Hydrothermal synthesis and characterisation of zeolites from metakaolin and water glass

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Abstract. Zeolites were synthesised from two types of metakaolin mixed with water glass and in some samples with water. The mixtures were autoclaved for 24 hours at 130°C. Autoclaved samples were ground to analytical fineness and tested by X-ray diffraction and differential thermal analysis. Polished samples embedded in epoxy resin were studied using of electron microprobe including BSE imaging and WDX analysis of chemical composition of zeolites. Samples with the highest zeolite content were studied by SEM. The obtained results showed that the dominant synthesised zeolite in autoclaved samples is mineral chemically close to chabazite, less phillipsite. Zeolite Na-P1, gmelinite and boggsite were also identified by XRD analyses. The total content of zeolites is up to 29 wt. % in the sample prepared from a mixture containing metakaolin MK1/sodium water glass/water in weight ratio 1.5/2.5/1. The Si/Al of synthesised zeolites varies between 2.1 and 3.2.

1. Introduction

Natural zeolites are aluminosilicates with a porous structure, classified as tectosilicates. Tectosilicates have a spatial bond of SiO4 tetrahedra. Most tectosilicates have several other ions in their crystal structure, such as Ca, K and Na. These elements can only enter the structure of the mineral if less valent ion replaces part of the Si4+ ions. In most cases it is Al3+ [1].

Zeolites are characterised by a three-dimensional bond between SiO4 and AlO4 tetrahedra defined by sharing corner oxygens [2]. Unlike other tectosilicates, zeolites have larger cavities in their crystal structure connected to each other by channels. Also, the number of pores in the structure of zeolites is significant. The size of these pores varies depending on the Si:Al ratio in the zeolite structure [3, 4]. Zeolites can retain large amounts of water and other substances. Water from the zeolite structure (so-called zeolite water) can be removed by slow heating [5].

To date, about 67 natural zeolites have been discovered, according to the International Zeolite Association. These minerals are mainly bound to volcanic rocks, in which they form fillings of cavities or amygdales. It can also be found in pegmatites, sedimentary rocks and hydrothermal veins [6].
The most common zeolites are heulandite, clinoptilolite, chabazite, stilbite, phillipsite, natrolite and analcime [7, 8].

More than 250 zeolites were prepared by hydrothermal synthesis [9]. From a structural point of view, zeolite groups (zeotypes) can be distinguished, which are identified by a three-letter code derived from a typical zeolite belonging to that group [10].

Synthetic zeolites can be prepared from a lot of chemical compounds containing Al and Si, and a lot of scientists deal with this problematic [f.e. 11–15].

Many authors tried to use natural and waste raw materials in the production of synthetic zeolites. For example, blast furnace slag [16–17], waste glass [18], fly ash [19–20], waste kaolin [21–22], natural kaolin or bauxite [23–24], aluminium waste [25], diatomite [26–27], rice husk ash [28], ash from corn cobs [29], volcanic glass [30], aluminium cans [31] or ash from bamboo leaves [32] can be used for the synthesis of zeolites.

Thanks to retaining water and other substances, zeolites are used in a wide range of applications. They are used for example as sorbents [33–34], molecular sieves [35–36], membranes [37], ion exchangers [38], catalysts [39], additive to fertilizers [40], water softeners [41], in papermaking industry [42] and animal nutrition [43].

Several researchers in the cement industry tried to use natural and synthetic zeolites as a supplementary cementitious material [44–48].

Joshaghani [45] deals with the use of zeolite as a cement replacement in concrete production. The author replaced Portland cement with zeolite in the amount of 15, 25 and 35 wt. %. Sixteen mixtures with different proportions of zeolite, with different sizes of aggregate particles and different w/c (water to cement ratio) were prepared. It was found that concrete permeability decreased when cement was replaced by up to 25 wt. % of zeolite. When the zeolite amount in the mixture is 35 wt. %, then tensile and compressive strengths of concrete decrease within 90 days. The used w/c of 0.37 seems to be the best in terms of reaching the highest strengths of the resulting concrete.

Sičáková et al [46] studied the long-term properties of composites with the addition of natural zeolite. Cement was doped with zeolite in an amount of 8, 13 and 25 wt. %. In one case, microsilica was added to the mixture. Concretes based on zeolite-doped cement show higher bulk density in 3 years of testing than concrete with ordinary Portland cement, on the contrary, 28-day strengths were lower. Higher zeolite content (25 wt. %) in the mixture reduced the compressive strength of the resulting concrete.

In this work, the initial results of the synthesis of zeolites from two different metakaolines in a mixture with sodium water glass are presented. The aim of the work is to verify the suitability of using two types of metakaolins, which differ in their composition and origin of the raw material. Metakaolin Mefisto L05 is made of claystone and Mefisto K05 is made of kaolin. Another goal of the work was to study in more detail the chemistry of synthesized zeolites using electron microprobe. Work on this topic should lead to the production of a material with a high zeolite content, which could be used as a supplementary cementitious material.

2. Materials and methods

The following raw materials were selected for the hydrothermal synthesis of zeolites: metakaolines Mefisto K05 (in the text as MK1) and Mefisto L05 (in the text as MK2), which are kaolinitic clays calcined at 750°C, sodium water glass and water.

The chemical composition of metakaolines was studied on the X-ray spectrometer PANanalytical Axios PW4400/30 with Rh lamp, 40 kV/40 mA. The SiO2 content of the water glass was determined by the gravimetric method, Na2O by the atomic mass spectroscopy and H2O gravimetrically by loss of drying and ignition according to ČSN 72 0102 [49]. The chemical composition of raw materials is given in tables 1 and 2.
Table 1. Chemical composition, loss of drying and silicate module of sodium water glass; values in wt. %.

| Sodium water glass |       |
|--------------------|-------|
| Na$_2$O            | 12.28 |
| SiO$_2$            | 21.74 |
| Loss of drying     | 41.95 |
| Silicate module    | 1.65  |

Table 2. Chemical composition and loss of ignition of metakaolines; values in wt. %.

|        | MK1   | MK2   |
|--------|-------|-------|
| SO$_3$ | 0.05  | 0.09  |
| P$_2$O$_5$ | 0.07 | 0.17  |
| TiO$_2$ | 1.56  | 1.23  |
| SiO$_2$ | 53.32 | 53.21 |
| Al$_2$O$_3$ | 37.09| 42.94 |
| Fe$_2$O$_3$ | 3.34 | 0.92  |
| MgO    | 0.88  | 0.28  |
| CaO    | 2.64  | 0.20  |
| Na$_2$O| 0.00  | 0.00  |
| K$_2$O | 1.23  | 0.78  |
| Loss of ignition | 2.10 | 1.59  |

Samples dried at 60°C and ground below 0.09 mm were analysed on the Bruker D8 Advance with Cu anode ($\lambda$Kα=1.5418 Å) with variable divergent aperture screens at Φ-Φ reflective Bragg-Brentano parafocusation geometry. Quantitative phase analysis was performed using the Rietveld method. In the case of amorphous phase determination, a standard (finely ground CaF$_2$) of 20 wt. % was mixed with the sample. The results of X-ray diffraction of metakaolines are given in table 3.

Table 3. XRD phase analysis of metakaolines (values in %).

| Phase           | MK1 | MK2 |
|-----------------|-----|-----|
| Mullite         | 7.7 | 1.0 |
| Quartz          | 4.7 | 6.3 |
| Anatase         | 1.2 | 1.9 |
| Kaolinite       | 4.2 | 3.6 |
| Illite/muscovite| 4.9 | 4.1 |
| Microcline      | 6.8 | -   |
| Amorphous phase | 70.5| 83.1|

Differential thermal analysis (DTA) was done on the dried and ground samples. The measurement was performed on device Perseus STA 449 (Netzsch) in the temperature range 35–1000°C with heating rate 10°C/min in dynamic atmosphere of synthetic air (N$_2$/O$_2$ 80/20).

Samples of autoclaved mixtures ground below 0.09 mm were embedded in epoxy resin, ground on SiC papers with several grits and polished with diamond paste on polishing machine Struers Labo-Pol 30. Polished samples were coated with a thin layer (30 nm) of carbon in vacuo. Analyses of zeolites were carried out on electron microprobe Cameca SX-100. The following phases were used as standards: sanidine (Si, Al, K), albite (Na), apatite (P), Rb-Ge glass (Rb), wollastonite (Ca), celestite (S, Sr), halite (Cl), barite (Ba), hematite (Fe), LiF (F), BN (N), rhodonite (Mn), ZnO (Zn), chalcopyrite (Cu), vanadinite (Pb). In point analyses, an acceleration voltage of 15 kV, beam current of 4 nA and beam diameter of ~1µm were used. Peak counting times (CT) were usually 20 s (for N 120 s), CT for each background were half of that of peak. Raw counts were converted to wt. % using standard PAP.
procedure. Contents of the elements mentioned above, which are not included in the tables, were consistently below the detection limits usually ranging between 300 and 1000 ppm, in case of Pb, Sr, N and F between 2000 and 3000 ppm. Photographs of the samples were taken in BSE.

Scanning electron microscopy (SEM) analysis was performed on a TESCAN MIRA3 device operating at 10 kV. Powder sample was placed under a sample holder where scans were acquired at different points within the sample with different magnifications.

2.1. Mixtures preparation

The required amount of metakaolin was weighed. Subsequently, sodium water glass was added in and the mixture was stirred in a mixer at medium speed for 5 minutes. Then, water (for MS1, SK1) was added to the mixture, followed by stirring for another 10 minutes. Mixtures MS2 and SK2 were stirred for 15 minutes. The resulting mixtures were casted into a 20 × 20 × 100 mm silicone mould and subsequently cured at room temperature for 48 hours (for mixtures marked with the letter "a"). After that, the samples were demoulded and autoclaved for 24 hours at 130°C. The mixtures marked "b" were autoclaved in the form of a gel/liquid mixture immediately after stirring. The mixture proportions are given in table 4.

| Table 4. Mixture proportions, values in grams. |
|-----------------------------------------------|
| Sample | MK1  | MK2  | Sodium water glass | Water |
| MS1a   | 177.8 | 302.2 | 120               |
| MS2a   | 222   | 377.8 |                   |
| MS1b   | 177.8 | 302.2 | 120               |
| MS2b   | 222   | 302.2 |                   |
| SK1b   | 177.8 | 302.2 | 120               |
| SK2b   | 222   | 377.8 |                   |

3. Results

3.1. XRD analysis

Autoclaved samples consist mainly of the amorphous component, which is most represented in the sample MS1a, the least in the samples SK (table 5). Except for the amorphous component, the following phases were identified by XRD analyses: quartz [SiO₂], muscovite [KAl₃(AlSi₃O₁₀)(OH)₂], anatase [TiO₂], trona [Na₂H(CO₃)₂·2H₂O], mullite [3Al₂O₃·2SiO₂], kaolinite [Al₂O₃·2SiO₂·2H₂O], thermonatrite Na₂CO₃·H₂O and microcline [KAlSi₃O₈]. The results of Rietveld analysis are summarised in table 5. Zeolites in the samples are represented by chabazite [(Ca,K₂,Na₂)[Al₂Si₆O₁₈]·12H₂O], phillipsite [Na₃[Al₂Si₆O₁₈]·2H₂O], boggosite [Ca₈Na₃(Si,Al)₆O₉·70H₂O] and gmelinite [Na₉(Si₈Al₄)O₂₄·11H₂O]. Also, Na-P1 zeolite [Na₆Al₆Si₁₀O₃₂·12H₂O] was identified, but it wasn’t possible to determine its percentage in the sample, whereas this phase is missing in the program evaluating the quantity of individual components in the sample. Highest zeolite contents (up to 29%) were found in SK samples (table 5).

3.2. DTA analysis

Autoclaved mixtures ground below 0.09 mm were analysed by differential thermal analysis and the measurement was performed in temperature range 35–1000°C with heating rate 10°C/min. The results of DTA analysis are shown in figure 1 and table 6. The dehydration temperature of zeolites is characterised by an endotherm in the range of 139 to 285°C (table 6, figure 1) and most closely corresponds to the published curves for chabazite [50]. Other zeolites mainly occur in small amounts in the samples and probably therefore no visible changes were recorded for these zeolites in the DTA, TG and DTG curves.
Table 5. XRD phase analysis of autoclaved samples.

| Sample   | MS1a | MS1b | MS2a | MS2b | SK1b | SK2b |
|----------|------|------|------|------|------|------|
| Phase    |      |      |      |      |      |      |
| Quartz   |      |      |      |      |      |      |
| Muscovite/illite | 5.3  | 3.1  | 4.4  | 4.2  | 0.7  | 0.9  |
| Phillipsite | 2.0  | 3.8  | 6.6  | 1.9  | 6.9  | 8.7  |
| Gmelinite | 1.2  | 1.9  | -    | 1.7  | -    | -    |
| Mullite   | 0.9  | 0.7  | 0.7  | 1.1  | -    | -    |
| Trona     | 3.9  | 5.3  | 3.1  | 1.9  | -    | -    |
| Thermonatrite | 0.5  | -    | -    | -    | -    | -    |
| Chabazite | 2.7  | 7.0  | 2.8  | 6.9  | 16.5 | 17.3 |
| Kaolinite | 0.2  | 1.8  | -    | 1.3  | -    | -    |
| Zeolite Na-P1 | ?    | ?    | ?    | ?    | 0.4  | 0.7  |
| Anatase   | 1.8  | 1.3  | 1.8  | 1.8  | 2.8  | 3.0  |
| Boggsite  | -    | -    | -    | -    | 11.9 | 10.2 |
| Microcline |     |     |      |      |      |      |
| Amorphous phase | 76.1 | 69.5 | 74.9 | 71.2 | 46.9 | 44.9 |
| Sum of zeolites | 5.9  | 12.7 | 9.4  | 10.5 | 26.2 | 29.0 |

Not very significant endotherm in the range of 400–600°C visible on DTG curves for all samples and in the case of SK samples also on the DTA curve probably indicates the loss of crystal water from the zeolite structure. The exotherm in the range between 859 and 874°C, which is most evident in the SK2 mixture is apparently related to the destruction of the framework of the minerals and probably the transformation of zeolite into basic members of the plagioclase group. However, we have not verified this by XRD or WDX analysis. The total loss of mass of the samples heated to a temperature of 1000°C is in the range from 11.4 to 15.8%, whereas the highest loss of mass was analysed in samples SK1 and SK2, which contain the highest content of zeolites.

Table 6. Thermoanalytical data of autoclaved samples.

| Sample   | Temperature of dehydration (°C) | Total loss of mass up to 1000°C (%) | Temperature of transformation, destruction of framework of zeolite (°C) |
|----------|---------------------------------|------------------------------------|---------------------------------|
| MS1a     | 139-201                         | 14.15                              |                                  |
| MS1b     | 144-195                         | 13.75                              |                                  |
| MS2a     | 150-194                         | 13.02                              |                                  |
| MS2b     | 140-182                         | 11.43                              |                                  |
| SK1b     | 145-200                         | 15.08                              |                                  |
| SK2b     | 152-285; 499                    | 15.84                              | 874                             |

3.3. WDX analysis and SEM

Autoclaved samples were analysed by electron microprobe to identify the chemical composition of synthetised zeolites. It has been found that the synthesized zeolites by their chemistry do not correspond to the published data for individual minerals, but chemically they are in some cases close to them. The main monovalent cations that enter the structure of the zeolite is Na, significantly less K, Ca and NH₄. These constituents are isomorphically substituted in the crystal structure of the mineral. In addition, the zeolites also contain trace amounts of Fe, Mg and F (tables 7–8). Contents of other elements (S, P, Zn, Cu, Sr, Ba, Pb, Rb) are mostly negligible (below 0.02 apfu) (tables 7 and 8). It was found that the most abundant zeolite composition in the samples is close to chabazite-(Na), less phillipsite, which also corresponds to the results of XRD analyses (see table 5). The representative WDX analysis of chabazite-(Na) are shown in the table 7 and phillipsite in table 8. In the MS samples,
a number of particles of unreacted components are visible in the backscattered electron images (figure 2 a–d), while in the SK samples the spherical aggregates of zeolites already significantly dominate (figure 2 e, f). Samples with the highest content of zeolite (SK1 and SK2) were studied using a scanning electron microscope. Zeolite aggregates have been found to be up to 30 micrometers in size. Two types of zeolites with different structures were found in the SK1 sample (figure 3 a, b).

Figure 1. TG, DTG and DTA curves of autoclaved samples.
**Figure 2.** BSE images of autoclaved samples: a) MS1a, b) MS1b, c) MS2a, d) MS2b, e) SK1b, f) SK2b; spherical aggregates represent zeolites; ant – anatase, Kfs – potassium feldspar, php – phillipsite.
4. Discussion
Crystallisation of zeolites takes place quickly in samples with MK1, zeolite content in these samples is up to 29%. This can be due to the fact that metakaolin MK1 contains a larger amount of K-feldspars and mullite, from which a large amount of zeolites can be formed by hydrothermal synthesis [51, 52]. Formation of thermonatrite and trona in MS samples probably relates to the reaction of unreacted Na with airborne CO$_2$ and water (in the case of trona). Higher amounts of zeolites were formed in samples autoclaved in the form of gel/liquid immediately after stirring the mixture. In the case of samples which were firstly cured at room temperature for 48 hours and subsequently autoclaved, the contents of formed zeolites are slightly lower (see table 5).

The used metakaolines contain only a small amount of Ca and K and water glass has a high Na content, it was probable that predominantly Na will enter the zeolite structure and thus Na-rich members of chabazite, phillipsite and gehlenite were formed. In the ternary diagram of Na$_2$O-K$_2$O-CaO we can see that sodium is the dominant element in the structure of most zeolites (figure 4). Only, in 6 point analysis, K-rich members of zeolites were identified (figure 4).

In some analysis, minute inclusion of a foreign phases, such as quartz or feldspar, were detected to be enclosed in zeolites. Thus, it is probable that some of the analyses correspond to a mixture of zeolite and unreacted components originated from raw materials and the contents of Si, Al and alkalis are significantly affected in these cases.

Compared to other research, in our work metakaolin with calcination temperature 750°C was mixed with water glass, in contrast, in Novembre et al [53] metakaolin calcined at 650°C was mixed with a solution of NaOH and SiO$_2$ in various proportions. The mixture has been cured at a temperature of 68°C and ambient pressure. Na-A zeolite began to form after about 8 hours, hydroxysodalite after 190 h and Na-P zeolite after 382 hours.

In work of Pereira et al [54], zeolite-A was synthesised from two types of calcined kaoline, white and red. The calcination temperature of kaoline was 600°C and the endurance was 12 hours. The used metakaolins had slightly higher contents of K$_2$O and TiO$_2$ compared to the metakaolines used in our research. The metakaolin was then mixed with NaOH in a NaOH/metakaolin ratio of 8:1. The mixture was heated at 80°C for 24 hours. The synthesised zeolites had the following chemical composition 43.52-44.35 wt. % SiO$_2$, 33.82-34.39 wt. % Al$_2$O$_3$, 19.82-20.59 wt. % Na$_2$O and traces of Ti, Fe, Mg, Ca, Mn and K. In the case of our research, zeolites with a more variable chemical composition are formed (see tables 7 and 8). As verified in our study, it’s not necessary to add NaOH as a reagent.

Figure 3. SEM images of zeolites: a) sample SK1b, b) sample SK2b.
to the mixture. Water glass can also perform this function, but the growth rate of the zeolite isn’t probably so fast.

Table 7. WDX analyses of zeolites with a chemical composition close to chabazite-(Na),
apfu values are recalculated on the 24 atoms of O per formula unit; n.a. – not analysed,
b.d.l. – below detection limit.

|          | MS1a | MS2a | SK1b | MS1b |
|----------|------|------|------|------|
| SO₃      | 0.03 | 0.13 | 0.02 | 0.03 |
| P₂O₅     | 0.05 | 0.04 | 0.03 | 0.02 |
| SiO₂     | 42.01| 45.63| 56.05| 52.84|
| Al₂O₃    | 17.61| 20.67| 22.56| 22.19|
| MgO      | 0.07 | 0.10 | 0.26 | 0.19 |
| CaO      | 0.20 | 0.20 | 0.91 | 1.52 |
| SrO      | 0.10 | 0.13 | 0.04 | 0.03 |
| BaO      | b.d.l.| b.d.l.| b.d.l.| b.d.l.|
| FeO      | 0.35 | 0.41 | 0.31 | 0.35 |
| MnO      | 0.01 | 0.04 | 0.04 | 0.05 |
| Na₂O     | 7.27 | 7.30 | 6.84 | 7.96 |
| K₂O      | 0.69 | 0.54 | 3.58 | 3.35 |
| (NH₄)₂O | 0.83 | 1.94 | b.d.l.| b.d.l.|
| Cl       | 0.17 | 0.12 | 0.04 | 0.05 |
| F        | 0.23 | 0.18 | 0.21 | b.d.l.|
| SiO₅/Al₂O₃| 2.39 | 2.21 | 2.48 | 2.38 |
| S⁶⁺      | 0.004| 0.016| 0.001| 0.007|
| P⁵⁺      | 0.008| 0.006| 0.004| 0.004|
| Si⁴⁺     | 8.032| 8.738| 8.079| 8.022|
| Al³⁺     | 3.968| 4.184| 3.892| 3.970|
| Mg²⁺     | 0.020| 0.026| 0.056| 0.027|
| Ca²⁺     | 0.040| 0.036| 0.143| 0.226|
| Sr²⁺     | 0.012| 0.012| 0.013| 0.033|
| Ba²⁺     | b.d.l.| b.d.l.| 0.002| b.d.l.|
| Fe²⁺     | 0.056| 0.058| 0.037| 0.038|
| Mn²⁺     | 0.002| 0.006| 0.004| 0.008|
| Na⁺      | 2.694| 2.430| 1.958| 2.314|
| K⁺       | 0.168| 0.118| 0.666| 0.641|
| NH₄⁺     | 0.183| 0.425| b.d.l.| b.d.l.|
| Cl⁻      | 0.056| 0.034| 0.010| 0.010|
| F⁻       | 0.140| 0.098| 0.100| b.d.l.|
| Si/Al    | 2.02 | 1.87 | 2.07 | 2.02 |
| Si+Al    | 12.00| 11.99| 11.97| 11.99 |

It is known from several studies that the Si/Al content in zeolite, which is used as a supplementary material, significantly affects the properties of the resulting cement. Further research shows that the zeolites with a higher Si/Al ratio have higher pozzolanic activity [55]. In our study, zeolites have a SiO₂/Al₂O₃ varying between 2.1 and 3.2 (see tables 7 and 8). These materials could have relatively high pozzolanic activity. Verification of these properties will be the subject of further research.
Table 8. WDX analyses of zeolites with a chemical composition close to phillipsite, apfu values are recalculated on the 32 atoms of O per formula unit; b.d.l. – below detection limit.

|         | MS2b | MS1b | SK1b | SK2b |
|---------|------|------|------|------|
| SiO₂    | b.d.l. | b.d.l. | b.d.l. | b.d.l. |
| P₂O₅    | b.d.l. | b.d.l. | b.d.l. | b.d.l. |
| SiO₂    | 50.60 | 51.42 | 49.71 | 55.74 |
| Al₂O₃   | 20.24 | 20.82 | 21.54 | 22.25 |
| Si/Al   | 2.12  | 2.12  | 1.96  | 2.12  |
| Si + Al | 15.84 | 15.75 | 15.51 | 16.67 |

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5. Conclusion
The results presented in this publication represent initial data for the synthesis of zeolites from Czech metakaolins and water glass. Metakaolin Mefisto K05 proved to be a more suitable raw material in a mixture with water glass in the synthesis of zeolites. This is probably because the original raw material contains a higher amount of feldspar, from which zeolites are formed. A mixture with a zeolite content of up to 30% was prepared by hydrothermal synthesis and studied by XRD, DTA and WDX analysis. The synthesised zeolites correspond to their chemical composition close to Na-rich members of chabazite and phillipsite and the Si/Al varies between 2.1 and 3.2. Work on this topic continue and lead to developing of a high-grade zeolite material that could be used as a substitute for Portland cement in the concrete industry.

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