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# Evaluation of potential applications of recycled moulding and core sands to production of ceramic building materials

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#### Abstract

This study summarises the properties of ceramic materials containing used moulding sand, from processed and recycled mould and core mixes. The sand preparation procedure involves crushing and separation of metallic parts. Thus obtained substance acts as a substitute for natural quartz sand, commonly used as a leaning agent in ceramic plastic bodies to be formed into ceramic-based construction materials. The study summarises the basic functional parameters, structure and microstructure of ceramic materials made from plastic bodies containing variable qualitative proportions of used sand. The issues addressed in the paper include the potential threats associated with manufacturing and disposal of these types of materials. Potential hazards include atmospheric emissions of hazardous gaseous substances in the form of polycyclic aromatic hydrocarbons (PAHs) as derivatives of organic binders used for manufacturing of moulding and core sand mixes. These substances are formed in the process of combustion of ceramic products or can be produced when heavy metals are released from the ceramic matrix. This process can occur throughout the entire service life of ceramic products under the specific conditions. Applicability of used sand in this disposal scheme is well proved by good parameters of thus obtained ceramic materials and positive test results evidencing the absence of atmospheric emissions of hazardous substances and low-level leaching of heavy metals.

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#### 1. Introduction

The Polish foundry engineering sector typically uses about 1 million tons of good-quality natural silica sands. Silica sand acts as the quartz matrix and when mixed with other substances (binders, hardening agents and organic admixtures), the sand is used for preparing the moulding mix to obtain moulds and cores required for casting operations [1]. However, in typical processes, moulding sand and core sand can be used only once. In practice that means that when the casting process is over, the sand is treated as waste and dumped on open dumping sites, practically with no potential for their re-use in the production cycle [2,3]. This method of disposing of the used moulding sand has become a major environmental problem which might become even worse unless some action is taken promptly. On the other hand, used sand mix

\*Tel.: +48 126172393; fax: +48 126172452. E-mail address: pytel@agh.edu.pl contains significant amounts of silica components, mostly β-quartz, so it seems reasonable to attempt to re-use it outside the foundry engineering sector. A good example here is the manufacturing of construction materials, particularly the technologies that require huge amounts of natural quartz sand. Depending on the type of construction materials, quartz sand can play a different role; in most cases it acts as the source of crystalline quartz [4]. Accordingly, duly processed used moulding sand might become an alternative for natural quartz sand [5,6] In order to be able to effectively recycle the used moulding and core mix to ensure their effective disposal and re-use, it is required that the original properties of natural quartz sand be brought back to the largest extent. The process must involve the crushing of aggregated portions of sand mix formed in the course of knock-out operations, without making the grains finer. Besides, metallic and non-metallic substances, the remnants of the casting operations, have to be removed. However, this method of sand mix processing does not remove the remainders of the binder agents, used for preparing green mix, from the surface of the quartz matrix grains. Hence on the grain surface there is still a thin, adhesive and water-insoluble layer of the binder agent. That is why silica materials obtained from the moulding mix recycled in the manner described before can be used only in those manufacturing technologies that involve their heat treatment [7–13], At high temperatures the remainders of binder agents, particularly of organic origin, are oxidised and thus formed gaseous products shall be released to the atmosphere, together with the flue gas. The main products of the oxidation reaction are CO2 and H2O which are not particularly noxious. however there is also a possibility of atmospheric emission of dioxins and furanes, posing a threat to all living organisms. In the case considered here these substances come in the form of polycyclic aromatic hydrocarbons (PAHs) [14–18]. If the emission levels of potentially harmful products of oxidation of organic binders, mostly polycyclic aromatic hydrocarbons (PAHs), dioxins and furanes, do not exceed the admissible values, those sands might be well used in indicated applications [19,20]. Oxidation of such binders is accompanied by release of a specified amount of thermal energy, becoming and additional source of heat, which should reduce the fuel consumption required to heat a vast mass of feed materials to the specified process temperature. An example of such technology is manufacturing of ceramic construction materials, involving the use of silty minerals, mostly illite and montmorillonite [21]. On account of their mineralogical composition, these materials exhibit good plastic properties and demand huge amounts of process water to achieve the required consistence, adequate to the widely applied plastic forming methods. The presence of large amounts of process water prolongs the drying time, increases the unit costs of production, and what is more, leads to excessive shrinking during the drying, causing deformations and cracks to appear on semi-finished products being dried. All these are consequences of a negative feature of silty minerals, referred to as excessive sensitivity to drying. For that very reason, silty minerals displaying this property should not become the single components of plastic bodies used for manufacturing of ceramic construction materials. It is necessary, therefore, to use leaning additives. As their grains are much coarser than those of silty minerals, such materials lead to reduction of their plasticity and hence of the demand for process water. In the consequence, that reduces the shrinking and helps limit the tendency to defects during the drying process, which adversely affect the quality of finished products. A typical leaning agent, that has been used for that purpose, is natural quartz sand. However, according to the author's hypothesis, the potential leaning materials that can be added are the used moulding and core mix from the foundry processes, in which the amounts of crystalline silica exceeds 95% of their mass [1]. It is reasonable to recommend this group of waste products as the substitute of natural quartz sand in plastic bodies intended for production of ceramic construction materials. However, the re-use of waste moulding and core mix in manufacturing of this type of ceramic materials is possible only when the following requirements are met:

- in accordance with principles of sustainable development, manufacturing and use of ceramic construction materials made from recycled moulding mix should not negatively

- impact on the environment or the impacts produced must not be more serious than when traditional manufacturing technologies are chosen, and
- there is no deterioration of quality of ceramic materials obtained using the recycled materials when compared to materials manufactured from traditional components.

Except above mentioned also leachability of heavy metal ions is important feature if foundry wastes are used as raw material. Literature gives some data dealing with this subject [22–28] which points that leachability test should be performed for waste bearing materials.

# 2. Experimental

#### 2.1. Design of the test procedure

The main objective of this study is to determine the characteristics of ceramic materials made from recycled moulding and core sand. The design of the research programme is based on the assumption that silica products from recycled moulding and core sand should act as substitutes for natural quartz sand, which typically plays the role of a leaning agent in manufacturing of ceramic construction materials [5]. The effectiveness of this approach is evaluated on the basis of a comparative analysis of key functional parameters and microstructure analyses of the two types of ceramic products: the reference material and experimental products differing in quality of the recycled materials. Further evaluation of reused moulding and core mix as alternatives for natural quartz sand involves the analysis of potential environmental impacts associated with manufacturing and use of ceramic building materials containing used sands. That is why a qualitative EGA-evaluated gas analysis is performed of the gaseous phase emitted to the atmosphere during the burning of ceramic materials. Besides, the authors tested the leaching of selected heavy metals, which might potentially get released from the ceramic matrix during the entire service life of ceramic components.

#### 2.2. Materials

The main components of ceramic products, both the reference and experimental material mixes, is silty mineral in the form of Tertriary Krakowiec clay (IKK). The conventional leaning agent in component mix to prepare the reference material is the natural quartz sand (PK-GL). This sand is used to obtain the moulding and core sand in the foundry plants which later provided the used moulding and core sand for the purpose of the research programme. In the case of experimental products, natural sand is replaced by an equivalent amount of silica material from the processing of used mould mix from different foundry plants, using different production technologies and different binders to prepare the fresh sand mix.

Particular batches of ceramic products used in the experimental programme contain four types of recycled materials

- mixture of moulding and core sand containing an organic binder in the form of furane and phenol-formaldehyde resins (sample depiction WK-II),
- mixture of moulding and core san containing bentonite as a mineral binder (sample depiction WK-III),
- used moulding sand from shell moulding processes containing hydrolysed ethyl silicate as an inorganic binder (sample depiction WK-IV), and
- used mix containing water–glass (sample depiction WK-V).

These are components of plastic mixes which were further utilised to manufacture the ceramic products in laboratory conditions.

#### 2.3. Composition of plastic mixes

Underlying the composition of the plastic bodies is the assumption that these mixes used to obtain both the reference and experimental products should contain the same proportion of the leaning agent – 30% by weight. That is why the composition of those mixes is identical in quantitative terms, the differences between them being qualitative. Qualitative differences between the compositions of experimental products prepared in laboratory conditions, with respect to the reference material (WK-I), are achieved by substituting adequate amounts of natural silica sand by the silicate material from the recycled moulding and core mixes. Samples of ceramic materials obtained with the use of waste moulding masses are depicted as given in point Section 2.2.

# 2.4. Sample preparation

All mix components, carefully weighted to the predetermined proportion, are first dry-homogenised, then water is added in the amount ensuring the 'normal consistency', to meet the requirements of the sample forming process. Mixes prepared in that manner are then subjected to further homogenisation. For that purpose, they are placed inside tightly closed containers to prevent humidity variations, and kept in those conditions for 7 days. Afterwards all mixes are subjected to mechanical processing with the use of a laboratory worm press, to make them fully homogenous. Thus prepared component mixes are used for forming two types of laboratory samples: cubic ones with the nominal edge length 50 mm and those shaped like rectangular prisms  $60 \times 35 \times 10 \text{ mm}^3$ , further referred to as bricks. Afterwards the samples are dried in a two-cycle process: drying in natural conditions at room temperature and in the atmosphere of the ambient air and drying in a thermal chamber enabling the control of temperature in the range 20–105 ( $\pm$ 5) °C and of the flow rate of the drying medium (i.e. dry air), in accordance with the predetermined programme. After drying, the samples are sintered in laboratory conditions to establish their final properties, in an electric furnace with an incorporated microprocessor control system ensuring most precise control of temperature fluctuations and stabilising the temperature throughout the entire process of thermal treatment.

Burning is conducted at two different temperatures: 960 and 1050 °C. Finally, we obtain 2 batches of ceramic samples and five series in each batch, differing in the mix composition. The burning process in the laboratory conditions is shown as sample sintering curves in Fig. 1.

#### 3. Methods

#### 3.1. Basic processing parameters and physical features

During sample processing, basic parameters were monitored and controlled on all subsequent stages: sample preparation, drying and sintering. Parameters which were controlled were: the amount of process water  $W_z$ , the extent of shrinking during drying  $S_s$  and burning  $S_w$ , as well as the total shrinkage  $S_c$ . In accordance with the harmonised standard PN-EN 771 [29], with the applicable sections of the harmonised standard PN-EN 772 [30], compressive strength  $f_b$  and water absorption  $w_m$  were also tested. In accordance with the methodology set forth in the standard PN-B-12016:1970 [31], the resistance of ceramic samples to low temperatures, to negative impacts of marl grains and of soluble salts were tested. Beside the scope of the relevant standards, the open porosity  $P_o$  and bulk density  $\rho_o$  were established by the hydrostatic weighing method.

#### 3.2. Microstructural examinations

In order to explain the differences in functional qualities of ceramic products containing used moulding and core mixes, the author conducted the microstructure tests using a scanning electron microscope JOEL (model JSM 5400). Prior to the tests the samples were subjected to the process of etching in 5% solution of HF, to better expose the crystalline phases. Thus prepared samples were then covered with thin carbon layer and observed under the scanning microscope.

#### 3.3. Mass spectrometry analysis of gaseous products

The qualitative analysis of gaseous products of ceramics burning is performed in the specialist set-up comprising a thermal weight TA Instruments (model SDT 2960) integrated with a quadrupole mass spectrometer STA of the Thermostar type (Balzers

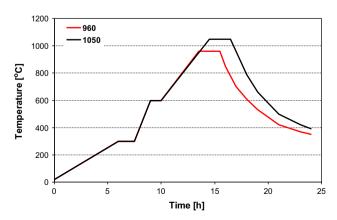


Fig. 1. Sample sintering curves.

Instruments). This set-up enables the recording of thermal characteristics (DTA and TG) and the qualitative analysis (EGAevaluated gas analysis) of the gaseous phase produced during the sample heating. The feed material for analytical samples are dried brick-shaped elements prepared in laboratory conditions, made from plastic bodies containing waste from foundry plants, which were not given any previous heat-treatment. Tests are run on samples weighing about 60 mg, crushed in an agate mortar to achieve the grain size below 63 µm. Measurements are taken in the atmosphere of synthetic air, being a mixture of nitrogen and oxygen, flowing through the chamber at the rate of 100 cm<sup>3</sup>/min. Measurements involve the online recording of the sample mass (TG curve) assuming the thermal weight sensitivity 1 µg, and of thermal effects (DTA curve) and EGA curves of particular gaseous components. During the measurements the samples are heated in the temperature range 20–1000  $^{\circ}$ C at the rate of 10  $^{\circ}$ C/min.

The emission levels of selected polycyclic aromatic hydrocarbons during full scale technological trial of ceramic bodies incorporating waste moulding masses firing were measured with the use of mobile laboratory equipped with automatic analysers which were operating on the basis of gas chromatography principles.

# 3.4. Heavy metals leaching test

At that stage tests are performed to determine the level of selected metal leaching from the burned ceramic materials containing the waste moulding and core sand, in comparison to the reference samples. Tests are run on eluats prepared in accordance with the requirements specified in the harmonised standard PN-EN 12457-2 [32] and the procedure to determine the heavy metals contents and interpret the data meets the criteria set forth in the harmonised standard PN-EN ISO 11885 [33]. The amounts of trace elements in eluats are determined by the ICP-AES method (atomic emission spectrometry with induction excited plasma),

using an emission spectrometer ICP (Perkins-Elmer, model Plasma 400). Measurements are taken to establish the trace amounts of chromium, zinc, cadmium, lead, nickel, arsenic, molybdenum, barium and copper.

#### 4. Results

# 4.1. Characteristics of ceramic samples

Results are compiled in Table 1.

#### 4.2. Microstructure of ceramic products

The most typical microstructure images are shown in Fig. 2.

#### 4.3. Environmental impact assessment

Results of tests performed to check the functional quality of investigated materials have relevance only as the preliminary data in assessing whether used moulding and core sand mixes can be utilised in manufacturing of ceramic-based construction materials. Functional quality becomes a necessary yet still insufficient criterion in assessing their applicability.

Another factor determining the applicability of the used mould and core mixes, containing different binder agents, is the absence of negative environmental impacts of this technological solution. Accordingly, the required tests include measurements of potentially hazardous gaseous emissions involved in the manufacturing technology, particularly the ceramic burning processes and leaching of heavy metals as it takes place throughout the whole service life of ceramic construction materials. Tests were run on selected ceramic materials obtained in laboratory conditions.

Test data in the form of TG, DTA and EGA graphs are shown in Figs. 3–5.

Properties of mixes and ready ceramic materials.

Parameter	Sample designation							
	WK-I	WK-II	WK-III	WK-IV	WK-V			
W <sub>z</sub> , %	17.7	17.0	17.7	17.6	19.2			
S <sub>s</sub> , %	6.3	5.2	6.1	6.1	6.2			
Burning temperatu	re 960 °C							
S <sub>w</sub> , %	0.2	0.3	0.3	0.1	0.1			
S <sub>c</sub> , %	6.5	5.5	6.4	6.2	6.3			
w <sub>m</sub> , %	$13.6 \pm 0.67^{(a)}$	$15.2 \pm 0.48^{(a)}$	$12.9 \pm 0.71^{(a)}$	$15.6 \pm 0.53^{(a)}$	$15.3 \pm 0.49^{(a)}$			
$\rho_{\rm o}$ , kg/dm <sup>3</sup>	$1.9 \pm 0.02$	$1.86 \pm 0.01$	$1.90 \pm 0.02$	$1.85 \pm 0.0.01$	$1.84 \pm 0.0.01$			
Po, %	$25.9 \pm 0.41$	$28.4 \pm 0.13$	$24.5 \pm 0.23$	$29.0 \pm 0.27$	$28.1 \pm 0.59$			
$f_{\rm b}$ , MPa	$36.9 \pm 2.61$	$31.3 \pm 3.05$	$38.1 \pm 2.87$	$40.1 \pm 2.78$	$28.9 \pm 3.65$			
Burning temperatu	re 1050 °C							
S <sub>w</sub> , %	0.4	0.6	0.7	0.5	0.9			
S <sub>c</sub> , %	6.7	5.8	6.8	6.6	7.1			
w <sub>m</sub> , %	$12.7 \pm 0.52$	$13.8 \pm 0.39$	$11.3 \pm 0.69$	$13.9 \pm 0.45$	$13.5 \pm 0.57$			
$\rho_{\rm o}$ , kg/dm <sup>3</sup>	$1.92 \pm 0.02$	$1.89 \pm 0.01$	$1.93 \pm 0.02$	$1.88 \pm 0.02$	$1.87 \pm 0.02$			
Po, %	$24.3 \pm 0.43$	$26.1 \pm 0.39$	$21.8 \pm 0.33$	$26.1 \pm 0.51$	$25.3 \pm 0.43$			
$f_{\rm b}$ , MPa	$43.9 \pm 2.35$	$21.4 \pm 3.05$	$43.2 \pm 3.51$	$40.7 \pm 2.76$	$38.4 \pm 1.55$			

 $<sup>^{(</sup>a)} \pm$  - standard deviation.

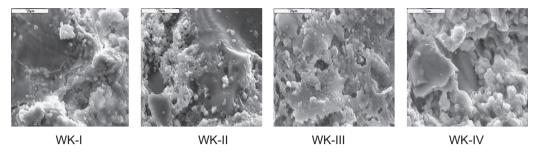


Fig. 2. Microstructure of ceramic samples.

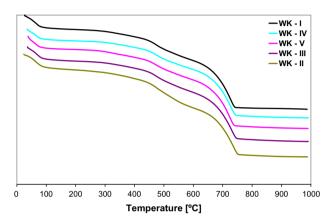


Fig. 3. TG curves of the tested samples.

In Table 2 the concentrations of selected gaseous pollutants in flue gases emitted during the full scale trial into the environment by tunnel furnace used for firing of the ceramic bodies incorporating waste moulding sand are presented.

Results of heavy metals leachability expressed as the average of three determination tests are summarised in Table 3. Apart from measurement data, Table 3 gives also the critical values of leaching levels specified in the regulation RMGiP [34], which deals with criteria and procedures for admission of wastes to be dumped on the open-space dumping sites. That applies to three categories of wastes: neutral wastes, other than hazardous or neutral and hazardous. Results of metal determination tests reveal that the level of leaching of these elements slightly exceeds the critical levels for the category of neutral wastes, yet these values are still much lower than the admissible levels specified the two remaining categories of wastes: hazardous waste and other than hazardous and neutral.

### 5. Results discussion

Experimental data summarised in Table 1 lead us to the conclusion that the addition of silicate material from recycled moulding or core sand to the component mix does not adversely impact on technological parameters or functional features of finished ceramic products. This component, just like natural silica sand, acts as leaning agent to be added to the silty mineral. Ceramic plastic bodies containing silica minerals display most favourable rheological behaviour, allowing for smooth sample forming and thus obtained samples of ceramic products do not exhibit any external defects, even after drying and burning. As

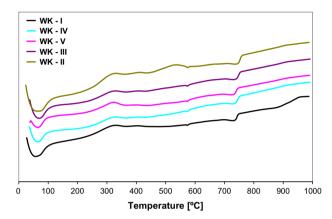


Fig. 4. DTA curves of tested samples.

regards the properties of manufactured ceramic materials and their functional features, they satisfy the regulatory criteria to be met by porous-structured ceramic materials. Comparison of functional parameters of ceramic materials containing recycled moulding or core sand (samples WK-II–IV) and those displayed by the reference sample (WK-I) reveals that the properties of the two products are similar. The presence of those additives does not effect on properties of ceramic materials associated with durability at low temperatures (frost-resistance) and resistance to negative impacts of marl grains and of soluble sulphate salts, which, if present, usually causes efflorescence on the surface of the material.

These findings are well corroborated by microstructure test data. The analysis of microstructure images of the types of materials does not reveal any major differences and porosity of the two samples is similar, too. It is reasonable to suppose, therefore, that the waste materials from foundry plants act as inert additives which do not react chemically with the remaining components of the ceramic body, or which enter into chemical reaction in a minor degree only. Such behaviour is most characteristic of a leaning agent added to silty minerals in the form of natural silica sand. As regards the functional qualities of investigated ceramic products, it is reasonable to state that silica minerals obtained from recycled moulding or core sand is a good alternative to natural silica sand.

The results of analyses performed by the thermal methods (Figs. 3 and 4) reveal a marked similarity between the TG and DTA plots for all investigated samples, which is indicative of similar character of chemical reactions and physical transformations occurring when the samples are heated even though the samples' compositions may differ in qualitative terms. A thorough analysis of the TG plots reveals a continuous, not sharp, decrease

Table 2
Emission of volatile organic compounds in flue gases.

Compound	Unit	Emission value	Acceptable value	
		Measurement 1	Measurement 2	
Benzene	kg/h	0.6545	0.3718	0.97
Toluene	kg/h	0.2318	0.1584	1.12
$\sum$ Xylene	kg/h	0.0578	0.0704	0.63
$\sum$ Aromatic hydrocarbons	kg/h	0.9533	0.6132	7.79
$\sum$ Alifatic hydrocarbons	kg/h	0.1902	0.2101	2.72

Table 3 Leaching of heavy metals from ceramic samples containing used moulding and core sand.

Analysed component	Sample designation					Admissible critical leaching levels liquid/solid phase = $10  \text{L/kg}$ for:			Reference data according to	
	WK-I	WK-II	WK-III	WK-IV	WK-V	Neutral wastes	Other than neutral and hazardous wastes	Hazardous wastes	[13]	[28]
	Leaching of the given component mg/kg of dry mass								mg/L	
Chromium	0.47	0.17	0.16	0.14	0.41	0.5	10	70	_a	0.027
Zinc	0.82	0.83	0.43	0.93	0.20	4	50	200	0.013	0.380
Cadmium	0.06	< 0.01	0.01	< 0.01	< 0.01	0.04	1	5	0.015	0.003
Lead	0.52	0.43	0.77	0.81	0.58	0.5	10	50	_a	0.063
Nickel	0.14	0.09	0.25	0.47	0.30	0.4	10	40	0.061	0.048
Arsenic	1.05	1.11	1.64	1.25	0.77	0.5	2	25	_(a)	0.047
Molybdenum	1.39	1.73	0.71	0.97	0.81	0.5	10	30	0.422	_a
Barium	0.18	0.21	0.16	0.18	0.14	20	100	300	0.020	0.707
Copper	0.08	< 0.01	< 0.01	< 0.01	< 0.01	2	50	100	0.025	0.148

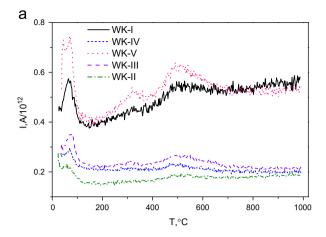
<sup>&</sup>lt;sup>a</sup>No data available.

of the mass of samples. The intensity of this process differs, the lower intensity is registered in the temperature range up to 450 °C. From 500 °C the process intensity gets higher or even higher at 670 °C, right through to 700 °C when the process is over. These effects correspond to endothermic effects registered on the DTA plots, indicative of hydration of ceramic body components and dehydroxylation of silty minerals. The other effect registered on DTA curves is somewhat blurred, which can mean that the silty mineral used in the experiments contains minerals differing in their internal structure and that is why their de-hydroxylation temperatures may be different. A most striking point is the absence of high-temperature exothermic effects to be revealed on DTA curves, typically associated with crystallisation of newly-formed phases. This absence can be due to too low temperatures applied during the burning process for new phases (e.g. mullite) to synthesise.

The analysis of EGA plots (Fig. 5) for samples containing additives in the form of used moulding sand reveals a good similarity between their patterns. Minor differences are associated only with quantitative aspects relating to differences in the volume of released vapour (Fig. 5a) or carbon dioxide (Fig. 5b) in the analysed ceramic products. In the case of CO<sub>2</sub>, these differences are attributable to variable proportions of organic binder residues left in the moulding sand, whilst in the case of H<sub>2</sub>O the differences may be indicative of the presence of other forms of water, apart from OH<sup>-</sup> groups, associated with the structure of silty minerals. Assuming the required precision and discrimination capability of the applied measurement method, test results reveal no emissions

of hazardous substances, such as polycyclic aromatic hydrocarbons (PAHs), that could be threatening to the environment. Similar results have been obtained in experimental programs reported elsewhere [19]. The absence of flammable components, like CO, or hydrocarbons (called organic carbon, mainly CH<sub>4</sub>) as well as harmful toxic wastes, like dioxine or furane shows that the process parameters, like air intake and time of firing were set correctly, allowing all the organic resin, as well as their degradation products to burn completely. Additionally, absence of SO<sub>3</sub> is positive, because in case of sulphur bearing resins, it won't cause additional contamination of flue gases. Results obtained are in agreement with literature data [12]. The results therefore can be treated as positive, evidencing the absence of negative environmental impacts of manufacturing technologies of ceramic-based construction materials containing used moulding or core sand mix. Results shown above were additionally verified during full scale technological trial. Ceramic bodies were manufactured using waste moulding sand as a raw material in ceramic furnace used for bricks firing. Table 2 presents the concentration of harmful gaseous compounds in flue gases from furnace used in trial test. Data show that the level of emission of harmful substances is lower comparing to acceptable values, what is in agreement with literature data [16].

Results of experiments performed to test the extent of leaching of selected heavy metals from the ceramic matrices of particular types of ceramic materials are summarised in Table 3. Tests reveal that the level of leaching of these elements slightly exceeds the critical levels for the category of neutral wastes, yet these values



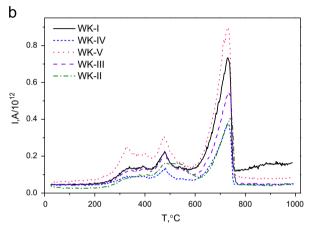


Fig. 5. EGA curves for gaseous products: (a) for water and (b) for carbon dioxide.

are still much lower than the admissible levels for the two remaining categories of wastes: hazardous waste and other than hazardous and neutral. Moreover, it can be concluded, that similarly to published data [13,28], among heavy metals analysed in present paper and showed in Table 3, slight increase in leachability comparing to control sample (WK-I) can be observed only in case of Pb, Ni and As. In case of other heavy metal ions, the leachability stays on the same level, or even decrease.

All things considered, the proposed solution whereby natural silica sand to be used as a mix component is replaced by silicate material from the recycled moulding and core sand allows for manufacturing of good-quality ceramic materials provided the process regimes are strictly observed. Those materials show mechanical properties typical for construction materials and also fulfil requirements for durability in low temperatures. Also there is no negative action of marl or soluble sulphates.

Furthermore, environmental impacts observed during the manufacturing and the service life of ceramic construction materials containing used moulding sand are similar to those registered when traditional materials are used. The results indicated that the bricks incorporating foundry wastes present sufficient compressive strength for civil construction, which is the same of the traditionally bricks produced with only red clay. Furthermore, its production cost will be less that of the traditional bricks, since less clay and natural quartz sand are used in its production.

#### 6. Conclusions

Results of tests carried out to explore the potential applications of recycled moulding and core sands to the manufacturing of ceramic construction materials lead us to the following conclusions:

- Disposal of used moulding sand in manufacturing of ceramic materials for the construction sector is possible provided the wastes are first subjected to the processing treatment involving the crushing, homogenisation and removal of the casting remnants.
- From the standpoint of process technology, these waste materials can become a component of plastic bodies for manufacturing of construction materials, in which the recycled sands act as leaning additive.
- Waste materials analysed in this study in combination with the widely applied clayey minerals are used to manufacture:
- plastic bodies exhibiting excellent rheological properties while the finished products do not have any external defects after drying and burning, and
- high-quality ceramic products having good functional features meeting the criteria set forth in the relevant standards for ceramic materials with porous shards.
- Waste materials considered in this study contain also flammable organic substances, such coal and remainders of organic binders, so their calorific value is relatively high. These components may act as 'secondary fuels' which are burnt during the burning stage, releasing heat, thus reducing the fuel demand required for the burning processes.
- Environmental impacts observed during the manufacturing and the service life of ceramic construction materials containing used moulding sands are similar to those registered when traditional materials are used. It means that the level of heavy metals leachability, as well as emission of harmful gaseous substances, heterocyclic aromatic hydrocarbons among them, are lower comparing to acceptable limits.
- From the standpoint of process technology, these waste materials can become a component of ceramic plastic bodies for manufacturing of construction materials, in which the recycled sands act as leaning admixtures.

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#### References

- J.L. Lewandowski, Tworzywa na formy odlewnicze, Wydawnictwo Akapit, Kraków, 1997.
- [2] J.L. Lewandowski, J. Dańko, R. Dańko, Used Foundary Sands. Characteristic and Classification, Archives of Foundry Engineering 2 (3) (2002) 91–96.

- [3] W. Solarski, J. Zawada, J.L. Lewandowski, J. Dańko, Ecological characteristic of core sand in phenol CO<sub>2</sub> process, Acta Metallurgica Slovaca 8 (2002) 59-63.
- [4] J. Małolepszy, Materiały budowlane, Podstawy technologii i metody badań Uczelniane Wydawnictwa Naukowo-Dydaktyczne AGH, Kraków, 2004 (in Polish).
- [5] Projekt wynalazczy p.t. "Sposób przetwarzania i wykorzystania zużytych mas odlewniczych", zgłoszenie patentowe nr P-389 371 z mocą od dnia 23.10.2009.
- [6] Z. Pytel Properties of ceramic materials obtained with addition of foundry scrap materials V Konferencja Naukowo-Techniczna, MATBUD 2007, Kraków 2007 s. 447-454 (in Polish).
- [7] F. Pezarski, Z.b. Maniowski, A. Baliński, I. Izdebska-Szanda, E. Smoluchowska, Attempts at utilization of the used moulding and core sands in manufacture of building ceramics, in: Proceedings of International Conference on Modern Foundry Technologies – Environmental Protection, Kraków, 6-8 września, 1995, s. 56-60 (in Polish).
- [8] U. Lahl, Recycling of waste foundry sands, Science of Total Environmental 114 (1992) 185–193.
- [9] C.M.F. Vieira, S.N. Monteiro, Incorporation of solid wastes in red ceramics – an updated review, Revista Materia 14 (3) (2009) 881–905.
- [10] J. Brandstetr, J. Rusin, Use of waste molding sands in various branches of industry from the view point of the customer, Slevarenstvi 48 (7–8) (2000) 320–323.
- [11] E. Richter, B. Gemende, H. Schone, Technolgies for reuse and utilization of used foundry sands, Environmental Protection Engineering 25 (3) (1999) 47–57.
- [12] A Czernichowski, Z. Ferenc, J.W. Wandrasz Waste, molding sands as a source of raw materials, Ceramika-Materiały Ogniotrwałe 50 (2) (1998) 46–49
- [13] R. Alonso-Santurde, A. Coz, N. Quijorna., J.R. Viguri, A. Andrés, Valorisation of foundry sand in clay bricks at industrial scale, Journal of Industrial Ecology 14 (2) (2010) 217–230.
- [14] K. Srogi, Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: a revive, Environmental Chemistry Letters 5 (2007) 179–208.
- [15] R.S. Dungan, Polycyclic aromatic hydrocarbons and phenolics in ferrous and non-ferrous waste foundry sands, Journal of Residuals Science and Technology 3/4 (2006) 203–209.
- [16] H.-H. Liu, H.-H. Yang, Ch.-D. Chou, M.-H. Lin, H.-L. Chen, Risk assessment of gaseous/particulate phase PAH exposure in foundry industry, Journal of Hazardous Materials 181 (2010) 105–111.
- [17] S. Bonassi, F. Merlo, R. Puntoni, Bladder cancer and occupational exposure to polycyclic aromatic hydrocarbons, International Journal of Cancer 44 (1989) 648–651.
- [18] F. Perera, et al., Detection of polycyclic aromatic hydrocarbons-DNA adducts in white blood cells of foundry workers, Cancer Research 48 (1988) 2288–2291.

- [19] Z. Pytel, Production and exploitation of ceramic building materials having founder waste materials, Archives of Foundry Engineering 8 (2) (2008) 49–55 (Special Issue).
- [20] Z. Pytel, Application of wastes from foundry processes for manufacturing ceramic building materials – part I, Ceramic Materials 61 (3) (2009) 201–207.
- [21] B. Stefańczyk, Budownictwo ogólne, t. 1: Materiały i wyroby budowlane, rozdz. 3: Ceramika budowlana, Wyd. Arkady, Warszawa, 2005, (in Polish)
- [22] R.E. Miquel, J.A Ippolito, A.A. Porta, R.B.B. Noriega, R.S Dungan, Use of standarized procedures to evaluate metal leaching from waste foundry sands, Journal of Environmental Quality 42 (2) (2013) 615–620.
- [23] An. Deng, Contaminants in waste foundry sand and its leachate, International Journal of Environmental and Pollution 38 (4) (2009) 425–443.
- [24] R.S. Dungan, N.H. Dess, The characterization of total and leachable metals in foundry molding sands, Journal of Environmental Management (2008) 90 (1) (2009) 539–548.
- [25] S. Ji, L. Wan, Z. Fan, The toxic compounds and leaching characteristics of spent foundry sands, Water Air and Soil Pollution 132 (3–4) (2001) 347–364.
- [26] J. Kargulewicz, M. Holtzer, The elution of have metals (Cd, Cu, Pb and Zn) from used moulding sands vs conditions of the elution process, Archives of Metallurgy 46 (1) (2001) 33–42.
- [27] R. Siddique, G. Kaur, A. Rajor, Waste foundry sand and its leachate characteristic, Resources Conservation and Recycling 54 (2010) 1027–1036.
- [28] Y. Zheng, Preparation, properties, formation mechanism of autoclaved bricks from waste foundry sand, Applied Mechanics and Materials 174– 177 (2012) 697–700.
- [29] PN-EN 771-1: 2006: Wymagania dotyczące elementów murowych, cz. 1: Elementy murowe ceramiczne.
- [30] PN-EN 772-1: 2001/Ap1: 2002: Metody badań elementów murowych, Część 1: Określenie wytrzymałości na ściskanie.
- [31] PN-B-12016: 1970: Wyroby ceramiki budowlanej, Badania techniczne.
- [32 [PN-EN 12457-2: 2006: Charakteryzowanie odpadów, Wymywanie. Badanie zgodności w odniesieniu do wymywania ziarnistych materiałów odpadowych i osadów, cz. 2: Jednostopniowe badanie porcjowe przy stosunku cieczy do fazy stałej 10 l/kg w przypadku materiałów o wielkości cząstek poniżej 4 mm (bez redukcji lub z redukcją wielkości).
- [33] IPN-EN ISO 11885: 2009: Jakość wody Oznaczanie 33 pierwiastków metodą atomowej spektrometrii emisyjnej z plazmą wzbudzaną indukcyjnie.
- [34] Rozporządzenie Ministra Gospodarki i Pracy z dnia 7 września 2005 r., Dziennik Ustaw Nr 186, Poz. 1553.