

# EMISSION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AND BENZENE, TOLUENE, ETHYLBENZENE AND XYLENE (BTEX) FROM THE FURAN MOULDING SANDS WITH ADDITION OF THE RECLAIM

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In this paper, the results of decomposition of a moulding sand with furfuryl resin also on a quartz matrix and with additions of a reclaimed material, under industrial conditions, are presented. 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. The dependence of the emitted PAHs and BTEX group substances and ignition losses on the reclaim fraction in a moulding sand are of a linear character of a very high correlation coefficient  $R^2$ . On the bases of the derived equations, it is possible to determine the amount of the emitted hazardous substances from the moulding sand containing the known fraction of the reclaim.

*Key words:* foundry, moulding sands, BTEX, PAHs, reclaim

## INTRODUCTION

Application of synthetic resins as binding agents for moulding and core sands constitutes a threat for the natural and work environment. This is caused by generating, under an influence of high temperatures of liquid metal, highly toxic substances. Depending on the kind of resin applied - under an influence of temperatures - such substances as: furfuryl alcohol, formaldehyde, phenol, compounds from the BTEX and PAHs groups, can be formed and released. These compounds are released into the atmosphere when a mould is poured with liquid metal, during a mould cooling, and when castings are knocked out. or eluted during storing of spent foundry sands [1-11].

The results of investigations of thermal decompositions of moulding sands prepared with various kinds of furan resins, in which fresh sand was a matrix, are given in the paper [12]. Presently nearly each foundry plant, which is using moulding sands with furfuryl resins, applies as a matrix the reclaimed material. A reclaim originated from the mechanical reclamation always contains certain amounts of organic substances, either as binder left overs (not removed in the reclamation process) or organic substances condensed on quartz grains. When a liquid metal influences moulding sands prepared with reclaim additions, the emission of substances from the

BTEX and PAHs group increases. The results of laboratory examinations of thermal decompositions of a moulding sand with furfuryl resin on a quartz matrix, with various additions of the reclaimed material, were presented in paper [13]. Whereas in this paper, the results of decomposition of a moulding sand with furfuryl resin also on a quartz matrix and with additions of a reclaimed material, but under industrial conditions, are presented.

The obtained results allow to determine the maximum amount of reclaim added to the molding that gives no consequences of deterioration of the working and environmental conditions.

## MATERIALS AND TESTING METHODO-LOGY OF INVESTIGATIONS

Moulding sands with urea-formaldehyde resin (1 %) modified by furfuryl alcohol (content of a furfuryl alcohol is about 80 %), hardened by mixture (0,5 %) of sulfonic acid and inorganic acid were used in tests. Moulding sands were preparing from fresh quartz sand and reclaim.

Moulding sands of the following composition were tested: SP100 – matrix 100 % fresh quartz sand; R50P50 – matrix 50% fresh quartz sand and 50 % reclaim; R100 – matrix 100 % reclaim.

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.

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A sample of the investigated moulding sand of a cylinder shape of dimensions  $\Phi$  50 x 50 mm, weight about 150 g, was poured with liquid cast iron of a temperature of 1 350 °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.

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 PAHs was carried out by means of the system consisting of the gas chromatograph Trace GC Ultra. The device HPLC Dionex 3 000 with fluorescent detection was used for the liquid chromatography.

At the determination of compounds from the PAHs group a part of hydrocarbons was condensing on the formed dust particles and together with them was deposited on the filter placed in the capsule before the polyurethane foam. Therefore at determining the total amount of generated PAHs the polyurethane foam as well as the dust on the filter were analysed.

## RESULTS AND DISCUSSION

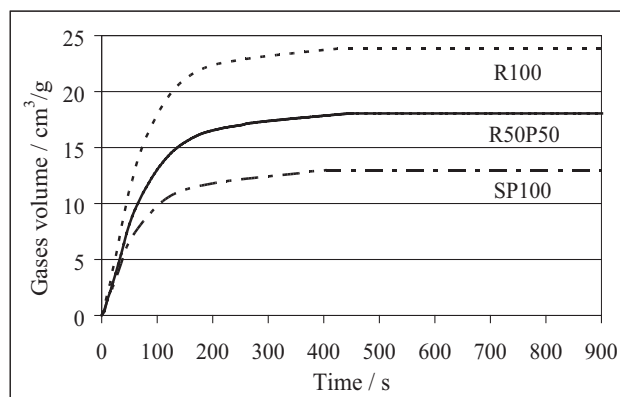
### Measurement of emitting gases amounts

The diagram showing the amount of generated gases with respect to time is presented in Figure 1, while the rate of their evolution in Figure 2.

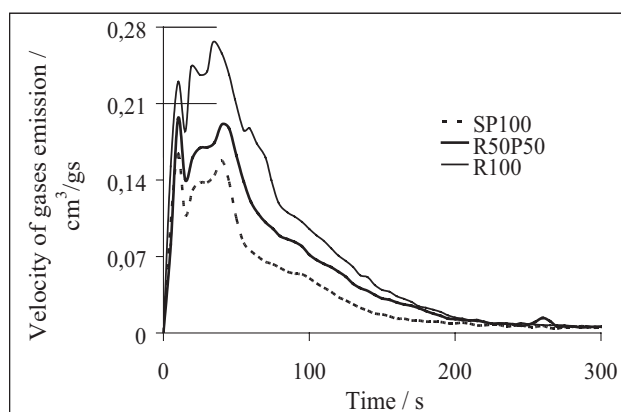
### Measuring the content of components from the btx group

Quantitative data of the emissivity of components from the BTEX group are listed in Table 1.

An addition of the reclaim to the moulding sand matrix causes a distinct increase of the emitted gases volume. Two maxima of emission rates were seen in the curves describing the kinetics of gases emissions. The gases emission rate nearly doubles when the fresh sand in



**Figure 1** Emissivity of gases in time, from the investigated moulding sands after pouring the mould with cast iron of a temperature of 1 350 °C



**Figure 2** Velocity of gases emission, from the investigated moulding sands after pouring the mould with cast iron of a temperature of 1 350 °C

**Table 1 Results of the BTEX content emitted from the moulding sands during the thermal decomposition**

Sample	BTEX content in emitted gases mg/kg moulding sand			
	B	T	E	X
SP 100	333,137 ± 33,31	2,826 ± 0,28	0,621 ± 0,06	0
R50P50	512,516 ± 51,25	18,148 ± 1,81	0	0
R100	956,602 ± 95,66	91,144 ± 9,11	1,184 ± 0,11	7,723 ± 0,77

B-Benzene, T-Toluene, E-Ethylbenzene, X- Xylen

the matrix is completely substituted by the reclaim. Along with an increasing volume of emitted gases, at the increasing fraction of the reclaim, the increased benzene concentration is visible (from 333 mg/kg - for the fresh sand matrix, to 950 mg/kg - for the reclaim matrix only).

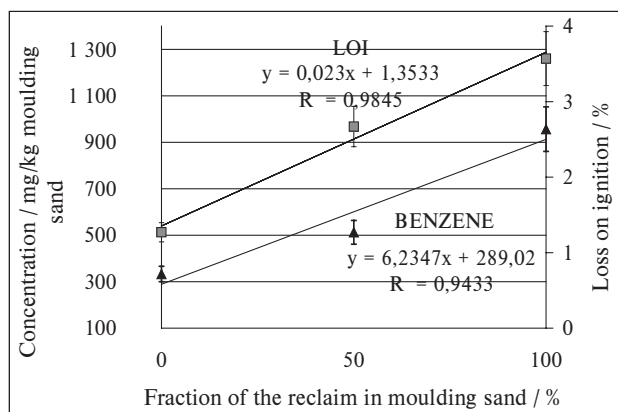
### Determination of the PAHs group substances

Analytical results of the content of substance from the PAHs group in gases emitted during moulds pouring are listed in Table 2.

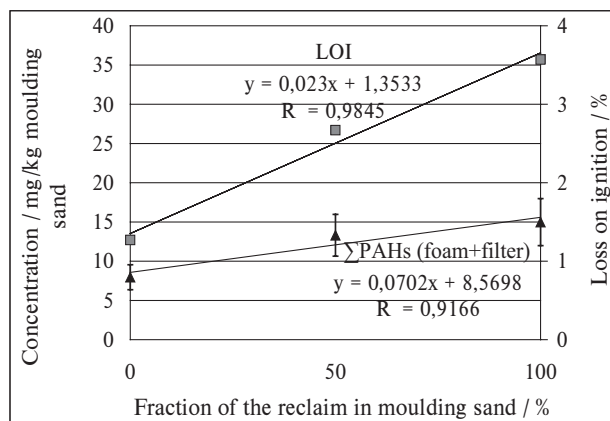
**Table 2 Analytical results of the total PAHs content, emitted from moulding sands deposited on the filter together with dusts as well as on the polyurethane foam**

Sample	Foam	Filter	TOTAL
	µg/kg moulding sand		
SP100	3 421 ± 684	4 537 ± 907	7 958 ± 1592
R50P50	5 386 ± 1077	7 920 ± 1584	13 306 ± 2661
R100	13 251 ± 2650	1 733 ± 347	14 983 ± 2997

In practice only naphthalene, which has the lowest boiling point (218 °C) and simultaneously the highest vapour pressure out of the tested PAHs, was adsorbed on the polyurethane foam. The content of the remaining PAHs adsorbed on the foam is minimal. In case of the moulding sand R100 additionally fluorene, phenanthrene and fluoranthene i.e. substances which boiling



**Figure 3** Dependence of the emission of benzene and loss on ignition on the reclaim fraction in the moulding sands matrices.



**Figure 4** Dependence of the generated PAHs substances (total emission was taken into account, i.e. substances found on the filter and polyurethane foam) and loss on ignition on the reclaim fraction in the moulding sands matrices.

points do not exceed 400 °C, are adsorbed on the foam in higher amounts. The amount of the PAHs adsorbed on the filter, for this moulding sand, constitutes only approximately 10 % of all substances emitted from this group. In case of two remaining moulding sands (SP100 and R50P50) approximately 40 % of the determined PAHs was collected on the foam and 60 % on the filter. Mainly fluoranthene, pyrene, benzo(a)-pyrene, indene(1,2,3-cd)pyrene and benzo(b)-fluoranthene (for sands: SP100 and R50P50), were found on the filter. Whereas for the sand R100 fluorene and phenanthrene occurred in large amounts. A special attention draws large amounts of carcinogenic benzo(a)pyrene.

A significant increase of the amount of the emitted PAHs substances is seen, when the reclaim fraction in matrices of tested moulding sands increases (Table 2).

### Correlation between ignition losses and the btex and PAHs concentrations in emitted gases

The dependence of the generated BTEX substances and ignition losses on the reclaim fraction in the moulding sand is presented in Figure 3.

The dependence of the generated PAHs substances and loss on ignition on the reclaim fraction in the moulding sands matrices is presented in Figure 4.

The reclaim addition to the moulding sand matrix causes a significant increase of loss on ignition of this sand. The dependence of loss on ignition on the reclaim percentage fraction is of a linear function character, which can be described by the equation:  $y = 0,023x + 1,32$ ;  $R^2 = 0,9944$ .

Both, the dependence of the emitted PAHs and BTEX group substances and loss on ignition on the reclaim fraction in a moulding sand are of a linear character of a very high correlation coefficient  $R^2$  (above 0,9).

On the bases of the derived equations, it is possible to determine the amount of the emitted hazardous substances from the moulding sand containing the known fraction of the reclaim. Since changes of the moulding

sand loss on ignition are of a similar pathways, it is also possible to estimate the amount of these generated substances on the basis of this parameter.

## CONCLUSIONS

The performed measurements of the PAHs and BTEX group substances emitted from moulding sands which matrices contained various amounts of the reclaim, under an influence of liquid cast iron high temperatures, allowed to estimate the reclaim addition influence on the harmfulness of the given moulding sand.

1. Applying the reclaim in the matrix of the moulding sand with the tested resin, causes:
  - increased amounts of generated gases (nearly twice at 100 % of the reclaim in relation to the fresh sand matrix), which for sure favours occurrence of casting defects of the gaseous porosity type;
  - significant increase of the PAHs substances, which - to a high degree - condense on matrix grains.
  - significant increase of the BTEX group substances, mainly benzene;
  - amounts of the generated PAHs and BTEX substances are linearly dependent on the reclaim fraction in the moulding sand. The correlation coefficient of this dependence is very high.
2. On account of a similar character of the dependence of the PAHs and BTEX substances emitted from the moulding sand and loss on ignition of this moulding sand on the reclaim fraction in the matrix, it is possible to estimate - with a good approximation - the amount of emitted substances from the sand with the known reclaim addition to its matrix on the basis of this parameter. Since an estimation of loss on ignition is much less laborious and time consuming and does not require specific equipment, utilising such dependence is very important for assessing the harmfulness of the given moulding sand.

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## REFERENCES

- [1] M. Holtzer, M. Kubecki, R. Dańko, S. Żymankowska-Kumon, A. Bobrowski, 4th International Symposium on High-Temperature Metallurgical Processing: TMS 2013 Annual meeting & exhibition, San Antonio, 2013, Proceedings of a Symposium 643-650. DOI: 10.1002/9781118663448.ch77.
- [2] M. Holtzer, B. Grabowska, S. Żymankowska-Kumon, D. Kwaśniewska-Królikowska, R. Dańko, W. SolarSKI, A. Bobrowski, *Metalurgija* 51 (2012) 4, 437-440.
- [3] C. D. N. Humfrey, L. S. Levy & S. P. Faux, *Food and Chemical Toxicology* 34 (1996) 1103-1111. DOI: 10.1016/S0278-6915(97)00081-1.
- [4] M. G. Ribeiro & W. R. P. Filho, *Journal of Hazardous Materials A136* (2006), 432-437. DOI: 10.1016/j.jhazmat.2006.01.019.
- [5] P. Scarbel, C. E. Bats & J. Griffin, *AFS Transactions* 114 (2006), 435-445.
- [6] G. R. Crandell, J. F. Schifo, G. Mosher, *AFS Transactions* 06-031 (2006) 10, 1-17.
- [7] D. Fabbri, I. Vassura, *Journal of Analysis and Applied Pyrolysis* 75 (2006), 150-158.
- [8] J. R. Fox, M. Adamovits, C. Henry, *AFS Transactions* 110 (2002), s. 1299-1309.
- [9] H. W. Dietert, A. L. Graham, R. M. Praski, *AFS Transactions* 84 (1976), 221-228.
- [10] J. F. Schifo, J. T. Radia, G. R. Crandell, G. Mosher, *AFS Transactions* 111 (2003), 1193-1190.
- [11] G. Crandell, 13th CIATF International Conference on Environmental Protection, Leipzig, 2000, Proceedings of a Conference.
- [12] M. Kubecki, M. Holtzer, S. Żymankowska – Kumon, *Archives of Foundry Engineering* 13 (2013) 2, 85-90.
- [13] M. Holtzer, R. Dańko, M. Kubecki, S. Żymankowska-Kumon, A. Bobrowski, A. Kmita, M. Górny, 71st World Foundry Congress, Bilbao 19-21 May 2014 (in print).

**Note:** The responsible translator for English language: "ANGOS" Translation Office, Krakow, Poland