

Comparison of the Emission of Aromatic Hydrocarbons from Moulding Sands with Furfural Resin with the Low Content of Furfuryl Alcohol and Different Activators

S. Żymankowska-Kumon *, A. Bobrowski, B. Grabowska

AGH University of Science and Technology, Faculty of Foundry Engineering, Reymonta 23, 30-059 Kraków, Poland * Corresponding author. E-mail address: szk@agh.edu.pl

Received 01.06.2016; accepted in revised form 02.09.2016

Abstract

No-bake process refers to the use of chemical binders to bond the moulding sand. Sand is moved to the mould fill station in preparation for filling of the mould. A mixer is used to blend the sand with the chemical binder and activator. As the sand exits the mixer, the binder begins the chemical process of hardening. This paper presents the results of decomposition of the moulding sands with modified urea-furfuryl resin (with the low content of furfuryl alcohol below 25 % and different activators: organic and inorganic) on a quartz matrix, under semi-industrial conditions. Investigations of the gases emission in the test foundry plant were executed according to the method extended in the Faculty of Foundry Engineering (AGH University of Science and Technology). Article presents the results of the emitted chosen aromatic hydrocarbons and loss on ignition compared with the different activators used to harden this resin. On the bases of the data, it is possible to determine the content of the emitted dangerous substances from the moulding sand according to the content of loss on ignition.

Keywords: Environment protection, Moulding sands, Resin, Aromatic hydrocarbons, BTEX, Emission

1. Introduction

The second favorite method of metalcasting industry's for producing cast elements (the first is moulding sands with bentonite called green sands) is no-bake moulding system which has proven its worth as an efficient means to produce medium and low volumes of difficult castings in both ferrous and nonferrous metals [8].

In the no-bake process, sand is mixed with a chemical binder and activator and the next moulded around the cope and drag halves of the tooling. After a precise period of time (from for example 10 sec to as long as the foundry requires depending upon mould volume), the sand mixture hardens (it similar to a brick in strength) to form the mould halves. Then, a refractory coating may be applied to both mould halves before they are brought together to form one complete mould for pouring.

Moulding sand with self-hardening furan resin - called nobake process - it takes furan resin as adhesion initiator and mixes with activator to produce sand moulds, the sand moulds can harden under room temperature [10].

The advantages and disadvantages of moulding sand with furan resin are presented in Figure 1. The sand moulds do not need to be oven dry, so it shortens the period of production and save energy, and also sand moulds are serried, and reduce the intensity of work.

ADVANTAGES	DISADVANTAGES
HIGH QUALITY OF THE RAW MATERIALS	
PRECISE SIZES OF METALS CASTINGS	HIGH COST OF RESIN
CLEAR OUTLINE OF THE METAL CASTINGS	
SMOOTH SURFACE OF THE METAL CASTINGS	
GOOD APPEARANCE QUALITY IS GOOD	UNFRIENDLY FOR ENVIRONMENT
CONSISTENT OF MICROSTRUCTURE	

Fig. 1. The advantages and disadvantages of moulding sand with furan resin

Most of the furan/furfuryl resins in use today are condensation products from furfuryl alcohol, formaldehyde and urea. The urea is responsible for the more or less high content of nitrogen in these resins. A furan/furfuryl resin with 75 % furfuryl alcohol contains 3,5 % nitrogen, on average. A simple method of reducing the nitrogen content is by raising the furfuryl alcohol to 90 % and more [10]. However, this also entails a number of disadvantages: resins are highly reactive, curing is difficult to control (especially during the warm season). Resins with high content of furfuryl alcohol are very fragile. The time for demoulding must be observed exactly because the curing process lacks elasticity. In another way parts of the mould may break away during demoulding. These parts must then be repaired/glued, which is a very time-consuming process. And the last - price of resins is defined almost exclusively by the furfuryl alcohol component, i.e., the resins are extremely liable to the development of raw material prices of furfuryl alcohol.

This type of resin will less negatively influence the natural environment and work conditions during moulding sands preparations and forming, than the currently used resins [3, 4]. Simultaneously a significant different type of activator in binder, should limit the emission of aromatic hydrocarbons [5-9].

The results of tests of thermal decompositions of moulding sands prepared with furfuryl resin and different kinds of activators (matrix from fresh sand), are given in this paper. The results of measurements of emissions of chosen aromatic hydrocarbons (especially from BTEX group) from moulding sands are presented in paper [10-12].

2. Materials and methodology

Moulding sands with modified urea-furfuryl resin of the free furfuryl alcohol content below 25 %. In addition, it contains the following: 0,1-0,2 % of free formaldehyde, 2,5-3,2 % of nitrogen, < 3,0 % of ethyl alcohol, and < 2 % ethanediol. Resin was hardened by different activators:

- A1 (an aqueous solution of paratoluenesulfonic acid);
- A2 (mixture of organic acids with very low content of free sulfuric acid < 0,25 %);
- A3 (phosphoric acid).

Moulding sands were preparing from fresh quartz sand. Studies of the gases emission in the test foundry plant were executed according to Polish Patent No. PL 398709 [4-7, 11]. Gases emitting from the sample, after pouring it with liquid cast iron of a temperature of about 1300°C are adsorbed on active carbon (during the chosen aromatic hydrocarbons measurement). For the extraction of these compounds used diethyl ether [5, 7]. Parameters of the process are presented in figure 2 [4-7, 11].

METHOD	Gas chromatography with flame-ionising detector (GC-FID)
COLUMN	Capillary, RXI 5Sil-MS (Restek)
DIMENSIONS	Length 30 m Internal diameter: 0,25 mm

Fig. 2. Parameters of GC-FID analysis

3. Results and discussion

3.1. Measurement of emissivity of gases

The Figure 3 presenting the content of generated gases in dependence on time, while the rate of gas evolution in Figure 4. Additional data is shown in Table 1. Depending on used activator the kinetics curves are different. The smallest volume (approx. 14 dm^3) were recorded for moulding sand based on activator A1. Gas evolution rate was the most intense (the maximum attained in the first five seconds the process).

Table 1.

Results of gases emission					
	Gases emission from the moulding sands				
Sample	Gas volume, dm ³ /kg moulding sand	Maximum gas evolution rate (dV/dt), dm ³ /kg·s	Time of maximum gas evolution rate, s		
A1	13,93	0,17	5		
A2	14,95	0,18	15		
A3	15,42	0,15	50		

The biggest volume of gases (approx. $15,5 \text{ dm}^3$) was recorded for moulding sand based on activator A3, but the process was the least intense (maximum reached after 50 seconds the process). Generally, two maxima of emission rates were seen in the curves describing the kinetics of gases emissions. This involves the gradual release of organic compounds: simple and complex, during the whole process of cooling of casting.

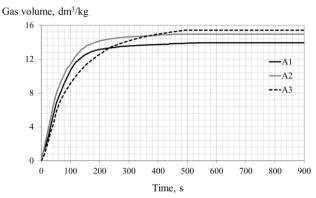


Fig. 3. Emissivity of gases in dependence on time from the tested moulding sands

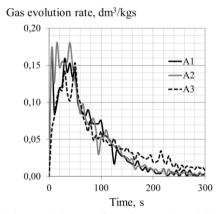


Fig. 4. Gas evolution rate from the tested moulding sands

3.2. Measurement of aromatic hydrocarbons content

Quantitative data of the emissivity of chosen aromatic hydrocarbons (from BTEX group) during the thermal decomposition of moulding sands are presented in Table 2.

Table 2.

Results of the content of chosen aromatic hydrocarbons				
Aromatic hydrocarbons content in emitted gases,				tted gases,
Sample	mg/kg moulding sand			
-	В	Т	Е	Х
A1	654,51	18,30	0,00*	0,00*
A2	601,23	10,12	0,00*	1,16
A3	200,87	4,78	0,57	2,88
B – Benzene, T – Toluene, E – Ethylobenzene, X – Xylenes				
* below the sensitivity of GC-FID device				

The chosen aromatic hydrocarbons content (from BTEX group, especially carcinogenic of benzene) is dependent on the type of activator. The most damaging are the activators based on organic acids. As a result of study the most eco-activator is A3, where benzene content was 3 times lower than for moulding sand based on activator A1 or A2. The content of other BTEX compounds remained at a low level, below the sensitivity of GC-FID device, which was caused by disintegration of these compounds (at a temperature of 1300°C) with creation a basic structure of benzene.

3.3. Dependence between loss on ignition, volume of gases and benzene concentration

The dependence of the generated benzene concentration, volume of emitted gases and loss on ignition in the moulding sands is presented in Table 3.

In the obtained results is observed that the dependence of emission of benzene on loss on ignition is of a linear function character, which can be described by the equation: y = 11341x - 14144, with a correlation coefficient $R^2 = 0.8367$ (Fig. 5). On the bases of the results, it is possible to deduce that the higher the value of loss on ignition, the higher benzene content. Based on the derived equation for this relation, it is possible to estimate the content of the emitted dangerous substances from the moulding sand taking into account the value of loss on ignition.

Table 3.

Data of the emissivity from thermal decomposition of tested moulding sands

Sample	Benzene content in emitted gases, mg/kg moulding sand	LOI, %
A1	654,51	1,31
A2	601,23	1,29
A3	200,87	1,27

Benzene content, mg/kg moulding sand

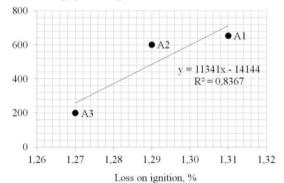


Fig. 3. Dependence of the benzene content and loss on ignition in the moulding sands with tested resin based on different activators

4. Conclusions

The executed measurements of chosen aromatic hydrocarbons (from BTEX group) emitted from moulding sands, under an influence of high temperatures, allowed to assess the activator addition influence on the harmfulness of the given moulding sand. Applying the different activators causes:

- depending on the used activator, gases emission is varied as the content of the generated aromatic hydrocarbons (from BTEX group);
- characteristic increase of aromatic hydrocarbons (from BTEX group), mainly benzene, especially using activators based on organic acids;
- content of the generated aromatic hydrocarbons (from BTEX group, mainly benzene) are linearly dependent on loss on ignition. The correlation coefficient of this dependence is relatively high.

Due to the similar character of the dependence of aromatic hydrocarbons (from BTEX group) emitted from the moulding sand and loss on ignition, it is possible to assess the content of emitted substances from the moulding sand on the basis of this factor. Assessment of loss on ignition is much less difficult and time-consuming. Measurement does not require specific equipment, utilising such dependence is important for appraisal the harmfulness of the given moulding sand with tested resin based on different activators.

Acknowledgements

The work was supported by the Project AGH No 11.11.170.318/13.

References

- [1] Dietert, H.W., Graham, A.L. & Praski, R.M. (1976). Gas evolution in foundry materials. Its source and measurement. *AFS Transactions*. 84, 221-228.
- [2] Fabbri, D. & Vassura, I. (2006). Evaluating emission levels of polycyclic aromatic hydrocarbons from organic materials

by analytical pyrolysis. *Journal of Analysis and Applied Pyrolysis.* 75, 150-158.

- [3] Fox, J.R., Adamovits, M. & Henry, C. (2002). Strategies for Reducing Foundry Emissions. AFS Transactions. 110, 1299-1309.
- [4] Holtzer, M., Bobrowski, A., Dańko, R., Kmita, A., Kubecki, M., Żymankowska-Kumon, S. & Górny, M. (2014). Emission of polycyclic aromatic hydrocarbons (PAHs) and benzene, toluene, ethylbenzene and xylene (BTEX) from the furan moulding sands with addition of the reclaim. *Metalurgija*. 53(4), 451-454.
- [5] Holtzer, M., Dańko, J., Lewandowski, J.L., Solarski, W., Dańko, R., Grabowska, B., Bobrowski, A., Żymankowska-Kumon, S., Sroczyński, A., Różycki, A., Skrzyński, M. (2013). Polish Patent No. PL 398709.
- [6] Holtzer, M., Grabowska, B., Żymankowska-Kumon, S., Kwaśniewska-Królikowska, D., Dańko, R., Solarski, W. & Bobrowski, A. (2012). Harmfulness of moulding sands with bentonite and lustrous carbon carriers. *Metalurgija*. 51(4), 437-440.
- [7] Holtzer, M., Kubecki, M., Dańko, R., Żymankowska-Kumon, S., Bobrowski, A. (2013). Research on the influence of moulding sand with furan resin on the environment. 4th International Symposium on High-Temperature Metallurgical Processing, 643-650. DOI: 10.1002/978111-8663448.ch77.
- [8] http://www.afsinc.org, 2016-03-15, 8:52.
- [9] http://www.huttenes-albertus.co.uk, 2016-02-12, 09:52.
- [10] http://www.iron-foundry.com, 2016-04-09, 14:12.
- [11] Kubecki, M., Holtzer, M. & Żymankowska-Kumon, S. (2013). Investigations of the temperature influence on formation of compounds from the BTEX group during the thermal decomposition of furan resin. Archives of Foundry Engineering, 13(2), 85-90.
- [12] Palmer, W.G. & Scott, W.D. (1981). Lung cancer in ferrous workers: a review. Am. Ind. Hyg. Assoc. J. 42, 329-340.
 DOI: 10.1080/15298668191419848.