d.	2.0
Xylain	40	0.16	2.38	4.66	0.4
Liptain	160	1.30	2.82	7.36	1.6
Vitrain	60	0.72	3.63	7.62	0.6
Coal and coal lithotypes (LA-ICP-MS)					
P4F	240	3.08	5.70	34.66	2.4
P4F/f	440	6.38	14.10	46.15	4.4
BC	550	1.04	4.40	8.25	5.5
BC/f	1750	2.92	8.70	11.02	17.5
Combustion products TPP Maritsa East 2 (LA-ICP-MS)					
P1WP	735	6.74	6.94	90.19	1.2
P1WP/f	509	6.96	9.61	92.61	0.8
P1WP/n	405	6.39	9.94	90.34	0.7
P1WP/l	375	6.48	5.39	90.44	0.6
P1WP/s	601	7.64	7.85	91.71	1.0
P1WP/k1	446	7.24	6.25	90.38	0.7
P2WP	325	5.51	8.14	90.19	0.5
P2WP/f	384	5.12	17.59	86.35	0.6
P2WP/n	233	3.04	15.50	73.90	0.4
P2WP/l	543	4.88	5.81	83.78	0.9
P2WP/s	497	10.87	6.37	91.37	0.8
P3WP	<295	13.99	5.52	89.66	<0.5
P3WP/f	<410	11.31	25.56	85.77	<0.7
P3WP/n	213	4.29	8.09	88.34	0.3
P3WP/l	<355	6.13	7.42	89.51	<0.6
P3WP/s	289	23.67	18.72	91.52	0.5
P3WP/k1	629	33.44	22.29	85.57	1.0
P3WP/k2	<460	4.97	36.44	83.33	<0.7
P3WP/k3	<315	3.59	9.56	83.82	<0.5
P5FA	376	6.05	1.36	94.01	0.6
P5FA/n	195	4.82	1.58	93.46	0.3
P5FA/l	362	5.42	1.29	93.43	0.6
P5FA/s	291	10.72	2.79	94.95	0.5
P6FA	781	7.32	2.37	94.01	1.3
P7BA	<170	4.91	4.14	70.48	<0.3
P7BA/n	66	3.67	3.57	64.28	0.1
P7BA/l	<75	6.18	4.03	84.66	<0.1
P7BA/s	<140	13.12	6.38	89.65	<0.2
P8/k1	310	48.42	31.49	90.27	0.5
P8/k2	152	9.81	2.30	99.33	0.2
Clays (ICP-MS aqua regia digestion)					
Blue clay	28	3.90	0.22	n.d.	0.4
Yellow clay	28	4.22	0.46	n.d.	0.4
Black clay 1	69	3.87	1.46	85.74	1.0
Black clay 2	432	2.93	0.26	n.d.	6.4

* Samples provided by Mini Maritsa Iztok EAD; WP, waste product; FA, fly ash; BA, bottom ash; f, fine fraction (<0.063 mm); n, non-magnetic; l, slightly magnetic; s, highly magnetic; k*n*, sample piece No.

be suggested that Hg associates with Fe-oxide/hydroxide film or associate with transformed framboidal pyrite. Some portion of Hg might be included in gypsum and basanite, formed during desulfurization (Kairies et al., 2006). Among the samples formed at limited airflow conditions (P8/k1 and P8/k2), sample P8/k1 (with high pyrrhotite content) has higher Hg concentrations. Concentrations of Hg in combustion products are generally lower than the clarke value.

Conclusions

The Maritsa East coals have Hg contents up to 2.6 times higher than clarke values. The dominant mode of occurrence is pyrite. Organic matter and clay minerals contain lesser amount of Hg. Fusain contains highest Hg content among different coal lithotypes, probably due to its sorption ability. The relation established between Hg concentrations and Fe, S and A^d and pyrite content in P4F and BC could not be found in the technological coal samples, probably because of the various lithotypes and mineral composition. The major concentrators of Hg in combustion waste are hematite, glass and char. In accordance with the adopted directives of EC for Hg emissions, TPP Maritsa East 2 has applied the methods of Nalco for flue gas desulfurization and capture of Hg^0 and Hg^{2+} using activated carbon and halogenides.

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