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Citation for published version (APA):

Kaja, A. M., Lazaro Garcia, A., & Yu, Q. (2018). Effects of Portland cement on activation mechanism of class F fly ash geopolymer cured under ambient conditions. *Construction and Building Materials*, 189, 1113-1123. <https://doi.org/10.1016/j.conbuildmat.2018.09.065>

Document license:

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DOI:

[10.1016/j.conbuildmat.2018.09.065](https://doi.org/10.1016/j.conbuildmat.2018.09.065)

Document status and date:

Published: 20/11/2018

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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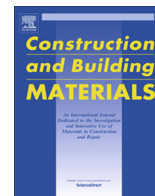
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Effects of Portland cement on activation mechanism of class F fly ash geopolymer cured under ambient conditions

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HIGHLIGHTS

- A small cement addition enables ambient curing of class F fly ash-based geopolymer.
- Setting of class F-based geopolymer is greatly accelerated by the cement addition.
- Cement addition promotes the formation of calcium rich products at early age.
- The optimal cement dosage is associated with the silica content in alkali activator.
- The presence of calcium rich products impedes the gel formation at later ages.

ARTICLE INFO

Article history:

Received 22 June 2018

Received in revised form 14 August 2018

Accepted 12 September 2018

Keywords:

Class F fly ash geopolymer

Ambient curing

Portland cement

Setting time

Reaction kinetics

Structural formation

Compressive strength

ABSTRACT

This study addresses the influence of a small Portland cement addition on the reaction kinetics and phase evolution of ambient cured class F fly ash-based geopolymer. The results show that setting time and reaction kinetics can be controlled by tailoring the precursor and activator characteristics, primarily the Ca/Si molar ratio. Calcium ions, dissolved from cement phases, contribute to a faster precipitation of products and in consequence, to a denser microstructure of composite pastes and a higher early age mechanical performance. However, excessive cement content impedes the gel formation due to hindered hydration of cement in high alkalinity at later ages and low compatibility between calcium deficient and calcium rich phases which lower the silica availability. It is found that the optimal dosage of cement in fly ash F based geopolymeric system is depending on the total silica content, 5 wt% and 7.5 wt% for silicate-based activator with a silica modulus of 1.2 and 1.5, respectively.

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1. Introduction

The demand for sustainable development in concrete industry has been arising constantly during the recent years [1]. Tightened regulations concerning greenhouse gas emission as well as financial motivation have shifted the direction of concrete development from traditional Portland cement-based materials towards by-products-based materials such as geopolymers. The use of industrial by-products to design new binders contributes to a reduced CO₂ emission associated with the manufacture of Portland cement and lower costs. Extensive laboratory research has been performed on geopolymeric binders over the last years. Duxson et al. [2] proposed a model based on the Si/Al atomic ratios in metakaolin based

geopolymers, linking composition of the raw materials with microstructure and mechanical properties, which allows tailoring the mix design for specific applications. Criado et al. [3] showed that the phase assemblage among the geopolymeric systems can differ substantially depending on activator characteristics. Bakharev et al. [4] investigated the effect of curing temperature on the microstructure and mechanical properties of fly ash-based geopolymers, suggesting a significant influence of thermal conditions on geopolymers performance as well as dependence of the initial mix design on the optimal curing conditions. Nevertheless, there are yet only few full-scale geopolymer productions over the world. As was shown by Bakharev et al. [4], the external heat supply in order to ensure the sufficient rate of geopolymerization generates an additional variable in designing geopolymers. In contrast to alkali activated calcium rich systems, special accommodations must be applied in production of geopolymers to provide the

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required amount of heat with a suitable method, especially for large concrete casting [5,6]. Concerns about long-term durability are also a limiting factor in a widespread geopolymers adoption.

Recently, special attention has been paid to alkali-activated systems consisting of fly ash and cement. These hybrid materials can be produced without thermal treatment, while maintaining a high content of fly ash in the binder. It has been suggested that an intermixing of the geopolymeric binder with calcium source hinders the formation of zeolites which can have an adverse effect on mechanical performance of geopolymers at later ages [7,8]. Moreover, Krivenko et al. [9] reported that hybrid binders possess better abilities to bind sodium ions. This can, in turn, prevent the efflorescence occurrence. The presence of a calcium source has also been proved to influence considerably the setting time of alkali-activated materials [10]. The impact of calcium ions in hybrid systems is assigned to the provision of nucleation sites for the precipitation of products, thus leading to an accelerated hardening [11]. As calcium ions possess similar ionic radius to sodium ones, their role is also attributed to charge balancing function in structure formation [12].

The activation of a hybrid cement and fly ash geopolymers can be very complex due to the different nature of cement hydration and fly ash geopolymerization process. Garcia-Lodeiro et al. [13] investigated the structure development and mechanical properties of hybrid system (70 wt% of fly ash/ 30 wt% of cement) under ambient temperature and high alkalinity conditions. It was observed that at the early ages of activation, C-S-H and N-A-S-H gels are formed simultaneously in the systems with additional calcium source. At longer periods, C-S-H gel transforms into C-A-S-H gel, since this phase is thermodynamically more stable in the highly alkaline environment. A similar effect was observed for N-A-S-H gel, leading to the formation of (N,C)-A-S-H, which subsequently evolves towards less polymerized C-A-S-H structure [14].

On the other hand, Yip et al. [15] proved that whereas a calcium source (cement, ground granulated blast furnace slag) up to 20 wt% in hybrid systems can have a positive impact on mechanical performance of these materials, a higher calcium source dosage (40 wt%) causes a decrease in compressive strength compared to the plain geopolymer sample. Moreover, the studies of Nath et al. [16] and Suwan et al. [17] show that the compressive strength of geopolymers can be considerably improved even within a small range of cement addition (5–10 wt%), however, the mechanism behind this phenomenon still remains unclear. Even though recent studies explored in depth the compatibility between C-S-H and N-A-S-H gels in fly ash-cement systems as well as synthetic gels systems [13,18], there is still lack of knowledge regarding the influence of cement dosage on the formation of geopolymeric structure and accordingly mechanical performance of these materials.

In this study, the alterations in the geopolymerization process in the presence of a low amount of cement are addressed in detail. Mixtures with cement dosages up to 10 wt% and two different values of the activator modulus are investigated in order to systematically understand the kinetics of the gel formation, characteristics of the formed phases and their interaction. The Vicat needle test was used to determine the setting behaviour and isothermal calorimetry was applied to monitor the heat release during the activation process. The gel structure was assessed employing Four-

ier transform infrared spectroscopy (FTIR). Phase development was determined by X-ray diffraction (XRD) and thermogravimetry analysis (TGA). The microstructural development was analysed by using scanning electron microscopy (SEM). In addition, the mechanical strength of the samples at different curing periods was determined. The present results provide fundamental insights on the greatly shortened setting behaviour and enhanced early age mechanical performance, which are critical parameters for the manufacture of these hybrid materials at ambient conditions.

2. Experimental

2.1. Materials

Class F fly ash (FA) and Ordinary Portland Cement (OPC, provided by ENCI, the Netherlands) were used as solid precursors in this study. Their chemical composition, determined by X-ray fluorescence, is presented in Table 1. In order to minimize the effect of the particle size of the raw materials on the final performance of geopolymeric pastes, solid precursors with similar particle size distribution were selected, as presented in Fig. 1. The particle size distribution (PSD) was measured by laser diffraction (Mastersizer 2000, Malvern).

Two alkaline activators were prepared by mixing sodium silicate solution (27.69% SiO₂, 8.39% Na₂O and 63.92% H₂O by mass) with analytical sodium hydroxide pellets (99 wt%) and demineralized water. The equivalent sodium oxide content in both activators was kept constant (8 wt% of the binder). This level of alkali content has been proved to be optimal for a sufficient dissolution rate of low calcium fly ash [4,19]. Skvara et al. [20] found that optimum compressive strength of fly ash based geopolymers can be achieved when Na₂O content in sodium silicate activator ranges between 7% and 9% by mass of fly ash. Similar observations were reported by Winnefeld et al. [21], who stated that increasing the Na₂O content in an activator solution has a positive effect on strength development, whereas higher amounts than 9 wt% of fly ash are not recommended. Another important feature characterizing the activator solution is the silica modulus (Ms), described as the molar ratio between silicon oxide and sodium oxide. The content

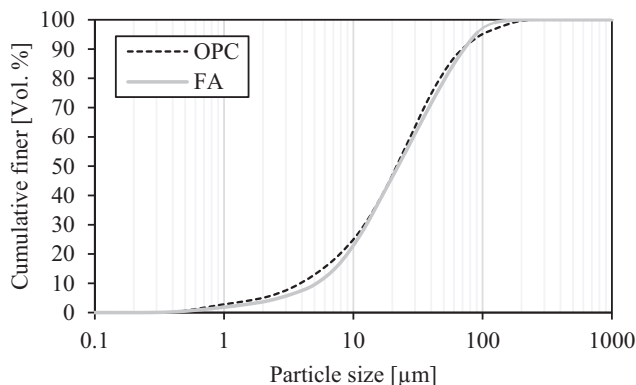


Fig. 1. Particle size distribution of the investigated materials.

Table 1
Chemical composition of the raw materials.

Raw material	Mass fraction wt. %											
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	Na ₂ O	TiO ₂	Mn ₃ O ₄	P ₂ O ₅	LOI
OPC	63.71	20.27	4.8	3.43	1.58	2.91	0.53	0.26	–	–	–	2.51
Fly ash	4.44	54.62	24.42	7.21	1.43	0.46	1.75	0.73	1.17	0.11	0.86	2.8

of silica in activating solution considerably influences early age development of the geopolymeric structure. Rees et al. [22] proved that a silica concentration of approximately 0.6 M is sufficient to shift the reaction mechanism from hydroxide activation towards silicate activation. Moreover, it has been widely proved that silicate species in initial solution enhance the formation of a geopolymeric structure, and increasing silicate concentration leads to a more homogenous and denser microstructure of geopolymeric products [23,24]. In this study two silica moduli (Ms) of 1.2 and 1.5 were applied, based on the previous study [25].

2.2. Sample preparation and test methods

Alkali solutions were first prepared and cooled down to room temperature (20 ± 1 °C) one day prior to further application. For compressive strength measurements, geopolymeric pastes were produced following the mix proportions shown in Table 2. The liquid to binder ratio was kept constant as 0.5 for all the mixtures. Dry powders were firstly mixed for one minute in a Hobart mixer. Subsequently, the sodium silicate solution was added to the homogenized solid precursors and mixed for another 4 min. Fresh pastes were cast into plastic molds ($40 \text{ mm} \times 40 \text{ mm} \times 160 \text{ mm}$) and covered with plastic foil to prevent moisture loss. After 24 h of curing, samples were demolded (pastes based solely on fly ash were demolded after 3 days of curing) and sealed cured at room temperature of about 20 °C until the testing age. The compressive strength of all samples was determined according to EN 196-1 [26] after 7 and 28 days of curing. The average values were obtained from 3 measurements for each sample. The initial and final setting time measurements were conducted with a Vicat needle test setup according to EN 196-3 [27].

The reaction kinetics of the investigated systems were determined with an isothermal calorimeter (TAM Air, Thermometric) at 20 °C. Powders were firstly mixed with sodium silicate solutions for 2 min and about 10 g of pastes were transferred to sealed ampoules that were then loaded into the calorimeter. In order to evaluate the cumulative heat, the integration of heat flow curve was performed between 30 min and 140 h.

The FT-IR spectra of geopolymeric samples were collected using a PerkinElmer FrontierTM MIR/FIR Spectrometer with the attenuated total reflection (ATR) method (GladiATR). The analyses were performed on pastes without terminating the hydration during the first 28 days of activation. All spectra were scanned 50 times from 2000 to 600 cm^{-1} at a resolution of 4 cm^{-1} .

For the microstructure analysis, the activation process was stopped by immersing the paste specimens in isopropanol for 24 h and subsequent drying in the oven at 40 °C for 3 days. Selected sections were sputtered with gold by using an Emitech

K550X sputter coater (current 25 mA, coating time 2 min). The Phenom ProX scanning electron microscope (SEM) was used with an accelerating voltage of 15 kV. Point analyses were conducted on polished samples with the Element Identification (EID) software package with fully integrated Energy Dispersive Spectrometer (EDS) (more than 120 points were taken for each measurement).

The X-ray diffraction (XRD) analysis and thermogravimetric analysis (TGA) were carried out on powder samples. To stop the activation process, pastes were firstly crushed and immersed in isopropanol for 24 h, then dried for 5 h at 40 °C and ground. A D2 PHASER X-ray Diffractometer with Co X-ray tube and a step size of 0.02° for a 2θ range of $10\text{--}50^\circ$ was used to determine the phase composition of pastes. About 40–70 mg of powdered samples were thermally treated using a Jupiter STA 449 F1 Netzsch instrument. The samples were firstly isothermally held at 105 °C for 2 h and then heated up to 1000 °C at the rate of 5 °C/min with nitrogen as the carrier gas.

3. Results and discussion

3.1. Setting behavior

Table 3 shows the Vicat test results of the designed mixes. This method is universally accepted and specified since the simple procedure allows to obtain satisfactory results when Portland cement hydration at normal conditions is concerned [28]. It should be pointed out, however, that during the alkali activation different mechanisms of stiffening and hardening take place. Therefore, considering the practical aspects of hybrid systems manufacture it has to be taken into account that the properties of alkali activated materials at the setting point can differ substantially from the cement paste properties. Nevertheless, this test provides useful information about the hardening process and can be supportive to explain the mechanism of alkali activation. It should be noted that in overall cement addition leads to a reduced workability, nevertheless the difference is rather limited. The flow, determined fol-

Table 3
Setting behavior of alkali activated pastes.

Mixture	Initial setting time [min]	Final setting time [min]
P0M1.2	>24 h	>24 h
P5M1.2	210	300
P7.5M1.2	130	180
P10M1.2	80	115
P0M1.5	>24 h	>24 h
P5M1.5	350	520
P7.5M1.5	190	300
P10M1.5	110	145

Table 2
Mix proportions of investigated geopolymeric pastes.

Mixture	Mass fraction wt.%		W/B ratio		L/B ratio
	Fly ash	Cement	Activator		
			Ms = 1.2 ^a	Ms = 1.5 ^a	
P0M1.2	100	–	0.30		0.5
P5M1.2	95	5	0.30		0.5
P7.5M1.2	92.5	7.5	0.30		0.5
P10M1.2	90	10	0.30		0.5
P100M1.2	–	100	0.30		0.5
P0M1.5	100	–		0.28	0.5
P5M1.5	95	5		0.28	0.5
P7.5M1.5	92.5	7.5		0.28	0.5
P10M1.5	90	10		0.28	0.5
P100M1.5	–	100		0.28	0.5

^apH measured with a Metrohm 780 pH Meter were 13.98 and 13.80 for activators with silica modulus (Ms) 1.2 and 1.5, respectively.

lowing EN 1015-3 but without jolts, reduces only from 31 cm to 30 cm in the case of M1.2, while it reduces from 28 cm to 26.8 cm in M1.5 series, with the cement dosage of 10% compared to the control samples.

While samples with the sole fly ash precursor are not able to set within 24 h, the present data show that even a very small amount of cement addition can considerably accelerate the setting. This behavior has also been reported by others [16,29]. Suwan et al. [29] suggested 5 wt% of cement content in the fly ash based binder as an optimum value to obtain reasonable setting times for practical applications of these materials. In the study of Yip et al. [15], the significant role of calcium ions at the early stages of alkali activation was emphasized by analysing the influence of different calcium sources in fly ash-based hybrid systems. It can be therefore assumed that calcium ions dissolved from the cement phases contribute to the hardening process. The present study additionally reveals that next to the cement content, the $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of the activator significantly influences the setting behavior of hybrid systems. Whereas the increasing cement content accelerates the hardening process of highly alkaline low-calcium systems, the setting time is substantially prolonged with a higher silica concentration in the alkaline solution. Considering the exothermic nature of cement hydration, an accelerated formation of geopolymeric structure in the presence of additional heat can also contribute to the faster setting of these binders.

According to Visser [30], dissolution of amorphous silica (in this study silica from fly ash) at high pH is an acidifying process. The accelerating effect of cement addition on the setting time can be explained considering the presence of calcium ions which pose significantly higher charge screening capacity of the silicic acid anions than sodium ions. It is known that in high alkalinity environment, negatively charged silicic acid monomers will repulse each other preventing condensation [31]. Calcium ions can therefore accelerate the formation of products due to the charge neutralization effect. Gaboriaud et al. [32] suggested that the presence of calcium ions in sodium silicate solution leads to the aggregation and subsequent densification of the gel network. Under high pH environment, however, their effect is associated with precipitation of calcium-silica products rather than gelation. As suggested by Visser [30], who analysed the mechanism of alkali-silica reaction in concrete, and confirmed in this study, from the fly ash dissolution point of view, precipitation occurs at lower silicic acid anions concentration in the presence of divalent cations (calcium) than monovalent cations (sodium).

3.2. Reaction kinetics

Fig. 2 shows the heat flow profiles and cumulative heat of designed systems normalized to the mass of the binder.

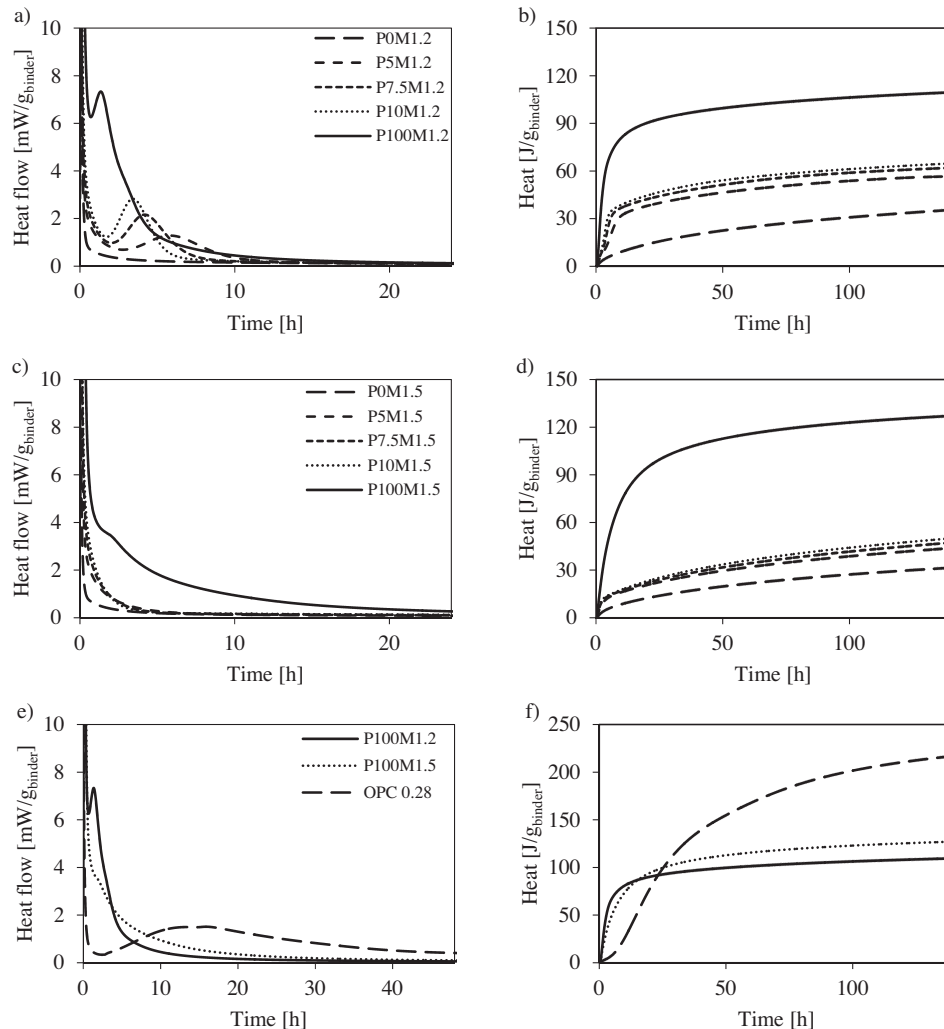


Fig. 2. Normalized heat flow a), c), e) and total heat b), d), f) curves of alkali activated pastes (note: additional water hydrated cement paste was prepared for comparison purpose, described as OPC 0.28, where 0.28 is the water to cement ratio). Binder is defined as fly ash and cement.

Regardless of the activator modulus, the heat flow curves of pastes based solely on fly ash do not reveal any peaks associated with products formation. With the presence of cement in the systems, the influence of the activator characteristics becomes more significant. For the samples activated with sodium silicate solution with a silica modulus of 1.2 and with additions of cement, an additional peak occurs between 2 and 6 h. This peak is attributed to the products formation. With the increasing cement content, the position of this peak shifts towards shorter times and rises in intensity. This behaviour is consistent with the setting time observations. Most likely, C-S-H-like structures are formed in these systems as a consequence of the reaction between calcium ions dissolved from cement phases and silica. On the contrary, no “main reaction peak” can be distinguished in the hybrid systems activated with sodium silicate solution with a silica modulus 1.5 (Fig. 2c). These observations can be attributed to the higher concentration of silica ions and lower concentration of OH^- in the activator.

Considering the impact of cement on the heat liberation in hybrid systems, the influence of high pH on the dissolution and hydration of cement phases has to be taken into account. Kumar et al. [33] studied the influence of sodium and potassium hydroxide on alite hydration. It was found that the hydration of alite in alkaline solution is accelerated. The rapid formation of portlandite in high pH, caused by the increased activity of hydroxyl ions, lowering the amount of calcium ions required to achieve supersaturation for portlandite, is the main reason for the acceleration of alite hydration. They also reported a reduction of calcium concentration and an increase in silicate content in the pore solution during the first few hours of hydration compared to water hydrated sample. This argumentation explains the setting behavior of the samples with higher silica concentration. Due to the fact that a smaller concentration of calcium ions in the solution is required for the products precipitation, insufficient calcium ions are dissolved for massive formation of calcium rich products and thus, more gradual formation of C-S-H-like phase is observed in these samples compared to the systems with a lower silica content. The shape of the heat flow profiles confirms these assumptions. Precipitation of C-S-H phases in samples with a lower silica content is more pronounced, suggesting a higher contribution of calcium ions. Whereas the setting time of samples with a lower silica content corresponds well to the occurrence of peak associated with C-S-H formation, the gradual precipitation of products in the systems with a higher initial silica content results in prolonged setting times.

In order to broaden the spectrum of information related to hydration of cement in highly alkaline conditions, calorimetric measurements were also conducted on the neat cement samples. Fig. 2e and f show the heat flow profile and cumulative heat of cement hydration with alkaline activators and water as a reference (selected $w/c = 0.28$ corresponds to w/c ratio of the alkali activated

cement sample with an activator modulus 1.5), respectively. It can be seen that cement hydration is considerably accelerated by a high alkalinity. Due to the high pH of the used activators and the presence of silica species, induction period is eliminated. The overall heat liberation by the end of 140 h curing, however, is considerably higher in the case of cement with only water. It is concluded that a high alkalinity solution contributes to an accelerated products formation during the first few hours of curing while further hydration is drastically inhibited. Comparing the hydration curves of cement activated with solutions with a silica modulus of 1.2 and 1.5, similar conclusions can be drawn. The higher amount of heat generated at the beginning of activation process due to products formation results in the retardation of further structure development in sample activated with solution M1.2.

3.3. Infrared spectroscopy analysis of activation process

The fly ash FTIR spectrum consists of vibrational bands assigned to both glassy and crystalline phases. In order to count a large spectrum of component bands from the raw materials as well as reaction products, in this study, a straightforward approach is applied based on the identification of the “main” band position in the region $1100\text{--}800\text{ cm}^{-1}$, attributed to Si–O–T bond asymmetric stretching vibrations (T = Si, Al). It has been well documented that the shifts in the position of this band indicate structural changes of investigated materials, especially the polymerization degree of the silica network [34]. From Fig. 3a it can be seen that the band assigned to T–O stretching vibrations in fly ash spectrum shows the peak at around 1033 cm^{-1} . This peak consists of group of bands assigned to quartz, mullite and glassy phase. The location of the major vibrational band at low frequencies- around 1033 cm^{-1} indicates a relatively high amorphous content of fly ash used in this study [34,35]. In dry cement, the position of the main peak is considerably shifted towards lower wavenumbers due to the different nature of main phases. The band located at around 915 cm^{-1} is assigned to crystalline calcium silicates [36].

Two sodium silicate solutions used in this study characterized by different silica and water contents were also examined by FTIR. Previous studies on sodium silicate solutions have shown that the position of the main bands is determined by molecular weight of units formed in the solution [37,38]. Larger silicate structures contribute to the bands at higher vibrational frequencies. It is also known that the size of the structural units increases with the increasing silica modulus and decreasing pH [39,40]. In this study both activators exhibit very high pH (see Table 2) hence the main peaks occur at relatively low wavenumbers, attributed to small silicate units. The infrared spectrum of these highly alkaline solutions is dominated by two component bands near 975 and 921 cm^{-1} . Their presence is assigned to the vibrations of small linear silicate

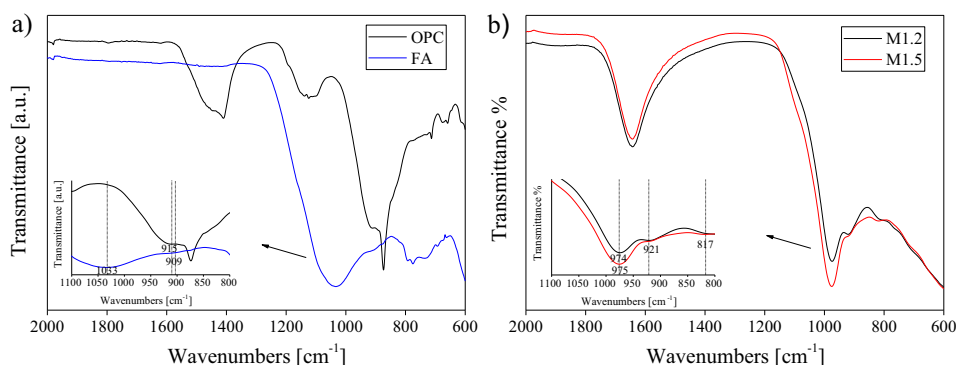


Fig. 3. FTIR spectra of a) fly ash and cement, b) sodium silicate solutions.

species (dimer, trimer, tetramer) and monomeric and dimeric species, respectively [41]. The fact that the position of the main peak is only slightly changed for activators with different silica modulus indicates that in high alkalinity small silicate species are dominant and only slightly larger units can be observed in solution with a higher silica modulus. Rees et al. [24] also reported that the higher the pH of solution the higher silica concentration can be used to maintain the monomeric nature of silicate species. It has to be mentioned, however, that larger silicate units (oligomers) can also be present in these solutions but they are not distinguished in this study due to the overlapping of the bands. Silicate monomers and small species are found to participate in the dissolution process of fly ash and enhance the attainment of steady gel [24]. From this study it appears that in the presence of calcium source silicate species are involved in the C-S-H-like gel precipitation at the beginning of activation process which limits their availability to further support the dissolution process.

The FTIR spectra of the investigated samples were collected after scheduled curing periods without any mechanical or chemical intervention in the activation process. Therefore, the analogy of the spectra shape and peak positions of early age samples spectra and spectra of sodium silicate solution used to activate samples can be observed. For samples based solely on fly ash, a shift in the position

of the main peak at around $973\text{--}975\text{ cm}^{-1}$ towards lower wavenumbers can be observed during the first 24 h of curing. The rate of this shift seems not to be influenced by the initial silica content in the activator. Changes in the main peak position are mainly attributed to the dissolution of fly ash, resulting in the occurrence of silica and alumina species (depolymerisation). Even though the dissolution of the raw materials occurs, three-dimensional structure formation is not observed, which is in line with the setting and hardening behaviour of pastes presented in the previous sections. The rate of geopolymerisation is, therefore, not controlled by the dissolution process [42]. The shift of the main peak towards higher wavenumbers observed between 24 h and 7 days is attributed to the formation of the gel network. The peak is shifted towards higher wavenumbers for sample with a higher initial availability of monomeric silica which can promote the structure formation [43]. Nevertheless, after longer curing periods (28 days) the position of the main peak becomes stable, regardless of the used activator. Most likely, the influence of silica from activator becomes less prominent at later ages due to a considerably higher contribution of the silica from fly ash in products.

In the presence of cement in the system, a similar behavior in the main peak position can be observed. However, the shift of the main band towards lower wavenumbers during the first hours

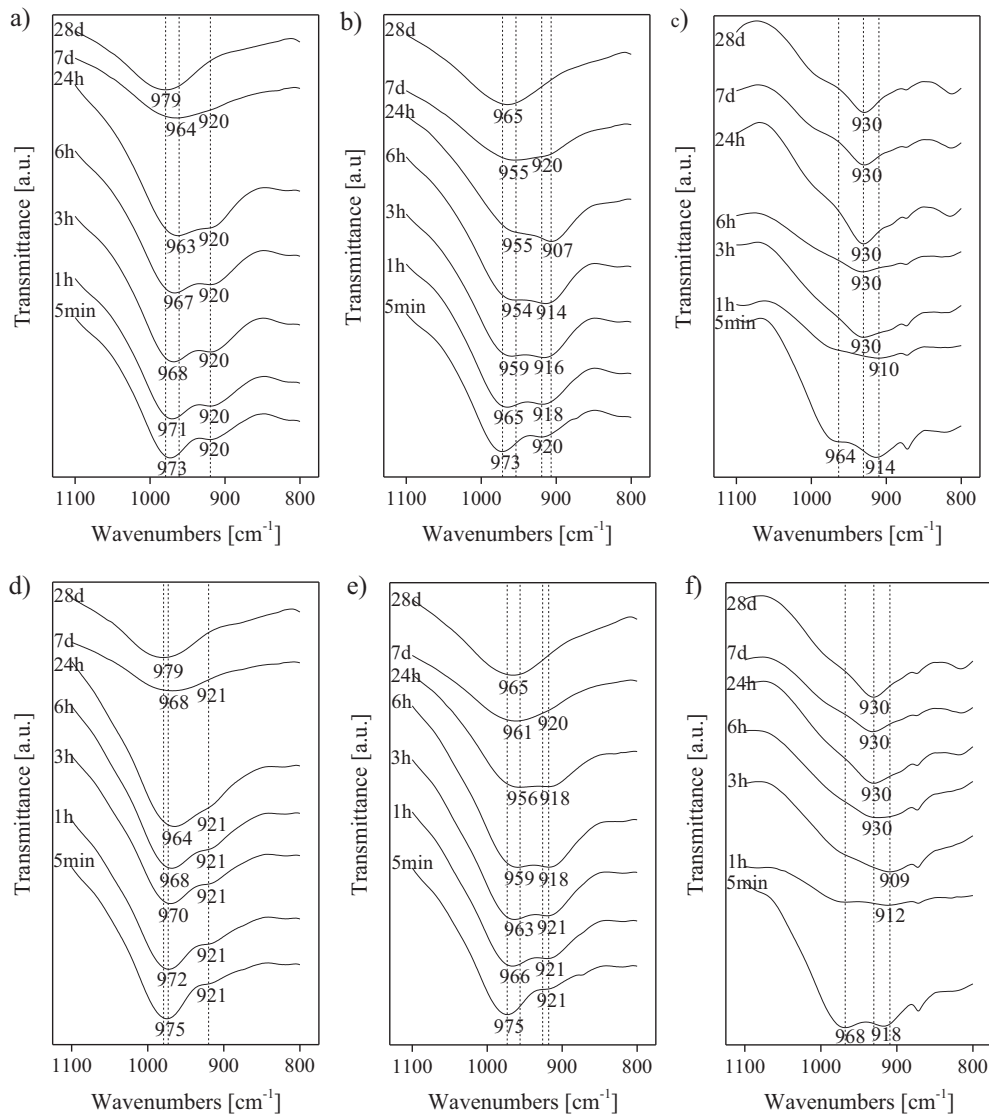


Fig. 4. FTIR spectra of the geopolymeric pastes during activation process a) P0M1.2, b) P10M1.2, c) P100M1.2, d) P0M1.5, e) P10M1.5, f) P100M1.5.

of activation is more significant. The reason for this phenomenon most likely lies in the fact that another band at around 920 cm^{-1} becomes dominant. This can be explained by the presence of cement since this behavior was not seen in sole fly ash based samples. From the study of Taylor [44], Zhang et al. [45] and Zhang et al. [46], it appears that the band located in the region $900\text{--}920\text{ cm}^{-1}$ reflects the stretching of $\text{Si-O}-(\text{M, Fe})$ bond, where M is an alkali metal or an alkali-earth metal, or Si-OH . Therefore, this behavior can indicate the formation of “primary” C-S-H phases in the presented systems, which is in line with the calorimetric measurements (Section 3.2). This conclusion can be further confirmed by analyzing the position of this band in sole cement based samples (Fig. 4c and f). During the first few hours of activation, shifts towards lower wavenumbers (around 910 cm^{-1}) can be observed. Subsequently, after 1 h for sample with a lower initial silica content and after 3 h for sample with a higher initial silica content, a shift towards higher wavenumbers occurs. In both cases, however, during the activation process up to 28 days, spectra are dominated by the peak at around 930 cm^{-1} , originating from unreacted phases, confirming limited reaction of cement in highly alkaline medium. Differences in the rate of C-S-H phase formation depending on the initial silica content in samples based solely on cement are also reflected in composite samples. Changes in the peak position for samples with a lower silica content reflect changes observed during cement activation (C-S-H precipitation) whereas in samples with higher silica dosage the formation of C-S-H-like structures is hindered and the mechanism of activation process is closer to geopolymerization.

3.4. Microstructure

Since the previous methods show that cement addition has significant influences on the structure formation of alkali-activated fly

ash based samples especially during the first day of activation process, SEM images were collected from the representative samples after 24 h of curing (Fig. 5). Comparison between samples based solely on fly ash, with 10 wt% of cement and based solely on cement demonstrates densification of the structure with the increasing cement content (the cracks observed within the samples are believed to be caused by sample preparation, drying procedure or due to irradiating the specimen with an electron beam applied to early age samples). Accelerated hydration of cement in high alkalinity contributes to the substantial increase in the amount of the formed products.

Based on these observations, chemical characterization of the cement alkali activation products in the hybrid systems with 10 wt% of cement was performed on polished samples (see Fig. 6a). Polished sections of the gel surrounding unreacted cement particles were examined with EDS point analysis.

Fig. 6b displays the plot of the Ca/Si atomic ratio against Na/Ca atomic ratio for these gels in hybrid samples activated with sodium silicate solutions with silica modulus M1.2 and M1.5. After 24 h of activation chemical composition of gels formed significantly varies, however, the graphical display of atomic ratios is able to show the range of the chemical composition of main activation products. In order to provide sufficient statistical information, 15 sections were investigated and from each section 8 points were measured, resulting in 120 points (see Fig. 6). All measurements were performed on the cracks-free areas. As expected, a higher silica content from activator contributes to a higher content in the gel formed. Not only Ca/Si atomic ratio is lower in the sample with a higher initial silica content but also Al/Si atomic ratio. The phases exhibit an Al/Si atomic ratio of 0.15 and 0.12 for P10M1.2 and P10M1.5, respectively. This observation strongly suggests that calcium ions dissolved from the cement phases react mainly with silica species initially present in the pore solution whereas alumina is derived from the fly ash dis-

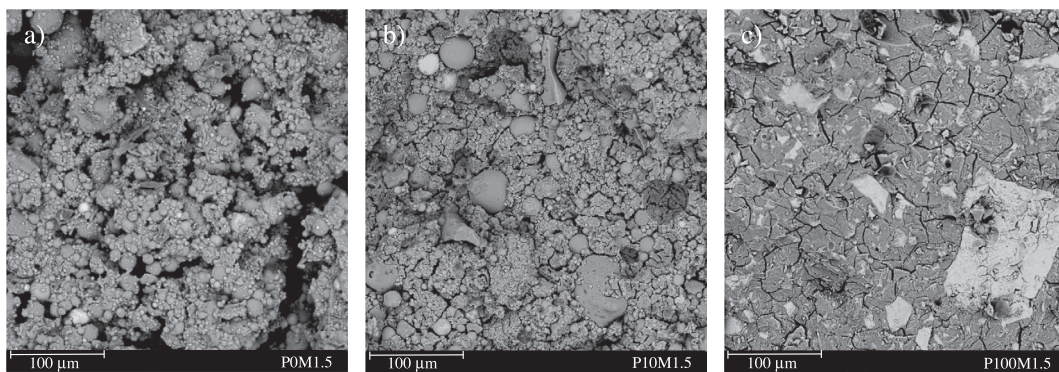


Fig. 5. SEM micrographs of a) P0M1.5; b) P10M1.5 c) P100M1.5 after 24 h of curing.

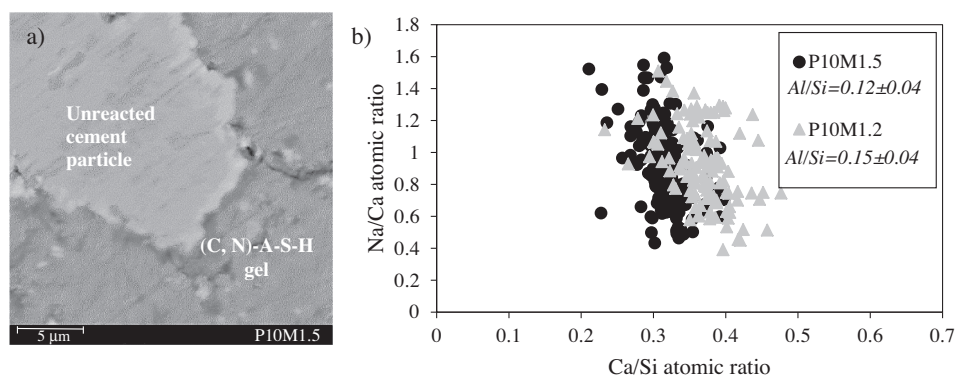


Fig. 6. a) Backscattered electron image of the cement particle surrounded by main activation product after 24 h of curing of the sample P10M1.5; b) Atomic Na/Ca versus Ca/Si ratios of the gel surrounding cement particles in hybrid samples after 24 h of activation.

solution. The observed contribution of alumina in the early age products agrees with the dissolution process described with FTIR study. On the other hand, the Na/Ca atomic ratio remains similar regardless the activator used, which correlates well with the fact that the same amount of Na₂O was incorporated into the systems with both activators. In general, it should be noticed, however, that an intake of alkalis and silica from activator into these calcium rich gels is very high. The Na/Si ratio ranging between 0.25 and 0.45 is substantially higher than the values of around 0.1–0.3 observed for N-A-S-H gels when similar activators were applied to activate fly ash [47,21]. The phases formed are also more abundant in alkalis compared to calcium containing (N,C)-A-S-H gel with intervals of $0.0 \leq \text{CaO/SiO}_2 \leq 0.3$, $0 \leq \text{Na}_2\text{O/Al}_2\text{O}_3 \leq 1.85$ and $0.05 \leq \text{Al}_2\text{O}_3/\text{SiO}_2 \leq 0.43$ [13]. On the one hand, the high silica content in these gels suggests a higher polymerization of silica than in C-S-H phases and therefore a better compatibility with N-A-S-H gels (three-dimensional structure of products should be maintained). On the other hand, however, a high uptake of silica and alkalis limits their availability for N-A-S-H structure formation.

3.5. Phase characterization

Fig. 7 shows the XRD patterns of pastes after 28 days of activation together with the patterns of the used raw materials. The XRD analyses reveal that at ambient conditions mostly amorphous phases are formed during the activation of fly ash, cement and composite samples. The formation of amorphous products, associated with N-A-S-H phase, is reflected in the occurrence of a hump between 20 and 40° which is slightly shifted towards higher values than that in original fly ash [36]. The XRD patterns of alkali activated cement samples show that after 28 days of curing no crystalline portlandite is detected among hydration products. Moreover, the existing alite confirms the limited hydration of cement after accelerated hydration period reported in Section 3.2. Traces of monocarbonate are observed in cement based samples which is in line with the XRD measurements and phase modelling performed by Alahraiche et al. [48] on fly ash-cement composite sample hydrated in the presence of alkalis. As ettringite has been reported to destabilize at high pH [48], this phase is not detected among the products. Sulphate ions are most likely bound within amorphous C-S-H phase, as suggested by Richardson et al. [49] who investigated alkali activated cement with 30 wt% of fly ash substitution.

During the alkali activation mostly amorphous products are formed. These products consist of evaporable water present in large pores (which should be removed during arresting hydration with isopropanol), loosely bound water and tightly bound water absorbed in small pores or existing as condensed hydroxyl group on the surface of the gel [23]. Therefore, in order to examine the gel formation in investigated systems the thermogravimetric analysis was performed (Fig. 8). An initial idea was to distinguish the products with loosely and tightly bound water, which give the peak in the range of 50–200 °C, by applying an isothermal holding at 105 °C for 2 h during the heating process. It appears, however, that regardless of the chemical composition of the starting materials the weight loss peak occurs at the similar temperature in all alkali activated systems. The TG curves show that more water is trapped/bound in the samples based on cement compared to fly ash-based samples after 7 and 28 days of curing. This observation implies a greater ability of C(N)-S-H products to bound water. Analogously, in composite samples more water is bound after 7 days of curing (weight loss observed in the temperature range of 105–250 °C) than in sole fly ash based samples, indicating faster precipitation of products or/and different nature of calcium rich phases which are able to bound water more strongly. After 28 days, however, no substantial difference can be observed between the amount of bound water in neat fly ash samples and hybrid samples when 10 wt% of cement is used. Therefore, it can be concluded that the presence of calcium rich products has harmful effect on the structural development of geopolymers at later ages. This effect is more prominent in the samples with lower initial silica content in the pore solution, where the formation of products with higher C/S was reported, implying the incompatibility of the gels formed. The harmful effect of cement on the later age formation of geopolymeric structure can be caused by high intake of sodium ions into calcium rich products formed at the beginning of activation process, as was shown by EDS point analysis.

Next to the presence of cement in geopolymeric systems, the Na₂O/SiO₂ molar ratio in activator highly influences the binding properties of these materials. A higher amount of water is bound in samples prepared from alkali solution with a higher silicate modulus and a weight loss occurs at slightly higher temperatures, regardless of the presence of cement. Therefore, it can be concluded that more products are formed in these systems during the investigated curing periods or/and the products exhibit higher density trapping a higher amount of water in the structure. This is

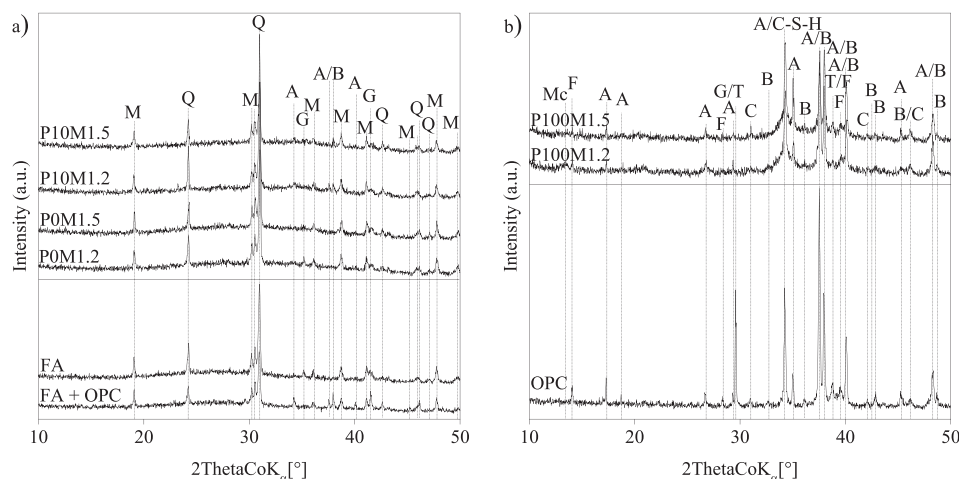


Fig. 7. XRD diffractograms of the raw materials and activated samples a) fly ash and fly ash-cement based pastes, b) cement based pastes after 28 days of curing. Legend: Q – quartz, M – mullite, H – hematite, A – alite, B – belite, T – tricalcium aluminate, F – ferrite, G – gypsum, C – calcite, Mc – monocarbonate, C-S-H – calcium silicate hydrate.

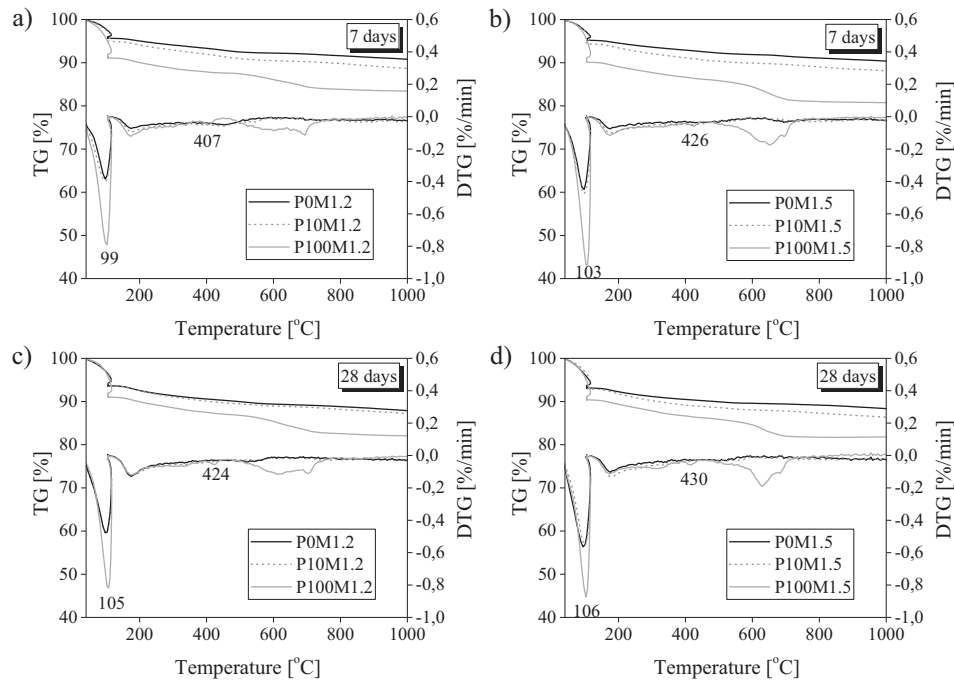


Fig. 8. Mass loss (TG) and derivative mass loss (DTG) curves for alkali activated pastes.

consistent with the higher rate of polymerization observed with the FTIR.

The analyses of cement-based samples also indicate that after 7 days of curing, the hydration of cement is very limited, as the weight loss remains almost the same up to 28 days, whereas the slight shift towards higher temperatures is observed suggesting the higher ordering of products. Interestingly, in cement samples a small amount of portlandite is detected after both 7 and 28 days of hydration, which could not be observed with XRD technique due to detection limits or low crystallinity of portlandite formed. The position of the weight loss peak assigned to portlandite dehydroxylation depends on the activator characteristics and the age of the samples and ranges between 407 and 430 °C. The amount of calcium hydroxide is very small and according to the XRD data it probably exists in poorly crystalline form. Considering that samples were cured and stored under controlled sealed conditions, a significant extent of carbonation is not expected to occur. Therefore, the presence of weight loss peak at temperatures between 500 and 750 °C assigned to calcium carbonates in neat cement samples is mostly derived from the raw material and to a limited extent from carbonation during the experiments [50].

3.6. Mechanical performance

The 7 and 28 days compressive strength of geopolymers and geopolymer composites with Portland cement are presented in Fig. 9. In general, it can be seen that samples with a higher initial silica content exhibit a better mechanical performance at investigated periods, which is in line with the FTIR and thermal analyses. Next to the higher silica content, cement addition has also a positive effect on mechanical performance of the investigated samples. Increasing the amount of cement causes a substantial improvement in compressive strength at the early age. Even a very small amount of cement in the binder (5 wt%) enables a dramatic increase in the 7-d compressive strength, exceeding 200% of the values for samples based solely on fly ash.

Tailby et al. [51] assumed that in alkali-activated hybrid halloysite-cement systems cured at elevated temperatures the

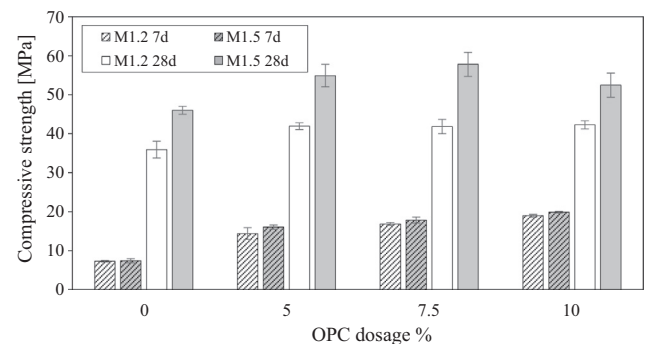


Fig. 9. Compressive strength of geopolymeric pastes after 7 and 28 days of curing.

competition for silicon between C-S-H and geopolymeric products occurs and consequently a too fast formation of geopolymeric structure hinders the cement hydration. From the present study it appears, however, that at ambient conditions formation of calcium-rich phases is favored at the beginning of activation process and, as a consequence, cement highly contributes to the strength development. Nevertheless, after longer curing periods (28 days) mechanical performance of geopolymeric samples is negatively affected by the excess of calcium source. Even though the compressive strength of all the samples with cement addition is higher than the reference, the rate of strength development appears to decrease with an increasing cement content. These observations are consistent with the results reported by Dombrowski et al. [52] who suggested 8% of $\text{Ca}(\text{OH})_2$ addition as an optimal value. It can be therefore concluded that cement addition into alkali activated fly ash-based binder has positive effects on the early age strength development, while the amount has to be determined with caution as otherwise the long-term performance can be expensed. In this study, an optimal amount of 7.5 wt% when the activator solution M1.5 is applied and around 5% with the solution M1.2 was found. Yip et al. [15] suggested that the decrease in compressive strength can be attributed to the local alterations in

Si/Al ratio caused by the leaching of Si and/or Al between calcium rich and calcium deficient products to obtain equilibrium in the system. The present study concludes that cement hydration in high alkalinity is considerably accelerated within the first few hours of curing, whereas after 7 days, the hydration process is strongly inhibited. Moreover, kinetics of the formation of calcium rich phases is higher for samples with a lower silica content initially available in the pore solution. As the lower content of cement was beneficial for the strength development of samples with a lower initial silica content, it can be therefore assumed that too fast precipitation of calcium rich products results in a decrease in mechanical performance of geopolymeric materials, most likely due to less-well interlocked structure of products formed. Moreover, the presence of calcium-rich phases has been found to retard structural development at later ages. Significant influence on geopolymeric structure formation can be attributed to the reduced silica availability from the binder in composites systems (dilution effect) as well as high intake of silica and alkalis into calcium rich phases.

4. Conclusions

This study focuses on the reaction kinetics and phases evolution of alkali-activated fly ash-cement hybrid systems with varying cement content and activator $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio. Characterization of setting behavior, activation heat release, phase development and their interaction, and subsequently evaluation of the influence of these parameters on the mechanical performance were carried out by applying various techniques including Vicat setting, isothermal calorimetry, FTIR, TG, XRD, SEM, EDS and strength tests. Based on the obtained results, the following conclusions are drawn:

- 1) Setting time of alkali activated hybrid fly ash – cement systems is considerably accelerated due to the presence of cement (5–10 wt%) and can be tailored by modifying the cement dosage and activator modulus. Retarding behavior observed with increasing silica content from activator became more remarkable in the hybrid systems.
- 2) Within 24 h of activation process in hybrid systems, the formation of calcium rich gel phases was observed. These phases were characterized by high intake of alkalis and silica. The alkali content of the gel products formed increased with the reduction of silica content of the activator.
- 3) Kinetics of the calcium rich gel formation was found to decrease with a higher silica content that led to prolonged setting times. A higher initial content of silica resulted in the formation of (N,C)-A-S-H gel with lower Ca/Si and Al/Si atomic ratios.
- 4) In alkali activated hybrid fly ash – cement systems with 10 wt% of cement content, only amorphous products were formed up to 28 days of ambient temperature curing. In samples based solely on cement traces of monocarbonate were detected.
- 5) Between 7 and 28 days of activation, harmful impact of calcium rich products on the gel formation was observed. This phenomenon could be caused by the high intake of alkalis and silica of the (N,C)-A-S-H gel since the effect was less pronounced in samples with a higher initial content of silica from activator.
- 6) The cement addition showed beneficial effects on the early age mechanical performance of geopolymers, whereas further strength development was adversely affected. This was caused by impeded three-dimensional structure formation and retarded gel formation in the presence of calcium

rich products. 5 wt% and 7.5 wt% of cement addition were recommended for fly ash activated with sodium silicate solution with silica modulus of M1.2 and M1.5, respectively.

Conflict of Interest

None.

Acknowledgements

The authors would like to acknowledge the financial support by NWO (The Netherlands Organisation for Scientific Research) for funding this research (project no. 12824). Furthermore, the authors wish to express their gratitude to the following sponsors of the Building Materials research group at TU Eindhoven: Rijkswaterstaat Grote Projecten en Onderhoud; Graniet-Import Benelux; Kijlstra Betonmortel; Struyk Verwo; Attero; Enci; Rijkswaterstaat Zee en Delta-District Noord; Van Gansewinkel Minerals; BTE; V.d. Bosch Beton; Selor; GMB; Icopal; BN International; Eltomation, Knauf Gips; Hess AAC Systems; Kronos; Joma; CRH Europe Sustainable Concrete Centre; Cement & Beton Centrum; Heros; Inashco; Keim; Sirius International; Boskalis; NENERGY; Millivision; Sappi and Studio Roex (in chronological order of joining).

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