Dathe and Dehn *Int J Concr Struct Mater* (2024) 18:1
https://doi.org/10.1186/s40069-023-00627-y

International Journal of Concrete Structures and Materials

RESEARCH Open Access

Alkali Activation of Common Clay Deposits: Evaluation of the Suitability by an IR Spectroscopic Method

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Abstract

In the context of a sustainable use of resources with the aim of the reduction of the CO_2 footprint, the development of alternative concrete materials has attracted a great deal of attention. In this context, geopolymers, obtained from common clay deposits, are found to be interesting construction materials with very versatile properties. In this paper, a completely novel approach for the evaluation of the suitability of clays for the geopolymer formation is investigated. The method is based on simple and easy-to-handle IR spectroscopic measurements, through which the surface area under the OH stretching band in the IR spectrum of the clay can directly be correlated to the amount of reactive clay components. These reactive components are required for the success of the alkali activation of the clays in order to access geopolymers. Based on the theoretical reaction pathway of the geopolymer formation, the linear relationship between the OH stretching band area and the reactive components can be used for the estimation of the required activator amount for the alkali activation of calcined clays and predict the quality of the casted geopolymer mortar in terms of strength. This new method not only gives an insight into the suitability of a common clay for the geopolymer formation, but also facilitates a straightforward alkali activation procedure without tedious preliminary testing of the required activator amount.

Keywords Alkali activation, Clay, IR spectroscopy, Geopolymer binder, Clay activation index

1 Introduction

The components of clays are mainly based on the mineral relicts of their parent rocks. This fact causes a vast variety of clay deposits to occur. Most common clays are associated with sheet silicates, which are vital for the alkali activation of clays, since they comprise suitable hydroxyl groups for the calcination process prior to the alkali activation (Emmerich, 2011). Despite the sheet silicates also other minerals, such as quartz, hematite and feldspar, can be found in clay deposits. These minerals are inert towards calcination and activation processes (Xu & Deventer, 2000).

The alkali activation of raw materials has been studied in more depth recently, since it provides versatile access to novel construction materials. These materials are referred to as alkali activated binders or geopolymer binders, depending on the calcium content of the raw material (Herrmann et al., 2015). Furthermore, alkali activation represents a suitable and environmental friendly alternative to the cement production, which has a negative influence on the carbon dioxide content in the atmosphere (Damtoft et al., 2008). So far, the focus has been mainly on the alkali activation of fly ash, slag and metakaolin (Provis & Deventer, 2014) and not so much on common clays, due to the complexity of the clay material itself. This versatility of common clays causes

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Journal information: ISSN 1976-0485 / eISSN 2234-1315.

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difficulties, since it is necessary to investigate the exact mineral composition of the clay before the activation to evaluate the right conditions for the calcination and subsequent activation of the raw material (Slaty et al., 2013). The calcination as well as the activation processes are extremely important not only for the development of new construction materials, but also for the application of calcined clay as an additive for ordinary concrete, due to its pozzolanic activity (Avet et al., 2016; Garg & Skibsted, 2016). Although there is a close relationship between the pozzolanic activity and the alkali activation, the hardening of the binder is caused by a different chemical reaction and makes a comparison difficult.

To obtain a geopolymer binder based on common clays, the raw material must be calcined first. During this step, the crystalline nature of the sheet silicates is destroyed under elevated temperatures and at the same time the hydroxyl groups of the crystal structure are eliminated in the form of water (White et al., 2012). The calcination process significantly impacts both the crystallinity of the material and its solubility in a basic pH solution. The amorphous material obtained after calcination represents the starting material for the alkali activation. During the alkali activation process, an aqueous base and water glass are commonly added to the calcined clay which leads to the formation of a geopolymer precursor. This precursor then undergoes a condensation reaction and forms an amorphous aluminosilicate network (Fig. 1) (Davidovits, 1994).

One of the major factors to consider during this process is the amount of base and water glass that is required for the geopolymer formation. Based on the studies of Davidovits et al. in 1994 it can be assumed that for 1 mol of metakaolin (which is a dehydroxylated form of kaolinite) 2 mol of water glass and in total 2 mol of base are required. However, if a calcined clay is used instead of pure kaolinite, which consists of a variety of mineral components, the situation becomes more complex. Therefore, it is necessary to determine the number of reactive components within clay deposits before the alkali activation. The amount of reactive components in the clay strongly depends on the OH groups present in the structure, since during the calcination process the clay structure is losing its OH groups in the form of water. This leads to the formation of so-called reactive centres, where the OH groups were present before, and the subsequent formation of geopolymer precursors. The positions of these reactive centres can then be cross-linked during the activation process via a condensation reaction (Dathe et al., 2021; Pacheco-Torgal et al., 2008).

Encouraged by this, a suitable method for the investigation of the amount of reactive components in clay deposits was developed. Therefore, a clay activation index, which represents the alkali activation potential of common clays, based on an IR spectroscopic method, is introduced. This clay activation index allows to estimate the suitability of a certain clay for the geopolymer formation, but also gives an estimation of the amount of activator that is required for the alkali activation of the calcined clay.

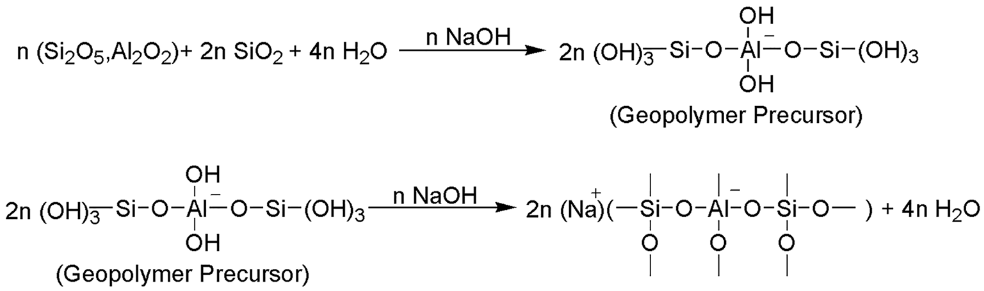
2 Materials and Methods

2.1 Clay Materials

Eight different deposits of common and materials (clays A–H) were analysed by powder X-ray diffraction (XRD) and simultaneous thermal analysis (STA) to gain information about their composition (Table 1). The phase components usually exhibit error values around ± 2%.

For the qualitative analysis of the composition of the clays the programme EVA™ was used, whereas the quantitative analysis was obtained by Rietveld analysis of the data, employing the programme PROFEX.

MetaMax® from BASF was used as reference material, since it is a high-reactivity pure metakaolin product, which shows no contamination of other minerals. The chemical purity of the kaolinite was investigated by powder XRD and STA. As aqueous base a 50 wt.% sodium hydroxide solution and as water glass a sodium metasilicate with a molar proportion of SiO_2 to Na_2O of 3.4 was used.



$$n\,(Si_2O_5,Al_2O_2) + 2n\,SiO_2 + 4n\,H_2O \xrightarrow{n\,NaOH} 2n\,(OH)_3{-}Si{-}O{-}\overset{OH}{\underset{OH}{\overset{|}{\underset{|}{Al^-}}}}{-}O{-}Si{-}(OH)_3$$

(Geopolymer Precursor)

$$2n\,(OH)_3{-}Si{-}O{-}\overset{OH}{\underset{OH}{\overset{|}{\underset{|}{Al^-}}}}{-}O{-}Si{-}(OH)_3 \xrightarrow{n\,NaOH} 2n\,(\overset{+}{Na})(-\overset{|}{\underset{\underset{|}{O}}{Si}}-O-\overset{|}{\underset{\underset{|}{O}}{Al^-}}-O-\overset{|}{\underset{\underset{|}{O}}{Si}}-O-) + 4n\,H_2O$$

(Geopolymer Precursor)

Fig. 1 Process of the formation of geopolymers based on metakaolinite (Davidovits, 2011)

Table 1 Composition of the clays A to D (in %)

Mineral component	Clay A	Clay B	Clay C	Clay D	Clay E	Clay F	Clay G	Clay H
Albite	–	–	4	–	–	3	2	–
Phyllosilicates	94	65	61	33	93	77	82	24
Quartz	2	28	29	44	2	20	12	74
Orthoclase	4	4	4	2	–	–	4	2
Anatase	–	3	1	1	2	–	–	–
Anhydrite	–	–	–	1	–	–	–	–
Haematite	–	–	2	–	–	–	–	–
Amorphous content	–	–	–	19	–	–	–	–
Phyllosilicates								
Kaolinite	78	40	23	12	87	68	5	6
Muscovite	16	10	19	21	6	9	4	18
Smectite	–	5	3	–	–	–	–	–
Montmorillonite	–	–	–	–	–	–	71	–
Chlorite	–	–	3	–	–	–	2	-
Strata chlorite/smectite	–	5	3	–	–	–	–	–
Strata illite/smectite	–	5	10	–	–	–	–	–

2.2 Analytical Methods

Powder X-ray diffraction (XRD) was carried out using a D8 Advance diffractometer (Bruker GmbH Karlsruhe, Germany) with a Lynxeye Detector (5° opening angle). Experiments were carried out with Cupper Kα radiation in a 2θ area between 5 and 70° in steps by 0.02° with a scanning time of 0.2 s. The quantitative analysis was carried out with the software PROFEX Version 4.1.0, by using an internal standard of 10 wt.% corundum.

Infrared spectroscopic measurements (IR) were carried out on a Bruker Tensor 27 FT-IR Spectrometer, with a modified ATR-IR Diamond setup. During the measurements, attention was paid on constant pressure on the sample.

Simultaneous thermal analysis (STA) About 100 mg of the raw materials were heated up to 1000 °C with a heating rate of 10 K/min under nitrogen atmosphere in corundum crucible, using a STA 409 apparatus (Netzsch, Selb, Germany).

Scanning electron microscopy (SEM) images were obtained using a Philips XL 30 FEG environmental scanning electron microscope (ESEM; FEI Europe, Eindhoven, The Netherlands). For the measurements all samples were glued onto aluminium SEM-holders using conductive tape (Leit-C, Plano GmbH, Wetzlar, Germany). To improve the quality of the SEM images, the samples were sputtered with a thin conductive layer (5 nm Au/Pd 80/20) and were investigated using an acceleration voltage of 20 kV.

2.3 General Preparation of the Clay Samples

Prior to the activation process, all clays were calcined in 1 kg charges, which were tempered to 700 °C for 3 h in a muffle oven under air. Afterwards, different components were added to the calcined clay to obtain mortar specimens (according to a slightly modified EN 196-1:2005-05 approach). Firstly, the calcined clay was placed in the mixer with the aqueous base. After 30 s of stirring, sand was added over 30 s and subsequently water glass was added to the mixture while the mixture was stirred (140 rpm). Afterwards, the mortar was stirred for another 30 s under stirring (280 rpm) and the specimens were cast in steel moulds.

Before the IR measurements of the clay, the samples were ground and sieved to obtain a particle size ≤ 32 µm. Furthermore, the clays and the material for the calibration were well dried under vacuum to remove any residual water. For the IR spectroscopic measurements of the common clays non-calcined samples were used. For the generation of the calibration curve (Fig. 4a) a certain amount of pure kaolinite was added to the calcined kaolin.

2.4 Strength Measurements

The compressive strength of the mortar specimens was determined according to EN 196-1:2005-05 with a TESTING Bluhm & Feuerherdt GmbH servo hydraulic compression and bending test device of the type RT 200/10-1s. After casting, the specimens were stored at

20 °C with a relative humidity of 65% for 7 days until the specimens were tested.

3 Results and Discussion

In order to measure the clay activation index of the clay samples and evaluate the activator amount that is needed for the alkali activation of common clay deposit, it is important to know the amount of reactive components within the clay. As mentioned before, this reactive amount is directly associated with the OH groups that are present in the clay. Therefore, IR spectroscopic measurements were utilised to gain information about the composition of the clay and the presence of hydroxyl groups.

3.1 Description of the Experimental Setup

The developed experimental IR setup is shown in Fig. 2. The setup consists of a modified diamond ATR-IR unit from “PIKE Technology”. In order to obtain a constant pressure on the sample, a load cell was installed in axial position to the pressure stamp. With the aid of a fine thread, the contact pressure can be adjusted precisely. To guarantee a constant sample volume, a plate with a drilling was drafted on top of the IR diamond. This not only gives the possibility to use a certain sample volume, but also enables an efficient cleaning of the instrument after the measurement.

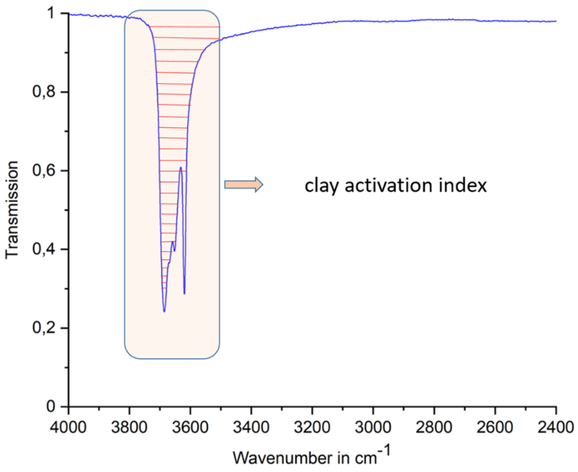


Fig. 3 Example of an IR measurement of a clay using the before described experimental setup

In Fig. 3, an example of an IR spectrum of a clay material using the before described setup is shown. The important region for the determination of the clay activation index is in the area of 3800–3500 cm^{-1}.

3.2 Calibration of the Experimental Setup

As starting point for this method, different mixtures of pure kaolinite with amorphous calcined kaolin, which was used as hydroxyl free support material, were

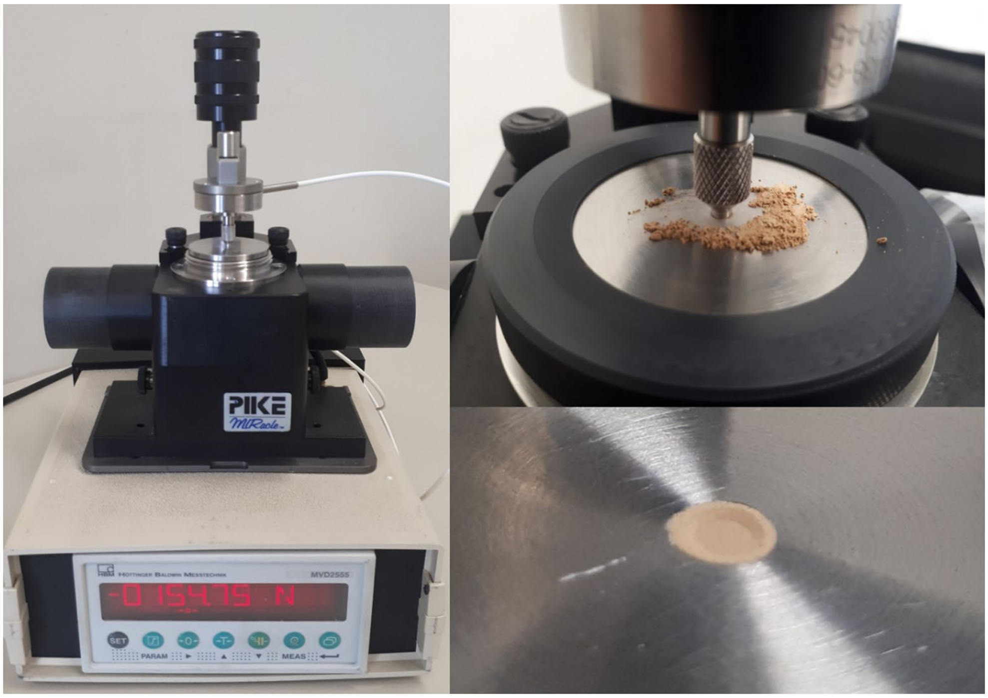


Fig. 2 Picture of the experimental IR setup for the determination of the clay activation index of common clays

prepared. The proportion of the mixtures were 0 to 100 wt.% of the kaolinite content with a stepwise increase of 5 wt.%. Kaolinite was the mineral of choice, since it represents the sheet silicate with the most hydroxyl groups and therefore a material that can easily be used for alkali activation (Prost et al., 1989). The samples were dried under vacuum prior testing to ensure that no free water influences the measurement. The purity of the samples was previously determined by powder XRD and STA measurements. Also, the samples were analysed via SEM imaging, showing the sheet like structure of the clay minerals. The mixtures were then further examined by the before introduced ATR-IR setup. As expected, an increase of the surface area of the OH stretching band around 3800–3500 cm^{-1} was observed moving from mixtures with a small kaolinite content to a higher kaolinite content (Fig. 4). To verify this observation quantitatively, the surface area under the OH stretching band was integrated and plotted against the kaolinite content, resulting in a linear correlation. Based on this, it can be assumed that the kaolinite content/the amount of OH groups correlate directly with the number of reactive centres present after the calcination process.

3.3 Clay Activation Index of Common Clays

After the calibration procedure, the clays were also analysed by ATR-IR spectroscopy using the developed setup (Fig. 5). Fig. 5 provides a clearer overview by displaying only four of the investigated clays. It is essential to note that all clays underwent vacuum drying before being utilised in this study.

The integrals of the OH IR stretching bands of the different clays were then related to the calibration curve obtained before (Fig. 6). Since, the integral is related to the amount of OH groups present in the clay sample, which is crucial for the alkali activation process, it can be converted into the clay activation index based on the calibration shown before. The clay activation index varies from 0 to 100% depending on the content of the active species within the clay that can be used for the alkali activation process.

3.4 Application of the Clay Activation Index for the Alkali Activation of Clays

The observations made during the ATR-IR spectroscopic measurements and the calculated clay activation indexes were now applied to the design of a suitable mixture of calcined clay, water glass and base during the alkali activation process to form a geopolymer binder mortar. Therefore, clays were calcined prior to the alkali activation process.

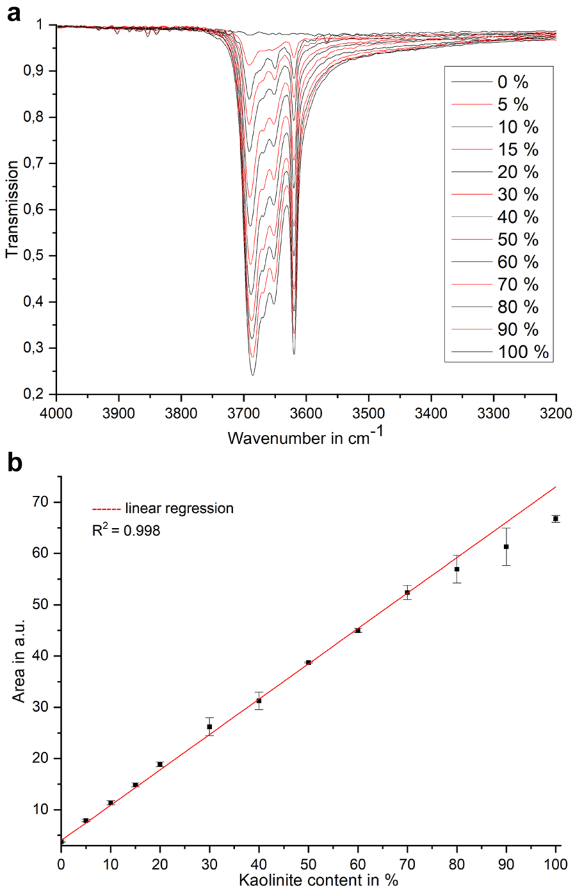


Fig. 4 **a** Investigation of different kaolinite/kaolin mixtures by IR spectroscopy and **b** the relationship between the area under the OH stretching bands and the kaolinite content

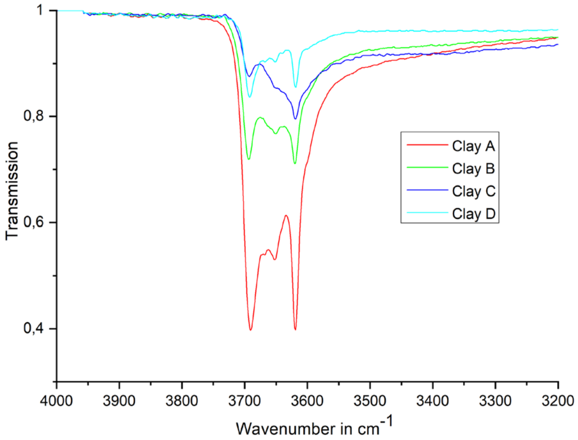


Fig. 5 Investigation of four different clay deposits by ATR-IR spectroscopy

For the mixing design for the alkali activation procedure, it was assumed that a high hydroxyl content within a clay and thus a high clay activation index is related to large amounts of reactive centres. Therefore, a high clay activation index should also result

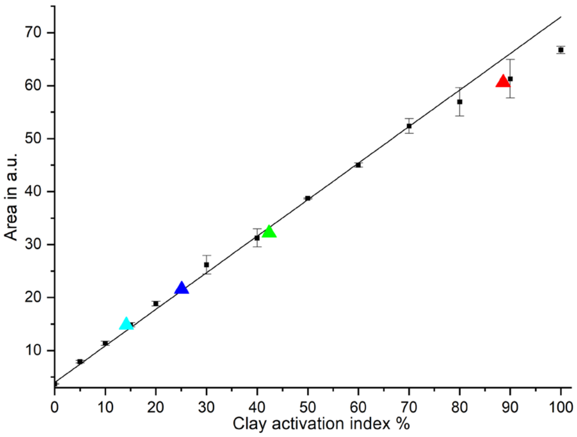


Fig. 6 The relationship between the surface area under the OH stretching bands and the clay activation index of the common clays (**A** red; **B** green; **C** blue; **D** light blue) and the kaolinite/kaolin calibration curve (black)

Table 2 Alkali activation mixtures based on the IR spectroscopic determination of the clay activation index

Calcined clay sample	Clay activation index in %	NaOH in mol	Na_2SiO_3 in mol
Clay A	88.6	1.77	1.77
Clay B	42.4	0.85	0.85
Clay C	25.1	0.5	0.5
Clay D	14.2	0.28	0.28
Clay E	95.3	1.9	1.9
Clay F	64.4	1.29	1.29
Clay G	20.2	0.4	0.4
Clay H	4.3	0.09	0.09
Ref. pure metakaolin	100	2	2

All mixtures consisted of 450 g calcined clay, 1350 g CEN-sand and the calculated activator amount

in good mortar quality after the alkali activation. The stoichiometry of the different components was based on Davidovits' studies, in which 1 mol of metakaolin, 2 mol of water glass and in total 2 mol of base were used (Davidovits, 1994). The previously defined clay activation index (Fig. 6) can now be utilised to calculate the required activator dosage (Table 2). In this context water glass as well as the aqueous base were both considered as activators, since the addition of base without water glass to the calcined clay only leads to the formation of a crystalline material (zeolite) (Christophliemk, 1989). In case of a lower clay activation index, the clay demands a smaller amount of activator solution, because the amount of reactive centres responsible for forming geopolymer precursors is lower. The reference mixture with a pure metakaolin (MetaMax®) consumes the highest amount of activators during the chemical reaction.

For the examination of the geopolymer binder specimens, which were obtained by the alkali activation described before, the compressive and flexural tensile strength was measured (Fig. 7).

These investigations have shown, that almost all specimens hardened without any special treatment (heat, etc.), which was not observed when random mixtures of calcined clay, activators (water glass, base) and sand were used. This already shows the success of this IR spectroscopic method for the evaluation of the necessary activator content for the alkali activation. Only clay H did not harden and consequently no compressive and flexural tensile strength measurements could be carried out.

As expected, the reference material MetaMax®, with the highest clay activation index, has shown the highest compressive strength among all clay materials. The compressive strengths then decrease with decreasing clay activation index from clay E to clay G. Therefore, the clay activation index is not only a great tool to estimate the suitability of common clays for the alkali activation, but it also gives clear information about the mixing design for the alkali activation procedure. Only in the case of clay D a slight inconsistency can be witnessed, since clay D shows a little higher compressive strength than clay G, despite the lower clay activation index. This points out, that not only chemical processes, like the alkali activation process, are responsible for the mortar performances but also physical effects, such as the grain size or the porosity, influence the material characteristics.

The obtained results were also verified via SEM imaging. Clays with a high activation index, and a therewith-associated high compressive strength, such as clay E, show a well-structured binder surface, whereas samples with a lower clay activation index, such as clay D, exhibit a more inhomogeneous microstructure that leads to a fragile connection between the particles.

4 Conclusions

The current study has shown a linear correlation between the surface area of the ATR-IR OH stretching band in kaolinite mixtures, and the kaolinite content using the developed ATR-IR setup. Based on this correlation and a subsequent calibration, the clay activation index, which gives insights into the amount of reactive components after the calcination process, of various common clays was determined. This allowed the calculation of the activator (water glass and base) amount required during the alkali activation of the calcined clay based on Davidovits' proposed geopolymer formation. This completely novel approach simplifies the alkali activation of clay material

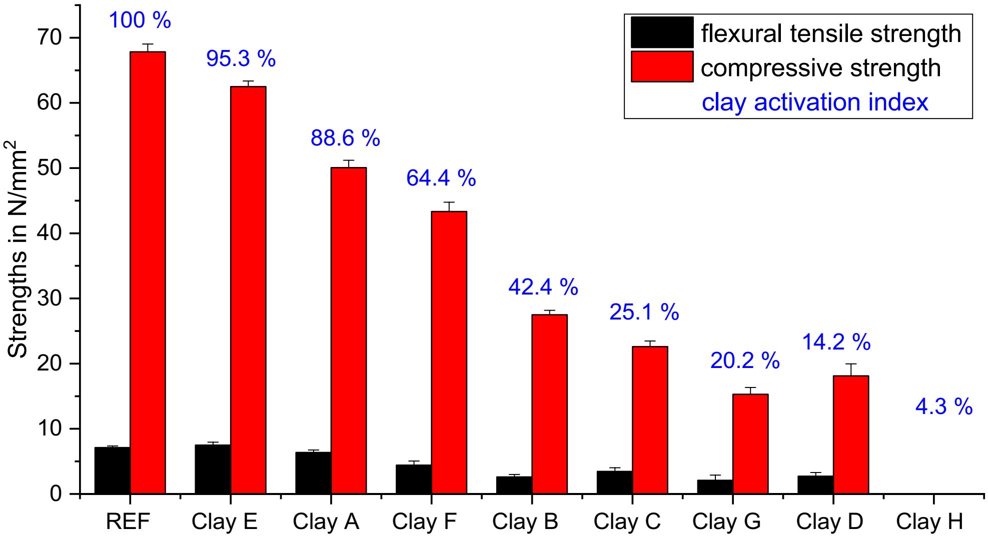


Fig. 7 Compressive strength and flexural tensile strengths of the geopolymer mortars, sorted by decreasing clay activation index

enormously and provides a straightforward access to a variety of geopolymer binders without the need of preliminary empirical and often iterative testing of the necessary activator amount. Tests of the compressive as well as the flexural tensile strength have underlined the stability of the geopolymer binders after the activation process and therefore shown the success and the wide applicability of this method.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40069-023-00627-y.

Additional file 1. Appendix: Powder X-ray diffractograms: **Figure S1.** Powder X-ray diffractograms of clay A. **Figure S2.** Powder X-ray diffractograms of clay B. **Figure S3.** Powder X-ray diffractograms of clay C. **Figure S4.** Powder X-ray diffractograms of clay D. **Figure S5.** Powder X-ray diffractograms of clay E. **Figure S6.** Powder X-ray diffractograms of clay F. **Figure S7.** Powder X-ray diffractograms of clay G. **Figure S8.** Powder X-ray diffractograms of clay H. Selected SEM images: **Figure S9.** SEM image of clay D. **Figure S10.** SEM image of mortar D after the alkali activation. **Figure S11.** SEM image of clay E. **Figure S12.** SEM image of mortar E after the alkali activation. **Figure S13.** SEM image of clay H. **Figure S14.** SEM image of mortar H after the alkali activation.

Acknowledgements

This work would not have been accomplished without the Faculty of Chemistry and Mineralogy of Leipzig University. We also like to thank the staff of the Competence Center for Material Moisture (CMM) from KIT for the support during this work, and the German Research Foundation (DFG) for funding (Projektnummer 325967999).

Author contributions

FDa: conducted the experimental study, analysed the test results and drafted the manuscript. FDe contributed to the conception of the manuscript and supervision.

Funding

Open Access funding enabled and organized by Projekt DEAL. This study was supported by the German Research Foundation (DFG) for funding (Projektnummer 325967999).

Declarations

Ethics approval and consent to participate

All authors of the manuscript confirm ethical approval and consent to participate following the Journal's policies.

Consent for publication

All authors of the manuscript agree on the publication of this work in the *International Journal of Concrete Structures and Materials*.

Competing interests

Authors report no conflict of interest.

Availability of data and materials

All data relevant to this manuscript are given either in the manuscript or in Additional file 1: Appendix.

Received: 8 April 2023 Accepted: 31 July 2023

References

Avet, F., Snellings, R., Diaz, A. A., Haha, M. B., & Scrivener, K. (2016). Development of a new rapid, relevant and reliable (R3) test method to evaluate the pozzolanic reactivity of calcined kaolinitic clays. *Cement and Concrete Research, 85*, 1–11.

Christophliemk, P. (1989). *Henkel Kommanditgesellschaft, Verfahren zur kontinuierlichen Umwandlung von Metakaolin in feinstteiliges zeolithisches Natriumaluminiumsilikat*. 0085902B1, 05.04.89 (patent in German)

Damtoft, J. S., Lukasik, J., Herfort, D., Sorrentino, D., & Gartner, E. M. (2008). Sustainable development and climate change initiatives. *Cement and Concrete Research, 38*(2), 115–127.

Dathe, F., Strelnikova, V., Werling, N., Emmerich, K., & Dehn, F. (2021). Influence of lime, calcium silicate and portlandite on alkali activation of calcined common clays. *Open Ceramics, 7*, 100152.

Davidovits, J. (1994). Geopolymers: Man-made rock geosynthesis and the resulting development of very early high strength cement. *Journal of Materials Education, 16*, 91–138.

Davidovits, J. (2011). *Geopolymer Chemistry & Applications* (3rd ed.). Institut Geopolymere.

Emmerich, K. (2011). EMU Notes in Mineralogy: Advances in the Characterization of Industrial Minerals. Vol. 9, G. Christidis, Ed., Mineralogical Society, pp 129–170.

Garg, N., & Skibsted, J. (2016). Pozzolanic reactivity of a calcined interstratified illite/smectite (70/30) clay. *Cement and Concrete Research, 79*, 101–111.

Herrmann, A., König, A., & Dehn, F. (2015). *Proposal for the classification of alkali-activated binders and Geopolymer binders*. Cement International.

Pacheco-Torgal, F., Castro-Gome, J., & Jalali, S. (2008). Alkali-activated binders: A review Part 1. Historical background, terminology, reaction mechanisms and hydration products. *Construction and Building Materials, 22*, 1305–1314.

Prost, R., Dameme, A., Huard, E., Driard, J., & Leydecker, J. P. (1989). Infrared Study of Structural OH in Kaolinite, Dickite, Nacrite, and Poorly Crystalline Kaolinite at 5 to 600 K. *Clay and Clay Minerals, 37*, 464–468.

Provis, J. L., & van Deventer, J. S. J. (2014). *Alkali-activated materials, State-of-the-Art report, RILEM TC 224-AAM*. Springer.

Slaty, F., Khoury, H., Wastiels, J., & Rahier, H. (2013). Characterization of alkali activated kaolinitic clay. *Applied Clay Science, 75–76*, 120–125.

White, C. E., Provis, J. L., Riley, D. P., Proffen, T., Perander, L. M., & van Deventer, J. S. J. (2012). *Characterization and description of the structure of metakaolin by total scattering, density functional theory, and X-ray spectroscopy. Concrete Repair, Rehabilitation and Retrofitting III*. Taylor & Francis Group.

Xu, H., & van Deventer, J. S. J. (2000). The geopolymerisation of alumino-silicate minerals. *International Journal of Mineral Processing, 59*, 247–266.

Publisher's Note

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