Original Article

Characterization of geopolymers prepared using powdered brick

Jan Fořt\textsuperscript{a,b,*}, Radiměř Novotný\textsuperscript{b}, Eva Vejmelková\textsuperscript{a}, Anton Trník\textsuperscript{a,c}, Pavla Rovnaníková\textsuperscript{d}, Martin Keppert\textsuperscript{a}, Vojtěch Pommer\textsuperscript{a}, Robert Černý\textsuperscript{a}

\textsuperscript{a} Department of Materials Engineering and Chemistry, Faculty of Civil Engineering, Czech Technical University in Prague, Thákurova 7, 166 29 Prague 6, Czech Republic
\textsuperscript{b} Institute of Technology and Business in České Budějovice, Okružní 517/10, 370 01 České Budějovice, Czech Republic
\textsuperscript{c} Department of Physics, Faculty of Natural Sciences, Constantine the Philosopher University in Nitra, A. Hlinku 1, 94974 Nitra, Slovakia
\textsuperscript{d} Institute of Chemistry, Faculty of Civil Engineering, Brno University of Technology, Žižkova 17, 602 00 Brno, Czech Republic

\textbf{Abstract}

Geopolymerization of waste products can contribute to the solution of current environmental issues related to depletion of natural resources. In this paper, several geopolymer mixes are prepared using waste brick in powdered form, while different alkaline activators and curing conditions are applied. Experimental results show that the reaction rate at early age decreases with the increasing silicate modulus as well as with the rise of curing temperature; the reaction is though significantly slower than, e.g., for metakaolin-based geopolymers because of the low content of amorphous phase in the brick. The most compact microstructure is observed for geopolymers with highest reaction rate at early age; with increasing silicate modulus of the activator and decreasing curing temperature the compactness gradually decreases and the specific pore volume increases. Thermal analysis shows a decreasing weight loss with increasing silicate modulus for all temperatures, while dehydration of N-A-S-H and C-A-S-H gels are identified as the most important factors. Dehydroxylation of muscovite is found for the mixtures cured at temperatures up to 60 °C only, and decomposition of calcium carbonate just for 20 °C curing. Most crystalline phases detected by X-ray diffraction analysis in designed geopolymers are identical to those found in the raw precursor, which indicates only a partial geopolymerization and presence of a significant amount of unreacted particles. For geopolymers cured at 60 °C and 80 °C, formation of zeolitic phases is observed. While sodalite and chabazite are found only in mixtures with higher reaction rate, gismondine appears in geopolymers with higher silicate modulus.

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* Corresponding author at: Department of Materials Engineering and Chemistry, Faculty of Civil Engineering, Czech Technical University in Prague, Thákurova 7, 166 29 Prague 6, Czech Republic.
E-mail: jan.fort@fsv.cvut.cz (J. Fořt).

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1. Introduction

The massive utilization of cement-based composites currently faces a growing criticism related to their significant contribution to carbon dioxide production and depletion of natural resources. The environmental risks of cement production are also accompanied by an increased health hazard for humans [1]. One of the possible solutions to overcome the mentioned issues can be found in using alkali-activated binders (often denoted as geopolymers) which represent an alternative binder type with desired durability properties and lower negative effects on the environment [2–7]. The recycling of various waste or by-products by incorporating them into construction materials poses an opportunity for waste disposal and mitigation of associated environmental negatives [8]. Therefore, quite a few geopolymer-related studies were carried out for fly ash and blast furnace slag [9–14].

Geopolymer mix design involves an application of suitable alkaline activators and curing conditions [15–17]. Regarding the optimal silicate modulus of the activator, several studies concluded that this ratio needs to be identified, together with molar ratios in particular precursors to provide a comprehensive and applicable output for materials engineers [18–20]. Lee at al. [21], concluded that the optimized length and temperature of the curing period could substantially contribute to the improvement of compressive strength. A detailed information on material’s curing, composition of precursors, or amount of applied activators is important not only for functional assessment; relevant data are required also for the evaluation of environmental factors [22].

Thanks to the extensive research of high-amorphous precursors [23–27] a paradigm associated with the unsuitability of low-amorphous precursors for geopolymerization was broken and the benefits of using waste bricks for geopolymerisation were revealed [28–32]. This trend complies with the suggestion of Mohajeran et al. [33] to pay attention to research of locally available materials despite the lower material reactivity compared to other resources [34]. Notwithstanding, neither coherent knowledge nor guidelines are available regarding the linkage between the applied silicate modulus, influence of increased temperature curing on reaction kinetics, development of chemical bonds, or formed reaction products. These points were reflected in several studies aimed at the investigation of SiO$_2$/Al$_2$O$_3$ molar ratios to provide understanding of geopolymers formation in order to maximize the mechanical performance [35, 36]. This field was found as promising also by Robayo Salazar et al. [37] who designed brick-based geopolymers with compressive strength of up to 60 MPa, which was significantly higher than in the previous works of Reig et al. [38] and Puertas et al. [39].

In this paper, reaction kinetics, microstructure and composition of geopolymers based on powdered brick are analyzed, taking into account the variations in silicate modulus of the alkaline activator and curing conditions. A comprehensive set of characterization methods including isothermal calorimetry, scanning electron microscopy, mercury intrusion porosimetry, X-ray diffraction, and thermal analysis is used in the investigations, making possible to identify the effects of principal parameters of mix design and curing on the course of chemical reactions during the hardening process and the corresponding changes of reaction products.

2. Materials and methods

2.1. Raw materials and geopolymer mixes

As a precursor for the preparation of geopolymers a waste brick powder produced during the bricks grinding process was used. The material delivered by a brick company from the Czech Republic was sieved firstly by using 125 µm sieve to reach adequate fineness and consequently dried at 105 °C for 48 h to remove excessive moisture. The particle size distribution was analyzed on the laser diffraction principle using an Analysette 22 Micro Tec plus (Fritsch) device. The mean particle size was approximately 50 µm.

At the preparation of geopolymer mixtures, for one batch 1000 g of waste brick powder, 350 g of sodium silicate (water glass with the silicate modulus of 1.6, produced by Vodní Sklo, a.s., Czech Republic), 250 g of distilled water, and sodium hydroxide pellets (produced by Fichema, a.s., Czech Republic) in four different amounts (77.85 g, 47.5 g, 27.5 g, and 12.85 g) were used. The silicate modulus of the combined sodium silicate-sodium hydroxide activator was 0.8, 1.0, 1.2, and 1.4 for the particular mixes, which were denoted as G0.8, G1.0, G1.2, and G1.4 accordingly. Geopolymer samples of 20 mm × 20 mm × 100 mm were cast into molds and cured at 20, 40, 60, and 80 °C for 7 days. Then, they were demolded and placed in a climatic chamber for another 21 days at 20 °C and 50% relative humidity.

2.2. Experimental methods

TAM Air eight-channel calorimeter (TA Instruments) was used for monitoring the development of reaction heat of prepared geopolymers. Each calorimetric channel is a twin type, consisting of a reference chamber and a sample. The ampoules of the calorimeter have a volume of 20 ml. The operating temperature range is 5 °C–90 °C, the detection limit is 4 µW.

Scanning electron microscopy (SEM) was the primary method for analyzing the microstructure of geopolymers. The SEM images were obtained using a TESCAN MIRA3 XMU device. The samples were gilded for the SEM observations Mercury intrusion porosimetry (MIP) was used to characterize the pore structure. A combination of Pascal 140 and Pascal 440 porosimeters (Thermo Scientific) was employed in the measurements.

The chemical and mineralogical composition was determined by X-ray fluorescence (XRF) spectroscopy (Thermo ARL 9400 XP) and X-ray diffraction (XRD) analysis (PANalytical XPertPRO equipped by CoKα X-ray tube, 40 kV, 30 mA). The XRD data were evaluated using a HighScorePlus software package (version 3.0.5) and JCPDS PDF2 database. The Rietveld analysis was done by Topas software. The quantification of the amorphous portion was performed using an internal standard (ZnO, 10%).

Thermal analysis (TA) was carried out by a Labsys Evo analyzer (Setaram). In the measurements, finely ground samples were prepared and placed into an alumina cup with a volume...
of 100 mm$^3$ with the sample mass of about 80 mg. The TA was conducted in the temperature range from 25 to 1 000 °C with a heating rate of 5 °C/min in an argon atmosphere (flow rate 40 ml/min).

3. Results and discussion

3.1. Brick powder

The XRF spectroscopy showed that the waste brick powder consisted of 58.8% SiO$_2$, 19.6% Al$_2$O$_3$, 5.7% Fe$_2$O$_3$, 6.9% CaO, 2.8% MgO, 2.9% K$_2$O, and 1.5% Na$_2$O which indicated its suitability as a precursor of geopolymer mix. The XRD analysis revealed quartz (SiO$_2$) as a dominant compound (26%), albite (NaAlSi$_3$O$_8$) and muscovite (KAl$_2$[AlSi$_3$O$_10$](OH)$_2$) were present by 13% each, hematite, microcline, orthoclase, illite, diopside and akermanite were found in the amounts lower than 5%. The amorphous phase content was 28%.

3.2. Geopolymers

3.2.1. Reaction heat evolution

The heat evolution rate (specific heat power) of the analyzed geopolymers is presented for two characteristic cases of samples cured at 40 °C and 80 °C in Figs. 1, 2.

For the specimens cured up to 60 °C the reaction heat development curves were similar in shape during the initial time period of 20–30 h. For all analyzed geopolymers, only one peak appearing immediately after mixing was observed (Fig. 1), which corresponded to the initial adsorption of the alkaline solution on the surface of brick particles and the following breakdown of the Si–O and Al–O bonds (see, e.g., Ref. [40]). The amount of produced heat decreased with the increasing silicate modulus of the activator and the peak maxima increased with the increasing temperature, indicating the corresponding changes in the reaction rate. The expected polymerization from the deconstructed products formed during the initial reaction phase could not be identified up to 60 °C because the generated heat decreased fast and the data obtained for times higher than 20 h were within the error range of the applied method.

The geopolymers cured at 80 °C exhibited also a second peak on the specific heat power vs. time curve corresponding to the polymerization of deconstructed compounds and formation of the aluminosilicate gels (Fig. 2). However, the effect of silicate modulus of the activator, SM, was very significant here. While for SM = 0.8 the peak was observed at 2.5 h and was very pronounced, for SM = 1.0 it appeared at 18.5 h in a form of a broad maximum, and for SM = 1.2 it only began to build up at −30 h. The magnitude of the first peak decreased with increasing SM similarly as in the case of lower curing temperatures but it was significantly higher.

A direct comparison of results obtained in this paper with other investigators could not be done because calorimetric analyses of heat evolution in brick-based geopolymers were not found in common databases. A qualitative agreement was achieved with the data reported by Yao et al. [41] for geopolymers prepared using metakaolin as a precursor. They observed a decrease of reaction rate with increasing silicate modulus and its increase with increasing curing temperature. However, the second peak on the reaction heat development curves was found already for room temperature curing. The reason for the observed differences was in the reactivity of the applied precursors. While metakaolin belongs to typical representatives of high-amorphous materials with the amorphous content above 90%, the brick powder used in this paper contained only 28% of the amorphous phase.

3.2.2. Microstructure

Fig. 3 shows a comparison of SEM images of materials with different SM which were cured at room temperature. The compact plates formed during the alkali-activation process presented the most characteristic feature. The cracks, mainly visible for G1.0 and G1.2, could be attributed to the shrinkage of reaction products. The most compact structure was observed for the G0.8 sample, with increasing SM the compactness gradually decreased. These results agreed well with the analysis of reaction heat development in Section 3.2.1; the most compact microstructure corresponded to the highest reaction rate.

The effect of curing temperature on the microstructure of analyzed geopolymers is presented in Figs. 4–7. G0.8 samples with the lowest SM (Fig. 4) had for the curing temperatures of 20–40 °C a similar structure, characterized by a high amorphous content. For 60 and 80 °C, the microstructure was free of cracks. G1.0 samples (Fig. 5) revealed for rising temperatures a more compact structure than G0.8 but cracks were
Fig. 3 – SEM images of studied geopolymers cured at room temperature.

Fig. 4 – SEM images of G0.8.

Fig. 5 – SEM images of G1.0.

Fig. 6 – SEM images of G1.2.

Fig. 7 – SEM images of G1.4.
oberved in all cases. G1.2 samples (Fig. 6) showed microcracks for 20 °C and 40 °C curing but for 60 °C and 80 °C cracks were no longer present and the reaction products were dense. These cracks were observed also by Messina et al. [42] and can be assigned to the sample preparation. G1.4 (Fig. 7) exhibited a different microstructure of reaction products than the other geopolymers; they were made up of larger units that were further covered by smaller formations. As the curing temperature increased to 80 °C, the small formations did not occur. Apparently, also the observed effects of curing temperature on microstructural changes corresponded well with the analysis of reaction rate in Section 3.2.1.

The specific pore volume, as determined by MIP, increased with the increasing silicate modulus (Fig. 8) which correlated well with the SEM results; the most compact microstructure was observed for G0.8 (Fig. 3).

Fig. 9 shows, on a typical example of G1.4, that the specific volume decreased with increasing curing temperature. This was in a good agreement with the increasing reaction rate found by isothermal calorimetry (Section 3.2.1).

3.2.3. Composition

The results obtained by the thermogravimetric analysis of studied geopolymers are plotted in Figs. 10 and 11. The weight loss (Figs. 10a–d) was significantly affected by both curing conditions and silicate modulus of the alkaline activator. The lowest weight loss was observed for G1.4 mixtures with lowest NaOH dosage; the weight loss ranged from 10.89% (20 °C) to 12.18% (80 °C). On the other hand, the most significant weight loss was found for G0.8 mixture with highest NaOH dosage; it varied from 12.37% (20 °C) to 14.25% (80 °C).

The differential thermogravimetry analysis (Fig. 11a–d) showed that the free water evaporated up to approx. 95 °C; between 95 and 130 °C the adsorbed water was removed. A further weight loss around 150–200 °C could be assigned to the dehydration of N-A-S-H and C-A-S-H gels [15]. A bimodal peak around 100–150 °C was observed also by other authors, who associated it to a weight loss of zeolitic phases [40]. However, Bernal et al. [43] concluded that this reaction could not be conclusively revealed by thermogravimetry due to the overlap with a wide dehydration peak at similar temperatures. The gradual decomposition process took place up to approximately 600 °C. Within this temperature interval, the evaporation of chemically bound water was the most significant factor, which appeared as most distinct for mixtures cured at 80 °C. The small humps around 400 °C indicated a decomposition of sodium carbonate originating in atmospheric carbonation of unreacted sodium hydroxide [44]. The minimum at ~500 °C could be attributed to the dehydroxylation of muscovite [45]; it was most distinct for mixtures cured up to 40 °C. For temperatures higher than 600 °C, geopolymers cured at 20 °C showed a shallow minimum at ~700 °C which indicated decomposition of calcium carbonate [29,43,46].

The mineralogical composition of studied geopolymers is summarized in Table 1. The XRD analysis identified quartz (SiO₂), albite (NaAlSi₃O₈) and muscovite (KAl₂(AlSi₃O₁₀)(OH)₂) as dominant compounds in all mixtures. Diopside (CaMgSi₂O₆), akermanite (Ca₂MgSi₂O₇), hematite (Fe₂O₃), illite (K₀.65Al₂(Al₀.65Si₃.65O₁₀)(OH)₂), orthoclase (KAlSi₃O₈), and microcline (KAlSi₃O₈) were found in lower amounts. The main crystalline phases identified in designed geopolymers were identical to those found in the raw precursor (see Section 3.1), which indicated only a partial geopolymerization and presence of a significant amount of unreacted particles in the geopolymers.

The contents of quartz, hematite and orthoclase gradually decreased with increasing curing temperature (Table 1). For the geopolymers cured at 60 °C, the formation of zeolitic phases was observed. The total zeolite amount then further increased to 80 °C curing but the identified phases were the same. On the other hand, the silicate modulus of the alkaline activator, SM, affected the type of zeolitic phase in a significant way. Sodalite (Na₈(Al₆Si₄O₁₆)Cl₂) was found only in mixtures with SM = 0.8, i.e., the highest dosage of sodium hydroxide. The geopolymers with SM = 1.0, 1.2 and 1.4 contained gismondine (CaAl₂Si₂O₈·4H₂O), and those with SM = 1.0 also chabazite (Ca₃Na₂K₂MgAl₂Si₄O₂·4H₂O).

The occurrence of sodalite or chabazite was observed in geopolymers based on Class F coal fly ash or kaolinite and activated by NaOH solution [47]. However, a general lack of literature describing in detail the geopolymerization of ceramics did not make possible a direct comparison of obtained results with relevant studies for similar precursors.
4. Conclusions

Waste powdered bricks were used as precursors for the preparation of geopolymers. The mix design included variations in silicate modulus (SM) of the alkaline activator and curing conditions. The experimental investigations based on the application of materials characterization techniques for analyzing reaction rate, microstructure and composition of studied geopolymers led to the following main results:

- The reaction rate at early age monitored using the time development of specific heat power measured by isothermal calorimetry decreased with the increasing silicate modulus of the activator and increased with the increasing curing temperature.
- The overall course of reactions in the precursor-activator system was for the applied powdered brick qualitatively similar to more frequently used precursors, such as metakaolin, but significantly slower because of the low content of amorphous phase in the brick powder.
- The most compact microstructure, according to the SEM analysis, was observed for geopolymers with SM = 0.8, which were also characterized by the highest reaction rate; with increasing SM the compactness gradually decreased and the specific pore volume, as determined by MIP, increased.

Fig. 10 – a–d). Relative mass change of geopolymers cured at 20 °C, 40 °C, 60 °C, and 80 °C, respectively.

Fig. 11 – a–d). Differential thermogravimetry curves of geopolymers cured at 20 °C, 40 °C, 60 °C, and 80 °C, respectively.
The decrease of specific volume with increasing curing temperature found by MIP was in a good correlation with the results of SEM experiments showing microcracks for 20 °C and 40 °C curing but dense reaction products without cracks for the curing temperatures of 60 °C and 80 °C.

Thermal analysis showed a decreasing weight loss with increasing SM for all curing temperatures, the evaporation of free and adsorbed water and dehydration of N-A-S-H and C-A-S-H gels being the most important factors for all analyzed geopolymers. Dehydroxylation of muscovite was found for curing temperatures up to 60 °C only, and decomposition of calcium carbonate just for 20 °C curing.

The main crystalline phases identified by XRD analysis in designed geopolymers were identical to those found in the raw precursor, which indicated only a partial geopolymerization and presence of a significant amount of unreacted particles.

The contents of quartz, hematite and orthoclase gradually decreased with increasing curing temperature. For the geopolymers cured at 60 °C, the formation of zeolitic phases was observed. The total zeolite amount then further increased to 80 °C curing but the identified phases were the same.

The type of zeolitic phase observed in the studied geopolymers was affected by SM in a significant way. Sodalite (Na8[Al6Si12O36]Cl2) was found only in mixtures with SM = 0.8, i.e., the highest dosage of sodium hydroxide. The geopolymers with SM = 1.0, 1.2 and 1.4 contained gismondine (CaAl2Si2O8·4H2O), and those with SM = 1.0 also chabazite (Ca4Na2K2MgAl2Si4O12·6H2O).

Summarizing the results of materials characterization experiments, the waste powdered brick analyzed in this paper can be considered as a prospective precursor for the preparation of geopolymers, despite its low amorphous content. It should be noted that it can be obtained not only as waste from brick production but also from the construction and demolition waste. In addition, a rethink of used brick powder as not only a precursor for activation but also a fine non-reactive aggregate may provide a feasible approach in materials design. Another interesting application range, e.g. for immobilization of heavy metals or radionuclide absorption and fixing, can be found in the combined geopolymer-zeolitic structures formed by geopolymerization of brick powder after curing at 60 °C and 80 °C.

**Conflicts of interest**

The authors declare no conflicts of interest.

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