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# Analysis of Spent Moulding Sands with Binders of Various Thermal Degradations, in an Aspect of a Possibility of a Directional Mould Degassing

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## Abstract

The results of investigations of spent moulding sands taken from the mould in which the metal core cooling system - to increase the cooling rate of the ladle casting - was applied, are presented in the hereby paper. The changes of the spent moulding sand at the casting external side being the result of degradation and destruction processes of organic binder, were analysed in this publication. Since the reclaimed material, obtained as a result of the mechanical reclamation of spent sands of the same type, is used as a grain matrix of the moulding sand, the amount of a binder left from the previous technological cycle is essential for the sound castings production. On the bases of investigations of the thermal analysis, ignition losses, dusts contents and pH values of the samples taken from the spent sand the conditions under which the process of gases displacing in the casting mould was realised as well as factors limiting the efficient mould degassing - were considered in this study. The possible reason of a periodical occurrence of an increased number of casting defects due to changing gas volume emission, being the reason of the realised technological process, was indicated.

**Keywords:** Spent moulding sands, Thermal analysis, Organic binders, Ignition loss

## 1. Introduction

The known, European producer of massive high-dimensional castings (ladles, ingot moulds) of spheroidal and vermicular cast irons wrestles with problems of uneven cast iron structure occurrence and with defects related to gasified castings at the wall cross-section. This state is caused by a significant difference in the cooling rates of two sides of the casting walls. Outer sides having access to the surroundings - due to better conditions of the heat dissipation - are cooling fast, while metal layers from the

casting core side - which form a closed space - are cooling much more slowly.

The inner ladle part is reproduced by a relatively thin layer of the moulding sand formed on the metal core (Fig. 1). In order to increase the casting cooling rate, and specially its inner side, forced cooling of metal core by means of water mist, was applied. The moulding sand reproducing the inner ladle part undergoes a total burning. Since the metal core has several openings and from its inside the metallic conduit with injective suction is led outside the mould the gases, from the burned moulding sand and from metal, can flow easily (Fig. 1).

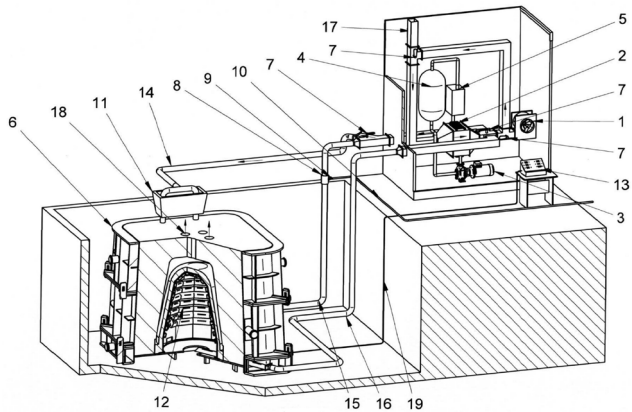


Fig. 1. System of a mould cooling: 1 – ventilator, 2 – heat exchanger, 3 – water pump, 4 – tank of working medium, 5 – peak load boiler, 6 – casting mould, 7 – control valve, 8 – jet pump, 9 – metering valve, 10 – water conduit, 11 – pouring tank, 12 – pipe coil, 13 – electronic control module, 14 – pipe conduit of hot air, 15 – conduit of cold mixture: air – water mist, 16 – conduit of hot mixture: air – water vapour, 17 – air conduit: system – atmosphere, 18 – overflow and outlet openings of cooled air, 19 – multi-strand cable connecting temperature sensors – control assembly

Moulding sands reproducing the outer casting surface, due to a significantly thicker layer, undergo the thermal destruction and degradation to a different degree. Since the reclaimed material, obtained as a result of the mechanical reclamation of spent sands of the same type, is used as a grain matrix of the moulding sand, the amount of a binder left from the previous technological cycle is essential for the sound castings production. The moulding sand increased layer from the moulding box side of a changing thickness resulting from the ladle shape, can be a factor increasing the casting gassing.

## 2. Methodology of testing

### 2.1. Materials taken for tests

The urea-formaldehyde resin modified by furfuryl alcohol, hardened by mixture of organic (from sulphonic acids group) and inorganic acids (modified by special additions) is applied by the Company for making the casting mould. The reclaimer obtained by the mechanical reclamation is used as the matrix [1].

The state of the spent moulding sand taken during the casting knocking out is presented in this publication. On account of the casting shape, materials for tests were taken from three places of various moulding sand burning degrees. The places of sampling are shown in Figure 2.

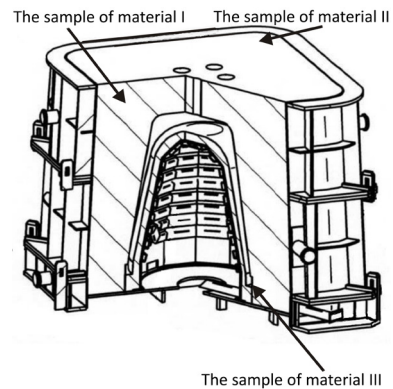


Fig. 2. Places in the casting mould from which materials were taken

The sample of material I – was taken from the place nearest the casting, where the direct metal influence caused losing the bonding properties of a binder (material I was in a loose state). This burned moulding sand consisted of a mixture of matrix grains with binders of various degradation degree on surfaces. Numerous grains were covered by a lustrous coating indicating that the pyrolysis effect occurred and carbonizate (process coke) was formed, as a result of degassing of organic substances under oxygen-free conditions (Fig. 3).

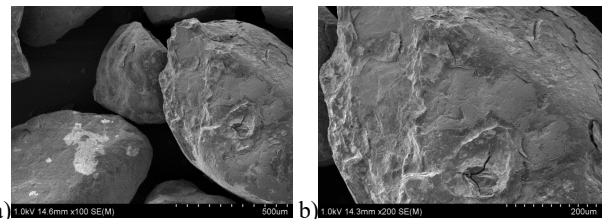


Fig. 3. Spent furan moulding sand after casting knocking out from the mould: a) Magnification x100, b) Magnification x200

The sample of material II – was taken from the middle part of the mould, between the casting and the moulding box. This moulding sand was not burned (remained in the mould), but was within the space of the liquid metal temperature influence (moulding sand was hot).

The sample of material III – was taken from the moulding box corner. This material was in a lump form. The moulding sand was not subjected to the liquid metal temperature during the casting making (moulding sand was cold) (Fig. 4).

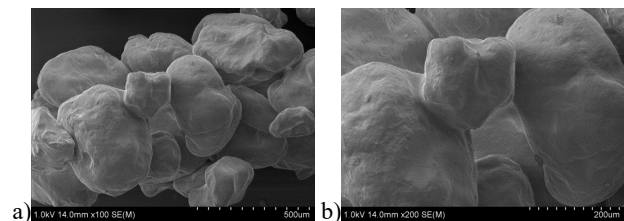


Fig. 4. Furan moulding sand after bonding and mechanical crushing: a) Magnification x100, b) Magnification x200

## 2.2. Thermal analysis

Thermal investigations were performed by means of the thermal analyser NETZSCH STA 449 F3 Jupiter®, which allows performing TG and DTG measurements, under the same measuring conditions, it means at the same temperature increase rate ( $10^{\circ}\text{C}/\text{min}$ ), at the gas flow rate ( $40\text{ ml}/\text{min}$ ). Each sample was measured both in the oxygen atmosphere (air) and in the oxygen-free atmosphere (argon). Samples subjected to the thermal analysis TG were of masses app. 15 mg. Platinum crucibles, allowing to perform the temperature measurements up to  $1000^{\circ}\text{C}$ , were used [2-4].

## 2.3. Mass decrements in dependence of the temperature - ignition losses

The most important criteria of assessing the quality of spent moulding sands with organic binders or the reclaim, are ignition losses [5, 6]. The sampled materials were subjected to investigations of the temperature influence on the degradation and destruction of a binder applied in the moulding sand (furan resin). Samples of materials II and III were crushed and sieved through the  $0.8\text{ mm}$  sieve, before testing. Materials in a loose form were roasted in the silite furnace. Investigations of the temperature influence on the degradation and destruction state were carried out on two 30 g samples, weighted into quartz crucibles. The presented in this study results are averaged values. Investigations of ignition losses were done in the temperature range from  $300^{\circ}\text{C}$  to  $950^{\circ}\text{C}$ , which is assumed as warranting burning of all organic products. The roasting time was 2 hours.

## 2.4. Mass decrements in dependence on time – ignition losses

Samples were also subjected to a roasting process, and mass decrements were tested in dependence on time of their roasting in the silite furnace of a temperature  $520^{\circ}\text{C}$ . Tests were performed on two 30g samples and their average values are presented in this paper. Investigations were carried out at various roasting times: from 15 to 120 minutes.

## 2.5. Sieve analysis

The sieve analysis was performed for two 50 g samples. Sieving was done on the laboratory sieve shaker LPeZ-2e. The obtained results were elaborated by the LabaSit program.

## 2.6. Analysis of fractions technologically unsuitable for the grain matrix

An important factor influencing the moulding sand quality is the grain matrix state (sand, reclaim) in respect of dusts content (fractions technologically unsuitable – particles size less than  $0.1$

mm). This parameter was determined on 100 g samples blown through by the air flowing with a velocity of  $1\text{ m}/\text{s}$  for 4 minutes in the fluidising column of a diameter of  $50\text{ mm}$ . The results presented in this paper are the arithmetic mean from two samples.

## 2.7. Determination of the pH value

The determination of the tested material pH value was done for 50 g sample to which  $50\text{ cm}^3$  of distilled water was added, mixed and left for 1 hour.

The pH value of the obtained solution was determined by means of the microcomputer pH-meter CP-105. The measurement was performed after the calibration of the device, to avoid an eventual error related to electrode properties. Two buffer solutions of the strictly determined pH values are needed for this calibration: e.g. for contaminated acidic waters of pH 7 and pH 4.

## 3. Analysis of results

In order to determine the destruction temperature of the binder, applied by the Company, the thermal analysis of this binder was performed. The FR 75A resin was mixed with the hardener PU-6 according to the proportion recommended by the producer (ratio: binder/hardener = 2). Vapours of materials forming the binder were mixed under conditions of a fast heat abstraction due to a very strong exothermic reaction of the resin with the hardener without the grain matrix.

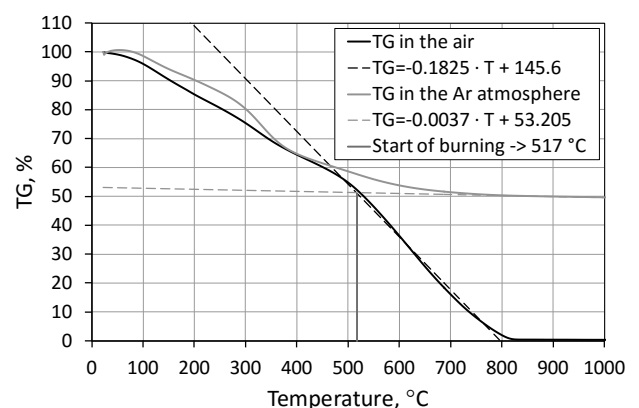


Fig. 5. Selection of the destruction (burning) temperature of the resin applied by the foundry

The thermal analysis results (performed in the oxygen and oxygen-free (Ar) atmosphere) as well as the developed by the author method of estimating the required destruction temperature of the organic binder, are presented in Figure 5. The determined destruction temperature of the resin applied by the producer was app.  $520^{\circ}\text{C}$  [3].

The moulding sand samples taken from the mould after the casting knocking out from the moulding box were roasted in the silite furnace at temperatures:  $300^{\circ}\text{C}$ ,  $440^{\circ}\text{C}$ ,  $480^{\circ}\text{C}$ ,  $500^{\circ}\text{C}$ ,

520°C, 600°C, 700°C, 840°C and 950°C, and the obtained results were shown in Figure 6. The spent sand taken from places being directly near the casting (material I) was burned to the highest degree. Under the liquid metal temperature influence binding properties were lost (material was loose). The further inside the mould the more limited temperature influence and - in consequence - the binder degradation decreased and ignition losses increased. Gases generated by the binder destruction and degradation occurring near the casting, are moving outside the mould and displacing air (oxygen) from the ceramic mould which limits the total burning of the binder. The thermal analysis presented in Figure 5 indicates that under oxygen-free conditions at higher temperatures the binder destruction process slows down. Not total burning of the binder in the moulding sand layer between the casting and the moulding box, significantly hinders the remaining gases migration. The heat wave flowing from the cooling casting towards the box, additionally generates gases, due to the binder degradation, and this process occurs regardless of the atmosphere.

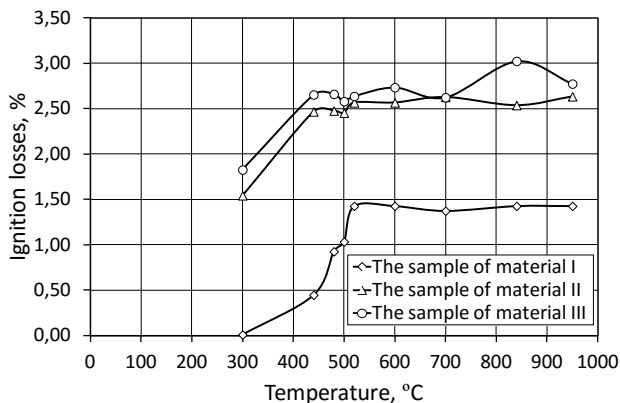


Fig. 6. Ignition losses of the tested spent moulding sand samples in dependence on the temperature

As can be noticed in Figure 6 mass decrements of the material I occurring due to roasting at various temperatures, stabilise from a temperature of 520°C, it means from the temperature determined - on the bases of the thermal analysis and the developed model - as the one warranting the efficient thermal destruction of the applied organic binder. Ignition losses at temperatures of 520°C and 950°C (temperature of the total destruction of organic binders) are of the same value. The sample of material I is degraded to a significant degree since at a temperature of 300°C, too low for the binder destruction, none mass decrement occurred due to roasting. As it was mentioned previously, the sample of material I is a mixture of grain matrix covered by binders of a various degradation degree. Therefore during the roasting temperature growing up to 520°C ignition losses were increasing. The difference between percent mass decrements between material I and II equals app. 1.5% (at a temperature of 300°C). This indicates the successive degradation of the moulding sand in dependence on the space of the temperature influence.

The results presented in Figure 6 also confirm that the temperature sufficient to remove the bound binder and its total

destruction is 520°C, since from this temperature value ignition losses are at a similar level for all samples. Small fluctuations within the temperature range from 520°C to 950°C can be the result of the partial segregation of spent moulding sand particles, which can influence the unitary result. In case of the sample of material III the highest ignition losses and the least regular distribution of mass decrements were obtained.

The treatment time is an essential parameter of assessing the thermal degradation and destruction degree of the determined volume of the moulding sand. Therefore, for the assumed temperature of 520°C, investigations of the ignition losses of the tested samples were carried out within the range: from 15 to 120 minutes. The achieved results were presented in Figure 7.

The investigations indicate that regardless of the amount of spent binders on the grain matrix surface the determined operation time of the determined temperature is required to cause the total organic binder destruction. When performed in the mould, the total burning process will need a longer time due to a directional influencing by a temperature. Differences between ignition losses of spent moulding sand samples are results of the temperature obtained in the given place and the time of its influence. Having in mind the given above results (compare Fig. 6 and 7) indicating that longer than 2 hours' time of roasting the sample of material I at higher temperatures did not cause increasing ignition losses, it can be assumed that this time (2 h) is sufficient to achieve the total binder destruction.

In case of materials II and III ignition losses were increasing proportionally to the binder degradation state in the mould occurring during the technological process.

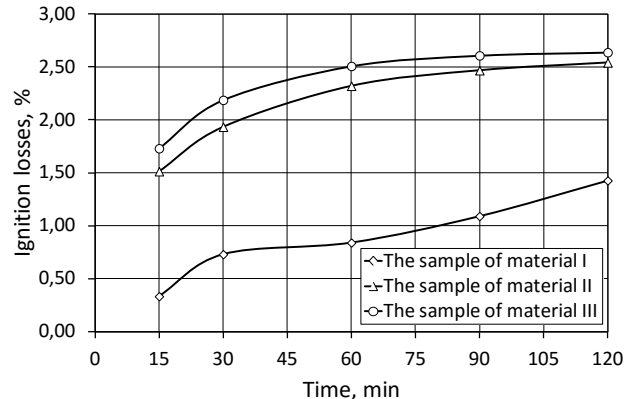


Fig. 7. Ignition losses of the tested spent moulding sand samples at a temperature of 520°C, in dependence on the roasting treatment time

When investigating the influence of the roasting time on the degradation of the tested samples of materials and - as a final effect - on the binder destruction, it can be noticed that the process is the most intensive at the beginning (for shorter times). In case of materials II and III ignition losses, for 15 min, constituted app. 60% of their final value. When the obtained result is compared with the thermal analysis, it confirms a significant thermal decomposition of a resin (polymer) at a temperature of 520°C. It can be assumed that the remaining time is necessary for burning this part of a binder which was not decomposed (with

taking into account the way of ignition losses testing). The attention should be also directed to a different character of the ignition losses changes of the sample of material I. The sample of the moulding sand, which was significantly degraded due to its direct contact with the liquid metal, was more intensely losing mass after longer roasting times.

Grain sizes of the matrix influence significantly technological properties of moulding sands as well as the surface quality of the obtained castings. The sieve analysis of the moulding sand samples indicates differences in grain sizes. The sample of material I is characterised by the smallest grain diameters, which is presented in Table 1. This indicates a partial loss of the binder coating, which underwent degradation as the result of the temperature influence.

Table 1.  
Selected parameters of the sieve analysis of the tested materials

Material	Calculated values of the sieve analysis				
	$d_a$ [mm]	$S_t$ [cm <sup>2</sup> /g]	$F_g$ [%]	GG [%]	Main fraction
Sample 1	0,430	60,35	89,90	61,37	0,400/0,320/ 0,200
Sample 2	0,494	53,11	82,67	60,58	0,400/0,320/ 0,200
Sample 3	0,504	52,58	80,17	59,88	0,400/0,320/ 0,200

The sample of material II of spent moulding sand was taken in a lump form and then crushed and sieved by 0.8 mm sieve. Since the moulding sand grain refinement was done mechanically, grain diameter values were larger, and the particle size was not significantly decreased due to the sand thermal degradation and volumetric decrease of binder coatings. Along with the change of a distance from the casting, the amount of the main fraction changes. It is the largest near the casting and the smallest at the moulding box wall. The thermal degradation and destruction causes more uniform decomposition of moulding sands than the mechanical operations. The thermal degradation process caused an improvement of the grain matrix uniformity, determined as the GG value (larger GG value – more uniform grain matrix).

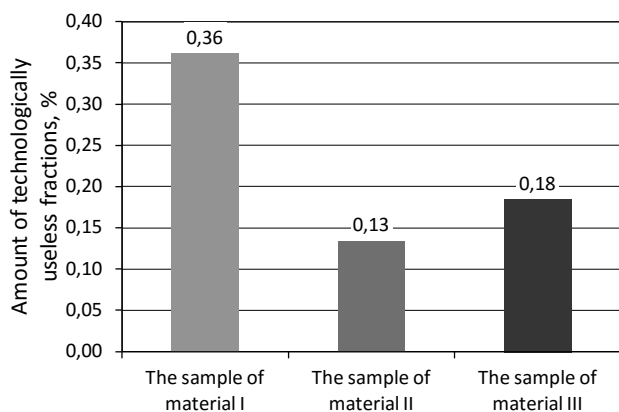


Fig. 8. Amount of technologically useless fractions in individual samples of spent moulding sands

The spent moulding sand taken near the casting, due to the highest thermal destruction and degradation of the binder, was characterised by large amounts of technologically useless fractions (Fig. 8). The thermal decomposition of a matrix grains binder generates, as a result of losing cohesion forces, the determined amount of dusts from a binder which did not undergo carbonization on the matrix grains surface or the total burning. A mechanical crushing of spent moulding sand (from the remaining parts of the mould) generates smaller amounts of technologically useless fractions. Not total burning of the organic binder requires, before the next cycle of the moulding sand preparation, the application of a pneumatic classification to improve the moulding sand permeability (removal of small particles) and to decrease the binder demand.

In dependence on the thermal degradation degree of the spent moulding sand the obtained grain matrix should be characterised by the higher pH value. pH values of individual materials taken for investigations are presented in Figure 9. The smallest pH value was found in the sample of material III, which contained the largest amount of an acidic hardener (not being under a temperature influence) used for resin binding. The least acidic solution was obtained from the sample of material I of the highest binder degradation.

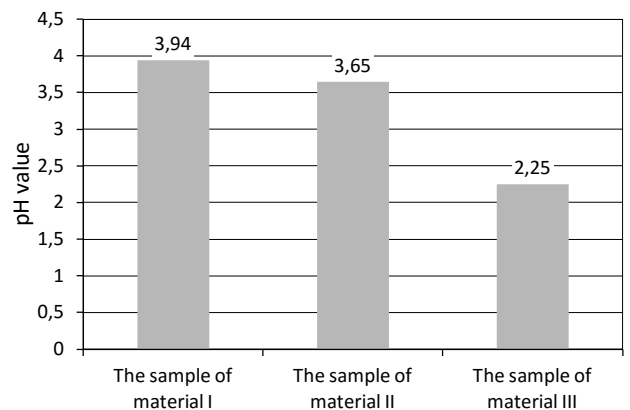


Fig. 9. The pH values of samples of materials taken for tests

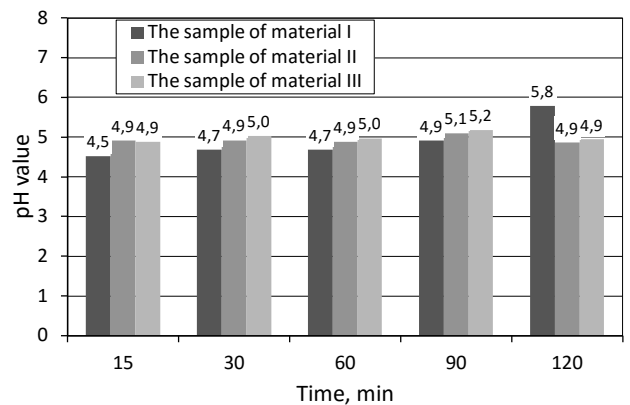


Fig. 10. Determination of pH values of solutions obtained after roasting at a temperature of 520°C of the tested materials, in dependence on the process duration time



The results of pH values of solutions prepared on samples of the tested materials for various times of their roasting, are presented in Figure 10. When the process was realised at the same temperature, being in this case 520°C, none essential pH changes were found.

All obtained results of measured pH values of the tested materials are presented in Figure 11. The roasting temperature increase was - in all cases - decreasing the acidity of solutions prepared from materials roasted at various temperatures. Within the roasting temperature range: 440°C to 520°C, nearly constant pH value occurs. It was only when the temperature was above 700°C that the pH value of the tested materials was changing. It can indicate that the acidic hardener was chemically decomposed and requires further investigations.

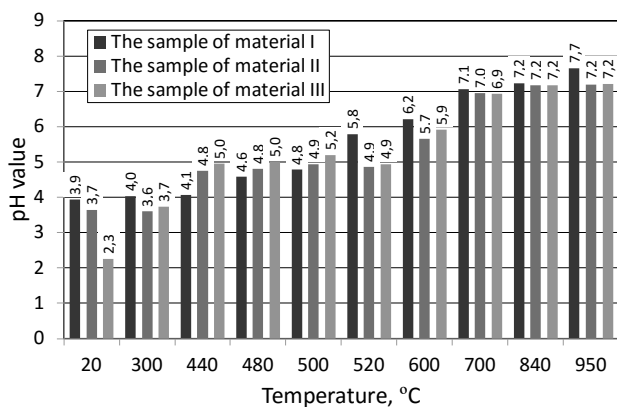


Fig. 11. The pH values of solutions obtained from the samples of materials after their roasting for 2 hours, in dependence of the process temperature

## 4. Conclusions

The general example of a degradation of spent moulding sands for a wide assortment of ladles and ingot moulds, presented in this study, shows the basic problem related to a large segregation of spent sands in respect of their burning. Binder decomposition processes occurring in the mould, in spite of the installed degassing systems, cause certain effects influencing the produced castings quality. Another essential factor causing defects formations in the produced castings is the preparation of moulding sands of various binder contents. The main error is caused by the lack of averaging of spent moulding sands subjected to the reclamation process. Moulds are disassembled in the cooling area, where - during the ladle taking out from the box - the most burned moulding sand is poured out (sample of material I), together with the casting. Not burned moulding sands (material II and III) together with the box are placed on the shake out grid, where due to vibrations are crushed out from the moulding box. This shake out grid is directly connected with the

mechanical reclamation system of the Company. On account of this, first of all the moulding sand of the highest content of spent binders feeds the reclamation system. The burned moulding sand is periodically taken from the cooling area and poured - through the shake out grid - into the mechanical reclamation system. The mechanical reclamation system operates each material batch with the same intensity, and - in consequence - the final reclaim contains various amounts of spent binders. If additionally, a various assortment of the foundry products is taken into account, it can be seen that finally the mechanically reclaimed material with various residues of binders is used in the production of successive moulding sand batches. This situation constitutes a factor destabilising the composition of the moulding sand with the reclaim and can be the reason of the periodical defects occurrence, signaled by the Company. These defects could be the result of a low efficiency of the mould degassing system when there is an increased gas volume emission from the moulding sand.

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