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Assessment of Harmfulness of Phenolic Resins Hardened by CO_2 in an Aspect of Emission of Substances from BTEX and PAH Groups

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Abstract

Out of moulding sands used in the foundry industry, sands with organic binders deserve a special attention. These binders are based on synthetic resins, which ensure obtaining the proper technological properties and sound castings, however, they negatively influence the environment. If in the initial state these resins are not very dangerous for people and for the environment, thus under an influence of high temperatures they generate very harmful products, being the result of their thermal decomposition. Depending on the kind of the applied resin under an influence of a temperature such compounds as: furfuryl alcohol, formaldehyde, phenol, BTEX group (benzene, toluene, ethylobenzene, xylenes), and also polycyclic aromatic hydrocarbons (PAHs) can be formed and released.

Keywords: Environment Protection, Phenolic Resin, BTEX, PAH, Foundry

1. Introduction

Foundry engineering belongs to an industrial branch of an increased professional risk. During the whole casting production process employees are exposed to dangerous, harmful and uncomfortable factors related, among others, to emissions of harmful substances. One of the reasons of such emission are binding agents applied in foundry practice (e.g. resins or lustrous carbon carriers applied in bentonite sands) and hardeners undergoing thermal decomposition at high temperatures. Due to this, several more of less harmful organic compounds are formed. In dependence on the applied resin (phenolic, phenol-formaldehyde, urethan, furfuryl-urea, alkyd), under a temperature influence can be formed and released such compounds as: furfuryl alcohol, formaldehyde, phenol, BTEX group and also polycyclic aromatic hydrocarbons (PAHs) [1-9].

These substances and also dusts are mainly generated during mould pouring with liquid metal (a temperature of liquid foundry alloys on ferrous basis is: 1350-1550°C). Forming volatile organic compounds (VOC) can penetrate to mould parts located further from a casting, condense on matrix grains and when a mould is cooling and castings are knocked out they can be either released to the environment or eluted during storing of spent foundry sands [10-13]. More and more strict rules concerning the environment protection and growing social pressure are the reason that foundry plants are looking for new, more friendly moulding sands and cores technologies or for modifications of currently applied to limit the emission of harmful substances and unpleasant odours during sands preparation, pouring, cooling and castings knocking

out. These elements decide to a high degree on the foundry sector image. Simultaneously this situation is forcing materials producers to develop such binders which will meet the requirements. Changes of binding materials for moulding and core sands will occur more evolutionary than revolutionary. They will progress in three main directions: environment protection, technology (among others: prolongation of a storing time of moulds and cores, higher dimensional accuracy of castings, improved casting quality) and the production yield. Thus, a long-lasting success of a foundry plant can provide: yield, quality and environment. In the scope of the environment protection the following elements should be taken into consideration: composition of initial raw materials, emission of harmful substances during moulding sands preparation, during making moulds and cores, pouring, cooling and knocking out as well as the possibility of the reclamation and reusing of spent foundry sands. When binding agents of a decreased contaminations emission are applied, foundry plants can reduce investments of devices required for capturing and rendering harmless these dangerous substances [14-16].

An assessment of harmfulness of moulding sands applied for moulds and cores is based on two main elements:

- emissivity of harmful gases during preparation of sands, formation, pouring the mould with liquid metal, mould cooling and casting knocking out;
- elution of dangerous substances from spent foundry sands during their storing or functional utilisation.

Therefore when assessing an influence of the given sand on the environment these two aspects should be taken into account. Only such investigations provide the total assessment of the tested sand harmfulness. The main source of the dangerous substances emission are operations of pouring, cooling, castings knocking out and making cores. In foundry plants applying green sands it can be even 90 % of the whole emission [17]. Inorganic dangerous substances are mainly emitted during casting melting and cleaning processes. Organic dangerous substances constitute up to 96 % of all harmful substances emitted from a typical foundry plant. Organic compounds are emitted during mixing operations at making moulds and cores and during storing of cores, when organic binders were applied. To this group belong also catalysts e.g. triethylamine, protective coatings on alcohol bases, models separators. However, the largest amount of dangerous organic substances is emitted during pouring, cooling and castings knocking out when bentonite sands with additions of lustrous carbon carriers or sands with organic binders are used. Under an influence of high temperatures of liquid metal, at insufficient amounts of oxygen, a complete decomposition of organic substances occurs and (as a result) numerous new compounds are formed.

Among substances generated under an influence of high temperatures on binding materials, applied for moulding sands, especially harmful are PAHs (polycyclic aromatic hydrocarbons) and BTEX (benzene, toluene, ethylbenzene and xylenes). Therefore investigations leading to thorough getting to know the conditions of their formation, which should allow - in the future - for such control of the foundry process parameters which will limit the formation of these dangerous substances, are necessary.

The presented results constitute a fragment of the wide scope of research (performed in the Faculty of Foundry Engineering, AGH University of Science and Technology, within the realised developmental project) on harmfulness of materials applied in foundry processes, comprising investigations of various types of resins (furan, alkyd, phenolic, phenol-formaldehyde, for the alfa-set process) and bentonites with various lustrous carbon carriers, permanent moulds protective coatings and metallurgical slag.

2. Investigated resins

The subject of investigations were alkaline phenolic resins soluble in bases and hardened by CO_2. These resins are intended for production of moulds and cores for iron, steel cast and non-ferrous metals castings. They are characterized by a small emission of odours during a cores production and during mould pouring with liquid metal. They have a good knocking out ability and provide a good quality of casting surfaces. These resins were supplied by two producers present in the Polish market:

- Resin 1 – intended for production of moulds and cores for castings of ferrous alloys. It is applied as an addition to moulding sands in an amount of 2,5 parts by mass. It contains the following dangerous substances: KOH up to 25 %, phenol < 0,1 % and formaldehyde < 0,5 %.
- Resin 2 – intended mainly for production of moulds and cores for castings of light, non-ferrous metals. It is applied as an addition to moulding sands in an amount of 3 parts by mass. It contains the following dangerous substances: KOH up to 18 %, phenol < 0,2 % and sodium tetraborate < 8,5 %.
- Resin 3 – intended for production of moulds and cores for ferrous alloys castings. It is applied as an addition to moulding sands in an amount of 2,5 parts by mass. It contains the following dangerous substances: KOH up to 18 %, phenol < 1 % and ethylene glycol up to 5 %.
- Resin 4 – intended for production of moulds and cores for ferrous alloys castings. It is applied as an addition to moulding sands in an amount of 2.5 parts by mass. It contains the following dangerous substances: KOH up to 25 %, phenol < 0,1 % and formaldehyde < 0,5 %.

All moulding sands for investigations were prepared on a basis of the standard high-silica sand from Szczakowa.

3. Methodology of investigations

Investigations of the gases emission in the test foundry plant were performed according to the original method developed in the Faculty of Foundry Engineering, AGH UST [1, 7, 18].

A sample of the investigated moulding sand, on a basis of high-silica sand, of a roll shape of dimensions Φ 50 x 50 mm, and a mass of app. 150 g, compacted by a moulder's rammer stroke, is poured with liquid cast iron of a temperature of 1350°C. The liquid metal mass poured into the mould was 9 kg. The composition of each moulding sand was in agreement with the producer's requirements (standard composition). Gases emitting from the sample - after pouring it with liquid metal are led by means of a steel pipe via the drying system and the capsule with active carbon (during the BTEX measurement) or z polyurethane foam[1] (during the PAHs measurement) into a tightly sealed

[1] Raw Polyurethane Foam 0,022 g/cm^2 density (RESTEK) for collection of semivolatiles (pesticides, PCBs, PAHs).

container with liquid, from which they push out the liquid. The weight of displaced liquid was measured as a function of time. The whole mould (of a mass of 24 kg) was made of green sand. The measuring time was up to 15 minutes (in dependence on the intensity of gases emission).

Measurements of the BTEX emission: two layers of active carbon, separated from each other, were placed in a glass tube. One layer (1) containing 700 mg of active carbon constituted the basic adsorption place, while the second layer (2) containing 200 mg of active carbon was of a control character, providing information on an eventual 'breakthrough' of the first layer[2]. The active carbon layer with adsorbed organic substances was extracted in carbon disulphide. The analysis was carried out by the gas chromatography method with the application of the flame-ionising detector (FID).

Measurement of the PAHs emission: at determining compounds from the PAHs group a part of hydrocarbons condensed on dust particles and deposited, together with them, on a filter placed inside a capsule in front of a polyurethane foam. Therefore for the determination of the total amount of generated PAHs both the polyurethane foam and dusts on the filter were analysed. In order to do that, the filter and foam were extracted by toluene for 16 hours in the Soxhlet extractor and then separated from sand grains in hexane. After vaporising the hexane excess and cleaning by means of silicagel, the PAHs were separated in dichloromethane. The PAHs analysis was performed by the gas chromatography method coupled with the mass spectrometer (GC-MS).

The developed method allows to determine the total amount of emitted gases as well as their emission rate.

4. Results and their discussion

4.1. Measurements of the emitted gases amounts

For every tested resin the amounts of the emitted gases were recorded every 5 seconds. The diagram showing the amount of generated gases in respect to time is shown in Fig. 1, while their emission rate is shown in Fig. 2.

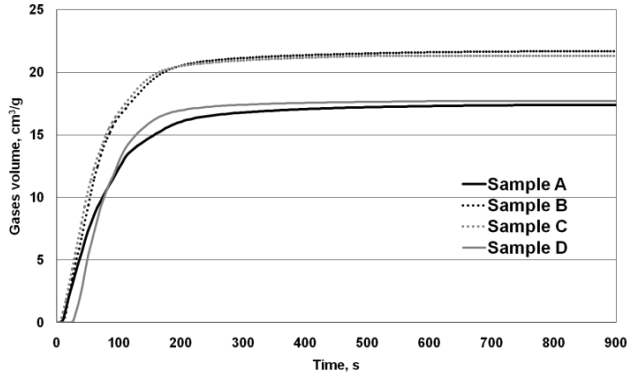

Fig. 1. Emissivity of gases from the tested moulding sands versus time

[2] Both layers of active carbon (1 and 2) were analysed. It was assumed that if the BTEX amount in the control layer (2) was lower than 10 % of these compounds in the main adsorption layer (1), none 'breakthrough' occurred and the measurement was correct.

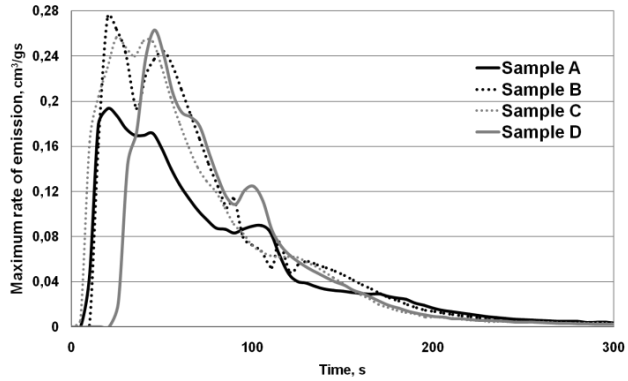

Fig. 2. Emission rates of gases from the tested moulding sands

4.2. Measurements of the BTEX group content

Quantitative data of the emission of the BTEX group compounds in recalculation for 1 kg of mass are given in Table 1.

Table 1.
Results of analyses of the BTEX group gases generated in tests on a semi-technical scale.

Sample	Gases volume, dm³/kg Moulding sand	Gases emission mg/kg moulding sand				Maximum rate of emission, dV/dt, cm³/g·s	Time of maximum rate, s
		Benzene	Toluene	Ethylobenzene	Xylenes		
A (LOI = 1,61 %)	17,373	325,886	29,333	0,225	1,859	0,193	20
B (LOI = 2,01 %)	21,673	317,891	23,169	0,204	4,143	0,275	20
C (LOI = 2,07 %)	21,185	353,225	21,277	0,162	2,943	0,256	25
D (LOI = 1,38 %)	17,709	237,773	3,154	0,064	0,871	0,263	46

The example of the chromatogram obtained for BTEX substances contained in gases emitted from the mould being poured under semi-technical conditions is presented in Fig. 3 (1 – analytical sample, 2 – control sample).

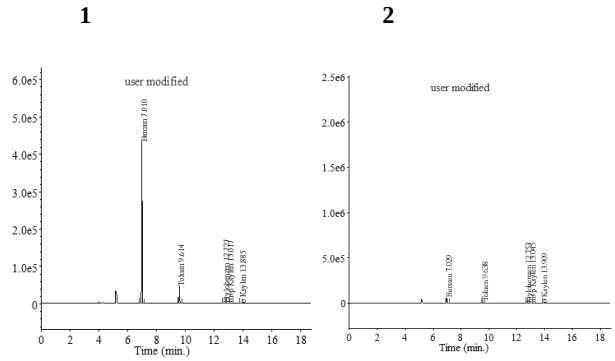

Fig. 3. Report from the chromatographic analysis of BTEX gases emitted from the moulding sand with resin A (sample 1A – analytical, sample 1B – control)

4.3. Measurements of the PAH group concen-tration

The results of analyses of substances from the PAH group in gases emitted during pouring moulds with cores made of the given resin (C and D) are listed in Table 2. The analyses of the PAH substances on the foam and on the filter, where dusts were gathered, are given. 16 the most often analysed substances from this group are shown.

Table 2. Content of substances from the PAH group in gases generated by the tested resins

Name of substances	**µg/ kg moulding sand, filter**		**µg/ kg moulding sand, foam**		**Total**	
	C	**D**	**C**	**D**	**C**	**D**
naphthalene	0,16	0,13	382,23	3,66	382,39	3,79
acenaphthylene	0,82	0,75	119,92	43,35	120,74	44,1
acenaphthene	0,03	0,02	5,47	1,94	5,5	1,96
fluorene	0,65	0,19	10,49	4,56	11,14	4,75
phenanthrene	19,49	2,02	0,51	7,25	20	9,27
anthracene	17,99	7,47	10,49	6,80	28,48	14,27
flouranten	41,97	28,40	0,70	1,42	42,67	29,82
pyrone	26,98	20,93	0,97	1,12	27,95	22,05
benz(a)anthracene	11,99	6,95	< 0,15	< 0,15	12,14	7,1
chrysen	5,55	3,29	< 0,01	< 0,07	5,56	3,36
benzo(b) fluoranthene	0,75	0,52	< 0,01	< 0,15	0,76	0,67
benzo(k) fluoranthene	1,57	0,34	< 0,01	< 0,07	1,58	0,41
benzopyrone	1,05	0,49	< 0,27	< 0,07	1,32	0,56
indeno(1,2,3-cd)pyrone	0,37	0,31	< 0,07	< 0,52	0,44	0,83
dibenzo(ah) anthracene	0,04	0,16	< 0,10	< 0,45	0,14	0,61
benzo(ghi)perylene	0,08	0,07	< 0,07	< 0,52	0,15	0,59
Total	**127,41 ± 25,48**	**71,76 ± 14,20**	**532,13 ± 104,93**	**< 72,51 ± 14,20**	**659,54 ± 130,41**	**144,27 ± 28,40**

5. Conclusions

- The higher ignition losses reveals the given resin (at 950°C) the more gases it emits during the mould pouring with liquid metal (resins B and C have higher ignition losses and generate more gases than resins A and D).
- A higher benzene content was found in gases emitted during pouring the mould with core with resin C, than in gases when the remaining resins were used. Whereas in case of resin A gases contain more toluene. However, these differences are within the measuring error, being 10-20 %.
- The smaller benzene amounts were formed when resin D was used (nearly 1/3 less than when resins B, C and A were used). Also amounts of toluene in case of resin D were 4-5 times lower than in case of the remaining resins.
- Thus, resin D is the most environment friendly in an aspect of the BTEX gases emission.
- Also, in case of resin D the maximum emission rate of gases occurs at the latest (after 46 seconds), which is advantageous from the point of view of a castings porosity.
- The main gaseous compounds from the PAHs group, generated from resin C are naphthalene and acenaphthene, while from resin D acenaphthylene. The emission of carcinogenic benzopyrone is in case of these both resins very small.
- The PAHs content in a gas phase generated from resin C is nearly one order of magnitude larger than from resin D.

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