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ECOLOGICAL ASPECTS OF THE PERFORMED THERMAL RECLAMATION

EKOLOGICZNE ASPEKTY REALIZACJI REGENERACJI TERMICZNEJ

The thermal analysis results of the selected group of binders and the thermal reclamation of one spent moulding sand with organic binder, are presented in the paper. The reclaiming process of the quartz matrix was performed on the basis of the own method of selecting the reclamation temperature. Taking into account thermogravimetric (TG) analysis results of the binder, the temperature range – required for performing the efficient reclamation of spent moulding sand containing this binder – was indicated. In order to confirm the assumptions, the thermal reclamation operations were carried out at a temperature similar to the determined on the TG basis and – for comparisons – at lower and higher temperatures. During the reclamation operation the reclaim samples were taken for the loss on ignition testing, aimed at the determination of the process efficiency. Temperature in the reclaimer chamber and gas consumptions were also recorded. On the bases of the thermal analyses, loss on ignition, gas consumption and temperatures of the reclaimed moulding sand bed the recommendations for the realisation of the thermal reclamation were given. These recommendations will allow a better, than currently available, process control in an aspect of decreasing the pyrolysis effect and limiting the emission of substances harmful for the environment.

Keywords: spent sands, thermal analysis TG, organic binders, thermal reclamation, loss on ignition

W publikacji przedstawiono wyniki badań analizy termicznej wybranej grupy spoiw i regeneracji termicznej jednej zużytej masy ze spoiwem organicznym. Proces odzysku osnowy kwarcowej przeprowadzono w oparciu o sformułowany własny sposób doboru temperatury regeneracji. Na podstawie zrealizowanych badań analizy termograwimetrycznej (TG) spoiwa wskazano zakres temperatury, wymaganej do przeprowadzenia skutecznej regeneracji termicznej masy zużytej z jego udziałem. W celu potwierdzania przyjętych założeń wykonano zabiegi regeneracji termicznej w temperaturze zbliżonej do wyznaczonej na podstawie TG oraz dla porównania w niższej i wyższej temperaturze. W trakcie trwania zabiegu regeneracji pobierano próbki regeneratu do badania strat prażenia, w celu określenia skuteczności działania procesu. Podczas regeneracji rejestrowano temperaturę w komorze regeneratora oraz zużycie gazu. Na podstawie zestawienia analiz termicznych, strat prażenia, zużycia gazu oraz temperatury złoża regenerowanej masy podano wytyczne do realizacji regeneracji termicznej, w warunkach pełniejszej niż dotychczas kontroli procesu w aspekcie zmniejszenia zjawiska pirolizy i emisji związków szkodliwych do otoczenia.

1. Introduction

An important problem concerning the thermal reclamation of spent moulding and core sands is the thought over, proper selection of its realisation method, allowing to achieve the expected purpose at retaining the environment protection conditions and satisfactory economic effect. The modern structural solutions, which are able to meet the mentioned above challenges, are looked for. The operation parameters of devices are selected to make the process as efficient as possible at as small as possible energy consumption. Simultaneously, in view of more and more demanding regulations concerning the environment protection, the newly designed devices and technologies must fulfil the up-to-date standards, legal acts, and general conventions of respecting the natural environment.

The thermal reclamation of spent moulding sands is related to a generation of the determined reclamation temperature. Applying of unfounded too high temperature ranges or too long times, increases the process costs, making the grain matrix purification the uneconomical process. Investigations of the thermal reclamation of various resins applied in moulding and core sands are aimed at looking – based on the accurate analysis – for essential assumptions of the proper thermal reclamation ways.

Since the thermal reclamation of spent moulding and core sands is related to the thermal degradation of organic compounds (resins) the special attention is required to prevent the emission of harmful compounds – negatively influencing the natural environment – during the quartz matrix reclamation.

2. Burning process of spent binders

The burning effect contains several chemical and physical processes interrelated with each other by complex dependencies. Several chemical reactions, simple and chain, proceeding

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with various rates and described by complex kinetic equations occur in this process [1,2].

During a heating process, after reaching the determined temperature, chemical bonds in organic substances start breaking, which generates new decomposition products mainly gaseous (volatile substances). This effect is called the thermal destruction. At sufficiently high temperature chemical bonds in macroparticles are intensely breaking and the majority of them are destroyed. The process grows very rapidly and leads to a total destruction of an organic binder. The destruction process mechanism and the chemical composition of products depend on the macroparticle built, heating rate, final temperature and thermal effects of endothermic reactions. The thermal destruction under strictly determined conditions (without contact with oxygen and other oxidising elements) causes the pyrolysis effect [1]. In case of spent moulding and core sands, in which the binder amount is small (up to app. 1.5%), during burning in a fluidised bed (air mixing moulding sand layers) the pyrolysis effect can be only temporary. The higher probability of the pyrolysis occurrence is during the mould pouring with liquid metal, when the binder destruction occurs as a result of heat transferred by liquid metal into the mould. In the mould space some places with a limited oxygen presence occur, since air contained in pores of the formed moulding sand is displaced by gases generated during pouring and thermal destruction of sand in the mould as well as destruction of moulding sand being in the vicinity of solidifying metal.

The thermal analysis is the basic method allowing to trace the organic binder decomposition: degradation, destruction (eventually with the pyrolysis process) and under favourable conditions total burning of resin. The thermal analysis performed in this study was aimed at the determination of changes of the mass of the organic binder sample at the temperature range: 20-1000°C, under oxygen and oxygen-free conditions, as well as at obtaining the thermal binder characteristic essential for the optimisation of conditions of performing the thermal reclamation of spent moulding sands. The selection of the minimal reclamation temperature and the process realisation time are the main criteria of the efficient thermal reclamation in the device of the determined operation intensity [3-5].

3. Materials and the investigation methodology

Thermal investigations were carried out by means of the thermal analyser NETZSCH STA 449 F3 Jupiter®, which allows to make TG and DTG measurements, under the same measuring conditions, it means at the same temperature increase rate (10°C/min) and the same gas flow rate (40 ml/min). The measurement for each sample was performed in the oxygen (air) and oxygen-free (argon) atmosphere. Samples subjected to the thermal, TG analysis were of a mass of app. 15 mg. Platinum crucibles, enabling measurements up to 1000°C, were used in measurements.

4 sets of materials (resin and hardener/catalyst) used for preparing the moulding or core sands were applied in investigations. Each resin was mixed with its hardener according to the proportions recommended by the producer. Individual pairs of materials are presented in Table 1. In case of binder I and II the components were mixed under conditions of a fast heat abstraction due to a very strong exothermic reaction between resin and hardener without the grain matrix. In case of binder III and IV, resin mixed with hardener was placed for 1.5 min into the furnace heated to a temperature of 220°C (the hot-box process).

TABLE 1

Compositions of binders applied in investigations

Material	Kind of resin	Hardener/catalyst	Ratio: resin/ hardener
Binder I	Urea-formaldehyde resin modified by furfuryl alcohol 1.0 part by mass	Mixture of sulphonic and inorganic acids modified by special additions 0.5 part by mass	2
Binder II	Urea-furfuryl resin 1.0 part by mass	Activator in a form of aqueous solution of paratoluenesulphonic acid 0.5 part by mass	2
Binder III	Urea-furfuryl resin 1.2 parts by mass	Hardener prepared on the ammonium bases 0.12 parts by mass	10
Binder IV	Urea resin modified by furfuryl alcohol 1.5 parts by mass	Aqueous solution of sulphonic acid with urea and inhibitors 0.3 parts by mass	5

The moulding sand in the hot-box technology was prepared acc. to the following composition (binder III):
– high-silica sand – 100.0 parts by mass
– resin – 1.5 parts by mass
– hardener – 0.3 parts by mass

The moulding sand IV, after mixing according to the producer recommendations, was shot into the core-box of a shape of the bend-test specimen. Cores were made with using experimental shooting machine LUT-c of the Multiserw Morek Company. Shooting pressure was 5.2 MPa, shot time: 1 s and blowing through time: 2 s. Cores were made – at a temperature of 220°C – in various hardening times being: 15, 30, 60 and 120 s. Shaped samples, after cooling, were crushed in a jaw crusher and sieved (0.8 mm) [6]. The material obtained in such a way was subjected to the thermal reclamation treatments. The thermal treatment of spent core sands was performed in the experimental thermal reclaimer, the operation of which was presented in other publications of the author [7-9].

When the reclaimer chamber was heated to the required temperature and the fluidising air temperature reached 100°C, the spent moulding sand from the hot-box process was loaded. The charge of 10 kg was reclaimed at temperatures: 400, 500, 600 and 700°C, with the bed mixing according to the sequence (5s_5s_5s). This means that, to each section of the reclaimer bottom, air mixing was successively supplied for 5 seconds. During the reclamation process small samples of the reclaim were taken – after: 1, 2, 4, 8, 16 and 32 min. – to determine ignition losses. Samples after the determined reclamation times were roasted in the silite furnace. The results presented in this paper are average values from two reclaim

samples, which were heated for two hours at a temperature of 950°C in the furnace.

4. Analysis of the results

The thermal analysis results of two binders of a similar chemical composition (furane resins) are presented in Figure 1. It can be stated that the thermal degradation process, it means a conversion of organic compounds into volatile products, reveals itself by the mass change of the tested sample. The thermal analysis results under oxygen-free conditions are presented in Figure 2. The degradation process both in the argon and air atmosphere occurred with a similar intensity. As long as in the oxygen presence the tested binders underwent degradation and destruction causing the total burning of resins at a temperature over 800°C, under the oxygen-free conditions the destruction process caused the pyrolysis effect, which resulted in leaving more than 40% of the sample mass.
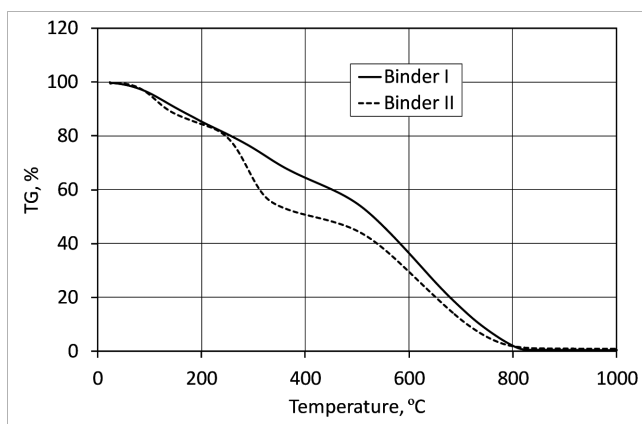

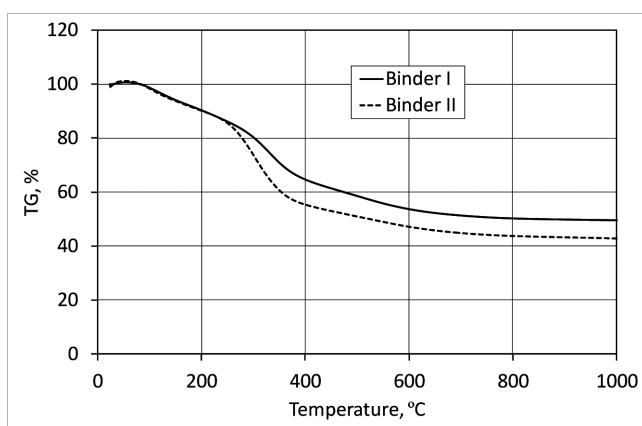Fig. 1. Thermal analysis in the oxygen atmosphere (air) – binder I and II

Fig. 2. Thermal analysis in the oxygen-free atmosphere (argon) – binder I and II

The thermal analysis results of binders used in the hot-box technology are shown in Figures 3 and 4. As can be seen, the decomposition and burning processes of the investigated organic substances occur with various intensities, but pathways of both curves are of similar shapes. Different compositions of both resins cause that organic compounds of binders III and IV are burning at different temperatures (in the air), while under

oxygen-free conditions the pyrolysis effect causes that – within the tested temperature range – the significant part of the sample mass remains. Binder III requires a higher temperature for its total destruction, and in the argon atmosphere its thermal degradation is more difficult. Various susceptibilities to the destructive temperature influence of individual binders is essential in the melting temperature context of the cast foundry alloy. The more difficult is the thermal destruction process of synthetic resin the application to foundry alloys of higher melting and pouring temperatures of this resin is possible.
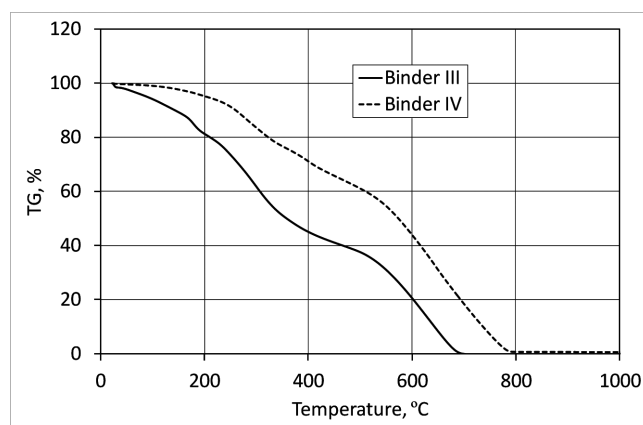

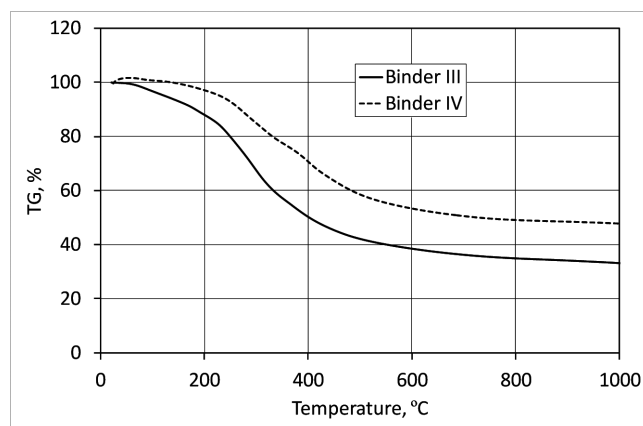Fig. 3. Thermal analysis in the oxygen atmosphere (air) – binder III and IV

Fig. 4. Thermal analysis in the oxygen-free atmosphere (argon) – binder III and IV

In all cases of the thermal analysis, both in the oxygen and oxygen-free atmosphere, it was noticed that rectilinear segments occurred in the obtained TG diagrams. The linear functions were selected for these ranges (at the example of binder IV) and it was assumed that the point of their intersection determines the temperature, at which the binder burning process starts. The method of determining – on the thermal analysis basis – the required temperature from which the thermal degradation (identified with the final burning) starts, developed by the author, is presented in Figure 5. This temperature can be interpreted as the minimal temperature required for the thermal reclamation. In case of the tested binder a temperature of 570.5°C was determined as the one from which the burning process starts and thus the expected efficient thermal reclamation process.
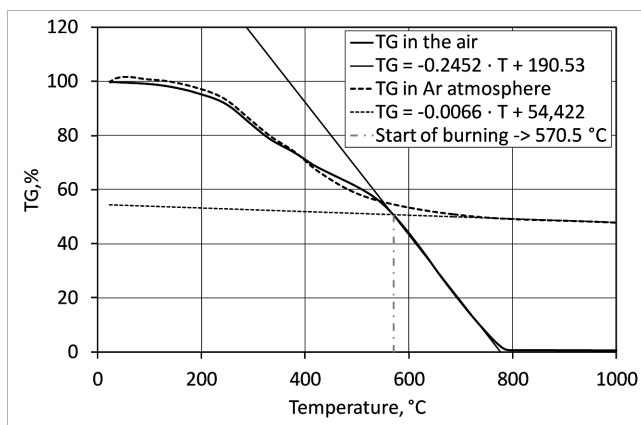
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Fig. 5. Selection of the burning temperature – binder IV

Fig. 7. Gas consumption during the reclamation process in dependence on the assumed process temperature

Loss on ignition for various reclamation temperatures of spent core sands are presented in Figure 6. The realisation of this process at a temperature of 400°C, for the longest reclamation time did not warrant a good matrix purification, leaving more than 0.20% of not burned resin. The spent moulding sand reclaimed at a temperature of 500°C contained – in the final moment – still 0.10% of organic substances remains. Increasing the reclamation temperature to 600°C, caused that for the longest reclamation time the matrix purification was significantly better, comparable with loss on ignition at a temperature of 700°C. The binder maximal degradation process was, of course, faster at higher temperatures.
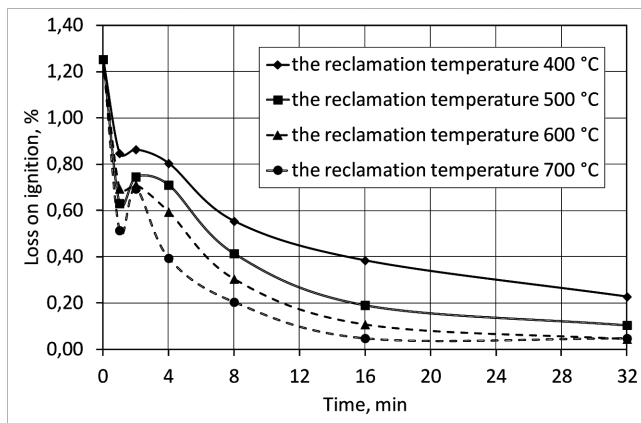
It was shown that the lower process temperature the gas consumption smaller, however in the initial reclamation phase when the moulding sand – to be reclaimed – was heated to the reclamation temperature the gas consumption was similar.

Fig. 8. Recorded temperatures and gas consumptions during the reclamation at a temperature of 600°C, bed mixing by air from the recuperator

Fig. 6. Loss on ignition of the reclaim in dependence on the reclamation temperature and time

The distribution of temperatures in the reclaimer, from the moment of charging the spent moulding sand of the room temperature up to the moment of reaching the temperature assumed for the reclamation, is presented in Figure 8. It can be noticed, that for approximately 10 minutes the moulding sand is heated to the assumed reclamation temperature. During this time, at temperatures lower than the given one, the degradation of spent binders into gaseous products occurs. Loss on ignition, presented in Figure 6 confirm the occurring effects. In a very short time, at lower temperatures, a significant mass loss – related to the emission of gases -occurs. As it was emphasised in the introduction the process, from the one side, should be efficient and effective but, from the second side, should meet the ecological requirements. On the basis of the performed analysis it can be stated that the general belief that at a higher temperature the reclamation process occurs more efficiently, warranting more effective burning of a spent binder, is not fully correct. When a spent moulding sand, the most often being of an ambient temperature, is charged into the reclaimer it is not possible to perform its reclamation at high temperatures omitting the gasification phase and causing the

In accordance with the proposed mode the reclamation temperature of 570.5°C was determined for the core sand (binder III). Changes of loss on ignition in dependence on the temperature and time of the process, presented in Figure 6, confirm the assumption. The reclamation carried out at a temperature of 600°C occurred efficient for the matrix grains purification from spent binders. At a lower reclamation temperature the spent binder destruction was realised with a less efficiency. In turn, the application of a higher temperature did not caused any significant effect but a higher gas consumption. Gas consumptions at various reclamation temperatures are presented in Figure 8.
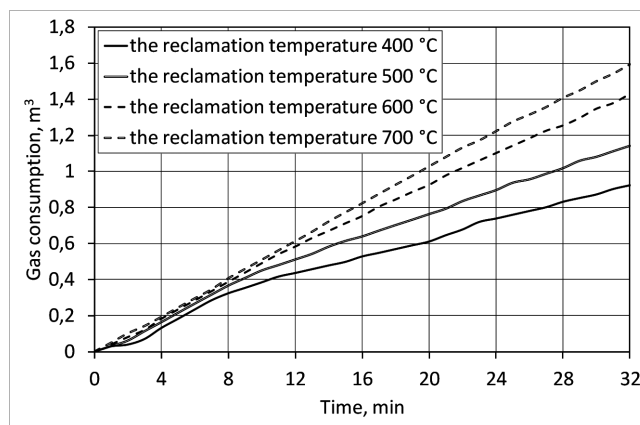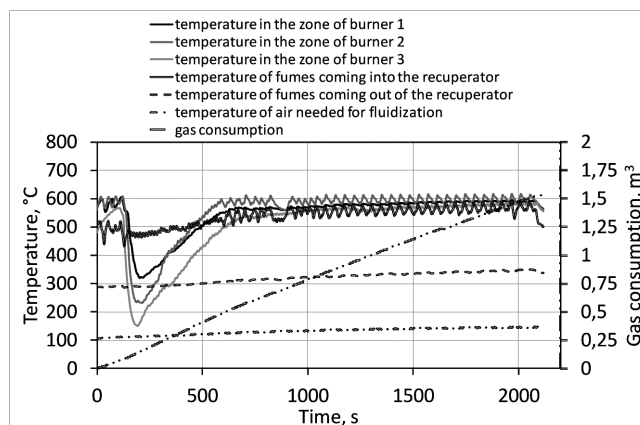
final destruction. In view of this fact, it seems that the more rational mode of operation is to perform the spent moulding sands reclamation at the lowest possible temperature, however warranting the efficient binder destruction (determined e.g. by the method presented in this study). However, due to ecological reasons, the main emphasis should be put on a combustion of gases formed during the reclamation which are formed when the bed is heated. The amount of these volatile products is very large, since in 10 minutes (time of the bed heating to the required temperature) it was equal 80% of the initial mass of the spent moulding sand with binder III. If we look at the thermal analysis, especially realised in the argon atmosphere (Fig. 5), we can see how much volatile products are formed, which under free flow conditions are emitted into the atmosphere. Thus, the recommended installation (presented in paper [9]) with the application of the reactor combusting gases seems – on the bases of the performed studies – justified.

5. Conclusions

The presented above analysis indicates that the thermal reclamation process, due to ecological reasons, should be realised according to the following scheme of operations:
– selection of the proper minimal reclamation temperature for the given binder, e.g. on the thermal analysis bases,
– realisation of the thermal reclamation in the reclaimer chamber at the established temperature,
– supplying the proper amount of oxygen (from the air) to limit the pyrolysis effect and efficiently realised the organic binder destruction, fluidal mixing of the reclaimed moulding sand bed,
– equipping of the reclaimer chambers with additional reactors combusting volatile products and causing their final destruction.

The described above operations can contribute to lowering the thermal reclamation realisation costs. Heating the large reclaimer chamber to a lower temperature (determined e.g. by the thermal analysis) causing the spent binder destruction and the realisation of additional combustion in the reactor of a much smaller volume, can contribute to a significant energy saving, simultaneously making the system more efficient also from ecological reasons.

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