

Influence of the Reclaim Addition to the Moulding Sand Matrix Obtained in the ALPHASET Technology on the Emission of Gases - Comparison with Moulding Sand with Furfuryl Resin

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Abstract

This study focuses on the ALPHASET process of mould making (Ester-Cured Alkaline Phenolic No-Bake). The cross – linking of alkaline phenolic resole resin by adding at least one kind of organic esters is the secondary popular system (after the technology of molding sands with furfuryl resins) with the advantages including low odour, virtually no smoke, easy to stripping, good finishing, low veining, minimal erosion, and very good hot strength. The phenolic resoless used in the system are prepared typically by reacting 30-55% formaldehyde solution with less phenol using a strong alkali catalyst, such as sodium hydroxide or potassium hydroxide at the temperatures of below 110°C (pH > 7). After removing parts of water this yields a thermal set phenolic resin solution with solid content 50-70%. In order to significantly increase strength and to improve the moisture and humidity resistance of sand mould, it is necessary to mix a little silicene solution addition with resin binder (about 0.1 – 0.3% based on the amount of resin binder).

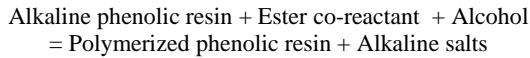
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1. Introduction

Nowadays, sand casting is commonly used to form wide variety of metal components with intricate shape and geometries. Automotive components such as engine blocks, manifolds, cylinder heads and transmission cases are among typical components made of sand casting process besides other vast applications. This study focuses on the ALPHASET process of mould making (Ester-Cured Alkaline Phenolic No-Bake). The

cross – linking of alkaline phenolic resole resin by adding at least one kind of organic esters is the secondary popular system (after the technology of molding sands with furfuryl resins) with the advantages including low odour, virtually no smoke, easy to stripping, good finishing, low veining, minimal erosion, and very good hot strength. The phenolic resoless used in the system are prepared typically by reacting 30-55% formaldehyde solution with less phenol using a strong alkali catalyst, such as sodium hydroxide or potassium hydroxide at the temperatures of below

110°C (pH > 7). After removing parts of water this yields a thermal set phenolic resin solution with solid content 50-70%. In order to significantly increase strength and to improve the moisture and humidity resistance of sand mould, it is necessary to mix a little silicic acid solution addition with resin binder (about 0.1 – 0.3% based on the amount of resin binder). The alkali in the phenolic resin reacts with the ester to form alkali metal ions.



A variety of ester hardeners can be used in the system. Since the binders are free of nitrogen and sulfur, they afford foundry engineering advantage of nodular iron, cast steel and aluminum casting [1-4].

Typically, 1.5 to 2.0% binder based on sand and 20 to 25% co-reactant based on the resin are used to coat washed and dried silica sand in most core and molding operations.

Both the resin and co-reactant are water soluble, permitting easy cleanup. Physical strength of the cured sand is not as high as that of the acid-catalyzed and urethane no-bakes at comparable resin contents. However, with care in handling and transporting, good casting results can be obtained.

When moulds with organic binders poured with liquid metal alloys of high temperatures (app. 1400 - 1550°C), a binder thermal decomposition occurs and various substances such as polycyclic aromatic hydrocarbons (PAHs) and BTEX (benzene, toluene, ethylbenzene, and xylenes) are generated. A significant part of these compounds is emitted to the atmosphere during a mould pouring and then cooling, however a part of them condenses in intergranular spaces in moulding sands and emits during castings knocking out [5,6].

Presently nearly each foundry plant, which is using moulding sands with ALPHASET resins, applies as a matrix the reclaimed material, in amounts from 50 to nearly 100%. 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. The reclaimed material loss on ignition (LOI) constitute a measure of organic substances presence. When a liquid metal influences moulding sands prepared with reclaim additions, the emission of substances from the BTEX and PAHs group increases [5, 6].

The impact of thermal destruction of molding sands with the regenerate and ALPHASET resin at the emission of compounds from the BTEX group and PAHs is presented in the article. The obtained results allow to determine the maximum amount of regenerate added to the molding that gives no consequences of deterioration of the working and environmental conditions.

Mechanical reclamation

In reclaiming ester – cured alkaline phenolic systems alkali metals can react with the sand surface during casting forming silicates. The alkali salts can change the sand surface chemistry, and remain in the sand [7,8].

This can interfere with reclaimed sand re-bonding. It can also make the reclaimed sand appear “dry” by absorbing water from resin. In general, for mechanical reclamation sodium salts show

less effect than potassium. Therefore use of sodium – based resin on mechanical reclaimed sand is preferred. Also, water additions of 0.2 – 0.3% based on sand during re-bonding can improve performance. It is possible to reuse the regenerated from the mechanical recovery of 60 -80%.

Thermal reclamation

The effect of alkali salts on thermal regenerated sands is even more dramatic than on mechanical reclaimed sands [9,10].

The salts can react with silica sand forming silica glass. These sintered silicates can foul the reclaimer. In addition, sodium and potassium salts can build- up in reclaimed sands and reduce re-bonding strengths. To prevent this special additives are added (0.6 – 1.0%) to the shakeout sand just prior to its entry into a thermal reclaimer. These mineral additives minimize sintering temperature of compounds. The additive complexes with alkali metals and removes them as fines. Water additions may be helpful in improving re-bonding strengths. Potassium – based resins may provide better performance on higher quality thermal reclaim sands. In case of the thermal reclamation the reclaimed material can substitute fresh sand nearly in 100%. However, it is necessary to introduce the mentioned above additions into the moulding sand subjected to this reclamation.

2. Materials and testing methodology of investigations

Moulding sands Ester-Cured Alkaline Phenolic No-Bake were used in tests. Dangerous components contained in a resin (pH app. 14): NaOH, KOH, methyl alcohol CH₃OH, phenol C₆H₅OH, formaldehyde. Fresh quartz sand, Szczakowa (0.20/0.16/0.32, sintering point 1400°C) and reclaim (LOI = 0,78%). Reclaimed materials were obtained from spent moulding sands of the same composition as the fresh moulding sand in investigations.

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 [11].

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 [12]. Station for research of the volume and harmfulness of gases compounds from the materials used in foundry and metallurgical processes (Poland) [13].

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 foam (during the PAHs measurement). The part of PHAs was condensing on the formed dust particles and together with them was deposited on the filter. The total amount of generated PAHs the polyurethane foam as well as the dust on the filter were analysed.

At the determination of compounds 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 PAHs analysis was performed according to the ISO 11338-2:2003 standard. The device HPLC Dionex 3 000 with fluorescent detection was used for the liquid chromatography. Ignition losses were determined according to the Procedure 117-87-S [14].

3. Investigation results and their discussion

3.1. Measuring of the loss on ignition

The results of ignition losses of the tested moulding sands and initial reclaim, which constituted addition to a matrix, are shown in Table 1. The reclaimed material added to the moulding sand matrix causes a significant increase of the ignition loss. The moulding sand on the matrix being 100% of the reclaim (R100) has ignition losses nearly twice as high than the moulding sand on the matrix of 100% fresh sand (SP100) (0.91 and 1.41%, respectively). Dependence of ignition losses on the percentage content of the reclaim is of a linear character and can be described by the equation: $y = 0.0049x + 0.9483$; $R^2 = 0.9316$ (Fig. 4).

3.2. Measurement of emitting gases amounts

At each test the amount of emitting gases was recorded every 5 seconds. The diagram showing the amount of generated gases with respect to time is presented in Fig. 2 and table 1, while the rate of their evolution in Fig. 3. An addition of the reclaim to the moulding sand matrix causes a distinct increase of the emitted gases volume. The total amount of gases is, in practice, formed in the first 100 seconds from pouring the core by liquid metal. On the curves of gasses emission rates 3 maxima are seen. They probably correspond to: peak I – expansion of air plus the evaporation of free moisture; peak II – about 30 seconds identified as the release of combined water (water of crystallization) in the binder and/or aggregate; and II peak – after 50-80 seconds, attributed to the general break down of the organics in the binder.

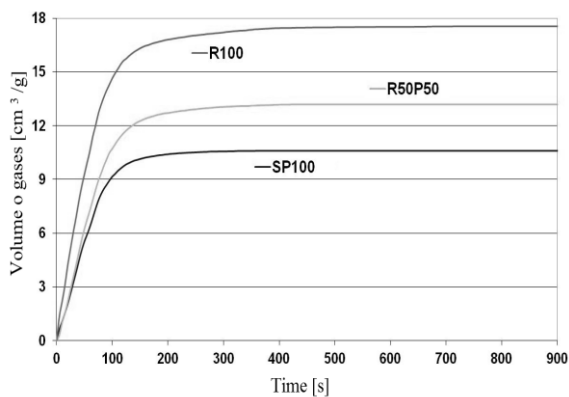


Fig. 2. Emissivity of gases in time, from the investigated moulding sands after pouring the mould with cast iron of a temperature of 1350°C

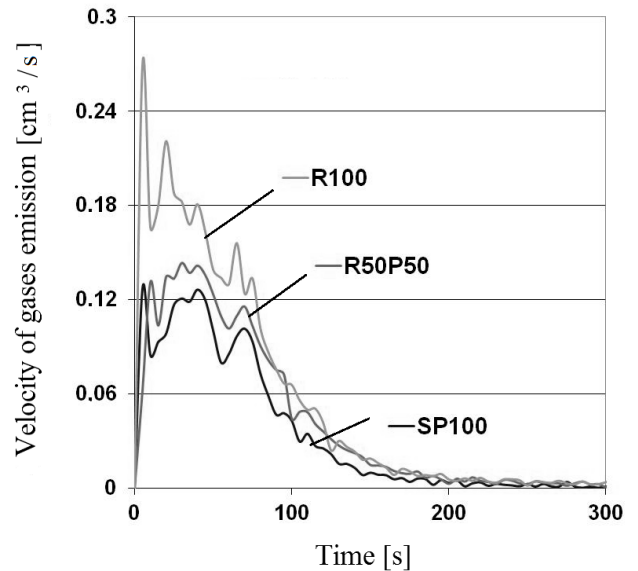


Fig. 3. Velocity of gases emission, from the investigated moulding sands after pouring the mould with cast iron of a temperature of 1350°C

3.3. Measuring the content of components from the BTEX group

Quantitative data of the emissivity of components from the BTEX group counted over for 1 kg of a moulding sand, are listed in Table 1.

The main component is benzene. Amounts of the remaining substances from the BTEX group are two orders of magnitude lower.

Table 1.

Volume of generated gases and results of the BTEX content emitted from the moulding sands during the thermal decomposition (temperature 1350°C)

Sample name	LOI, %	Volume of gases [dm³/kg]	Content of BTEX mg/ kg				ΣBTEX
			Benzene	Toluene	Ethylbenzene	Xylenes	
SP100	0.91	11.303	246.7	2.1	0.3	0.02	249.12 ± 24.9
R50P50	1.27	13.773	332.2	5.3	0.3	0.02	337.8 ± 33.8
R100	1.40	16.766	446.3	8.4	0.6	0.5	455.8 ± 45.6

Along with an increasing volume of emitted gases, at the increasing fraction of the reclaim, the increased benzene concentration is visible (from 247 mg/kg - for the fresh sand matrix, to 446 mg/kg - for the reclaim matrix only).

The dependence of the generated benzene and loss on ignition on the reclaim fraction in the moulding sand is presented in Figure 4.

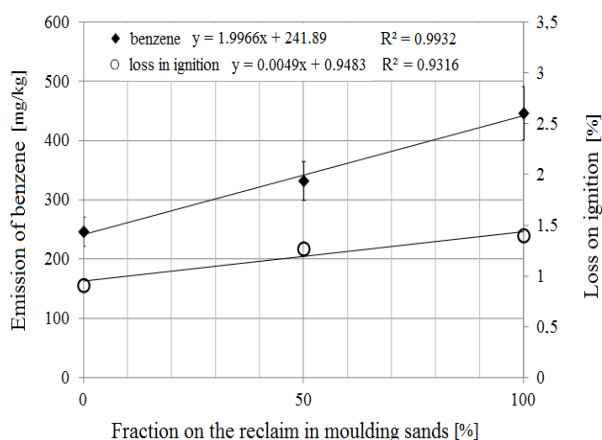


Fig. 4. Dependence of the emission of benzene and loss on ignition on the reclaim fraction in the moulding sands matrix

3.4. Determination of the PAHs group substances

Analytical results of the total content (which were deposited on the filter together with dusts as well as on the polyurethane foam) of substance from the PAHs group in gases emitted during moulds pouring are listed in Tables 2.

In case of all tested moulding sands the emission of naphthalene was the highest (from 30 to 40% of all emitted PAHs),

Such substances as: fluoranthene, pirenene, chrysene and benzo(a)pirene were emitted in relatively large amounts. They were mainly settling on a filter together with dusts (boiling points of these substances are above 400°C).

The total emission of the PAHs group substances from tested moulding sands was constant (within the limiting error), regardless of the reclaim fraction in the moulding sand, and thus regardless of ignition losses.

On the bases of the derived equations, it is possible to determine the amount of the emitted BTEX, and especially benzene, 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.

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

Compound	Concentration, µg/kg		
	SP100	R50P50	R100
1 Naftalen	1664	2175	2021
2 Acenaftalen	2.3	3.7	0
3 Fluoren	20.2	65.1	32
4 Fenantren	172.8	449.3	399
5 Antracen	86.6	97.7	260
6 Fluoranten	595.8	570.4	755
7 Piren	583.4	590.4	684
8 Benzo(a)antracen	203.3	231.2	100
9 Chryzen	545.1	733.2	83
10 Benzo(b)fluoranten	374.0	364.3	279
11 Benzo(k)fluoranten	139.6	146.5	79
12 Benzo(a)piren	480.8	479.7	330
13 Dibenzo(a,h)antracen	-----	-----	2
14 Benzo(g,h,i)perylene	360.8	476.0	296
15 Indeno(1,2,3-c,d)piren	48.3	488.4	364
16 Σ WWA	5276.3 ±	6870.8 ±	5685 ±
+/- 20%	1055.3	1374	1137

The comparison of the emission of substances from the BTEX and PAHs group from the tested moulding sand from the ALPHASET technology and from the moulding sand with furfuryl resin (of the furfuryl alcohol content < 25%), are shown in Table 3.

Table 3.

Comparison of the BTEX and PAHs emission during the thermal decomposition of the binder based on the furfuryl resin and on the resin from the ALPHASET technology [15]

Resine	Sample name	V, dm³/kg	ΣBTEX mg/kg	Benzene mg/kg	LOI %	ΣPAHs mg/kg
Furfuryl resin	SP100	14.95	666.4	654.7	1.32	11.76
	R50P50	19.33	1297.1	1198.6	2.18	23.64
	R100	24.67	1906.1	1770.4	3.15	25.56
ALPHASET resin	SP100	11.03	249.1	246.7	0.91	5.28
	R50P50	13.77	337.8	332.2	1.27	6.87
	R100	16.77	455.8	446.3	1.40	5.69

4. Conclusions

1. 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.
2. Applying the reclaim in the matrix of the moulding sand with the tested resin, causes:

- increased amounts of generated gases relation to the fresh sand matrix, which for sure favours occurrence of casting defects of the gaseous porosity type;
 - significant increase of the of the BTEX group substances, mainly benzene;
 - amounts of the generated BTEX substances are linearly dependent on the reclaim fraction in the moulding sand. The correlation coefficient of this dependence is very high.
3. On account of a similar character of the dependence of the 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.
 4. The emission of substances from the PAHs group is, in practice, constant (within the limiting error), regardless of the reclaim fraction content in the moulding sand.
 5. The emissivity of substances (from the BTEX and PAHs group) harmful for the environment from the moulding sand with the ALPHASET resin is 2 to 5 times smaller than the emission from the moulding sand with the furfuryl resin (even of the furfuryl alcohol content < 25%).

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