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BTEX EMISSIONS FROM BioCo2 BONDED MOULDING SANDS

EMISJA ZWIĄZKÓW ZALICZANYCH DO GRUPY BTEX Z MASY WIĄZANEJ SPOIWEM BioCo2

Abstract

The aim of the research was to determine the volume of BTEX emission (benzene, toluene, ethylbenzene and xylenes) from BioCo2 bonded moulding sands. BioCo2, a new polymer binder, is a water solution of two - component polymer composition (polyacrylic acid and dextrin).

Research on gas emissions were performed according to the method developed at Faculty of Foundry Engineering, AGH University of Science and Technology. The measurement of BTEX samples adsorbed on activated carbon was made with the use of gas chromatography (GC-FID) and was followed by a qualitative and quantitative analysis. The research showed that the volume of BTEX emissions was lower in BioCo2 bonded moulding sand than in resin-bonded sand Kaltharz U404.

Key words: *moulding sands, polymer binders, gas emissions, gas chromatography*

Streszczenie

Przedstawione badania emisji gazów miały na celu określenie poziomu wydzielania związków chemicznych: benzenu, toluenu, etylobenzenu i ksylenów (BTEX) z masy wiązanej nowym spoiwem polimerowym BioCo2. Spoiwo stanowiło roztwór wodny dwuskładnikowej kompozycji polimerowej poli(kwas akrylowy)/dekstryna. Przeprowadzone pomiary emisji gazów wykonano według metody opracowanej na Wydziale Odlewnictwa AGH. Metoda pomiarów emisji umożliwiała pobranie próbek zaadsorbowanych gazów BTEX na węglu aktywnym w celu ich analizy jakościowej i ilościowej przy zastosowaniu techniki chromatografii gazowej (GC-FID). Na podstawie przeprowadzonych badań stwierdzono, że poziom emisji BTEX badanej masy podczas procesu zalewania ciekłym metalem był niski w porównaniu z poziomem emisji mas wiązanych żywicą Kaltharz U404.

Słowa kluczowe: *masa formierska, spoiwo polimerowe, emisja gazów, chromatografia gazowa*

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1. Introduction

In terms of gas emission, the pouring and cooling of foundry moulds is one of the processes that is feared the most by engineers. Gas emission, i.e. the tendency of moulding and core sands to release gases as a result of a high temperature of molten metal poured into the sand mould cavity, is important for technology and the environment [1].

The high temperature of poured liquid alloy causes complicated chemical transformations of moulding sands components and coating, e.g. organic components, additives, organic binders, stabilizers. The chemical composition of these substances determines if emitted gases are organic or inorganic (Fig. 1). The following gases may occur in the process: water vapour, CO, CO_2, NH_3, HCN, SO_2, H_2S, PH_3, phenol, formaldehyde, benzene, toluene, ethylbenzene, xylenes, isocyanates, polycyclic aromatic hydrocarbons (PAHs) and dioxins [2, 3].

The amount of emitted gases depends on the percentage of high-emission components of the moulding sands and above all the percentage of organic substances and water. The high temperature of liquid metal causes the thermal decomposition of organic components and the formation of numerous, new compounds [4].

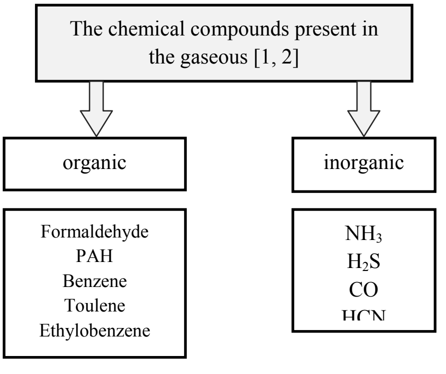

Fig. 1. Sample gas products released during the process of pouring and cooling of moulds

It is predicted that moulding and core sands will evolve in the coming years which will be caused by the modification of binders. The changes will be related to environmental protection, productivity, and technology. There are plans to extend the storage time of moulding sands to achieve a greater dimensional accuracy of castings and improve the quality of castings [5].

To restrict the emission of toxic gases, attempts are made to create binders that include more environmentally friendly solvents or to limit the amount of organic solvents in the binders. Ultimately, it is water that is going be the solvent which after evaporation is harmless for human body and the environment [5].

An interesting solution is a polymer binder in which the evaporation of water bonds the moulding sands and no chemical reaction occurs. Therefore, it is non-toxic [5]. Protein and starch solutions are also used in the foundry as binders of core and moulding sands. Modified starch from the group of polysaccharides deserves particular attention as this biopolymer is widely distributed, easy to acquire, biodegradable and cheap [6]. Polymer binder BioCo2 may be also included in this group of binders.

2. Methodology of research

2.1. Materials and reagents

The following substances were used during the research:

- polymer binder: polyacrylic acid polymer composition / dextrin, 60% aqueous solution (BioCo2 binder),
- quartz sand from Szczakowa with a grain size of 0.2 / 0.16 / 0.32,
- activated carbon for gas chromatography of 0.5÷1 nm (18÷35 ASTM), Merck,
- pure carbon disulfide, CZDA, ODCZ. FP (CS2), Polish Chemical Reagents "POCH".

2.2. The stand for determining the gas volume and BTEX emission

The research on BTEX emission during the pouring and cooling of moulding sand was carried out according to the original method developed at AGH University of Science and Technology, Faculty of Foundry Engineering, Krakow, Poland [7]. A cylindrical sample with a diameter of 50 mm, made of BioCo2 bonded moulding sand was placed in a mould made of moulding sand with bentonite and poured with liquid cast iron at a temperature of 1400^{O}C [8]. The sample was rapidly heated to a temperature of about 1400^{O}C on its surface, and to about 900^{O}C inside. The sample passed through the temperature range of 400÷900^{O}C in which the majority of volatile substances are emitted.

The analysed sample was prepared in such a way that the ratio of sand to binder is 100:3. It was thermally cured (conventionally tempered). During the process of pouring all emitted gases were led through exhaust system, then drying system and then through the adsorber (activated carbon in a container) in which organic compounds contained in gases were adsorbed. Adsorption occurred in two separate layers: control and measurement layer of the activated carbon. Control layer was used to detect gases which were absorbed on the first measurement layer.

Additionally, the measurement system allowed for simultaneous on-line tracking of the kinetics of gas emission at the interval of 5 s and for the measurement of volume. The built-in pressure-water system coupled with a scale and a computer recorded changes of liquid’s weight caused by the gas movement.

2.3. Preparing samples for chromatographic tests and BTEX determination

The scale of BTEX emission from the moulding sand was determined and the gas identification was made with the use of chromatographic test with a gas chromatograph HP 5890 Series II with flame-ionizing detector (FID).

It should also be noted that for each group of chromatographically analysed gases a suitable methodology and measurement parameters are required.

A container with two layers of activated carbon separated by glass wool was used to prepare the samples for chromatography (Fig. 2).

Gases adsorbed on both activated carbon layers were subjected to extraction in the carbon disulfide. After 15 min, 0.5 ml of the substance was sampled and placed in a containers suitable for gas chromatography testing (GC) (Fig. 3) [4].

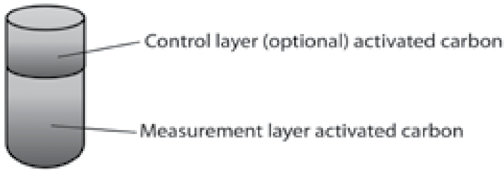

Fig. 2. Scheme of container with the activated carbon

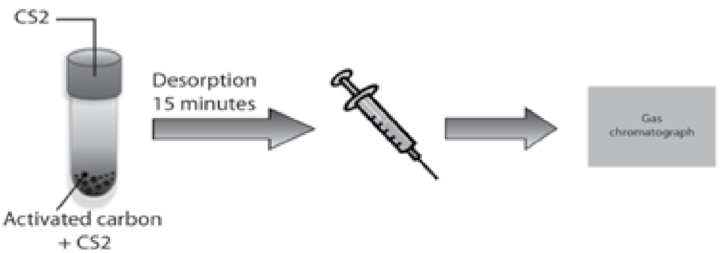

Fig. 3. Scheme of sample preparation for the test in a gas chromatograph

3. The results and analysis

Research on the BioCo2 bonded polymeric binder allowed us to obtain results (Tab. 1) on the volume of gas emitted from the BTEX components bonded with the BioCo2 polymer binder, and the speed of the process. For the purpose of comparison, the results of the tests on the emissions of BTEX from resin Kaltharz U404 bonded moulding sands and bentonite bonded moulding sands were also featured in the Table 1.

Studies of gas emission (Fig. 4) showed that the volume of collected decomposition products from the sample of the BioCo2 bonded moulding sand is ca. 0.12 dm^3 (per 1 kg of the moulding sand).

Table 1. The results of the gas emission of the BTEX group for BioCo2 bonded moulding sand and resin Kaltharz U404 and bentonite bonded moulding sands

Sample of the moulding sand	Composition, parts by weight	Volume of gas, dm^3/kg sand moulding	Gas emission, mg/kg moulding sand				Max. velocity of emission, $cm^3/g \cdot s$
			B*	T*	E*	X*	
Moulding sand with BioCo2 binder	Binder 3 Sand 100	12.40	133	3.00	0.02	0.04	0.12
Moulding sand with Kaltharz U404	Binder 1 Hardener 0,5 Sand 100	33.00	384	56.95	0.30	2.64	0.27
Moulding sands with bentonite	Technology of ENVIBOND	22.19	371	15.52	0.06	0.47	0.17

* – B – benzene, T – toluene, E – etylobenzene, X – o-, m-, p-xylene

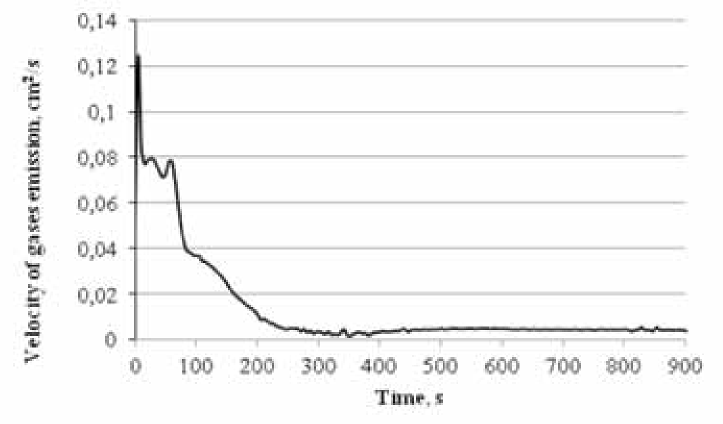

Fig. 4. The volume of gas emitted from the sample of BioCo2 bonded moulding sand in the process of pouring with molten metal

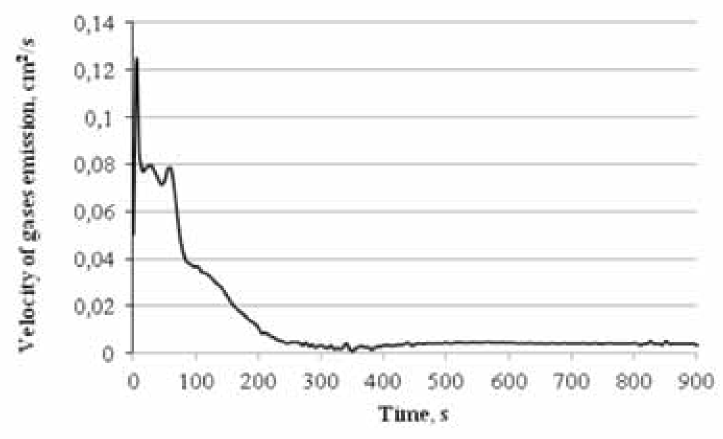

Fig. 5. Kinetics of gas emission from BioCo2 bonded moulding sand

The analysis of the curve presenting the kinetics of gas release (Fig. 5) showed that the polymer binder in moulding sand decomposed heavily in several stages (three characteristic speed peaks). The highest volume of gas was emitted during the first 100 s. This is the time interval in which the main gas products are formed from the destruction of the binder.

The course and the intensity of the decomposition process may be related to the evaporation of solvent water followed by the release of constitutional water and eventually the deterioration of the binder and the formation of low molecular weight gaseous products and carbonization.

In the course of gas emission we may set apart two peaks with the greatest kinetics of release. The first peak is formed immediately after the pouring of molten metal into fittings and the second peak approximately 90 s later.

The results of the BTEX gas emission from the BioCo2 bonded moulding sand are shown in Table 1. The study shows that the analysed BioCo2 bonded moulding sand is characterized by low emissions of BTEX during pouring in comparison with resin furan Kaltharz U404 (Kaltharz U404, Hüttenes Albertus) bonded moulding sand and bentonite (technology ENVIBOND, S&B Industrial Minerals) bonded moulding sand. Benzene was the main BTEX compound emitted. In addition, small amounts of toluene, ethylobenzene and o-, m-, p-xylenes were detected.

On the basis of the data in Table 1 we may note that that BioCo2 bonded moulding sand is characterized by more than 2.5 times lower benzene emissions compared with Kaltharz U404, or bentonite bonded moulding sands.

4. Conclusions

Currently applied moulding sands consist of many binders that release numerous volatile compounds in the atmosphere. The presence of the compounds may negatively influence the health of the people working with moulding sands. During pouring and cooling the concentration of the compounds may probably exceed the occupational exposure limit. Therefore, the lower the volume of the BTEX compound emission, the more ecological the components of the moulding sands are.

The results show that the use of a BioCo2 binder is recommended in foundry due to its low gas emission, especially BTEX emission.

It has been proved that the release process from moulding sands is violent and the highest level is recorded during the first 100 s. Despite that, among all analysed moulding sands, the lowest volume of gas was released from the BioCo2 bonded moulding sand. Also, the results of the chromatographic tests show that the lowest emission of BTEX was observed in the BioCo2 bonded moulding sands.

Taking into account the results of the research on the BioCo2 binder and the knowledge about the chemical composition of the binder (60% of water and the composition of components that are made only of carbon, hydrogen and oxygen); it seems sensible to classify the BioCo2 binder as an ecological binder.

In addition, because of the appropriate technological properties, easy availability and low cost of components and their biodegradability, the new polymer binder is an interesting and environmentally friendly binder for moulding and core sands.

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