Influence of lime, calcium silicate and portlandite on alkali activation of calcined common clays

Felix Dathe [a], Vera Strelnikova [a], Nadja Werling [b], Katja Emmerich [b], Frank Dehn [a,*]

[a] *Institute for Concrete Structures and Building Materials, Karlsruhe Institute for Technology (KIT), Gotthard-Franz-Straße 3, 76131 Karlsruhe, Germany*
[b] *Competence Center for Material Moisture, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany*

ARTICLE INFO

ABSTRACT

The application of calcite rich common clays has marked impact on the formation of alkali-activated binders. Experiments have shown that the carbonate decomposition can be well controlled via the calcination procedure, whereby the majority of the decomposition and the subsequent CO_2 release occurs above the calcination temperature of 750 °C. The decarbonation of the calcite can mostly be separated from the dehydroxylation of the layered silicates. Depending on the composition of the raw clay material, the $CaCO_3$ decomposition leads either to the formation of lime or other Ca rich minerals. The mechanical properties of the alkali-activated binders were investigated and despite the very low amounts of layered silicates of the clay raw materials and the high content of unreactive minerals, compressive strengths of above 20 MPa of the mortars could be obtained. The presence of lime in calcined clays up to an adequate amount has a positive effect on post-solidification and the carbonation resistance of the mortars.

1. Introduction

Recently, geopolymer (GP) and alkali-activated binders (AAB) have attracted a great deal of attention in research as alternative to conventional binding materials [1]. In contrast to the state-of-the-art construction material cement, the CO_2 footprint can be tremendously reduced through the application of such alternative binders in the field of civil engineering.

Both geopolymers and alkali-activated binders can be obtained from condensation reactions of Si and Al-rich precursors in the presence of a base. This process is also referred to as alkali activation. The transition from a geopolymer to an alkali-activated binder depends strongly on the soluble Ca content of the raw material, since this is crucial for the formation of different amorphous phases, such as N-A-S-H (low Ca content), C-A-S-H, C-(N)-A-S-H, and C–S–H(I) (very high Ca and low Al content) [2]. The nature of these amorphous phases is very complex and key to ongoing studies [3]. In general, GPs are considered as Ca-poor AABs with a high Al and Si content and whereas products resulting from fly ash with more than 7 wt% of CaO (according ASTM C618, type F) or 10 wt% CaO (according to EN 450–1), respectively, are classified as AAB, a lower calcium content is thought to result in the formation of a geopolymer. Further classification criteria are based on the Ca content within the

crystallographic structure of the reaction products (<20 wt% CaO → geopolymer [4]) or the performance of the concretes/mortars (<10 wt% CaO → geopolymer [5,6]).

For the production of alkali-activated binders, usually industrial by-products, such as fly ash (FA) and ground-granulated blast-furnace slag (GGBS), have been used. The exploitation of these industrial by-products for the production of construction materials has been emphasised recently, especially with respect to a circular economy [7]. However, the availability of fly ash and slag in the European area is limited. This is mainly due to the continuous decrease of coal production and mining in the context of the energy revolution and the use of sustainable energy resources. In addition, the amount of ground-granulated blast-furnace slag lag from iron production cannot cover the global demand for mineral binders.

For these reasons, common clays have been investigated as precursors for the production of alkali-activated binders and as substitute in conventional cementitious systems with the ultimate aim of decreasing the amount of required cement clinker [8]. The term common clays is referring to structural clay products, which are fine grained and typically exhibit plastic behaviour when exposed to water [9] The main benefit of using common clays as precursors for alternative binders is the great availability since clay deposits are distributed widely around the globe. A

further advantage of using clays for the GP production, are the moderate temperatures in the range of 700 °C–850 °C, which are required for the calcination. Consequently, only H_2O is released by the decomposing of the clay minerals and no CO_2 is formed as by product during the thermal treatment. The calcium-poor geopolymer binders, resulting from the alkali activation of these calcined clays, are very different from conventional cementitious systems in terms of their mineralogical properties and their microstructure. The very high thermal stability, the resistance towards acids [10–14] and the good mechanical performance [2,15,16] are particularly worth mentioning here.

Despite these advantages, the consumption of NaOH and the therewith-associated rapid decrease of pH of the binder during the condensation reaction is challenging since the basicity of binders is one of the most important material parameters in concrete technology. To protect the steel reinforcement of corrosion processes, a constant pH value above 11 is required to maintain the durability of the structure.

In ordinary Portland cements, the basicity results from the hydration product portlandite ($Ca(OH)_2$). The formation of $Ca(OH)_2$ in the microstructure of the cement will automatically stabilise the pH value at a constant level above 13 [17,18]. However, since during the hardening process of alkali-activated binders no portlandite is formed and the generation of sodium carbonates from sodium hydroxide through the presence of CO_2 in the air takes place [19], the basicity of the binder is reduced [20]. The consumption of NaOH and the thereof resulting reduction in the pH value influences in the corrosion of steel reinforcement [21–23].

As part of this study, calcite rich common clays were investigated as precursors for alkali-activated binders. Earlier studies focused almost exclusively on the utilisation of kaolin-rich deposits, which contain only very low amounts of calcium carbonate [24]. However, since carbonates, such as calcite and dolomite, are often geologically associated with layered silicates, the investigation of calcite rich common clays to produce AABs seems logical. Spurred by this, the author's attention in this area has turned towards the exploration of calcite rich common clays and their alkali activation. To investigate the influence of calcite on the alkali activation, the calcination temperature has been varied and the formation of CaO and the impact on the AAB properties have been explored. In that sense, the mechanical properties, such as the compressive and tensile strengths, of specimens made of alkali-activated common clays, have been measured. The investigation on calcium carbonate bearing clays for alkali-activation leads us to the grey area between the calcium-free geopolymers and calcium-rich alkali-activated binders and all because of the low solubility of the calcium carbonate and the high reactivity of lime.

In addition, the carbonation resistance has been looked at in detail, since through the formation of CaO from $CaCO_3$, an internal buffer is formed, which can react with the CO_2 from the air and consequently counteracts the-afore mentioned reduction in pH value.

2. Materials and methods

2.1. Raw materials

As part of this study two naturally occurring common clays were used, namely one clay from the Rhine Graben (Clay1) and one from a clay pit in central Germany (Clay2), both clays are secondary clay deposits. As a reference material (denoted as Refclay), a kaolin with a high purity of kaolinite from Hampshire UK mixed with 25 wt% $CaCO_3$ was utilised. For the reference materials pulverised $CaCO_3$ with a purity of >98.5% and a grainsize d_{50} of 1 μm as well as pulverised $Ca(OH)_2$ with a purity > 96% were selected (Carl Roth GmbH & Co.KG, Karlsruhe, Germany). All materials were milled and sieved to a grainsize below 90 μm and the particle sizes were determined by a particle size Analyser CILAS 1064 (LG), (3p instruments, Odelzhausen, Germany). The mineral composition of the two common clays was determined via powder X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses (Table 1 and Table 2).

As activators, a saturated NaOH solution with a concentration of 19.05 mol/L (50 wt%) and sodium silica solution Betol39T were blended. The applied water glass is based on a solution of sodium silicate with a solute concentration of 34.5 wt% and a molar ratio of SiO_2 and Na_2O of 3.4 (Woellner, Ludwigshafen, Germany).

2.2. Analytical techniques

2.2.1. Powder X-ray diffraction (XRD)

For the powder X-ray diffraction analysis a D8 Advance diffractometer (Bruker GmbH Karlsruhe, Germany) with a Lynxeye Detector (5° opening angle) was used. Experiments were carried out with Copper 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.

2.2.2. X-ray fluorescence (XRF)

The elementary composition was determined using a S4 Explorer for the raw clay and the surface of the AAB specimens investigated by a M4 Tornado (Bruker GmbH Karlsruhe, Germany) using energy dispersive X-ray fluorescence (XRF) spectrometer.

2.2.3. 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).

2.2.4. Simultaneous thermal analysis (STA) coupled Mass spectrometry (MS)

About 100 mg of the raw materials were heated up to 1000 °C with a heating rate of 10 K/min under nitrogen (50 mL/min)/synthetic air (25 mL/min) atmosphere (Jupiter 449, Netzsch, Selb, Germany). The coupled mass spectrometer was a Quadrupol 409 (Aeolos, Netzsch, Selb, Deutschland).

2.3. Calcination

100 g of each clay were calcined at different temperatures in a laboratory muffle furnace (Heraeus Instruments, Hanau, Germany). Based on the STA results, one of the following temperatures 650, 700, 750, 800 and 850 °C was selected. These temperatures are based on the decomposition of the carbonate species and crystallisation of lime or calcium silicates in the clays. The clays were analysed quantitatively and qualitatively via powder XRD after the thermal treatment. After the calcination, the clays were milled with a vibrating mill to destroy the small aggregates that were formed.

Table 1
Proportions (wt.%) of the mineral phases within the common clays and the references clay obtained from powder XRD analysis and particle size from laser granulometric measurements.

	Clay1 Rhine Graben	Clay2 central Germany	Kaolin Hampshire UK
Calcite	25.4 ± 0.5	27.5 ± 0.5	0
Dolomite	4.9 ± 0.5	0	0
Quartz	21.3 ± 0.5	26.5 ± 0.5	3.2 ± 0.5
K-feldspar	2.5 ± 0.8	0	0
Plagioclase	5.3 ± 0.4	3.8 ± 0.8	0
Kaolinite	8.7 ± 1	14.5 ± 1	94.5 ± 1
Muscovite/Illite	16.6 ± 1	15.0 ± 0.5	2.2 ± 0.5
Smectite	6.7 ± 0.4	10.0	0
Microcline	1.7 ± 0.5	0	0
Chlorite	4.8 ± 0.6	2.5 ± 0.5	0
Hematite	0	1.8 ± 0.5	0
Particle size			
d(0,5)% < [μm]	8.5	27.8	9.4

Table 2
Elemental compositions of the raw materials determined by XRF analysis. LOI = loss of ignition.

Constituents	SiO$_2$	Al$_2$O$_3$	CaO	Fe$_2$O$_3$	MgO	Na$_2$O	K$_2$O	LOI
Clay1	44.5	11.5	14.4	4.7	3.1	0.7	2.1	18.0
Clay2	45.3	17.5	15.7	8.1	0.2	1.5	0.8	12.5
Kaolin	44.3	42.9	0.1	0.7	0.1	0.3	0.1	10.5

2.4. Determination of the lime content

The soluble calcium content was determined by the following procedure developed by Franke [25]. Therefore, 50 g of the calcined clay samples were taken and completely sieved to 0.063 μm. Weighted with the accuracy of 0.001 g, 1.0 g of the sieved sample was mixed with 12 mL of ethyl acetoacetate and 80 mL of 2-butanole. The mixture was heated under reflux for 3 h and subsequently filtered. The precipitate was washed with 2-propanole and the washing liquid was combined with the mother liquor. To this clear solution, the indicator (TYP) was added, and the solution was titrated with 0.1 M HCl until a colour change from colourless to yellow occurred. This titration was carried out twice.

2.5. Alkali activation

After the calcination, the clays were mixed with the alkali activator solution and sand. The resulting mortars were then cased based on DIN EN 196–1 [26]. Hereby, two different sample sizes were cased 2*2*8 cm and 4*4*16 cm. For a better workability, the powder grain content of the used CEN standard sand was removed by sieving <125 μm. The mix ratio is shown in Table 3.

The development of the formulation started from the theoretical hypothesis given from Davidovits [27] for the optimal proportion for a geopolymer network. From the former research done on zeolite materials is known that the most stable ratio of silicon to aluminium is 3 to 1 because of the fourfold bonding of Al as energetic unstable coordination sphere. Considering this aspects and calculating with pure metakaolin as precursor, a theoretical optimal proportion of precursor to sodium silicate and sodium hydroxide can be achieved estimating a complete reaction. On the other hand, the practical realization is often difficult due to the different water demand of each calcined clay and the actually reactive amount of metaclay after the calcination process. Several different mixing designs were investigated always with the aim to minimise the activator amount with regard to environmental aspects. The chosen formulation was free of shrinkage cracks, showed good setting time and the specimens did not show efflorescence on the surface. However, a certain amount of activator had to be added to achieve an adequate workability for constructional applications which was determined via the slump test.

The portlandite containing metakaolin mortar "Ca(OH)$_2$ Metakaolin Mortar" was cased with the same mix design from the calcined kaolin clay from the UK (Kaolin). There for 10 wt% of the metakaolin was replaced by portlandite Ca(OH)$_2$.

2.6. Determination of the physical properties

Like in DIN EN 196–1 [26] described, the fresh mortars were tested

Table 3
Alkali activation procedure.

Mortar	Alumosilicate precursor calc. clay (750 °C; 850 °C)	Activator solution Betol39T + NaOH (50 wt%)	CEN standard sand 125 μm–2 mm
Mix ratio	450 g	450 g Betol39T, 225g NaOH (162 g sodium silicate, 112.5 g NaOH, 400.5 g H$_2$O)	1350 g

for their slump, density and solidification time based on DIN EN 196–3:2017–03 [28]. All three clays show a comparable water demand, so that the water binder ratio of 1:1 led to a stiff fresh mortar with a resulting slump test around 15–20 cm. All samples were demoulded 24h after casting and stored wrapped in foil at 65% relative humidity and 20 °C until further tests were carried out. The compressive and flexural strengths were measured 7 and 28 days after casting on a ToniPRAX testing station Model 2031 (Toni Technik, Germany).

2.7. pH value

The hardened mortars were ground and powdered. 5 g of this powder <90 μm, were suspended in 50 mL distilled water and the pH value of this suspension was measured with a pH electrode.

2.8. Carbonation tests

Based on EN 13295:2004[29], a accelerated carbonation testing was performed on 4*4*16 cm mortar pricks after 7 days of curing wrapped in foil at 65% relative humidity (RH) and 20 °C. The specimens were transferred to a carbonation cabinet, with an atmosphere of 2% CO$_2$ atmosphere and 65% RH. After a certain time of CO$_2$ exposure, the depths of carbonation were determined by cracking the specimens and spraying a 1% phenolphthalein solution on the freshly broken surface. After 60 s, the carbonation depth was measured on four sides of the specimens and an average value was calculated. Hereby it became obvious, that the carbonation depth was not dependent on the determination time. Similar observations were already reported by Gluth et al. [1].

3. Results and discussion

3.1. Characterisation of the raw materials

The two clays and the reference material were analysed by simultaneous thermal analysis (STA, Fig. 1). During the STA experiments, different phase transitions were observed. At around 100 °C the loss of water bound in the materials can be observed. All three clays showed a dehydroxylation of the clay minerals, especially the dehydroxylation of kaolinite, around 520 °C. However, differential scanning calorimetry (DSC) and the thermogravimetric analysis (TG) of this decomposition process are overlapping with the dehydroxylation of the minerals. The CO$_2$, formed by the decomposition of dolomite, could be detected starting at 700 °C by STA coupled to a mass spectrometer (see supporting information) [30]. Further, mass losses starting at around 700 °C occurred, which result from the decomposition of the dolomite and calcite in the raw materials. At temperatures above 850 °C, all carbonates were decomposed. Afterwards no further mass losses could be observed by TG. However, for Clay1 and Clay2 the formation of a high temperature phase could be observed at 902 °C via differential scanning calorimetry and for the reference clay the formation of spinel phase at high temperatures consisting of Si and Al could be witnessed at 994 °C.

To gain further insight into the before described phase transitions, the clays were calcined at different temperatures (650, 700, 750, 800, 850, 950 °C) and the resulting materials were analysed via powder X-ray diffraction (Fig. 2). Clay1 consists of a broad range of minerals and the calcination at 650 °C results in the disappearance of kaolinite and dolomite. Nevertheless, still a strong reflex, which can be attributed to calcite, can be observed. When Clay1 is calcined at higher temperatures,
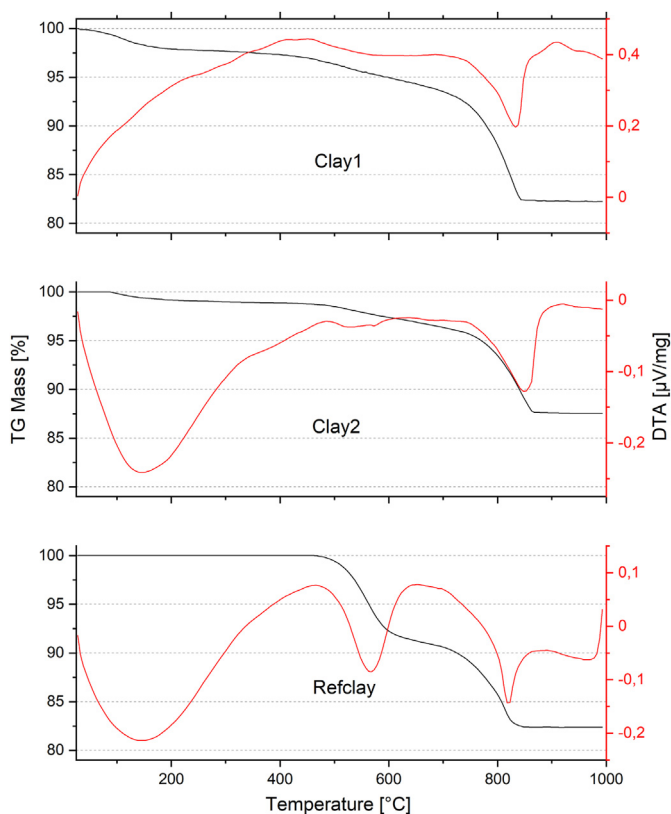
Fig. 1. STA measurements of the three investigated clays heated from room temperature to 1000 °C; Sample weight 100 mg, atmosphere 75 ml/min N_2.

the intensity of the calcite reflex is decreased, however, only very little recrystallisation of calcite to lime does occur even at a calcination temperature of 850 °C. With Rietveld analysis only a lime content of 2 wt% could be determined. The calcium oxide within the clay (14.4 wt% in the raw material) forms most likely an insoluble amorphous phase during the thermal treatment, which is not detectable via powder X-ray diffraction.

Qtz Quartz; Cal Calcite; L Lime; Kln Kaolinite; Gh Gehlenite; Wo Wollastonite; Dol Dolomite; Per Periclase
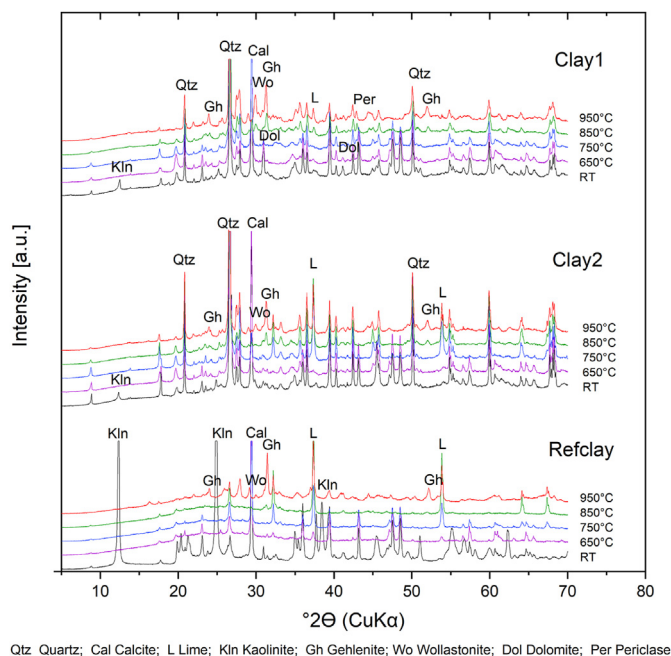
Fig. 2. Powder X-ray diffractograms of the two clays and the reference material, which were calcined at different temperatures (RT, 650, 750, 850, 950 °C).

This is confirmed by the fact, that when Clay1 is calcined at temperatures above 902 °C, different calcium minerals, such as Gehlenite (Ca_2Al [$AlSiO_7$]) and Wollastonite ($CaSiO_3$) can be observed. The transition of the Calcite to Gehlenite and Wollastonite via an amorphous transition state is favoured over the formation of crystalline lime. In addition, the variation of the calcination duration could not change the outcome of the powder diffraction experiments.

In the case of Clay2, the decomposition of calcite starting at 750 °C leads mainly to the formation of lime 10 wt% (15.7 wt% in the raw material). However, again not the whole amount of calcite is converted into lime. At 850 °C gehlenite and wollastonite can already be observed, which shows that not all the calcium is bound in the form of crystalline lime after the calcination. At higher temperatures above 950 °C the lime reacts further with the aluminosilicate to form more gehlenite.

For the reference clay, kaolinite is decomposing when the material is calcined at temperatures in the range of 650–750 °C. At a calcination temperature of 850 °C the complete decomposition of calcite to lime can be observed. When the Refclay is heated up further to 950 °C, the lime and the amorphous metakaolin forms gehlenite ($Ca_2Al[AlSiO_7]$). Also, small reflexes belonging to wollastonite ($CaSiO_3$) can be detected.

The information gathered by powder XRD is underlined by the measurement of soluble free calcium in the calcined clays according to the method described by Franke [25]. The results are depicted in Fig. 3. It becomes obvious, that the soluble content of calcium follows different trends for the three clays. Whereas for Clay1 with 14.4 wt% CaO in the raw material only 1.7 wt% calcium oxide is soluble after the complete decarbonation of the calcite, in Clay2 9.3 wt% out of 15.7 wt% in the at 850 °C calcined material are soluble. In the case of the reference clay, consisting of 14 wt% CaO in the raw material, a soluble CaO content of 13.6 wt% was determined.

3.2. Exploration of the mortars

Alkali activations of the calcined common clays and the reference kaolin were carried out to obtain mortars prisms. Hereby it has to be mentioned that CaO is quite reactive and reacts with water to form $Ca(OH)_2$ with an exothermic reaction enthalpy of 65 kJ/mol. This high exothermic heat release may influence hardening process and leads to changes in the mechanical strength development. The compressive strengths of these specimens were analysed depending on the calcination temperature of the clays 28 days after casting (Fig. 4). All three mortars show an enhancement of the compressive strength until a calcination
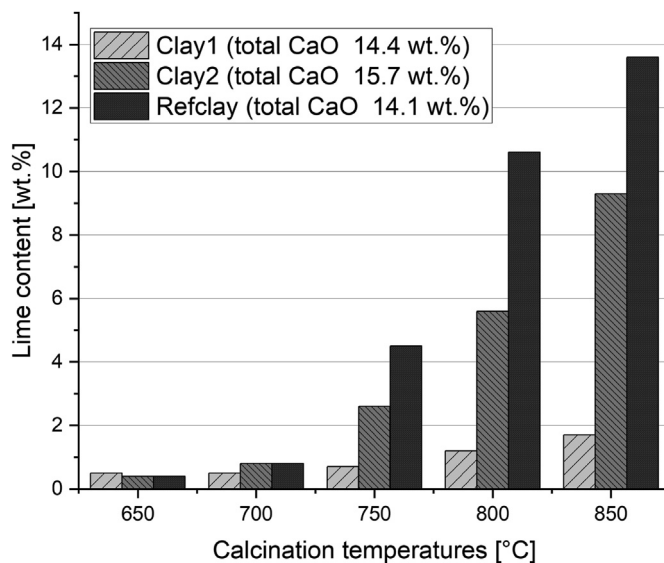

Fig. 3. Calcium oxide content depending on the calcination temperatures. The soluble CaO content was determined according to Franke et al. [25].
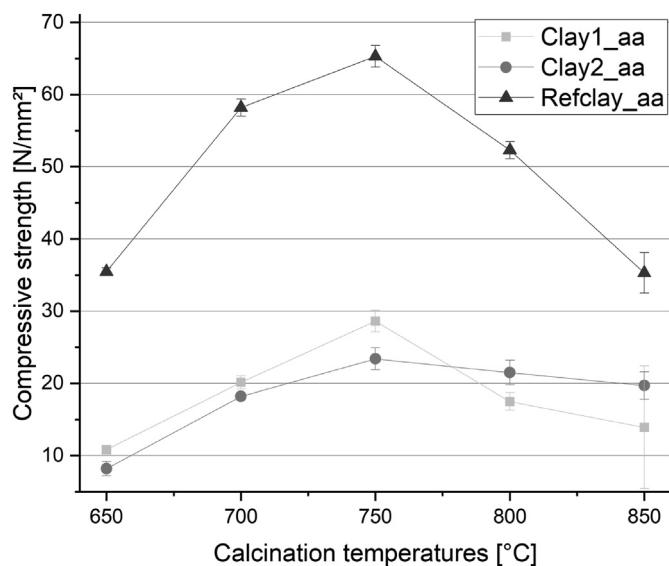
Fig. 4. Compressive strengths of the two alkali activated clays and the alkali activated reference clays depending on the calcination temperature. Strengths were measured 28 days after casting.

temperature of 750 °C. Hereby a maximum compressive strength of 65.3 MPa could be obtained for Refclay, whereas compressive strengths of 28.6 MPa for Clay1 and 23.4 MPa for Clay2 were measured. The reason for the lower compressive strengths of the clays, in comparison with the reference clay, is the lower amount of reactive layer silicates, which can be calcined and converted into the strength giving N-A-S-H phases. Whereas the reference clay contains 94.5 wt% kaolinite, Clay1 consists of 8.9 wt% and Clay2 14.5 wt% kaolinite. When the clays are calcined at temperatures above 750 °C a tremendous decrease of compressive strength can be witnessed. For that reason, the optimal calcination temperature for the investigated clays was chosen to be 750 °C. At this temperature, that CO_2 release is quite low and the mechanical properties are optimal considering a constructional application.

Comparable calcite-free clays show usually a very similar increase of the compressive strength up to calcination temperatures of 750 °C. However, such calcite-free clays do not exhibit a significant loss in compressive strengths in temperature ranges between 750 °C and 900 °C. Only when calcination temperatures above 900 °C are applied, a decrease in compressive strength is observed for calcite-free clays, due to the formation of unreactive spinels formed from the metaclay minerals [31]. The observed loss of compressive strength up to 50% is therefore a direct consequence of the presence of high calcium contents, since Ca species influence the hardening process of the binder paste.

Based on the results of the compressive strengths in dependence of the calcination temperature, only clays calcined at 750 °C and 850 °C were considered for further testing.

During the casting of the specimens, also the properties of the fresh mortar properties were explored. There was a major change in workability and the solidification time observed depending on the calcination temperature of the clays.

With constant activator/clay ratio for the alkali activation, the workability of the mortars is clearly increased for all three clays when the calcination temperature is enhanced. This is based on the fact, that the particle size is enhanced with increasing calcination temperature, as laser granulometric measurements have shown (Table 4). This leads to a reduced water consumption and consequently to a higher flow spread of the fresh mortars. As shown in Table 4, the slump test results of all three materials were significantly increased.

Especially for the mortar cased from Clay1 calcined at 850 °C, an inhomogeneous solidification was observed, whereby the softer binder covers solidified areas. This inhomogeneous solidification also leads to a

high standard deviation of the obtained compressive strengths (Fig. 6).

To study the inhomogeneous solidification further, the mortars casted of Clay1 were analysed in more detail by powder X-ray diffraction and micro x-ray fluorescence. Thereby it could be shown, that two phases were formed with very different crystallographic and mechanical properties (Fig. 5). In the hard areas crystalline sodium silicate hydrate (Na_2SiO_3 x H_2O) crystallised (Fig. 6). This observation can most likely be attributed to the fact that the activator solution of Betol39T does not react with the amorphous clay minerals to form N-A-S-H or C-A-S-H phases, but directly crystallises and forms Na_2SiO_3. This leads to a local inhomogeneous distribution of aluminium and calcium as shown in Fig. 5.

The compressive strength development over the first 28 days (Fig. 7) shows that there is a significant post solidification from 7 days to 28 days. Such a development is typical for cementitious systems or slag based AABs, since a reaction is occurring through which strengthening crystalline phases, such as calcium silicate hydrate (CSH) phases, are formed. Also in the case of the calcite containing clays, the post solidification could be due to the formation of CSH phases. This assumption is supported by the appearance of the typical reflex of CSH phases in the XRD of the reference clay after six days (Fig. 9). In contrast, for alkali-activated calcite free clays, which form N-A-S-H phases, usually no major post solidification can be observed over time (see Fig. 7).

3.3. Lime consumption

The solidified binder paste was analysed by powder XRD 7 days after casting (Fig. 8). These investigations show that the calcite stays untouched by the activation process. In addition, a lot of other minerals such as Quartz, Albite, Hematite and Muscovite show an inert behaviour. The binder paste of Clay2 calcined at 850 °C shows no Ca species in crystalline form, such as lime. This finding points towards the fact, that Ca is taking part in the alkali activation reaction and is consumed during this reaction.

A similar behaviour can also be observed for the alkali-activated reference clay (Fig. 9). Again, CaO in the binder is consumed over the time and Ca species are implemented into amorphous networks. Further, the beginning formation of calcium silicate hydrate phases can be observed.

3.4. Carbonation resistance

Since measurements of the pH values of the ground mortars have shown higher values than expected (Fig. 10), the question arose whether the CaO within the mortar can protect the specimen from carbonation, similar to the role of $Ca(OH)_2$ in concrete systems.

As it is shown in Fig. 9, the pH value inside the mortars is decreased over time. Starting from 14, due to the pure NaOH used for the activation, the pH value is reduced to 10.8 after 90 days for a calcium free metakaolin mortar. In contrast, the investigated calcite containing clays show a higher pH value after 90 days, which was found to be between 12 and 13. Based on these results, accelerated carbonation experiments were carried out (Fig. 10).

For comparison, a reference mortar consisting of pure metakaolin without any calcium content was also investigated, named further as

Table 4
Particle size, slump test and hardening time for 750 °C and 850 °C alkali activated calcined clays.

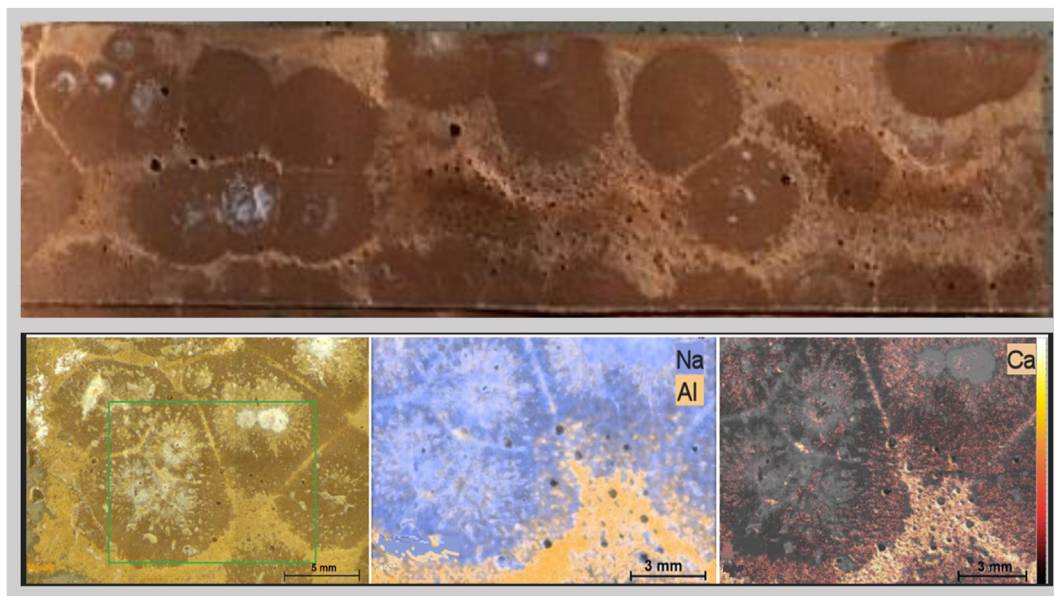|	Particle size d(0.5)% < [μm] 750 °C → 850 °C	Slump test [cm] 750 °C → 850 °C	Solidification time [h] 750 °C → 850 °C
Clay1_aa	10.5 → 13.5	15,5 → 20	5 → 2
Clay2_aa	30.5 → 35.4	17 → 21.5	6 → 1.5
Refclay_aa	9.4 → 12.1	15.5 → 19.5	4,5 → 2.5

Fig. 5. Top: surface of the mortar specimen of Clay1_aa calcined at 850 °C. Bottom: the inhomogeneous distribution of Al, Na and Ca determined by μXRF.
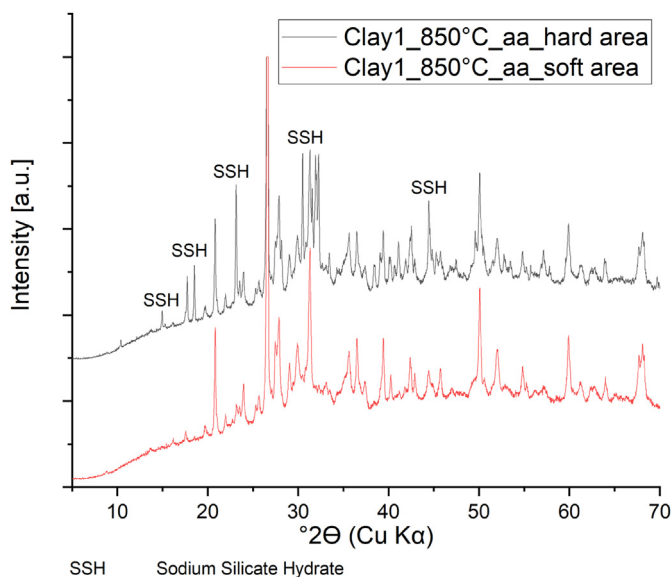

Fig. 6. Powder X-ray diffractograms of the inhomogeneous solidification measured on two different parts of one specimen casted from Clay1, soft and hard area. The Formation of Sodium Silicate Hydrate is shown.

Fig. 7. Post-solidification of the mortar specimens between 7 and 28 days after casting.

"Metakaolin Mortar". It becomes obvious that the carbonation depths of the clays significantly differ from the Ca-free mortar. The carbonation depth was measured by spraying phenolphthalein on the fresh broken cross-section of the specimens. After 90 days the calcium free system shows a carbonation depth of 9.5 mm. In comparison, the three investigated clays show a carbonation depth between 4.8 and 7.2 mm. That underlines that the attack of CO_2 on the specimen is occurring much slower due to an enhanced OH^- content in the pore solution.

3.5. Replacement of lime by portlandite

Based on the before described results, two CaO-free mortars were casted, since very high CaO contents were found to have a negative impact on the solidification time and the compressive strength. More precisely, a standard metakaolin mortar, referred to as "Metakaolin
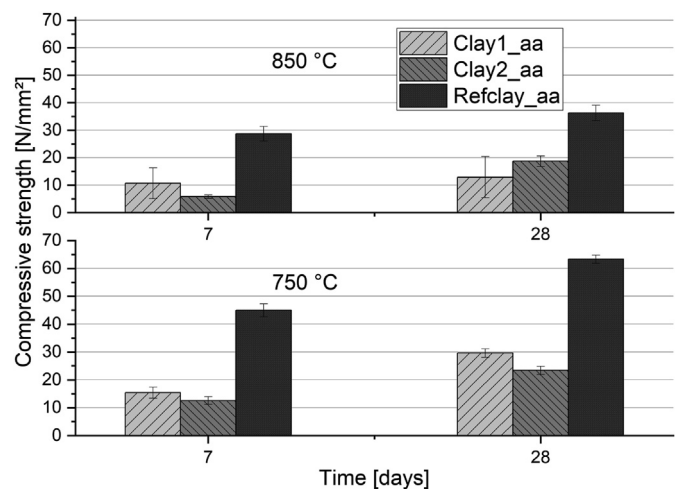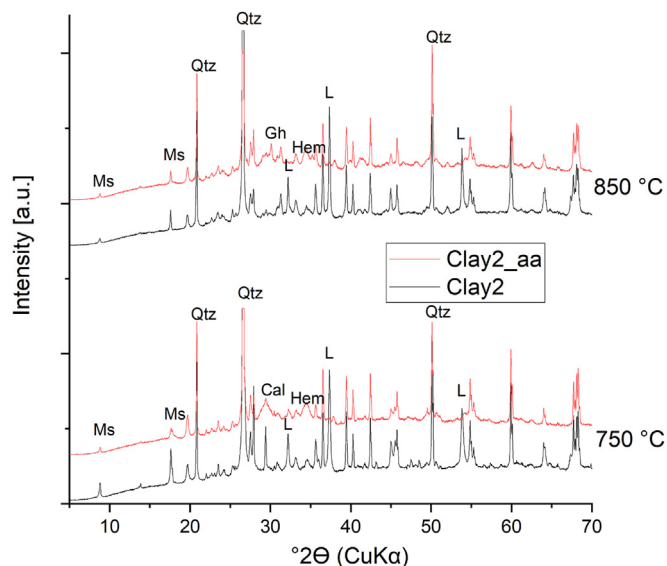
Mortar" and a metakaolin mortar mixed with $Ca(OH)_2$, denoted as "$Ca(OH)_2$ Metakaolin Mortar", were utilised for the investigations. The intention was hereby to implement an alternative Ca-source beside CaO, which does not react that exothermically with water and is therefore thought to be a more unreactive Ca species in the context of this study.

The $Ca(OH)_2$ Metakaolin Mortar was casted replacing 10 wt% of the metakaolin binder by $Ca(OH)_2$. The resulting specimens reached to a compressive strength of 61.3 MPa (Metakaolin Mortar) and 60.7 MPa ($Ca(OH)_2$ Metakaolin mortar). The fresh mortar properties were similar. The investigation of the mechanical properties have shown that the $Ca(OH)_2$ does not have a negative impact on solidification time and the mechanical properties, as seen before for the CaO containing clays. Also, the accelerated carbonation tests of the $Ca(OH)_2$ Metakaolin Mortar show a very high carbonation resistance. Again, as seen before for the calcite containing clays, the soluble Ca is consumed after the alkali activation and most likely imbedded in amorphous Al and Si containing phases. 24 h after casting the XRD investigation show that the crystalline portlandite hast been completely dissolved. The Results of the accelerated carbonation tests are shown in Fig. 11, the admixture of $Ca(OH)_2$

Fig. 8. Powder X-ray diffractograms of binder paste casted from calcined Clay2 at two different calcination temperatures.

Qtz Quartz; Cal Calcite; L Lime; Gh Gehlenite; Ms Muscovite; Hem Hematite

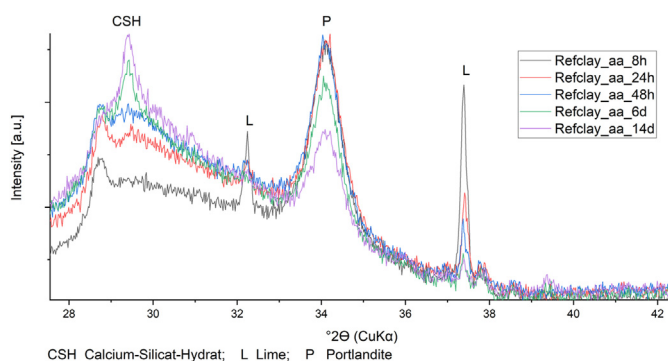CSH Calcium-Silicat-Hydrat; L Lime; P Portlandite

Fig. 9. Powder X-ray diffractograms of the reference clay mortar showing the CaO consumption over the time of 14 days.
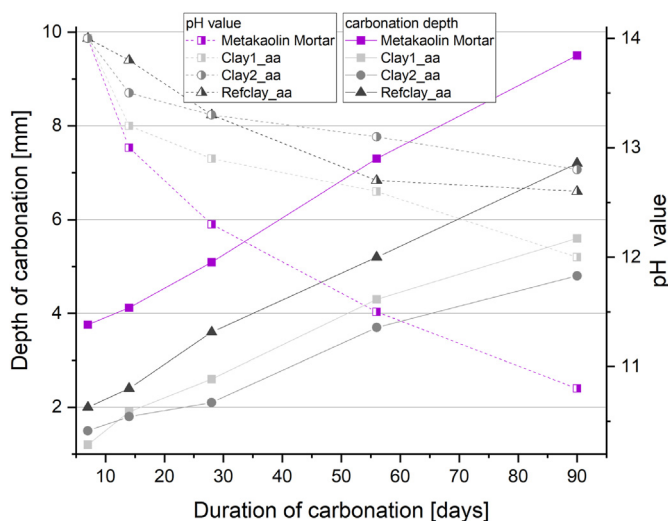

Fig. 10. Accelerated carbonation test 2% CO_2 atmosphere. The depths of carbonation of all three mortars made of the clays calcined at 750 °C and the overall pH value of the hardened mortars are shown. A comparable Ca-free metakaolin mortar is used.
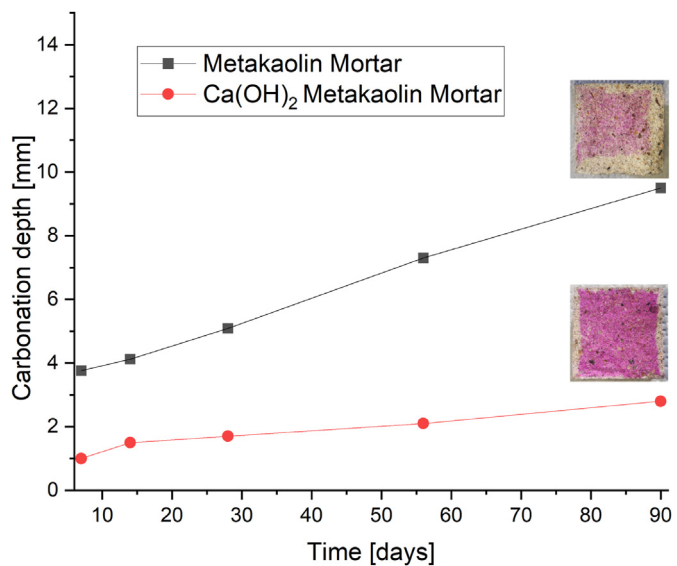

Fig. 11. Carbonation depth of $Ca(OH)_2$ tuned metakaolin mortar. The pictures in the graph show the freshly broken cross sections sprayed with phenolphthalein.

leads to a 3 times higher carbonation resistant compared to the Ca free system. The results show that after 90 days the carbonation depth of the Ca free Metakaolin Mortar is 9.5 mm while the tuned Mortar shows a carbonation depth of 2.8 mm. After 270 days the Ca free specimens are completely carbonated while the tuned $Ca(OH)_2$ Metakaolin Mortar show a carbonation depth of 14 mm.

One observation made on all alkali-activated specimens was that the casting side of the beams always shows a much lower carbonation depth than the sides that were in the mould while casting. The surface of the specimens, that has contact to air while setting, seems to be much denser than the other sides this lowers the diffusion rate of CO_2 in to the specimen. These observations have to be further investigated in the different scientific setup.

4. Conclusions

Calcium-rich common clay deposits have gained more and more attention recently in the field of construction materials, due to the frequent occurrence of such clay deposits. In this context, also the utilisation of calcium rich common clays as precursors for the alkali activation and formation of alternative binders has been considered.

In this work, the authors investigated the influence of calcium compounds on the properties of the alkali-activated binders. Hereby, it could be shown that, if calcium was present in the form of calcite, the two investigated common clays showed expected mechanical properties after calcination and alkali activation. However, if calcite decomposition occurs during the thermal treatment, the properties of the alkali-activated binders are altered tremendously. Although the calcination of Clay1 and Clay2 leads to calcite decomposition, different reaction products are observed. Whereas Clay1 forms an amorphous Ca-rich transition phase, the thermal treatment of Clay2 leads to the formation of crystalline lime. The formation of lime has an enormous impact on the mechanical properties, such as the setting behaviour and the workability of the mortars. With very large lime amounts, undesired damage processes can be observed, such as the crystallisation of sodium silicate, which leads to an inhomogeneous solidification of the binder. Ultimately, this makes the binder not suitable for any application as construction material. However, lime in adequate amounts leads to an increase in basicity and consequently an enhancement of carbonation resistance, which is beneficial for the application of such binders in steel reinforced components. Combined whit the high acid resistance that alkali activated systems

naturally show an application in agriculture buildings could be an interesting place of use.

As part of this work, the authors could show that the calcium carbonate decomposition can be well controlled via the calcination process. It became obvious that for pure calcium carbonate, the carbonate decomposition and the dehydroxylation of the layered silicates can be separated via the temperature. Only for MgCa carbonates, such as dolomite, the decarbonation and dehydroxylation takes place simultaneously within a similar temperature range. Based on this, the desired amount of lime can be adjusted via the calcination of the calcite-rich common clays without any recrystallisation processes of the amorphous layered silicates. The consideration of the free lime content is not only important for the formation of alkali-activated binders but has also to be considered when common clays are applied as additives in conventional cementitious systems.

The mechanical properties of the alkali-activated binders were investigated and despite the low content of layered silicates that are reactive after calcination, and the high content of unreactive minerals (60 wt% quartz, Illite) compressive strengths of above 20 MPa of the mortars could be obtained. Considering the kaolin content in Clay1 with 9 wt% and Clay2 with 15 wt%. We are convinced that after the addition of additives, such as super plasticizers and retarders, and the optimisation of the activator species, compressive strengths of 32.5 MPa similar to standard ordinary Portland cementitious systems are feasible. Such investigations are part of our ongoing studies.

The investigations have confirmed that even low amounts of free lime lead to an increase of basicity and have therefore a positive impact of the carbonation resistance of the mortars. Thereby, no negative effect on the mechanical properties was observed and even a post-solidification of 50% from 7 to 28 days of the mortars were observed for the first time in the field of alkali-activated binders based on common clays.

In ongoing studies, the mechanism of the $CaCO_3$ decomposition in combination with different clay minerals should be clarified further, since it can react either to form lime, as expected, or to form Ca-rich amorphous phases, which leads to an immobilisation of the calcium.

Funding

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.

References

[1] G.J.G. Gluth, K. Arbi, S.A. Bernal, D. Bondar, A. Castel, S. Chithiraputhiran, A. Dehghan, K. Dombrowski-Daube, A. Dubey, V. Ducman, K. Peterson, P. Pipilikaki, S.L.A. Valcke, G. Ye, Y. Zuo, J.L. Provis, RILEM TC 247-DTA round robin test: carbonation and chloride penetration testing of alkali-activated concretes, Mater. Struct. 53 (2020) 1–17, https://doi.org/10.1617/s11527-020-1449-3.

[2] J.L. Provis, J.S.J. van Deventer, Alkali Activated Materials: State-Of-The-Art Report, RILEM TC 224-AAM, Springer Netherlands, Dordrecht, The Netherlands, 2014.

[3] F. Pacheco-Torgal, J. Castro-Gomes, S. Jalali, Alkali-activated binders: a review, Construct. Build. Mater. 22 (2008) 1305–1314, https://doi.org/10.1016/j.conbuildmat.2007.10.015.

[4] A. Buchwald, The Influence of Calcium on the Condensation of (Alumino-) Silicates in Alkali-Activated Binders, Habilitation, Weimar, 2012.

[5] A. Herrmann, A. Koenig, F. Dehn, Structural concrete based on alkali-activated binders: terminology, reaction mechanisms, mix designs and performance, Struct. Concr. 19 (2018) 918–929, https://doi.org/10.1002/suco.201700016.

[6] A. Herrmann, A. Koenig, F. Dehn, Proposal for the classification of alkali-activated binders and Geopolymer binder, Cem. Int. 2015 (2015) 63–69.

[7] e.V. Verband kommunaler Unternehmen, Statusbericht der deutschen Kreislaufwirtschaft, 2018.

[8] A. Trümer, Calcinierte Tone als Puzzolane der Zukunft – Von den Rohstoffen bis zur Wirkung im Beton, 2020. Weimar.

[9] H.H. Murray, in: Applied Clay Mineralogy: Occurrences, Processing and Application of Kaolins, Bentonites, Palygorskite-Sepiolite, and Common Clays, first. ed., Elsevier, Amsterdam, 2007.

[10] A. Mehta, R. Siddique, Sulfuric acid resistance of fly ash based geopolymer concrete, Construct. Build. Mater. 146 (2017) 136–143, https://doi.org/10.1016/j.conbuildmat.2017.04.077.

[11] N.K. Lee, H.K. Lee, Influence of the slag content on the chloride and sulfuric acid resistances of alkali-activated fly ash/slag paste, Cement Concr. Compos. 72 (2016) 168–179, https://doi.org/10.1016/j.cemconcomp.2016.06.004.

[12] A. Koenig, A. Herrmann, S. Overmann, F. Dehn, Resistance of alkali-activated binders to organic acid attack: assessment of evaluation criteria and damage mechanisms, Construct. Build. Mater. 151 (2017) 405–413, https://doi.org/10.1016/j.conbuildmat.2017.06.117.

[13] T. Bakharev, J.G. Sanjayan, Y.-B. Cheng, Resistance of alkali-activated slag concrete to acid attack, Cement Concr. Res. 33 (2003) 1607–1611, https://doi.org/10.1016/S0008-8846(03)00125-X.

[14] H.J. Zhuang, H.Y. Zhang, H. Xu, Resistance of geopolymer mortar to acid and chloride attacks, Procedia Eng 210 (2017) 126–131, https://doi.org/10.1016/j.proeng.2017.11.057.

[15] C.-K. Ma, A.Z. Awang, W. Omar, Structural and material performance of geopolymer concrete: a review, Construct. Build. Mater. 186 (2018) 90–102, https://doi.org/10.1016/j.conbuildmat.2018.07.111.

[16] A. Koenig, A. Wuestemann, F. Gatti, L. Rossi, F. Fuchs, D. Fessel, F. Dathe, F. Dehn, F. Minelli, Flexural behaviour of steel and macro-PP fibre reinforced concretes based on alkali-activated binders, Construct. Build. Mater. 211 (2019) 583–593, https://doi.org/10.1016/j.conbuildmat.2019.03.227.

[17] R. Pouhet, M. Cyr, Carbonation in the pore solution of metakaolin-based geopolymer, Cement Concr. Res. 88 (2016) 227–235, https://doi.org/10.1016/j.cemconres.2016.05.008.

[18] P. Hewlett, in: Lea's Chemistry of Cement and Concrete, fourthth ed., Elsevier, Burlington, 2004.

[19] N. Werling, F. Dehn, F. Krause, A. Steudel, R. Schuhmann, K. Emmerich, Solubility OF precursors and carbonation OF WATERGLASS-free geopolymers, Clay Clay Miner. (2020), https://doi.org/10.1007/s42860-020-00096-4.

[20] A. Koenig, H. Mahmoud, O. Baehre, F. Dehn, Alkalinity and its consequences for the performance of steel-reinforced geopolymer materials, Molecules 25 (2020) 2359, https://doi.org/10.3390/molecules25102359.

[21] F. Tittarelli, A. Mobili, C. Giosuè, A. Belli, T. Bellezze, Corrosion behaviour of bare and galvanized steel in geopolymer and Ordinary Portland Cement based mortars with the same strength class exposed to chlorides, Corrosion Sci. 134 (2018) 64–77, https://doi.org/10.1016/j.corsci.2018.02.014.

[22] C. Monticelli, M.E. Natali, A. Balbo, C. Chiavari, F. Zanotto, S. Manzi, M.C. Bignozzi, Corrosion behavior of steel in alkali-activated fly ash mortars in the light of their microstructural, mechanical and chemical characterization, Cement Concr. Res. 80 (2016) 60–68, https://doi.org/10.1016/j.cemconres.2015.11.001.

[23] M. Criado, I. Sobrados, J.M. Bastidas, J. Sanz, Corrosion behaviour of coated steel rebars in carbonated and chloride-contaminated alkali-activated fly ash mortar, Prog. Org. Coating 99 (2016) 11–22, https://doi.org/10.1016/j.porgcoat.2016.04.040.

[24] N. Beuntner, Zur Eignung und Wirkungsweise calcinierter Tone als reaktive Bindemittel-komponente im Zement, 2018. München.

[25] B. Franke, Bestimmung von Calciumoxyd und Calciumhydroxyd neben wasserfreiem und wasserhaltigem Calciumsilikat, Z. Anorg. Allg. Chem. 247 (1941) 180–184, https://doi.org/10.1002/zaac.19412470115.

[26] European Committee for Standardization, Methods of Testing Cement - Part 1, Determination of strength, 2016.

[27] J. Davidovits, in: Geopolymer: Chemistry and Applications, fifth ed., Institut Geopolymere, Saint-Quentin, 2020.

[28] European Committee for Standardization, DIN EN 196-3:2017-03, Prüfverfahren für Zement - Teil_3: Bestimmung der Erstarrungszeiten und der Raumbeständigkeit; Deutsche Fassung EN_196-3:2016, Beuth Verlag GmbH, Berlin.

[29] European Committee for Standardization, Products and Systems for the Protection and Repair of Concrete Structures—Test Methods—Determination of Resistance to Carbonation, 2004. Brussels, Belgium.

[30] R.M. McIntosh, J.H. Sharp, F.W. Wilburn, The thermal decomposition of dolomite, Thermochim. Acta 165 (1990) 281–296.

[31] A. Buchwald, M. Hohmann, K. Posern, E. Brendler, The suitability of thermally activated illite/smectite clay as raw material for geopolymer binders, Appl. Clay Sci. 46 (2009) 300–304, https://doi.org/10.1016/j.clay.2009.08.026.