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Research Paper

Micromechanical properties of geopolymers with different calcined clay precursors

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ABSTRACT

Geopolymers and supplementary cementitious materials (SCM) are potential substitutes for ordinary Portland cement (OPC). Calcined common clays appear to be well suited as raw materials for the production of geopolymers. Due to the multiphase composition of common clays, it is necessary to study geopolymers first, which are prepared of individual calcined clay minerals. Nanoindentation was used to investigate the mechanical properties of metakaolinite, metasmectite, and metaillite geopolymers. For geopolymer production Si:Al ratios between 1:1–3:1 and NaOH concentrations ranging from 4 to 10.79 mol/L were used. All geopolymers were prepared without the use of commercial waterglass. All three clay minerals could be constituents of a natural common clay. Additionally, mercury porosimetry was used to determine the porosity and average pore radius of the samples. The porosity of the studied geopolymers (20.3–31.6%) was in the range found for cement pastes. The average pore radius decreased with increasing concentration of NaOH or increasing Si:Al ratio. Hardness and average pore radius of the geopolymers with the same precursor showed a negative correlation. The highest hardness (1.09 GPa) of all geopolymers was reached by one produced with the metasmectite precursor. On average, the metakaolinite geopolymers reached a hardness of 0.19 GPa and a Young's modulus of 4.72 GPa, the metasmectite geopolymers reached values up to 0.60 GPa and 18.88 GPa. The metaillite geopolymers showed an average hardness of 0.26 GPa and an average Young's modulus of 8.43 GPa. A positive correlation of the Si:Al ratio and the hardness was determined. The hardness values found in this study were comparable to hardness values of cement pastes.

1. Introduction

Clay minerals can be used in many different industries, e.g. for paper production, molding foundries, or in construction industry. This study used three different clay minerals, which are commonly part of natural clay deposits. Kaolinite is the main clay mineral in kaolin deposits, and smectites in bentonites. Illites are contained in most clay deposits, either as minor component or as main clay mineral. Natural common clays, which are widely available all over the world, are a mixture of all the mentioned clay minerals. Due to their availability natural common clays could be a cheap source of clays, especially for construction industry which needs huge amounts of raw materials. The use of clays to produce environmentally friendly binders could reduce the CO_2 emissions of construction industry tremendously. The cement industry is responsible for 5–8% of the annual worldwide CO_2 emissions (McLellan et al., 2011). A large proportion of the emissions originates from the combustion of limestone ($CaCO_3$) during the production of the cement clinker (He et al., 2019). Geopolymers and supplementary cementitious materials (SCM) are potential substitutes for ordinary Portland cement (OPC). Natural clays to be calcined for geopolymer production or to be used as SCM contain no or low amounts of carbonates and calcination takes place at temperatures below the thermal decomposition of the carbonates. Thus, applying SCM or using geopolymers, produced with clay precursors, as a binder in construction can reduce the CO_2 emissions between 40 and 80% (McLellan et al., 2011; Davidovits, 2013). Other studies found lower reductions of the CO_2 emissions, depending on the country and the availability of precursors. Fly ash geopolymers reduce the emissions by about 9%, which is significantly lower than for geopolymers with clay precursors (Turner and Collins, 2013; Sandanayake et al., 2018). While SCM substitute only a certain amount of OPC, geopolymers are OPC-free binders. Unlike OPC which is a hydraulic binder and SCM which show either hydraulic or pozzolanic activity,

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geopolymers are alkaline activated binders. Alkaline activated binders are subdivided in high Ca and low Ca/Ca-free types (Dehn et al., 2017). Geopolymers belong to the low Ca/Ca-free alkaline activated binders.

Geopolymers are inorganic polymers with a 3-dimensional structure which are produced of aluminosilicate precursors under highly alkaline conditions. Calcined clay minerals can be used as precursors. The precursors are activated with a highly alkaline solution like NaOH/KOH or waterglass, which leads to a polycondensation and the formation of geopolymer binders. During the first step of geopolymer production the calcined clay minerals are dissolved. The second step includes the reorganization and diffusion of monomers and forming of oligomers due to association of the Si- and Al-tetrahedra. The consolidation of the 3-dimensional geopolymer network takes place in a third step during polycondensation.

Many studies on geopolymers have shown that adequate compressive strengths (up to 80 MPa for paste) can be reached (Pouhet and Cyr, 2016; Lahoti et al., 2017; Samantasinghar and Singh, 2018; Si et al., 2020). To reduce the costs of geopolymers and make them more competitive to OPC in construction industry, it would be beneficial to use calcined common clays as precursors. Common clays are a mixture of different clay minerals and calcined common clays appear to be well suited as precursors for geopolymers. Due to their multiphase composition, it is necessary to study geopolymers produced of individual clay minerals first. While there are many studies on macroscopic compressive strength of geopolymers (Pouhet and Cyr, 2016; Lahoti et al., 2017), less information about micromechanical properties is available especially for geopolymers produced with different calcined clay mineral precursors. Nanoindentation can be used to investigate the micromechanical properties of geopolymers (Škvára et al., 2006; Němeček et al., 2011; Pelisser et al., 2013; Das et al., 2015; Luo et al., 2020; Si et al., 2020).

This study investigates the micromechanical properties and microstructure of geopolymers produced with three different calcined clay mineral precursors (metakaolinite, metasmectite, and metaillite). Nanoindentation measurements were conducted to evaluate the hardness dependent on the used calcined clay mineral precursor. Additionally, mercury porosimetry was used to investigate the porosities of the geopolymers. By comparing the properties of the hardened geopolymers, the suitability of the different calcined clay minerals as a precursor was evaluated.

2. Materials & methods

2.1. Solid precursors

As clay mineral precursors for the geopolymers, three different materials were chosen. The materials differed in the main clay mineral. First KBE-1, a Bavarian kaolin (Amberger Kaolinwerke Eduard Kick GmbH & Co. KG, Hirschau, Germany) with kaolinite as main clay mineral was used. Second Ceratosil® WG, a bavarian bentonite (Clariant Produkte Deutschland GmbH, Frankfurt am Main, Germany) with the main clay mineral smectite. The third material was Arginotec INX, an illitic clay (Arginotec GmbH & Co. KG, Huenxe, Germany).

KBE-1 mainly consisted of a kaolinite ($\geq$ 93 wt%), which was low b-axis error-ordered and consisted of 46–47 wt% ordered kaolinite and 50–51 wt% disordered kaolinite. 93% BB/7% BC stacking sequences were identified for the disordered kaolinite. No additional ~b/3 stacking errors were found for 88% of BB sequences (Izadifar et al., 2020). The Hinckley Index of 1.63 was characteristic of a well-ordered kaolinite (Izadifar et al., 2020). As accessory minerals dioctahedral mica (muscovite), quartz, and anatase were present (Table 1).

The main phase of Ceratosil® WG was a dioctahedral smectite (montmorillonite) with accessory silicates, cristobalite/opal-C and carbonates (Table 1). The structural formula for the montmorillonite was $Ca_{0.1}Na_{0.1}Mg_{0.01}$ $(Si_{3.96}$ $Al_{0.04})$ $(Al_{1.48}Fe_{0.09}Mg_{0.51})$ $O_{10}(OH)_2$. The montmorillonite was classified as a medium-charged cis-vacant montmorillonite (Werling et al., 2022).

Table 1
Mineral phases (in wt%, from Werling et al., 2022).

Phase	KBE-1	Ceratosil WG	Arginotec INX
Kaolinite	93	–	5.4
Montmorillonite	–	67.1	–
Dioctahedral illite	–	–	76.4
Dioctahedral mica	5.5	2.4	–
Biotite (Phlogopite)	–	–	7.8
Zeolite (Heulandite)	–	0.9	–
Quartz	1	–	0.4
Cristobalite/Opal-C	–	13.3	–
K-Feldspar	–	10.4	4.4
Plagioclase	–	4.1	1.1
Calcite	–	1.9	2.4
Anatase	$<$ 0.5	–	–
Anhydrite	–	–	1.4
Apatite	–	–	0.7

Arginotec INX mainly consisted of a dioctahedral trans-vacant interlayer-deficient mica (2M_1 polytype, Werling et al., 2022). Small amounts ($\leq$ 10 wt%) of other clay minerals (kaolinite and trioctahedral mica) and accessory silicates, quartz, carbonates, sulphates, and phosphates could be detected (Table 1). The structural formula for the illite was $K_{0.75}$ $(Si_{3.5}$ $Al_{0.5})$ $(Al_{1.25}Fe_{0.5}Mg_{0.25})$ $O_{10}(OH)_2$ (Werling et al., 2022).

In the subsequent manuscript the terms metakaolinite, metasmectite, and metaillite will be used when referred to the calcined bulk material of KBE-1, Ceratosil WG, and Arginotec INX.

In addition to the clay mineral precursors, amorphous silica (Amosil®, HPF – The Mineral Engineers, Frechen, Germany) and industrial produced crystalline aluminum hydroxide powder (Hydrafil®, HPF – The Minerals Engineers, Frechen, Germany) were used for the adjustment of the Si:Al ratio of the geopolymers. Amosil® consisted of 99 wt% SiO_2 and Hydrafil® of 99.5 wt% Al_2O_3 with only minor impurities (Table 2).

For the production of the geopolymers in this study, no commercial waterglass was used. Waterglass in geopolymer production is commonly used for the adjustment of the Si:Al ratio. But, first by the use of commercial waterglass the environmental benefits compared to OPC are reduced, because of the CO_2 emissions due to the raw materials used for waterglass production. Second, waterglass itself polymerizes and this polymerization would disguise the properties of the geopolymers produced of the calcined clay minerals. In this study solid amorphous SiO_2 or crystalline $Al(OH)_3$ were used to in−/decrease the Si:Al ratio of the natural clay mineral precursors.

2.2. Alkaline activator

For alkaline activation ultra-pure NaOH solutions (Carl Roth GmbH & Co.KG, Karlsruhe, Germany) with concentrations of 10.70 mol/L (32%), 7.96 mol/L (25%), 6.1 mol/L (20%), 5 mol/L, and 4 mol/L were used.

3. Methods

Nanoindentation was carried out with a Nano Indenter® G200 X (KLA, Milpitas, California, USA). The hardness and Young's modulus of

Table 2
Oxide compositions of supplements (in wt%).

	Amosil®	Hydrafil®
SiO_2	99	–
Al_2O_3	0.3	99.5
Fe_2O_3	0.03	0.01
CaO + MgO	0.03	0.1
$Na_2O + K_2O$	0.03	–

the samples were measured using the test method NanoBlitz3D and a diamond Berkovich indenter tip. Arrays of 28 × 28 indents within a test area of 30 μm × 30 μm and with an indentation load of 3 mN were conducted. Between 400 and 780 indents were evaluated for each geopolymer sample. Hardness and Young's modulus were determined according to Oliver and Pharr (1992).

Mercury porosimetry was carried out with a AutoPore V 9600 (Micromeritics Instrument Corporation, Norcross, Georgia, USA). The results were evaluated using the associated software MicroActive. The maximum injection pressure used was 420.6 MPa and the measurement contact angle was 141.3°.

4. Experimental procedure

4.1. Calcination of the clay minerals

The calcination was carried out with a heating rate of 10 K/min in a L9/12/B180 furnace under air (Nabertherm GmbH, Lilienthal, Germany). The bulk materials were heated in unglazed ceramic crucibles to the final temperature and placed in a desiccator for cooling down to room temperature. For metakaolinite 700 °C, for metasmectite and metaillite 750 °C were chosen as final temperature. The calcination temperatures were selected based on the optimal activation studied in previous experiments (Werling et al., 2022). The optimal activation temperature varies depending on the material due to structural changes after dehydroxylation and resulting solubility of the main clay minerals.

4.2. Geopolymer production

Different geopolymers with Si:Al ratios between 1 and 3 were produced according to stoichiometric mixing ratios. The mixing was carried out with a Roti®-Speed stirrer (Proxxon S.A., Wecker, Luxembourg). The geopolymer samples were stirred starting with 5000 rpm and a gradual increase to a maximum of 10.000 rpm. A fixed Na:Al ratio of 1:1 resulted in varying s/l ratios for the geopolymers dependent on the concentration of NaOH which was used. During pretesting some of the mixing ratios proved to be not producible. Main reason for limitations during production was a bad workability due to high viscosity of the mixtures. Therefore, only the geopolymers with a good workability were used for further experiments (Table 3). For a good workability s/l ratios from 0.8 to 1.44 proved to be suitable.

For the geopolymer mixtures with Si:Al ratios deviating from the inherent ratio of the calcined clay mineral, amorphous SiO_2 or $Al(OH)_3$ were used as powdered additive. The SiO_2 or $Al(OH)_3$ powder was mixed with NaOH for pre-dissolution, 24 h before the production of the geopolymer. The powdered calcined clay minerals were mixed with the previously prepared SiO_2 or $Al(OH)_3$/NaOH solution or pure NaOH and stirred for 5 min. After homogeneous mixtures were obtained, the geopolymers were cast in cylindric plastic molds (PE cylinders, Kulzer GmbH, Hanau, Germany) with a diameter of 25 mm. The geopolymers in the molds were put on a vibration table (Vortex Genie 2, Scientific Industries Inc., Bohemia, New York, USA) for 2 min to release macroscopic air bubbles. Especially in more viscous samples this step was required. After vibrating the geopolymers were stored at room temperature, the molds were sealed with lids to prevent carbonation during the hardening process at ambient conditions which was observed before (Werling et al., 2020). After 3 days the geopolymers were demolded, the height of the hardened geopolymer discs was about 5 mm.

Table 3
Si:Al ratio, solid/liquid (s/l) ratio and NaOH concentration of studied geopolymers.

Sample	Si:Al [mol/mol]	s/l [g/g]	NaOH concentration [mol/L]
K1	1:1	0.89	10.79
K2	2:1	0.86	6.1
K3	2:1	1.07	7.96
K4	3:1	0.80	4
K5	3:1	0.98	5
K6	3:1	1.16	6.1
K7	3:1	1.44	7.96
C3	1:1	0.83	6.1
C6	2:1	1.0	4
C5	2:1	1.24	5
C4	2:1	1.25	6.1
I3	1:1	0.97	4
I2	1:1	1.08	5

4.3. Sample preparation for nanoindentation

After demolding, the geopolymers were left in lab atmosphere (21 °C, 50–60% r.H.) for additional 7 days for further drying. To reach a smooth sample surface for nanoindentation the surface of the geopolymer cylinders was grinded and polished in multiple steps. A MetaServ 250 grinder and polisher (Buehler, Leinfelden-Echterdingen, Germany) was used with different abrasive papers. The grinding was performed starting with a rougher abrasive paper (P2500; 8 μm) and finished with P6000 (2 μm). After polishing, the samples were cleaned from loose particles with compressed air. No diamond suspensions (or similar) were used for polishing, to avoid the need for an ultrasonic treatment to remove residual suspension particles.

4.4. Sample preparation for mercury porosimetry

One of each geopolymer discs was crushed after demolding and hardening for 7 days in lab atmosphere (21 °C, 50–60% r.H.). For mercury porosimetry a total of 2–3 g of fragments with a size between 2 and 4 mm were used. After crushing and before the measurement, the fragments were dried at 105 °C for 24 h.

5. Results and discussion

5.1. Micromechanical properties

The hardness of the metakaolinite geopolymers varied across the sample surface (Fig. 1). Some areas showed very low hardness values after hardening which could indicate incorporated particles of unreacted material. On average, all geopolymers with the metakaolinite precursor showed evolved hardness, except geopolymer K4 (Fig. 2). K4 was prepared with the lowest used concentration of NaOH (4 mol/L) and it could be assumed that metakaolinite was not activated sufficiently using this NaOH concentration. In earlier research it was already shown that

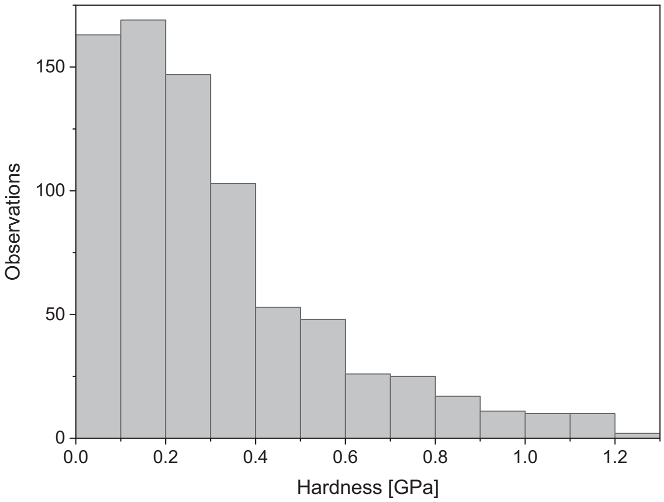

Fig. 1. Histogram for distribution of hardness over the surface of geopolymer K7.

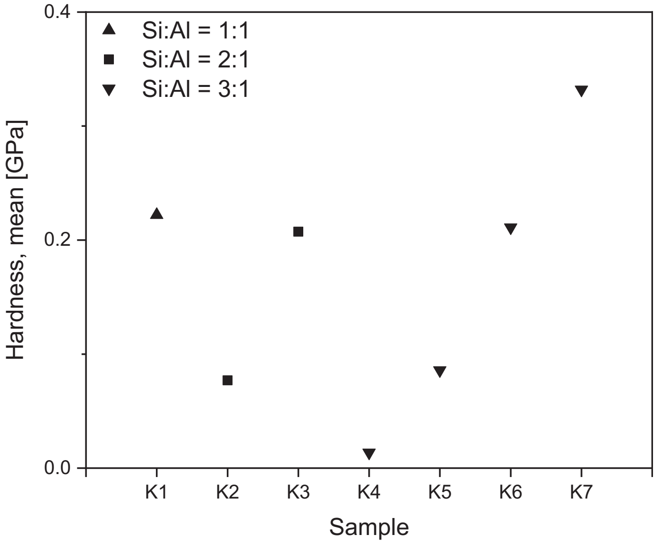

Fig. 2. Mean values for hardness of metakaolinite geopolymers.

the concentration of the activator solution influences the solubility of the precursor (Werling et al., 2022) and strength development of geopolymers (Heah et al., 2013).

The geopolymers with the metakaolinite precursor developed a hardness between 0.01 GPa for K4 and 0.33 GPa for K7. K1, with a Si:Al ratio of 1:1, showed a hardness of 0.22 GPa. K2 and K3 were prepared with a higher Si:Al ratio of 2:1. K3 was prepared with a higher NaOH concentration (7.96 mol/L) compared to K2 and developed a higher value of hardness (0.21 GPa compared to 0.08 GPa for K2). K4 – K 7 were produced with the highest Si:Al ratio of 3:1. As mentioned before, K4 did not develop significant hardness (0.01 GPa). The hardness of K5 – K7 increased with the concentration of NaOH. K5, prepared with 5 mol/L NaOH, showed a hardness of 0.09 GPa. K6 was produced with 6.1 mol/L NaOH and had a hardness of 0.21 GPa. As previously indicated, K7 developed the highest hardness of the metakaolinite geopolymers (0.33 GPa). The hardness showed a positive correlation with the concentration of NaOH. The same trend was observed for Si:Al ratio and hardness.

The values obtained for the metakaolinite geopolymers were in the range of values determined in previous studies (Pelisser et al., 2013; Zhang et al., 2017). According to Zhang et al. (2017) partially developed geopolymer gels develop a hardness in the range of 0.1 GPa $\leq$ H $\leq$ 0.35 GPa. Completely reacted and hardened geopolymers reach a hardness between 0.35 GPa $\leq$ H $\leq$ 1.5 GPa (Zhang et al., 2017). These values were obtained for geopolymers produced with a commercial waterglass (sodium silicate solution). Waterglass itself has a hardness development, additional to the hardness of metakaolinite geopolymer. This could explain the lower values of “partially developed geopolymer gels” for geopolymers produced without commercial waterglass like the ones investigated here.

The hardness of geopolymers produced with the metasmectite precursor varied across the sample surface (Fig. 3), as observed for metakaolinite geopolymers before. Four different geopolymers were produced from the metasmectite which showed a hardness between 0.29 and 1.09 GPa (Fig. 4).

C3, which was the only metasmectite geopolymer prepared with a Si:Al ratio of 1:1, developed a hardness of 0.66 GPa. For the samples prepared with a Si:Al ratio of 2:1, C5 showed a higher hardness (1.09 GPa) compared to C4 (0.29 GPa), although C4 was prepared with a higher concentration of NaOH (6.1 mol/L). Comparing the hardness of C5 and C6 (0.35 GPa), the same positive correlation with NaOH concentration as for metakaolinite geopolymers could be observed. C6 with a lower concentration of NaOH showed a lower hardness than C5. C4 seemed to be out of line, because it even developed less hardness compared to C3 with the same NaOH concentration but a lower Si:Al ratio. It is noteworthy, that metasmectite geopolymers showed higher values for hardness compared to metakaolinite ones.

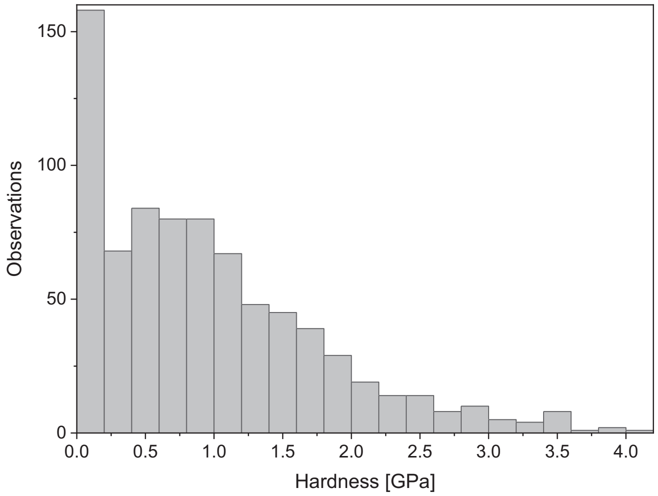

Fig. 3. Histogram for distribution of hardness over the surface of geopolymer C5.

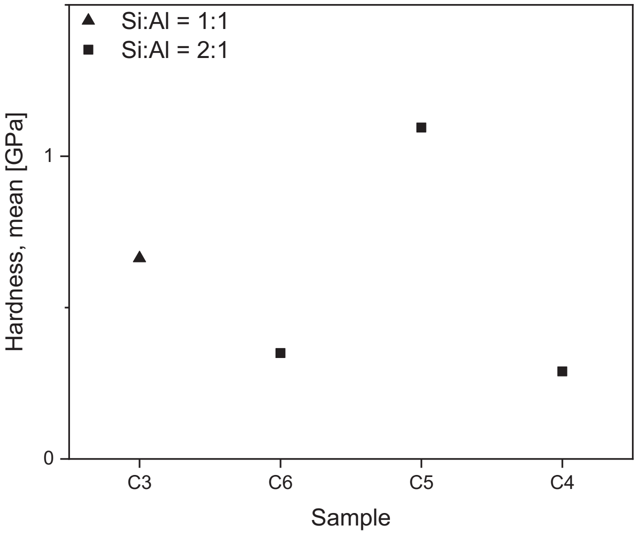

Fig. 4. Mean values for hardness of metasmectite geopolymers.

Only two geopolymers were producible for the metaillite precursor. The water demand of the precursor was very high and not all of the mixtures could be mixed homogeneously. A variation of the hardness across the sample surface was observed (Fig. 5) as for all geopolymers before. The mean values for hardness of the geopolymers with metaillite precursor was in a range of 0.24–0.28 GPa (I2 – I3; Fig. 6), which was lower than for the geopolymers with metasmectite precursor. The lower values for hardness could be explained by the mixture properties. I2 and I3 were producible, but the mixtures were difficult to homogenize and very viscous. Furthermore, the geopolymers with metaillite were only producible with the lowest concentrations of NaOH (4 and 5 mol/L) and a Si:Al ratio equal to natural kaolinite (1,1). For higher NaOH concentrations and Si:Al ratios, higher values for hardness could be expected. Therefore, it would be important to enhance the production process so that metaillite geopolymers with higher NaOH concentrations could be produced. As the metaillite geopolymers still developed hardness values in the range of the metakaolinite geopolymers, it could be assumed that metaillite is suitable as a precursor for geopolymer production, too.

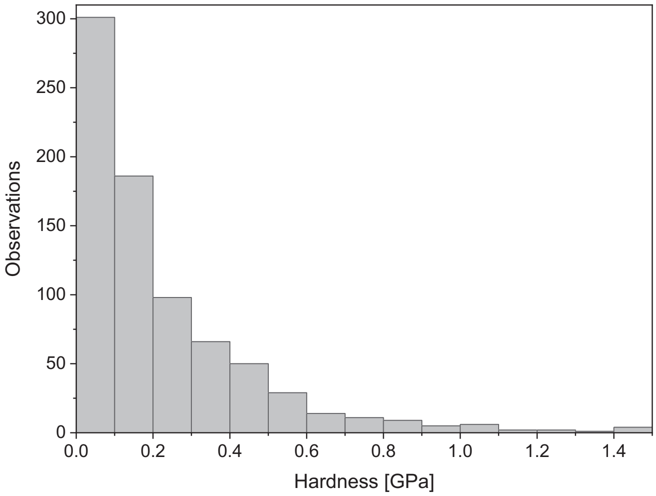

Fig. 5. Histogram for distribution of hardness over the surface of geopolymer I2.

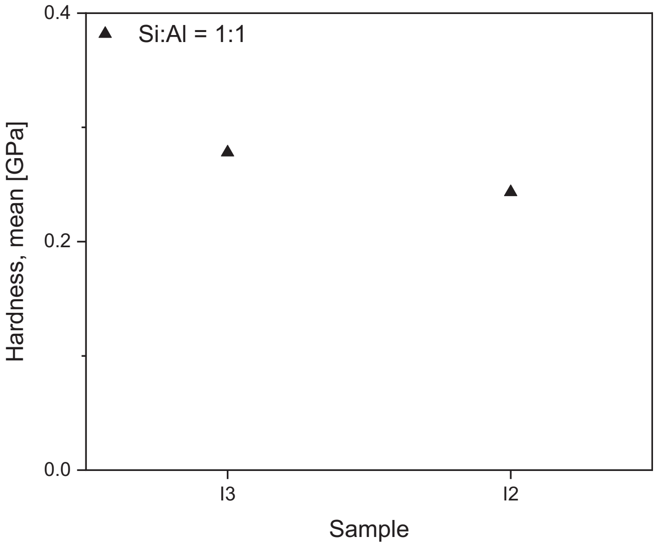

Fig. 6. Mean values for hardness of metaillite geopolymers.

Besides hardness, Young's modulus was determined by nanoindentation (Table 4). The values for Young's modulus were mainly in the range found in preliminary research for metakaolinite based geopolymers (Pelisser et al., 2013; Zhang et al., 2017). According to Zhang et al. (2017) partially developed geopolymer gels showed Young's moduli of 2 GPa ≤ E ≤ 5.5 GPa and geopolymer gels after completed reaction 5.5 GPa ≤ E ≤ 25 GPa. Only geopolymer K4 was significantly out of this range. As explained before K4 most likely contained large amounts of unreacted material.

Table 4
Average of Young's modulus (E) of geopolymers.

Sample	E average [GPa]	Standard deviation [GPa]
K1	5.98	4.09
K2	2.91	2.25
K3	5.70	3.28
K4	0.42	0.18
K5	2.04	2.58
K6	3.57	1.86
K7	8.09	3.93
C3	13.42	9.60
C6	17.30	10.68
C5	30.22	12.32
C4	14.57	9.17
I3	6.72	4.38
I2	10.13	5.14

Hardness and Young's modulus of cement pastes were already studied by nanoindentation measurements and model calculations. Model calculations yielded values in the range of 0.73 (low density CSH) – 1.27 GPa (high density CSH) for hardness of cement paste and values for Young's modulus from 23.4 (low density CSH) – 31.4 GPa (high density CSH) (Zhu et al., 2007). By nanoindentation measurements of cement pastes a maximum hardness of 1.1 GPa and Young's modulus of 26.6 GPa were determined by Pelisser et al. (2013). Vandamme et al. (2010) measured a maximum hardness of 0.812 GPa and Young's modulus of 31.35 GPa, which was in the same order of magnitude. The Young's moduli of the herein studied geopolymers were below the values for cement paste. Only C5 showed a modulus close to the value determined by Vandamme et al. (2010). The Young's moduli followed the trends determined for hardness, e.g. for metakaolinite geopolymers K4 showed the lowest and K7 the highest modulus. Comparing the moduli of the different geopolymers, the metasmectite geopolymers showed the highest values and the metakaolinite geopolymers the lowest. The maximum hardness reached by C5 (1.09 GPa) was as high as the maximum hardness for cement paste of 1.1 GPa determined by Pelisser et al. (2013) and even higher as 0.812 GPa of Vandamme et al. (2010). Based on these results, it could be stated that the micromechanical properties of the prepared geopolymers were comparable to those of cement pastes. As an average hardness for OPC pastes 0.5 GPa is given in literature (Škvára et al., 2006). The average hardness of the herein studied geopolymers was 0.35 GPa (excluding K4 with no significant development of hardness). Therefore, the geopolymers with metakaolinite, metasmectite, and metaillite precursors could be a possible replacement for cement concerning hardness and Young's modulus.

As it was possible to produce geopolymers with all three calcined clay minerals, it could be assumed that geopolymer production should be possible with a mixture of calcined clay minerals, like calcined common clays, as well.

5.2. *Porosity*

In addition to the micromechanical properties, the porosity of the samples was studied by mercury porosimetry measurements. The geopolymers with metakaolinite precursor showed porosities between 20.3 and 31.6% (Table 5). The average pore radii varied significantly between the samples, a decrease with increasing concentration of NaOH was observed. Furthermore, geopolymers with a lower Si:Al ratio showed a higher average pore radius for the same concentration of NaOH. The pore radii were in a range of 231–854 nm. K4 with no significant development of hardness showed the biggest average pore radius. The sample with the highest hardness of the metakaolinite geopolymers (K7) had the lowest average pore radius of 231 nm.

The porosities of the geopolymers with metasmectite and metaillite precursors were in the same dimension as for the metakaolinite geopolymers. For metasmectite geopolymers porosities between 27.2 and 31.6% were determined (Table 6). The porosity of the metaillite geopolymers was slightly lower (23.4–25.8%; Table 6). The average pore radii of the metasmectite geopolymers (274–490 nm) were in the range of the metakaolinite geopolymers, except C4. The metaillite geopolymers had an average pore radius between 98 and 130 nm which was

Table 5
Porosity (%) and average pore radius (nm) of metakaolinite geopolymers.

Sample	K1	K2	K3	K4	K5	K6	K7
Porosity [%]	29.2	22.5	28.4	20.3	23.6	21.5	31.6
Average pore radius [nm]	301	779	368	854	495	414	231

Table 6
Porosity (%) and average pore radius (nm) of metasmectite and metaillite geopolymers.

Sample	C3	C6	C5	C4	I3	I2
Porosity	27.2	28.8	30.6	31.6	23.4	25.8
Average pore radius [nm]	490	320	274	14	130	98

comparable to the geopolymers with the other precursors.

K4 showed the lowest porosity (20.3%) of all geopolymers, but the largest average pore radius (854 nm) by far. This observation correlated with the absence of hardness in this sample. K7, which showed the highest hardness of the metakaolinite geopolymers, developed the highest porosity (31.6%). The porosity values of the metakaolinite geopolymers in this study were within the range shown in former research for porosity of metakaolin based geopolymers between 28.5 and 30.9% (Aredes et al., 2015). The average pore radius of K7 (231 nm) was among the lower values of the herein studied geopolymers. Sample C4 developed a significantly lower average pore radius (14 nm) than all other geopolymers. This can only be interpreted to a limited extent as C4 was outside of any trend for hardness before. Therefore, it has to be assumed that the pore radii values are out of the range as well. C5 and C6 followed the same trend as the metakaolinite geopolymers. C6 developed a lower porosity than C5, already indicated by the lower hardness shown before. The average pore radius (320 nm) was higher compared to C5 (274 nm). I2 and I3 showed comparable values for porosity and average pore radius. Due to the comparable hardness of these samples this result was expected.

According to literature the porosity measured by mercury intrusion equals the open porosity of a material (Aredes et al., 2015). In preliminary research unblended cement pastes (with no addition of supplementary materials) showed values of 20–49% for open porosity. Blended cement pastes with addition of fly ash or silica fume showed open porosities in the same range (Day and Marsh, 1988). All of the produced geopolymers in this study were within that range.

A negative correlation between hardness and average pore radius of the geopolymers with the same precursor was observed. A higher average pore radius indicates more, bigger macropores in the geopolymer which will lead to a pore network with lower strength. It is more likely to hit a pore with the indenter during nanoindentation which will lead to measuring more areas without significant hardness. The addition of silica (e.g. silica fume) to fly ash geopolymers led to an increase in porosity of geopolymer pastes, but to a decrease in geopolymer mortars due to filler properties (Dutta et al., 2010). With the amorphous silica used in this study no such effect was observed. It was shown before that the Si:Al ratio has no significant influence on the porosity of metakaolinite geopolymers (Aredes et al., 2015).

6. Summary

All of the studied geopolymers showed a development of hardness, except one metakaolinite geopolymer produced with the lowest concentration of NaOH (4 mol/L). The concentration of the 4 mol/L NaOH was too low to adequately activate the metakaolinite in that case. For the geopolymers produced with metakaolinite precursor a geopolymer sample produced with 7.96 mol/L NaOH and a Si:Al ratio of 3:1 developed the highest hardness. For geopolymer samples which had an equal Si:Al ratio, an increase in hardness with concentration of NaOH could be observed. Metakaolinite geopolymers prepared with the same concentration of NaOH showed that the hardness increased in positive correlation with the Si:Al ratio. This trend was observable for two of the metasmectite geopolymers as well. The metasmectite geopolymer produced with 5 mol/L NaOH and a Si:Al ratio of 2:1 developed the highest hardness of all samples. The metaillite geopolymers were prepared with only slightly different concentrations of NaOH (5 mol/L and 4 mol/L) and showed similar values for hardness. A negative correlation of average pore radius and hardness was observed for geopolymers produced with the same precursor. The suitability as a geopolymer precursor was determined for all three calcined clay minerals, conditional of the improvement of production for some mixtures. Preliminary research already noted that a general statement about the optimal activation procedure is not possible, not even within the same group of clay minerals (e.g. montmorillonite). Properties like layer structure, morphology, particle size, etc. are influencing the activation process (Khalifa et al., 2020). The observations led to the assumption that a mixture of the herein studied clay minerals, e.g. in form of natural common clays, could be suitable for the production of geopolymers after determining the optimal production parameters. The use of calcined common clays would be favorable concerning the costs and availability of precursor materials for geopolymer production.

CRediT authorship contribution statement

N. Werling: Conceptualization, Validation, Investigation, Writing – original draft, Visualization. **R. Schwaiger:** Formal analysis, Investigation, Writing – review & editing. **F. Dathe:** Investigation, Writing – review & editing. **F. Dehn:** Writing – review & editing, Funding acquisition. **K. Emmerich:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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