

Conditions of synthesis and structure of metakaolin-based geopolymers: application as heavy metal cation sorbent

Magdalena Król¹, Kamila Brylewska^{1, 2, *}, Arkadiusz Knapik¹, Kamil Kornaus¹,
Włodzimierz Mozgawa¹

¹AGH University of Science and Technology, Faculty of Materials Science and Ceramics, al. Mickiewicza 30, 30-059 Kraków, Poland

²Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland

*Corresponding author: e-mail: kamilaaa@agh.edu.pl

This study presents the synthesis of geopolymer materials designed for application as self-supporting zeolite membranes. For this purpose, batches of metakaolin activated with sodium silicate and sodium hydroxide were used. During synthesis, it was assumed that low temperatures are sufficient to receive the membranes. The composition of raw materials and temperature of activation were selected in such a way so as to correspond to the basic chemical compositions and synthesis conditions of sodalite as well as zeolites A and X. Additionally, the structural and textural properties of geopolymers were determined. The results show that it is possible to obtain composite zeolite structures in an amorphous matrix. A number of synthesized materials were used in the sorption of selected heavy metal cations (Ni^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+}). It was concluded that the investigated geopolymerization process may be applied to obtain a material with potential use as a heavy metal sorbent.

Keywords: metakaolin, geopolymers, structural and textural properties, heavy metal sorbent.

INTRODUCTION

Geopolymers are inorganic polymers that belong to a group of amorphous aluminosilicates with structural elements similar to those of crystalline zeolites. Their 2- or 3-dimensional structure is based on alumina $[\text{AlO}_4]$ and silica $[\text{SiO}_4]$ tetrahedra joined together with oxygen atoms. The negative charge of $[\text{AlO}_4]$ is compensated by the presence of alkali metal ions (e.g. Na^+ or K^+).

Geopolymers synthesis (geopolymerization) involves chemical reaction between alumina and silicate rich materials in the presence of alkali activators, i.e. NaOH, KOH or water glass. This exogenous process gives rise to oligomers (dimers and trimers) which are proper structural units of geopolymers. Those units create dimensional framework¹. Exact course of geopolymerization depends mainly on the nature of both aluminosilicates and alkali reagents, ion-exchange capacity and the structure of the precursor materials. Nevertheless, most investigators concur that the formation of geopolymers involves the dissolution of aluminum and silicon compounds present on the surface of aluminosilicates, the polymerization of active surface groups, and the formation and eventual curing of gel².

Owing to high content of Al and Si, natural materials such as clay but also fly ash and blast furnace slag are often used to synthesize geopolymers. Due to the presence of numerous contaminants, those reactants do not suit purpose of model surveys. For this reason, kaolin or preferably its metastable and disordered form – metakaolin is used instead. Transformation of kaolin into metakaolin takes place at 550–800°C and involves dehydroxylation of strongly bound hydroxyl ions in Al layers, which leads to layered structure^{3–5} and further to geopolymer's mechanical properties improvement^{6–9}.

Additives other than metakaoline or kaoline are also used in the synthesis of geopolymers, including calcium hydroxide, slag or ash. They are active as binders and

builders in the geopolymer matrix, but do not significantly affect the deterioration of the final products^{10–11}.

Geopolymers properties are determined by the selection of the reagent used, which is associated with availability, cost, and the potential applications of the product. The quality of the produced geopolymer is also affected by the type and concentration of the alkali activator, drying temperature and time of polycondensation. Sodium and potassium hydroxide are the most common alkalis⁷. Several studies confirmed their high compressive (after exposure to a pressure of over 90 MPa for 28 days) and flexural (10–15 MPa) strength, resistance to weather conditions, low porosity, and little shrinkage¹². As a consequence, geopolymers are used in the construction industry, chemical engineering, environmental protection, and as additives to cements or alkali-slag binders¹³. Research was also conducted on the fire, frost, acid, sulphates, and seawater resistance of materials based on metakaolinite and fly ash¹⁴.

One of the application spectrum of geopolymers is environment protection. The ongoing degradation of natural environment, connected mostly with human activity, has been a significant influence for some time now. The contamination of water and air is connected mainly to the presence of heavy metal cations. For this reason materials with advantageous sorption properties are highly desired. Geopolymers are environmentally friendly materials, used as adsorbents of heavy metal cations¹⁵. There are many studies^{16–17} showing that geopolymers are characterized by high porosity and capacity and therefore they are used in immobilization of heavy metals to removal them from aqueous solution. For example Yuanyuan Ge¹⁶ described synthesis of porous geopolymeric spheres by a solidification method and their use as adsorbents for the removal of Cu(II) from aqueous solution. Zhang et al.¹⁸ studied geopolymers based on fly ash and immobilized Cr^{6+} , Cd^{2+} , and Pb^{2+} ions and Yousef¹⁹ studied the impact of zeolitic tuffs on

the adsorption capacity of geopolymer products. It was confirmed that this material can have high adsorption capacity regarding methylene blue and Cu^{2+} . Other studies²⁰ based on the synthesis of geopolymers from metakaolin and silica fume and its use as adsorbents for decontamination of Cs^+ and Pb^{2+} ions.

The aim of this work was to study the influence of the synthesis conditions (chemical composition of substrates and activation temperature) on the structure of synthesized geopolymers. Additionally, the purpose of this work was to obtain zeolite phases in the stable geopolymer matrix. Geopolymers have similar structure to zeolites, and they are often referred to as zeolitic precursors. This paper also examines the correlation between the structure of the obtained geopolymers with their sorption properties towards heavy metal cations (Ni^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+}).

EXPERIMENTAL

Material preparation

Kaolin, a raw clay material, which had been extracted from the Maria III national polish deposit, was used in the study. Kaolin was calcined at 800°C for 2 h in a chamber furnace to obtain metakaolin. Its chemical composition (recalculated to oxides), determined by XRF (WDXRF, Axios max 4kW, PANalytical), normalized to 100% was follows (in wt.%): 58.50 (SiO_2), 39.23 (Al_2O_3), 0.72 (Na_2O), 0.61 (Fe_2O_3), 0.61 (TiO_2), 0.14 (MgO), 0.09 (CaO), 0.01 (K_2O).

Metakaolin was activated with a solution of sodium silicate (39 wt.% of SiO_2 and Na_2O , $\text{SiO}_2/\text{Na}_2\text{O}$ (molar ratio = 2.5, POCH) and sodium hydroxide (pure NaOH, POCH) in order to receive zeolite structures in an amorphous geopolymer matrix. Two series of samples (A and B) with different $\text{SiO}_2/\text{Al}_2\text{O}_3$, and the same $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ molar ratios were prepared. Two different temperatures of sample activation ($T_{\text{activation}}$ is the same as curing temperature) – 368 K (A series) and 353 K (B series) – were applied, since geopolymer polycondensation requires the external provision of energy¹³. Geopolymerization reaction is endothermic process. The time of activation was 24 h. During synthesis, it was assumed that low temperatures are sufficient to receive the membranes, and that standard high-temperature processes used in the ceramic industry, such as sintering or firing, are not required. The conditions of preparation are summarized in Table 1.

Table 1. Conditions and phase composition of obtained materials

Sample	$T_{\text{activation}}$ [K]	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$	Solid phase/ H_2O
A1	368	2.00	1.00	1.25
A2		2.25		
A3		2.50		
B1	353	2.00	1.00	1.25
B2		2.25		
B3		2.50		

Material modification

The sorption of heavy metal cations (Ni^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+}) was carried out with the A1 and B1 samples, because in the case of those samples, the most zeolite phases were obtained.

For this purpose, the materials were triturated to obtain a particle size below 0.125 mm. 5 ml of a salts as: $\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ (0.01 mol/dm³) was added to 0.1 g of the sample, shaken for 24 h, centrifuged, washed three times with distilled water, and then dried.

Research methodology

The phase composition of the samples was investigated by XRD (PANalytical; CuK_α radiation with a wavelength of 1.5406 Å). Measurements were performed in the 5–90° 2θ angle range (the presented diffractograms show the range from 5 to 40°) for 4 h, with an 0.008 increment, using a graphite monochromator. Phases were identified using the HighScore Plus application and the ICDD (International Centre for Diffraction Data).

Qualitative and quantitative analysis of the parent material and the geopolymer samples before and after sorption were carried out with XRF (WDXRF, Axios Max 4 kW, PANalytical).

Low-temperature nitrogen sorption was performed with a Micromeritics ASAP 2000 device after 24 h of activation of the studied samples at 400°C. The BET (Brunauer-Emmett-Teller) equation and was used for determination of the overall specific surface (S_{BET}).

The microstructural analysis of the samples was performed using a scanning electron microscope (FEI Nova NanoSEM 200).

FT-IR spectra were measured with a vacuum spectrometer (Bruker VERTEX 70V), using the standard KBr (Merck) pellet method for mid-infrared (MIR). The spectra were recorded with a 4 cm⁻¹ resolution, over the course of 128 scans.

RESULTS AND DISCUSSION

Chemical composition

According to the literature^{2,21}, the initial contents of Si, Al and Na allow the type and contribution of crystalline and amorphous phases to be controlled (Table 1). The parameters that have a significant impact on the final properties of geopolymers are Si/Al and Na/Al ratios. The former affects the dissolution, hydrolysis and condensation of geopolymerization reactions. The proposed values are in a range that ensures high strength and durability of the resulting products²².

XRD studies

During the calcination of kaolin, kaolinite transforms into amorphous metakaolinite²³. In the diffraction patterns of both sample series (A and B), no significant reflections originating from kaolinite phase were observed (Fig. 1). However, peaks indicating the presence of unreacted silica from the starting kaolin were present, as well as reflections originating from quartz²⁴. With exception of B3 sample, among sodalite, zeolites X and A, at least one was present in every sample which

confirmed that geopolymerization enables the synthesis of zeolite phases sunk in the geopolymer matrix. The rise in the baseline (i.e. halo - $2\theta = 10\text{--}20^\circ$) indicates the expected amorphous component of the studied samples². This is more noticeable in the case of the A-series (A1 and A2), which was activated at a higher temperature. Depending on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio in the starting materials, and on the temperature of activation, various zeolite structures in an amorphous geopolymer matrix were obtained. For the B3 sample with a low aluminum content ($\text{Si}/\text{Al} = 1.25$), zeolite structures were not observed, unlike in the case of the A3 sample, which had the same composition, but was activated at a different temperature. According to the available reports²⁴, the formation of zeolite structures is promoted only when both aluminum and sodium are present at high concentrations. It is worth mentioning that the initial water content affects the geopolymerization process, i.e. the structure and other properties of the obtained geopolymers²⁵.

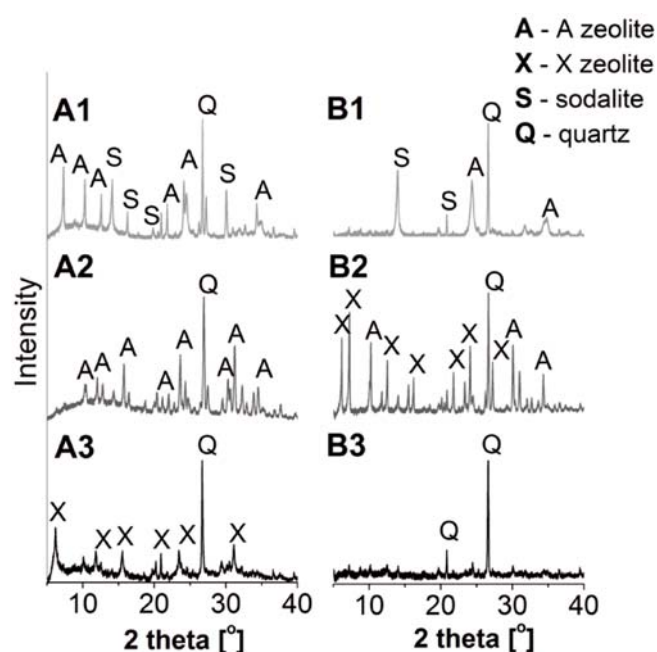


Figure 1. Diffraction patterns and phase compositions of the obtained geopolymers

IR studies of geopolymers

Figure 2 presents the mid-infrared (MIR) spectra for the aforementioned samples (series A and B). IR absorption spectra made it possible to obtain information about the structure of the zeolite samples after geopolymerization. Considering the chemical compositions of the starting material and of the materials after geopolymerization, Si-O bond vibrations in the range of $1000\text{--}400\text{ cm}^{-1}$ could have been expected. However, the most interesting range is $800\text{--}500\text{ cm}^{-1}$, which is typical for vibrations of overtetrahedral structural units (i.e. single- or double-rings)²⁶. For both series, intensive bands originating from the stretching vibrations of the O-H groups were observed at $3490\text{--}3460\text{ cm}^{-1}$ ²⁷. The most intensive band was registered for materials with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.25. The highest intensity of the band is related to the most of OH groups in the structure of this material, which may originate from zeolite forms or kaolinite hydration products (amorphous gel). The O-H

bending vibrations at 1650 cm^{-1} are likely associated with the presence of weakly bound water molecules on the surface or in so-called zeolite cages²⁸. The band at about 1450 cm^{-1} is associated with carbonate groups, which had most likely formed in the partial reaction between sodium hydroxide and atmospheric CO_2 during the thermal activation of geopolymers²⁹. This band is observed for both series of samples, and is particularly intensive for A1 and A3 samples, for which the analysis of diffraction patterns showed the presence of sodalite. The highest band intensity for the A3 sample is associated with the presence of large amounts of crystalline phases as well as sodium originating from sodium hydroxide, present during the geopolymerization reaction.

Intensive bands at $1200\text{--}400\text{ cm}^{-1}$, observed for all samples, correspond to the vibrations of Si-O-Si and Si-O-Al groups, typical of aluminosilicate structures. X-ray analysis revealed that the character of the samples was both amorphous and crystalline, with the latter related to the presence of zeolite (Fig. 1). The analysis of MIR spectra showed the presence of bands at $1010\text{--}990\text{ cm}^{-1}$, indicating asymmetrical stretching vibrations of Si-O-Si and Al-Si-O bonds in $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedrons in the geopolymer framework³⁰.

Bands associated with occurrence of symmetrical vibrations, which allow the degree of polymerization to be determined, were noted at $900\text{--}500\text{ cm}^{-1}$. Depending on the position of pseudolattice vibrations corresponding to overtetrahedral structural units, bands specific to a given type of zeolite were registered³¹. Therefore, in the case of A3, characterized by $\text{Si}/\text{Al} = 1.25$, bands at 880 and 750 cm^{-1} were recorded. Their presence results from the vibrations specific to D6R (six-membered rings) in the framework of zeolite X. Similar results were noted for B2, but the intensity of the band was low. The presence of the crystalline phase of zeolite A in samples A1, A2, B1 and B2 was confirmed. Thus, in the case of samples with average aluminum content (A2 and B2), the oscillation band of double four-membered rings (560 cm^{-1}) presented in the structure of zeolite A was observed³². This band exhibited the highest intensity only in the case of these materials. The bands specific to vibrations of double four-membered rings (D4R) are also observed for A1 and B1, but their intensity is low. In the case of samples with low aluminum content (A3 and B3), for which no peaks specific to the crystalline phase of zeolite A were recorded in the diffraction patterns, the 560 cm^{-1} band was observed. This can be related to the condensation of tetrahedra to D4R, which is one of the presumed mechanisms of the formation of zeolite structures³³.

The bands at 700 cm^{-1} were also analyzed. Their presence indicates that the generated geopolymer structure formed as a result of a reaction between aluminosilicate and the alkali solution. This is the reason for the presence of the Si-O-T (T = Si or Al) band, which was especially pronounced in the case of the A1 and B1 samples, but is also observed for other materials.

A certain correlation between the positions and intensities of bands and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios can be noted (Fig. 2). For higher concentrations of silica in the geopolymer structure, all bands shift towards lower frequencies and their intensity increases.

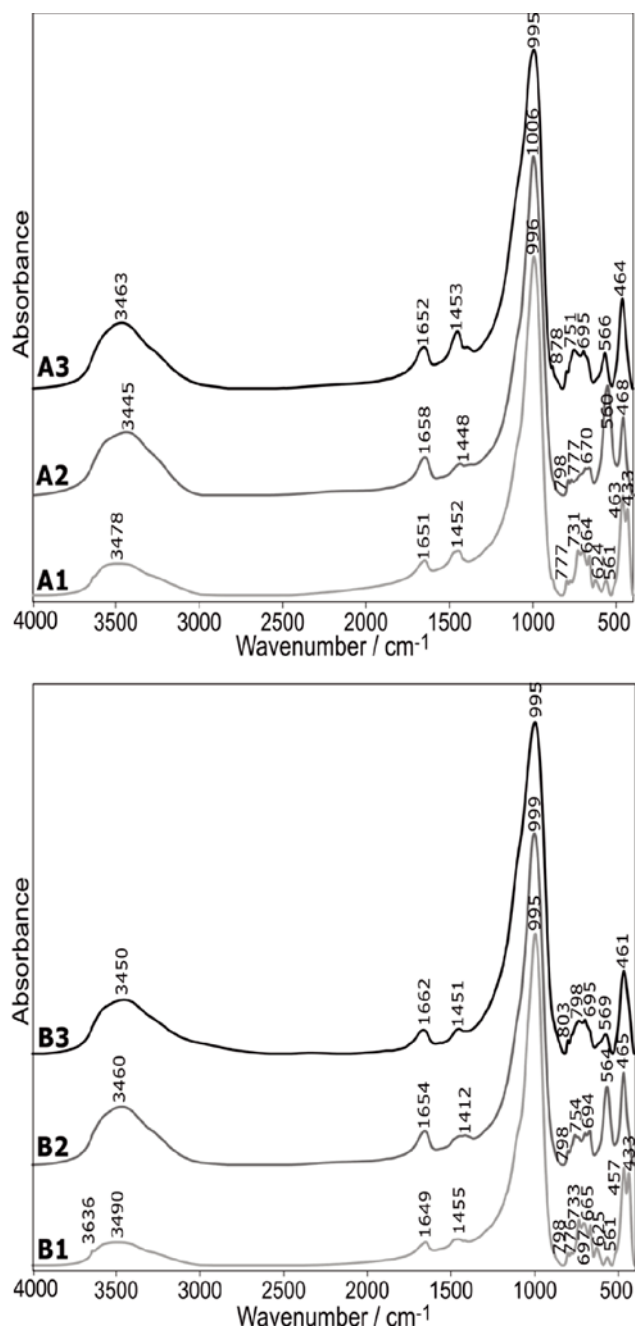


Figure 2. IR spectra of the obtained geopolymers

Physicochemical studies

The BET results showed that the most developed surface was observed for the samples activated at high temperature ($S_{\text{BET}(A_2)} = 262$ and $S_{\text{BET}(A_3)} = 115 \text{ m}^2/\text{g}$). The only B-series samples for which considerable surface area was observed was B2 ($S_{\text{BET}(B_2)} = 46 \text{ m}^2/\text{g}$). The A1 ($5 \text{ m}^2/\text{g}$) and B1 ($7 \text{ m}^2/\text{g}$) samples exhibited relatively low values. The smallest surface area equal to about $3 \text{ m}^2/\text{g}$ was observed for B3 sample. This is likely due to the occurrence of a compact matrix with densely occurring small pores. In the case of materials that had a large specific surface area, high values of S_{micro} ($S_{\text{micro}(A_2)} = 241$, $S_{\text{micro}(A_3)} = 100$, $S_{\text{micro}(B_2)} = 41 \text{ m}^2/\text{g}$) were found. One of the implications is the presence of multiple active sites with the ability to bind to metal ions³⁴.

Figure 3 shows the SEM images of representative samples from each series: A1 and B1, activated at 368 and 353 K, respectively. The micrographs show the homogeneous character of the studied samples. The surface of geopolymers is built of homogeneously and regularly

distributed particles with a spherical shape. Fine spherical crystals of sodalite (1 at the picture) and cubic grains of zeolite A (2 at the picture) were observed. The grains form large agglomerates, and the size of an individual grain in both cases is comparable, i.e. about $1\text{--}2 \mu\text{m}$. For the remaining samples (data not shown), the same trend was observed.

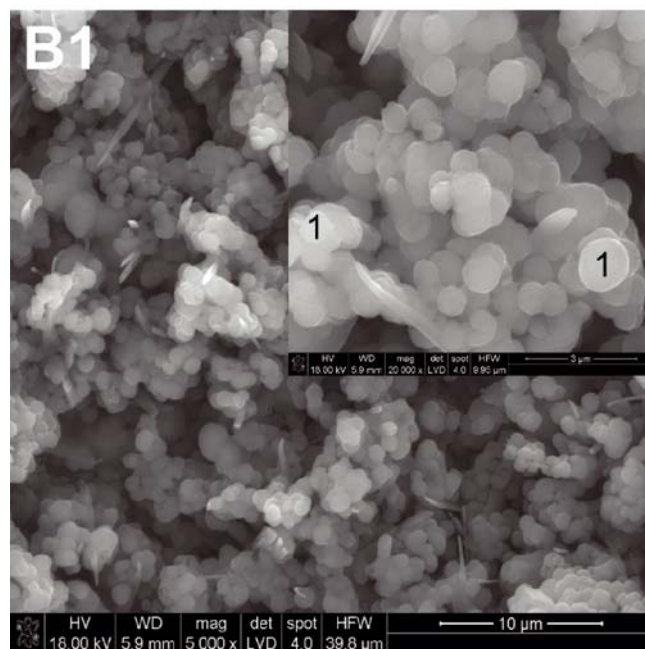
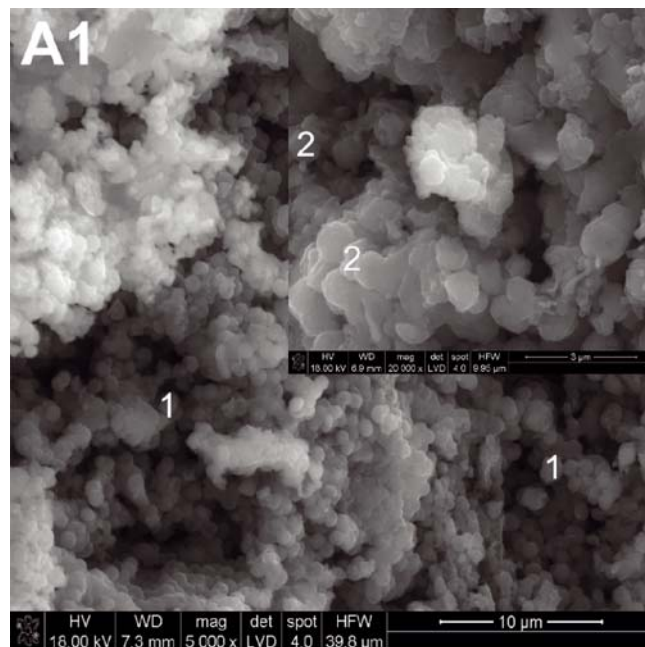


Figure 3. SEM micrographs of geopolymers respectively from samples A1 and B1

IR studies of sorption of heavy metal cations on geopolymers

The sorption of heavy metal cations from aqueous metal salts was carried out for the A1 and B1 samples. The registered spectra are presented in Figure 4.

According to Mozgawa³⁵, the immobilization of heavy metals causes noticeable changes in IR spectra. A cursory analysis of the MIR spectra (Fig. 4) recorded for the investigated geopolymer materials after the sorption

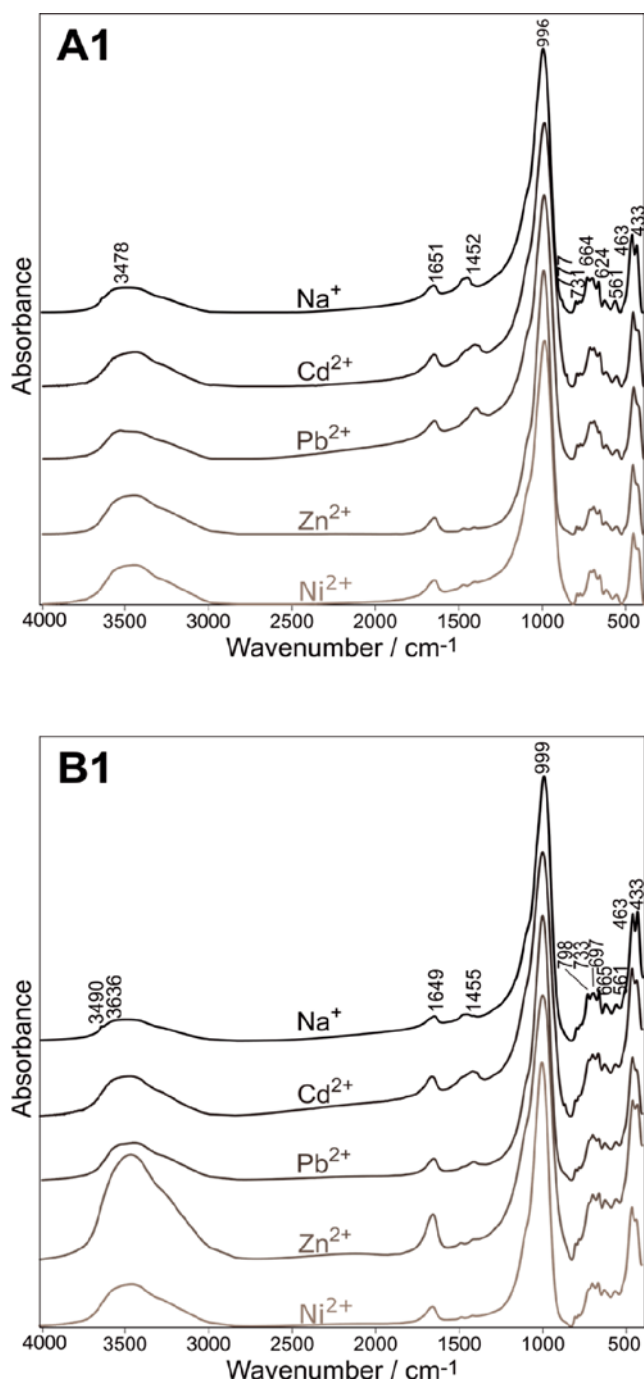


Figure 4. IR spectra after sorption of heavy metal cations on A1 and B1 samples

of heavy metal cations indicates that they do not differ significantly. Changes related to vibrations originating from O-H groups should be observed in the frequency range of $3100\text{--}3700\text{ cm}^{-1}$. This band is composed of several bands of varying nature and location within the zeolite framework, including bands corresponding to silanol (Si-OH) group/bond vibrations on the surface of grains or on the surface of mesopores, silanol groups/bonds in framework defects, and bridged acid groups (Si-OH-Al)³⁶. The impact of the sorbed cations on the geopolymer structure is clear when the fragments of spectra in a narrower range of wavenumbers ($700\text{--}500\text{ cm}^{-1}$) are compared (Fig. 4). For B1 sample a considerable increase in the intensity of bands corresponding to particular ions is observed, in the following order: $\text{Pb}^{2+} < \text{Cd}^{2+} < \text{Zn}^{2+} < \text{Ni}^{2+}$. When comparing the band intensities with the size of the ionic radii ($\text{Na}^+ - 116\text{ ppm}$, $\text{Pb}^{2+} - 133\text{ ppm}$, $\text{Cd}^{2+} - 109\text{ ppm}$, $\text{Zn}^{2+} - 88\text{ ppm}$, $\text{Ni}^{2+} - 72\text{ ppm}$), the following correlation can be noted: the decrease in the size of cationic radii is accompanied by an increase in the intensity of the bands corresponding to stretching vibrations of OH groups. In the case of the A1 sample, the observed dependence is different: $\text{Cd}^{2+} < \text{Zn}^{2+} < \text{Ni}^{2+} < \text{Pb}^{2+}$. These changes may be connected to the different nature of cations that coordinate hydroxyl groups, and, more specifically, their behavior in aqueous media. This is the result of hydration and the difference in the tendency of the analyzed cations to form water complexes in an aqueous environment.

In the range of pseudolattice vibrations ($800\text{--}600\text{ cm}^{-1}$) for all materials, clear shifts of bands towards lower frequencies and a slight change in intensities were observed. Changes in IR spectra occur because of the exchange of Na^+ ions with heavy metal cations³⁷. Ion exchange causes changes in the space surrounding the ring, the charge and radius of cations, and the deformation of the ring.

The observed changes in the IR spectra were confirmed via the chemical composition analysis (values in percentage terms) performed both before and after the sorption of heavy metals (Table 2). The composition of the studied samples changed after the sorption of selected cations. These materials may subsequently find potential use in the sorption of heavy metals from aqueous solutions.

Table 2. Chemical composition of geopolymers before and after the sorption of heavy metal cations

Chemical composition	A1					B1			
	0	Ni	Zn	Cd	Pb	0	Ni	Zn	Cd
SiO ₂	53.31	35.69	35.77	35.20	35.66	53.31	36.46	34.81	35.91
TiO ₂	0.51	0.31	0.30	0.26	0.26	0.51	0.29	0.27	0.24
Al ₂ O ₃	42.49	31.16	30.38	31.80	31.29	42.49	31.84	30.87	32.22
Fe ₂ O ₃	0.43	0.26	0.27	0.23	0.23	0.43	0.22	0.23	0.22
CaO	0.07	0.18	0.16	0.11	0.13	0.07	0.07	0.07	0.08
MgO	0.14	0.19	0.12	0.14	0.14	0.14	0.14	0.12	0.13
NiO ₂	0.01	2.98	0.00	0.00	0.01	0.01	2.74	0.01	0.01
CuO ₂	0.00	0.54	0.01	0.01	0.03	0.00	0.01	0.01	0.01
ZnO ₂	0.00	0.01	2.28	0.01	0.01	0.00	0.00	2.23	0.01
CdO ₂	0.00	0.00	0.00	0.51	0.00	0.00	0.00	0.00	0.52
PbO ₂	0.05	0.02	0.02	0.03	3.81	0.05	0.02	0.02	0.01
Na ₂ O	1.96	27.88	30.06	30.86	27.80	1.96	27.57	30.72	30.08
K ₂ O	0.57	0.31	0.30	0.41	0.25	0.57	0.29	0.30	0.21
other	0.46	0.47	0.33	0.43	0.38	0.46	0.35	0.34	0.35

CONCLUSIONS

The study demonstrated that it is possible to synthesize composite geopolymer materials containing crystalline phases of zeolites. The selection of the appropriate synthesis conditions yielded zeolite structures, i.e. zeolites A and X as well as sodalite. The type of zeolite structure depends largely on the type of reagent (Si/Al ratio) and the temperature of activation. A number of techniques, including infrared absorption spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) confirmed the presence of crystalline zeolite structures in the amorphous geopolymer matrix. An attempting to sorb selected heavy metals on the obtained materials confirmed their effectiveness in the adsorption of cations from aqueous solutions.

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