

# Analysis of Structural Changes in Starch-Aluminosilicate Binder and Molding Sand with its Participation after Physical Curing

K. Kaczmarek \*, B. Grabowska, S. Cukrowicz, A. Bobrowski, S. Żymankowska-Kumon

AGH University of Science and Technology, Faculty of Foundry Engineering,  
Reymonta 23, 30-059 Krakow, Poland

\* Corresponding author. E-mail address: karolina.kaczmarek@agh.edu.pl

Received 26.05.2018; accepted in revised form 20.08.2018

## Abstract

The organo-inorganic commercial binder Albertine F/1 (Hüttenes-Albertus) constituting the starch-aluminosilicate mixture was directed to structural studies. The paper presents a detailed structural analysis of the binder before and after exposure to physical curing agents (microwaves, high temperature) based on the results of infrared spectroscopy studies (FTIR). An analysis of structural changes taking place in the binder system with the quartz matrix was also carried out. Based on the course of the obtained IR spectra, it was found that during the exposure on physical agents there are structural changes within the hydroxyl groups in the polymeric starch chains and silanol groups derived from aluminosilicate as well as in the quartz matrix (SiO<sub>2</sub>). The curing of the molding sand takes place due to the evaporation of the solvent water and the formation of intramolecular and intermolecular cross-linking hydrogen bonds. Type and amount of hydrogen bonds presence in cured molding sand have an impact on selected properties of molding sand. Results indicates that for molding sand with Albertine F/1 during conventional heating a more extensive network of hydrogen bonds is created.

**Keywords:** Conventional heating, Microwave-Curing, Starch-Aluminosilicate binder, FTIR, Hydrogen bonds

## 1. Introduction

In technology of molding sands, the selection of materials and choice of curing methods are two important aspects of the production of proper molds and cores. However, in order to meet the demands of industry, not only the quality of materials, but also economic and environmental aspects of technology should be taken into account while preparing forms [1, 2]. Therefore, the method of microwave curing of molding and core sands seems to be an interesting alternative to energy-consuming and time-consuming conventional curing (drying). Interest in the method of microwave hardening of molding, core and ceramic coatings dates back to the 60's and 70's of the last century [3–5]. Over the years,

justifiability of the use of the microwave curing of molding sands with furfuryl resins [6, 7] and furfuryl-urea resins [8], liquid molding sands with organic binders [9], core molding sands with thermosetting binders [10]. The vast majority of research works in recent years related to the microwave curing of molds and cores with the use of inorganic binder concerns molding sands with water glass. The results of these tests confirm not only the legitimacy of using microwave radiation for technological but also economic reasons [11–14]. However, in the field of microwave curing of molding sands with organic binders at the Faculty of Foundry Engineering UST AGH a number of research works were carried out related to the assessment of the effect of radiation on the properties of molding sands containing the composition of polymer binders, among others BioCo type

binders and starch binder based on sodium carboxymethyl starch. As part of the work carried out, it was proved that by using microwave radiation as a curing agent, the highest strength properties of the molding sands were obtained in comparison to other curing methods [15–19].

Considering the fact that in the research works the most effective application of the microwave radiation in the molding sand technology with the use of organic or inorganic binders was confirmed in the aforementioned research work, action was taken to evaluate the possibility of binding the molding sands with an organic-inorganic binder on the example of Albertine F/1 (Hüttenes-Albertus). This commercial binder (in form of extra-fine powder) is a mixture of starch with aluminosilicates used commonly for modification of green sands with bentonite. However - according to the manufacturer - it can also be used as a main binder in presence of water for thermosetting molding sands [20]. The technological tests were conducted and its results were compared to the effects of curing the same molding sand through conventional heating (drying) [21]. Also in this case, the tests of selected molding sand properties confirmed that it is possible to microwave-curing the composition of quartz sand with the Albertine F/1 binder, however, compared to the conventional heating method, much lower values, e.g. tensile and bending strength, were achieved - the results are shown in the Fig. 1. After 1 and 4 hours of storage, the microwave-cured molding sand was characterized by significantly lower tensile strength (4-7 times lower) and bending strength (4-6 times lower) in comparison to conventionally cured molding sand. After 24 hours of storing the strength of a conventional and microwave cured molding sands reached a similar level -  $R_m^u \sim 1.2$  MPa and  $R_g^u \sim 2.5$  MPa [21].

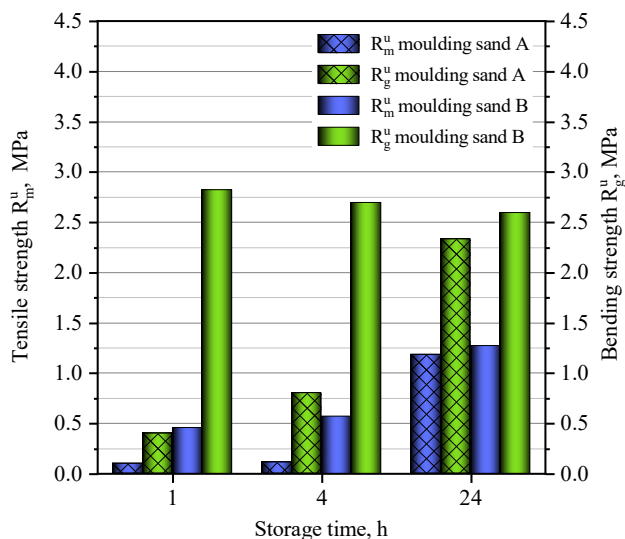


Fig. 1. The bending and tensile strength of cured molding sands with the participation of Albertine F/1 depending on the storage time: A - conventionally cured, B - microwave cured

This paper attempts to explain the observed phenomenon and answer the question: why the microwave-cured samples of molding sands bonded with a starch-aluminosilicate binder initially exhibit lower values of technological properties (eg.  $R_m^u$ ,  $R_g^u$ ) than cured by conventional drying? In order to explain this

question, structural studies were carried out by infrared spectrometry (IR) with the aim the formation of a network of bonds in the starch-silicate binder alone, as well as in the binder-matrix system before and immediately after the curing agent, when the differences of molding sand properties are the most visible. The efforts have been made to complete the knowledge in the field of application of binders based on starch and aluminosilicates, through a structural tests aimed at clarifying the dependence of selected properties of molding sands on the curing method.

## 2. Methodology

### 2.1. Materials

The binder applied in research was commercial product Albertine F/1 (Hüttenes-Albertus). The composition of the commercial binder is described in the Table 1.

Table 1. The composition of Albertine F/1 [20]

Composition	Content, %
content of starch derivatives with different swelling capacities (insoluble polymer)	75–79
heat-resistant materials; aluminosilicates (bentonite)	8–14
water content	10–12
ash content	<1.0

The matrix of molding sand was extra-fine quartz sand Sibelco Europe. Distilled water (Avantor Performance Materials Poland S. A) was also used to plasticize the binding material.

### 2.2. Preparation of samples

Albertine F/1 binder was tested as a starting material (uncured), a mixture with water (2.0 parts by weight of water per 1.0 parts by weight of binder) and cured physically. Samples of model molding sand (~10 g for each test) were prepared with the proportion of molding sand components: 1.0 pbw binder, 1.0 pbw water, 3.0 pbw matrix. The term "model molding sand" was used in the paper to emphasize the difference between the molding sand subjected to structural and technological tests. In the model molding sand compounds, the proportion of the binder in relation to the sand matrix was deliberately overestimated in order to be able to record on the IR spectra absorption bands coming from all components present in the mixture.

The prepared binder samples and model molding sands were cured under the following conditions:

- microwave curing process was carried out in the microwave device INOTEC MD 10940; microwave power of 800 W, frequency 2.45 GHz, sample irradiation time binder and molding was set at 120 s, and the temperature in the microwave was approx. 100°C; samples subjected to

microwave curing were placed in a 21-liter chamber on a rotating plate activated after switching on the microwave device. The nominal output power of the device used was 1200 W;

- conventional drying at 100°C. The curing process was carried out in a SUP-65 laboratory dryer for 15 min; samples directed for drying by the conventional method in a laboratory dryer were placed in a 75-liter chamber with gravitational air circulation. The rated power of the device was 1500 W.

The conventional drying and microwave cured conditions were proposed based on the results of preliminary structural research of binder and molding sands with other starch-based binders [15, 16, 19]. After exposure to physical agents, the samples were allowed to cool. Cooled samples of Albertine F/1 and samples of model molding sand were gently ground in a mortar. The spectra for the samples were recorded no later than 1 hour after the curing agent stopped.

### 2.3. Structural studies

Infrared structural studies were carried out using a transmission technique (FTIR) using the calibrated instrument: Digilab Excalibur FTS 3000 Mx FT-IR Spectrometer with a DTGS detector. The selected range of wavenumbers was 4000-600  $\text{cm}^{-1}$ , the resolution was set at 4  $\text{cm}^{-1}$  for 32 scans of the sample. Uncured samples were applied with a thin layer on the surface of the pellet. The solid samples were measured in the form of KBr pellets with a sample/KBr ratio 1/200 mg.

## 3. Results and analysis

### 3.1. Structural analysis of Albertine F/1 binder

Figure 2 shows the IR spectra of the Albertine F/1 binder before and after exposure to physical agents.

In the IR spectrum for the initial sample in the region of 3415  $\text{cm}^{-1}$  the maximum associated with the presence of hydrogen bonds within the binder was observed. The addition of water to the binder causes a significant intensification of the band in this range, its maximum being slightly shifted to higher wavenumbers. In the range 3800-3000  $\text{cm}^{-1}$ , the wide band corresponding to the vibrations of the free O-H ( $\text{H}_2\text{O}$ ) group and hydrogen bonds does not disappear after crosslinking. The use of curing physical agents on the moistened binder causes changes in the shape and shifting of the bands towards the higher wavenumbers (spectrum 3: 3433  $\text{cm}^{-1}$ , spectrum 4: 3445  $\text{cm}^{-1}$ ). This indicates changes occurring in the area of hydrogen bonds, also those occurring in the starch-water and aluminosilicate-water interaction, and the presence of this band and the shift of maxima result from the vibration of hydrogen bonds in the cured sample and the presence of water bound in the binder. The fact that this band is very wide may result from overlapping bands coming not only from the starch, but also from the aluminosilicate in the system. Namely, in the IR spectra at higher wavenumbers, the "broadening" of the band arm

towards 3500  $\text{cm}^{-1}$  may be due to the presence of the water-stretching group -OH located between the aluminosilicate layers [22]. Thus, in the case of a conventionally cured sample, a more intense band was noticed in comparison to the sample spectrum at higher wavenumbers, which may be related to the more efficient formation of hydrogen bonds between the hydroxyl groups present in the starch and silanol groups derived from aluminosilicates. So that bonds can affect the strength properties of the molding sand after curing.

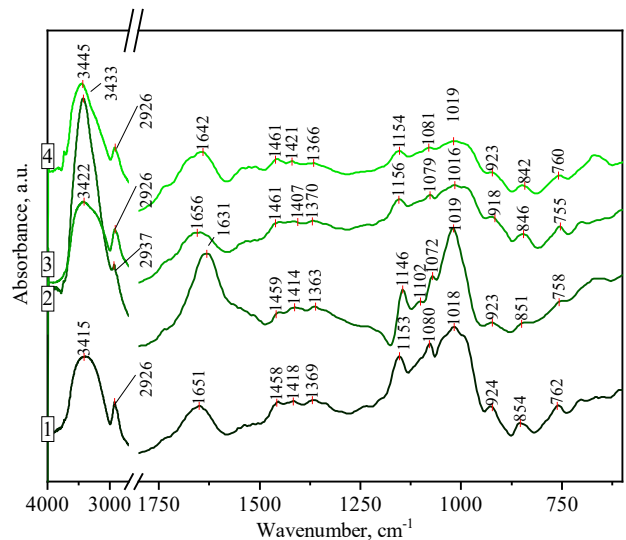


Fig. 2. IR spectra of the Albertine F/1: 1 binder - starting form, and the system with water: 2 - uncured, 3 - after microwave curing, 4 - after conventional curing

An intense and wide band with a maximum at  $\sim 1650 \text{ cm}^{-1}$  on the spectrum 1 was assigned to water adsorbed in the binder. This band in the moistened sample is shifted to  $\sim 1630 \text{ cm}^{-1}$  (spectrum 2), which was associated with the intensification of the band of water introduced into the binder [23]. The band in this region does not disappear after exposure of the moisten binder to physical factors, but its maximum shifts slightly to higher wavenumbers, so there is no complete evaporation of water from the system. It was noted that the intensity and bandwidth is comparable for both cured binder samples.

When comparing the shape of the IR spectra of the binder sample in the initial form (spectrum 1) and after exposure to physical factors (spectra 3 and 4), there are marked differences in the intensity of the bands in the range of 1200-950  $\text{cm}^{-1}$ . This fact can be assigned to the irreversible changes occurring in the starch structure due to the physical impact on the moisten binder Albertine F/1. On the IR spectra 1-4, the presence of bands with maxima at wavenumbers  $\sim 1020 \text{ cm}^{-1}$ ,  $\sim 1080 \text{ cm}^{-1}$  and  $1150 \text{ cm}^{-1}$  were observed, which are associated with vibrations characteristic of natural starch (vibrations: C-O stretching, C-H bending, and C-C stretching) and concern the ordering of the structure of this polymer in its natural form. The predominant share of starch in the Albertine F/1 binder is also confirmed by bands with maxima at  $\sim 760 \text{ cm}^{-1}$ ,  $\sim 851 \text{ cm}^{-1}$  and  $\sim 920 \text{ cm}^{-1}$  attributed to the presence of  $\alpha$ -1,4-glycosidic bonds (C-O-C) typical of native starch [23].

The bands at wave numbers  $\sim 920\text{ cm}^{-1}$  after curing did not undergo significant changes, which may indicate that due to the chosen crosslinking agents, the binder was not degraded and the  $\alpha$ -1,4-glycosidic bonds were broken.

Table 2 summarizes the details of the specific identification of characteristic absorption bands for the obtained IR spectra of the Albertine F/1 binder samples based on Figure 2.

Table 2.

Characteristic bands in the IR spectra of starch-aluminosilicate binder. Analysis based on literature data [23–29]

No. spectrum/ Wavenumber, $\text{cm}^{-1}$				Bands assignment
1	2	3	4	
3415	3422	3433	3445	S/A: O-H stretching
2926	2937	2926	2926	S: $\text{CH}_2$ deformation
1651	1631	1656	1642	S/A: deformation $\text{H}_2\text{O}$
1458	1459	1461	1461	S: $\text{CH}_2$ bending
1418	1414	1407	1421	S: $\text{CH}_2$ bending; C-O-O symmetrically stretching
1339	-	-	-	S: C-O-H bending, C-O-O twisting
1153	1146	1156	1154	S: C-O, C-C stretching
1080	1072	1079	1081	S: C-H bending A: Si-OH lattice
1018	1019	1016	1019	S: C-O stretching, $\text{CH}_2$
924	923	918	923	S: skeletal vibrations of glucopyranose ring (C-O-C)
854	851	846	842	S: C-H, $\text{CH}_2$ deformation A: Si-OH
760	-	764	760	S: C-C stretching

S – bands derived from a starch derivative; A - bands derived from aluminosilicate; S/A- overlapping bands

### 3.2. Structural analysis of molding sand with Albertine F/1 binder

The second measurement series (Figure 3) included the analysis of IR spectra recorded for model molding sand before and after curing.

From the point of view of the application of quartz matrix molding ( $\text{SiO}_2$ ) in molding sand production technology, the quartz grain surface quality is important due to the presence of Si-O-Si siloxane groups (on the 1-4 spectra, the band with the maximum at  $\sim 1080\text{ cm}^{-1}$  and the doublet of bands at  $798\text{--}776\text{ cm}^{-1}$ ) and single terminal silanol Si-OH and twin silanols  $\text{Si}(\text{OH})_2$  (on the IR spectra  $3800\text{--}3000\text{ cm}^{-1}$  and  $960\text{--}920\text{ cm}^{-1}$ ) [30–32]. Silanol groups on the  $\text{SiO}_2$  surface are important centers conducive to the binding effects of the polar groups present in the binder. However, the  $\text{SiO}_2$  surface activity from the point of view of chemical and adsorption processes is greater when adsorbed water is eliminated at elevated temperature ( $100\text{--}150^\circ\text{C}$ ). Above  $150^\circ\text{C}$ , in the case of  $\text{SiO}_2$ , hydroxyl groups may be removed from its surface (derived from silanol groups - Si-OH - which may affect the less efficient effect of molding sand curing [31, 33–36].

Analysing the IR spectra of model molding sands with an organic-inorganic binder, attention has been paid to the bands that

may indicate the interaction of the mineral matrix, aluminosilicate and starch derivative as a result of their exposure on a physical curing agent.

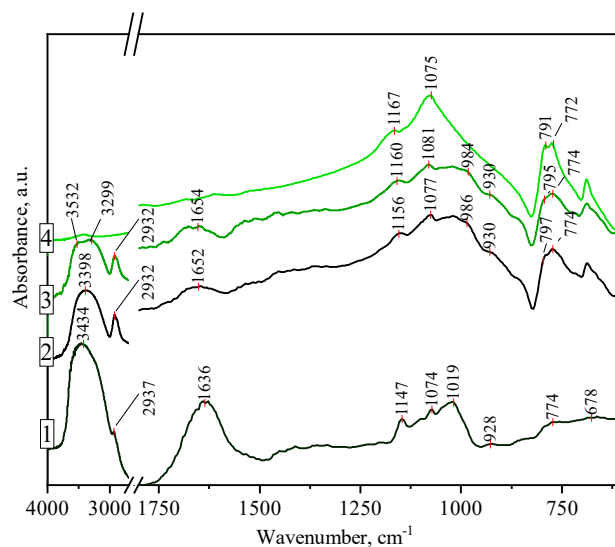


Fig. 3. IR spectra of molding sands with Albertine F/1: 1 - uncured, 2 - microwave cured, 3- conventionally cured and 4 - quartz sand

The band on the IR spectrum for the uncured molding sand sample (spectrum 1) at  $3434\text{ cm}^{-1}$  is associated with the stretch vibration of  $\text{H}_2\text{O}$  molecules. In turn, the band at a maximum of  $1636\text{ cm}^{-1}$  corresponds to the bending vibration of  $\text{H}_2\text{O}$  molecules. However, on the spectra of the cured molding sands (spectra 2 and 3) the band changed shape and maxima shifts were observed. And so, in spectrum 2 the maximum in the area of  $3398\text{ cm}^{-1}$  was interpreted as the effect of overlapping bands coming from hydrogen bonds in the area of the binder and the matrix. In contrast, the course of the band on the spectrum 3 showed two maxima at  $3532\text{ cm}^{-1}$  and  $3299\text{ cm}^{-1}$ , respectively. The first of them can be interpreted as intense tensile vibrations of silanol groups in the amorphous  $\text{SiO}_2$  structure, while the second one is attributed to the formation of intermolecular hydrogen bonding networks between polar groups present in the starch molecule (hydroxyl groups -OH and carbonyl  $>\text{C}=\text{O}$ ) during physical curing. In both cases the presence of bands in the  $3800\text{--}3000\text{ cm}^{-1}$  range was also associated with a marked change in the position and intensity of the band around  $1000\text{--}850\text{ cm}^{-1}$  interpreted as the vibrations of free silanol groups. It is noted that the band on the IR spectrum of the conventionally cured sample is more intense in the region of the maximum at  $\sim 984\text{ cm}^{-1}$  than the band corresponding to it in the spectrum of the microwave-cured sample (compare spectrum 3→2). Therefore, in selected conditions of thermal impact on the system containing  $\text{SiO}_2$  in the presence of water, silanol groups could be activated on the surface of the grains of the matrix. It could also result in the formation of a number of new silanol groups (Si-OH), which attached polymer chains of starch and aluminosilicates dispersed in the system at the surface of grains of sand with the formation of hydrogen bonds of the type  $\text{Si-O-H}\cdots\text{O-H}$ . Comparing the IR spectra of

both cured model molding sands, it can be assumed that it is the hydrogen bond network that determines the bond strength of the matrix with the Albertine F/1 organic-inorganic binder.

Conventional heating of the samples proceeds slowly and gently, therefore the formation of a hydrogen bond network between the starch molecules, aluminosilicates and the surface of the grains of the matrix proceeds smoothly. This is evidenced by wide and intense bands in the region of wavenumbers assigned to vibrations derived from hydroxyl and silanol groups as compared to samples irradiated with microwave. On the other hand, the rapid heating of the sample during exposure of the molding sand sample to microwave radiation probably caused fast water evaporation from aluminosilicate and weakening of intermolecular bonds between molding sand ingredients therefore the less successful effect of binding capacity in microwave field was observed.

Table 3 details the identification of characteristic absorption bands for the obtained IR spectra of the model molding sand samples with the participation of Albertine F/1 in uncured and cured form based on Figure 3.

Table 3.  
Characteristic bands in the IR spectra of model molding sand. Analysis based on literature data [23–29, 33, 34]

No. spectrum/ Wavenumber, cm <sup>-1</sup>				Bands assignment
1	2	3	4	
-	-	3532	-	A: inter layer h-bonds
3434	3398	3299	-	S: OH stretching (intermolecular) M: OH stretching
2937	2932	2932	-	S: CH <sub>2</sub> deformation
1636	1652	1654	-	S/A: deformation H <sub>2</sub> O
1147	1156	1160	1167	S: C-O, C-C stretching M: Si-O-Si asymmetric stretching
1074	1077	1081	1075	S: C-H bending M: Si-O stretching
-	986	984	-	A/M: Si-OH stretching
928	930	930	-	
-	797	795	791	M: Si-O-Si
774	774	774	772	

S - bands derived from a starch derivative; A - bands derived from aluminosilicate; S/A- overlapping bands, M- bands derived from the matrix

## 4. Summary

Based on the analysis of structural changes recorded on IR spectra, it can be noticed that in the curing process of molding sand with an organic-inorganic binder Albertine F/1 the key role is played by the presence of hydroxyl groups derived from binder material components and activated silanol groups on the surface of the quartz sand matrix.

Applied methods of the curing of the molding sand caused not only evaporation of plasticizer (water), but the formation of intramolecular and intermolecular cross-linking hydrogen bonds. The amount and type of hydrogen bond network determines the bond strength of the quartz sand matrix with the Albertine F/1

binder. In the freshly microwave-cured molding sand, the number of intermolecular hydrogen bonds within the all components is lower as evidenced by the IR spectra (region of 4000-3000 cm<sup>-1</sup>), which results in lower values of strength properties of the molding sand.

## Acknowledgements

The research has been conducted within the AGH statutory work no. 11.11.170.318/13.

## References

- [1] Burian, A. (2009). New ecological binder systems. *Slévárenství*. LVII(1-2), 6. (in Czech).
- [2] Lewandowski, J.L. (1995). *Materials for casting moulds*. Kraków: Akapit. (in Polish).
- [3] Skubon, M.J. (1978). Microwave Binders Curing of Core and Coatings. *AFS Transactions*. 86(183), 183-186.
- [4] Dench, E.C. (1970). US 3519517 A - Method of and means for microwave heating of organic materials.
- [5] Brown, L.H., Stephans, L.C. (1972). US 3692085 - A process for producing cores by microwave heating.
- [6] Lukacek, G. & Luther, J. (1981). Microwave accelerate core and mold curing. *Foundry M&T*. (05).
- [7] Kottke, R.H. (1981). Microwave curing applications of furan foundry binders. *AFS Transactions*. 89, 251-260.
- [8] Drożyński, D., Holzer, M., Kobot, M. & Lewandowski, J.L. (2000). Influence of water addition on mass strength with furfuryl urea resin cured under ambient conditions and using microwaves. *Solidification of Metals and Alloys*. 2(43), 133-138. (in Polish).
- [9] Samsonowicz, Z., Wilczyński, J. & Wikiera, R. (1980). Microwave hardening of liquid masses with an organic binder. *Prace Instytutu Odlewnictwa*. (38). (in Polish).
- [10] Pigił, M. (1998). Curing of cores in microwaves. *Acta Metallurgica Slovaca*. 4(spec.2), 102-106. (in Polish).
- [11] Granat, K., Nowak, D. & Stachowicz, M. (2010). The use of an innovative microwave curing method in the production of cast steel castings for the machine industry. *Archiwum Technologii Maszyn i Automatykacji*. 30(1), 19-27. (in Polish).
- [12] Stachowicz, M., Granat, K. & Nowak, D. (2011). The effect of the addition of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> on the residual strength of microwave-cured molding sands with water glass. *Archives of Foundry Engineering*. 11(spec.2), 203-208. (in Polish).
- [13] Stachowicz, M., Granat, K. & Nowak, D. (2012). Measurement of flexural strength as a method of assessing the quality of a binder on the example of masses with water glass. *Archives of Foundry Engineering*. 12(1), 175-178.
- [14] Stachowicz, M., Opyd, B., Granat, K. & Markuszewska, K. (2014). Effect of electrical properties of materials on effectiveness of heating their systems in microwave field. *Archives of Foundry Engineering*. 14(2), 111-114.
- [15] Grabowska, B., Sitarz, M., Olejnik, E., Kaczmarzka, K. & Tyliczszak, B. (2015). FT-IR and FT-Raman studies of cross-linking processes with Ca<sup>2+</sup> ions, glutaraldehyde and

- microwave radiation for polymer composition of poly(acrylic acid)/sodium salt of carboxymethyl starch – Part I. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*. 135, 529-535. DOI:10.1016/j.saa.2015.06.084.
- [16] Grabowska, B., Sitarz, M., Olejnik, E., Kaczmarek, K. & Tyliczszak, B. (2015). FT-IR and FT-Raman studies of cross-linking processes with Ca<sup>2+</sup> ions, glutaraldehyde and microwave radiation for polymer composition of poly(acrylic acid)/sodium salt of carboxymethyl starch – In moulding sands, Part II. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 151, 27-33.
- [17] Grabowska, B. (2009). Microwave crosslinking of polyacrylic compositions containing dextrin and their applications as molding sands binders. *Polimery/Polymers*. 54(7-8), 507-513.
- [18] Grabowska, B. & Holtzer, M. (2008). Application of spectroscopic methods for investigation of the course of poly(sodium acrylate) crosslinking with use of different crosslinking agents. *Polimery/Polymers*. 53(7-8), 531-536.
- [19] Kaczmarek, K.J. (2017). *Sodium carboxymethyl starch (CMS-Na) as a material for use in moulding sand technology*. Unpublished doctoral thesis. AGH University of Science and Technology. (in Polish).
- [20] Additives for molding and core sand - Hüttenes Albertus Chemische Werke GmbH. (n.d.). Retrieved March 6, 2016, from [http://www.huettenes-albertus.pl/produkty/dodatki\\_do\\_mas\\_formierskich\\_i\\_rdeniowych/index.html](http://www.huettenes-albertus.pl/produkty/dodatki_do_mas_formierskich_i_rdeniowych/index.html). (in Polish).
- [21] Kaczmarek, K., Grabowska, B., Drożyński, D., Kurleto, Ż. & Szymański, Ł. (2015). An assessment of the effectiveness of physical curing methods of molding sand bonded by binders based on starch and aluminosilicates. *Metallurgy and Foundry Engineering*. 41(3), 133-141.
- [22] Fil, B.A., Özmetin, C. & Korkmaz, M. (2014). Characterization and electrokinetic properties of montmorillonite. *Bulgarian Chemical Communications*. 46(2), 258-263.
- [23] Kizil, R., Irudayaraj, J. & Seetharaman, K. (2002). Characterization of Irradiated Starches by Using FT-Raman and FTIR Spectroscopy. *Journal of Agricultural and Food Chemistry*. 50(14), 3912-3918. DOI:10.1021/jf011652p.
- [24] Schuster, K.C., Ehmoser, H., Gapes, J.R. & Lendl, B. (2000). On-line FT-Raman spectroscopic monitoring of starch gelatinisation and enzyme catalysed starch hydrolysis. *Vibrational Spectroscopy*. 22(1-2), 181-190. DOI:10.1016/S0924-2031(99)00080-6.
- [25] Sekkal, M., Dincq, V., Legrand, P. & Huvenne, J.P. (1995). Investigation of the glycosidic linkages in several oligosaccharides using FT-IR and FT Raman spectroscopies. *Journal of Molecular Structure*. 349(95), 349-352. DOI:10.1016/0022-2860(95)08781-P.
- [26] Budarin, V., Clark, J.H., Hardy, J.J.E., Luque, R., Milkowski, K., Tavener, S.J. & Wilson, A.J. (2006). Starbons: New starch-derived mesoporous carbonaceous materials with tunable properties. *Angewandte Chemie - International Edition*. 45(23), 3782-3786. DOI:10.1002/anie.200600460.
- [27] Ambjörnsson, H.A., Schenzel, K. & Germgård, U. (2013). Carboxymethyl cellulose produced at different mercerization conditions and characterized by NIR FT Raman spectroscopy in combination with multivariate analytical methods. *BioResources*. 8(2), 1918-1932.
- [28] Vasko, P.D., Blackwell, J. & Koenig, J.L. (1972). Infrared and Raman spectroscopy of carbohydrates. Part II: Normal and coordinate analysis of  $\alpha$ -D-glucose. *Carbohydrate Polymers*. 23, 407-416.
- [29] Vasko, P.D., Blackwell, J. & Koenig, J.L. (1971). Infrared and Raman spectroscopy of carbohydrates. Part I: Identification of O-H and C-H related vibrational modes for D-glucose, maltose, cellobiose, and dextran by deuterium-substitution methods. *Carbohydrate Research*. 19, 297-310.
- [30] Musić, S., Filipović-Vinceković, N. & Sekovanić, L. (2011). Precipitation of amorphous SiO<sub>2</sub> particles and their properties. *Brazilian Journal of Chemical Engineering*. 28(1), 89-94. DOI:10.1590/S0104-66322011000100011.
- [31] Shokri, B., Firouzjah, M.A. & Hosseini, S.I. (2009). FTIR analysis of silicon dioxide thin film deposited by metal organic-based PECVD. *Proceedings of 19th International Plasma Chemistry Society*. 1-4. Retrieved from <http://www.ispc-conference.org/ispcproc/ispc19/791.pdf>.
- [32] Pasieczna-Patkowska, S. & Olejnik, T. (2012). Investigations of selected physicochemical properties modified with amine groups of mesoporous silica materials. *Adsorbenty i katalizatory: wybrane technologie a środowisko*. 68-91. (in Polish).
- [33] Kwon, K.D., Vellido-Rodriguez, V., Logan, B.E. & Kubicki, J.D. (2006). Interactions of biopolymers with silica surfaces: Force measurements and electronic structure calculation studies. *Geochimica et Cosmochimica Acta*. 70(15), 3803-3819. DOI:10.1016/j.gca.2006.05.016.
- [34] Comas-Vives, A. (2016). Amorphous SiO<sub>2</sub> surface models: energetics of the dehydroxylation process, strain, ab initio atomistic thermodynamics and IR spectroscopic signatures. *Physical chemistry chemical physics: PCCP*. 18(10), 7475-82. DOI:10.1039/c6cp00602g.
- [35] Krysztalkiewicz, A., Rager, B. & Maik, M. (1994). The effect of surface modification on the physicochemical properties of precipitated silica. *Fizykochemiczne Problemy Mineralurgii*. (in Polish).
- [36] Gu, C., Li, G., Hu, Y., Qing, S., Hou, X. & Gao, Z. (2012). Effect of calcination temperature of starch-modified silica on the performance of silica supported Cu catalyst in methanol conversion. *Journal of Fuel Chemistry and Technology*. 40(11), 1328-1335. DOI:10.1016/S1872-5813(13)60002-X.