Advanced oxidation and adsorption modification of dust waste from standard moulding sands

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Abstract

The article discusses the process of advanced oxidation (*AO*) with application of ultrasounds and surface modification of the dust waste collected during dry dedusting of processed moulding sands with bentonite binder. A beneficial effect of both *AO* and adsorption modification of dust waste, when performed with the selected type of polyelectrolyte, on the technological and mechanical properties of moulding sands prepared with an addition of this dust has been stated. In spite of the bentonite content in moulding sand reduced by 43% and replaced with modified dust waste, the mechanical properties, i.e. the compression and tensile strengths, examined on sand specimens have been improved by 10% and 13%, respectively, with no harm to other basic technological sand properties. At the same time, it was also possible to reduce by about 30% the emission rate of the main gaseous component from the *BTEX* group, i.e. benzene.

Keywords: Innovative Foundry Technologies and Materials, Environmental Protection, Moulding Sand with Bentonite Binder, Dust Waste, Advanced Oxidation, Polyelectrolytes

1. Introduction

In Poland, about 80% of all foundry moulds are made from standard sands with bentonite binder and coal dust, or with lustrous carbon carriers. The processing plants for sands of this type are equipped with wet or dry dust collecting systems. The sludge or dust formed during mould preparation is an unnecessary burden for the foundry. Besides the condensates of compounds generally considered *HAPs* (*Hazardous Air Pollutions*), it contains silica, deactivated bentonite, active bentonite, and thermally non-deactivated particles of organic binder-hardener systems (sulphonic acids, pyridine derivatives, esters, isocyanates, amines, copper salts, ammonium salts,

hexamethylenetetramine). Numerous studies [1, 2] have proved that coal dust, organic lustrous carbon carriers, cores with organic binders, and protective coatings based on alcohol or water are the main sources of hazardous air pollutions (*HAPs*), emitted during the process of casting production in standard moulding sands. The pollutants emitted in the largest volumes include benzene, toluene, o-, m-, p-xylene, naphtalene, hexane, and their derivatives. When core sands with organic binders are used, others *HAPs* are formed, to mention only phenol and formaldehyde, both of which can occur in large amounts. Besides the above mentioned *HAPs*, the process of casting manufacture in standard moulding sands is the source of the emission of other compounds included in the group of *HAPs*, like acetaldehyde, acrolein, aniline, pyrokatechine, o-, m-, p-

cresol, cumene, hexane, isophorone, methyl, indene, polyclic organic compounds, priopionaldehyde, styrene, triethylamine [3, 4]. Unfortunately, the exhaust systems used currently cannot remove all chemical compounds formed in a foundry mould during and after filling of its cavity with molten metal. Carbon-containing materials, directly adjacent to mould-metal interface, usually undergo a total or partial decomposition, but fragments more distant from this interface remain untransformed. Additionally, cooler parts of mould can absorb gaseous hydrocarbons formed in the mould regions of higher temperature. So, it should be expected that fractions of these gas volumes will undergo recondensation or absorption in regions more distant from the mould-metal interface, and as such will remain unaffected by exhaust system.

Apart from the chemical compounds mentioned above, the process of casting manufacture results in an organised and non-organised emission of dust, taking place at each stage of the casting production.

The data on *HAPs* emission (both gases and dust) from the Polish foundries are not complete, but even being incomplete they give us a rough picture of the type and scale of hazards created to natural environment [5]. The dust emission level reported to take place during the process of standard (bentonite) moulding sand preparation is 0,001 – 0,044 kg/Mg of moulding sand. Moulding sand processing and reclamation is the source of dust emissions amounting to 0,004 – 0,258 kg/Mg, depending on the type of dust extraction unit used by a foundry plant. The organised emission of contaminants from the casting process and mould cooling operation amounts to: up to 1,071 kg/h dust, up to 0,082 kg/h phenol, up to 0,1548 kg/h formaldehyde, up to 1,479 kg/h CO, up to 0,0475 kg/h ammonia, up to 0,0001 kg/h hydrogen cyanide, up to 0,0964 kg/h PAHs, up to 0,015 kg/h aliphatic hydrocarbons. The operation of casting knocking out and de-coring results in dust emission levels from 0,04 up to 6,9 kg/h.

The above data on the emission level of the hazardous dust and gaseous contaminants were determined using different types of the dust collecting units (wet filters, sprinkling filters, circulation filters, bag-type cloth filters), characterised by the dedusting efficiency varying from 31 to 95% according to the filter type.

Basing on the results of an analysis of the consumption rate of moulding materials by domestic foundries, it can be tentatively assumed that the amount of produced dust waste is 19 000 tons/year, which makes about 20% of all waste originating from standard moulding and core sands. However, the dust waste also contains full-value materials (their content has not been determined yet), which can undergo complete recycling (active bentonite, coal dust, organic lustrous carbon carriers) and be re-used without deteriorating the technological and ecological properties of moulding sands, providing the chemical compounds generally considered *HAPs* are partially or totally removed from the waste.

Problems related with advanced oxidation (*AO*) of selected chemical compounds to neutralise their negative effect were the subject of numerous investigations, not necessarily related with metalcasting. They included investigations of the kinetics of the reaction of oxidation and examination of various compounds formed in potable water [6-8], as well as the process of benzene [9, 3] and/or phenols [10] oxidation. At the close of the 90-ties of the past century, the first information appeared in technical literature on the application of *AO* process in foundry industry [1, 10-13]. In most general terms, advanced oxidation is defined as a process of oxidation taking place in water phase and including the formation of hydroxyl radicals, which are intermediate products of the oxidising process, controlling the transformation and/or decomposition of some specific impurities.

Thus, the process of advanced oxidation enables reducing the level of harmful and toxic emissions. Under certain conditions, the application of *AO* can transform large volumes of carbon into an active material, later used as an adsorbent of *VOCs* (volatile organic compounds) and *HAPs*. Depending on the content of oxidising agents and the value of pH under which the reactions are taking place, the decomposition of organic compounds due to oxidising can proceed by several different routes, which include direct oxidising, indirect oxidising, and direct photolysis. The, formed by *AO* process, radicals removing the impurities can become particularly reactive at high temperatures, which commonly occur in standard moulding sands on pouring them with molten metal. Theoretically it is possible for the radicals to get combined with the impurities like benzene, toluene and phenol by addition or adsorption. By these mechanisms, VOCs may undergo partial decomposition. The *AO* process can also operate through a mechanism that changes the adsorption properties of bentonite and of other compounds of standard moulding sands, thus increasing their adhesive properties.

2. The advanced oxidation of dust waste suspension

Studies were carried out on the dust waste collected by a dry de-dusting system operating in a processing plant for the bentonite-bonded and coal dust-containing moulding sands. The BET measurements of specific surface, the measurements of pore dimensions and of the total volume of pores present in dust waste with nitrogen used as an adsorbate have proved that the specific surface of the dust waste is 5,57 m^2/g, the size of mesopores is 3,786 nm, and the total volume of pores is 0,09984 cm^3/g. The advanced oxidation of dust waste was carried out with ultrasounds in the medium of water saturated with ozone, which was generated by an *OZOMATIC OSC-MODULAR 4HC* ozone generator fed with oxygen.

The heat of ozone formation is 144,7 kJ/mole, with the solubility in water amounting to 3 ppm at 20°C. Ozone is an unstable gas, decomposing to diatomic oxygen at room temperature. Its decomposition is accelerated by contact with solid surfaces, chemical compounds and high temperature. Considering these properties of ozone, it has been necessary to determine the conditions under which it will reach its maximum concentration in water as well as the kinetics of decomposition under real conditions.
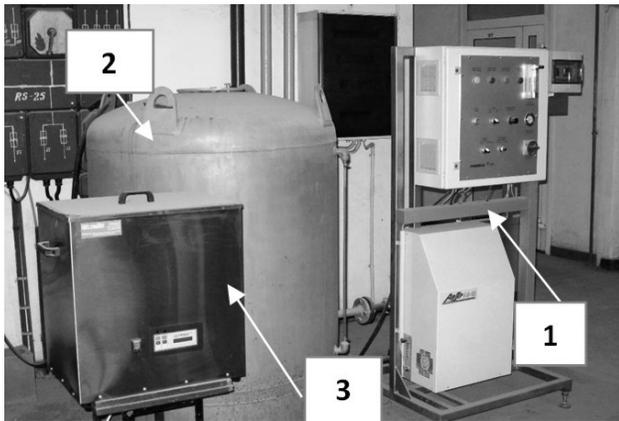
Fig. 1. Pilot stand for water saturation with ozone and for ultrasonic processing of dust waste from moulding sands
(1 – *Ozomatic OCS Modular 4HC* ozone generator,
2 – compensation tank, 3 – ultrasonic chamber)

The above investigations were carried out in several different configurations. Finally, it has been stated that the best water ozonation regime consists in 60 minute treatment with ozone in concentration of 4 g/Nm^3 (preliminary ozone treatment), followed by a break of 30 minutes, and further ozonation carried out for 30 minutes. This cycle produces water saturated with ozone in concentrations from 0,41÷0,43 mg/dm^3. The physico-chemical examinations using standard methods and Fourier transform infrared spectroscopy carried out on an Excalibur 3000 spectroscope with standard DTGS detector have confirmed the decay of activity in ozone-saturated water after the time longer than 210 minutes. This is indicated by the lack of differences in the values of the wave number of *IR* spectra and by the same values of the permanganate index, i.e. the oxidability index ($< 0,7 \pm 0,1$), obtained in water non-ozonised and ozonised for 60 minutes.

The dust waste was subjected to the ozonising process as a suspension in natural and ozonised water, applying the 21,5 kHz frequency ultrasounds for the time of 10, 20 and 30 minutes.

The particle size distribution in a waste dust suspension was measured by the light diffraction method (*Multi-Wavelength Particle Size Analyzer, model LS 13320* made by *Beckman Coulter*) after dispersion in water medium. The said method enables the determination of particle sizes in a wide range of values, i.e. from 40 nm to 2000 μm, yielding much better results in the case of polydispersive suspensions than the method of dynamic light scattering.

Figures 2÷4 show examples of particle size distribution in a waste dust volume. The obtained results indicate a favourable effect of ultrasounds on the reduction of maximum particle diameter size in the main fraction of dust waste. Compared to particles present in the dust waste not subjected to modification, this reduction is from 9% to 17% in the case of *AO* process and from 24% to 50% in the case of natural water. The highest effectiveness in reducing the maximum particle diameter size in the main fraction of dust waste was observed in the case of ultrasonic treatment carried out for 10 minutes on the dust suspension in natural water.
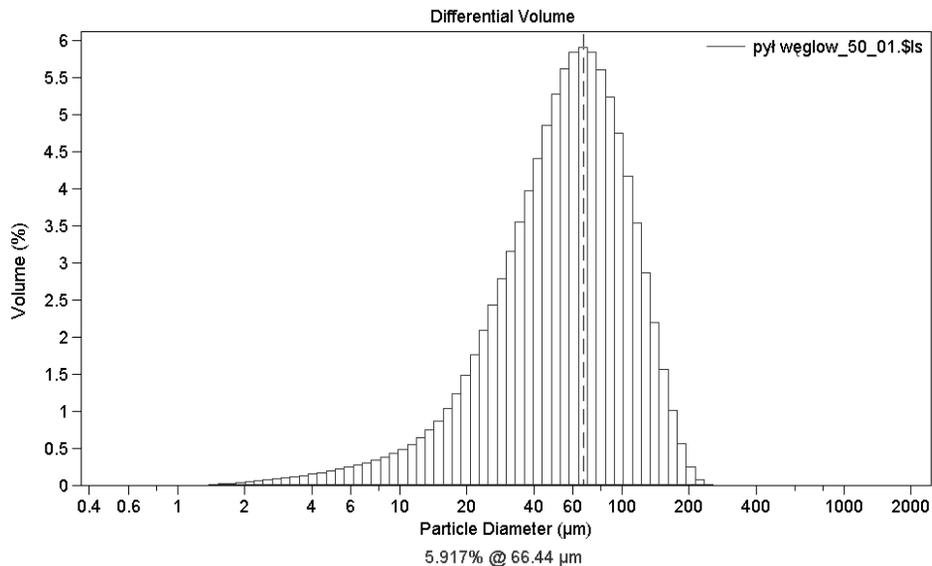

Fig. 2. Particle size distribution in the main fraction of non-modified dust waste determined by laser diffraction
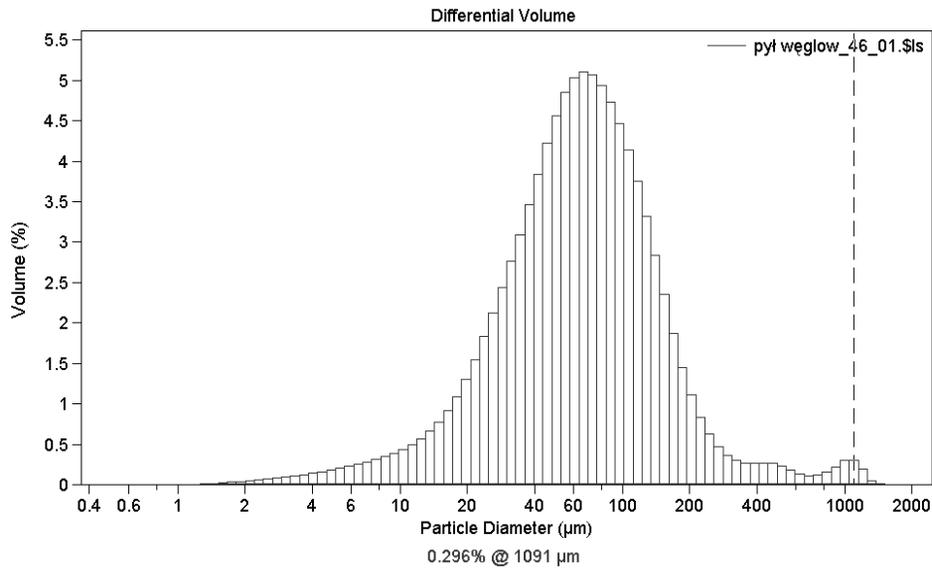(the dispersive medium is natural water)

Fig. 3. Particle size distribution in the main fraction of non-modified dust waste (particles of dimensions above 1000 μm) (the dispersive medium is natural water)
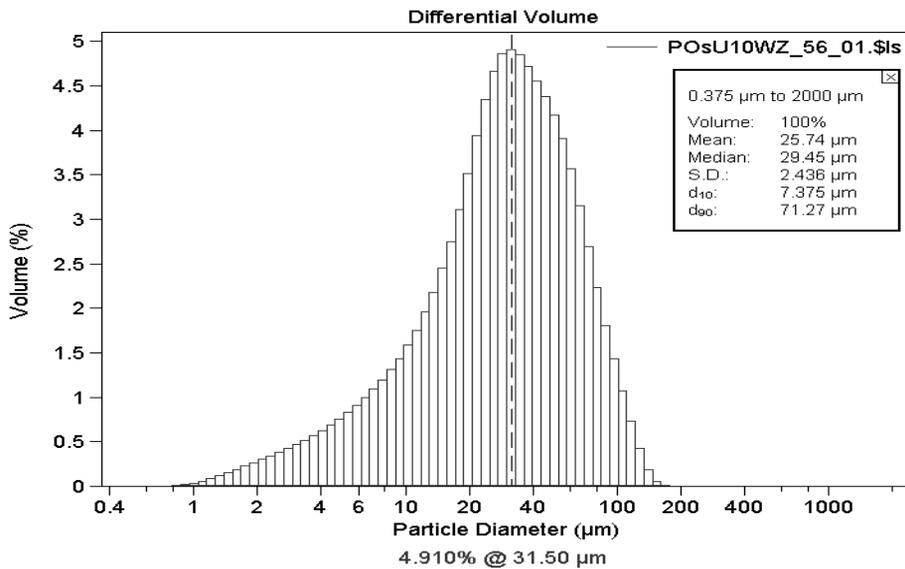

Fig. 4. Particle size distribution of 26 μm average value obtained in dust waste treated for 10 minutes with ultrasounds (the dispersive medium is natural water)

3. Adsorption modification of the dust waste suspension

Two basic types of polyelectrolytes, i.e. poly (sodium 4-styrene-sulphonate) of anione properties, designated as *PSS*, and polyethyleneimine, designated as *PEI*, enabling active control of surface charge through changes in the pH value of suspension, were chosen for investigations.

The characteristic features of the polyelectrolyte layers on phase boundaries were also determined, applying the research methods which enable measurement of the changing value of the electric potential of flow, and hence determination of the kinetics of the formation and structure of the polyelectrolyte layers of both anionic and kationic character, formed on solid surfaces. Changes in the electric potential are strictly correlated with the degree of the particle surface coverage with charge.

It has been stated that for the low-value range of ionic forces, the particles of *PSS* form oblong conformations, and the

shape of a single molecule can approach that of a rotating spheroid with the longer-to-shorter axis ratio exceeding considerably the value of 10. The increasing value of ionic forces results in more effective screening of the electrostatic forces and the particle assumes a more compact shape, which in close approximation can be described with semi-circle.

The polyelectrolyte *PEI* reveals different structure and conformation as regards branching of polymer chains forming its molecules. This is the reason why molecules of this polyelectrolyte assume a spherical shape with the hydrodynamic radius of 6,9 nm. Moreover, because of a large number of the amphoteric imine groups, the *PEI* molecules are characterised by high positive surface charge for the range of pH values > 10. Therefore, *PEI* molecules can be effectively adsorbed by the negatively charged surfaces, enabling effective modification of the suspension structure.

4. Technological properties of moulding sands with an addition of waste dust

The suspension of waste dust was subjected to an ultrasonic treatment carried out for the time of 10, 20 and 30 minutes, where the dispersing agent was water in natural condition and after ozone-treatment. After modifying treatment of the dust waste carried out under the conditions as stated above, the waste was dried at the temperature of 100^0C until a constant mass was obtained. Using thus prepared dust waste, moulding sands were made in which the content of bentonite binder and dust waste was constant and amounting to 7%. The dust waste was added in an amount from 1% to 4%, with 1% gradation. The moulding sand was prepared according to a respective standard [14], introducing to its composition the addition of 4% coal dust and using, as a wetting agent, natural or ozone-treated water, added in an amount considered optimum, i.e. 2,1%. From thus prepared moulding sands (14 different compositions), standard specimens were made and were next used in the determination of mechanical and technological properties, such as the compression strength, tensile strength, strength in the moisture condensation zone, permeability, friability, compactability and flowability.

Having analysed the results obtained so far, for further investigations to determine the type of gas emitted from moulding sand and the kinetics of this process under the real conditions of a foundry plant, the moulding sand containing water in an amount of 2,1%, coal dust in an amount of 4%, bentonite in an amount of 4%, and dust waste in an amount of 3% was selected. The main characteristics of this moulding sand composition are given in Table 1.

Figures 5÷11 show changes in mechanical and technological properties of the examined moulding sands compared to analogical properties of moulding sand *W*.

Table 1.
Characteristic features of moulding sand composition selected for the investigations of gas emission rate and chemical analysis (*BTEX*)

| Moulding sand type	Water type	Dust waste type
W	Natural	No ultrasonic treatment
D	Ozone-treated	No ultrasonic treatment
K1	Ozone-treated	Ultrasonic treatment for 10 minutes in natural water
D-PEI	Ozone-treated	No ultrasonic treatment, containing 2 ppm addition of PEI polyelectrolyte
K1-PEI	Ozone-treated	Ultrasonic treatment for 10 minutes in natural water, containing 2 ppm addition of PEI polyelectrolyte
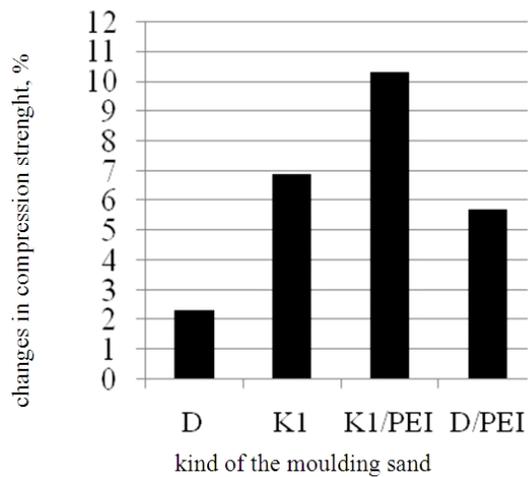
Fig. 5. Changes in compression strength of the examined moulding sand compared to the compression strength of reference sand *W*
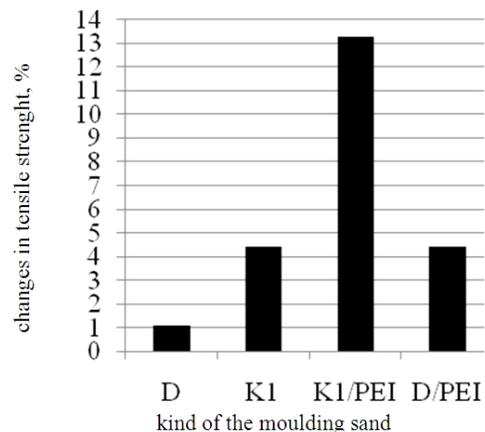

Fig. 6. Changes in tensile strength of the examined moulding sand compared to the tensile strength of reference sand *W*
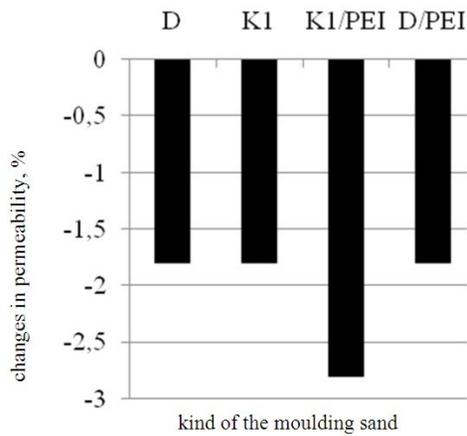
Fig. 7. Changes in permeability of the examined moulding sand compared to the permeability of reference sand *W*
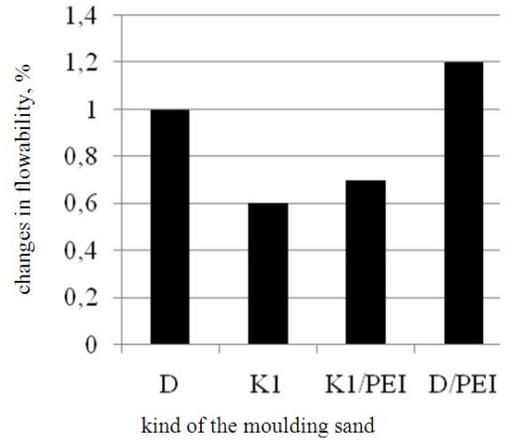

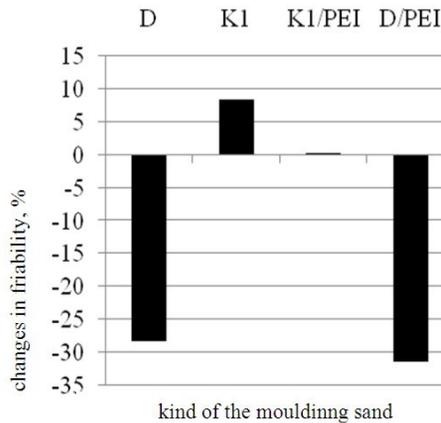Fig. 8. Changes in friability of the examined moulding sand compared to the friability of reference sand *W*
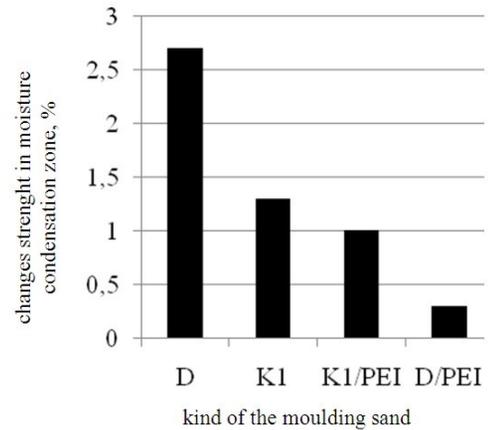

Fig. 9. Changes in compactability of the examined moulding sand compared to the compactability of reference sand *W*

Fig. 10. Changes in flowability of the examined moulding sand compared to the flowability of reference sand *W*

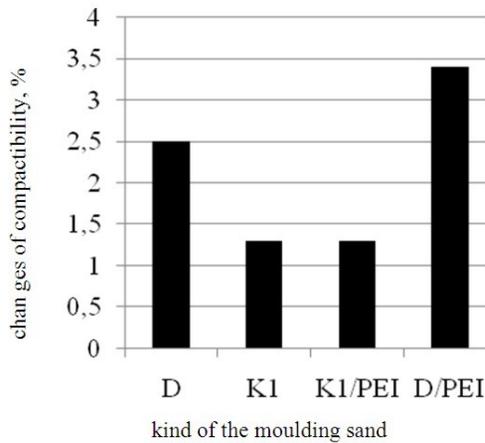Fig. 11. Strength in moisture condensation zone changing in the examined moulding sand compared to reference sand *W*

5. Analysis of gases from the BTEX group emitted by moulding sands containing an addition of dust waste

The gas emission rate from moulding sands designated with symbols *W*, *D*, *K1*, *D-PEI* and *K1-PEI* (Table 1) was analysed to determine the emitted gas volume and chemical composition (the content of benzene, toluene, ethylbenzene and xylene). Qualitative analysis of the emitted gas was carried out by the method of gas chromatography. For this purpose, the ϕ 50 x 50 mm specimens of the examined moulding sand were placed in a mould made from the standard bentonite-bonded mixture and were next poured with cast iron at a temperature of 1350°C. The total emitted gas volume determined in function of process

duration is shown in Figure 12, while Table 2 shows data on the emission rate of the examined gas types.

Table 2.
Gas emission rate (*BTEX*) from the examined moulding sand types

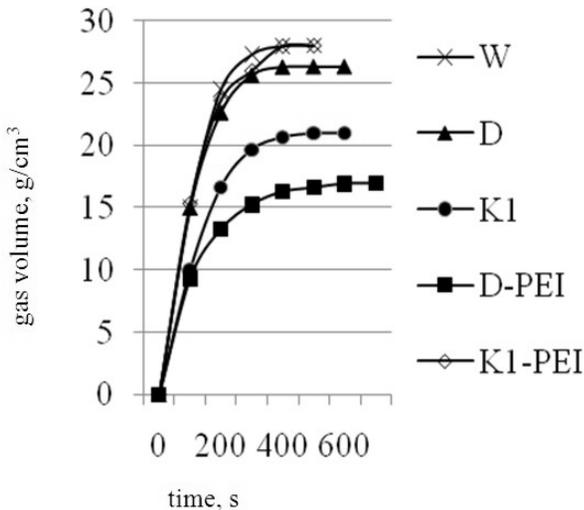| Moulding sand type	Gas emission rate from moulding sand in mg/kg			
	Benzene	Toluen	Ethyl benzene	Xylene
W	123,70	4,46	0,00	0,45
D	359,60	17,60	0,00	1,81
K1	211,74	8,60	0,00	1,52
D-PEI	90,56	4,46	0,13	0,53
K1-PEI	226,48	8,58	0,00	1,00

Fig. 12. Gas volume emitted from the examined moulding sand on pouring with cast iron

6. Conclusions

1. Adding to moulding sand 3% of dust waste as bentonite replacement with simultaneous use of ozone-treated water favourably affects an increase of the sand compression strength. Compared to the compression strength value of moulding sand with natural water, this increase amounts to about 2% in the case of dust waste without ultrasonic treatment and to about 7% in the case of ultrasonic treatment carried out in natural water for 30 minutes. The use of dust waste with the polyelectrolyte *PEI* adsorbed in an amount of 2 ppm increases the value of the moulding sand compression strength by approximately 6% when the dust waste is not subjected to ultrasonic treatment and by approximately 10% when the ultrasonic treatment in natural water is carried out for 30 minutes.

2. Adding to moulding sand 3% of dust waste replacing bentonite with simultaneous use of ozone-treated water favourably affects an increase of the sand tensile strength. Compared to the value of tensile strength obtained in moulding sand made with natural water, this increase amounts to about 1% in the case of dust waste without ultrasonic treatment and to about 4% when ultrasonic treatment is carried out in natural water for 30 minutes. The use of dust waste with polyelectrolyte *PEI* adsorbed in an amount of 2 ppm increases the value of the sand compression strength by about 4% when the dust waste is not subjected to ultrasonic treatment, and to about 13% when ultrasonic treatment in natural water is carried out for 30 minutes.

3. Changes in other technological parameters, such as the permeability (-1,8% to -2,8%), compactability (1,3% to 3,4%), flowability (0,6% to 1,2%), and strength in moisture condensation zone (0,3% to 2,7%), observed in moulding sand containing 3% dust waste as a bentonite replacement and mixed with ozone-treated water, are insignificant compared to analogical parameters of the moulding sand prepared with an addition of natural water and dust waste not subjected to ultrasonic treatment. Only in the case of friability, a considerable drop in the value of this parameter has been observed when the moulding sand was mixed with an addition of ozone-treated water and dust waste not subjected to ultrasonic treatment, with and without the adsorbed polyelectrolyte *PEI* (about 30%).

4. The lowest gas volume (calculated per 1 kg of the moulding sand) is emitted from the moulding sand containing 3% of dust waste replacing bentonite and ozone-treated water. The gas emission kinetics is similar in all types of the examined sands. Nearly all of the gas volume emitted by moulding sand is liberated during the first 200÷300 seconds of the measurement duration; the maximum gas emission rate is observed to occur during the first few seconds after pouring of the mould with liquid cast iron.

5. In the BTEX group, the main gaseous component is benzene. The lowest amount of *BTEX* compounds (benzene, toluene, ethylbenzene, xylene) was emitted by the sand containing 3% of dust waste replacing bentonite, without ultrasonic treatment, and with the adsorbed polyelectrolyte *PEI* and ozone-treated water.

6. The emission of ethylbenzene and xylene is minimum in all the examined moulding sands.

Acknowledgements

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