Green Foundry Life project (LIFE17 ENV/FI/000173)

Action B1: Emission different binder systems during small-scale test casts.

Method 1. Testing foundry at AGH-UST- laboratory tests.

Confidential

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1. INTRODUCTION

The intensively developing foundry industry consumes large amounts of natural resources, energy and metals as well as generates significant amounts of gases and solid wastes, which influence the natural environment and work conditions. Therefore the adjustment of foundry plants to the sustainable development strategy is the necessary condition of the foundry industry development [1-3]. Foundry plants should realise that the responsibility for the environment and for financial results are not mutually excluding. Taking care of the environment and introducing more environment friendly changes can cause the production increase and its costs decrease, can improve the recognition of the company name, strengthen relations with customers and improve profitability of the company. By implementing the environment management systems and the proper management of materials and wastes, applying recycling, the foundry plants can matter greatly in a sustainable consumption of natural resources. The adjustment of foundry plants to the sustainable development strategy is a necessary condition of the foundry industry development. It means, the necessity of taking into consideration - in strategic decision makings and production operations - the mutual dependence between the environment and social and economic aspects. The sustainable development is based on innovative operations being the effect of research, i.e. science [4].

The introduction of water glass as a binder in the early 1950s was very important in increasing the production efficiency of moulds and cores.

Processes using water glass-hardened CO_2 or organic hardeners contributed to improving the quality of the work environment and the natural environment. The rapid development of foundry industry in the second half of the 20th century and the increasingly complex shapes of castings, it was necessary to use binders based on organic compounds. However, the increasingly stringent requirements for environmental protection and the increased public awareness based on the principle of sustainable development caused that the attention was again paid to inorganic binders based on alkaline silicate solutions.

This is especially important for cores, which usually make up to 10% of the volume of the mould, but emit up to 70% of volatile organic compounds in the foundry.

There are many different types of chemical binders. They divide into two main types: organic and inorganic [5, 6].

2. BINDERS FOR MOULD AND CORE SANDS

2.1. ORGANIC BINDERS

Furan resins: Furan resins are synthetic resins obtained in polycondensation of furfuryl aldehyde (furfural) with phenol (furan-phenol resins) or with ketones (especially acetone), and in polycondensation of furfuryl alcohol (furfurol) with formaldehyde (furan-formaldehyde resins), with urea and phenol (furan-urea-phenol resins) and with other substances [7]. These resins undergo cross-linking under an influence of heating or chemical agents. Some of these

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resins found applications in casting. The initial raw material is furfuryl aldehyde, obtained from agricultural left-over e.g. straw, corn cob, sugar cane (Fig. 1).

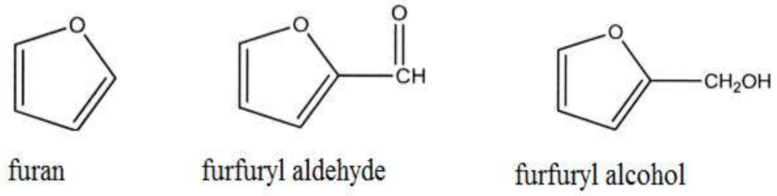


Figure 1. Raw materials for production of furan resin

Phenol-formaldehyde resins ("**resole**" resins) are obtained by reaction of phenol with excess formaldehyde in an alkaline environment (a formaldehyde/phenol ratio higher than one). Resole resins include methylene ($-CH_2-$) and hydroxymethylene groups ($-CH_2OH-$) [8]. One disadvantage of acid-cured phenolic no-bake resins is their relatively poor storage stability.

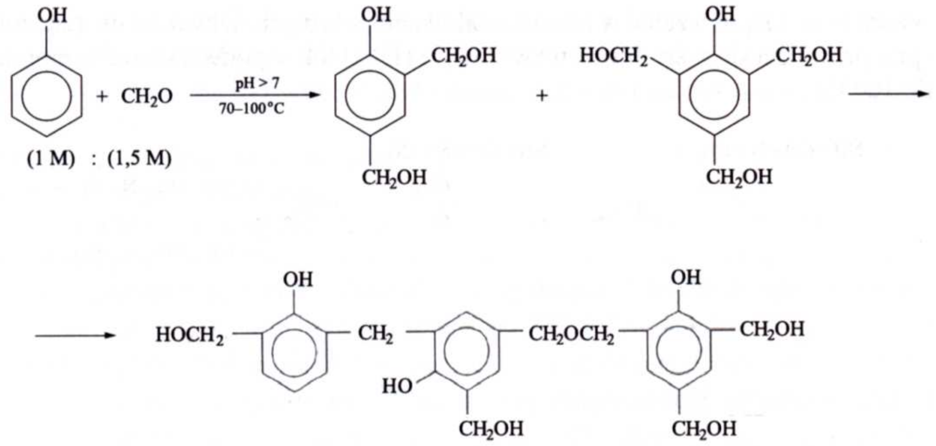
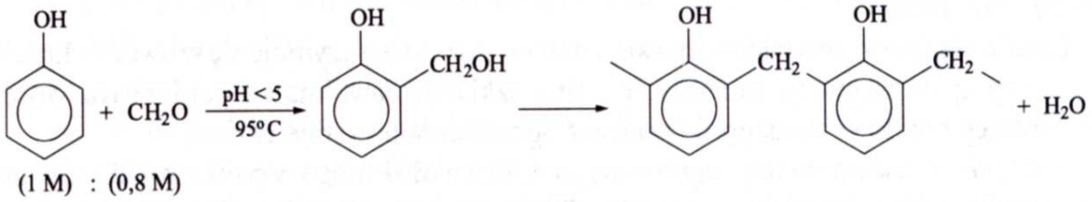


Fig. 2. Scheme of formation PF "resol" resin

Novolac resins are obtained during the reaction of phenol with formaldehyde in acidic medium, using a slight excess of phenol. (Fig. 3).



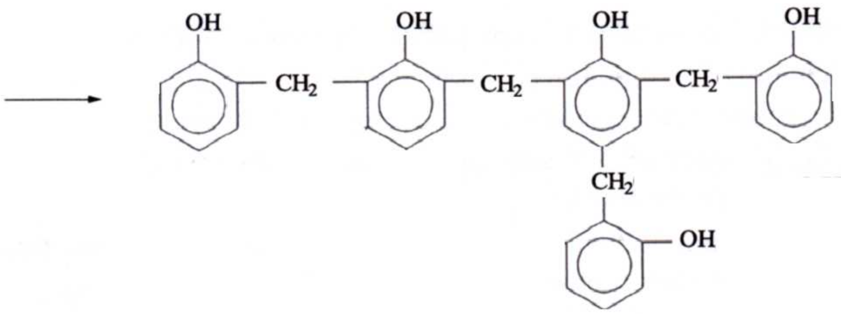


Fig. 3. Scheme of formation PF "novolac" resin

Since novolac resins contain only methylene groups (-CH_2-) and do not contain methylol groups (-CH_2OH-) such as resole resins, the same heating of these resins does not cause further cross-linking reactions and (they are thermoplastic). Only the addition of a formaldehyde-releasing compound causes end hardening. This binder component is added to the sand in the form hexamethylenetetramine (as a hardener), that decomposes at 160 ^{0}C into ammonia and formaldehyde when heated.

When pre-coated sand contacts the heated pattern, the hexamethylenetetramine decomposes and the formaldehyde cross-links the resin binder to form the characteristic strong bond. The presence of hexamethylenetetramine in sand mould does not cause bonding and to harden it the mixture needs to be heated to a predetermined temperature.

2.2. INORGANIC BINDERS

Inorganic binders are typically made out of synthetics such as sodium silicate, cement, phosphate and sulphite lye. The natural inorganic binders are clays and bentonites. Besides being environmentally friendly, inorganic binders when attached to cores also improve the casting quality. There is a growing interest in developing an inorganic binder that has the same structural capabilities as organic ones in terms of the core structural integrity, shake – out properties and casing quality. The following inorganic binders are based on silicate compounds: CORDIS (Huttenes –Albertus), alternative warm – box binder (AWB – Nemak Dillingen), INOTEC (ASK Chemicals), SOLOSIL, AMASILIK, NUCELPON, CARSIL, GEOSET (Ashland) and GEOPOL (SAND TEAM) [8].

CORDIS process [9]

CORDIS is the inorganic binder, in which the only solvent is water This binder is composed of the modified aqueous solution of sodium silicate (Cordis resin) and the pulverized addition named Anorgit. In dependence of the binder type its matrix consists of the combination of phosphate, silica and borate groups. Properties of the given binder type can be controlled by the aimed combinations and changes of the matrix structure. Inorganic additions are used for improvement of binder properties. By the combination of these all additions important properties of sands such as fluidity or durability of cores during their long-term storage, can be controlled. The moulding sand containing CORDIS is shot into the core box heated to a temperature of 120-160oC, in dependence of the core geometry. The hardening process is irreversible and constitutes a combination of the dehydration and chemical reaction. When a moulding sand is introduced into the core box a preliminary hardening of a sand occurs and the external shell is formed on the core. This stage contains hardening obtained only due to drying and of a purely physical character. In addition, in dependence on the applied CORDIS binder, the chemical hardening process can be initiated and in result the core strength can be higher. Benefits of CORDIS binder include improved shake out, significantly reduced down-time required for casting dies cleaning, reduction of gas porosity from sand cores and better surface finish by using finer sand. CORDIS binder achieve cold bending strengths between 3.5 and 5.5 MPa, depending on the sand and additive. No fumes or odors are released during the casting and there is no condensate in the die.

SOLOSIL TX process

The SOLOSIL TX binder (name reserved for FOSECO) is the inorganic thermo-setting binder, based on water glass, of properties comparable to organic binders and environment friendly. This binder consists of two components: solution of modified sodium silicate (app. 2 % of a module of 2.0 to 2.4) and fine powder containing various minerals.

The hardening occurs in the core box heated to 150 ^{o}C. An introduction of the appropriate addition into a binder significantly improves the cores strength. The strength increase is caused not only by the physical (thermal) hardening of sodium silicate, but also by decreasing the humidity level caused by this addition. Apart from the composition, the amount of these additions is very important. Additions introduced into the binder, apart their ability of the core dehydration, decrease the wettability of liquid metal vs. mould and decrease the binder viscosity, which causes a fluidity increase of the core sand. Apart from the physical (temperature) hardening of the binder the chemical reaction of reactive SiO_2 also occurs in sodium silicate and in some mineral components of the addition. At the total dehydration the cores maximum strength is achieved, but precautions should be taken to avoid brittleness of cores caused by their over-drying. The introduced mineral additives have also to prevent the chemical and physical penetration of liquid metal into the sand depth. The production of cores based on sodium silicate matrix should be characterised by as short as possible cycle time to achieve yields of the sands with organic binders. This time is determined by the cores drying stage. For its optimization (e.g. hot airflow flux, core box temperature) the computer simulation is used.

The SOLOSIL TX binder does not contain organic additions and due to that during the mould pouring none unpleasant smells are emitted (only water vapour).

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INOTEC technology

The INOTEC technology (ASK Chemicals) was created as a result of a continuous development of technologies based on inorganic binders. The INOTEC system is the new, 100% inorganic - that is free from emission - binder variant based on water glass, dedicated to the casting production, especially of aluminum, non-ferrous metals alloys and cast iron. This binder consists of three components: liquid mixture of silicates (1.8 - 2.5 %), highly mineralized activators (0.1 – 1.0 %) and if necessary, mineral material (1 - 30 %) added to high-silica sand. These component can be mixed in various proportions in dependence on the producer's requirements. During the casting production none fumes are generated. The INOTEC system can be utilized at the production of engine blocks and cylinder heads. Apart from visible advantages for the environment, the INOTEC technology is competitive due to technological properties of moulding and core sands as compared with traditional technologies based on water glass. The binder hardening occurs due to dehydration in the heated core box and the core blown through by hot air of a temperature: 180 – 200 ^{o}C. Technological advantages of the INOTEC technology:

- decrease of the moulding sand adhesion to the casting surface,
- improvement of the moulding sand knocking out ability, easy removal of cores from castings

AWB process

The AWB technology (developed by the Minelco, Nemak Dillingen and Audi Company) is applying modified water glass of a decreased viscosity. Due to this a binder can be easier mixed and homogenised with the moulding sand. The obtained moulding sand viscosity is similar to the one of the sand from the cold-box technology. The moulding sand hardening occurs as a result of the physical water removal, which is performed in two stages. In the first stage the hardening occurs in the core box (warmed to temperatures: 140 – 200 ^{o}C), which is connected with the vacuum pump for the water vapour removal. After app. 10 - 60 s, in dependence of the core size and shape, the hardened shell is formed, strong enough that it is possible to take out the core from the core box and its transport. The final hardening is performed by microwaves of a weak power. This stage is very important, since water remained in the core can dissolve binder bridges which shortens the storage time. Binding of sand grains occurs by silicate bridges. This process was developed for making engine blocks of aluminium alloys. Due to this, the energy consumption decreased by 30 % and emissions of greenhouse gases, wastes and sewages were highly reduced. Moulding sands made in the AWB technology are easily knocked out. These cores were verified at producing castings of cast steel, cast iron and non-ferrous metals alloys. Investigations indicated that, in order to achieve the same strength of cores made in the AWB technology as cores made in the cold-box technology (resin: activator = 0.8 % : 0.8 %) the application of 2.5 % of the AWB binder was necessary.

GEOPOL technology [10, 11]

Binders based on mineral polymers called geopolymers are classified in the group of inorganic binders for moulding and core sands. Geopolymers belong to the alkaline aluminosilicates group (they contain alkaline element sodium or potassium), formed by long tetrahedral chains of SiO_4^{4-} and. The negative charge of fragments containing aluminium is equilibrated by metal cations. The geopolymers are not formed due to geological processes. Geopolymers are artificially obtained e.g. from fly-ashes or slag. They are also called: "*polysialate"*.These binders undergo a gradual polymerisation, since due to a hardener activity, the binder viscosity increases and transformation into solid substance – polymer of a high binding ability – occurs. The syneresis effect does not occur. The polymerisation process result is the inorganic solid polymer of a characteristic structure. The polymerisation proceeding of this binder is quite different than sodium silicate gelling process in which the syneresis effect, i.e. liquid phase reducing from gel, occurs

Geopolymers demonstrate several advantageous features and therefore are finding applications in many domains. Mineral polymers added to concretes cause several times strength increase in relation to ordinary concretes, high fire resistance, high resistance to the chemical compounds and atmospheric factors influence. A geopolymer binder is a clear, viscous liquid of a small polymerisation degree and amorphous structure. Due to the hardener influence these binders undergo a gradual polymerisation, which causes a successive growth of viscosity of a liquid and its transformation into a solid – polymer of a high bounding ability. This binder is well water soluble. Application of various hardeners (the most often it is a mixture of organic esters) together with a temperature control, allows to control the polymerisation process rate, and due to that, it is possible to control the moulding sand suitability time to be formed and bounding time. The polymerisation course of geopolymer binders is completely different than the gelling process of water glass. Water glass due to the ester hardener actions forms - after the incubation time - practically in the same time the elastic gel, in which the whole liquid phase is contained. Then the syneresis effect occurs, i.e. the liquid phase educes from gel. Geopolymer binders undergo gradual polymerisation as the result of hardeners actions (the most often these are liquids or CO_2), which causes a successive increase of viscosity of a liquid and its transformation into solid substance, i.e. inorganic polymer. Geopolymer binders in the system remains intact. Such binding character, facilitates the casting knocking out and the spent sand reclamation is the investigations of moulding sands with geopolymer binders indicate, they are characterised by high strength, proper fluidity and permeability. In addition, these sands are distinguished by good knocking out and reclaimibility, which constituted the main drawback of moulding sands with water glass. In the case of a moulding with mineral matrix have a large cohesive strength, and their destruction character is determined as adhesive, since a binder breaks away from the matrix grain surface, while the structure of the binding bridge sand prepared on fresh sands the polymer binder addition is: 1.6 – 1.8 %, and when a moulding sand contains 75 - 100 % of a reclaim, the binder addition is: 1.8 - 2.0 %. The mechanical reclamation can be applied for these moulding sands and these sands do not require heating as moulding sands with water glass. A very important good point of geopolymer binders is their behaviour at high temperatures. In moulding sands with water glass the so-called first maximum of retained strength occurs at a temperature from 200 to 300 ^{o}C. Polymer binders do not have, in this temperature range, any tensile strength increase. However, after heating up to a temperature of 800 ^{o}C the final strength of cores with geopolymer binders euals 0.2 MPa, it means approximately 5-times less than of cores bound by water glass only.

The GEOPOL® technology is currently used in the foundries for three basic production processes/technologies:

- self-hardening moulding mixtures for moulds and cores production
- sand mixtures hardened by gaseous carbon dioxide or even moulds and cores production and
- the hot box technology with hot air hardening for cores.

In this technology, the hardening is caused by dehydration, so it means by a physical process

The GEOPOL® is odourless technology and generates no pollutants, so it has a minimal negative impact on the environment.

Cores applied in a foundry practice are exposed in moulds to significant thermal and mechanical loads. These loads value depends to a significant degree on the casting method. Cores are subjected to erosion caused by a high flowing rate of liquid metal, undergo metal penetrations and cause decreasing of a dimensional accuracy of castings. Taking into account, as an example, the gravity die casting, low-pressure and high-pressure castings, the pressure influencing the cores gradually increases and the cores must have higher and higher strength. When traditional moulding sand cores with organic binders - in amount of 1 - 3 % - are used, even 70 % of all VOC emitting from foundry plants originates from cores.

An increase of the core strength causes a decrease of its compliance, which prolongs the time needed for its removal and thus costs of the casting processing are growing.

SALT CORES

Numerous works aimed at minimising negative features of cores with chemically bound binders, led to the development of inorganic binders (sodium silicate based), and salt cores (inorganic salts based) soluble in water.

Salt cores, on account of being soluble in water, are easily removable from moulds and indicate high compliance due to which can take very complicated shapes. Solubility of cores in water is especially important in case of aluminium alloys castings, when too low temperature of liquid metal does not cause a total burning of a core and additional operations are needed for its removal. Salt cores have been known from 1970-th, but they were used only at multi-serial production of aluminium alloys castings, e.g. cooling channels in valves of gravitationally or under low pressure, cast engines [13].. The production process of salt cores as well as operations performed at high temperatures (pouring, cooling and solidification) do not emit VOC, which makes these cores environmentally friendly. These features of salt cores caused that they found wide applications in automotive and aircraft industry, where castings of complicated shapes were produced.

Water soluble cores must fulfill the determined technological requirements in order to achieve the optimal results:

- acceptable dimensional changes at their production, i.e. technological shrinkage max. 2 %,
- dimensional accuracy should be ± 0.2 mm;
- adequate mechanical strength (bending strength minimum 3 MPa);
- moisture resistance, both in volatile and liquid states;
- not causing secondary defects in castings (reactions with metal, or surface defects).

Cores can be classified in dependence on:

- production technology,
- chemical composition.

Salt cores can be produced by various techniques, but the most often the described below two technologies are applied:

a) Sintering and pressing under a high pressure with using the recrystallisation process. When the core obtains the required strength as a result of joining wet salt grains it is followed by the recrystallisation along grain boundaries. This method of manufacturing cores has certain limitations concerning reproduction of complicated internal spaces [5]
b) Shooting into the core box the mixture with the proper inorganic binder and hardening.

Another division of salt cores can be based on their composition, taking into account mutual relations of water : water soluble substance:

a) Cores produced mainly of water soluble substances, e.g. binary systems: NaCl – Na_2CO_3; KCl – K_2CO_3; KCl – NaCl, which strength is above 30 MPa.
b) Cores containing mainly water soluble substances and some other materials uniformly distributed in a water soluble substance, e.g. mixture of melted Na_2CO_3 and ceramic molecules of MgO [1].
c) Cores produced mainly of fire-resisting materials, which form a binder with a water soluble material, e.g. zirconium sand and sintered powdered Al_2O_3 as main components mixed with NaCl as a binder. Their strength was above 1.2 MPa.

The most often the mixture of Na_2CO_3, KCl and NaCl, is applied. After melting this mixture is used for making cores. Due to this, cores obtain the high compression strength and dimensional stability, so much needed for producing responsible castings. The drawback of such mixture constitutes its tendency for forming shrinkage cavities, micro porosities and hot cracks. Hot cracks can occur in salt cores when there is a volume change, e.g. during solidification. In addition, cores are subjected to erosions caused by a high rate of mould filling with liquid metal, by a metal penetration and by worsening of dimensional accuracy when the liquid metal temperature is approaching the salt melting temperature. Therefore special additions, of specific features and a determined granulation, are introduced into the mixture of pure salts. These additions increase a thermal strength of a core and decrease a possibility of surface defects on castings. Cores are often of complicated shapes. In such cases the mixture of components is melted and the obtained homogenous liquid is injected into the metal mould under a high pressure. After solidification a salt core is taken out from a mould. Such cores are applied in the die and gravity castings. On the other hand, for cores applied under high pressures four-component binary systems were developed: $NaCl$-Na_2CO_3, KCl-K_2CO3, KCl-$NaCl$, K_2CO_3-Na_2CO_3. Strength of cores made of a mixture $NaCl$-Na_2CO_3 was above 20 MPa at Na_2CO_3 content of app. 20 - 30 % and 50 - 70 %. The highest strength for the system $NaCl$-Na_2CO_3, equaled 30 MPa, was obtained at 70 % of Na_2CO_3 [6, 9]. As research by Peng Jiang very good properties were obtained for water-soluble cores composed of a mixture of $MgSO_4$ (magnesium sulfate) and Na_2SO_4 (sodium sulfate), hardened by microwave heating. Two parameters decide on the salt cores quality: resistance to moisture influence (service life) and solubility. An addition of 3 % of kaolin into potassium carbonate solution increases two-times the tensile strength of cores and decreases the moisture absorption rate by 14 %. These cores have a low emission of gases (9.5 mL/g). The water –soluble core can greatly improve the production efficiency of complex castings, This process has greater prospects in forming magnesium alloy castings.

GREENSANDS

In comparing the greensand technology and chemically bonded, two main parameters are taken into account.

- Amount and kind of used raw materials - in the greensand the average addition of bentonite equals 8% . Taking into account the sand recycling, it can be assumed that app. 7.5 % of this bentonite will be used again in further cycles (assuming that app. 0.5 % of bentonite will have to be substituted by a fresh material). In the typical technology of moulding sands with chemically hardened binders the addition of 1 - 3 % of a binder is used and all this amount is lost, due to a high temperature influence and in the reclamation process [17-19]. Such diversification of sands is essential for the process economy.
- The second essential factor influencing the technology selection is the problem of the environment protection. In case of greensands containing only bentonite and water, water vapour and CO_2 will be only evolving - in practice - into the environment. Problems are occurring when organic additions are introduced to green sands, e.g. carbon substances generating lustrous carbon.

Moulding sands with bentonite, it means greensand[1] is the most popular technology of manufacturing sand moulds, especially for cast iron castings. More than 70% of iron castings are produced in greensands. One of the reasons of such wide usage of moulding sands with bentonite is the possibility of its using several times [17-19]. It can be assumed that that 90 % of bentonite and the selected additions can be reclaimed and -after rebounding - used again.

The average composition of such moulding sand: 85-95 % of high-silica sand (but can be also olivine or zirconium sand), 5 to 10 % of bentonite, 2 to 5 % of water and - in case of making iron castings - 3 to 9 % of substances containing carbon, it means substances generating lustrous carbon. These can be: sea coal dust, brown coal, products from crude oil processing, starch, wood flour, synthetic resins, plastics, etc. Bentonite and water are acting as binders, while substances generating lustrous carbon prevent the metal oxidation, by producing the reducing atmosphere during the mould pouring with moulten metal. They produce the lustrous carbon layer not moistened by liquid metal, which prevents sand burn-on to the casting. Green sands can be used for producing moulds for castings of ferrous alloys as well as of non-ferrous metals alloys (magnesium, aluminium, copper alloys). Small, precise castings as well as large castings of a few tons can be cast.

At a uniform moulding sand compaction and at maintaining a precise control of its properties, castings of a very low dimensional tolerance are obtained. This process is characterised by a very good efficiency, as compared with several other processes of producing moulds, and is easily mechanized.

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[1] The process is called "green sand" casting not because the sand is green but because the sand is moistened with water and clay, rather than oil. The term Green Sand means the presence of moisture in molding sand and indicates that the mold is not baked or dried.

Green sands can be hand formed, but presently the machine forming technique with the application of automatic moulding machines: shaking and pressing, pressing or impulse-pressing, predominates. Specially beneficial is the flask-less formation, which is highly efficient and the produced moulds are very accurate.

The greensand technology is and still will be the one of the most important and the most widely applied moulding sands technology. These sands are cheap, environmentally friendly (provided that additions of substances containing carbon and generating at high temperatures often toxic gases and unpleasant odour, are not used) and - what is the most important - they are reversible. This technology is efficient: applying chemically bound moulding sands it is possible to produce 60-100 moulds/hour, while a modern foundry applying greensands is producing 600 moulds/hour.

3. ASSESSMENT OF THE HARMFULNESS OF THE MOULDING SANDS [14, 15]

Two aspects should be considered at the assessment of the given moulding sand harmfulness.

1. ***Moulding sands harmfulness for employees and for the environment caused by emissions of gaseous and dust contaminations occurring during the sands preparation, producing cores and moulds as well as at moulds pouring with moulten metal, cooling and castings knocking out:***
    - Evaporation of volatile compounds during producing moulds and cores (mixing, sands shooting, moulds making, storing, etc.);
    - Evaporation of unreacted initial components of resins (e.g. in case of phenol-formaldehyde resin: monomers of phenol and formaldehyde) as well as solvents of higher boiling points at the first seconds after a mould filling with liquid metal;
    - Emission of BTEX and other decomposition products occurred as the pyrolysis result of the main carbon chain of the polymer in further staMw dla odlwnictwa.ges of the casting production.
    - All chemically bound binders can create potential hazard for the health in case of long-lasting or recurring exposures to hazardous factors. The threat can occur both by inhalation and through the skin. Especially dangerous is a direct contact of an employee with unreacted resin or unhardened sand, during its preparation and during making moulds and cores. In extreme cases the skin contact with those substances can cause chemical burns, scars and allergies. Therefore using personal protection devices, such as gloves resistant to chemicals, safety goggles and protective clothing, is necessary.
    - during moulds pouring with moulten metal the binder thermal decomposition occurs. A majority of decomposition products occurs in trace amounts. Special

dangerous are decomposition products of substances containing carbon applied as additions for green sands.

2. The sand harmfulness for the environment is caused by elution of dangerous substances from spent sands. In dependence of the concentration of eluted substances - determined in the elution test - the given sand can be classified to one out of dumping grounds. In the situation when the spent sand will be further economically utilized, performing the elution test is also necessary due to a possible contact with employees or with the environment.

The emission of inorganic dangerous substances occurs mainly during melting and cleaning processes of castings and mostly these substances are metal oxides. Hazardous substances at work places can be gaseous, liquid or solid. Their dangerous operations can take place by the skin contact, by breathing or eating together with food. The main source of dust and gaseous contaminations are operations of moulds pouring with liquid metal, moulds cooling and castings knocking out. In the case of moulding sands with bentonite these operations generate up to 90 % of contaminations from the Hazardous Air Pollutants (HAPs) group.

In order to assess each technology, including the moulding and core sands technology, in the aspect of its influence on the environment and working conditions, the analysis of life cycles of all products should be performed. This analysis should start from the raw materials output (sand, bentonite, coal) via the binders production (resins, water glass) then the whole process of sands preparations and moulds making, pouring and cooling processes of moulds, castings knocking out. The analysis should be ended on the spent sands reclamation process and these sands utilisation or storage. Only two elements of life cycles of moulding and core sands, the most important in considerations of their harmfulness, are taken into account :

- moulding sand preparation process, making of moulds and cores, moulds pouring with moulten metals, moulds cooling and castings knocking out. This mainly concerns gaseous substances released to the environment during these processes.
- influence of spent moulding and core sands during their storage or recycling, the reclamation process, after reclamation wastes and possibilities of their utilisation, including storage. This concerns substances which could be eluted to the environment.

The emission into the air in foundry plans is not organised, it means it is difficult to detect and therefore hazardous for the environment and employees. The most important chemical compounds, which can be released during the castings production of various alloys and moulding sands with different matrices and binding materials, were determined on the bases of numerous references and own investigations. During moulds and cores productions such dangerous substances as e.g.: carbon monoxide, formaldehyde, phenol, furfuryl alcohol, isocyanides and amines, can be formed. The attention should be directed to the significant number of substances from the HAP group since a lot of them are carcinogenic or mutagenic. Apart from standard organic substances, which can be generated under the temperature

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influence at the determined chemical composition, substances from the PAH group or dioxanes and furans can be expected in waste gases.

The example of highly harmful moulding sands, especially at the stage of the mould pouring with moulten metal, are sands with bentonite and with additions of substances containing carbon, able to form lustrous carbon. Moulding sands with bentonite, without coal dusts belong to environment friendly sands (all components are of a natural origin). However, the introduction of coal dusts into this sand, causes that it becomes the most dangerous for the environment. When such mould is poured with moulten metal the additions containing coal are decomposed and toxic gases are emitted: NH_3, H_2S, PH_3, benzene derivatives, PAHs and BTEX, including highly carcinogenic benzo(a)piren. A part of these substances is released into the environment directly after the mould pouring with moulten alloy and another part is condensing on matrix grains. This part after successive cycles of sand circulations and after repeated mould pouring with moulten metal is also released into the environment. In several castings made in sands with bentonite, the application of cores is necessary. These cores are made most often by the cold – box, hot - box or coated sands technologies, which cause additional emissions of gases. During casting knocking out the burned moulding sand with bentonite is mixed with the burned core sand and such mixture is subjected to the reclamation. Thus, the remains from organic binders and not active bentonite are transferred to the reclaim, worsening its quality. This is specially disadvantageous when the moulding sand is only subjected to a partial reclamation, which encompasses the removal of dusts and improvement of the grain distribution of the return moulding sand.

Therefore investigations concerning moulding sands with bentonite are mainly focused on the development of such substitutes of seacoal, which would produce the same technological effect and be less harmful for the environment.

Since the majority of castings is produced in moulds on high-silica sand matrices, the special attention should be directed to the air contamination by crystalline respirable silica (SiO_2 particles of dimensions at least 100 times smaller than sand grains). Potential sources of the exposition to the respirable silica influence in the foundry plant are: transport of fresh sands and the reclaim, cores forming and production, castings knocking out and their treatment, reclamation of spent sands. The presence of respirable silica in the air increases the risk of serious illnesses such as: pneumoconiosis, lung cancer, kidney sicknesses.

In the foundry plant, which has the installation for the reclamation, sand grains are circulating and used several times. Mechanical rubbing processes during the preparation of moulds and during the mechanical reclamation, an exposure to thermal shocks and high temperatures, are causing that sand grains are cracking and breaking, which changes their shape and makes them useless in the foundry plant. When sand loses its properties and is not suitable for production of moulds and cores, it is removed from the foundry plant and treated as waste materials (Spent Foundry Sand - SFS). Main factors deciding on the SFS properties are: the alloy kind, casting process, applied moulding sand technology. Several possibilities of using the SFS can be found in references, among others in civil engineering. The SFS together with fly-ash can be used in production of blocks for building walls, for the production of fire-resistant mortars or bricks. The SFS constitutes a good material for foundations and for lower bases at building highways [7]. Foundry plants have the serious problem with the waste sands management. Only a part of spent moulding sands is subjected to the reclamation process and the obtained reclaim is used in the production of moulding sands. A significant part of the SFS must be managed outside foundry plants. There are several possibilities of the waste sands management outside foundry plants. However, such wastes must satisfy the determined requirements concerning their composition, contents of hazardous organic substances (which can be eluted), contents of heavy metals, coarseness, ability of water absorption, etc. In the case of spent sands, their harmfulness can be assessed by the contents of dangerous substances or by - more important for the environment - their inclination for elution. Main fields of a useful management of spent moulding and core sands are: the soil production, building of river embankments, or using sands with bentonite for removal of zinc and trichloroethylene from sewages [9]. The reclamation of spent sands becomes the need in the majority of foundry plants, due to increasing transport costs and raw materials prices. A foundry plant can choose either to store spent sands, to pay for fresh sands and their transport to the plant, pay for transport of spent sands and pay for their storage or to apply the reclamation. In case of the mechanical reclamation costs are much lower and contain electrical energy costs, buying and transporting of much smaller amounts of fresh sands (up to 10%), and disposal of 5-10% of after reclamation dusts, with taking into account that these dusts can be classified as dangerous. An additional advantage for the environment constitutes the lower emission of combustion gases since the transport is significantly limited. Three basic reclamation methods are applied: dry method (mechanical), wet method and thermal method. Each of them influences the environment in a slightly different way.

Very often occurs that: the better technological parameters achieved the more dangerous is the moulding sand. Therefore moulding sands which will allow to produce good castings at the minimal negative influence on the environment, are looked for. The example can be the moulding sand with water glass hardened by physical factors e.g. by drying. Another group of such moulding sands constitute hybrid sands, which are mixtures of inorganic components with organic ones, e.g. resin modified by bentonite nanoparticles or water glass with collagen additions. Apart from standard organic compounds, which can be formed under an influence of a temperature at the determined chemical composition, substances from the PAHs group or dioxins and furans be expected. The basic test, for the assessment of the possibility of utilising the SFS, is the elution test, performed according to the proper procedure. One of such tests is the Toxicity Characteristic Leaching Procedure (TCLP) developed by the Environmental Protection Agency (U.S. EPA) used for evaluating whether the given waste has toxic properties and can be dangerous. Since waste sands are usually mixtures of sands of various composition, originated from various technologies, the elution tests must be performed relatively often. The special attention was directed to elution of substances from the PAH group. All samples of moulding sands, regardless of their technology and the casting alloy grade, contained substances from the PAH group. The total concentration of these substances was changing in dependence of the kind of alloy and sand, but naphthalene constituted approximately 30% in each sand. Each substance from the PAH group had a higher concentration in spent moulding sands with bentonite, than in spent sands with chemically hardened binders. Out of all moulding sands with chemically bound binders the PAH concentration in sands with acid hardened furan resin and in sands with water glass hardened by CO_2 were lower than in phenol moulding sands hardened by esters. The kind of alloy poured into the mould, has a significant influence on the amount of substances from the PAH group. Concentrations of PAHs substances in moulding sands were in the following order: cast iron > aluminium alloys > cast steel. High concentrations of substances from the PAH group in moulding sands with bentonite is the effect of using organic additions for improving properties (e.g. substances generating lustrous carbon) and cores made of sands with furan or phenol resins. In addition, the moulding sand with bentonite circulates in cycles a few times which causes that these substances cumulate in the sand.

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4. GREEN FOUNDRY LIFE PROJECT (LIFE17ENV/FI/173)

The goal of this project is to demonstrate the new clean technology of moulding systems in practice. The new inorganic binder system is based on the sodium silicate (glass water) or aluminosilicate, which reduces the amount of harmful components indoor and in ambient air.

4.1. AGH –UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF FOUNDRY ENGINEERING

AGH – University of Science and Technology Faculty of Foundry Engineering is main research institution in investigations concerning influences of foundry processes and moulding sand technologies on the natural environment and work conditions.

Investigations of the gases emission in the test foundry plant were performed according to the original method developed in the AGH UST (Patent PL 224705 B1) (Fig. 1 and Fig. 2).

4.2. AGH –UNIVERSITY OF SCIENCE AND TECHNOLOGY ACTIONS

Action A1: Preparatory and foundry actions for pilot foundries sand recycling activities.

Action B1: Emissions of different binder systems during small – scale test casts.

Method 1. Testing foundry at AGH-UST - laboratory test;

Method 2. Tests in foundry plants – small scale chamber

4.3. ACTION B1: EMISSIONS OF DIFFERENT BINDER SYSTEMS DURING SMALL – SCALE TEST CASTS.

4.3.1. Method 1. Testing foundry at AGH UST –laboratory tests

4.3.2. Methodology and apparatus used

Investigation of the gases emission in the small test were performed according to the original method developed in the AGH. A sample of the investigated moulding sand of a cylinder shape of dimensions 50 mm x 50 mm, weight about 150 g is poured with liquid cast iron of a temperature of 1350^{o}C. Gases emitting from the sample – after pouring it with liquid metal are led by means of a steel pipe via the drying system and heating system and the capsule with activated carbon (during BTEX measurement) or polyurethane foam (during PAHs measurement) into pump.

Samples provided for the determination of compounds from BTEX group and PAHs were extracted with dichloromethane in a gas-tight vials for headspace analysis. BTEX analysis were performed using a headspace sampler for chromatographic separation HP-5MS column was used. The commercially available BTEX MIX standard in methanol was used for the quantitative analysis. PAHs analysis were performed using S/SL injector port in splitless mode for chromatographic separation ZB-PAH column were used, the commercially available PAHs MIX standard in acetonitrile/acetone/toluene mixture according with EPA 8310 (16 PAHs) was used for the quantitative analysis. Trace 1310 GC coupled with ITQ 1100 MS (Thermo Scientific).

Figure 4. Test station for measurement of BTEX and PAHs content in released gases

(laboratory- test)

CO_2, SO_2 and NO_X measurements were carried out with the GA40T plus analyzer. For measuring concentration of NO_X and SO_2 gases in the device were used electrochemical sensors. The infrared detector is responsible for CO_2 measurement. This analyzer enables measurement in the range of concentrations: CO_2 up to 25%, SO_2 up to 4000 ppm and NO_X up to 5000 ppm. GA-40 T plus is controlled by a microprocessor and via the RS 232 C interface is connected to a computer to read stored results and to work "on line". Gases from the flue gas channel are taken with the help of a probe tube and at the same time the temperature of the gases at the intake point is measured. Then they pass to the preheated dust filter with a permeability of 5µm and through a heated hose to the conditioner dryer. The steam separates here from the tested gas, which is fed to the external 5µm filter and then to the gas pump. Gas for CO_2, SO_2 and NO_X measurements was taken at a speed of 1.1 l/min and it constituted 16% of the total stream flowing through the test stand at the AGH foundry.

The CO content was measured using the GA-20 plus analyzer. An electrochemical sensor was used to measure CO concentration in the device. This analyzer enables measurement in the range of CO up to 15%. The GA-20 plus, like the GA-40 T plus, is controlled by a microprocessor and is connected to a computer in order to read the stored results and to work "on line". Gas for CO measurements was taken at a speed of 0.7 l/min and it constituted about 10 % of the total stream flowing through the test stand.

4.3.3. Materials and their characteristics

Moulding sands chemically hardening

There are many different types of chemical binders. They divide into two main types: organic and inorganic.

The introduction of water glass as a binder in the early 1950s was very important in increasing the production efficiency of moulds and cores.

Processes using water glass-hardened CO_{2T}or organic hardeners contributed to improving the quality of the work environment and the natural environment. The rapid development of foundry industry in the second half of the 20th century and the increasingly complex shapes of castings, it was necessary to use binders based on organic compounds. However, the increasingly stringent requirements for environmental protection and the increased public awareness based on the principle of sustainable development caused that the attention was again paid to inorganic binders based on alkaline silicate solutions.

This is especially important for cores, which usually make up to 10% of the volume of the mould, but emit up to 70% of volatile organic compounds in the foundry.

4.3.3.1. ORGANIC BINDERS

- **Furan resin: Kaltharz X 850 TN011 + Aktivator 100 T 3 (Hüttenes-Albertus)**

Furan resin: Kaltharz X 850 TN011 + Aktivator 100 T 3 (Hüttenes-Albertus) (code MF):
resin: free furfuryl alcohol – 85 ± 3%; free formaldehyde – 0.1 – 0.05%; nitrogen - <0,9%
hardener: Aktivator 100 T 3: aqueous solution of paratoluenosulfonic acid.
composition of moulding sand: silica sand – 98,5%; resin - 1%; hardener – 0.5%.

- **Phenol-formaldehyde resin (ALPHASET): Sinotherm 8255 + Aktivator J 120 (Hüttenes-Albertus)**

Phenol-formaldehyde resin (ALPHASET): Sinotherm 8255 + Aktivator J 120 (Hüttenes-Albertus) (code MA):
resin: free phenol - 1.0%; free formaldehyde - < 0.2%; content of nitrogen – 0%.
hardener: Aktivator J 120 - 0.3%, silica sand – 98.5%, resin Sinotherm 1.2%; hardener – 0.3%.

4.3.3.2. INORGANIC BINDERS

- **INOTEC inorganic binder system for cores (ASK CHEMICALS) (code MI):** composition of moululding sand: silica sand – 96.4%, binder INOTEC – 2.3%, promotor INOTEC – 1.3%.

- **CORDIS inorganic binder system for 1.**, binder CORDIS 8593 – 2%,

Anorgit 8610 – 1.3%.

- **GEOPOL – inorganic binder system (code MG):**

currently used for three basic technologies: a) for self-hardening, b) sand hardened by gaseous CO2 , c) hot– box technology with **hot air hardened. (SANDTEAM). GEOPOL 618, hardener SA 73:**composition of moulding sand: silica sand – 98.2%; GEOPOL 618 – 1.6%, organic hardener 73 – 0.24%.**)**

- **Greensand – ECOSIL SLE84 9 (CLARIANT)–activated bentonite with dust coal and carbon additive. (code MB)**

Composition of moulding sand: silica sand – 93% bentonite – 7%, water – 55 cm^3. Samples were dried at 100^{o}C for 4 h.

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4.3.4. Methodology

Collected samples with adsorbed gases were kept at 3-7°C until they were analyzed. Samples for the determination of compounds from the BTEX group and PAHs were extracted with dichloromethane.

In the case of BTEX, activated carbon constituting the adsorbent and dust retained on the quartz filter was analyzed. For PAHs, polyurethane X-2 foam and dust retained on the quartz filter were analyzed.

The obtained quantitative results were included in Table 1 (for BTEX) and Table 2 (for PAHs). To compare the tested moulding sands in terms of BTEX and PAHs emissions, two indicators were introduced: one calculated for 1 kg of moulding sand and the other calculated for 1 g of components included in the binder.

4.3.5. Designation of samples

MF - mould sand with furan resin
MA – mould sand with phenol-formaldehyde resin (ALPHASET),
MG – mould sand with GEOPOL binder,
MC – mould sand with CORDIS binder,
MB – greensand,
MI – mould sand with INOTEC binder

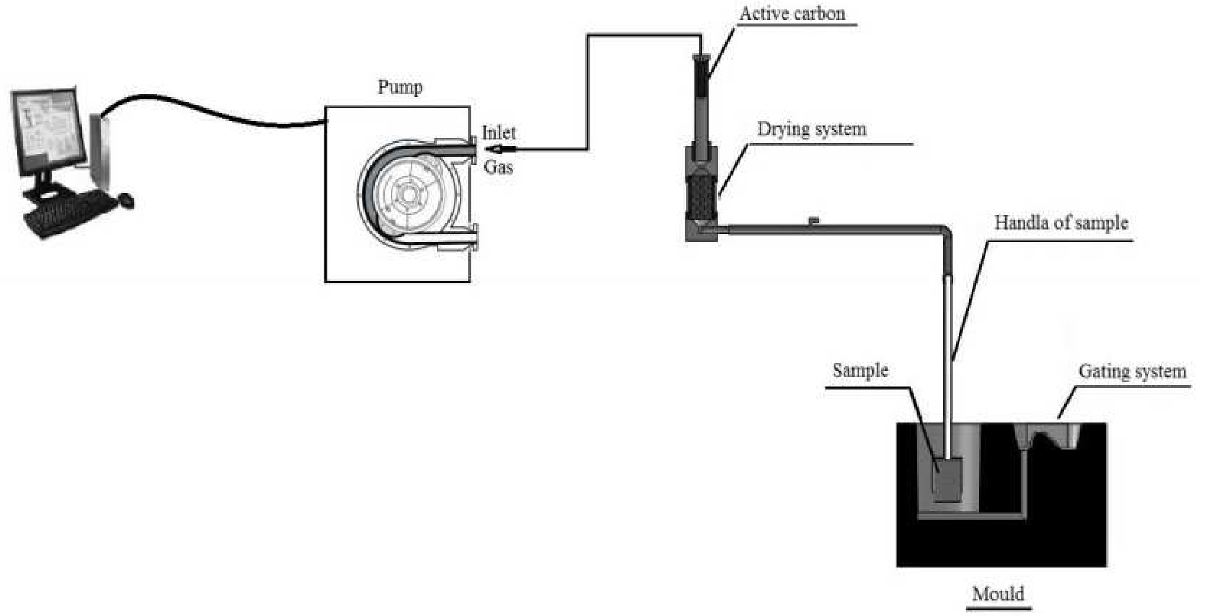


Fig. 5. Scheme of the station for measurement of BTEX and PAHs content in released gases (small-test)

5. RESULTS AND DISCUSSION

5.1. MOULDING SANDS WITH ORGANIC BINDERS

5.1.1. Measurement of BTEX

The tables (Table 1a-1c) contain the results of BTEX measurements calculated per 1 kg of moulding sand and calculated per 1 kg of binder.

Table 1. Quantity of BTEX compounds released during the test

Table 1a. Code: MFA+MFS (absorption layer + silica filter)

Type of moulding sand and code	Compound	Results, µg	Results, mg	Results, mg
		per sample	per 1 kg of moulding sand	per 1 kg of binder
Code: MFA+MFS Weight of sample, 138.046 g Content of binder, 1.5 %	Benzene	78 180	566.34	37 756
	Toluene	6520	47.23	3 149
	Ethylbenzene	70	0.51	34
	m + p xylene	301	2.18	146
	o- xylene	76	0.55	37
	Total	85 147	616.80	41 120

Table 1b. Code: MF-B (control layer B

Type of moulding sand and code	Compound	Results, µg	Results, mg	Results, mg
		per sample	per 1 kg of moulding sand	per 1 kg of binder
Code: MF-B Weight of sample, 138.046 g Content of binder, 1.5 %	Benzene	4 974	36.03	2 402
	Toluene	487	3.53	235
	Ethylbenzene	36	0.26	17
	m + p xylene	133	0.96	64
	o- xylene	27	0.20	13
	Total	5 657	40.98	2 732

Total MFA+MFS+MFB	Compound	Per sample, µg	Per 1 kg of moulding sand, mg	Per 1 kg of binder, mg
	BTEX	**90 804**	658	43 867

Table 1c. Code: MA

Type of moulding sand and code	Compound	Results, µg	Results, mg	Results, mg
		per sample	per 1 kg of moulding sand	per 1 kg of binder
Code: MA Weight of sample. 142.371 g Content of binder. 1.5 %	Benzene	66 013	463.67	30 911
	Toluene	3 711	26.07	1 738
	Ethylbenzene	119	0.84	56
	m + p xylene	515	3.62	241
	o- xylene	102	0.72	48
	Total	70 460	494.90	32 994

5.1.2. Measurement of PAHs

The tables (Table 2a-2b) contain the results of PAHs measurements calculated per 1 kg of moulding sand and calculated per 1 kg of binder .

Table 2. Quantity of PAHs compounds released during the test

Table 2a. Code: MFA+MFS

Type of moulding sand and code	Compound	Results, µg	Results, mg	Results, mg
		per sample	per 1 kg of moulding sand	per 1 kg of binder
Code: **MFA+MFS** Weight of sample 134.787 g Content of binder 1.5 %	Naphtalene	187	1.39	93
	Acenaphtylene	53	0.40	26
	Acenaphtene	4	0.03	2
	Fluorene	19	0.14	9
	Phenanthrene	204	1.52	102
	Anthracene	119	0.88	59
	Fluoranthene	354	2.63	176
	Pyrene	259	1.92	129
	Benz(a)anthracene	43	0.32	22
	Chrysene	58	0.43	29
	Benzo(b)fluoranthene	35	0.26	17
	Benzo(k)fluoranthene	21	0.15	10
	Benzo(a)pyrene	33	0.24	16
	Indeno[1,2,3-cd]pyrene	112	0.83	55
	Dibenz[a,h]anthracene	48	0.36	24
	Benzo[g,h,i]perylene	80	0.60	40
	Total	1 629	12.09	806

Table 2b. Code: MA

Type of moulding sand and code	Compound	Results µg	Results mg	Results mg
		per sample	per 1 kg of moulding sand	per 1 kg of binder
Code: MA Weight of sample 143.492 g Content of binder 1.5 %	Naphtalene	415	2.89	193
	Acenaphtylene	276	1.92	128
	Acenaphtene	4	0.02	2
	Fluorene	33	0.23	15
	Phenanthrene	71	0.50	33
	Anthracene	21	0.15	8
	Fluoranthene	143	1.00	66
	Pyrene	137	0.96	64
	Benz(a)anthracene	32	0.22	15
	Chrysene	40	0.28	19
	Benzo(b)fluoranthene	19	0.13	9
	Benzo(k)fluoranthene	11	0.08	5
	Benzo(a)pyrene	24	0.17	11
	Indeno[1,2,3-cd]pyrene	73	0.51	34
	Dibenz[a,h]anthracene	43	0.30	20
	Benzo[g,h,i]perylene	74	0.51	34
	Total	1 416	9.87	658

5.1.3. Measurements volume of gases and their release rate in time

5.1.3.1 Measurements volume of gases: BTEX and PAHs

Table 3 presents the total volume of gas emitted during BTEX and PAHs tests of MA and MF moulding sands and their average value.

Table 3. Contains the results of volume measurements of gases release during tests.

Moulding sand code	Realized gases from moulding sands during tests / 1 kg of moulding sands		
	from BTEX test [dm^3]	from PAHs test , [dm^3]	Average, [dm^3]
MF	13.988	14.942	14.466
MA	18.360	16.584	17.482

Dependence of the total volume of emitted gases and calculated per 1 gram of binder in time and their release rate in time are presented in Fig. 6a and 6b (MA-PAHs), Fig. 7a and 7b (MA-BTEX), Fig. 8a and 8b (MF+BTEX)

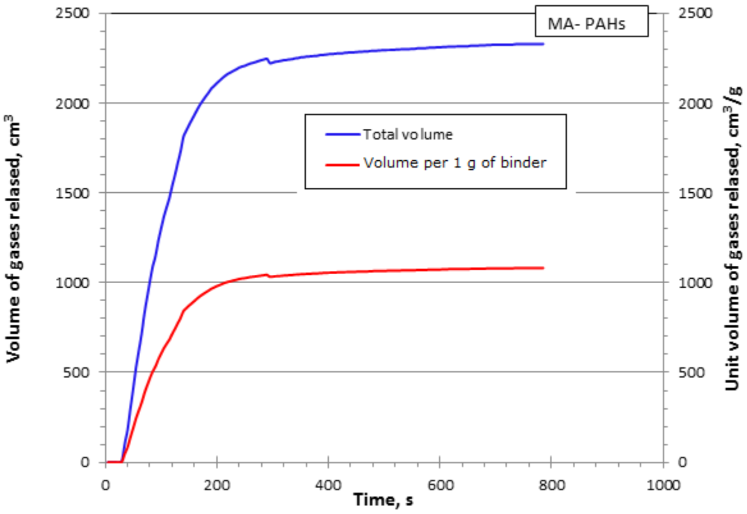


Figure 6a. Emissivity of gases in time, from the investigated moulding sand MA during PAHs measurements: blue line – total volume from sample, red line – volume calculated per 1 g of binder.

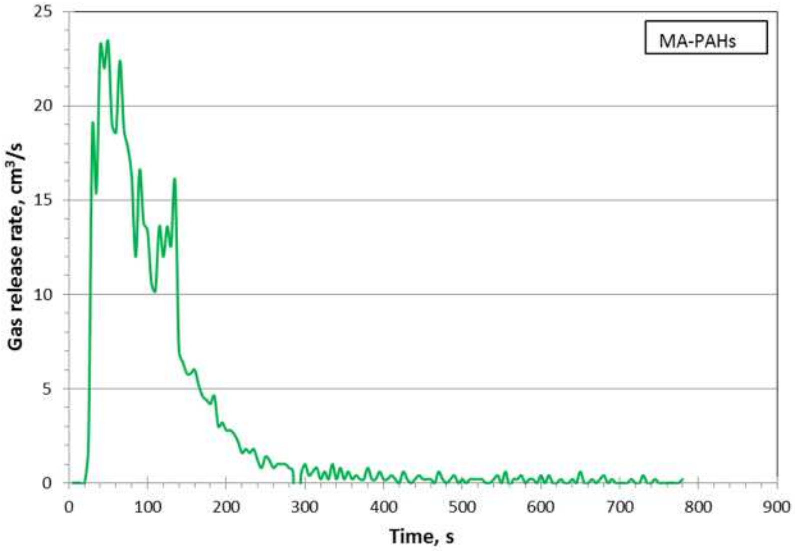


Figure 6b. Gas release rate in time, from the investigated moulding sands MA during PAHs dameasurements.

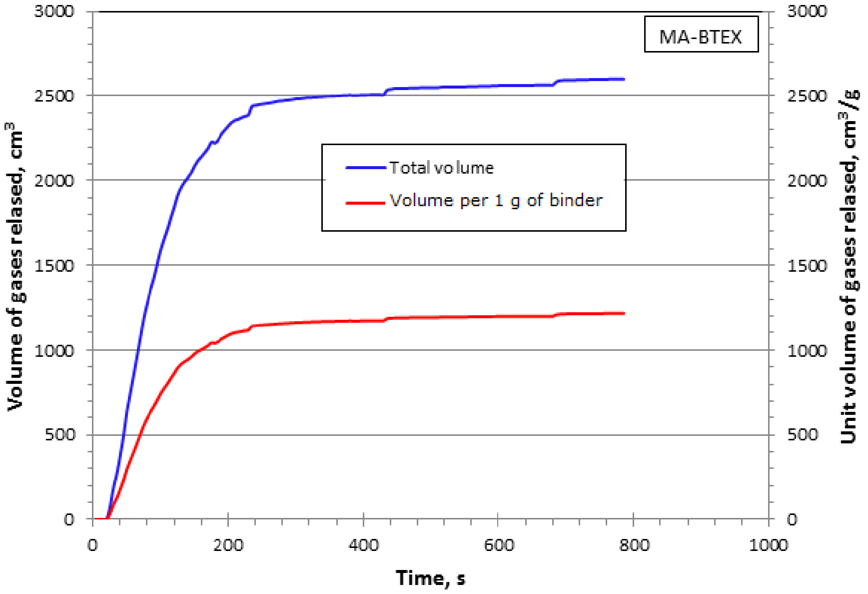


Figure 7a. Emissivity of gases in time, from the investigated moulding sands MA during BTEX measurements: blue line – total volume from sample, red line – volume calculated per 1 g of binder.

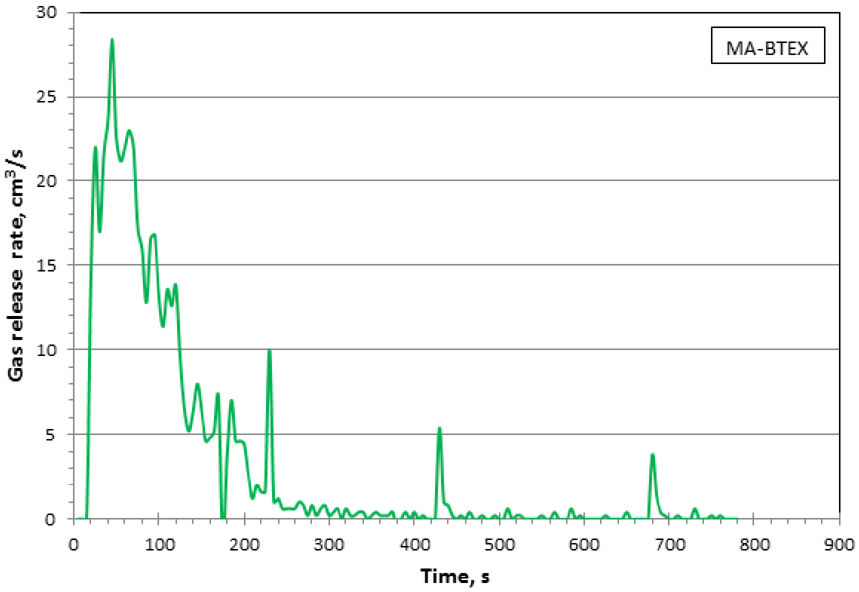


Figure 7b. Gas release rate in time, from the investigated moulding sands MA during BTEX measurements.

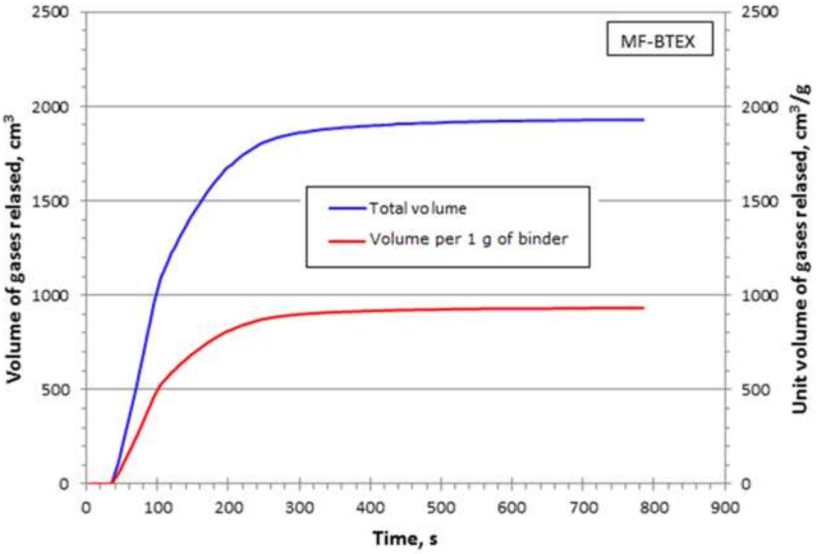


Figure 8a. Emissivity of gases in time, from the investigated moulding sands MF during BTEX measurements: blue line – total volume from sample, red line – volume calculated per 1 g of binder.

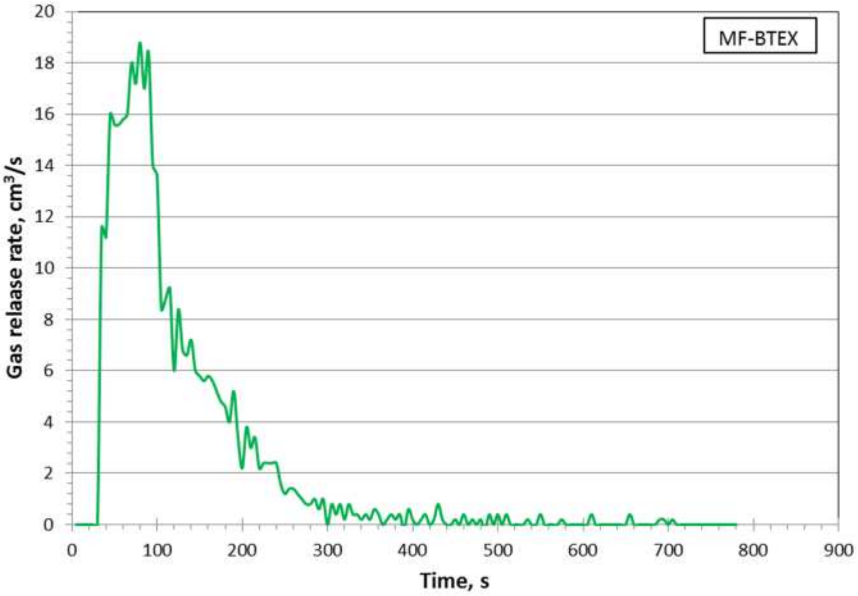


Figure 8b. Gas release rate in time, from the investigated moulding sands MF during BTEX measurements.

5.1.3.2 Measurements of gas emissions: CO, CO_2, SO_2 and NO_X

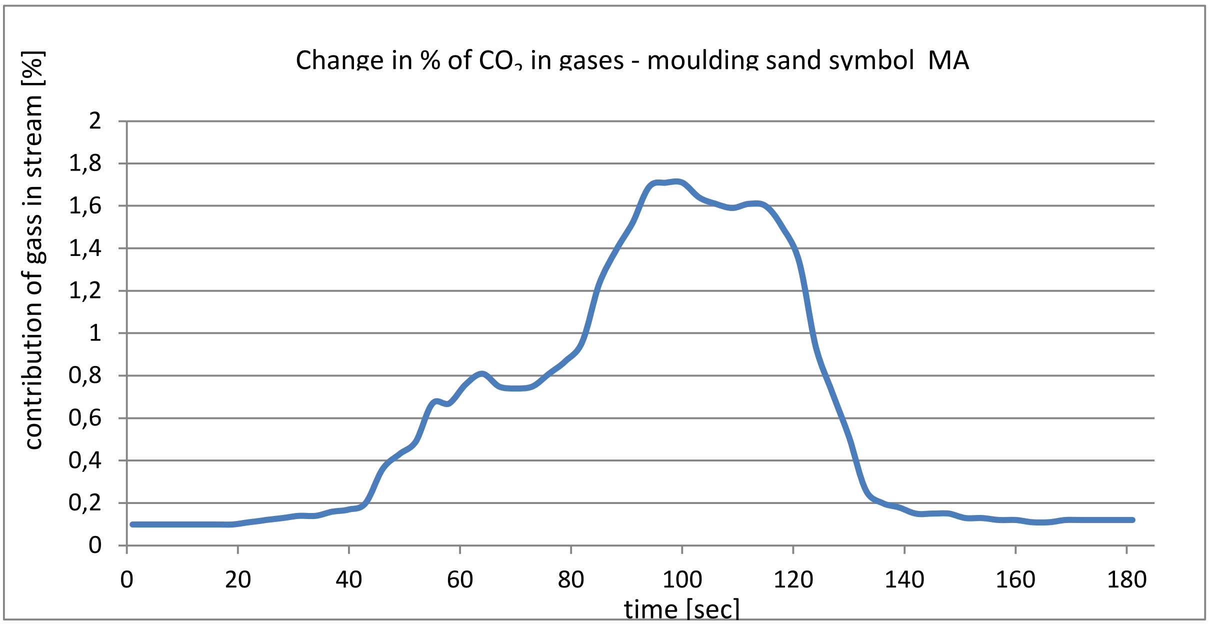
However, the figures 9a –c (for MA) and 10a-d (for MF) show graphically the volume of emissions of these gases for individual moulding sands and gases.
The table 4 below summarizes the results of gas emission: CO, CO_2, SO_2 and NO_X during laboratory tests.

Table 4. Emission of SO_2, CO, CO_2 and NO_x from moulding sands with organic binder

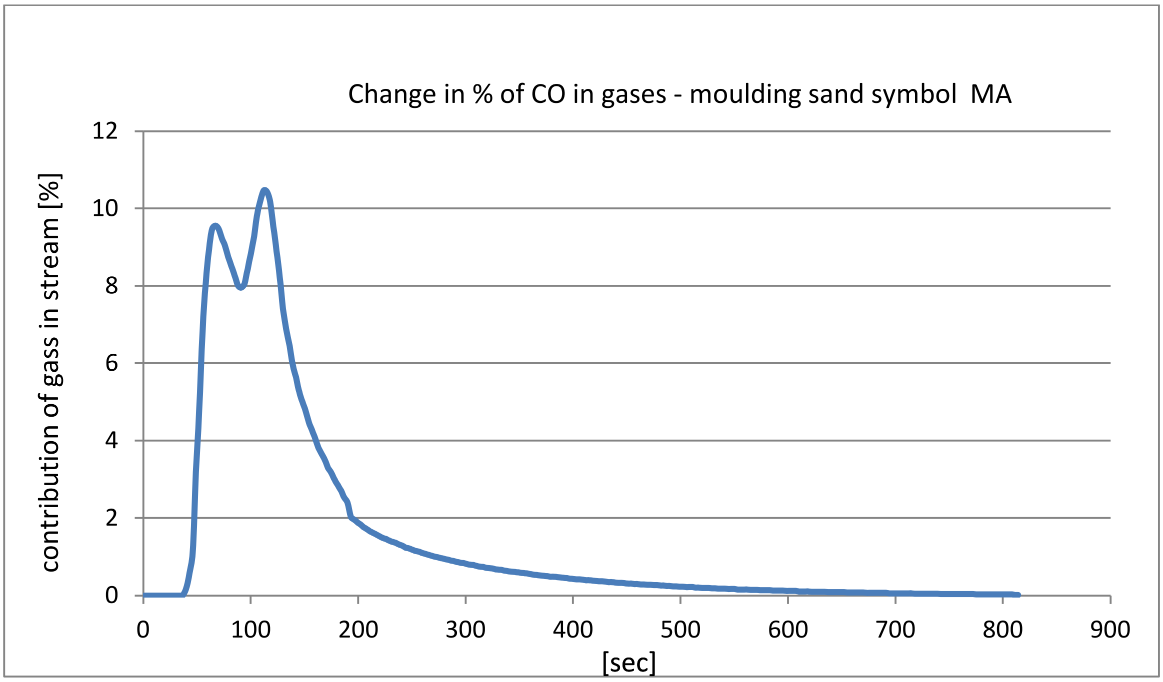
Moulding sand symbol	Amount of: SO_2, NO_x, CO, CO_2 emitted in experiment[1] and calculated per 1 kg of moulding sand[2]							
code	SO_2 [cm^3][1]	SO_2 [cm^3/kg][2]	NO_x [cm^3][1]	NO_x [cm^3/kg][2]	CO [cm^3][1]	CO [cm^3/kg][2]	CO_2 [cm^3][1]	CO_2 [cm^3/kg][2]
MF	1.4	10.5	0.011	0.08	98	738	6.7	50.4
MA	1.4	10.3	0.007	0.05	119	872	5.4	39.6

Moulding sand code MA

9a)

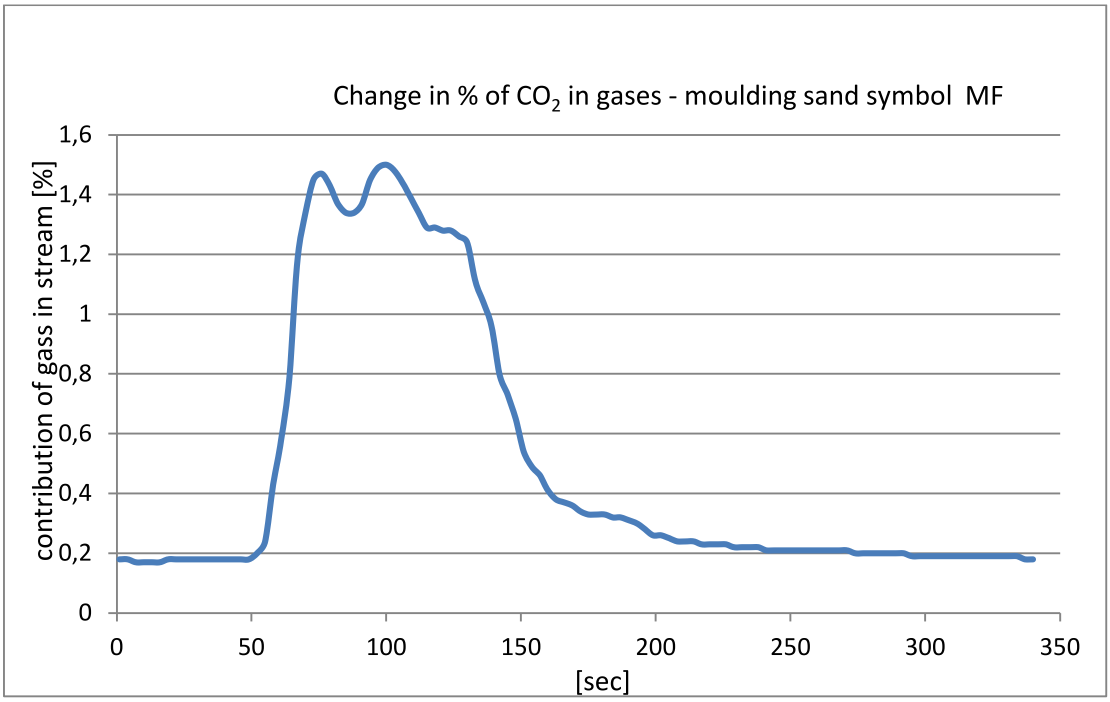


9b)

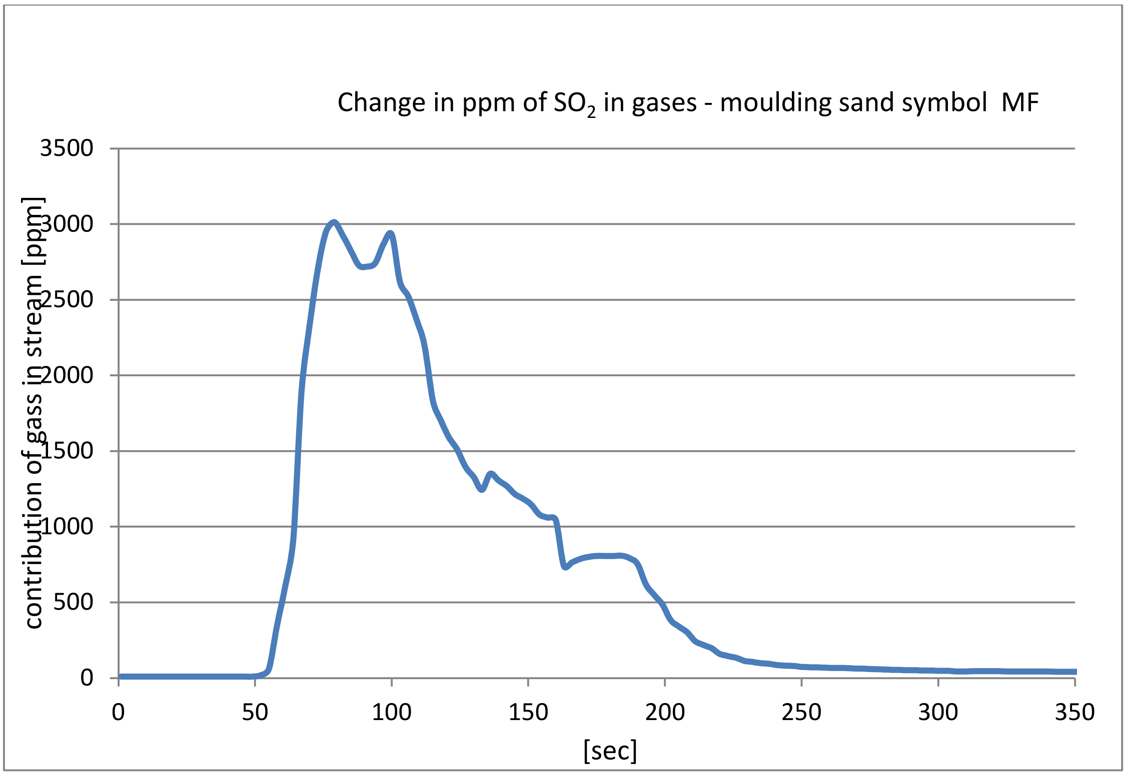


Moulding sand code MF

10a)



10b)



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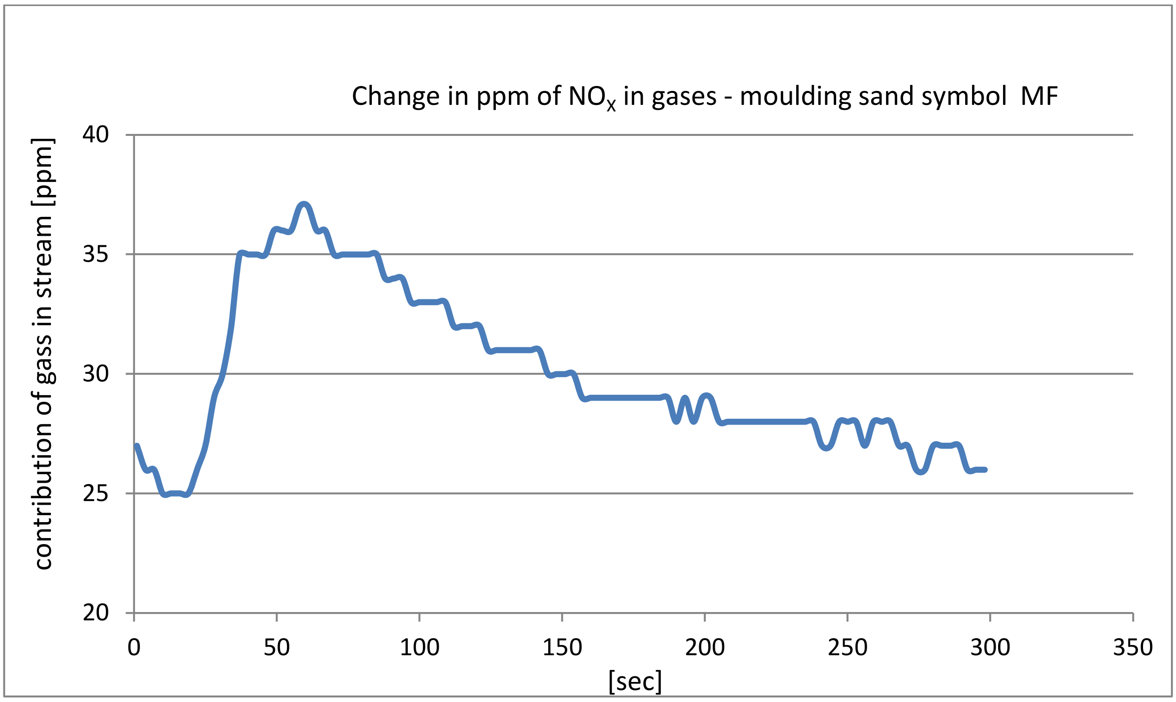
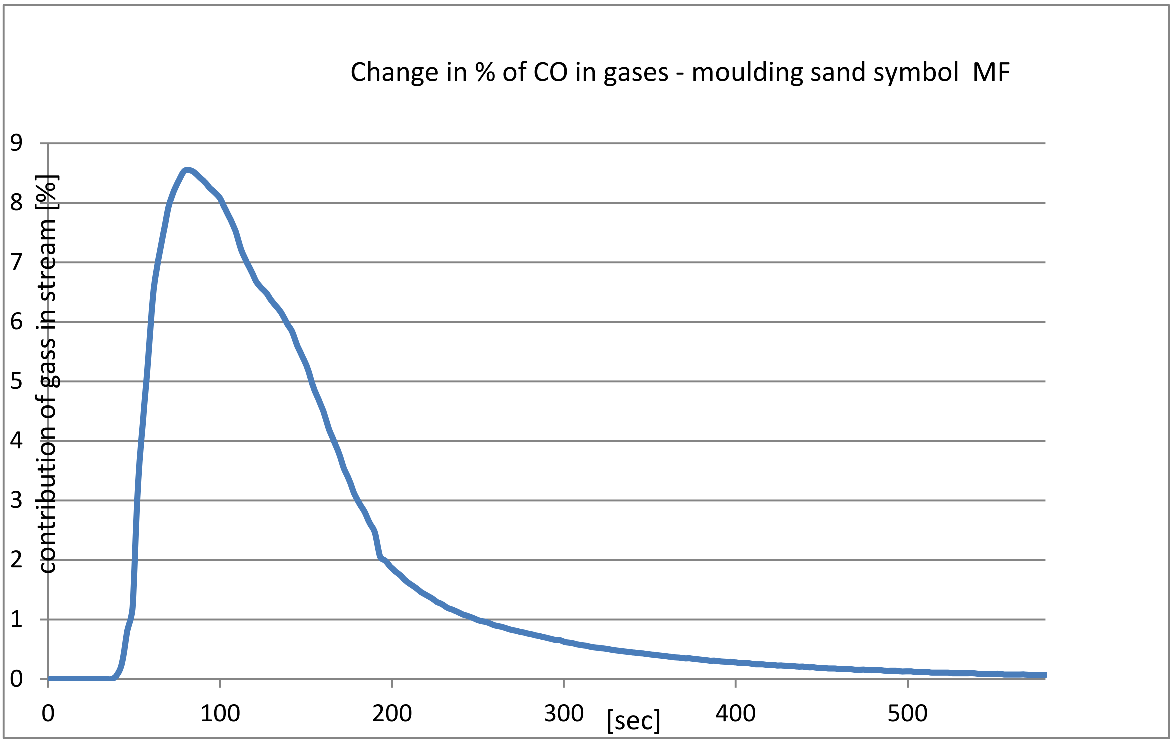
10c)



10d)



5.1.3.3 Conclusions for organic binders

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Table 5 contains of BTEX group emissions, and Table 6 of PAHs compounds emissions (calculation per 1 kg of binder and 1 kg of moulding sand).

Table 5. Total emission BTEX and benzene calculated per 1 kg of binder and 1 kg of moulding sand

CODE	Per 1 kg of binder, mg		Per 1 kg of moulding sand, mg	
Compounds	Total BTEX	Benzene	Total BTEX	Benzene
MF	43 852	40 158	658	602
MA	32 994	30 911	495	464

Table 6. Total emission PAHs and benzo(a)pyrene calculated per 1 kg of binder and 1 kg of moulding sand

CODE	Per 1 kg of binder, mg		Per 1 kg of moulding sand, mg	
Compounds	Total PAHs	Benzo(a)pyrene	Total PAHs	Benzo(a)pyrene
MF	806	16	12.09	0.24
MA	658	11	9.87	0.17

Based on the results obtained (in laboratory tests) for two mould sands with organic binders: furan resin (MF) and phenol-formaldehyde resin of resol type (MA), it can be stated that:

- gas emissions from both binders are high, which can negatively affect the quality of castings;
- his emission of gases begins immediately after pouring the liquid metal into the mould and lasts for about 200-250 s, reaching the maximum rate after about 100 s.
- both mould sands are characterized by high emission of BTEX (table 5) and PAHs (Table 6), with the MF releasing significantly larger amounts (about 20-25%) of gases from both groups,
- in gases from the BTEX group, benzene accounts for almost 95%.

5.1.3.4. Measurement of dust

Table 7 contains the results of measuring the amount of dust released during a test. These are average values from three tests (BTEX measurement, PAHs measurement and CO, CO_2, SO_2 measurement).

Table 7. Dust realized from moulding sands during tests.

Moulding sand code	Dust realized from moulding sands during tests / 1 kg of moulding sands			Average
	from PAHs test [g]	from BETX test [g]	from SO_2 test [g]	[g]
MF	0.09	0.04	0.04	0.06
MA	0.03	0.06	0.04	0.04

- MF releases larger amounts of dust (about 1/3) than MA mould sand.

5.2. MOULDING SANDS WITH INORGANIC BINDERS

5.2.1. Measurement of BTEX

The tables (Table 8a-8e) contain the results of BTEX measurements calculated per 1 kg of moulding sand and calculated per 1 kg of binder for inorganic binders

Table 8a. Code: MG

Type of moulding sand and code	Compound	Results		
		per sample µg	per 1 kg of moulding sand, mg	per 1 kg of binder mg
Code: MG Weight of sample. 129.521 g Content of binder 1.8 % (liquid SA 73)	Benzene	6 614	51.07	2 837
	Toluene	842	6.50	361
	Ethylbenzene	72	0.55	31
	m + p xylene	224	1.73	96
	o- xylene	39	0.30	17
	Total	7 792	60.16	3 342

Table 8b. Code: MC

Type of moulding sand and code	Compound	Results		
		per sample µg	per 1 kg of moulding sand,	per 1 kg of binder

			mg	mg
Code: MC Weight of sample. 146.081 g Content of binder 3.3 %, Cured at 180^{0}C	Benzene	2 393	16.38	496
	Toluene	724	4.95	150
	Ethylbenzene	71	0.49	15
	m + p xylene	222	1.52	46
	o- xylene	37	0.25	8
	Total	3 447	23.59	715

Table 8c. Code: MBA +MBS

Type of moulding sand and code	Compound	Results		
		per sample µg	per 1 kg of moulding sand, mg	per 1 kg of binder mg
Code: **MBA +MBS** Weight of sample. 136. 753 g Content of binder. 7 % Moisture : 2.7%	Benzene	21 172	154.82	2 218
	Toluene	1 151	8.41	120
	Ethylbenzene	71	0.52	7
	m + p xylene	249	1.82	26
	o- xylene	48	0.35	5
	Total	22 691	165.93	2 370

Table 8d. Code: MBB

Type of moulding sand and code	Compound	Results		
		per sample µg	per 1 kg of moulding sand, mg	per 1 kg of binder, mg
Code: MBB	Benzene	794	5.80	83
	Toluene	37	2.75	39
	Ethylbenzene	35	0.26	4

Weight of sample. 136. 753 g Content of binder. 7 %	m + p xylene	113	0.82	12
	o- xylene	18	0.13	2
	Total	1 336	9.77	140

Table 8e Code: MI

Type of moulding sand and code	Compound	Results		
		per sample, µg	per 1 kg moulding sand, mg	per 1 kg binder, mg
Code: MI Weight of sample. 148.678 g Content of binder 2.6% Cured at 150C	Benzene	2 148	14.44	556
	Toluene	776	5.22	201
	Ethylbenzene	77	0.51	20
	m + p xylene	292	1.96	76
	o- xylene	34	0.23	9
	Total	3 326	22.37	861

5.2.2. Measurement of PAHs

The tables (Table 9a-d) contain the results of PAHs measurements calculated per 1 kg of moulding sand and calculated per 1 kg of binder .

Table 9a. Code: MG

Type of moulding sand and code	Compound	Results		
		per sample, µg	per 1 kg of moulding sand, mg	per 1 kg of binder, mg
Code: MG	Naphtalene	18.85	0.15	8.19
	Acenaphtylene	14.64	0.11	6.36
	Acenaphtene	2.60	0.02	1.13
	Fluorene	13.77	0.11	5.98

Weight of sample 127.830 g Content of binder 1.8 %	Phenanthrene	28.70	0.22	12.47
	Anthracene	6.67	0.05	2.90
	Fluoranthene	54.63	0.43	23.74
	Pyrene	59.93	0.47	26.05
	Benz(a)anthracene	9.59	0.08	4.17
	Chrysene	17.91	0.14	7.78
	Benzo(b)fluoranthene	5.65	0.04	2.46
	Benzo(k)fluoranthene	2.73	0.02	1.19
	Benzo(a)pyrene	7.54	0.06	3.28
	Indeno[1.2.3-cd]pyrene	66.97	0.52	29.11
	Dibenz[a.h]anthracene	37.57	0.29	16.33
	Benzo[g.h.i]perylene	54.06	0.42	23.49
	Total	401.81	3.14	174.63

Table 9b. Code: MC

Type of moulding sand and code	Compound	Results		
		per sample, µg	per 1 kg of moulding sand, mg	per 1 kg of binder, mg
Code: MC Weight of sample 151.146 g Content of binder 3.3 %	Naphtalene	27.17	0.18	5.45
	Acenaphtylene	13.30	0.09	2.67
	Acenaphtene	2.89	0.02	0.58
	Fluorene	13.37	0.09	2.68
	Phenanthrene	24.09	0.16	4.83
	Anthracene	5.20	0.03	1.04
	Fluoranthene	45.09	0.30	9.04
	Pyrene	42.30	0.28	8.48
	Benz(a)anthracene	9.59	0.06	1.92
	Chrysene	14.10	0.09	2.83
	Benzo(b)fluoranthene	1.46	0.01	0.29
	Benzo(k)fluoranthene	0.01	0.00	0.00
	Benzo(a)pyrene	1.98	0.01	0.40
	Indeno[1.2.3-cd]pyrene	56.61	0.37	11.35
	Dibenz[a.h]anthracene	30.87	0.20	6.19
	Benzo[g.h.i]perylene	41.65	0.28	8.35
	Total	329.68	2.18	66.10

Table 9c. Code: MB

Type of moulding sand and code	Compound	Result		
		per sample, µg	per 1 kg of moulding sand, mg	per 1 kg of binder, mg
Code: MB Weight of sample 133.927 g Content of binder 7 %	Naphtalene	91.51	0.68	9.76
	Acenaphtylene	43.61	0.33	4.65
	Acenaphtene	3.37	0.03	0.36
	Fluorene	14.72	0.11	1.57
	Phenanthrene	38.17	0.29	4.07
	Anthracene	7.84	0.06	0.84
	Fluoranthene	145.32	1.09	15.50
	Pyrene	176.34	1.32	18.81
	Benz(a)anthracene	17.99	0.13	1.92
	Chrysene	23.33	0.17	2.49
	Benzo(b)fluoranthene	20.24	0.15	2.16
	Benzo(k)fluoranthene	10.99	0.08	1.17
	Benzo(a)pyrene	20.61	0.15	2.20
	Indeno[1.2.3-cd]pyrene	73.53	0.55	7.84
	Dibenz[a.h]anthracene	32.12	0.24	3.43
	Benzo[g.h.i]perylene	56.52	0.42	6.03
	Total	776.21	5.80	82.80

Table 9d. Code: MI

Type of moulding sand and code	Compound	Results		
		per sample, µg	per 1 kg of moulding sand, mg	per 1 kg of binder, mg
Code: MI Weight of sample 145.948 g Content of binder 2.6 %	Naphtalene	5.86	0.04	1.54
	Acenaphtylene	25.02	0.17	6.59
	Acenaphtene	2.81	0.02	0.74
	Fluorene	13.55	0.09	3.57
	Phenanthrene	26.44	0.18	6.97
	Anthracene	4.22	0.03	1.11
	Fluoranthene	44.35	0.30	11.69
	Pyrene	40.38	0.28	10.64
	Benzo(a)anthracene	5.72	0.04	1.51
	Chrysene	13.71	0.09	3.61
	Benzo(b)fluoranthene	1.97	0.01	0.52
	Benzo(k)fluoranthene	0.41	0.00	0.11
	Benzo(a)pyrene	2.28	0.02	0.60
	Indeno[1.2.3-cd]pyrene	47.04	0.32	12.40
	Dibenzo[a.h]anthracene	29.03	0.20	7.65
	Benzo[g.h.i]perylene	27.13	0.19	7.15
	Total	289.92	1.99	76.40

5.2.3. MEASUREMENTS VOLUME OF GASES AND THEIR RELEASE RATE IN TIME

5.2.3.1. Measurements volume of gases BTEX and PAHs

Table 10 presents the total volume of gas emitted during BTEX and PAHs tests and their average value.

Table 10. Contains the results of volume measurements of gases release during tests.

Moulding sand code	Realized gases from moulding sands during tests / 1 kg of moulding sands		
	from BTEX test [dm^3]	from PAHs test [dm^3]	Average, [dm^3]
MG	13.95	13.56	13.76
MC	12.73	10.11	11.42
MB	27.62	24.59	26.10
MI	8.62	9.14	8.88

Dependence of the total volume of emitted gases and calculated per 1 gram of binder in time are presented in Fig. 11 a, b (MG –PAH); Fig. 12 a, b (MG – BTEX); Fig. 13 a, b (MB-PAH), Fig 14 a, b (MB-BTEX)), Fig. 15 a, b (MC-PAH), Fig.16 a, b (MC-BTEX), Fig. 17 a,b (MI-PAH) and Fig. 18 a, b (MI-BTEX) and their release rate in time.

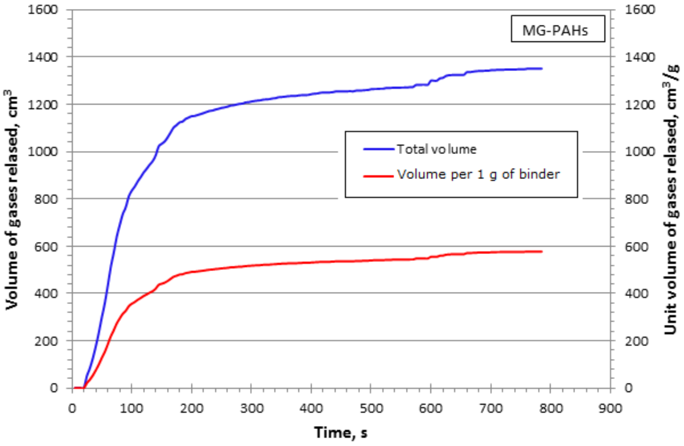


Figure 11a. Emissivity of gases in time, from the investigated moulding sands MG during PAHs measurements: blue line – total volume from sample, red line – volume calculated per 1 g of binder.

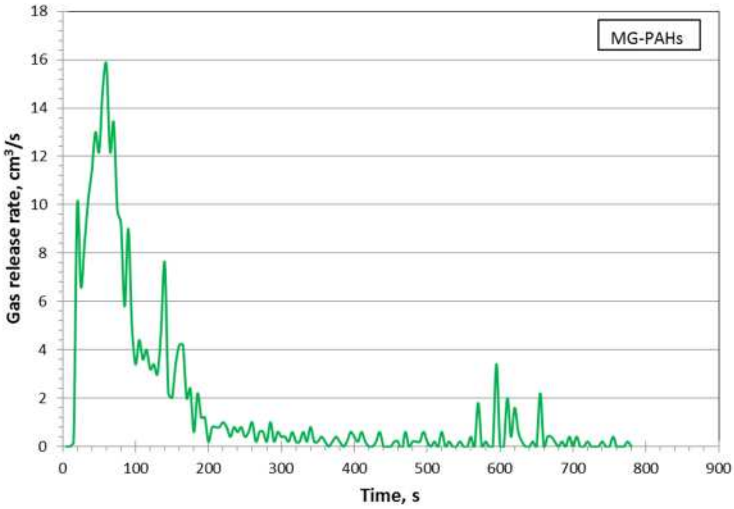


Figure 11b. Gas release rate in time, from the investigated moulding sands MG during PAHs measurements.

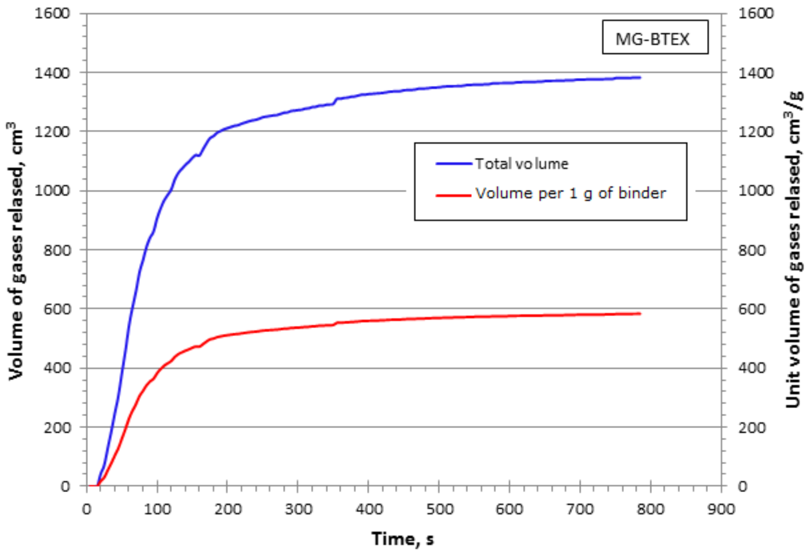


Figure 12a. Emissivity of gases in time, from the investigated moulding sands MG during BTEX measurements: blue line – total volume from sample, red line – volume calculated per 1 g of binder.

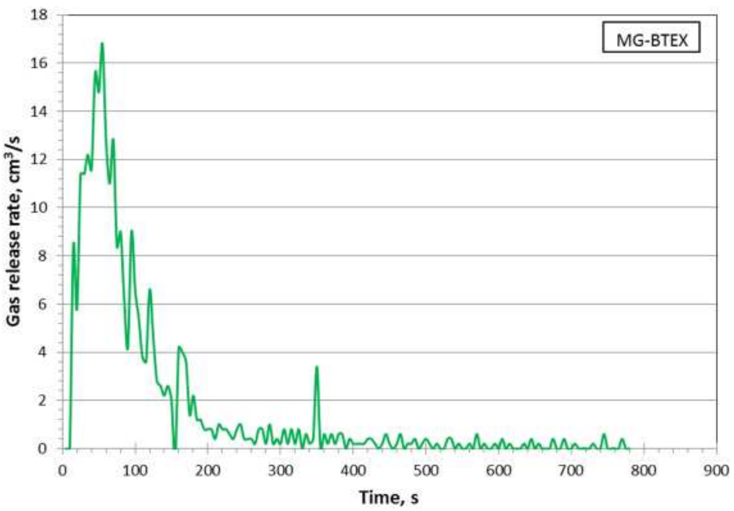


Figure 12b. Gas release rate in time, from the investigated moulding sands MG during BTEX measurements.

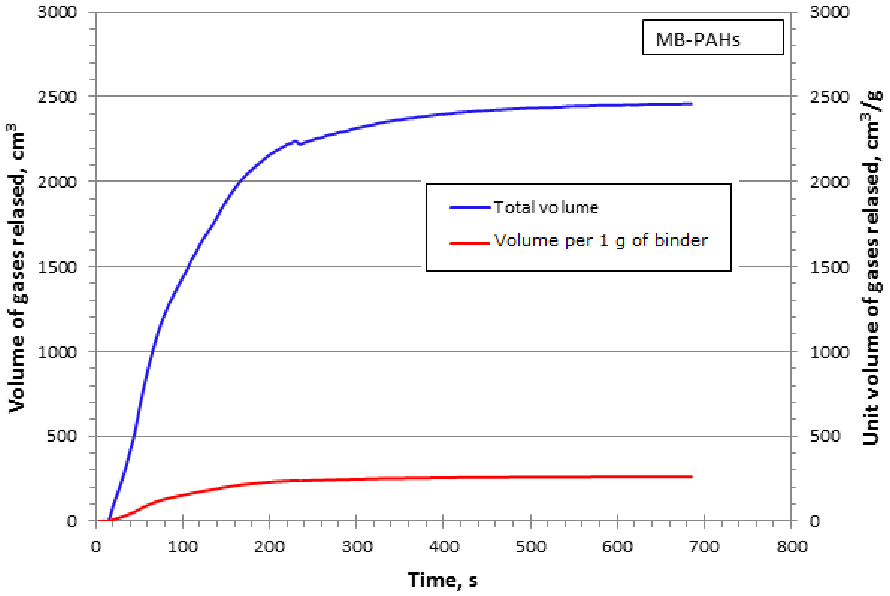


Figure 13a. Emissivity of gases in time, from the investigated moulding sands MB during PAHs measurements: blue line – total volume from sample, red line – volume calculated per 1 g of binder.

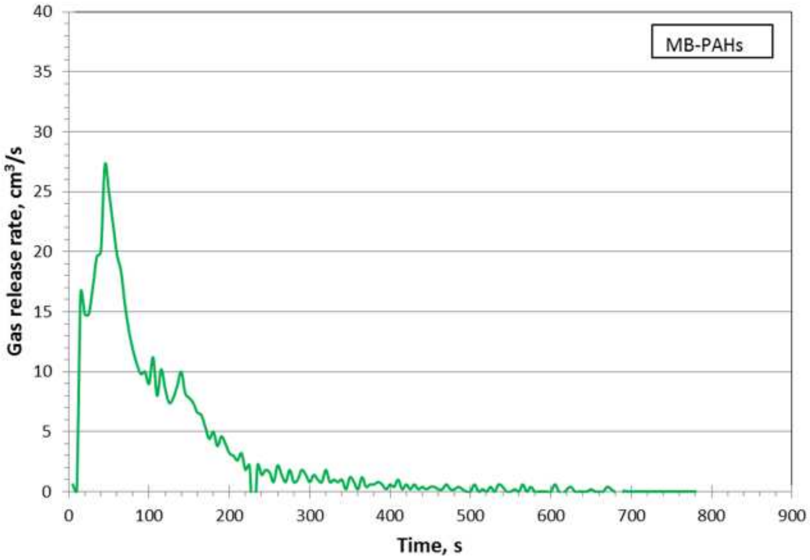


Figure 13b. Gas release rate in time, from the investigated moulding sands MB during PAHs measurements.

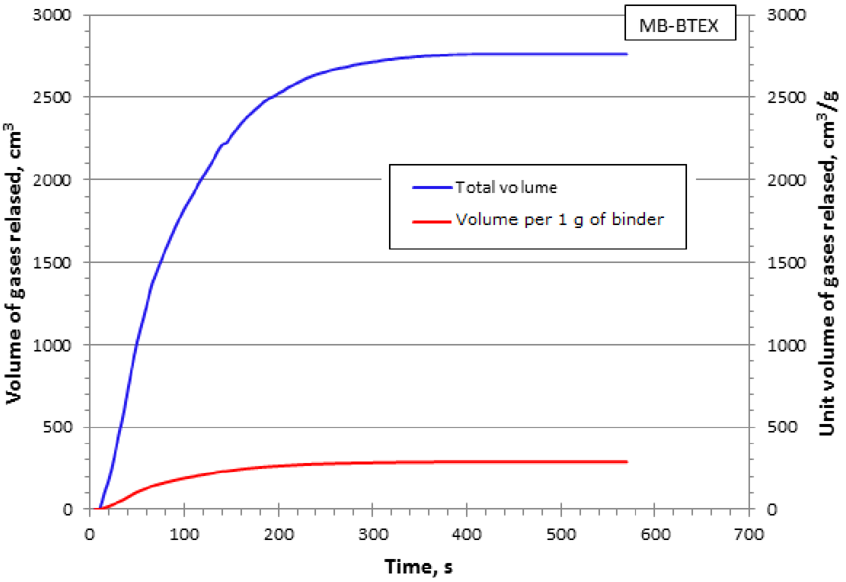


Figure 14a. Emissivity of gases in time, from the investigated moulding sands MB during BTEX measurements: blue line – total volume from sample, red line – volume calculated per 1 g of binder.

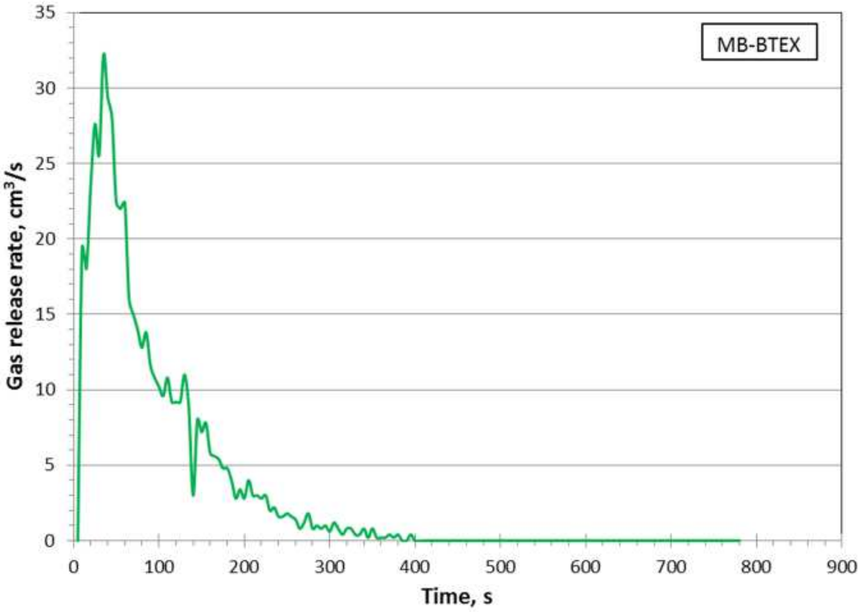


Figure 14b. Gas release rate in time, from the investigated moulding sands MB during BTEX measurements.

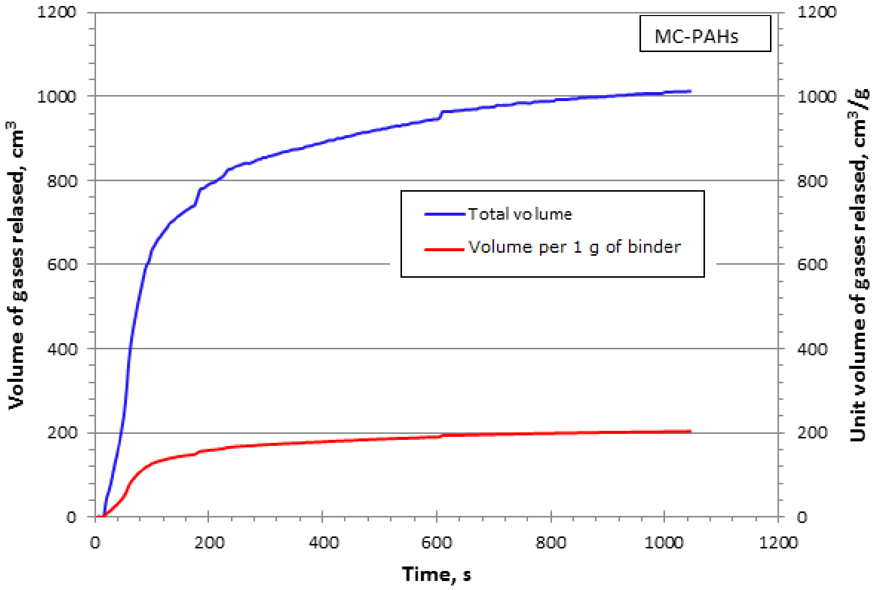


Figure 15a. Emissivity of gases in time, from the investigated moulding sands MC during PAHs measurements: blue line – total volume from sample, red line – volume calculated per 1 g of binder.

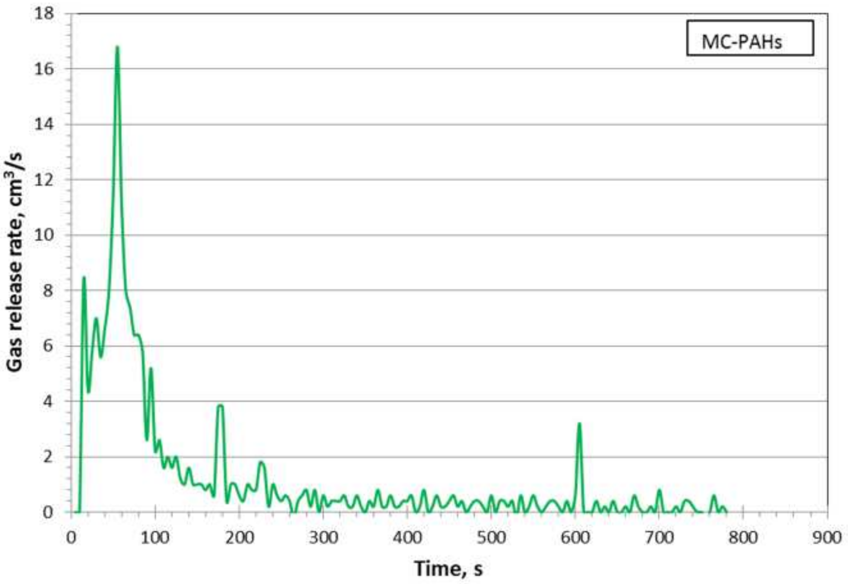


Figure 15b. Gas release rate in time, from the investigated moulding sands MC during PAHs measurements.

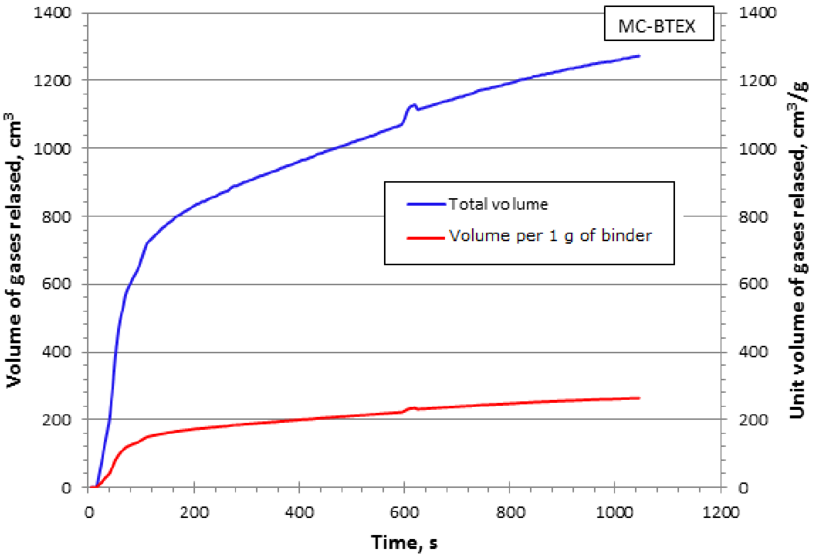


Figure 16a. Emissivity of gases in time, from the investigated moulding sands MC during BTEX measurements: blue line – total volume from sample, red line – volume calculated per 1 g of binder.

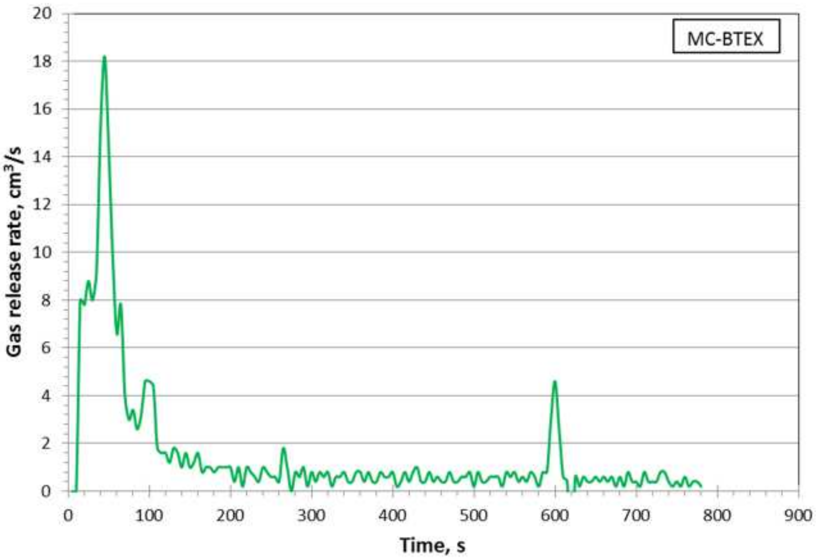


Figure 16b. Gas release rate in time, from the investigated moulding sands MC during BTEX measurements.

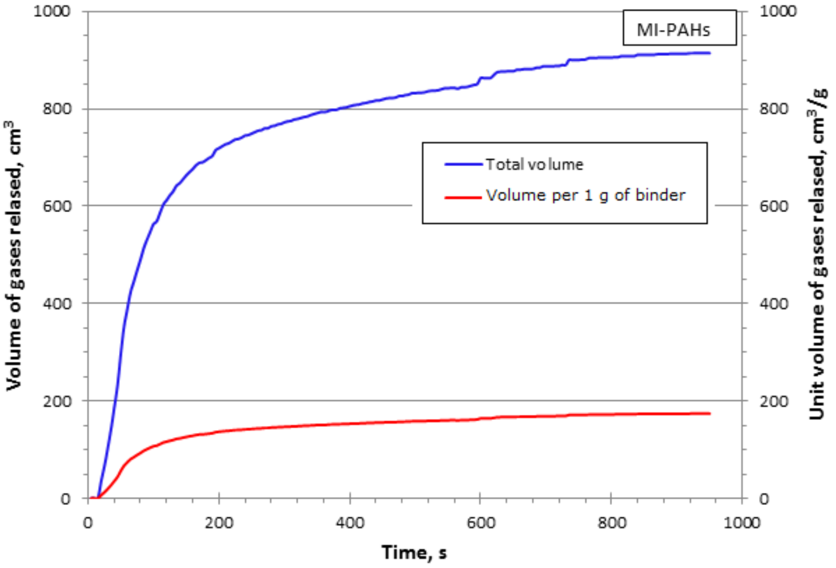


Figure 17a. Emissivity of gases in time, from the investigated moulding sands MI during PAHs measurements: blue line – total volume from sample, red line – volume calculated per 1 g of binder.

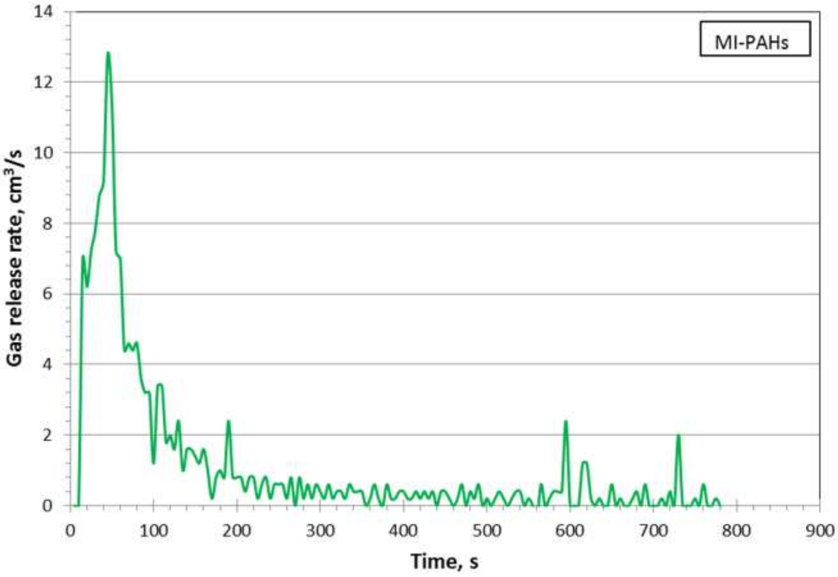


Figure 17b. Gas release rate in time, from the investigated moulding sands MI during PAHs measurements.

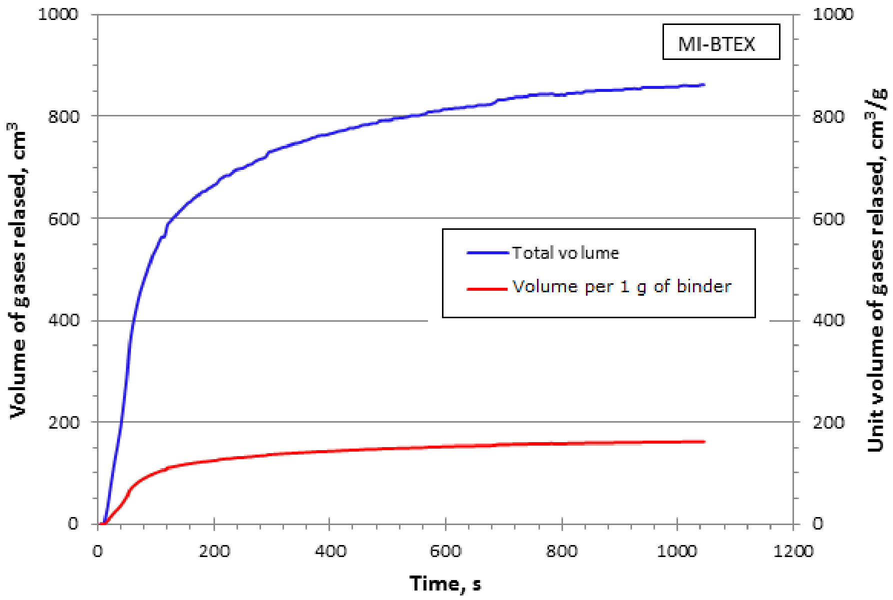


Figure 18a. Emissivity of gases in time, from the investigated moulding sands MI during BTEX measurements: blue line – total volume from sample, red line – volume calculated per 1 g of binder.

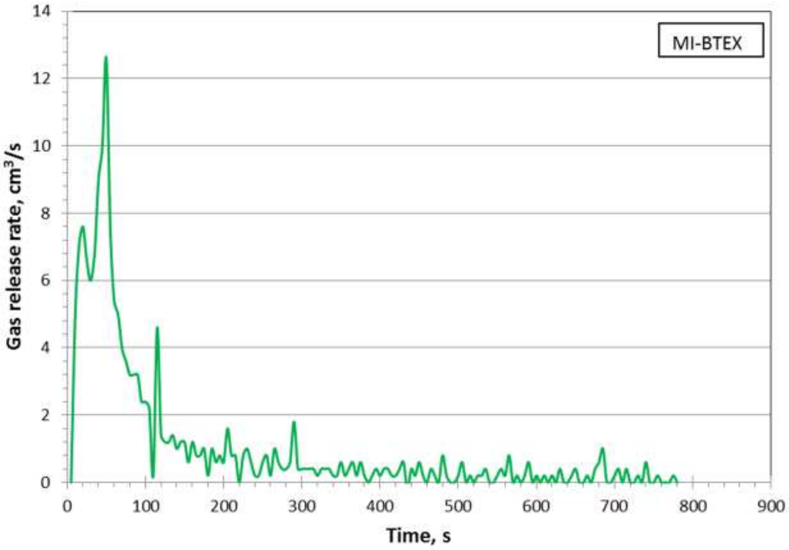


Figure 18b. Gas release rate in time, from the investigated moulding sands MI during BTEX measurements.

5.2.3.2. Measurements of gas emissions: CO, CO_2, SO_2 and NO_X

However, the figures 19 a –s show graphically the volume of emissions of these gases for individual moulding sands and gases.

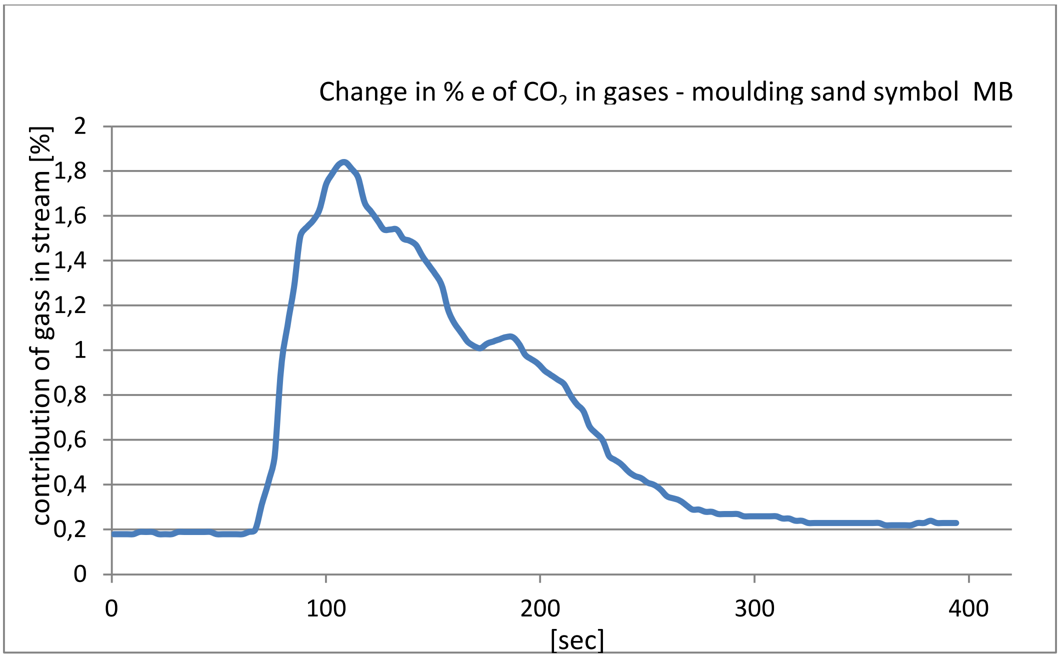
The table 11 below summarizes the results of gas emission: CO, CO_2, SO_2 and NO_X during laboratory tests.

Table 11. Emission of SO_2, CO, CO_2 and NO_x from moulding sands

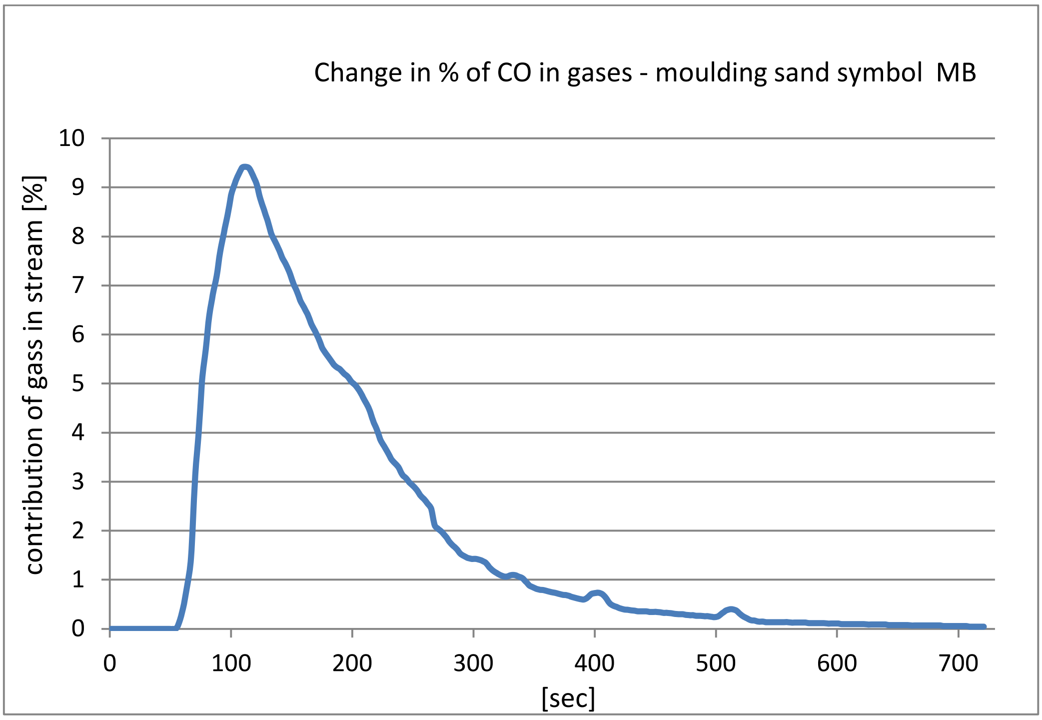
Moulding sand symbol	Amount of: SO_2, NO_x, CO, CO_2 emitted in experiment[1] and calculated per kilo of moulding sand[2]							
code	SO_2 [cm^3][1]	SO_2 [cm^3/kg][2]	NO_x [cm^3][1]	NO_x [cm^3/kg][2]	CO [cm^3][1]	CO [cm^3/kg][2]	CO_2 [cm^3][1]	CO_2 [cm^3/kg][2]
MG	0.11	0.82	-	-	53	394	7.2	53.6
MC	0.2	1.3	-	-	41	273	3.9	25.9
MB	1.9	13.7	-	-	134	965	10.1	72.7
MI	0.3	2.0	-	-	43	282	3.9	25.6

Moulding sand code MB

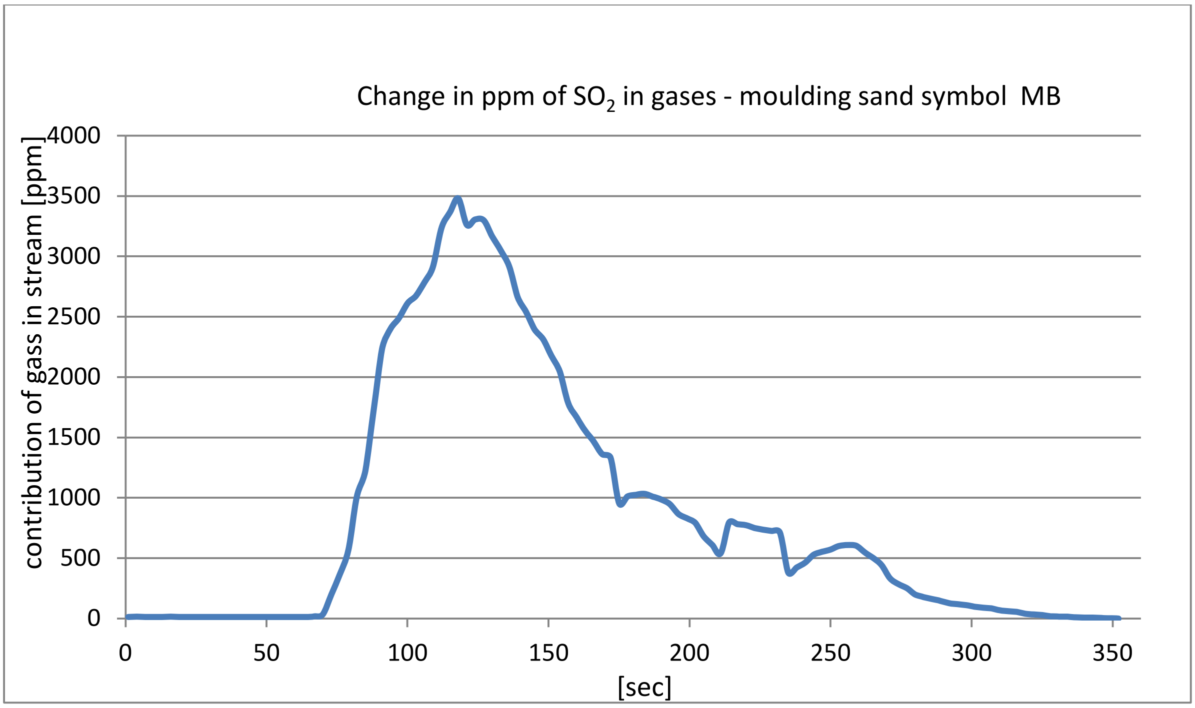
19a)



19b)

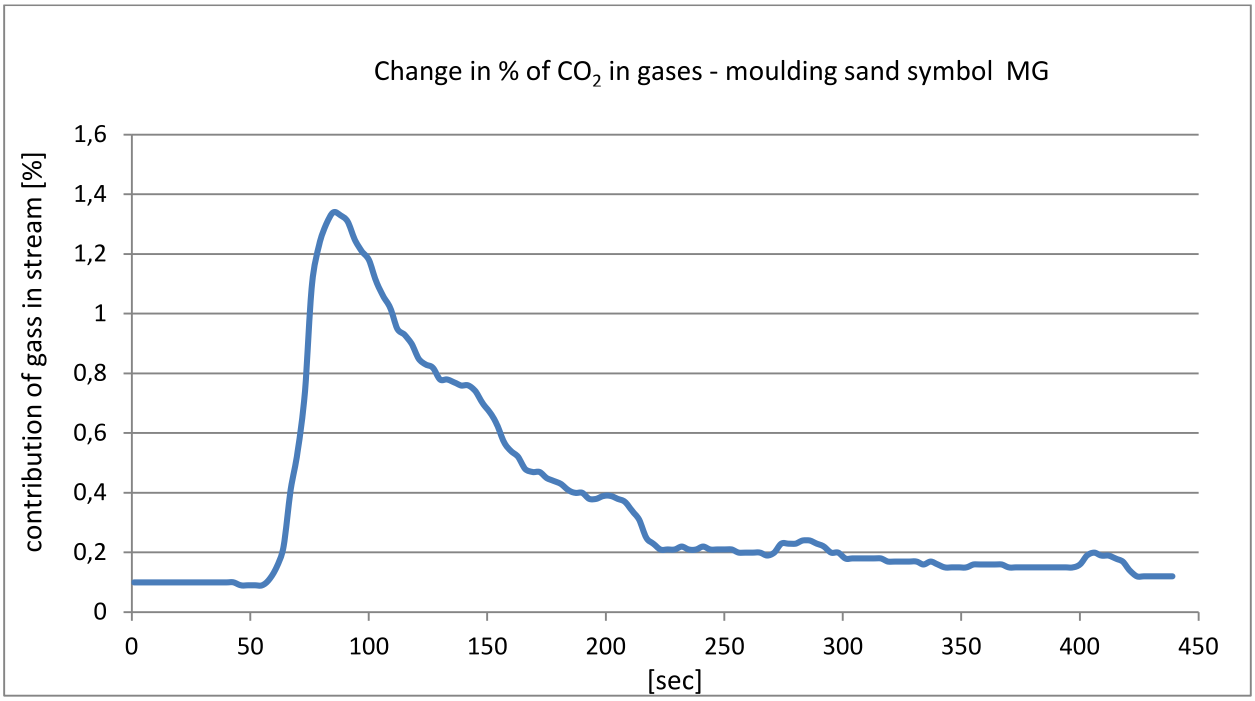


19c)


Change in ppm of SO_2 in gases - moulding sand symbol MB
contribution of gass in stream [ppm]
4000
3500
3000
2500
2000
1500
1000
500
0
0
50
100
150
200
250
300
350
[sec]

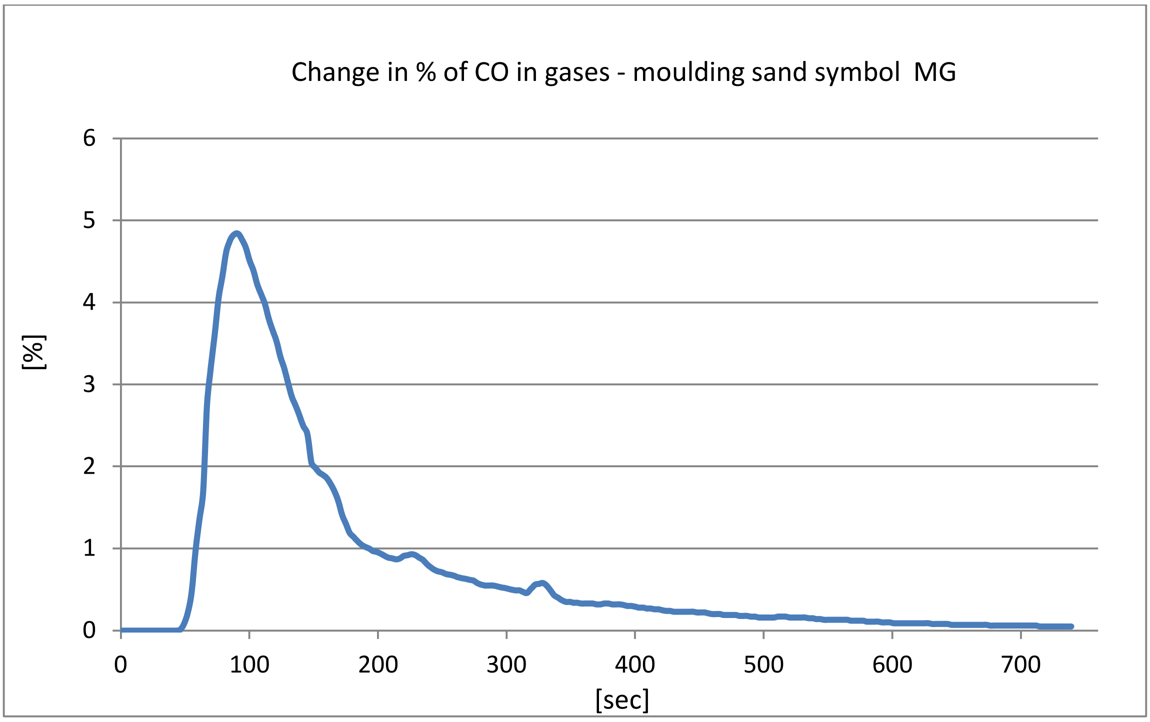
Mouldig sand code MG

20a)



Moulding sand code MG

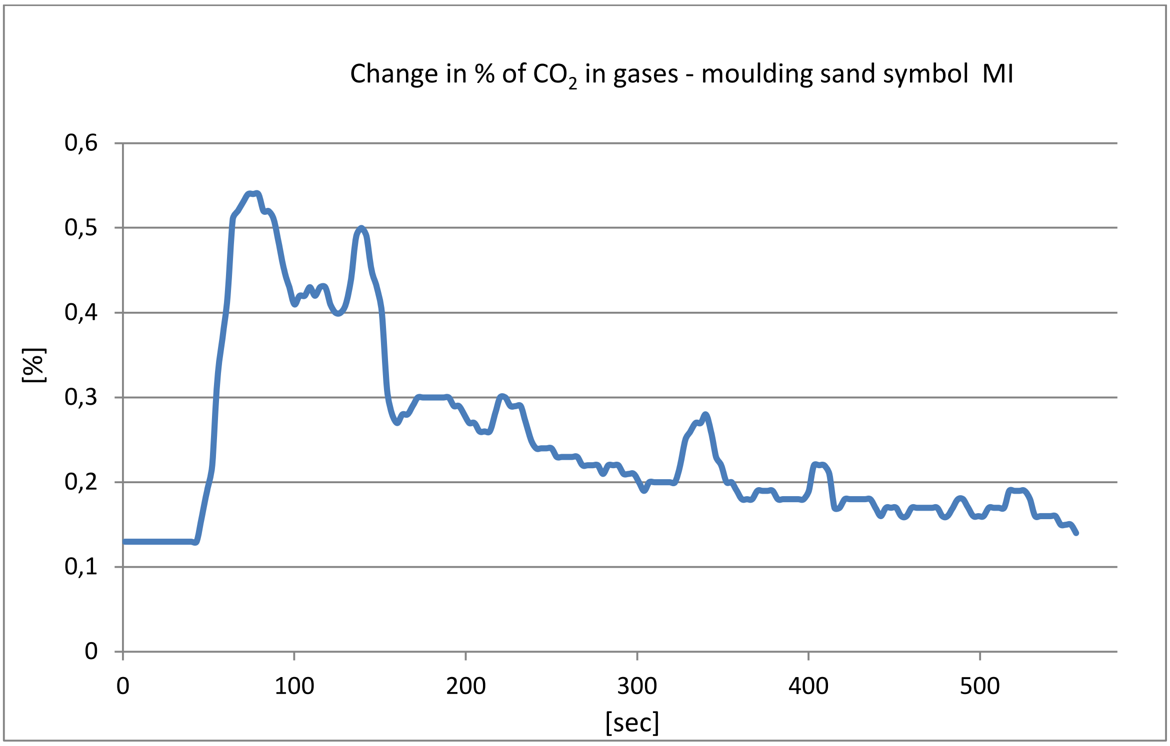
20b)



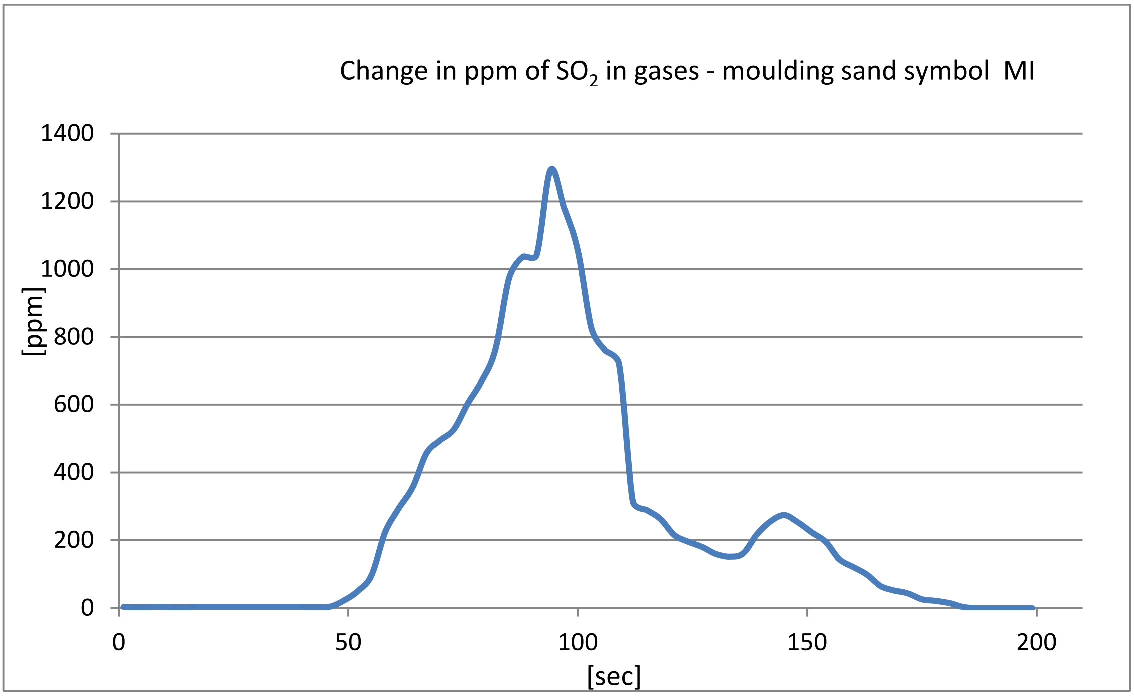
holtzer@agh.edu.pl

Moulding sand code MI

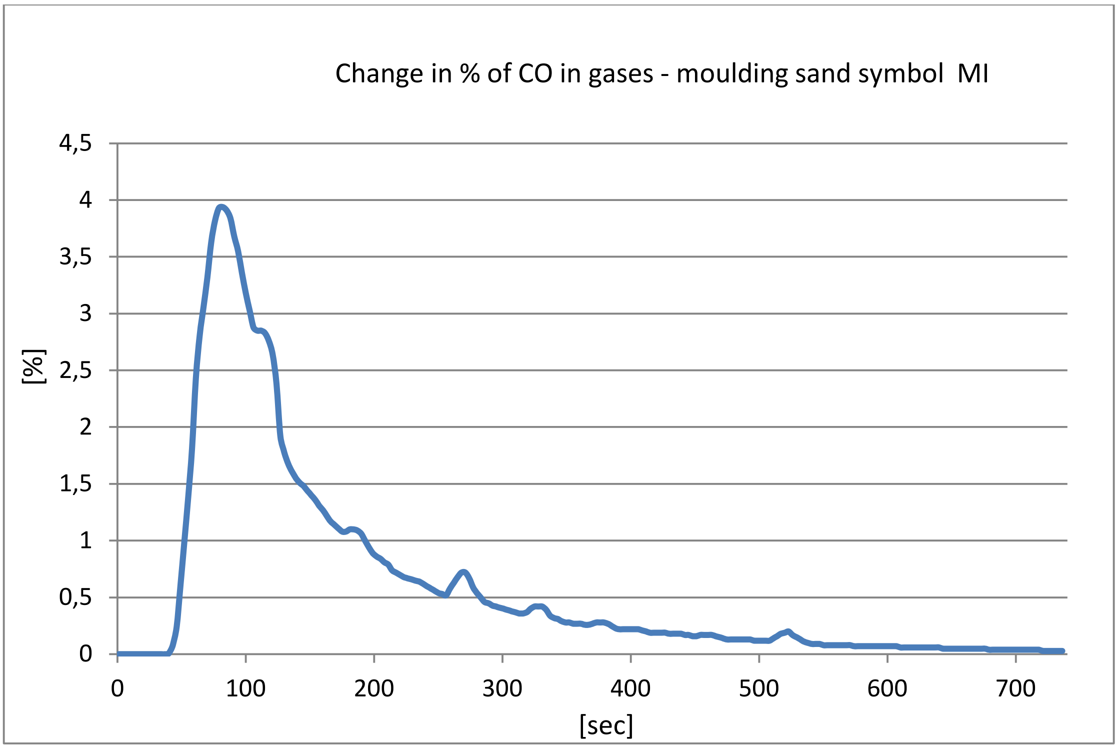
21a)



21b)

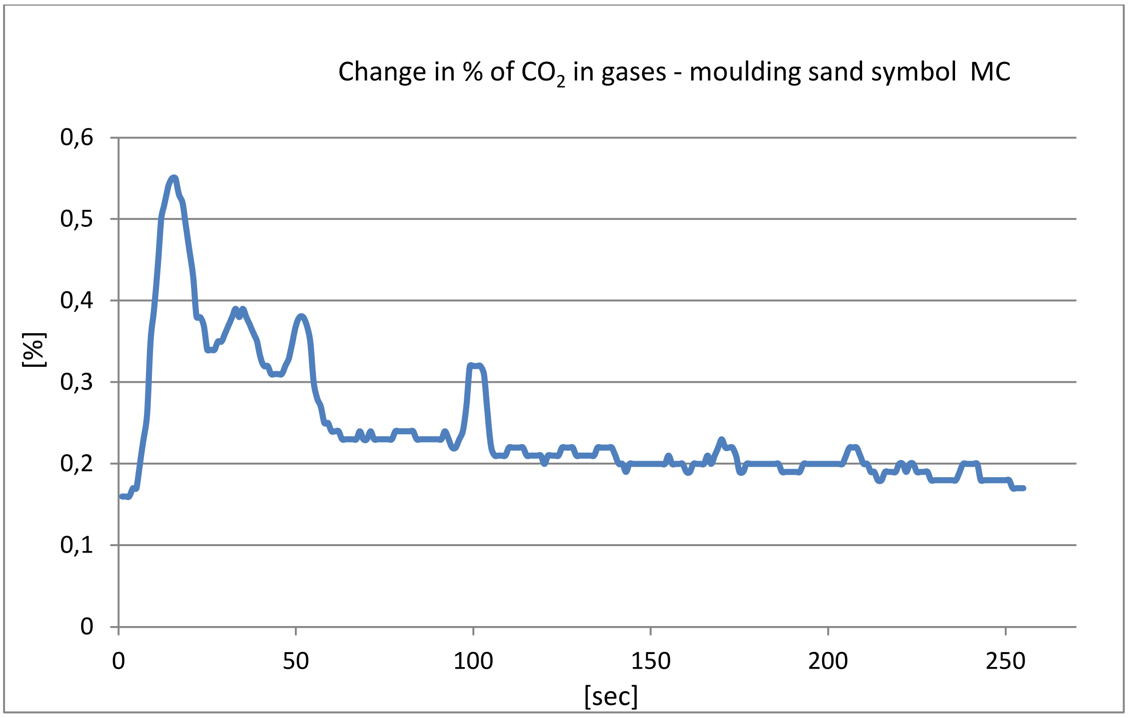


21c)

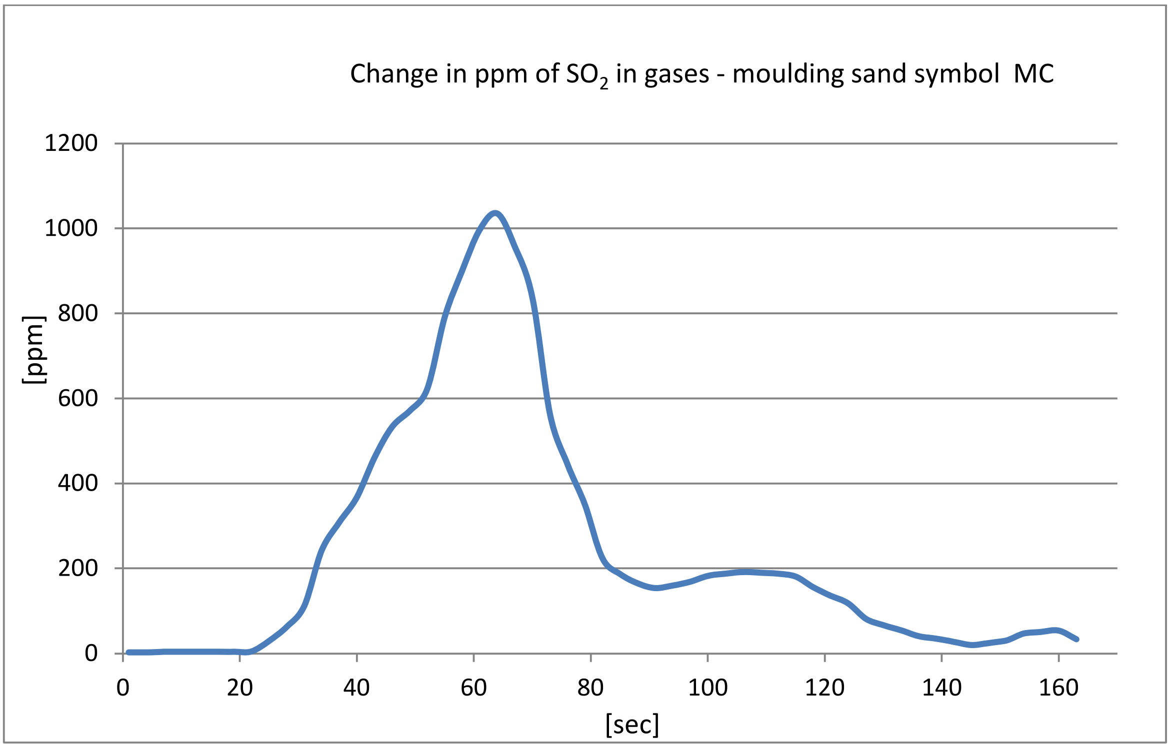


Moulding sand code MC

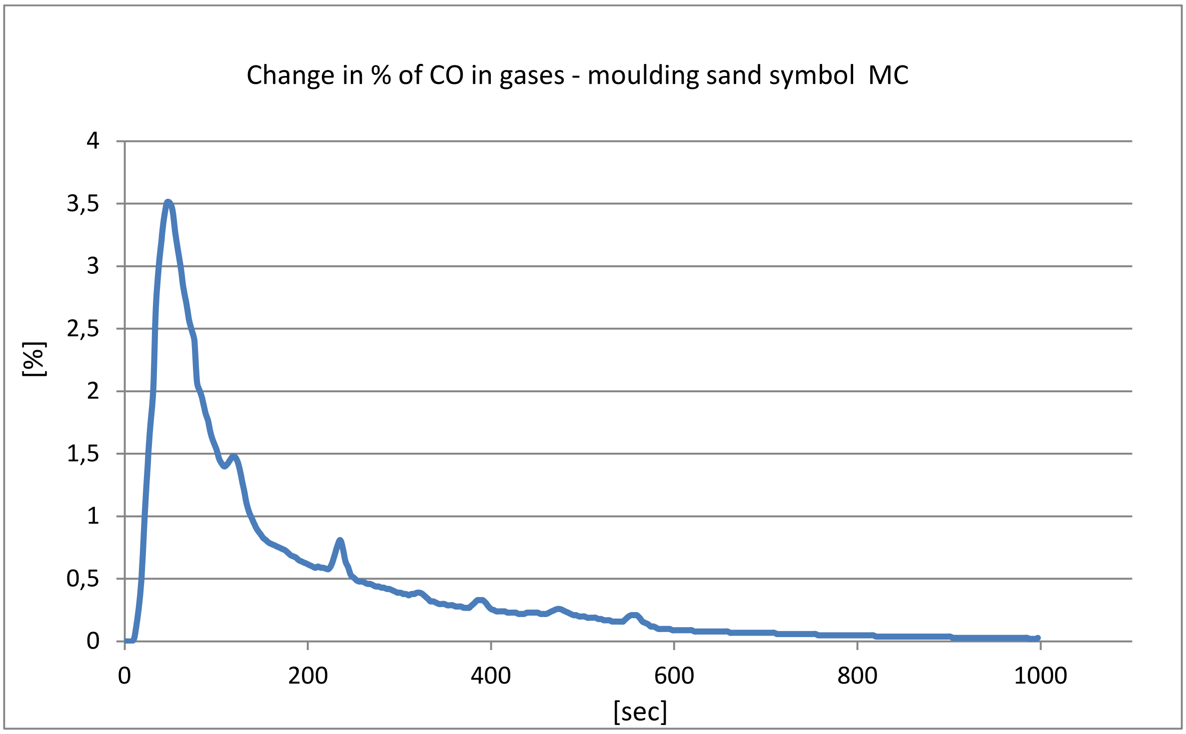
22a)



22b)


Change in ppm of SO_2 in gases - moulding sand symbol MC
[ppm]
1200
1000
800
600
400
200
0
0
20
40
60
80
100
120
140
160
[sec]

22c)


Change in % of CO in gases - moulding sand symbol MC
[%]
4
3,5
3
2,5
2
1,5
1
0,5
0
0
200
400
600
800
1000
[sec]

5.2.3.2. Conclusions for inorganic binders

Table 12 contains of BTEX group emissions, and Table 13 emissions of PAHs compounds (calculation per 1 kg of binder and 1 kg of moulding sand) moulding sand with inorganic binders**.**

Table 12. Total emission BTEX and benzene calculated per 1 kg of binder and 1 kg of moulding sand with inorganic binders

CODE	Per 1 kg of binder, mg		Per 1 kg of moulding sand, mg	
Compounds	Total BTEX	Benzene	Total BTEX	Benzene
MG	3342	2 837	60	51
MC	715	496	24	16
MB	2 510	2 301	176	161
MI	860	556	22	14

Table 13. Total emission PAHs and benzo(a)pyrene calculated per 1 kg of binder and 1 kg of moulding sand

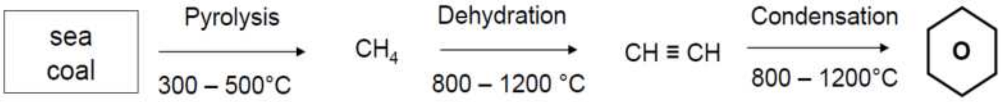
CODE	Per 1 kg of binder, mg		Per 1 kg of moulding sand, mg	
Compounds	Total PAHs	Benzo(a)pyrene	Total PAHs	Benzo(a)pyrene
MG	175	3.28	3.14	0.06
MC	66	0.39	2.18	0.01
MB	83	2.19	5.80	0.15
MI	76	0.60	2	0.02

Laboratory tests of inorganic binders (MC, MG, MI), including bentonite (MB) materials, under laboratory conditions showed that:

- Mould sands with inorganic binders under the influence of high temperature (Table 12 and Table 13) release some amounts of gases, but much less than one with organic binders.

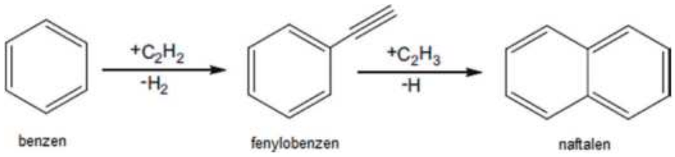
- Exception is the bentonite – based greensand system , which also contain carbon – based lustrous carbon formers (LCF) contribute to the BTEX emissions (coal dust, brown coal dust, synthetic resins, graphite).
- All mould sands with inorganic binders (silicate structure) emitted small amounts of BTEX compounds. The least of these types of compounds generate MC and MI and the most of the MG in which liquid organic hardener was used. MC and MI mould sands were heat cured. The main component of released compounds from the BTEX group is benzene.
- There is also a small emission of compounds from PAHs group in the case of sands with silicate binders.
- For inorganic binders, the maximum rate of gas evolution occurs at a lower temperature (<100°C) than for organic binders.
- For sands with bentonite high SO_2 emission is characteristic, which is the effect of using additives containing coal dust.

During pouring of liquid iron, the lustrous carbon formers (LCF) in the moulding sand system are pyrolyzed and form low-boiling aromatics like benzene, toluene, xylene and ethyl benzene (BTXE. At the same time, polycyclic hydrocarbons (PAH) which have with a high boiling point are formed. Therefore, BTEX aromatics are a topic of gaseous emissions , while PAHs are adsorbed by the moulding sand systems. These PAHs can create problems during waste disposal.



Formation of benzene from sea coal dust (pyrolysis, dehydration and condensation)

The formed benzene, is then forming naphthalene, which is subjected to successive reactions forming polycyclic aromatic hydrocarbons of a high boiling points.



Mechanism of naphthalene formation from benzene.

5.2.3.4. Measurement of dust

Table 14 contains the results of measuring the amount of dust released during a test. These are average values from three tests (BTEX measurement, PAHs measurement and CO, CO_2, SO_2 measurement).

Table 14. Dust realized from moulding sands during tests.

Moulding sand code	Dust realized from moulding sands during tests / 1 kg of moulding sands			Average
	from PAHs test [g]	from BETX test [g]	from SO_2 test [g]	[g]
MG	0.03	0.02	0.01	0.02
MC	0.02	0.02	0.02	0.02
MB	0.40	0.11	0.06	019
MI	0.03	0.01	0.01	0.02

- Among all the tested moulding sand with inorganic binders, the largest dust emissions have the green sands, which is caused by the addition of bentonite mix in the form of dust.

- Other sands with inorganic binders show a similar level of dust production.

5.3. GENERAL CONCLUSIONS

The Tables 15 and 16 presented emission BTEX and PAHs respectively from moulding sands with inorganic and organic binders.

Table 15. Total emission BTEX and benzene calculated per 1 kg of binder and 1 kg of moulding sand

CODE	Per 1 kg of binder, mg		Per 1 kg of moulding sand, mg	
Compounds	Total BTEX	Benzene	Total BTEX	Benzene
MF	43 852	40 158	658	602
MA	32 994	30 911	495	464
MG	3 342	2 837	60	51
MC	715	496	24	16
MB	2 510	2 301	176	161
MI	860	556	22	14

Table 16. Total emission PAHs and benzo(a)pyrene calculated per 1 kg of binder and 1 kg of moulding sand

CODE	Per 1 kg of binder, mg		Per 1 kg of moulding sand, mg	
Compounds	Total PAHs	Benzo(a)pyrene	Total PAHs	Benzo(a)pyrene
MF	806	16	12.09	0.24
MA	658	11	9.87	0.17
MG	175	3	3.14	0.06
MC	66	0.39	2.18	0.01
MB	83	2.19	5.80	0.15
MI	76	0.6	2.0	0.02

Comparative studies of moulding sands with organic and inorganic binders exposed at high temperature (1350 ^{o}C) carried out on a laboratory scale have shown that:

- moulding sand with organic binder generated 2 to 3 times more gas volume than other mouding sands,
- moulding sands with organic binder (MA and MF) showed significantly higher emission of compounds from the PAHs and BTEX group than moulding sand with inorganic binder (MI, MC, MG and MB); the difference was even 10 times;
- in the BTEX group, the main component emitted was carcinogenic benzene (up to 95%),

- in the PAHs group, the main component emitted was naphthalene, in addition, small amount of carcinogenic benzo (a) pyrene was also identified in these gases,

- the moulding sands with inorganic compounds, hardened with temperature (MI, MC), showed lower emissions of BTEX, whereas for moulding sands with inorganic binder, but hardened by organic hardener (MG),
- a particularly low emission from the group BTEX and PAHs were characterized by moulding sand with water glass (MI, MC) cured by hot air,
- green sand (MB) showed relatively low emission of compounds from the PAHs and BTEX groups because in the bentonite mixture the coal dust was partly replaced by more environmentally friendly components,
- in the case of moulding sands with organic binder (MF and MA) and green sand (MB), SO_2 was found in the tested gases. The presence of SO_2 in the gases from the moulding sand (MF) is the result of decomposition of benzenesulfonic acid which is used as a solvent, while the presence of SO_2 in gases from the MB moulding sand is associated with the sulfur content of carbon-containing additives introduced into bentonite,
- NOx oxides were found in gases released from MF and MA moulding sand, which are probably the result of the decomposition of compounds containing nitrogen e.g. urea, which is introduced to resin by manufacturers in order to extend resin life.

Due to the grate fraction of green sand in the production of cast iron, work is underway to develop environmentally friendly seacoal replacements.

As far as green sands are environmentally friendly, an introduction to them of sea coal dusts as a lustrous carbon source, makes these sands very harmful for employees and for the environment. The reason of this effect is mainly the harmfulness of products of coal dusts thermal decomposition (emission of PAHs and substances from the BTEX group). The highest concentrations of HAP were found for benzene, toluene, xylenes, ethylbenzene and naphthalene, which - in approximation - constituted 87 % of all emitted substances. Another substances formed when moulds with bentonite are poured with moulten metal are: phenol, dimethylphenol, trimethylbenzene, propylbenzene, methylnaphthalene, dimethylnaphthalene, ethyltoluene and cresol.

The high harmfulness of furan moulding sand, stricter environmental regulations and an increase in the prices of fufuryl alcohol (China's monopoly) mobilize binder producers to develop binders for more environmentally friendly moulding sands, and it seems that Alphaset technology may be one such alternative which to some extent confirmed by the above results.

5.3.1. MEASUREMENTS VOLUME OF GASES

Table 17 presents the total volume of gas emitted during BTEX and PAHs tests and their average value.

Table 17. Contains the results of volume measurements of gases release during tests.

Moulding sand code	Realized gases from moulding sands during tests / 1 kg of moulding sands		
	from BTEX test [dm^3]	from PAHs test [dm^3]	Average, [dm^3]
MF	19.31	20.14	19.73
MA	26.14	23.80	24.97
MG	13.95	13.56	13.76
MC	12.73	10.11	11.42
MB	27.62	24.59	26.10
MI	8.62	9.14	8.88

5.3.2. MEASUREMENT OF DUST

Table 18 contains the results of measuring the amount of dust released during a test. These are average values from three tests (BTEX measurement, PAHs measurement and CO, CO_2, SO_2 measurement).

Table 18. Dust realized from moulding sands during tests.

Moulding sand code	Dust realized from moulding sands during tests / 1 kg of moulding sands			Average
	from PAHs test [g]	from BETX test [g]	from SO_2 test [g]	[g]
MF	0.09	0.04	0.04	0.06
MA	0.03	0.06	0.04	0.04
MG	0.03	0.02	0.01	0.02
MC	0.02	0.02	0.02	0.02
MB	0.40	0.11	0.06	019
MI	0.03	0.01	0.01	0.02

5.3.3. MEASUREMENTS OF GAS EMISSIONS: CO, CO_2, SO_2 AND NO_X

Table 19. Emission of SO_2, CO, CO_2 and NO_x from moulding sands

Moulding sand symbol	Amount of: SO_2, NO_x, CO, CO_2 emitted in experiment[1] and calculated per kilo of moulding sand[2]							
code	SO_2 [cm^3][1]	SO_2 [cm^3/kg][2]	NO_x [cm^3][1]	NO_x [cm^3/kg][2]	CO [cm^3][1]	CO [cm^3/kg][2]	CO_2 [cm^3][1]	CO_2 [cm^3/kg][2]
MF	1.4	10.5	0.011	0.08	98	738	6.7	50.4
MA	1.4	10.3	0.007	0.05	119	872	5.4	39.6
MG	0.11	0.82	-	-	53	394	7.2	53.6
MC	0.2	1.3	-	-	41	273	3.9	25.9
MB	1.9	13.7	-	-	134	965	10.1	72.7
MI	0.3	2.0	-	-	43	282	3.9	25.6

FACULTY OF FOUNDRY ENGINEERING

ACADEMIC CENTRE FOR MATERIALS AND NANOTECHNOLOGY AGH

Green Foundry LIFE
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LIFE17 ENV/FI/000173

THERMAL ANALYSIS OF FOUNDRY BINDERS USING IN METAL CASTING.

Prepared by:
Dr Angelika Kmita

INTRODUCTION

TG/DTG/DSC MEASUREMENTS

Thermal analysis refers to any technique for the study of materials which involves thermal control. Measurements are usually made with increasing temperature, but isothermal measurements or measurements made with decreasing temperatures are also possible [1-6]. Table 1 shows a selection of thermal analysis techniques, illustrating the breadth of the field [1]. In fact, any measuring technique can be made into a thermal analysis technique by adding thermal control. Simultaneous use of multiple techniques increases the power of thermal analysis, and modern instrumentation has permitted extensive growth of application. The basic theories of thermal analysis (equilibrium thermodynamics, irreversible thermodynamics and kinetics) are well developed, but have to date not been applied to actual experiments to the fullest extent possible [1]. Thermal analysis refers to a variety of techniques in which a property of a sample is continuously measured as the sample is programmed through a predetermined temperature profile. Among the most common techniques are thermal gravimetric analysis (TG) and differential scanning calorimetry (DSC). In TG the mass loss versus increasing temperature of the sample is recorded. The basic instrumental requirements are simple: a precision balance, a programmable furnace, and a recorder. Modern instruments, however, tend to be automated and include software for data reduction. In addition, provisions are made for surrounding the sample with an air, nitrogen, or an oxygen atmosphere. In a DSC experiment the difference in energy input to a sample and a reference material is measured while the sample and reference are subjected to a controlled temperature program. DSC requires two cells equipped with thermocouples in addition to a programmable furnace, recorder, and gas controller [1]. Automation is even more extensive than in TG due to the more complicated nature of the instrumentation and calculations. A thermal analysis curve is interpreted by relating the measured property versus temperature data to chemical and physical events occurring in the sample. It is frequently a qualitative or comparative technique.

In TA the mass loss can be due to such events as the volatilization of liquids and the decomposition and evolution of gases from solids. The onset of volatilization is proportional to the boiling point of the liquid. The residue remaining at high temperature represents the percent ash content of the sample [1].

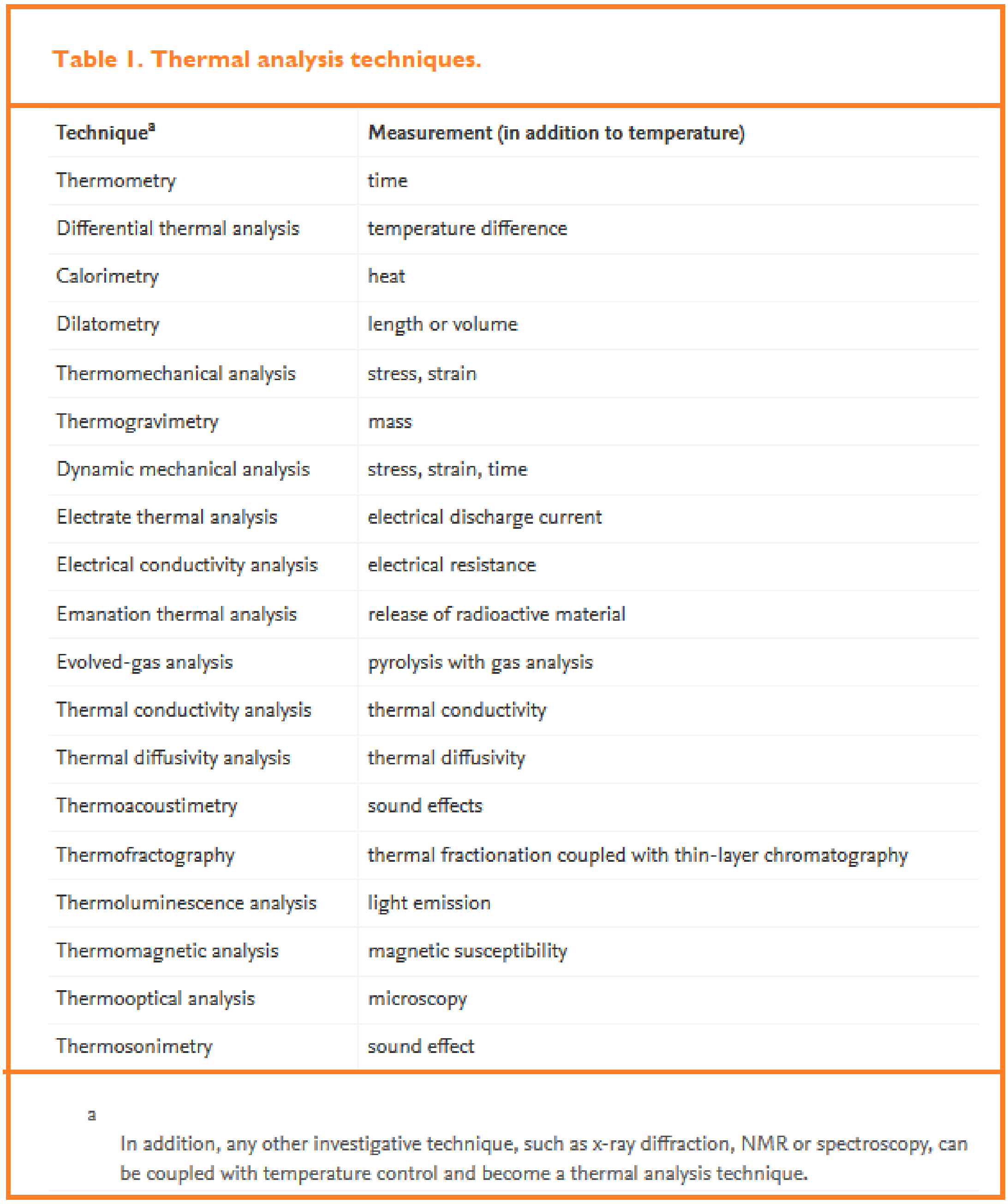

Table 1. Thermal analysis techniques.

Technique[a]	Measurement (in addition to temperature)
Thermometry	time
Differential thermal analysis	temperature difference
Calorimetry	heat
Dilatometry	length or volume
Thermomechanical analysis	stress, strain
Thermogravimetry	mass
Dynamic mechanical analysis	stress, strain, time
Electrate thermal analysis	electrical discharge current
Electrical conductivity analysis	electrical resistance
Emanation thermal analysis	release of radioactive material
Evolved-gas analysis	pyrolysis with gas analysis
Thermal conductivity analysis	thermal conductivity
Thermal diffusivity analysis	thermal diffusivity
Thermoacoustimetry	sound effects
Thermofractography	thermal fractionation coupled with thin-layer chromatography
Thermoluminescence analysis	light emission
Thermomagnetic analysis	magnetic susceptibility
Thermooptical analysis	microscopy
Thermosonimetry	sound effect

[a] In addition, any other investigative technique, such as x-ray diffraction, NMR or spectroscopy, can be coupled with temperature control and become a thermal analysis technique.

Thermogravimetry (TG), **derivative thermogravimetry** (DTG) and **differential scanning calorimetry** (DSC), were found to be suitable instrumental techniques for the study of foundry binders they need small amounts of sample and provide extensive qualitative and quantitative information. This technique makes it possible to carry out quantitative and semi quantitative analysis of the degradation of foundry binders it provides data about its composition and temperature range of thermal decomposition process.

BINDERS USED IN TESTS

The following samples were provided for the tests:

PHENOL-FORMALDEHYDE RESINS ("**RESOLE**" RESINS)
FURAN RESIN
GEOPOL
INOTEC PROCESS
CORDIS PROCESS
GREEN SAND

The tests were done according to the Table 1 (agreed with the customer).

Table 1. Program of tests

Testing at AGH University of Science and Technology (Poland)			
Cured binders used in foundry industry	Sample ID	Binder type	TG/DTG/DSC
	MB	natural clay	1
	MA	organic binder	1
	MF	organic binder	1
	MI	inorganic binder	1
	MC	inorganic binder	1
	MG	inorganic binder	1

TESTED SAMPLES:

METHODS AND EQUIPMENT

Equipment: TG/DTG/DSC/ analyser – Q 600 TA Instruments,

Method: TG/DTG//DSC method, temperature range 30-900 °C, heating rate 10 °C/min, inetr atmosphere (25 ml/min), corundum or graphite crucibles or with a hole in the lid (85 µl).

TG/DTG/DSC measurement was performed twice for a sample to check the repeatability of the measurements:

RESULTS AND DISCUSION

TG/DTG thermographs, DSC thermographs, numerical results.

TG/DTG/DSC analysis

MB sample:

The results showed that they are repeatable in term of specific temperatures determined for the sample. Fig. 1 and Fig. 2 shows: characteristic temperature range of thermal decomposition process and DSC effect.

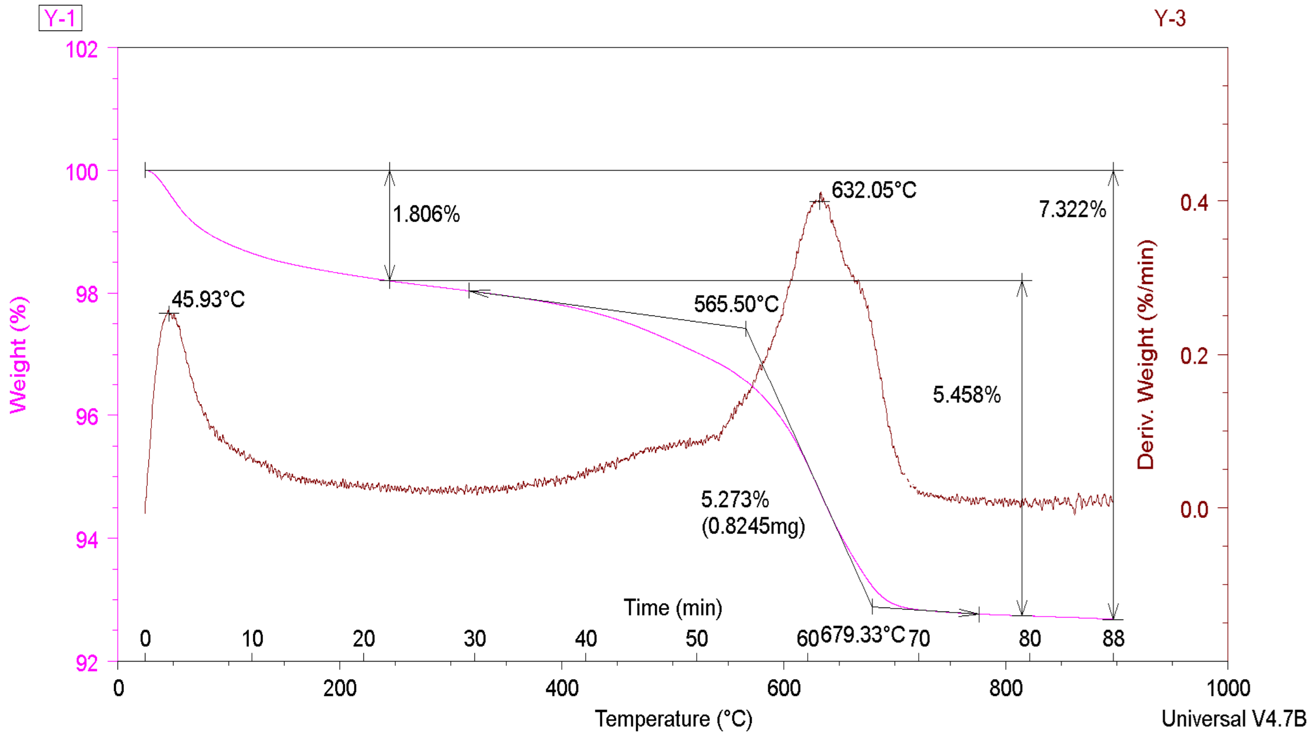

Fig.1 TG/DTG curves for **MB sample**

A comparison of measurements showed that in both cases the same processes and similar mass changes occur. The analyzed material decompose during a multistage process. In the first step, most probably water is evaporated. Thermal degradation of resin starts about 565 °C and it is a sum of two subsequent reactions, what is demonstrated via two signals at DTG curve (45.93/565.50 °C). A total mass loss is about 7.3 % mass. The results comparison was presented in Table 1 and on Fig. 1-2.

Table 1. Thermal parameters of samples from **TG** analysis (T_o - extrapolated 'onset' temperature of degradation, T_{DTG}- extremum of DTG peak, Δm - mass change)

Samle	T_o[°C]	T_{DTG} [°C]			Δm [%]			Solid residue [%]
					30-240 [°C]	240-820 [°C]	30-900 [°C]	
MB	**565.60**	**45.93**	**632.05**	**------**	**1.08**	**5.45**	**7.32**	**92.38**

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The analysis of DSC (Fig.2) results indicated that, similar to TG, DSC curves obtained in measurements. The analyzed material shows endothermic effect related to water evaporation (T= 28-81 °C) and reactions occurring during thermal degradation of resin. The observed effects are impossible to separate.

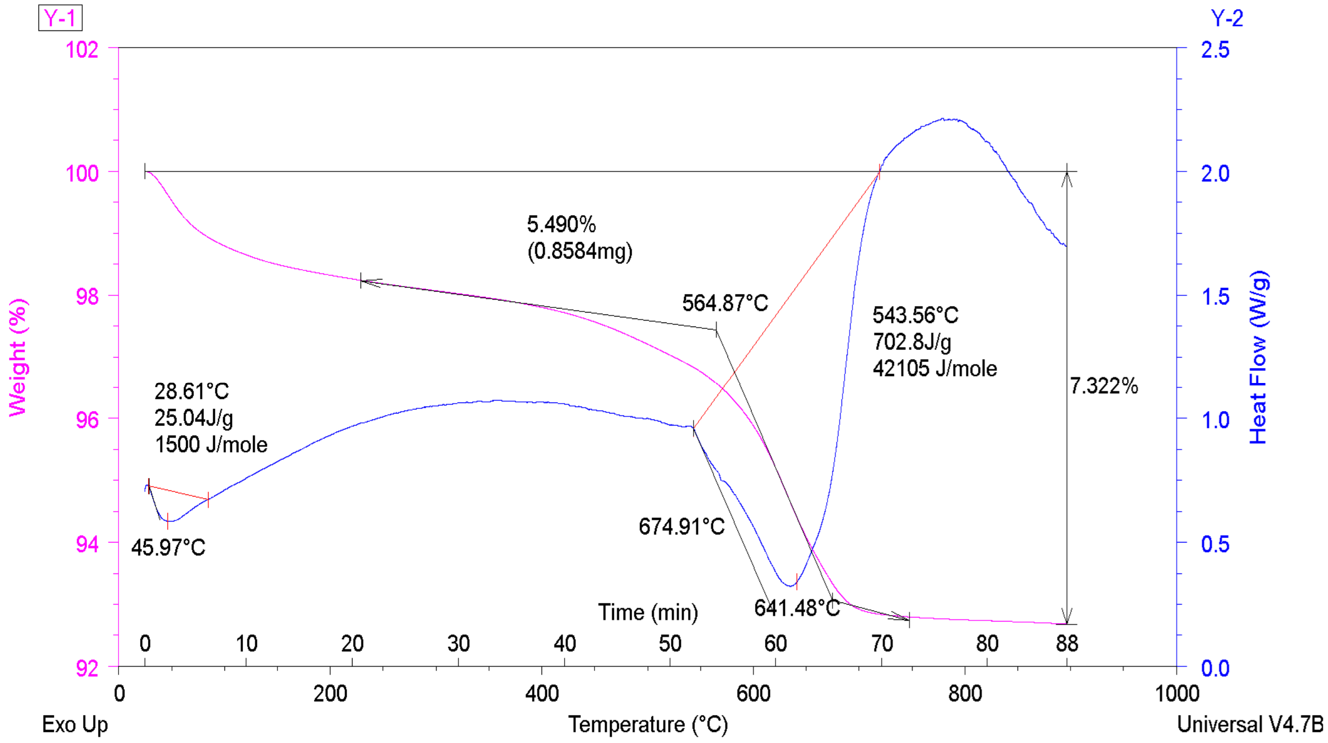

Fig.2 DSC curve and TG for **MB sample**

MA sample:

The results showed that they are repeatable in term of specific temperatures determined for the sample. Fig. 3 and Fig. 4 shows: characteristic temperature range of thermal decomposition process and DSC effect.

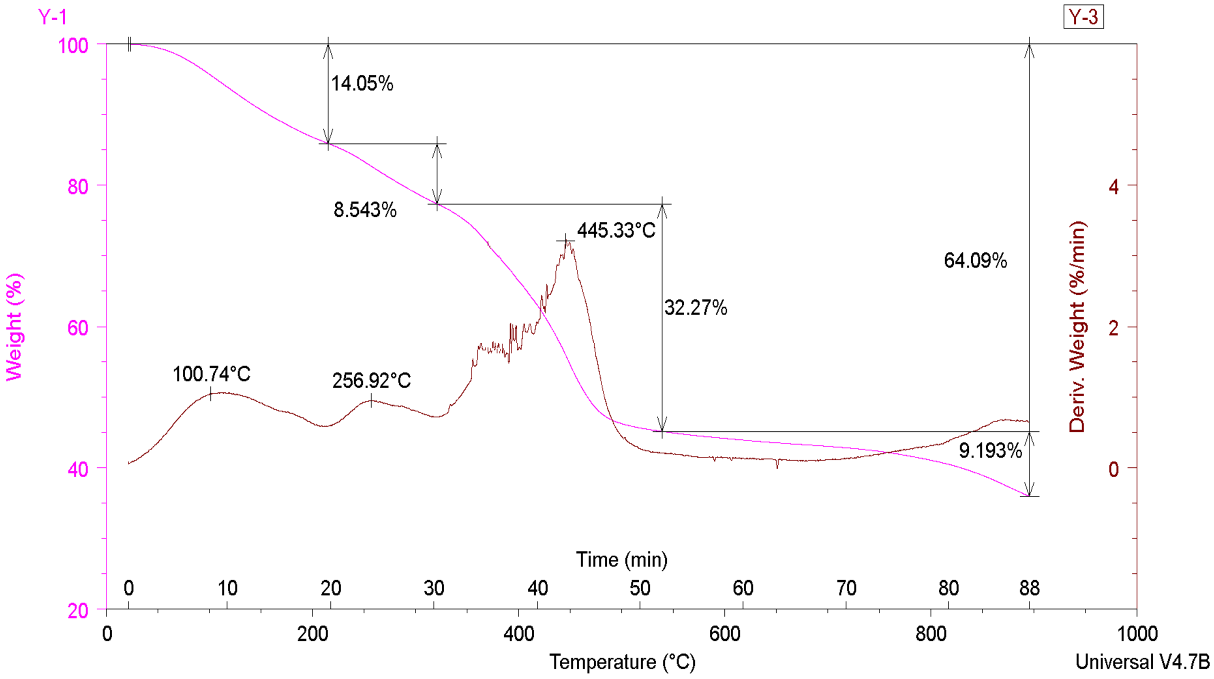

Fig.3 TG/DTG curves for **MA sample**

A comparison of measurements showed that in both cases the same processes and similar mass changes occur. The analysed material decompose during a multistage process. In the first step, most probably water is evaporated. Thermal degradation of resin starts about 393.65 ^{o}C and it is a sum of two subsequent reactions, what is demonstrated via two signals at DTG curve (370.29/445.33^{o}C). A total mass loss is about 64 % mass. The results comparison was presented in Table 2 and on Fig. 3-4.

Table 2. Thermal parameters of samples from **TG** analysis (T$_o$ - extrapolated 'onset' temperature of degradation, T$_{DTG}$- extremum of DTG peak, Δm - mass change)

10	**T$_o$[°C]**	**T$_{DTG}$ [°C]**				**Δm [%]**				**Solid residue [%]**
MA	393.65	100.07	256.92	370.29	445.33	**30-220 [°C]**	**220-320 [°C]**	**320-559 [°C]**	**30-900 [°C]**	35.91
						14.05	8.54	32.27	64.09	

The analysis of DSC (Fig.4) results indicated that, similar to TG, DSC curves obtained in measurements. The analyzed material shows 2 endothermic effect related to evaporation of solvents and reactions occurring during thermal degradation of resin. The observed effects are impossible to separate.

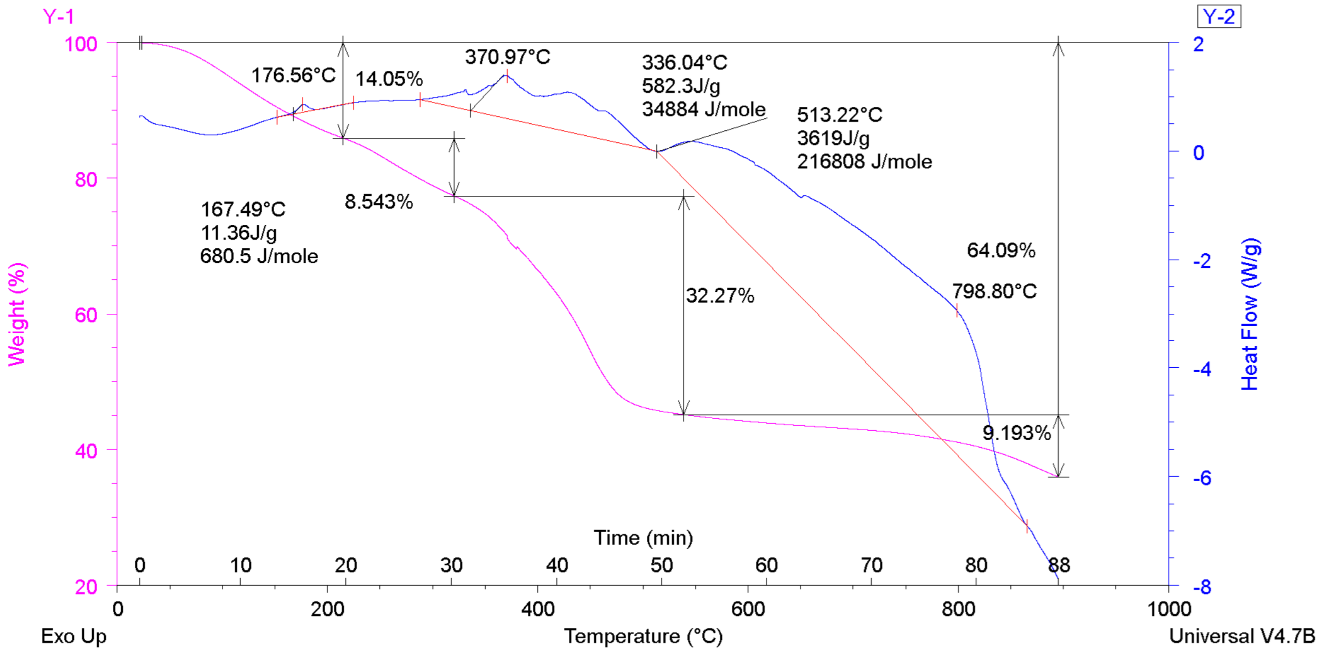

Fig.4 DSC curve and TG for **MA sample**

MF Sample:

The results showed that they are repeatable in term of specific temperatures determined for the sample. Fig. 5 and Fig. 6 shows characteristic temperature range of thermal decomposition process and DSC effect.

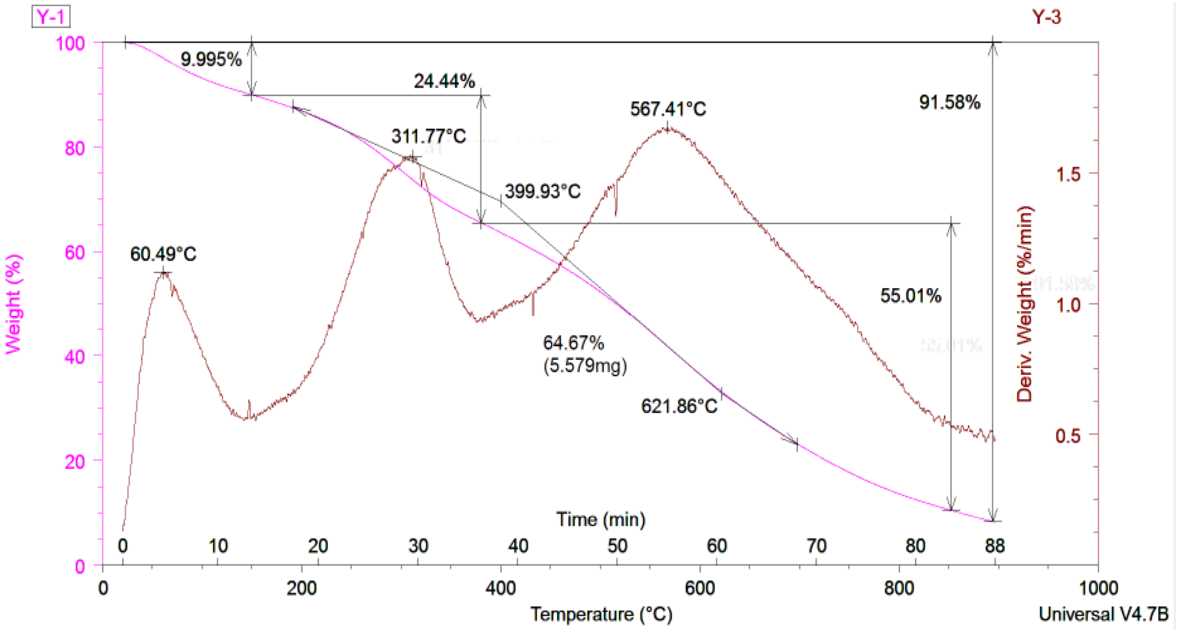

Fig.5 TG/DTG curves for **MF sample**

A comparison of measurements showed that in both cases the same processes and similar mass changes occur. The analysed material decompose during a multistage process. In the first step, most probably water is evaporated. Thermal degradation of resin starts about 19.567 °C and it is a sum of two subsequent reactions, what is demonstrated via two signals at DTG curve (311.77/567.41°C). A total mass loss is about 91 % mass. The results comparison was presented in Table 3 and on Fig. 5-6.

Table 3. Thermal parameters of samples from **TG** analysis (T_o - extrapolated 'onset' temperature of degradation, T_{DTG}- extremum of DTG peak, Δm - mass change)

Samle	**T_o[°C]**	**T_{DTG} [°C]**				**Δm [%]**			**Solid residue [%]**
						30-120 [°C]	**120-399 [°C]**	**399-900 [°C]**	
MF	197.56	60.49	311.77	567.41	--	9.95	24.44	55.01	8.42

The analysis of DSC (Fig.6) results indicated that, similar to TG, DSC curves obtained in measurements. The analyzed material shows 1 endothermic effect related to evaporation of solvents and reactions occurring during thermal degradation of resin (2 exothermic effects). The observed effects are impossible to separate.

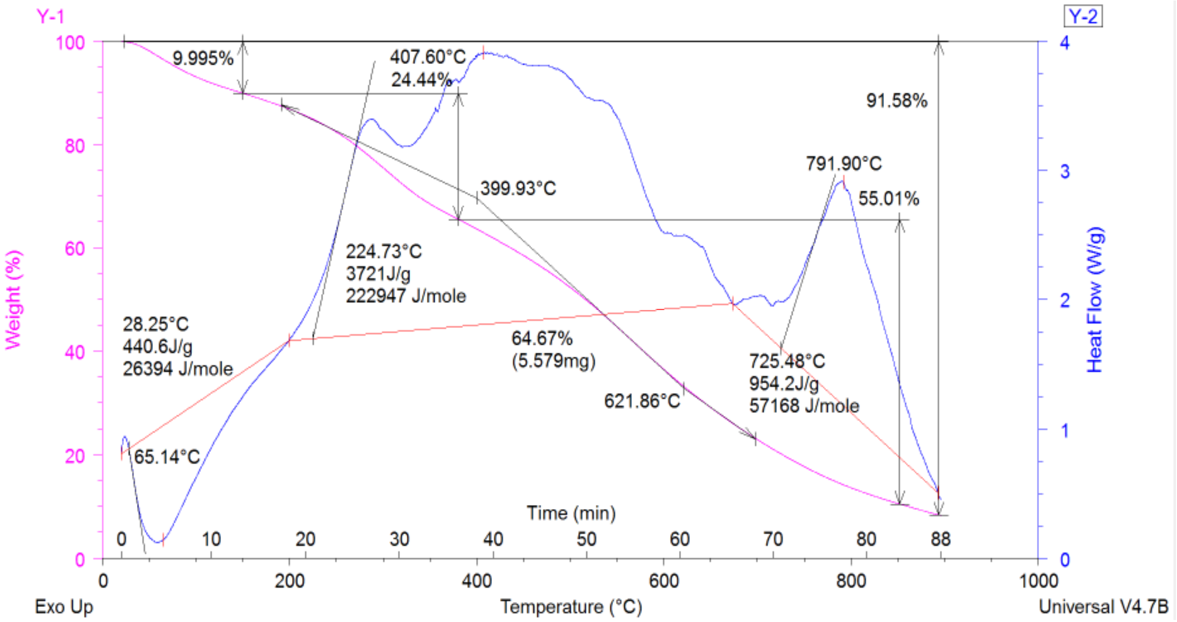

Fig.6 DSC curve and TG for **MF sample**

The presented results indicate that the analyzed material have been a similar way in all measurements, what suggests that it is homogeneous (Fig.6).

MG Sample:

The results showed that they are repeatable in term of specific temperatures determined for the sample. Fig. 7 and Fig. 8 shows characteristic temperature range of thermal decomposition process and DSC effect.

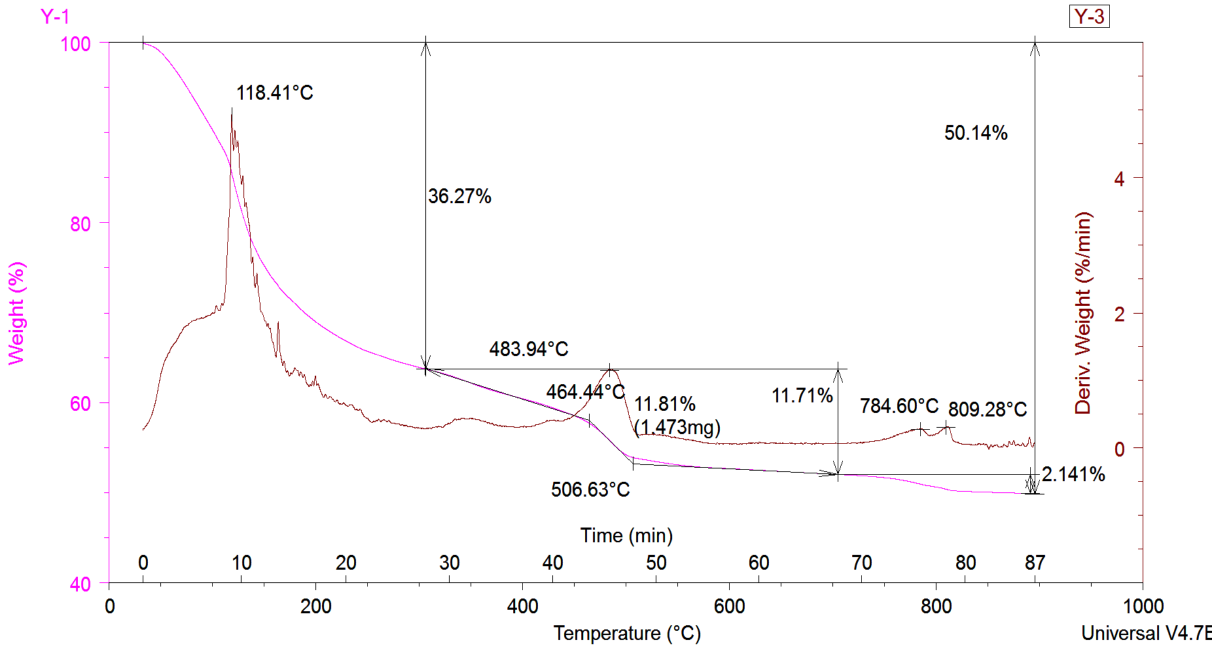

Fig.7 TG/DTG curves for **MG Sample**

A comparison of measurements showed that in both cases the same processes and similar mass changes occur. The analysed material decompose during a multistage process. In the first step, most probably water is evaporated. Thermal degradation of this material starts about 464 ^{o}C. On DTG curve we can see two signals (118.41/483.94^{o}C). A total mass loss is about 50 % mass. The results comparison was presented in Table 4 and on Fig. 7-8.

Table 4. Thermal parameters of samples from **TG** analysis (T_o - extrapolated 'onset' temperature of degradation, T_{DTG}- extremum of DTG peak, Δm - mass change)

Samle	T_o[°C]	T_{DTG} [°C]				Δm [%]			Solid residue [%]
						30-300 [°C]	300-720 [°C]	720-900 [°C]	
MG	464.4	118.4	464.9	784.6	809.2	36.27	11.71	2.14	49.8

The analysis of DSC (Fig.8) results indicated that, similar to TG, DSC curves obtained in measurements. The analyzed material shows 2 endothermic effect related to evaporation of solvents and reactions occurring during glass transaction (2 exothermic effects).

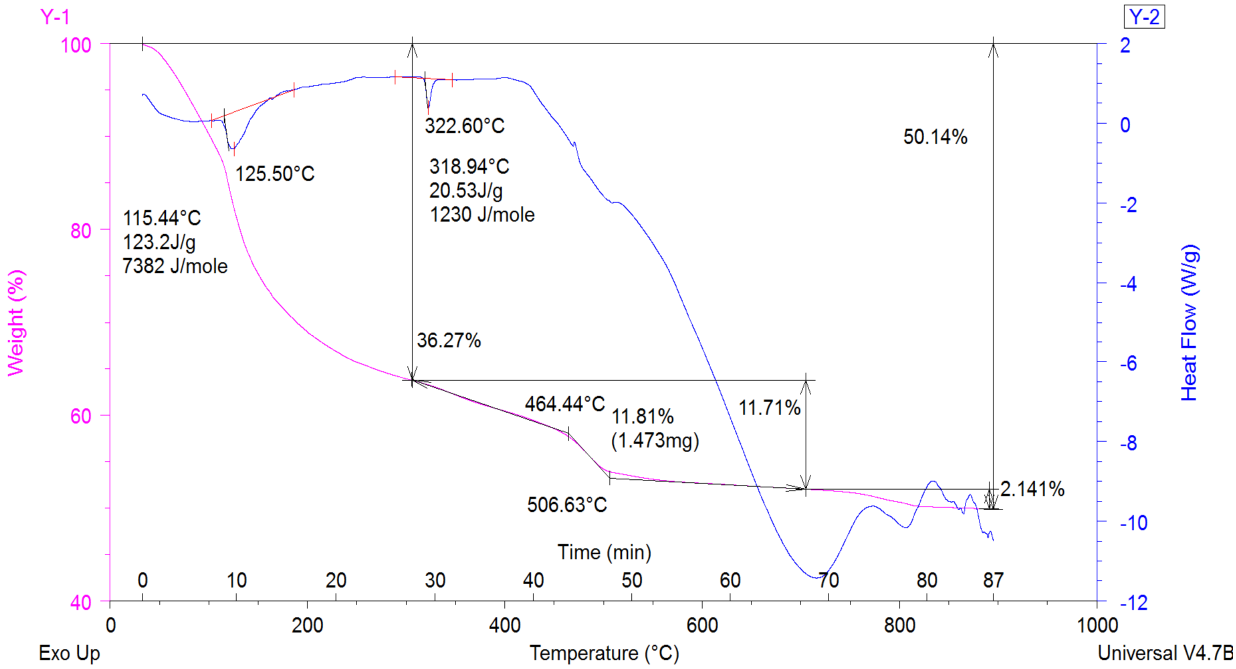

Fig.8 DSC curve and TG for **MG Sample**

MC Sample:

The results showed that they are repeatable in term of specific temperatures determined for the sample. Fig. 9 and Fig. 10 shows characteristic temperature range of thermal decomposition process and DSC effect. **This sample has been specially prepared by hardening at 300 °C for 10 min. before measurement**.

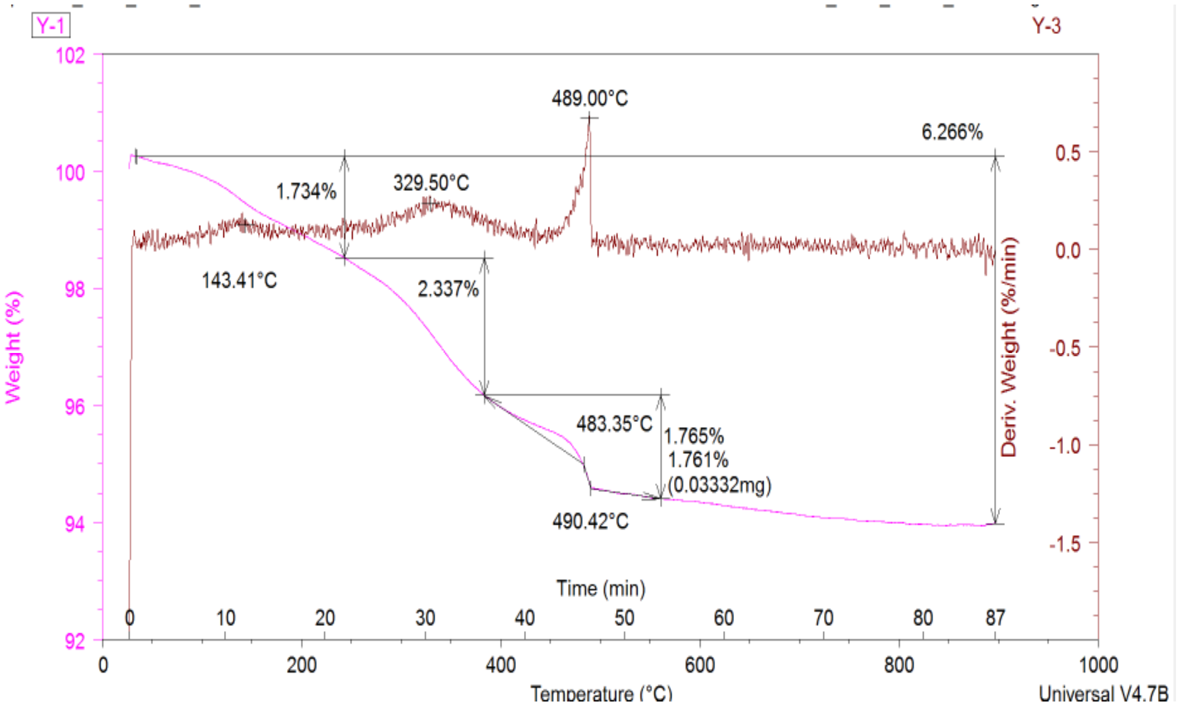

Fig.9 TG/DTG curves for **MC Sample**

A comparison of measurements showed that in both cases the same processes and similar mass changes occur. The analysed material decompose during a multistage process. In the first step, most probably water is evaporated. Thermal decompositiot of this material starts about 384.44°C. On DTG curve we can see one signal (489.00 °C). A total mass loss is about 6.26 % mass. The results comparison was presented in Table 4 and on Fig. 9-10.

Table 5. Thermal parameters of samples from **TG** analysis (T_o - extrapolated 'onset' temperature of degradation, T_{DTG}- extremum of DTG peak, Δm - mass change)

Samle	**T_o[°C]**	**T_{DTG} [°C]**				**Δm [%]**			**Solid residue [%]**
MC	**384.4**	**143.4**	**329.5**	**489.0**	**----**	**30-250 [°C]**	**250-384 [°C]**	**384-558 [°C]**	**93.74**
						1.73	**2.33**	**1.76**	

The analysis of DSC (Fig.10) results indicated that, similar to TG, DSC curves obtained in measurements.

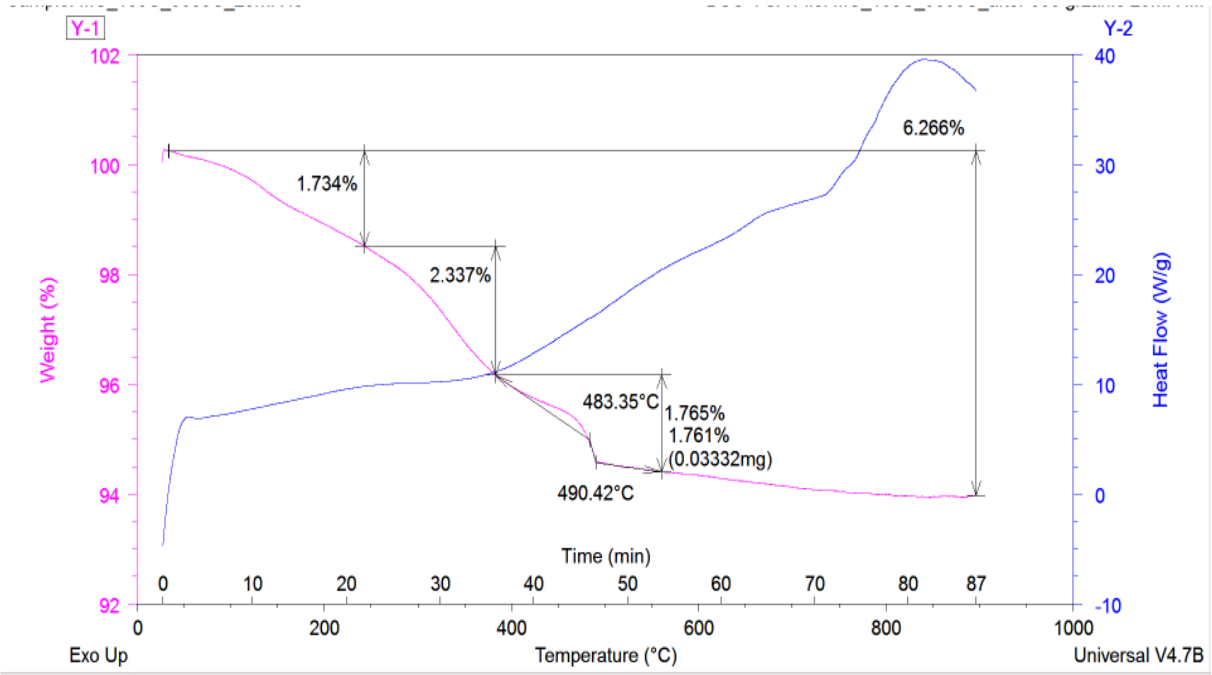

Fig.10 DSC curve and TG for **MC Sample**

MI Sample:

The results showed that they are repeatable in term of specific temperatures determined for the sample. Fig. 11 and Fig. 12 shows characteristic temperature range of thermal decomposition process and DSC effect. This sample has been specially prepared by hardening **at 300 °C for 10 min** before measurement.

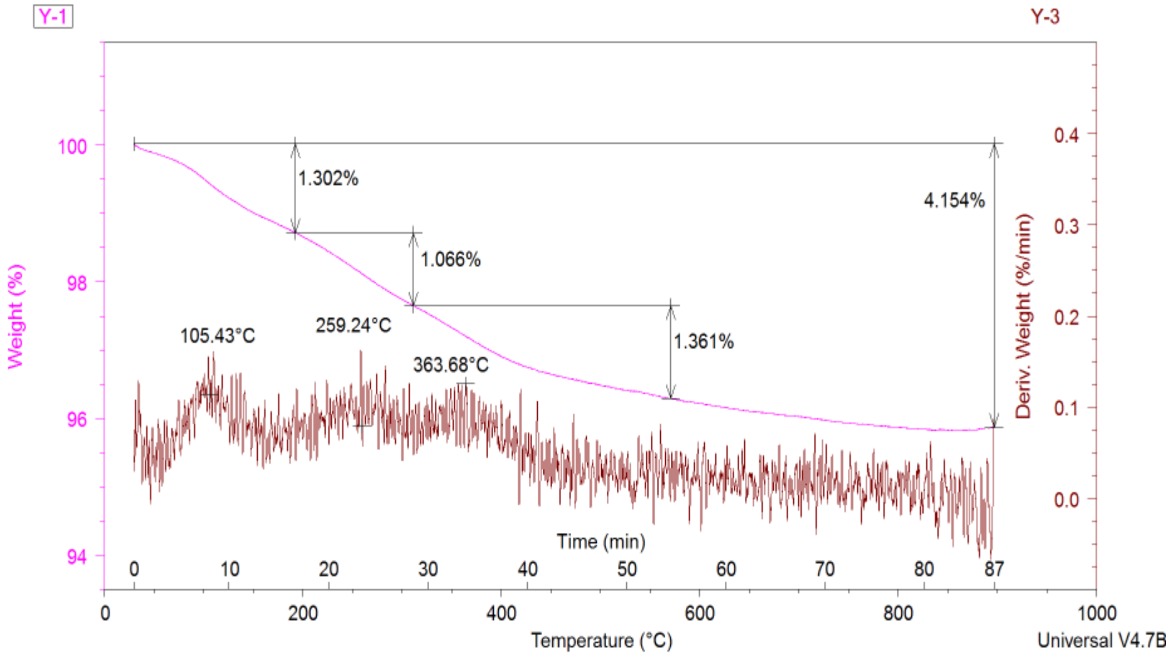

Fig.11 TG/DTG curves for **MI Sample**

A comparison of measurements showed that in both cases the same processes and similar mass changes occur. The analysed material decompose during a multistage process. In the first step, most probably water is evaporated. Thermal degradation of this material starts about 192.78 °C. On DTG curve we can see three signals (105.4/259.2/363.8 °C). A total mass loss is about 4 % mass. The results comparison was presented in Table 4 and on Fig. 9-10.

Table 6. Thermal parameters of samples from **TG** analysis (T_o - extrapolated 'onset' temperature of degradation, T_{DTG}- extremum of DTG peak, Δm - mass change)

Samle	T_o[°C]	T_{DTG} [°C]				Δm [%]				Solid residue [%]
MI	192.78	105.4	259.4	363.8	…	30-192 [°C]	192.-312. [°C]	312-575 [°C]	30-900 [°C]	95.85
						1.3	1.06	1.36	4.15	

The analysis of DSC (Fig.12) results indicated that, similar to TG, DSC curves obtained in measurements. The analyzed material shows endothermic effect related to evaporation of solvents and reactions occurring during glass transaction.

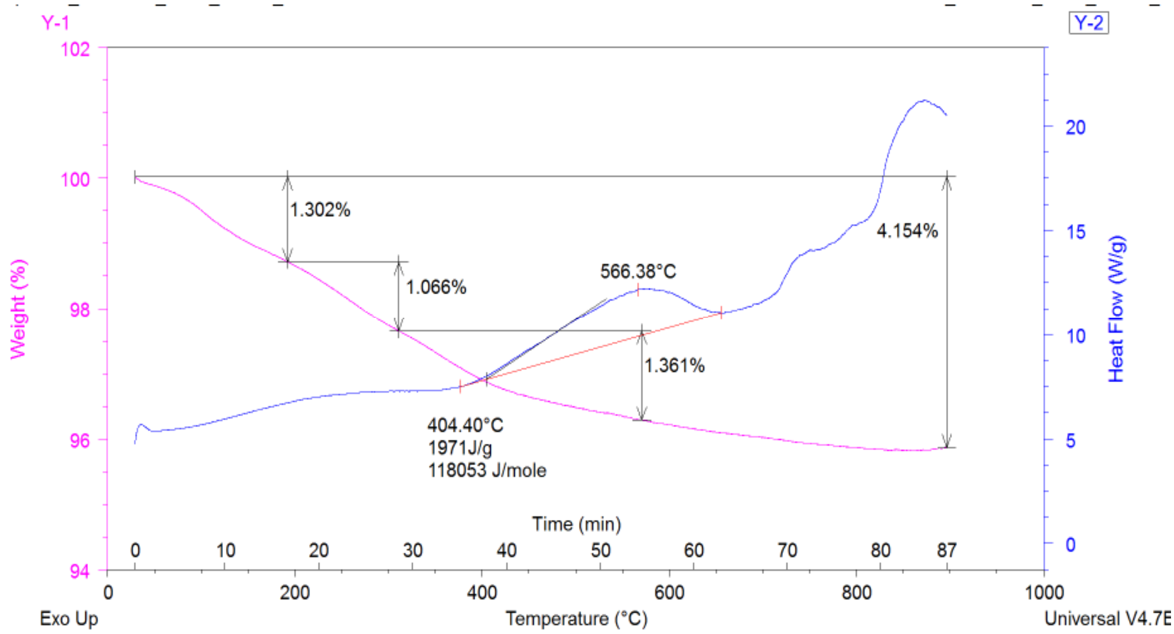

Fig.12 DSC curve and TG for **MI Sample**

The results showed that they are repeatable in term of specific temperatures determined for the samples. TG/DTG analysis showed characteristic temperature range of thermal decomposition process and DSC effect. Thermal analysis showed that tested materials decompose in two or three main stage with the specific energetic effects.

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