

The Influence of Reclaim Addition on the Emission of PAHs and BTEX from Moulding Sands with Furfuryl Resin with the Average Amount of Furfuryl Alcohol

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Abstract

In this paper, the results of decomposition of the moulding sand with furan-formaldehyde resin (with middle content of furfuryl alcohol about 50 %) 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.

Keywords: Environment Protection, Foundry, Moulding Sands, BTEX, PAHs, Reclaim.

1. Introduction

Moulding sands with furfuryl resins found wide applications in foundry plants of ferrous alloys not only in the country but also in Europe. However, due to probably carcinogenic properties of furfuryl alcohol the EU Directive¹ limits this substance content (in a monomer form) in resin to 25 %. Leading world companies producing binders for castings have been - since a couple of years

- performing intensive investigations on developing furfuryl resins, which would meet the requirements of this Directive.

However, it should be realised, that such drastic decrease of the furfuryl alcohol amount in new resins, in relation to the presently applied resins (these resins contain even up to 95 % of furfuryl alcohol) must involve additional costs, and in consequence will increase the price of such resins.

Therefore, first of all, the resins in which the furfuryl alcohol content is limited not so drastically, e.g. to the level of approximately 50 %, are being developed. This type of resins will - for sure - less negatively influence the natural environment and work conditions during moulding sands preparations and forming,

¹ Regulation (EC) No. 1272/2008.

than the currently used resins. Simultaneously a significant lowering of the furfuryl alcohol content in binders, should limit the emission of harmful substances from the PAHs and BTEX groups.

It is assumed, that an increased risk of suffering a lung cancer among foundry plant employees is related to inhaling gases and solid particles containing PAHs. These compounds are produced by pyrolysis of organic materials (binders, seacoal) in a limited oxygen supply and 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, 2, 4, 6, 8-14].

The PAH formed by pyrolysis can appear free in the gaseous form and adsorbed on to dust particles. The highest dust concentrations have been found where castings are removed from the moulds [3, 5, 15]

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. The results of measurements of emissions of substances from the PAHs and BTEX group for sands with additions of a reclaim and with furfuryl resin containing about 80 % of a furfuryl alcohol monomer, are presented in paper [7, 8].

These investigations had two purposes:

- determination in what way a decrease of a furfuryl alcohol content in resins influences a limitation of the PAHs and BTEX emissions;
- determination in what way a reclaim addition to the matrix influences a harmfulness of moulding sands with resin of a decreased furfuryl alcohol content.

2. Materials and testing methodology of investigations

Moulding sands with furan-formaldehyd resin Kalthartz 8117 (prod. Huttenes-Alberstus) (1 %) with a low content of free formaldehyde (0,1-0,2 %) and content of furfuryl alcohol about 50 %, hardened by Aktivator 500 T1 (0,5 %) being a mixture (pH < 1) of benzenesulfonic acid (15-20 %), paratoluenesulfonic acid (20-25 %), sulfuric acid (< 2 %) and xylenesulfonic acid were used in tests. Moulding sands were preparing from fresh quartz sand and reclaim from the same mould sand obtained in foundry plant. 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 [7-10, 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 ϕ 50 x 50 mm, weight about 150 g, was poured with liquid cast iron of a temperature of 1350°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 foam² (during the PAHs measurement). The whole mould (weight 24 kg) is made of green sand.

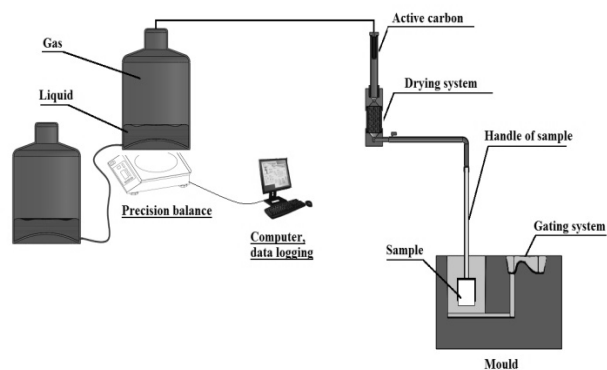


Fig. 1. Experimental stand for the determination of the emitted gases volume and the BTEX emission [10, 18, 19]

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, equipped with the capillary chromatographic column RTX 5MS (Restek) of a length 30 m and internal diameter 0,25 mm. The analysis of the PAHs group compounds was performed according to the standard ISO 11338-2:2003. The liquid chromatograph HPLC Dionex 3000 with a fluorescent detection was used.

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. Loss on ignition was determined by procedure AFS No. 117-87-S [16, 17].

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3. Results and their discussion

3.1. Measurement of emitting gases amounts

The diagram showing the amount of generated gases with respect to time is presented in Figure 2, while the rate of their evolution in Figure 3.

² Raw Polyurethane Foam 0,022 g/cm² density (RESTEK) for collection of semivolatiles (pesticides, PCBs, PAHs).

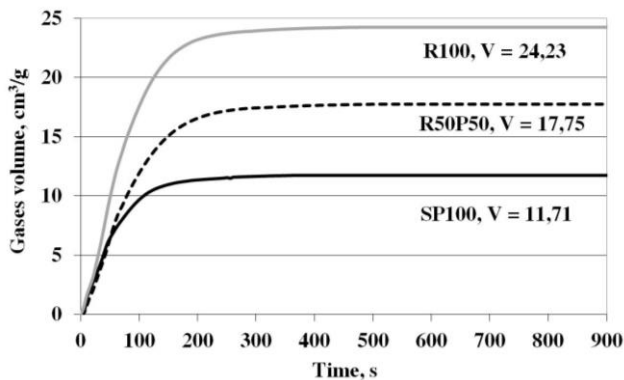


Fig. 2. Emissivity of gases in time, from the investigated moulding sands after pouring the mould with cast iron of a temperature of 1350°C

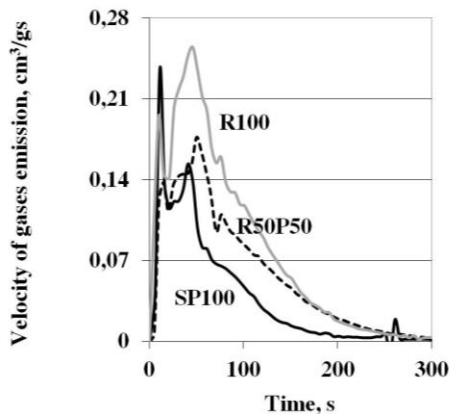


Fig. 3. Velocity of gases emission, from the investigated moulding sands after pouring the mould with cast iron of a temperature of 1350°C

3.2. Measuring the content of components from the BTEX group

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

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
	SP100	348,859	25,153	0,000
R50P50	896,077	55,769	0,713	2,029
R100	1074,677	86,663	1,172	6,159
B-Benzene, T-Toluene, E-Ethylbenzene, X- Xylene				

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 (at 10-20 s and 40-60 s). The gases emission rate nearly doubles when the fresh sand in 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 350 mg/kg - for the fresh sand matrix, to 1075 mg/kg - for the reclaim matrix only).

3.3. Determination of the PAHs group

Analytical results of the content of substance from the PAHs group in gases emitted during moulds pouring are listed in Table 2 and 3.

Table 2 shows the results of the PAHs substances emission from moulding sand R50P50, which were deposited on the filter and on the polyurethane foam, whereas in table 3 amounts of substances which were deposited on the filter together with dusts as well as on the polyurethane foam for all mould sands.

Table 2. The results of the PAHs substances emission which were deposited on the filter and on the polyurethane foam for moulding sand R50P50, after pouring the mould with liquid cast iron (in relation to 1 kg of a moulding sand)

PAHs	Sample R50P50 (50 % silica sand + 50 % reclaim), µg/kg moulding sand		
	Foam	Filter	Total
Naphthalene	5009	-	5009
Fluorene	49,7	90,7	140,4
Phenanthrene	20,0	765,5	785,5
Anthracene	56,9	243,4	300,3
Fluoranthene	2,3	3052,5	3054,8
Pyrene	1,8	2514,6	2516,4
Benz(a)anthracene	59,0	188,7	247,7
Chrysen	418,4	219,6	638,0
Benzo(b)fluoranthene	0,8	413,3	414,1
Benzo(k)fluoranthene	-	133,3	133,3
Benzo(a)pyrene	3,2	596,2	599,4
Dibenzo(ah)anthracene	0,5	-	0,5
Benzo(ghi)perylene	27,0	370,9	397,9
Indeno(1,2,3-cd)pyrene	-	354,3	354,3
Σ PAHs	5649±	8943±	14592±
	1130	1789	2918

Less substances from the PAHs group were deposited on the polyurethane foam than on the filter (on dusts). Moreover, the fraction of these substances in the foam was increasing with the reclaim increase in the sand.

In practice, the entire quantity produced 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 (about 90 %). The content of the remaining PAHs adsorbed on the foam was minimal. In case of the moulding sand R100 additionally fluoranthene, phenanthrene, pyrene and fluorene i.e. substances which boiling points do not exceed 400°C, are adsorbed on the foam in higher amounts (but each at 10-fold less than the amount of naphthalene). On the other hand, mainly fluoranthene and pyrene were deposited on the filter. They constituted 50 to 60 % of all PAHs present there. In the dusts deposited on the filter a significant amount of highly carcinogenic benz(a)pyrene was found. These amounts were very similar in all investigated sands.

Table 3. 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 (in relation to 1 kg of a moulding sand)

Sample	Foam	Filter	Total
	mg/kg moulding sand		
SP100	2,902	7,001	9,903
R50P50	5,649	8,943	14,592
R100	7,438	10,128	17,566

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 3).

3.4. Correlation between loss on ignition, volume of gases and the BTEX and PAHs concentrations in emitted gases

The dependence of the generated BTEX substances, volume of emitted gases and loss on ignition the reclaim fraction in the moulding sand is presented in Figure 4 a and 4 b.

The dependence of the generated PAHs substances and loss on ignition on the reclaim fraction in the moulding sands matrices is presented in Figure 5.

The reclaim addition to the moulding sand matrix causes a significant increase of loss on ignition of this moulding 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: $y = 0,0294x + 1,2567$; $R^2 = 0,9992$. The dependence of gases volume on the reclaim percentage fraction is of a linear function character, which can be described by the equation: $y = 0,1303x + 11,127$; $R^2 = 0,9991$.

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).

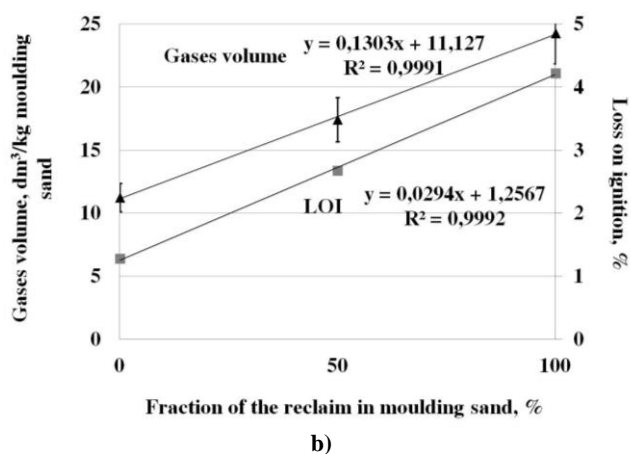
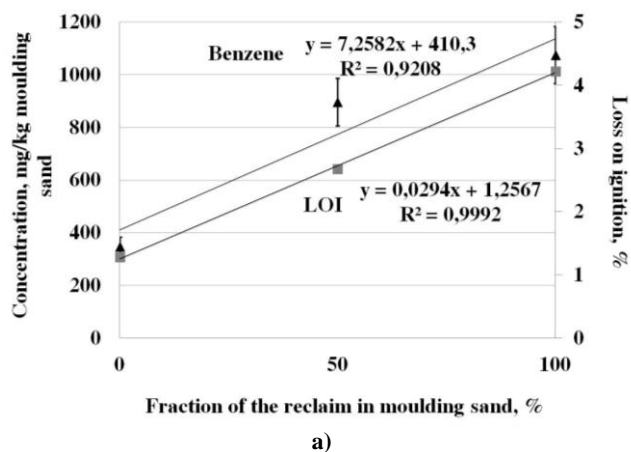


Fig. 4. Dependence of the emission of benzene (a), volume of emitted gases and loss on ignition (b) on the reclaim fraction in the moulding sands matrices

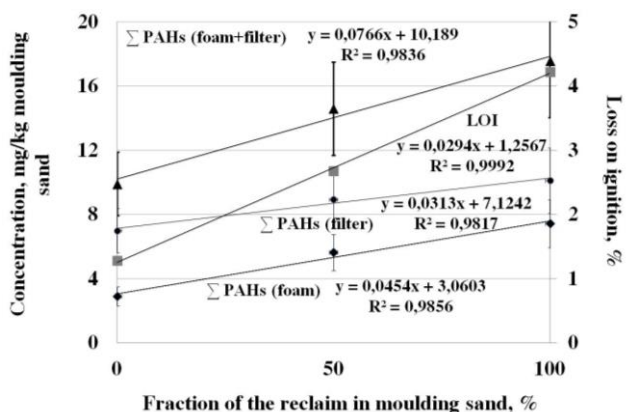


Fig. 5. Dependence of the generated PAHs substances (total emission was taken into account, i.e. substances found on the filter and polyurethane foam) and loss on ignition on the reclaim fraction in the moulding sands matrices

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.

4. 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.

Applying the reclaim in the matrix of the moulding sand with the tested resin, causes:

- increased amounts of generated gases (more than 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.

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.

On account of a similar character of the dependence of the gases volume 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 gases from the sand with the known reclaim addition to its matrix on the basis of this parameter.

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