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## HARMFULNESS ASSESSMENT OF MOULDING SANDS WITH A GEOPOLYMER BINDER AND A NEW HARDENER, IN AN ASPECT OF THE EMISSION OF SUBSTANCES FROM THE BTEX GROUP

### OCENA SZKODLIWOŚCI MASY FORMIERSKIEJ ZE SPOIWEM GEOPOLIMEROWYM I NOWYM UTWARDZACZEM W ASPEKCIE EMISJI ZWIĄZKÓW Z GRUPY BTEX

The harmfulness assessment of moulding sands with a geopolymer binder and a new hardener, in an aspect of the emission of substances from the BTEX group, was performed. Within the expedience project the new series of hardeners for the inorganic GEOPOL binder was developed. Before the introduction of the new system of moulding sands it was necessary to estimate their influence on the environment. To this aim the gasses emission from moulding sands subjected to the influence of liquid cast iron was tested with regard to the content of the gases from the BTEX group (benzene, toluene, ethylbenzene and xylenes). For the comparison the analogous investigations of the up to now applied moulding sands with the geopolymer binder, were performed. It was found that both systems of moulding sands binding emit similar amounts of gases, as well as similar amounts of substances from the BTEX group. Moulding sands with the GEOPOL binder are much more environmentally friendly than moulding sands with organic binders. The content of the BTEX group substances in gases emitted from moulding sands with the GEOPOL binder was approximately 10-times lower than in case of the moulding sands with organic binders.

*Keywords:* moulding sands, binder, geopolymers, gasses emission, BTEX

W ramach projektu celowego opracowano nową serię utwardzaczy dla spoiwa nieorganicznego Geopol. Przed wprowadzeniem nowego systemu mas formierskich konieczne było określenie ich wpływu na środowisko. W tym celu przeprowadzono badania emisji gazów z mas poddanych oddziaływaniu ciekłego żeliwa pod kątem zawartości w tych gazach związków z grupy BTEX (benzen, toluen, etylobenzen i ksyleny). Dla porównania przeprowadzono analogiczne badania dotychczas stosowanego systemu wiązania masy ze spoiwem geopolimerowym. Stwierdzono, że obydwie systemy wiązania mas formierskich emitują zbliżone ilości gazów, jak również związków z grupy BTEX. W porównaniu do mas ze spoiwami organicznymi można uznać, że masy ze spoiwem GEOPOL są wysoce przyjazne dla środowiska. Zawartość związków z grupy BTEX w gazach emitowanych z mas ze spoiwem GEOPOL była około 10-krotnie mniejsza niż w przypadku mas ze spoiwami organicznymi.

#### 1. Introduction

Organic dangerous substances constitute up to 96% of all hazardous substances emitted by the typical cast iron foundry. Organic substances are emitted during making moulds and cores (preparation of moulding sands, cores production and storage), when organic binders are applied. However, the largest amount of dangerous organic substances is liberated during pouring, cooling and knocking out moulds from moulding sands with bentonite and additions of lustrous carbon carriers or from moulding sands with organic binders. In foundry plants applying moulding sands with bentonite and lustrous carbon carriers it can constitute even 90% of the total emission of hazardous substances [1, 2].

Under an influence of liquid metal high temperature, at insufficient oxygen amount, the total decomposition of organic compounds occurs and – in result – numerous new substances are formed [3-10].

Inorganic dangerous compounds are emitted mainly from processes of casting melting and cleaning and these are mainly metal oxides.

Out of all substances generated when high temperatures are influencing binding materials applied for moulding sands, the special group – due to their extremely harmful influence – constitute polycyclic aromatic hydrocarbons (PAHs) and compounds from the BTEX group (benzene, toluene, ethylbenzene and xylenes) [11, 12].

On account of the development of new series of hardeners for the Geopol binder, the assessment of the influence of this new binding system on the environment and comparison with the hardeners used up to now, was necessary [1].

#### 2. Research methodology

Investigations of the gases emission in the test foundry plant were performed according to the original method de-

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veloped in the Faculty of Foundry Engineering, AGH UST [14].

The schematic presentation of the experimental stand is given in Figure 1.

A sample of the investigated moulding sand of a cylinder shape of dimensions  $\Phi 50 \times 50$  mm, weight about 150 g, was poured with liquid cast iron of a temperature of  $1350^\circ\text{C}$ . The liquid metal mass was 9 kg. Gases emitting from the sample, after pouring it with liquid metal are adsorbed on active carbon (during the BTEX measurement) or polyurethane foam (during the PAHs measurement). The whole mould (weight 24 kg) is made of green sand.

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 (Figure 2), into a tightly sealed container with liquid, from which they push out the liquid. The weight of displaced liquid was measured as a function of time.

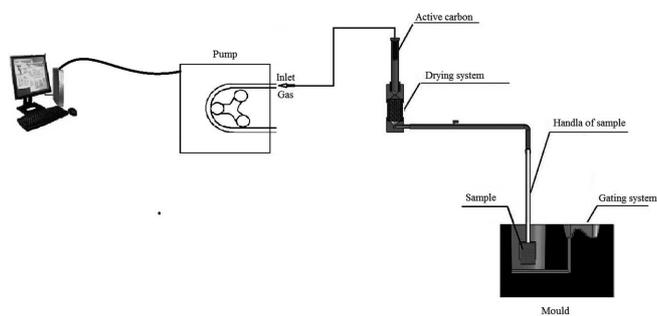


Fig. 1. Experimental stand for the determination of the emitted gases volume and the BTEX emission [11-15]

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

The identification of BTEX was carried out by means of the system consisting of the gas chromatograph Trace GC Ultra, equipped with the capillary chromatographic column RTX 5MS (Restek) of a length 30 m and internal diameter 0.25 mm.

### 3. Obtained results and their discussion

To estimate the harmfulness of substances emitted during pouring the moulding sand based on geopolymer binder with the new hardener, the comparative investigations were performed. As the reference point the moulding sands with the SA72 hardener, used up to date, was assumed. Four measurements were performed:

- 2 measurements for the moulding sand with the GEOPOL binder hardened by the SA72 hardener of the Sand-Team Company (used up to date).

- 2 measurements for the moulding sand with the GEOPOL binder hardened by the new KR72 hardener developed within the project ROW-III-315/2012.

The diagrams of the volumes of gases emitted during the process of the mould pouring with liquid metals are shown in Figure 3, while the gases emission rates in Figure 4.

On the bases of the results of the emission of compounds from the BTEX group it can be stated that both kinds of moulding sands (hardened by the SA72 and KR72 hardeners) do not constitute the higher endangering of the natural and work environments. Out of the gases emitted from the BTEX group the largest amount is of benzene, however its emission is nearly 10-times lower than in case of moulding sands with furfuryl resins.

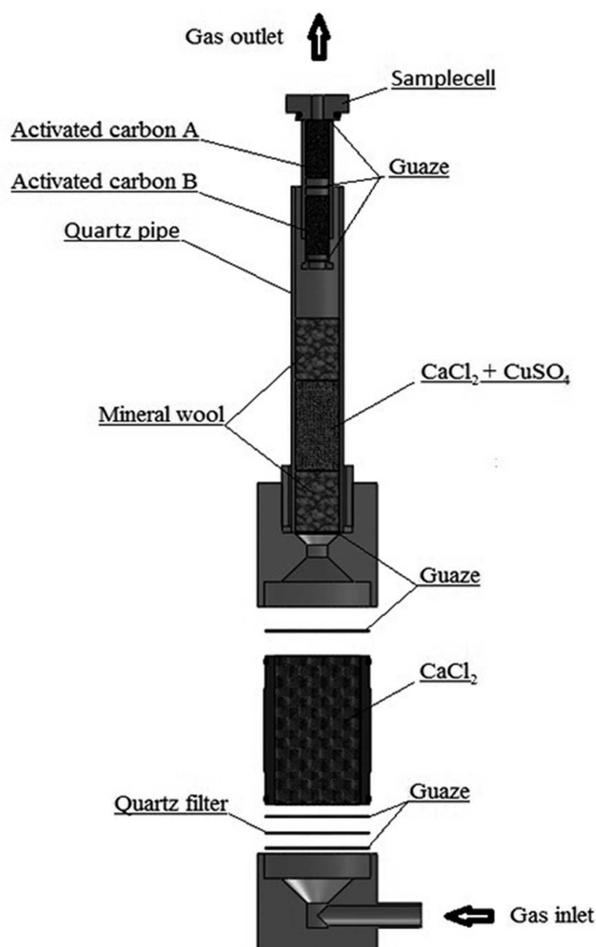


Fig. 2. Capsule for sampling gases for the BTEX content

Both, volumes of the emitted gases as well as amounts of substances from the BTEX group for two applied hardeners (SA72 and KR72) are comparable. On average, the volume of the gases emitted from moulding sands hardened by the KR72 is lower than from moulding sands hardened by the SA72 hardener. There are also certain differences in the benzene emission, in favour of the moulding sand hardened by KR72. These small differences can be the result of the measuring error but also of the fact that the moulding sand is not a homogeneous system in its whole volume. Therefore, it can be assumed that the harmfulness of both moulding sands (when

hardeners SA72 and KR72 were applied) is comparable in the range of the BTEX group emission.

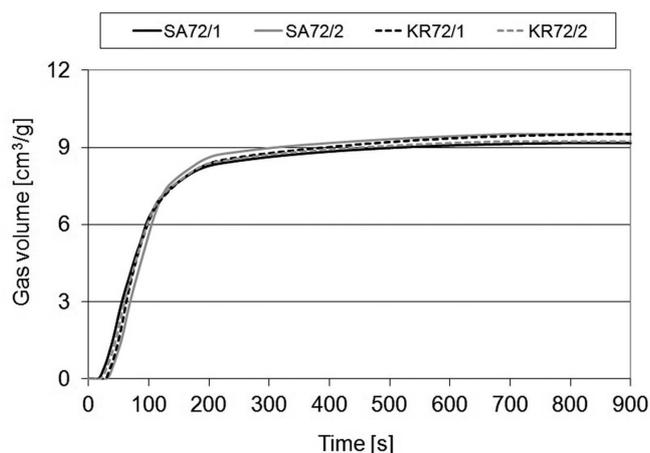


Fig. 3. Emissivity of gases in time, from the investigated moulding sands after pouring the mould with cast iron of a temperature of 1350°C

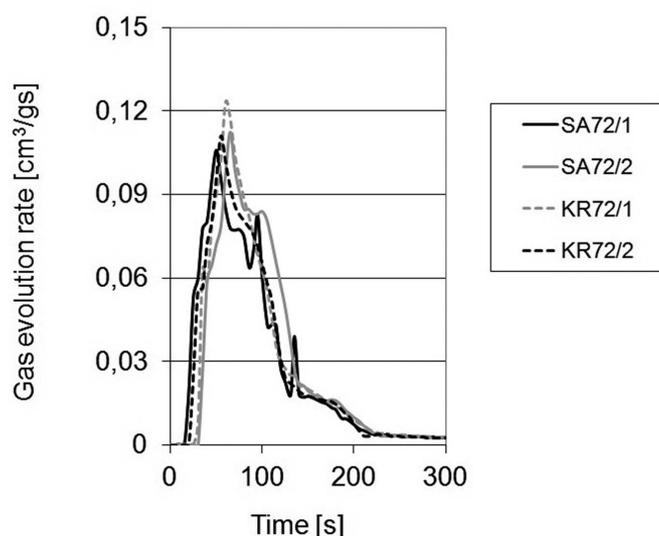


Fig. 4. Velocity of gases emission, from the investigated moulding sands after pouring the mould with cast iron of a temperature of 1350°C

The average volumes and emission rates of gases as well as the average BTEX content (from 2 measurements for each moulding sand) are given in Table 1.

TABLE 1

Results of gas volume and the BTEX content emitted from the moulding sands during the thermal decomposition (mg/kg moulding sand) (the average value for the two samples)

No	Sample	Gas volume, dm <sup>3</sup> / kg moulding sand	BTEX content in emitted gases, mg/kg moulding sand			
			Benzene	Toluene	Ethylo-benzene	Xylenes
1	SA72	9.909	37.00	0.58	0.015	-
2	KR72	9.277	33.37	0.49	0.041	0.058

#### 4. Conclusions

Assessments of harmfulness of moulding sands with the GEOPOL binder hardened by the SA72 hardener (of the SAND TEAM Company) and by the KR72 hardener (developed within the project) indicated:

- In practice, under conditions of measurements, only benzene is emitted from both moulding sands (with the SA72 hardener and with the KR72 hardener, developed within the project). Amounts of benzene are app. 10-times smaller than in case of moulding sands with organic binders and they should not be harmful for employees and for the environment.
- Moulding sands with the GEOPOL binder hardened by the developed hardener (from the KR series) are not hazardous for the natural and work environments and can be applied in sectors outside the foundry industry as raw materials, e.g. in road building, check dams, ground levelling, etc. It can be considered that moulding sands with the geopolymer binder hardened by the SA and KR series hardeners belong to sands friendly for the environment.
- Significantly lower amounts of the emitted gases as compared with moulding sands with organic binders should decrease the number of casting defects related to gases emitted from the moulding sand.

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#### REFERENCES

- [1] Report from the project No ROW-III-315/2012 (in Polish).
- [2] The assessment of harmfulness of binding materials used for a new generation of core and molding sands. Edited by M. Holtzera & R. Daňko. Wyd. Naukowe AKAPIT, Kraków 2013 (in Polish).
- [3] C.D.N. Humfrey, L.S. Levy & S.P. Faux, Food and Chemical Toxicology **34**, 1103-1111 (1996).
- [4] M.G. Ribeiro & W.R.P. Filho, Journal of Hazardous Materials **A136**, 432-437 (2006).
- [5] P. Scarbel, C.E. Bats & J. Griffin, AFS Transactions **114**, 435-445 (2006).
- [6] G.R. Crandell, J.F. Schifo, G. Mosher, AFS Transactions **114**, 819-835 (2006).
- [7] D. Fabbri, I. Vassura, J. Anal. Appl. Pyrolysis **75**, 150-158 (2006).
- [8] J.R. Fox, M. Adamovits, C. Henry, AFS Transactions **110**, 1299-1309 (2002).
- [9] H.W. Dietert, A.L. Graham, R.M. Praski, AFS Transactions **84**, 221-228 (1976).
- [10] J.F. Schifo, J.T. Radia, G.R. Crandell, G. Mosher, AFS Transactions **111**, 1173-1190 (2003).
- [11] A. Bobrowski, M. Holtzer, R. Daňko, S. Żymankowska-Kumon, Metalurgija International. **18** (7), 259-261 (2013).
- [12] M. Kubecki, M. Holtzer, A. Bobrowski, R. Daňko, B. Grabowska, S. Żymankowska-Kumon, Archives of Foundry Engineering. **12** (3), 67-72 (2012).

- [13] M. Holtzer, S. Żymankowska-Kumon, A. Bobrowski, R. Dańko, A. Kmita, Archives of Foundry Engineering. **13** (1), 39-43 (2013).
- [14] M. Holtzer, J. Dańko, J.L. Lewandowski, W. Solarski, R. Dańko, B. Grabowska, A. Bobrowski, S. Żymankowska-Kumon, A. Sroczyński, A. Różycki, M. Skrzyński, Polish Patent Nr PL 398709 (2013), Polish Patent Office (in Polish).
- [15] M. Holtzer, B. Grabowska, S. Żymankowska-Kumon, D. Kwaśniewska-Królikowska, R. Dańko, W. Solarski, A. Bobrowski, Metalurgija **51** (4), 437-440 (2012).

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