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INFLUENCE OF THE AMOUNT OF RESIN IN THE SPENT FURFURYL MASS ON THE THERMAL REGENERATION PROCESS

The aim of the study was to determine the influence of the amount of a commonly used binder in foundry work, furfuryl resin – on the course of the thermal regeneration of used moulding sand. The thermal regeneration procedure was carried out at a temperature of 525°C, the required temperature determined according to a specific procedure, and a lower and less effective temperature of 400°C. On the basis of the ignition losses, the influence of the regeneration temperature on the effects of the procedures carried out was compared. It was found that 400°C was too low to effectively clean the binder matrix, but that the more resin in the spent sand, the more intense the cleaning effect. When the required regeneration temperature for furfuryl resin of 523°C was used, higher binder degradation kinetics were observed due to the additional energy supplied to the process from the combustion of a large amount of organic material in the moulding sand.

Keywords: thermal reclamation; thermal analysis; ignition losses; furfuryl resin

1. Introduction

The organic binder content of the spent moulding sand depends on several factors:

- on the starting composition of the moulding or core sand, on the amount of resin added,
- on the type of grain matrix, whether the sand is fresh or whether a regenerate has been used, which can be obtained through the effects of mechanical, pneumatic, or thermal regeneration,
- on the multiple use of regenerate in the process circuit,
- on the casting alloy and its pouring temperature,
- on the size of the casting and the amount of heat accumulated in it, which influences the degradation and destruction of the organic binder,
- from the time the casting is held in the mould.

The aforementioned factors influence the state of the grain matrix, which can be coated with an organic binder in varying amounts and with a heterogeneous state of degradation or destruction of the binding material, associated with the pyrolysis of the organic compounds. By supplying heat through a thermal process to the moulding compound, the bound organic binder reaches a temperature at which the weakest chemical bonds in the chain begin to break. This phenomenon is called thermal degradation [1]. For both synthetic polymers and biopolymers, the term degradation refers to deterioration in the functionality of the polymer material and changes in its physical properties as a result of chemical reactions.

The thermal degradation phenomenon that occurs in polymer materials in the foundry industry is observed in the determination of the 'hot distortion' parameter. This factor allows us to simulate the behaviour of finished cores during heating. As presented in studies [2-3], depending on the furfuryl alcohol content of the urea-furfuryl resins used, the shapes, due to the thermal degradation of the binder that takes place, lost their initial physical properties and deformed as the temperature changed. For the resin with the lowest amount of furfuryl alcohol in its composition, the bonding properties deteriorated (the binder degraded) at a temperature of approximately 240°C.

The mechanism of the destruction process and the chemical composition of the products depend on the chemical structure of the macromolecule, the heating rate, the final temperature, and the thermal effects of the reactions taking place, which are endothermic reactions that require energy to proceed. The temperature range for the occurrence of degradation and destruction depends on the valence bond energy. Since this energy varies over a wide range, as shown in [1], the boundary between destruction and degradation is blurred, so that both processes can occur together.

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It should also be emphasised that the higher the temperature of the interaction with the resin (polymer) and the higher the heating rate, the [4]:

– the rate of thermal decomposition of the resin is higher,
– more low-molecular decomposition products are formed,
– there is a faster possibility of ignition and burning of the resin.

It is assumed that the thermal regeneration process has effectively cleaned the grain matrix of the binder if the roasting losses are below 0.1% [5]. Thermal regeneration issues, thermal degradation, or destruction of organic binders on the grain matrix are presented in [6-12].

2. Research methodology

2.1. Material used in the tests

For the tests, three portions of mass were prepared using the same grain matrix and the same organic binder and hardener, but with different contents in the prepared moulding mass. The composition of the moulding sand was as follows:

– grain matrix – quartz sand – 100 phr.
– urea-formaldehyde resin modified with furfuryl alcohol – 1.2 p.b.w. (moulding sand I), 2.4 p.b.w. (moulding sand II), 4.8 p.b.w. (moulding III),
– hardener, which is a mixture of sulphonic and inorganic acids modified with special additives – 50% p.b.w. to the binder, respectively.

The individual portions of the mass were prepared by first mixing the hardener with the grain matrix in a rotary mixer for 1.5 minutes, then the binder was added and mixed for another 1.5 minutes. The formed portions of the moulding compound were left to set for 24 hours. Individual portions of moulding compound with different binder contents were then crushed and sieved through a 0.8 mm sieve. The batches of material obtained in this way were subjected separately to thermal regeneration.

2.2. Thermogravimetric analysis

For thermogravimetric analysis, a 2:1 (resin:hardener) bonded binder sample was prepared and stirred under rapid heat dissipation due to the very strong exothermic reaction of combining resin and hardener without a grain matrix. After being set, the material sample was crushed and ground to powder in a mortar.

Thermogravimetric analysis tests were performed using a NETZSCH STA 449 F3 Jupiter® thermal analyser, for an assumed constant rate of temperature rise (10°C/min), with a gas flow rate (40 ml/min). Measurements were carried out in two atmospheres: anaerobic (argon) and aerobic (air) on resin samples weighing approximately 30 mg. Platinum crucibles were used for the measurements, which allowed measurements up to 1000°C [13]. The thermal analysis issues are presented in papers [1,14-16].

2.3. Thermal regeneration

The thermal treatment of the spent sand was carried out in an experimental thermal regenerator, the principle of which has been presented in other publications [17-22].

Fig. 1 shows a schematic diagram of the regenerator used in the study.

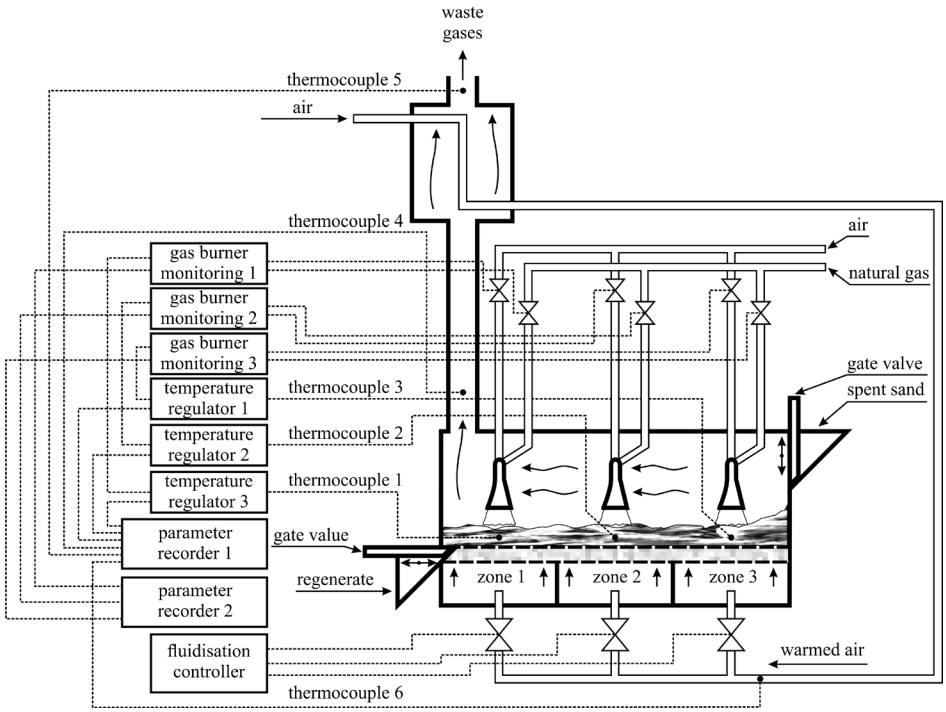


Fig. 1. Schematic diagram of the operation of a thermal regenerator [22]

The loading of the spent sand was carried out after the regeneration chamber had been heated to the required treatment temperature and the air temperature of the fluidisation (bed mixing) had reached approximately 100°C. The spent sand (batch of 10 kg) was regenerated at 400 and 525°C, with bed mixing in 5 s fluidisation followed by 5 s still bed. During the regeneration process (after 150, 300, 450, 600, 900, 1200 1500 and 1800 s), small portions of the regenerate were taken through the dump to determine the ignition losses. The grain matrix samples were subjected to roasting procedures in a silite furnace after the specified regeneration times. The results presented in this document are the average of two regenerate samples that were roasted in the oven for 2 hours at 950°C.

2.4. Microscopic examination

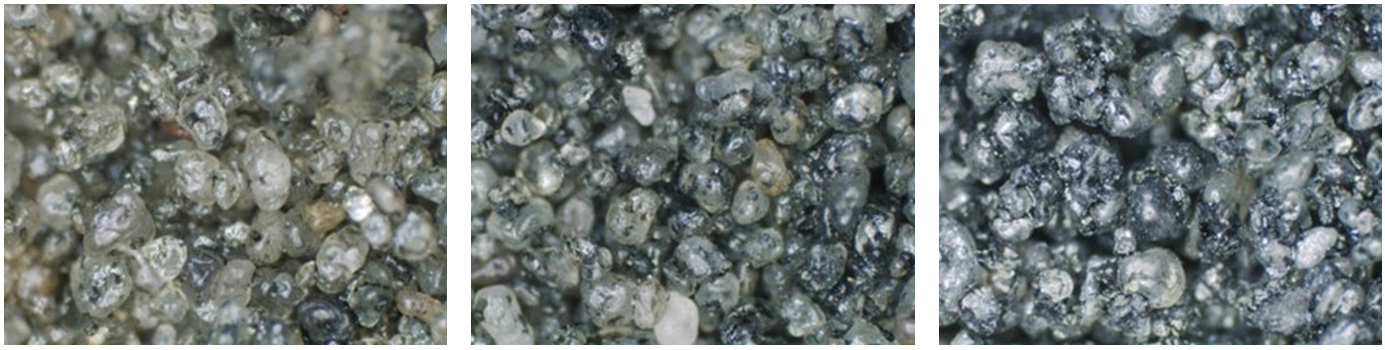
The surface morphology of the grain matrix is another criterion to assess the effects obtained from the regeneration treatments. Images were taken on the materials (regenerates) obtained as a result of treatment processes using a NIKON SMZ 745T stereoscopic optical microscope equipped with a DsFi1 camera, enabling digital image analysis with NIS-Elements BR software.

3. Analysis of results

Fig. 2 shows microscopic images of the materials prepared for thermal regeneration tests. The increasing amount of binder in the prepared moulding sand coats the quartz sand to a greater extent, and this translates into an increasingly less noticeable clean surface of the matrix grains.

The materials prepared in accordance with the respective proportions were subjected to a test for ignition losses. Fig. 3 shows the results obtained. Therefore, the initial content of the bound binder in the individual portions of the materials was estimated.

Thermal regeneration, as shown in other publications, requires the determination of temperature and time for successful treatment. The first parameter was determined according to the methodology presented in the article [22]. Fig. 4 shows the results of the thermogravimetric analysis of the bonded binder. The temperature required for the regeneration of the spent furfuryl sand was chosen to be approximately 521°C. Since the heating and cooling of the thermal regeneration chamber, to maintain a constant temperature, is associated with a certain inertia, a slightly higher regeneration temperature of 525°C was adopted. To compare the effects of thermal regeneration, a procedure was also performed at 400°C, which does not guarantee effective cleaning of the grain matrix of the binder.



a) b) c)

Fig. 2. Sand spent after crushing treatment (a) 1.2 p.b.w. of resin, (b) 2.4 p.b.w. of resin, (c) 4.8 p.b.w. of resin; magnification 50×

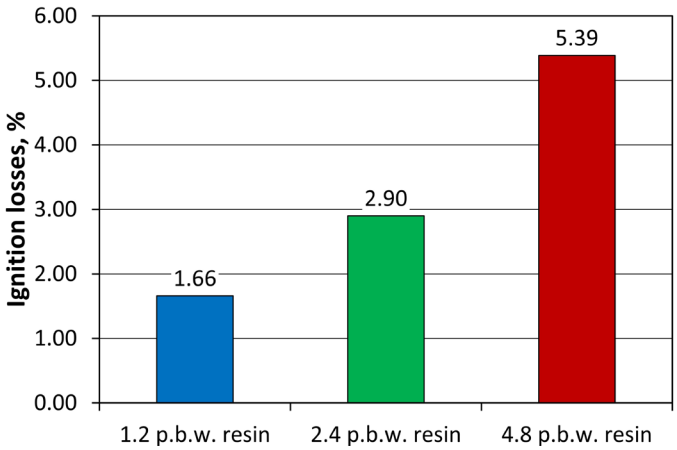


Fig. 3. Ignition losses of the initial moulding sands prepared for regeneration treatments

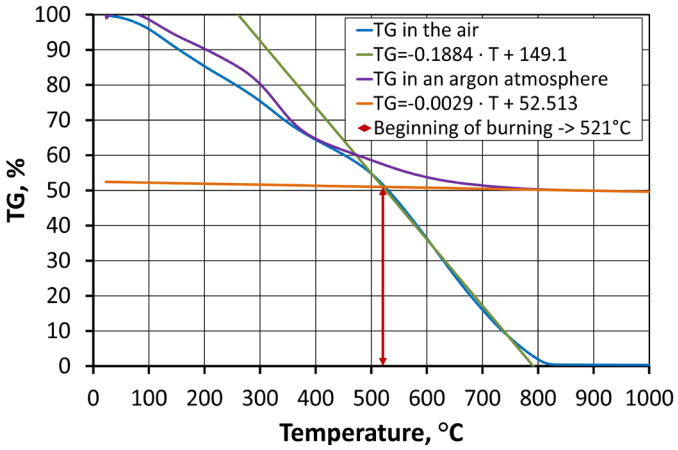


Fig. 4. Determination of the required thermal regeneration temperature of the tested binder, for a heating rate of 10°C/min and a constant gas flow rate of 40 ml/min

Figs. 5 to 7 show the results of the the ignition losses of material samples taken during the thermal reconditioning process carried out for three spent sands with different initial binder contents at 400°C and 525°C.

In the case of moulding sand with the lowest binder content (moulding sand I), it can be seen that 400°C is too low for effective cleaning of the grain matrix. Under the influence of the temperature, partial degradation of the binder occurs and a ignition losses of 0.5% were obtained over the time interval studied (Fig. 5). At higher temperatures, the process is more intense, the degradation process is greater, and for a process duration of 1800 s, the ignition losses were approximately 0.2%.

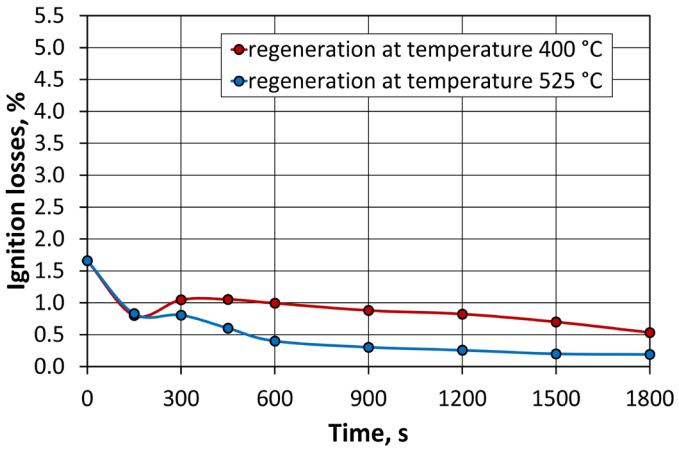


Fig. 5. Ignition losses of spent sand (moulding sand I) as a function of time, for different regeneration temperatures

Fig. 6 shows the results of ignition loss tests of moulding sand II with almost twice the content of bound binder in the sand used. At 400°C, the binder degradation process occurs at a high intensity during the initial period. With the passage of time, the ignition losses of the samples taken are decreasing, and 0.75% was obtained for the total process time. The ignition loss value indicates that the treatment temperature is too low to effectively purge the matrix of the bound organic binder. When a temperature of 525°C is used, the degradation of the bound resin occurs intensively for 600 seconds, followed by a very slow combustion process associated with the destruction of the binder, and ignition losses for the full process time were estimated at 0.15%.

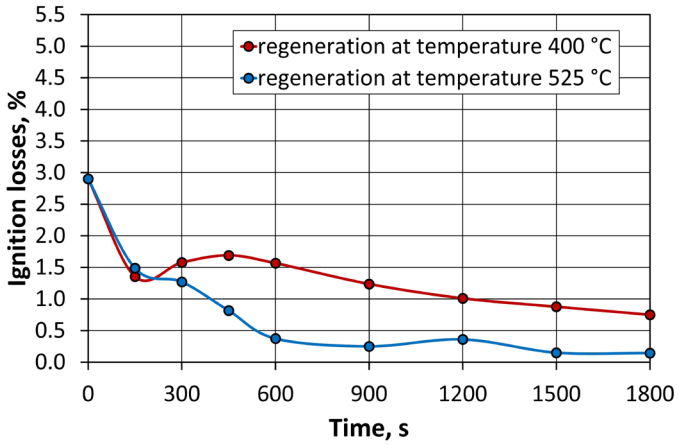


Fig. 6. Ignition losses of spent sand (moulding sand II) as a function of time for different regeneration temperatures

Fig. 7 shows the results of the ignition loss of the spent sand with the highest bound binder content (moulding sand III). The degradation of the binder material for both process temperatures occurred very intensively for about 300 seconds. Then, at the lower process temperature, the process was carried out at a lower intensity, and ignition losses of 0.5% were obtained after 1800 seconds. The higher process temperature intensifies the degradation and destruction procedure of the binder, and ignition losses for the full cycle were obtained at 0.1% (Fig. 7).

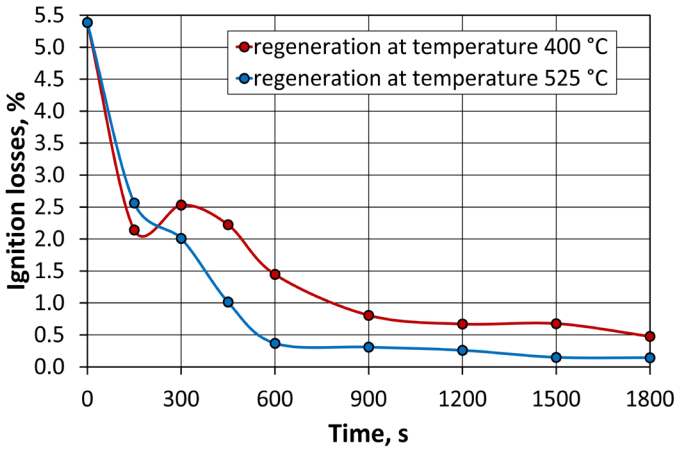


Fig. 7. Ignition losses of the spent sand (moulding sand III) as a function of time, for different regeneration temperatures

Figs. 5 to 7 show, for the initial thermal regeneration time, a significantly higher binder weight loss than for the continuation of the process. This is related to the operation of the unit. First, the grain matrix most heavily exposed to the burners, located on top of the layer of regenerated spent sand layer, moves to the dump (Fig. 1). Before the fluidisation process mixes and settles the bed evenly in the regenerator chamber, a greater decrease in ignition loss associated with the initial segregation of the regenerated spent sand is noticeable.

Figs. 8 and 9 present the ignition loss values of the spent sand with different binder values for a given regeneration temperature. It can be seen that, with a higher amount of bound binder weight in the spent sand, the process occurs with greater efficiency at a lower temperature (Fig. 10).

Fig. 10 shows microscopic images of the regenerated matrix after 1800 s, including the regeneration temperature and the amount of initial resin in the spent sand.

Analysing the microscopic images of the regenerates obtained after regeneration at 525°C of moulding sand III, it can be seen that the colour of the grain matrix is the brightest, indicating that the regeneration was most effective. The results of the surface morphology in Figs. 10e and 10f indicate that when the resin content of the regenerated spent sand is higher, regeneration occurs with greater efficiency.

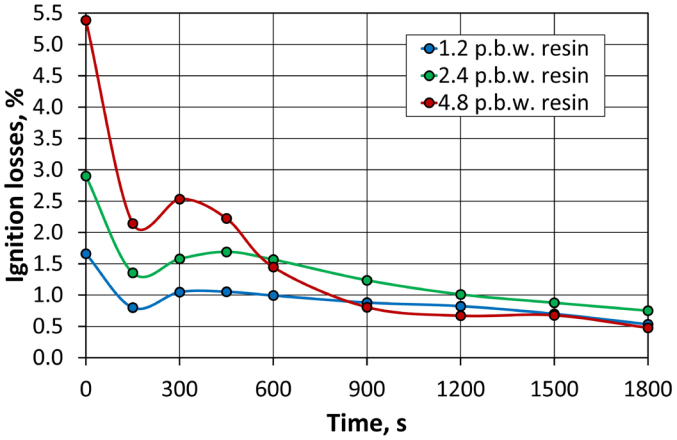


Fig. 8. The ignition losses of the spent sand of different compositions regenerated at 400°C as a function of time

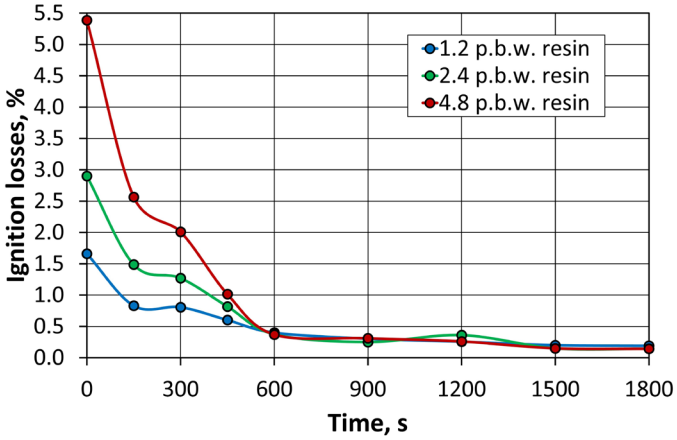


Fig. 9. The ignition losses of the spent sand of different compositions regenerated at 525°C as a function of time

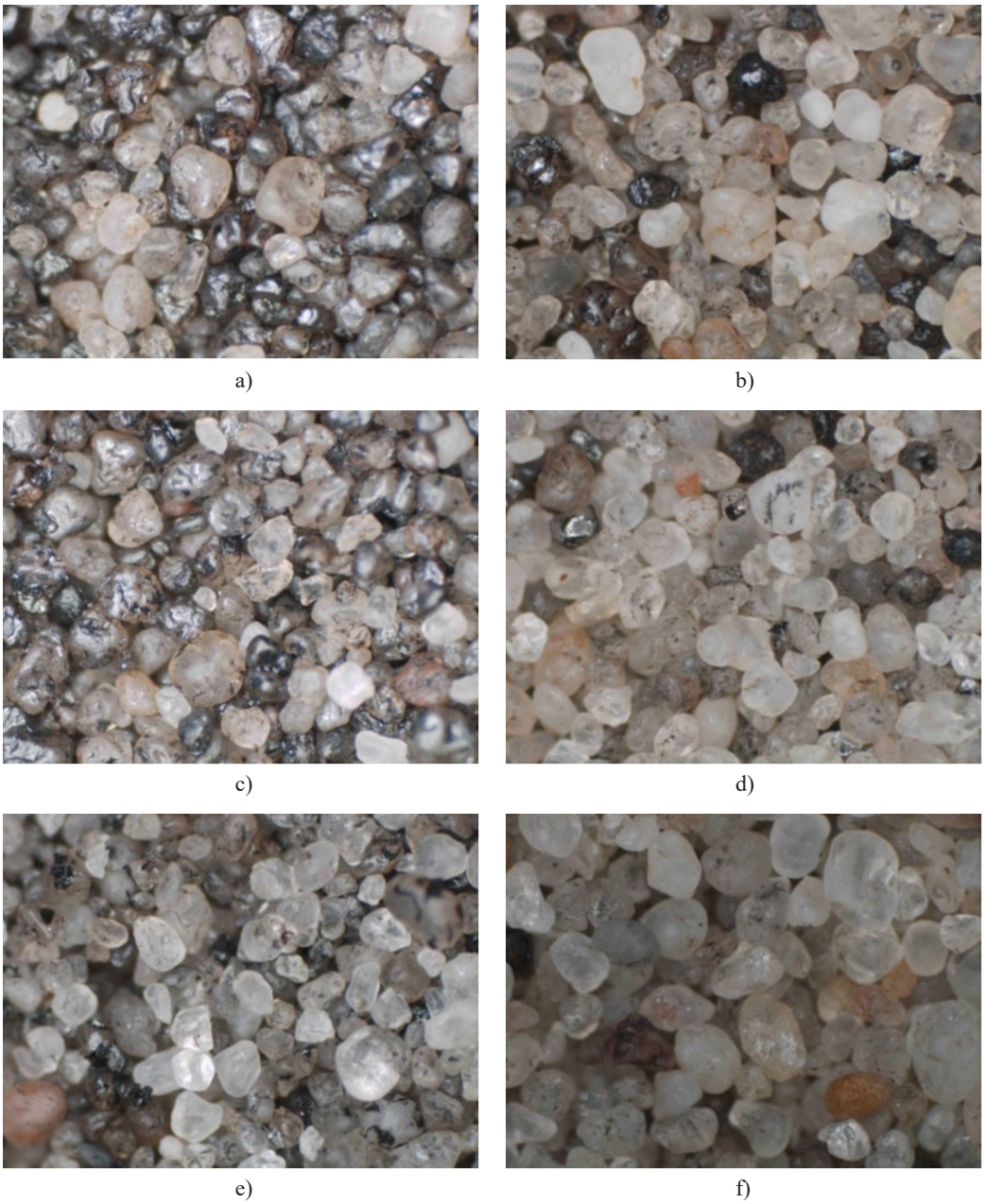


Fig. 10. Grain matrix after regeneration at (a) 400°C (moulding sand I), (b) 525°C (moulding sand I), (c) 400°C (moulding sand II), (d) 525°C (moulding sand II), (e) 400°C (moulding sand III), (f) 525°C (moulding sand II), magnification 50×

The reason for this is that a large amount of resin is burnt more intensively, which increases the temperature in the regenerator chamber. This, in turn, increases the kinetics of degradation and destruction of the fired binder. This process occurs when the spent binder is abundant so that the treatment being performed is sustained by the energy from the burnt resin. This effect was also shown in the work [23]. When the amount of resin in the spent sand is too small (for 1.2 and 2.4 p.b.w.), this effect does not occur. An increase in temperature was recorded during the regeneration of the spent sand (moulding sand III) both when regeneration at 400°C (a temperature increase of 500°C was observed) and at 525°C (a temperature increase to over 600°C – Fig. 11), confirming the above statement.

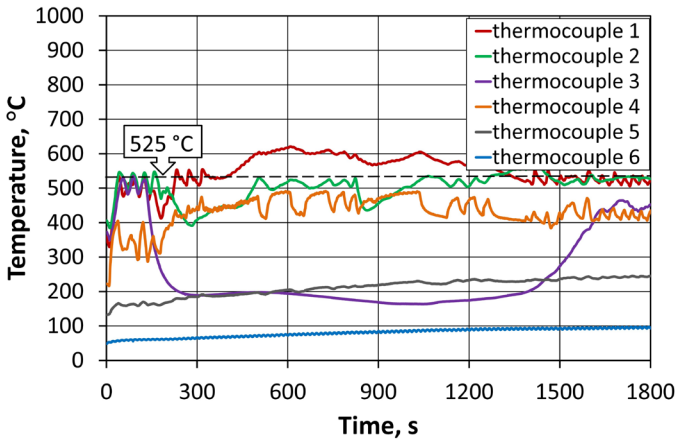


Fig. 11. Operating parameters recorded in the device chamber during the spent sand (moulding sand III) regeneration process at 525°C

4. Summary

The study showed that the thermal regeneration process is influenced by the amount of binder remaining in the spent sand. It was found that the more furfuryl resin in the moulding sand, the more intensive the regeneration, which translates into better cleaning of the matrix grains from the binder.

At a certain organic resin content in the spent sand, a self-regeneration process can arise that involves the supply of additional energy from the burnt binder to intensify the regeneration process. The exothermic reaction that occurs increases the kinetics of the process. When thermal regeneration of moulding sand moulding with spent furfuryl resin at the required temperature of 525°C, for different binder weights in the sand, the degradation process occurs with different intensities, while the destruction proceeds in the same way.

An interesting phenomenon was observed when a lower regeneration temperature was used for spent sand with a high content of bound furfuryl resin. The significant amount of energy generated from the combustion of the resin intensifies the process, resulting in better cleaning of the matrix grains from the spent binder than would result from the regeneration temperature used.

Tests have shown that for the thermal regeneration process to be effective, the required temperature of 525°C must be ensured in the regenerator chamber in the regenerated sand bed. The second important process parameter is the time required for the binder residue to burn off (destruction) after decomposition (degradation) at the set temperature.

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