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HARMFULNESS ASSESSMENT OF RESINS USED AS LUSTROUS CARBON CARRIERS IN BENTONITE MOULDING SANDS

OCENA SZKODLIWOŚCI ŻYWIC STOSOWANYCH JAKO NOŚNIKI WĘGLA BŁYSZCZĄCEGO W MASACH Z BENTONITEM

The assessment of harmfulness of two resins applied as a partial substitute of coal dust in moulding sands with bentonite – was performed in the paper. The emission value of compounds from the PAH and BTEX groups was assumed as the main harmfulness criterion. Also mixtures of the Kormix type prepared with additions of these resins were tested. Experiments were carried out in an argon atmosphere in a temperature range: 500-1300°C. The obtained emission values of these substances were recalculated for 1% of lustrous carbon content in each carrier. It was assumed in the calculations, that the NW 1 and NW 2 carriers contain approximately 55% of lustrous carbon while the Kormix mixture approximately 15%. The critical temperature of forming compounds of the PAH group for the NW 1 carrier is 900°C, while for the NW 2 carrier is 1100°C (this is a temperature, at which the emission abruptly increases). In case of formation of compounds from the BTEX group the critical temperature for both lustrous carbon carriers is a temperature of 900°C.

Keywords: moulding sand, bentonite, lustrous carbon carriers, harmfulness, resin

W artykule dokonano oceny szkodliwości dwóch żywic stosowanych jako częściowy zamiennik pyłu węglowego w masach z bentonitem. Jako kryterium przyjęto wielkość emisji związków z grupy WWA oraz BTEX. Zbadano również mieszanki typu Kormix sporządzane z dodatkiem tych żywic. Badania przeprowadzono w atmosfer argonu w zakresie temperatury 500-1300°C. Uzyskane wartości wielkości emisji tych związków zostały przeliczone na 1% zawartości węgla błyszczącego w każdym z nośników . Do obliczeń np. przyjęto, że nośniki NW 1 i NW 2 zawierają około 55% węgla błyszczącego, a mieszanki Kormix około 15%. Dla nośnika NW 1 temperatura krytyczną tworzenia się WWA jest 900°C, a dla nośnika NW 2 temperatura 1100°C (jest to temperatura, w której gwałtownie wzrasta emisja). W przypadku tworzenia się BTEX temperaturą krytyczną, dla obu nośników węgla błyszczącego jest temperatura 900°C.

1. Introduction

Lustrous carbon (LC) is very important in processes of iron casting in green sands. Its main task is a protection of casting surface against sand scorching and obtaining the required surface smoothness. LC is formed during pouring liqiud metal into mlds from additions containing carbon. The main source of LC until recently is coal dust [1-8]. However, mainly because of the environment protection and improvement of work conditions, the producers of bentonite form green sands are searching substitutes being more environmentally friendly: grphite dust, coke dust, carbon black, synthetic resin, gilsonite, lignite, aliphatic oil etc [9-12].

2. Methodology of investigations

Investigations of the emissivity of substance from the PAH and BTEX groups were performed in laboratory tests applying methodology and equipment described in [13, 14]. Polyurethane foam was used for adsorption of the PAHs, while active carbon for adsorption of BTEX substances. The tested sample was heated abruptly (it was placed in a furnace after it reached the needed temperature) and held at this temperature for the determined time. The analysis of the investigated substances was performed by the GC/MS method [15-18, 22].

3. Investigated materials

Two resins being the LC carriers for moulding sands with bentonite were investigated. They were marked as NW1 and NW2.

- ► NW 1: hydrocarbon resin HRC, German production of a LC content minimum 55%, water content maximum 0,4%, ash content – maximum 0,5%, softening point 95-115°C, benzo (a) pyrene content, maximum 50 mg/kg;
- ► NW 2: hydrocarbon resin W, indene-styrene type, Polish production of a LC content minimum 55%, melting tem-

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perature >100°C, boiling temperature >350°C, insoluble in water.

In addition, two bentonite mixtures prepared with additions of these resins and coal dust (the composition of these mixtures was selected in such a way as to have a lustrous carbon content at a level of 15%) were tested. They are marked as:

- Kormix 1 – coal dust + HCR resin;
- Kormix 2 – coal dust + WARTER resin.

4. The obtained results and their discussion

<u>LC carriers NW 1 and NW 2</u>

Concentrations of substances formed when the NW 1 sample was heated at the given temperature are listed in Table 1 and 2 (from the PAH group in Table 1 and from the BTEX group in Table 2).

The concentration results of substances (formed during heating the NW 2 sample at the given temperature) from the PAH group are given in Table 3, and from the BTEX group in Table 4.

TABLE 1

Concentration of the PAHs formed during an influence of the selected temperature on the NW 1 carrier (in recalculation to 1 g of a sample)

Organic compound	NW 1 a (700°C) [mg/g]	NW 1 b (900°C) [mg/g]	NW 1 c (1100°C) [mg/g]	NW 1 c (1300°C) [mg/g]
Naphthalene	2,13	6,15	22,72	3,52
Acenaphthylene	3,46	15,89	8,31	2,82
Acenaphthene	2,61	0,63	0,03	0,01
Fluorene	1,29	2,85	0,71	0,03
Phenanthrene	4,70	10,53	12,33	0,45
Anthracene	4,01	6,28	3,63	0,03
Fluoranthene	1,24	2,26	6,11	0,31
Pyrene	6,31	9,68	9,38	0,94
Benzo(a)anthracene	1,69	2,10	1,85	0,04
Chrysene	0,85	1,73	1,98	0,04
Benzo[b]fluoranthene	0,25	0,52	1,53	0,04
Benzo[k]fluoranthene	0,15	0,32	0,91	0,03
Benzo[a]pyrene	0,46	0,66	1,25	0,10
Indeno[1,2,3-cd]pyrene	0,01	0,04	0,28	0,26
Dibenzo[ah]anthracene	0,01	0,04	0,00	0,00
Benzo[ghi]perylene	0,14	0,18	0,30	0,02
SUM 16 PAH [mg/g]	**29,30**	**59,85**	**71,34**	**8,64**

TABLE 2

Concentrations of BTEX formed during an influence of the selected temperature on the NW 1 carrier (in recalculation to 1 g of a sample)

Organic compound	NW1B 1 (500°C) [mg/g]	NW1B 2 (700°C) [mg/g]	NW1B 3 (900°C) [mg/g]	NW1B 4 (1100°C) [mg/g]	NW1B 5 (1300°C) [mg/g]
Benzene	0,8	4,1	20,8	29,0	65,9
Toluene	4,6	7,5	15,9	17,2	1,0
Ethylbenzene	3,3	4,2	2,3	2,0	1,0
meta + para – xylene	2,9	4,4	6,5	5,9	0,2
o - xylene	0,6	1,3	1,2	1,0	0,0
SUM OF BTEX [mg/g]	**12,2**	**21,5**	**46,7**	**55,1**	**68,1**

TABLE 3

Concentrations of the PAH substances formed during heating the NW 2 carrier at the selected temperature (recalculated for 1 g of a sample)

Organic compound	NW 2 a (700°C) [mg/g]	NW 2 b (900°C) [mg/g]	NW 2 c (1100°C) [mg/g]	NW 2 d (1300°C) [mg/g]
Naphthalene	10,11	7,03	45,31	25,02
Acenaphthylene	1,23	0,56	12,75	11,79
Acenaphthene	0,41	0,29	1,26	0,10
Fluorene	1,28	0,72	6,83	0,57
Phenanthrene	1,03	0,59	11,95	10,70
Anthracene	0,35	0,16	5,57	1,53
Fluoranthene	0,11	0,08	2,30	8,64
Pyrene	0,10	0,06	1,73	6,86
Benzo(a)anthracene	0,23	0,14	2,62	1,38
Chrysene	0,19	0,08	2,37	1,68
Benzo[b]fluoranthene	0,06	0,03	0,88	1,92
Benzo[k]fluoranthene	0,07	0,03	0,95	2,19
Benzo[a]pyrene	0,05	0,00	0,80	2,39
Indeno[1,2,3-cd]pyren	0,00	0,00	0,17	1,43
Dibenzo[ah]anthracene	0,00	0,00	0,09	0,08
Benzo[ghi]perylene	0,00	0,00	0,03	0,96
SUM 16 PAH [mg/g]	**15,22**	**9,78**	**95,61**	**77,24**

TABLE 4

Concentrations of BTEX substances formed during heating the NW 2 carrier at the selected temperature (recalculated for 1 g of a sample)

Organic compound	NW2B 1 (500°C) [mg/g]	NW2B 2 (700°C) [mg/g]	NW2B 3 (900°C) [mg/g]	NW2B 4 (1100°C) [mg/g]	NW2B 5 (1300°C) [mg/g]
Benzene	2,3	33,4	85,1	173,1	163,2
Toluene	45,0	41,4	64,1	67,6	1,7
Ethylbenzene	21,2	15,6	14,7	1,7	0,0
meta + para – xylene	11,0	10,5	15,0	9,0	0,3
o - xylene	4,4	4,7	6,3	2,4	0,0
SUM BTEX [mg/g]	**83,9**	**105,6**	**185,2**	**253,8**	**165,2**

LC carriers: Kormix 1 and Kormix 2

The concentration results of compounds from the PAH and BTEX groups, formed during heating the Kormix 1 sample at the given temperature, are shown in Table 5-6, respectively.

The concentration results of compounds from the BTEX group – formed during heating the Kormix 2 sample at the given temperature – are shown in Table 7.

TABLE 5

Concentrations of substances from the PAH group formed during the selected temperature influencing the Kormix 1 mixture (recalculated for 1 g of a sample)

Organic compound	KORM_1 (700°C) [mg/g]	KORM_2 (900°C) [mg/g]	KORM_3 (1100°C) [mg/g]	KORM_4 (1300°C) [mg/g]
Naphthalene	0,65	6,23	8,44	1,04
Acenaphthylene	0,00	2,08	2,55	0,62
Acenaphthene	0,00	0,00	0,00	0,00
Fluorene	0,05	0,98	0,25	0,00
Phenanthrene	0,05	1,28	2,57	0,11
Anthracene	0,02	0,67	0,77	0,01
Fluoranthene	0,00	0,32	1,56	0,10
Pyrene	0,01	0,21	1,16	0,17
Benzo(a)anthracene	0,00	0,29	0,43	0,00
Chrysene	0,01	0,18	0,31	0,00
Benzo[b]fluoranthene	0,00	0,08	0,31	0,00
Benzo[k]fluoranthene	0,00	0,08	0,28	0,00
Benzo[a]pyrene	0,00	0,03	0,33	0,00
Inden[1,2,3-cd]pyrene	0,00	0,00	0,51	0,00
Dibenzo[ah]anthracene	0,00	0,00	0,00	0,00
Benzo[ghi]perylene	0,00	0,00	0,20	0,00
SUM of 16 PAH [mg/g]	**0,79**	**12,43**	**19,67**	**2,05**

TABLE 6

Concentrations of substances from the BTEX group formed during the selected temperature influencing the Kormix 1 mixture (recalculated for 1 g of a sample)

Organic compound	KORM1_B1 (500°C) [mg/g]	KORM1_B2 (700°C) [mg/g]	KORM1_B3 (900°C) [mg/g]	KORM1_B4 (1100°C) [mg/g]	KORM1_B5 (1300°C) [mg/g]
Benzene	0,4	5,0	30,8	39,0	6,7
Toluene	2,1	5,5	10,8	0,7	0,1
Ethylbenzene	1,4	2,6	1,2	1,6	0,7
meta + para – Xylene	2,9	4,4	5,9	4,8	1,7
o – Xylene	0,0	0,8	0,8	0,4	0,2
SUM BTEX	**6,8**	**18,3**	**49,5**	**46,5**	**9,4**

TABLE 7

Concentrations of the BTEX group substances formed during heating the Kormix 2 mixture at the selected temperature (recalculated for 1 g of a sample)

Organic compound	KORM2_B1 (500°C) [mg/g]	KORM2_B2 (700°C) [mg/g]	KORM2_B3 (900°C) [mg/g]	KORM2_B4 (1100°C) [mg/g]	KORM2_5 (1300°C) [mg/g]
Benzene	0,4	5,0	6,1	29,6	2,6
Toluene	1,3	4,8	4,6	0,4	0,0
Ethylbenzene	1,1	1,9	1,7	0,7	0,3
meta + para – Xylene	2,3	3,9	4,2	2,2	1,0
o – Xylene	0,0	0,7	0,6	0,2	0,1
SUM BTEX	**5,0**	**16,4**	**17,3**	**33,0**	**4,0**

In order to compare the harmfulness of all investigated LC carriers, the emission of compounds from the PAH and BTEX group was recalculated for 1% of the LC forming capacity (assuming the LC content for resins as being equal 55%, and for the Kormix mixtures as equal 15%). The results are presented in Table 8 and 9, respectively.

TABLE 8

Total emission of substances from the PAH group recalculated for 1% of LC, in dependence on the temperature (mg/1% LC)

LC carrier	**Decomposition temperature/Total PAHs content (mg/1 % LC)**			
	700°C	**900°C**	**1100°C**	**1300°C**
Kormix 1	0,053	0,829	1,311	0,137
NW 1	0,532	1,088	1,297	0,157
NW 2	0,277	0,178	1,738	1,404

TABLE 9

Total emission of substances from the BTEX group in recalculation for 1% of LC in dependence on the temperature (mg/1% LC)

LC carrier	**Decomposition temperature/Total BTEX content (mg/1%LC)**				
	500°C	**700°C**	**900°C**	**1100°C**	**1300°C**
Kormix 1	0,453	1,22	3,3	3,1	0,627
Kormix 2	0,333	1,09	1,153	2,2	0,267
NW 1	0,222	0,391	0,849	1,002	1,238
NW 2	1,525	1,92	3,367	4,615	3,004

The main compound from the PAH group, emitted from the Kormix 1 carrier is nafthalene, which constitutes app. 50% of all emitted PAH substances, in the whole tested temperature range. The maximum emission of these substances occurs at a temperature of 1100°C. For NW 1 and NW 2 carriers at temperatures of 700 and 900°C the acenaphthylene emission is higher than naphtalene. Only when the temperature equals 1100°C the amount of generated naphtalene significantly exceeds the acenaphthylene amount. In LC carriers from the NW group occur mainly: naphtalene, acenaphthylene, phenanthrene, anthracene and pyrene, while in carriers from the Kormix group: naphtalene, acenaphthylene, phenanthrene and fluoranthene are emitted [19, 20].

From the BTEX group substances, at lower temperatures: 500 and 700°C, the main component of the emitted gases is toluene, while from a decomposition temperature of 900°C the benzene concentration significantly exceeds the toluene concentration. The maximum emission of substances from the BTEX group occurs at temperatures: 1100-1300°C (NW carriers) and at temperatures: 900-1100°C (Kormix carriers).

In recalculation for 1% of the LC formation at temperatures 700 and 900°C the highest PAH emission indicates NW 1, while at temperatures 1100°C and 1300°C NW 2 carrier. The highest concentration of the BTEX substances occurred in case of the NW 2 carrier at the whole investigated temperature range (500-1100°C). The lowest concentration of these substances up to a temperature of 1100°C, exhibited NW1. The maximum concentration of BTEX substances for Kormix 1 occurred at a temperature of 900°C, for Kormix 2 at a temperature of 1100°C, for NW 2 at 1100°C and for NW 1 at 1300°C [21, 22].

5. Conclusions

- The LC carrier NW 2 exhibits a smaller emission of BTEX than NW 1 at the whole temperature range. The maximum emission is at 1100°C.
- The Kormix 2, which includes the LC carrier NW 2 is more friendly for environment because the emission of BTEX is smaller than from Kormix 1.
- At temperatures higher than 1100°C the BTEX emission dropped suddenly in cases of both Kormixes. The emission of PAHs from NW 1 is at its maximum at 1100°, but it is less than from NW 2 at the same temperature.
- Advantageous, from the point of view of work conditions, is a formation of very small amounts of benzo[a]pyrene in case of both lustrous carbon carriers.

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