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Influence of the Changes of the Structure of Foundry Bentonites on Their Binding Properties

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In this paper, the effects of the examination of the structure of calcium bentonites, activated by sodium carbonate, applied in the foundry industry as a binding agent for moulding sands, subjected to the effects of high temperature, were presented. The examination was conducted with the use of the infrared spectroscopy (FTIR) and X-ray analysis (XRD). In addition, the montmorillonite contents in the bentonite sample was determined with the use of the modern, Cu(II)-TET complex method and the technological properties of moulding sands containing the examined bentonites, such as: compactability, permeability, compression strength were examined.

Keywords: bentonite, foundry industry, determination of montmorillonite, FTIR analysis, X-ray analysis.

1. INTRODUCTION

Bentonite is one of the main binding materials used in a metal foundry practice for making moulds. In addition, bentonites are applied in other fields such as: drilling, food industry, crude oil processing. One of the most important parameters of foundry bentonites is their thermal resistance and strength at elevated temperatures [1–5]. A casting mould made of moulding sands with bentonite is poured with liquid metal alloy of a temperature approaching 1550 °C. The main component, which decides on the binding properties and thereby on the bentonite thermal resistance, is montmorillonite.

Montmorillonite belongs to the mineral group called smectites. These are laminar hydroxyaluminosilicates of aluminium, iron and magnesium, which are marked by packets 2 : 1 (two tetrahedrite silica-oxygen layers, and the oktahedrite metal-oxygen layer between them – Fig. 1) [6–9]. Exchangeable cations: Na^+, K^+, Ca^{2+}, NH^{4+} and others, as well as water particles are between the packets. A distance between packets in the montmorillonite structure depends on the exchangeable cation and increases along with a water saturation. Water stored in interpacket spaces causes montmorillonite swelling. Due to this, bentonites obtain colloidal and mechanical properties, allowing to make casting moulds. The bentonite ability to cations exchanges is being used for a sodium activation of calcium bentonites for foundry needs. A calcium bentonite activation is performed by means of sodium carbonate according to the following reaction:

$$Na_2CO_3 + Ca^{2+} \rightarrow 2Na^+ + CaCO_3.$$

The effect of this reaction is a significant increase of water absorption and an improvement of mechanical properties by the so-called activated bentonite. Calcium carbonate presence is characteristic for the activated bentonite. Under an influence of a temperature montmorillonite undergoes various transformations, which are the reasons of the loss of its binding properties.

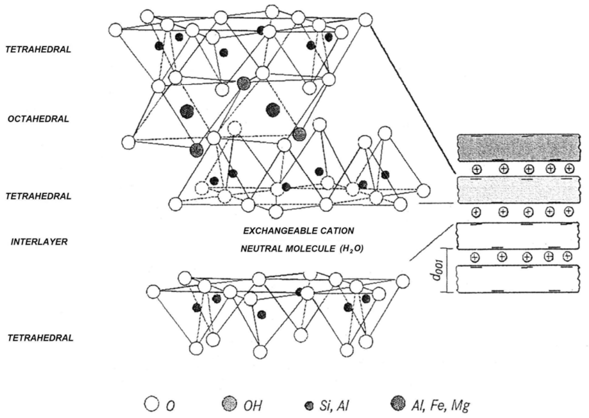

Fig. 1. Structure of bentonite [13]

Thus, the following processes can occur: dehydration, dehydroxylation, decomposition (transformation of a crystal structure into an amorphous form), recrystallization (once more formation of a crystal structure) [1, 3, 14, 15, 17, 19]. In the case of the activated bentonite an effect related to the $CaCO_3$ decomposition can occur [7, 10].

The purpose of this research was the determination of the influence of the temperature on structural changes occurring in two foundry bentonites: Special from company: ZGM "Zębiec" and S-Bentonite from company: S&B Industrial Minerals GmbH, activated with sodium carbonate, on the binding properties of the bentonite by determining the montmorillonite contents in the samples, using the copper complex adsorption method Cu(II)-TET. The structural analyses were conducted with the use of infrared spectroscopy (FTIR) and X-ray analysis (XRD).

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2. THE RESEARCH METHODOLOGY

In addition, the compactability, permeability and compression strength in the moulding sands, conducted with the use of the examined bentonites (bentonite contents – 8 %, compactability – around 45 %, water contents – around 2.5 %) were determined.

FTIR studies were carried out using Excalibur spectrometer equipped with a standard DTGS detector. All standards and technological samples were prepared using KBr technique. The spectra were collected with 4 cm^{-1} resolution in transmission mode and were taken in the frequency region from 4000 cm^{-1} to 400 cm^{-1}. The FTIR spectra were recorded for bentonite samples hold at temperatures 500, 550, 700, 900, 1000, 1100 and 1200 °C for 1 hour [5].

The X-ray analysis of the samples was conducted with the use of the Kristalloflex 4H type diffractometer, manufactured by Siemens, for the following conditions: anode voltage – 35 kV, beam current – 20 mA, anode – CuK$_{\alpha}$ = 1.54 Å. Database: ICDD PDF-2. The X-ray diffractograms were recorded for bentonite samples hold at temperatures 500, 700, 900, 1000, 1100 and 1200 °C for 1 hour.

The spectrophotometric method of the Cu(II)-triethylentetraamine complex (Cu-TET) was used to determine the montmorillonite contents in bentonites. The bentonite samples were heated to temperatures 500, 600 and 700 °C (heating rate – around 20 °C/min) respectively and were kept at the applied temperature for the period of 1 hour [6].

The technological analysis was conducted on the standard, cylinder shaped, ∅ 50 mm × 50 mm blocks, with the use of the LRuE-2e moulding sands analysing apparatus, manufactured by Multiserw Morek. The prepared blocks were heated in the furnace until they reached the specified temperature (300, 550, 700 °C) and then they were heated for the period of 1 hour; the heating rate was similar to the heating rate of pure bentonites. The samples were cooled down together with the furnace.

3. RESULTS AND DISCUSSION

3.1. XRD analysis

From the conducted phase analysis it emerged, that the analysed smectite collapsed at the temperature of 700 °C (the disappearance of the diffraction peaks (001) was observed) and its structure was totally destroyed at the temperature of 900 °C; that was proven by the disappearance of the remaining reflexes coming from the montmorillonite/beidellite phase (the graphic mark on the diffractogram).

The phase composition of the initial sample of the S-Bentonite comprised of: diocathedric sodium smectite (montmorillonite, beidellite), quartz and cristobalite SiO_2, calcite $CaCO_3$, as well as the (Na, Ca)(Si, Al)$_4$O$_8$ phases plagioclase (most likely albite). The phase composition of the initial sample of the Special bentonite was similar and comprised of sodium smectite (montmorillonite, beidellite), quartz SiO_2 and (Na, Ca)(Si, Al)$_4$O$_8$ plagioclase.

At the temperature of 900 °C, as a result of the smectite decomposition, the $SiO_2{\cdot}H_2O$ phase, also called the cristobalite opal appeared. In the sample of the S-Bentonite, at the temperature of 900 °C, the cristobalite disappeared. Above 1000 °C – three phases are present in both samples: quartz, cristobalite opal and albite. The diffractograms for both analysed bentonites are presented in Figs. 2 and 3.

The interplanar distances d_{hkl} for the examined casting bentonites are presented in Table 1. Within the limits of the basic temperature up to 700 °C, the values, which are characteristic for the montmorillonite structure were present; whereas beginning from 900 °C, the values for cristobalite opal, which appeared as a result of the montmorillonite decomposition, were present [10].

Table 1. Typical peaks and interplanar distances of two analysed bentonites

Temperature [°C]	S-Bentonite		Special	
	2Θ [°]	d_{hkl} [nm]	2Θ [°]	d_{hkl} [nm]
room	7.036	1.256	6.876	1.285
500	8.794	1.005	8.794	1.005
700	8.794	1.005	8.794	1.005
900	21.738	0.408	21.738	0.408
1200	21.738	0.408	21.738	0.408

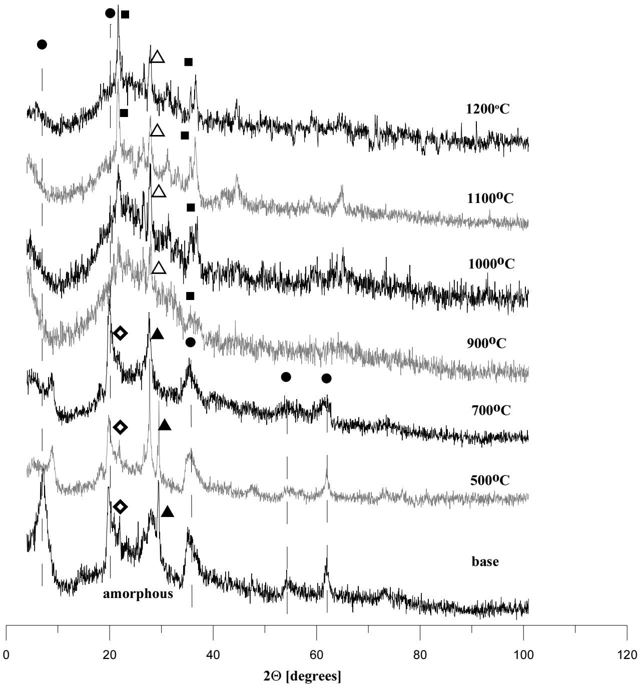

Fig. 2. X-ray diffractograms for S-Bentonite

3.2. FTIR analysis

In the analysed bentonites, two ranges of wavelengths, characteristic for those materials, can be seen in the spectrum obtained with the use of the FTIR method: 400 cm^{-1} – 1800 cm^{-1} and 3000 cm^{-1} – 4000 cm^{-1}.

The FTIR spectrum, obtained for the S-Bentonite is presented in Fig. 4 and the FTIR spectrum, for the Special bentonite, for the wavelength range 400 cm^{-1} – 1800 cm^{-1} is presented in Fig. 5. The identified, characteristic peaks for all bentonites, within the analysed range of wavelengths, are presented in Table 2.

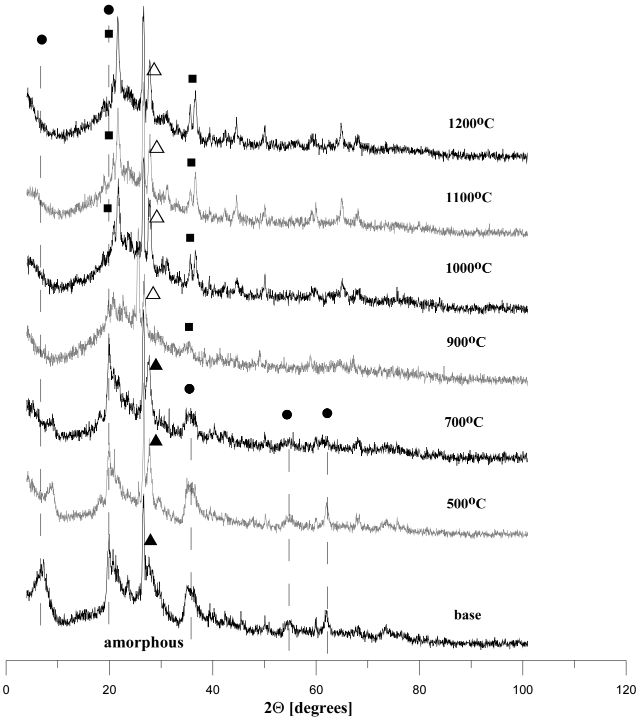

Fig. 3. X-ray diffractograms for Special bentonite. Phases: ● – montmorillonite, baidellite; ■ – cristobalite opal [SiO_2xH_2O]; ▲ – albite [$(Na, Ca)(Si, Al)_4O_8$]; Δ – albite [$NaAlSi_3O_8$]; ◊ – cristobalite

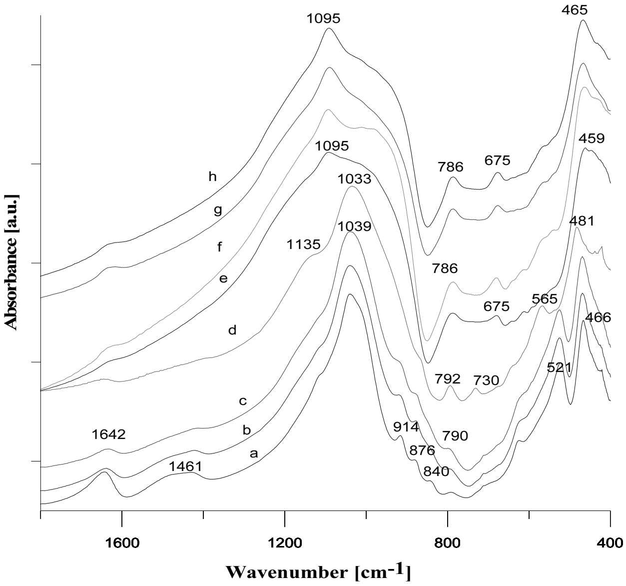

Fig. 4. IR spectrum of S-Bentonite in the wave numbers range: 1800 – 400 cm^{-1} before (a) and after heating to the following temperatures: b – 500 °C, c – 550 °C, d – 700 °C, e – 900 °C, f – 1000 °C, g – 1100 °C, h – 1200 °C

Bentonite held at temperatures 500 °C – 550 °C loses the adsorbed water both from the surface (dehydration) and from the interpacked spaces (Ist stage of dehydroxylation), which causes either a decreased intensity or a complete disappearance of bands at wave numbers of app. 3450 cm^{-1} and 1640 cm^{-1} [1, 14]. Such changes are visible in each investigated bentonite. Vibrations originated from OH group, at the wave number app. 3630 cm^{-1} are still visible.

Further temperature increase causes numerous changes in bentonites. At the temperature of 700 °C the band at a wave number of 3630 cm^{-1} (OH group) decays. This is related to the total (IInd stage) dehydroxylation of bentonite, i. e. the interpacked water loss [1, 14]. The Si-O band at the wave number 1114 cm^{-1} is shifted to 1140 cm^{-1} with a simultaneous intensity increase.

At temperature of 700 °C the band characteristic for carbonate ions decays. The band 915 cm^{-1} originated from the Al-Al-OH bond – is not seen any more in the spectrum of bentonite heated to this temperature. At temperature of 500 °C the band in the vicinity of 843 cm^{-1} (Al-Mg-OH) disappears also.

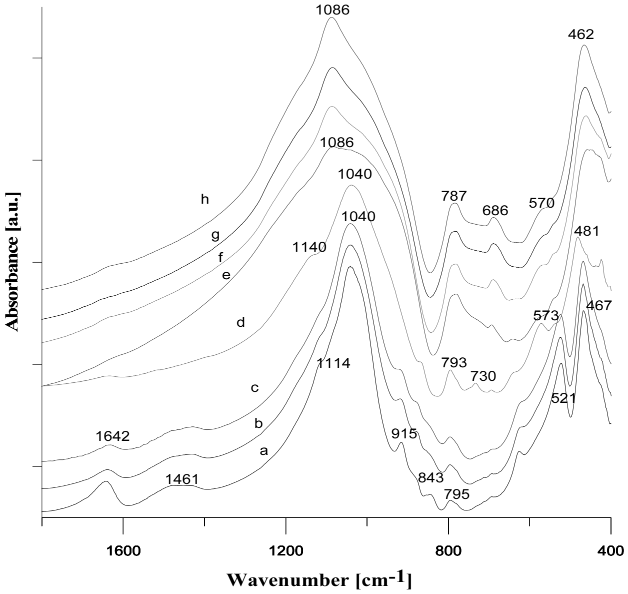

Fig. 5. IR spectrum of Special bentonite in the wave numbers range: 1800 – 400 cm^{-1} before (a) and after heating to the following temperatures: b – 500 °C, c – 550 °C, d – 700 °C, e – 900 °C, f – 1000 °C, g – 1100 °C, h – 1200 °C

Instead the band at the wave number 738 cm^{-1} appears, which can be related to the polymorphic change of quartz occurring at a temperature of 573 °C (low-temperature β-quartz turns into high-temperature α-quartz) [20]. It can be assumed that shifting of the band from the wave number 520 cm^{-1} to 573 cm^{-1} at the temperature of 700 °C is related to dehydroxylation [11, 12, 18]. Each temperature increase results in changing of bandwidth of the main Si-O band at the wave number app. 1040 cm^{-1}.

At temperature of 900 °C structural changes occur in bentonite samples. The intensity maximum of the band 1040 cm^{-1} corresponding to the Si-O vibrations shifts towards a higher wave number (1095 cm^{-1}) and its character indicates that it is more complex. These changes can indicate that the successive polymorphic quartz transformation occurs, (since at a temperature above 870 °C a high-temperature quartz turns into trydymite), but also can point out the degradation of the bentonite structure (montmorillonite) of laminar silicate into simple silicate and then into an amorphous form [20]. At the wave number of 680 cm^{-1} a new band appears and a further temperature increase from 900 °C to 1200 °C increases its intensity (probably a new crystal structure is being formed) [7, 8].

At the temperature of 900 °C the both bentonites structure were totally destroyed (disappearance of the remaining reflexes coming from the montmorillonite or beidellite phase on X-ray diffractogram and changes in IR spectrum) [10].

3.3. Analysis of the montmorillonite contents

Structural changes occurring in the montmorillonite under the influence of temperature lead to the loss of binding properties of the bentonite [1, 2]. The results of the analysis of montmorillonite contents in the examined bentonites, depending on the heating temperature, is presented in Fig. 6. After heating the bentonite at 500 °C, the montmorillonite in all analysed samples was practically unchanged. The differences between the bentonites begun to appear only after heating the samples to the temperature of 600 °C.

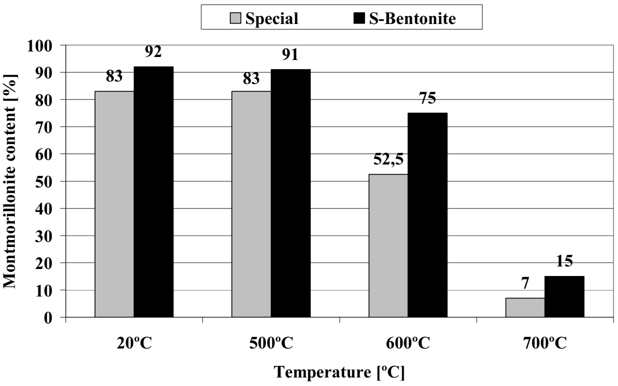

Fig. 6. Dependency of the montmorillonite contents in the examined bentonites on the heating temperature

The S-Bentonite proved to be more resistive to the temperature. After 1 hour at 700 °C, in all analysed bentonites, the montmorillonite contents fell practically to zero, and they lost their binding properties.

3.4. Technological analyses of moulding sands with bentonite

The results of compression strength analysis of the examined samples of moulding sands, heated at different temperatures are presented in Fig. 7.

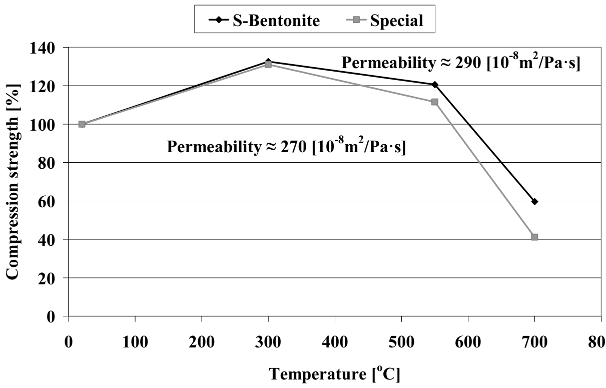

Fig. 7. Dependency of the compression strength of analysed moulding sands containing bentonites on the heating temperature

The relative changes in strength, determined in percent (%), are marked on the figure. It was assumed, that 100 % is the compression strength of the wet sample (green sample at ambient temperature). The analysis were conducted for the compactability equal around 45 %. The test results showed that the maximum compression strength was achieved for the temperature of around 300 °C. The S-Bentonite showed higher compression strength to high temperatures – the fall of the sample strength at 700 °C is lower than 50 %, as compared to the initial strength. The

Table 2. Listing of bands in the temperature range: 20 °C – 1200 °C for individual bentonites

T [°C]	20 °C		500 °C		550 °C		700 °C		900 °C		1000 °C		1100 °C		1200 °C		Bond
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	
Wavenumber [cm^{-1}]	3632	3633	3632	3633	3632	3633											-OH
	3455	3450	3455	3450	3455	3450											H-OH
	1642	1642	1642	1642	1642	1642	1642	1642									-H-OH
	1461	1461	1461	1461	1461	1461											CO_3^{2-}
		1114					1135	1140									Si-O
									1095	1086	1095	1086	1095	1086	1095	1086	Si-O
	1039	1040	1039	1040	1039	1040	1033	1040									Si-O
	914	915	914	915	914	915											Al-O-H
	876		876		876		876										AlFeOH
	840	843															Al-Mg-OH
	790	795	790	795	790	795	792	793	786	787	786	787	786	787	786	787	Si-O
							730	730									Si-O
									675	686	675	686	675	686	675	686	Si-O-Si
																	Si-O-Si
		623		623		623											Si-O-Al
							565	573	565	570	565	570	565	570	565	570	unknown
	521	521	521	521	521	521											Si-O-Al
							481	481									unknown
		466		466		466			459	462	466	462	466	462	466	462	O-Si-O

1 – S-Bentonite, 2 – Special.

permeability of both moulding sands containing bentonites was similar.

The result of the dehydration and dehydroxylation processes was visible decrease in the strength properties of moulding sands (at the temperature above 600 °C). This is consistent with previous studies about of thermal analysis of the bentonites [14, 16].

4. CONCLUSIONS

The conducted analysis of the influence of temperature on the properties and structure of bentonites used in the foundry industry as moulding sands binding materials confirmed that in all samples, the endothermic dehydratation and dehydroxylation processes occurred. The above mentioned processes were reflected in both, the results of the FTIR analyses (changes of the spectrum) and in the X-ray analysis (XRD) and in the thermal analysis [14].

The conducted technological examination of the moulding sands prepared with the use of bentonite showed the general characteristics of the influence of temperature on the compression strength. At the temperature of 700 °C moulding sands retained around 50 % of their original strength. When analysing the montmorillonite contents in pure bentonite for the same temperature it can be said that the bentonite should not retain any binding properties. The moulding sands contain also – apart from the bentonite – the quartz sand, working as base. In this case, the sand can work as an insulation for the binding material, ensuring that the bentonite was less exposed to the high temperatures during the heating process, thus, as a result, the heated moulding sands retained a significant percentage of strength.

The structural analysis were confirmed by the analysis of the binding properties of the bentonites, subjected to the effects of high temperature, what corresponds to the second stage of dehydroxylation (in the FTIR spectra, the disappearance of the bands from the OH groups can be observed). In the X-ray analysis, the disappearance of the diffraction peaks from the surfaces corresponding to the montmorillonite can be observed.

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