Preparation, structure and hydrothermal stability of alternative (sodium silicate-free) geopolymers

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Abstract In this contribution, we present the preparation and structural characterization of a new type of alternative (sodium silicate-free) geopolymer system. A new procedure of geopolymer synthesis based on the preparation of a reactive geopolymer precursor by direct calcinations of low-quality kaolin with Na/K hydroxides is introduced. The subsequent formation of geopolymer matrix does not require activation by alkaline silicate solution. The compact and hardened material was prepared only by adding a small amount of water. Besides the introduction of a new synthetic procedure, we focused also on the systematic study of chemical structure, mineralogical composition and hydrothermal stability of the prepared geopolymer systems as seen by solid-state NMR spectroscopy and powder X-ray diffraction (XRD). An important part of our contribution is the demonstration of structural and mineralogical changes induced by hydrothermal treatment and long-term aging of the prepared geopolymers. It was found that redistribution of basic structural units (SiO_4^{4-} and AlO_4^{5-}) and gradual formation of zeolite fractions can be related to the observed changes in mechanical properties. Up to a certain level, the presence of zeolites enhances the mechanical properties of the prepared geopolymer systems.

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However, the additional formation of a new generation of zeolite fractions, occurring over the long-term period causes an inversion of this trend and a dramatic reduction of mechanical strength. Nevertheless, formation of the geopolymer matrix by alkaline and thermal activation of low-quality kaolin has the potential to be used in ecological problems solving (solidification of powdered and dangerous waste materials).

Introduction

Geopolymers that belong to the family of aluminosilicate ceramics synthesized at room temperature have attracted commercial attention for their superior mechanical properties and relatively low production cost for a long time. Davidovits, in his pioneering works [1–5], defined geopolymers as the systems originating from the reaction of metakaolin with a concentrated solution of alkali silicate. It is supposed that during this process, the disintegration and gradual dissolution of metakaolinite is initiated. Subsequent rearrangement of aluminum species and their polycondensation with oligosiloxane molecules leads to the formation of an amorphous and/or partially ordered three-dimensional network of Si–O–Al bonds [1–2]. Depending on the initial Al/Si ratio, pH of solution, curing time and other factors [6] the resulting monolithic ceramic-like composites are composed of various combinations of polysialate, polysialate-siloxo, and polysialate-disiloxo repeating units. These building blocks are based on fully condensed silica tetrahedra $Q^4(n\text{Al})$, where n, ranging between 1 and 4, reflects the extent of aluminum substitution in the second coordination sphere. In several later

works, however, incomplete polycondensation of silanol groups was observed leading thus to the presence of hydroxyl-substituted Q^2 and Q^3 units [7, 8]. In addition, in some cases residual metakaolinite was found in final geopolymer composites [9–12]. Consequently, geopolymers—the systems prepared by alkaline activation of metakaolin—must be considered as very complicated nanocomposites that are difficult to define, with variable structure, composition and morphology.

Current trends in geopolymer chemistry are to develop new types of geopolymer systems at low energy requirements but still possessing good mechanical properties. As follows from the literature [13] and from our previous studies, one possible way how to achieve formation of such geopolymers is the reaction of metakaolin with a concentrated solution of NaOH. The main advantage of these techniques is utilization and/or solidification of waste materials like colored kaoline, fly ash or slag [11, 14–16]. In this contribution we introduce a quite novel and very promising procedure that is based on the preparation of reactive geopolymer precursor by direct calcinations of kaolin with sodium and potassium hydroxide.

However, the preparation and manufacturing of new types of geopolymers is only one part of our research. The expected application of these composites as building materials or solidifiers of dangerous substances requires also deep investigation of their long-term stability under various conditions. According to our best knowledge only a limited number of studies dealing with natural and/or artificial aging of geopolymers has been published [9, 17–21]. We believe that the stability of geopolymer materials is the critical parameter for their widespread application. As every chemical reaction can be accelerated by an increase in temperature, also aging of geopolymers can be artificially induced, e.g. by hydrothermal treatment. That is why we focused our work on the investigation of hydrothermal stability of these new geopolymer systems prepared by alternative procedures. In our investigation the prepared materials were treated under relatively soft conditions not far from natural state. From this point of view the testing of the prepared geopolymer systems under hydrothermal conditions is an invaluable aid for understanding the processes which normally continue for many years. Consequently the obtained results provide primary indications about long-term stability of geopolymers.

For deep structural characterization of the studied materials we combined X-ray diffraction (XRD) and solid-state NMR spectroscopy, the methods that are very informative and mutually complementary. While solid-state NMR can give information about structure of the amorphous phase, XRD can easily describe changes in mineralogical composition. ^{27}Al and ^{29}Si MAS NMR spectroscopy is capable not only to recognize tetrahedral or octahedral coordination of Al atoms but also makes it possible to distinguish various structure units according to the number of Al atoms in the second coordination sphere around the central Si atom.

In this contribution we present a set of preliminary results that are a part of a large project devoted to the investigation of stability of geopolymer composites prepared by conventional as well as alternative procedures from waste materials. We would like to demonstrate that the proposed new synthetic procedure leads to the formation of geopolymer materials with promising mechanical properties. Further we want to discuss structural changes occurring in these systems under laboratory and hydrothermal conditions that affect mechanical properties. Though the results of our investigation introduced in this contribution have not been quite completed yet, we believe that the concepts behind our experiments as well as our findings are of interest for all chemists who deal with the development and application of complex geopolymer systems.

Experimental section

Sample preparation

The geopolymer systems were synthetized from Czech kaoline (Merkur quarry, Kadaň; composition—10–15% illite, 40–50% quartz and 40–50% kaolinite, Table 1) with added sodium and potassium hydroxides (the weight ratio of raw materials: kaoline:NaOH:KOH = 6.5:1:1. This mixture was heated at 550 °C for 4 h. An appropriate amount of water was added to the cold mixture. The cubes ($2 \times 2 \times 2$ cm) were prepared from this paste-like material in the matrix. The prepared systems were placed in desiccator for 1 week. Subsequently mechanical strength of the prepared materials was measured after 1, 7 and 177 days of curing under laboratory conditions. Alternatively the prepared systems were exposed to hydrothermal conditions for 1–7 days at 100 and/or 140 °C.

Solid-state NMR spectroscopy

^{27}Al and ^{29}Si MAS NMR spectra were measured at 11.7 T using a Bruker Avance 500 WB/US NMR spectrometer equipped with double-resonance 4-mm probehead. ^{27}Al MAS NMR spectra were acquired at 130.287 MHz; spinning frequency was $\omega_r/2\pi = 13$ kHz; 20° pulse width was 1 μs; recycle delay 2 s; and the spectra were referenced to Al(NO$_3$)$_3$ (0.0 ppm). ^{29}Si MAS NMR spectra were acquired at 99.325 MHz; spinning frequency was $\omega_r/2\pi = 10$ kHz; 90° pulse width was 4 μs; recycle delay

Table 1 Chemical composition of the starting material

Oxide	SiO_2	Al_2O_3	Na_2O	CaO	K_2O	MgO	Fe_2O_3
Weight %	63	32	0.09	0.13	1.5	0.31	2.6

30 s; and the spectra were referenced to M_8Q_8 (–109.8 ppm). Relatively short repetition delay was used to detect predominantly Si sites combined with aluminum. On the other hand fractions of crystalline quartz are not quite quantitatively detected (corresponding signal is partially suppressed). Taking into account frictional heating of the samples during fast rotation [22] all NMR experiments were preformed at 308 K (precise temperature calibration was performed).

X-ray powder diffraction

Powder X-ray diffraction was recorded using 3000P Seifert computer, SRN, CoK_α radiation. Every sample was measured between 5–70 2Θ (step 0.05° 2Θ/s) for qualitative identification of phases. For quantitative identification was every sample measured 3-times with step 0.02° 2Θ/s.

SEM

The samples were investigated by FE-SEM (Field Emission Scanning Electron Microscopy) in Hitachi S-4700 Scanning Electron Microscope equipped with EDS analyzer from ThermoNoran D-6823. The microscope works with voltages from 500 eV to 30 keV; high voltage mode is required for samples where analytical signals are recorded, low voltages are used for non-conducting samples where metal coating should be avoided.

Mechanical testing

Pressure strength values were determined using a universal testing machine (FPZ 10/90, HECKERT/THÜRINGER INDUSTRIEWERKE, Germany) in accordance with international standard for the ceramics.

Results and discussion

As previously reported [9, 17, 23] ^{29}Si MAS NMR spectra of typical geopolymers consist of a single signal centered around –92 ppm with a broad upfield-shifted shoulder. While the main signal is usually attributed to fully condensed aluminum-substituted silica tetrahedra $Q^4(3Al)$ accompanied by minor fractions of $Q^4(2Al)$ and $Q^4(4Al)$ units, the highfield-shifted shoulder corresponds to

uncombined silica $Q^4(0Al)$. Similarly also ^{27}Al MAS NMR spectra of typical geopolymers are dominated by a single signal at ca. 58 ppm corresponding to tetrahedrally coordinated aluminum sites [1, 24]. Consequently these spectral parameters can be considered as a measure of the quality of a geopolymerization process.

Signal assignment mentioned in this contribution follows from the literature [5, 7, 13, 25, 26]. However, ^{29}Si NMR spectra are very complicated, with a large number of strongly overlapping NMR signals. Great problems follow from the fact that an increasing degree of condensation of hydroxyl groups leads to the gradual decrease in chemical shift while the same trend is observed with a decreasing degree of aluminum substitution. That is why in many cases the resulting NMR spectra are almost featureless. Consequently the reported signal assignment must still be regarded as tentative.

Preparation and structure of reactive geopolymer precursor

In general, the preparation of geopolymers without the adding of an alkaline solution of sodium silicate requires some kind of initialization which must lead to the formation of reactive siloxane groups, for instance by the dissolution of suitable inorganic components. In other words something like sodium silicate must be formed directly in the system. One possible way is the use of low-quality kaolin the composition of which (kaolinite, amorphous SiO_2, quartz etc.), makes it possible that typical geopolymers $(SiO_2:Al_2O_3:Na_2O/KOH:H_2O = (2–4):1:(0.24–0.3):(3.6–6)$ [17]) can in principle be prepared in the absence of sodium silicate.

The utilization of Na/K alkali mixture, as first described by Davidovits [1], was motivated by our effort to prepare thermally stable geopolymer systems. Recently it has been shown that K-systems exhibit better thermal stability compared with Na-systems [17, 18], and quite recently it has been found that in the mixed Na/K alkali systems potassium ions are preferentially incorporated into the geopolymeric binder while sodium ions are rather located in the reservoirs containing water molecules [24]. Consequently the increase in amount of K^+ ions in the geopolymer systems seems to be highly advantageous. However, taking into account the possible application of the geopolymer systems as a building material it is better to keep the amount of K^+ ions as low as possible because of the high cost of KOH. Consequently

the ratio KOH/NaOH—1:1 can be considered as a compromise choice.

The idea is based on the preparation of a reactive geopolymer precursor. It can be assumed that during calcination of the low-quality kaolin in the presence of alkaline hydroxides, the amorphous SiO_2 gel, quartz, and other silicate minerals can at least be partially decomposed, thus producing reactive free $Al(OH)_4^-$ and SiO_4^{4-} units. Simultaneously the transformation of Al^{VI} atoms to Al^{IV} can occur, while alkaline ions necessary to compensate negative charge on tetrahedrally coordinated Al atoms are directly supplied. The resulting powdered mixture after water addition could undergo polycondensation and formation of an amorphous geopolymer matrix. Hence we believe that calcination of a suitable low-quality kaolin with powdered hydroxides offers an interesting route to the creation of a reactive precursor that can subsequently be used to produce geopolymer systems.

To confirm our idea, the structural changes induced by calcinations of kaolin were probed in detail by solid-state NMR spectroscopy and powder X-ray diffraction. In conventionally prepared metakaolin, aluminum sites exhibit a very broad distribution involving interconnected units in tetrahedral, pentagonal and hexagonal coordination (^{27}Al MAS NMR spectrum, Fig. 1a). Consequently the extent of chemical coupling of SiO_4^{4-} tetrahedra with Al species in this system is relatively low. Predominantly partially combined silica units $Q^4(1Al)$ and $Q^4(2Al)$, and uncombined silica tetrahedra $Q^4(0Al)$, together with a minor fraction of partially condensed $Q^3(0Al, 1OH)$ units are formed (^{29}Si MAS NMR spectrum, Fig. 2a). On the other hand, as expected, a much more extensive disintegration and complex transformation of silicate minerals occurs during calcination of kaolin in the presence of alkaline hydroxides. An almost complete transformation of all aluminum sites to AlO_4^{5-} tetrahedra is clearly reflected by the signal at ca. 58 ppm in ^{27}Al MAS NMR spectrum (Fig. 1b). A small hump at ca. 65 ppm probably indicates a fraction of AlO_4^{5-} tetrahedra that are linked to residual layered structural motifs [27], while the weak signal at ca. 18 ppm reflects metastable Al sites in pentagonal coordination. Therefore it appears that this type of calcination leads to the formation of an aluminum-rich phase in which AlO_4 tetrahedra are linked by corner-shearing with SiO_4 units to form predominantly $Q^4(4Al)$ and $Q^4(3Al)$ building blocks (ca. –85 and –92 ppm, respectively; Fig. 2b). Furthermore this fact indirectly confirms that the added hydroxides are extensively incorporated into the aluminosilicate matrix, and produce extra-framework cations (Na/K) maintaining electronic neutrality on tetrahedrally coordinated Al atoms. However, the most advantageous property of the prepared system is the presence of unconsumed monomers and/or dimers of Na/K metasilicates containing potentially reactive functional groups Si–O⁻
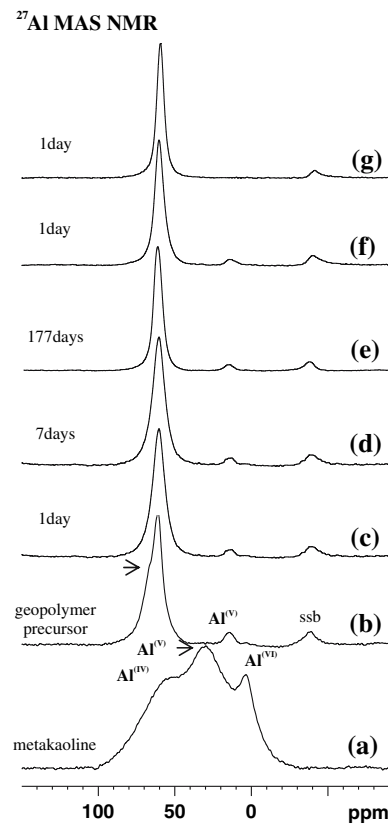

^{27}Al MAS NMR

Fig. 1 ^{27}Al MAS NMR spectra: (a) standard metakaoline; (b) geopolymer precursor, (**c**) geopolymer system after 1-day curing at RT; (d) system after 7-day curing at RT; (e) system after 177-day curing at RT; (f) geopolymer system after 7-days curing at RT and subsequent hydrothermal treatment at 100 °C (24 h); (g) geopolymer system after 7-day curing at RT and subsequent hydrothermal treatment at 140 °C (24 h)

(^{29}Si NMR signals at –72 and –78 ppm, respectively; Fig. 2b). As followed from XRD patterns (not shown here, diffractograms presented in Fig. 3 are processed to subtract broad baseline signals), the formation of these building units can be attributed to complete dissolution of amorphous SiO_2 fractions (broad reflections in the region from ca. 15 to 30°). While the diffraction signals of the amorphous SiO_2 phase completely disappeared, position and intensities of the diffraction peaks of illite and quartz are less affected (Fig. 3a, b). Chemical composition (molar ratio) of the resulting system is $SiO_2:Al_2O_3:Na_2O/K_2O = 3:1:1.1/0.8$. All the above-mentioned findings indicate that the direct calcinations of suitable low-quality kaolin with alkaline hydroxides lead to the formation of a reactive precursor possessing potentiality to produce geopolymer systems.

Geopolymerization of a reactive precursor and subsequent curing

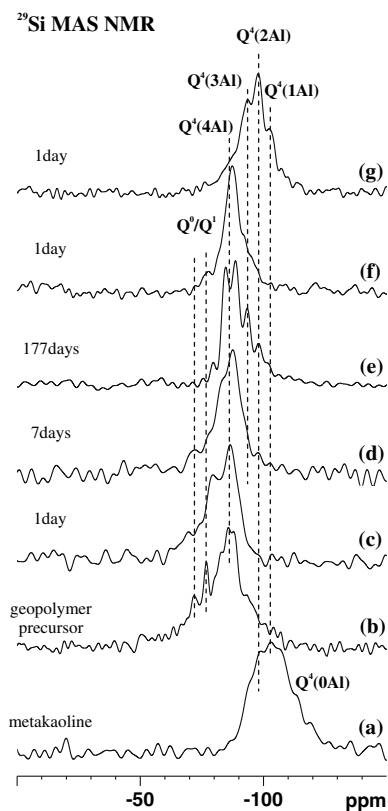After water addition, during 1-day curing at normal conditions, monomers and dimers of Na/K metasilicates

Fig. 2 ^{29}Si MAS NMR spectra: (a) standard metakaoline; (b) geopolymer precursor, (c) geopolymer system after 1-day curing at RT; (d) system after 7-day curing at RT; (e) system after 177-day curing at RT; (f) geopolymer system after 7 days curing at RT and subsequent hydrothermal treatment at 100 °C (24 h); (g) geopolymer system after 7-day curing at RT and subsequent hydrothermal treatment at 140 °C (24 h)

geopolymer, original minerals like quartz, illite and predominantly polysialate and polysiloxo-sialate structure units are presented, during half-year aging at normal conditions the whole system undergoes significant transformation. In general we observe rearrangement and increasing order of AlO_4^{5-} and SiO_4^{4-} tetrahedra, and gradual enrichment of the aluminosilicate phase by siloxane units. This is clearly reflected by the formation of narrow ^{29}Si NMR signals corresponding to $Q^4(4Al)$, $Q^4(3Al)$ and $Q^4(2Al)$ species (Fig. 2e). Further the improved arrangement corresponds to the increase in ^{29}Si NMR chemical shift. The obtained exact values of ^{29}Si NMR chemical shifts –84.8; –88.4; –93.4; and –97.6 ppm are in good accord with a previously published structural study of crystalline silicates [28]. As reflected by X-ray diffraction the observed gradual transition is accompanied by partial dissolution of quartz, and by the growth of a small fraction of zeolites (Fig. 3b–e). The amount of zeolite P (GIS) and/or phillipsite (PHI) is very small and does not fully correspond to the observed changes in the ^{29}Si NMR spectrum. This means that the observed redistribution of silica tetrahedra occurs predominantly in the amorphous phase and probably only partially ordered areas of some kinds of zeolite seeds are formed. This support previously published suggestions that a significant component of the binder phase in geopolymers is likely to be comprised of nanometer-sized crystalline structures [29]. We assume that during additional aging these partially ordered fractions could be converted to well-developed crystals.
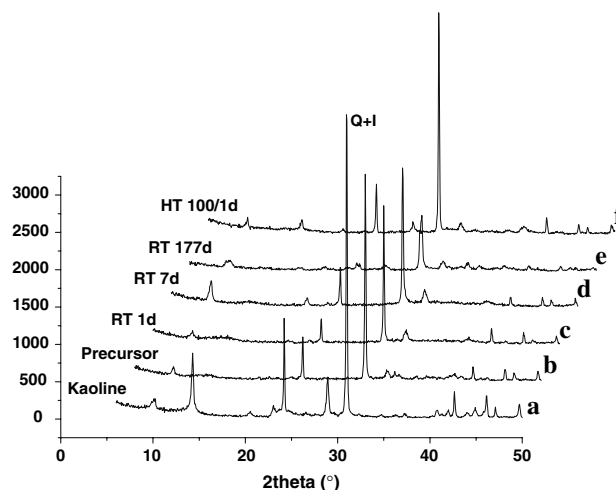
gradually condense to form an amorphous binding agent linking individual grains of the precursor (^{29}Si MAS NMR spectrum, Fig. 2c). As follows from ^{27}Al and ^{29}Si MAS NMR spectra (Fig. 1d and 2d) after the following 7-day curing, almost complete consumption of Q^0 and Q^1 structure units is reached, accompanied by disintegration of the residual layered structural motifs. The resulting material is predominantly formed by a three-dimensional framework of polysialate and polysiloxo-sialate structure units $Q^4(4Al)$ and $Q^4(3Al)$, and a small fraction of incompletely condensed aluminum substituted blocks probably $Q^3(nAl)$. These units are reflected by a shoulder at ca. –85 ppm (Figs. 2c, d). From the spectroscopic point of view the resulting material can be considered as a geopolymer system, and thus all these findings confirm that water initiates chemical reactions in the powdered geopolymer precursor leading to the formation of compact, monolithic and strengthened material.

Surprisingly structural evolution of this system is not finished. While immediately after the preparation of the

Fig. 3 X-ray difractograms of (a) kaoline; (b) geopolymer precursor; (c) system after 1-day curing at RT; (d) 7-day curing at RT; (e) composite after 177-day curing at RT; and finally (f) geopolymer composite after 7-day curing at RT and subsequent hydrothermal treatment at 100 °C (24 h)

Hydrothermal treatment of the prepared geopolymer composites

To induce crystallization and to accelerate structural changes that under normal conditions take many years, the prepared geopolymer composites were hydrothermally treated. Relatively moderate conditions of the treatment ($t < 140$ °C) were chosen to prevent extensive evaporation of capillary water and to keep the studied systems as close as possible to a normal state. At first it was found that one-day hydrothermal treatment at 100 °C of the geopolymer composite prepared by the above-mentioned procedure (7-day curing under laboratory conditions) significantly accelerated polycondensation of residual SiOH groups. This leads to completeness of the formation of a geopolymer-like phase exhibiting a high degree of order and uniformity. This is clearly reflected by narrow ^{27}Al and ^{29}Si NMR signals (Figs. 1f and 2f) indicating that the resulting geopolymer phase is nearly exclusively composed of $Q^4(4Al)$ and $Q^4(3Al)$ species. As reflected by XRD (Fig. 3f) this transformation is followed by crystallization and formation of relatively small amounts of zeolites (ca. 15%). On the other hand, one-day hydrothermal treatment at a slightly higher temperature (140 °C) causes an extensive dissolution of quartz, and dramatic rearrangement of AlO_4^{5-} and SiO_4^{4-} tetrahedra to form a semi-crystalline phase based on $Q^4(3Al)$, $Q^4(2Al)$ and $Q^4(1Al)$ units. During this process the amount of the amorphous geopolymer phase significantly increases. We found that quartz is gradually dissolved and the resulting building blocks are transformed through the amorphous geopolymer-like gel phase to crystallites of zeolites, the amount of which increases. This is clearly reflected by significant changes in signal intensity in XRD patterns (Fig. 4a) and by the formation of new ^{29}Si NMR signals at ca. –92.3; 100.2; and 105.6 ppm (Fig. 2g). The observed relatively
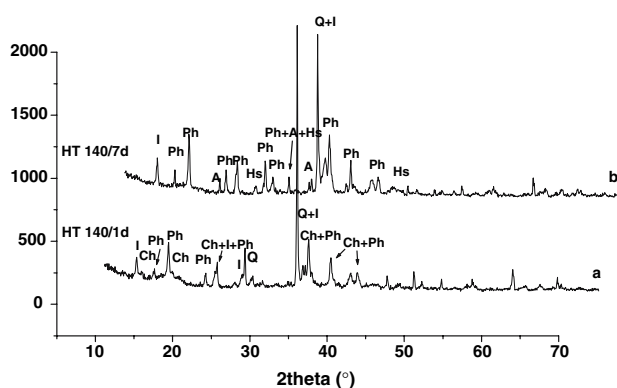
high reactivity of quartz is probably caused by the small size of the quartz particles. In our experiments we used finely-powdered kaolin exhibiting thus the high specific area. Owing to this fact the quartz particles can be more easily attacked by alkali ions during the calcination that occur above the melting points of NaOH (T_m = 318 °C) and KOH (T_m = 407 °C). These partially eroded quartz grains can subsequently participate in the transformation processes occurring during the hydrothermal treatment. During the initial period of hydrothermal treatment (1–4 days) the formation of two types of zeolites (chabasite and phillipsite) was observed, while during long-term treatment (t = 140 °C, 7 days) the amorphous phase is extensively converted to a new generation of minerals including analcime and feldspatoid hydroxisodalite (Fig. 4b).

Mechanical properties of the prepared geopolymer composites

In numerous papers [1, 15, 30] geopolymers are mentioned as potential building materials. That is why the discussion of mechanical properties and relationships with structural changes of the newly proposed alternative geopolymers is an inherent part of our investigation. Therefore we systematically measured compression strength of the studied systems after every step of the preparation procedure and aging process.

Although the alternative geopolymer systems prepared from the reactive precursor by 7-day curing exhibit all spectroscopic parameters like conventional geopolymers, their mechanical strength is relatively small (ca. 1 MPa). This fact can be explained by morphology and mechanism of the formation of these geopolymer composites. During the calcination with Na/K hydroxides, kaolinite is converted to a highly reactive metakaolinite maintaining size and shape of the original crystals that are in close contact with quartz grains (Fig. 5). Simultaneously dissolution of amorphous SiO_2 occurs leading to the formation of monomers and dimers of Na/K metasilicate. After addition of water, these monomer and dimer units strongly interact with the disturbed metakaolinite, providing primary strength to the resulting geopolymer matrix. This interaction is accompanied by the formation of linear Q^2 and subsequently branched Q^3 siloxane units (Figs. 2b–d). This indicates that strengthening of the geopolymer matrix is achieved by the gradual linking of aluminosilicate grains by polysiloxane chains to an infinite network. However, only a small fraction of monomers and dimers of Na/K metasilicate remains unconsumed after the calcination, and the resulting mixture after addition of water allows only a limited dissolution of the aluminosilicate material, because the majority of alkali cations is consumed to compensate
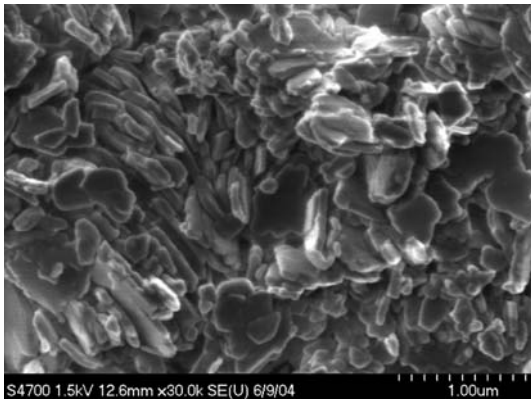

Fig. 4 X-ray difractograms of (a) geopolymer system after 7-day curing at RT and subsequent hydrothermal treatment at 140 °C (24 h); and (b) geopolymer system after 7-day curing at RT and subsequent hydrothermal treatment at 140 °C (7 days)

Fig. 5 Electron micrograph of the geopolymer precursor

negative charge on newly formed Al^{IV} sites. Consequently the amount of SiO_4^{4-} and AlO_4^{4-} structure units is not sufficient to form an extensive monolithic and infinite network (binding agent) that would be able to strongly link individual grains (Fig. 6).

An alternative explanation of the observed low mechanical properties can follow from the relatively low amount of water added to the geopolymer precursor to form the reaction mixture. The amount of water was optimized only with respect to the good processibility of the reaction mixture. That is why the amount of water was relatively low to keep the systems in pasty (creamy) consistence and not runny. This fact could lead to lower extent of geopolymer reaction and consequently to worse mechanical properties.

In general low mechanical strength does not allow applications of the prepared geopolymers as building materials. But the resulting product still can be applied as solidifier of dangerous and powdered substances. For such applications the requirements on mechanical properties are not so demanding. Nevertheless any future application of these alternative geopolymer systems requires very careful approach and detailed study of the long-term stability.

During half year aging of the prepared systems under laboratory conditions (room temperature, humidity and pressure), mechanical properties of the prepared geopolymer systems do not change notably, although significant changes in the structure of the prepared material were observed (Figs. 2 and 3). Despite compressive strength remained constant (about 1 MPa), the redistribution of siloxane structure units and the formation of zeolites clearly occurred. This indicates that the observed rearrangement does not change the overall morphology of the systems and the geopolymer binder still remains a continuous phase linking individual grains.

A quite opposite finding followed from the mechanical testing of hydrothermally treated samples. We found that under hydrothermal conditions, not brute, these materials very easily undergo not only significant structural and mineralogical changes but also dramatic changes in mechanical properties. Even one day of hydrothermal treatment at 100 °C leads to significant enhancement of mechanical strength from ca. 1 to 4 MPa. This enhancement can be attributed to the completion of geopolymerization reactions, as all monomers and reactive building blocks are consumed and simultaneously new reactive building blocks are formed from the dissolving quartz.

Much more extensive increase in mechanical strength occurs during hydrothermal treatment at 140 °C. Formation of zeolites like chabasite and philllipsite (Fig. 7) induced by higher temperature leads to hardening of the resulting geopolymer composites and maximum strength reaches up to 12–20 MPa after 1-day treatment. This follows from the fact that during this time period, the amounts of amorphous geopolymer phase reach maximum level while the amount of quartz is reduced. Gradual evaporation of capillary water increases the pH of the residual solution in the pores. That is why the dissolution of small quartz grains that are eroded by calcination with alkali hydroxides is significantly accelerated. In addition the increase in mechanical strength can be induced by the formation of a small amount of zeolites that can form secondary framework supporting the geopolymer matrix. But this trend is not continuously growing and exceeding of some limit leads to a loss of mechanical properties. It was found that during long-term hydrothermal treatment (4 days and more) amorphous geopolymer binder is consumed to form a new generation of secondary minerals, predominantly hydroxisodalite and analcime. Consequently the morphology of the geopolymer systems is changed to such extent that individual grains of the composite system are only slightly linked together. So above a certain level the presence of zeolites leads to a rapid decrease in mechanical properties and deterioration of the prepared geopolymer material.
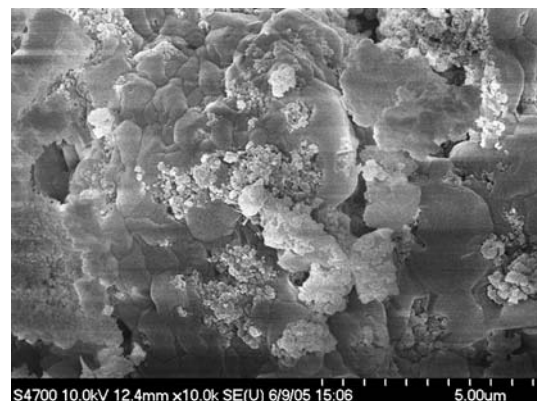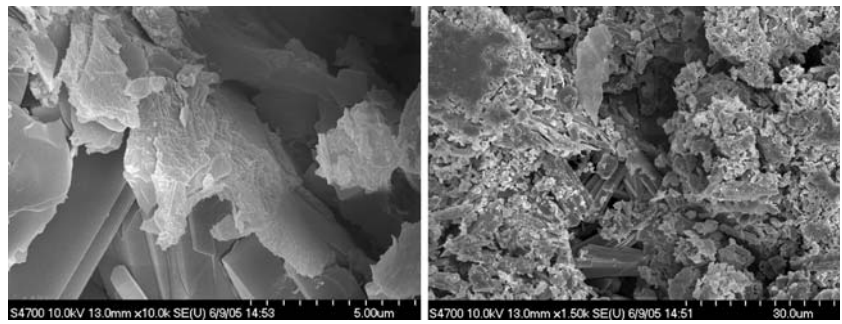

Fig. 6 Electron micrograph of the geopolymer system after 7 days curing at RT

Fig. 7 Electron micrographs (two scalings) of the geopolymer system after 7-day curing at RT and subsequent hydrothermal tratment at 140 °C (7 days). Phillipsite crystals are apparent

Conclusions

In this contribution the preparation and structural characterization of a new type of alternative (sodium silicate-free) geopolymer materials is demonstrated. The proposed quite new procedure of geopolymer synthesis is based on the preparation of a reactive geopolymer precursor by direct calcinations of low-quality kaolin with Na/K hydroxides. Such calcination leads to almost complete conversion of all aluminum sites into tetrahedral coordination and extensive chemical linking between $Si–O_4$ and $Al–O_4$ tetrahedra. Due to the presence of a sufficient amount of reactive building units based on SiOH bonds subsequent formation of a compact geopolymer composite does not require activation by alkaline silicate solution. Compact and hardened material was prepared by the addition of a small amount of pure water. However the small rate of quartz dissolution did not allow a large-scale yield of a geopolymer binding matrix, and consequently a very high strength of the resulting geopolymer system was not reached.

Besides the suggestion of a new synthetic procedure, we focused also on the systematic study of the chemical structure, mineralogical composition and hydrothermal stability of the prepared geopolymer systems. It was found that a temperature increase during hydrothermal treatment significantly accelerated the dissolution of quartz accompanied by a subsequent interaction of metasilicate units with Al–Si matrix. In initial steps this leads to an enrichment of the amorphous phase by silicon, and simultaneous redistribution of the basic structural units. Subsequent gradual formation of zeolite fractions significantly affects mechanical properties. Up to some level the presence of zeolites enhances mechanical properties of the prepared geopolymer composites. However, additional formation of a new generation of zeolite fractions occurring during longer periods causes inversion of this trend and dramatic reduction of mechanical strength. These changes are attributed to an extensive conversion of the amorphous geopolymer binding agent to crystals of zeolites. Consequently the morphology of the geopolymer systems is changed to such a degree that there is only a small possibility to link individual grains together.

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