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Strength Development of Metakaolin-Based Alkali-Activated Cement

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Abstract: Alkali-activated materials, sometimes called geopolymers, can be used as alternative cementitious materials to conventional Portland cement. Currently, there is a significant interest in these materials due to their low CO_2 footprint. The typical applications of alkali-activated materials are within civil engineering; however, potential applications as well cementing material within the oil and gas industry are also receiving emerging interest. This paper presents a systematic study of the compressive strength development from 1 to 28 days for metakaolin-based alkali-activated cement. The results show that the compressive strength is highly dependent upon the initial Si/Al ratio in the mix design, as well as the concentration of the activator solution. Furthermore, due to the relatively low initial reactivity of the metakaolin material used, different types of co-binders were included in the slurry composition to improve early strength development. The two different co-binders tested were another, more reactive metakaolin material and Blast Furnace Slag (GGBFS). It was found that both these co-binders performed as intended, by ensuring early strength development via precipitation of K-A-S-H and C-A-S-H gels, respectively, and also by enabling subsequent strength development due to improved dissolution of the low-reactive metakaolin.

Keywords: alkali-activated materials; geopolymer; metakaolin; well cement; co-binder

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1. Introduction

Portland cement has been used as construction material for nearly two centuries, where the cement is used as a binder material in concrete and mortar. However, the production of Portland cement represents about 6–8% of global anthropogenic CO_2 emissions. Therefore, there is a strong interest in finding alternative binder materials that have a significantly lower CO_2 footprint [1–3]. One potential alternative to Portland cement is alkali-activated materials (AAMs) or "geopolymers", which have already been used as construction material in several applications [2–4].

Alkali-activated materials are completely devoid of Portland cement, resulting in a considerably lower CO_2 footprint, but also having different reaction mechanisms and subsequent strength development. While Portland cement develops strength during a hydration reaction when the cement powder reacts with water and forms a C-S-H gel as the main strength-providing binder phase, the aluminosilicate precursors of AAMs react with an alkaline activator (usually NaOH, KOH, or their silicates) thereby forming other types of strength-providing reaction products. The calcium content of the precursors determines in large part which binder phases are formed, with a low Ca content leads to the formation of N-A-S-H or K-A-S-H phases and a high Ca content leads to the formation of C-A-S-H phases [5,6]. Typical high Ca precursors are Blast Furnace Slag (BFS) and Fly Ash Type C, whereas typical low Ca precursors are metakaolin and Fly Ash Type F. Low-calcium alkali-activated materials are often referred to as "geopolymers". It should be noted that regardless of the Ca content, the precursors of AAMs dissolve into monomeric or small oligomeric Si and Al species in the activator solution before the aluminosilicate binder phases precipitate. Therefore, the reactivity of the precursors (i.e., their dissolution potential) is of considerable importance for the subsequent strength development.

In addition to applications as construction material, Portland cement is also commonly used as a barrier material during cementing operations of wells for oil and gas production, CO_2 storage, and geothermal energy production [7–10]. During well construction, cement is pumped into the annulus outside the steel casing, both to provide support to the steel casing and to ensure zonal isolation in the well. Furthermore, cement is also pumped into wells during plug and abandonment (P&A) operations, to ensure that hydrocarbons and other downhole fluids do not leak into the environment after well abandonment [7,11,12]. There is currently a drive in the research community to find alternative well cementing materials as well, with geopolymers having been suggested as potential candidates [11–13]. Several different types of precursor materials have been used to prepare geopolymer well cements, such as fly ash [14–19], rock waste [20–22], and volcanic ash [23].

Metakaolin as precursor material during alkali activation has so far not been widely studied for well cement applications, which could be due to the relatively large water consumption of the platelike metakaolin particles [24,25], thereby causing potential slurry viscosity and pumpability issues. However, it has recently been shown that metakaolin-based geopolymers can have good potential as well cement during steam injection operations, due to their improved mechanical properties [26], and consequently, there is a need for further studies on the mechanical properties and strength development of these materials. With respect to sustainability, it should be noted that metakaolin is prepared by calcination of excavated kaolinite minerals, and therefore has a higher CO_2 footprint and environmental impact than other, typical AAM precursors such as BFS and fly ash which are waste materials. However, these precursors are waste materials from coal-fired steel production and coal power plants, respectively, and will consequently be of limited availability in future when use of coal is phased out. There will thus be a need to utilize AAM precursors other than BFS and fly ash, for example, metakaolin.

In this study, we prepared metakaolin-based alkali-activated cements with different Si/Al ratios and different activator concentrations, to determine the resulting effects on compressive strength over time. Metakaolin is usually very reactive during alkali activation, but the metakaolin material used in this study had relatively poor initial reactivity. It is however known that minor additions of other, more reactive aluminosilicate precursors that act as a "co-binder" in the slurry can also improve the reactivity and subsequent strength development of a poorly reactive main precursor [27,28]. Consequently, two different co-binders were included in the mix designs, to determine if the use of co-binders can improve the strength development of a poorly reactive metakaolin.

2. Materials and Methods

2.1. Materials

Two different sources of metakaolin (MK) were used in this study, one type provided by Metacaulim do Brasil and the other type provided by Imerys, denoted "MKB" and "MKF", respectively. Table 1 lists the chemical composition of these two metakaolin materials, as provided by their suppliers, as well as some physical properties. Ground Granulated Blast Furnace Slag (GGBFS) was provided by Swecem, and MicroSilica (MS) was provided by Elkem. Table 1 lists the chemical composition of GGBFS and MS, as provided by their suppliers, as well as some physical properties. A potassium silicate solution at a 1.6 molar ratio and 52% dry content was provided by Woellner, and a 12 M KOH solution was provided by Solberg. Distilled water was used to dilute the activator solutions to the selected concentrations.

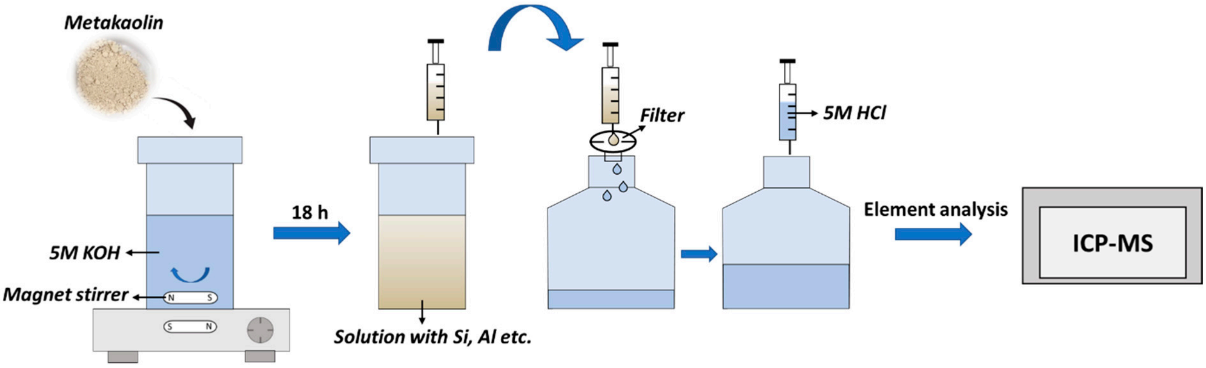
Table 1. Chemical composition and physical properties of metakaolin samples MKB and MKF, as well as Ground Granulated Blast Furnace Slag (GGBFS) and MicroSilica (MS) samples. Chemical composition was provided by the respective suppliers.

	Physical Properties		Main Oxide Composition (%)						
	d50 (µm)	Specific Gravity (g/cm^3)	SiO_2	Al_2O_3	CaO	Fe_2O_3	TiO_2	MgO	K_2O
MKB	25.3	2.6	70.3	23.4	0.1	1.6	1.7	0.1	0.3
MKF	6.29	2.4	51.4	43.6	0.1	-	5	-	-
GGBFS	10.0	2.9	35.8	12.7	33.7	0.2	2.2	12.8	0.8
MS	0.15	0.6	95.5	0.7	0.4	0.3	-	0.5	1.0

2.2. Characterization Techniques

X-ray diffraction analysis (XRD) was performed using a Bruker D8 Advance Eco diffractometer equipped with a Lynxeye detector (Cu-Kα radiation, 40 kV voltage, 25 mA current). The X-ray patterns were obtained in the 2Θ range of 5–90° using a 0.6 mm divergence slit during continuous rotation. Afterwards, the software DIFFRAC.EVA V6.1, implementing the PDF-4+ database from the International Centre for Diffraction Data (ICDD), was employed to identify mineral phases and visualize the data.

The solubility of Si and Al of metakaolin samples at alkaline conditions was determined by performing dissolution tests based on the following procedure [29,30]: 2 g of sample was added to 80 mL of 5 M KOH and stirred for 18 h at room temperature (20 °C). Subsequently, a suitable amount of the resulting solution was filtered and neutralized with 5 M HCl, before being sent for elemental analysis (ICP-MS), which was performed by an external provider (Eurofins). Figure 1 illustrates the solubility test procedure.



(a) Magnetic stirrer process (b) Solution filtration and neutralization (c) Results

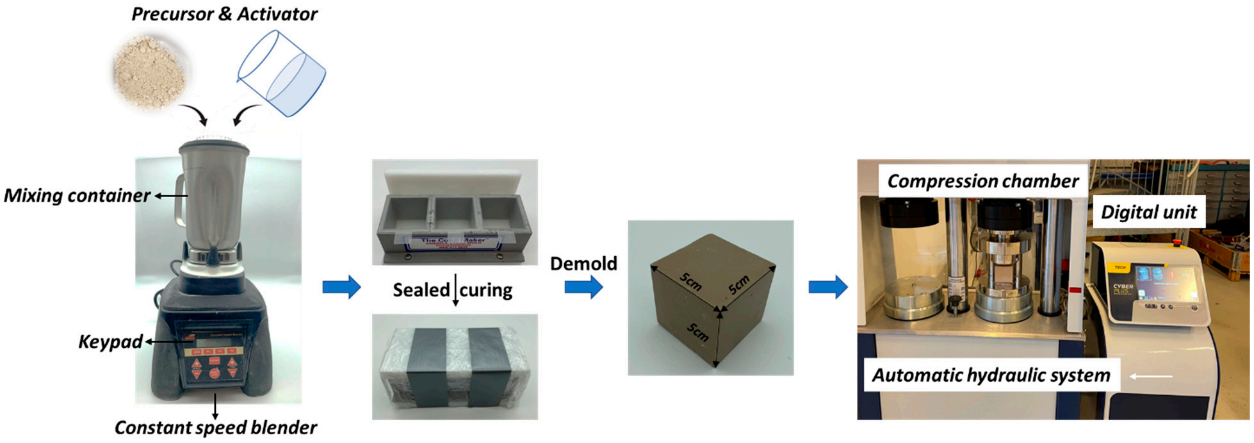
Figure 1. Overview of experimental procedure to determine solubility of Si and Al of metakaolin samples.

Unconfined compressive strength (UCS) was measured with a MATEST 300 kN compression machine, with a loading rate of 4000 psi/min according to API guidelines [31]. Particle size distributions (PSDs) were measured using a Mastersizer 3000 instrument provided by Malvern Panalytical, Norway, and rheological properties such as shear stress and shear rate were measured using an OFITE model 900 viscometer. The setting time of the cement slurries was determined by the Vicat method [32].

2.3. Sample Preparation

Cement slurries were prepared by mixing suitable amounts of the solid precursors with liquid activators, where metakaolin type MKB was used as the main precursor in all experiments, while MKF and GGBFS were also investigated as co-binders. Samples consisting of both MKB and MKF were denoted as "Bx Fy", where x and y is the percentage of MKB and MKF, respectively. Several samples of varying Si/Al ratios were prepared, where both potassium silicate and MicroSilica (MS) were used to adjust the Si/Al ratio. MicroSilica consists of amorphous silica particles of sub-micron sizes and are thus easily dissolvable. Estimations of the Si/Al ratio in the slurry were based upon the assumption that only the metakaolin part of the MKB samples dissolved, and that the quartz part remained inert. Increasing Si amounts in the slurry were obtained by increasing the ratio of potassium silicate/KOH in the activator, as well as the addition of MicroSilica in increasing amounts. Furthermore, several samples of varying KOH concentrations were prepared, where the increased KOH concentration was obtained by adjusting the amount of 12 M KOH vs. distilled water in the mixture. All samples were prepared with a solid/water ratio of 0.55.

The cement slurries were mixed in an OFITE model 25 constant speed blender according to the mixing procedure described in API 10B-2 [31], where the solid precursors were added to the liquid activator solution for 15 s at 4000 rpm, and the slurry was subsequently mixed at 12,000 rpm for 35 s. After mixing, the slurry was poured into 5 cm cubic molds, and cured in sealed conditions at room temperature (20 °C). It should be noted that 20 °C is a quite low temperature for most downhole applications, but this temperature was selected as it is relevant for tophole well sections. Room temperature is also relevant for civil engineering applications. The samples were de-molded after 1 day and the cubes were placed in sealed plastic bags and left to cure until designated time for UCS testing. Two replicates were tested for each sample, where the reported results are the average of these two measurements. Figure 2 illustrates the sample preparation procedure.



(a) Mixing process **(b) Curing process** **(c) Compression strength test**

Figure 2. Overview of experimental procedure during sample preparation and subsequent UCS testing.

3. Results and Discussion

3.1. Metakaolin Properties

The XRD patterns of the metakaolin samples MKB and MKF are shown in Figure 3, and it can be seen from the figure that MKB contains considerably more crystalline material than MKF, which is mostly quartz. This was also apparent in the XRF results with a relatively high SiO_2 amount and low Al_2O_3 amount for MKB (Table 1), which is most likely caused by the substantial amount of quartz in the sample. Furthermore, the XRD pattern of MKF contained a much more prominent amorphous "hump" at around 20–30° compared to MKB, which further indicates the substantial amorphous content of MKF. Figure 4 shows the cumulative particle size distributions (PSDs) of MKB and MKF, and it is seen that MKF consists of much finer particles than MKB, with d50 values of 6.29 µm and 25.5 µm, respectively.

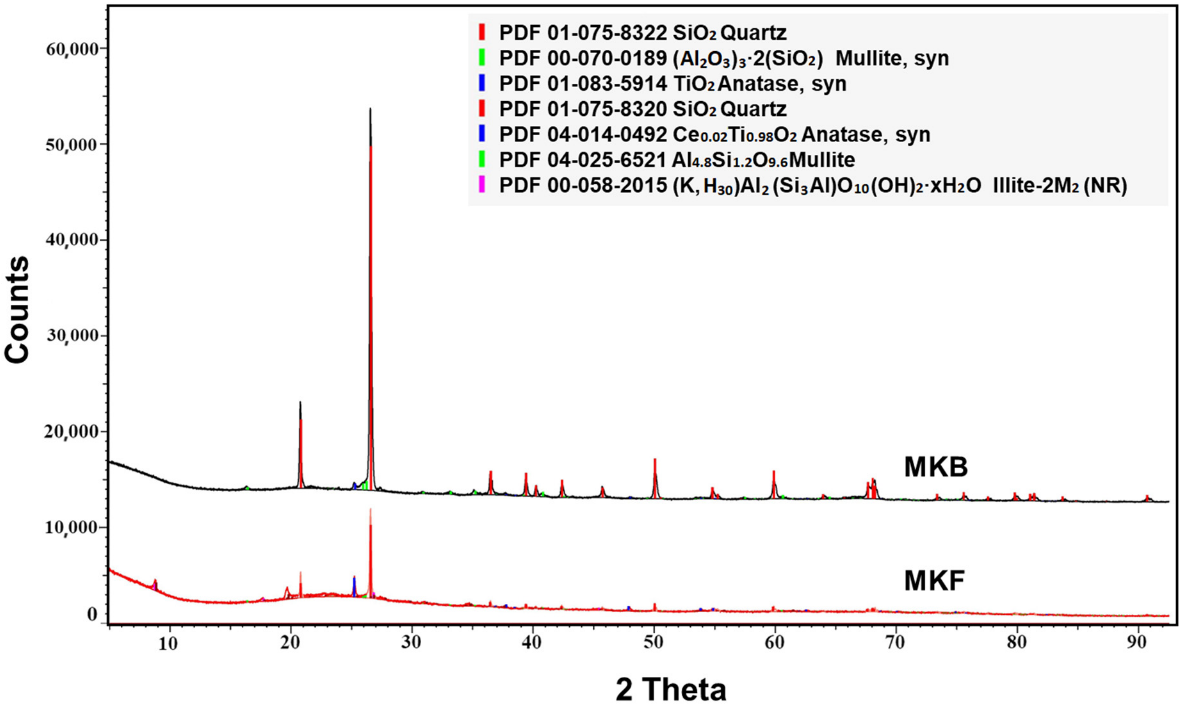


Figure 3. XRD patterns of metakaolin samples MKB and MKF.

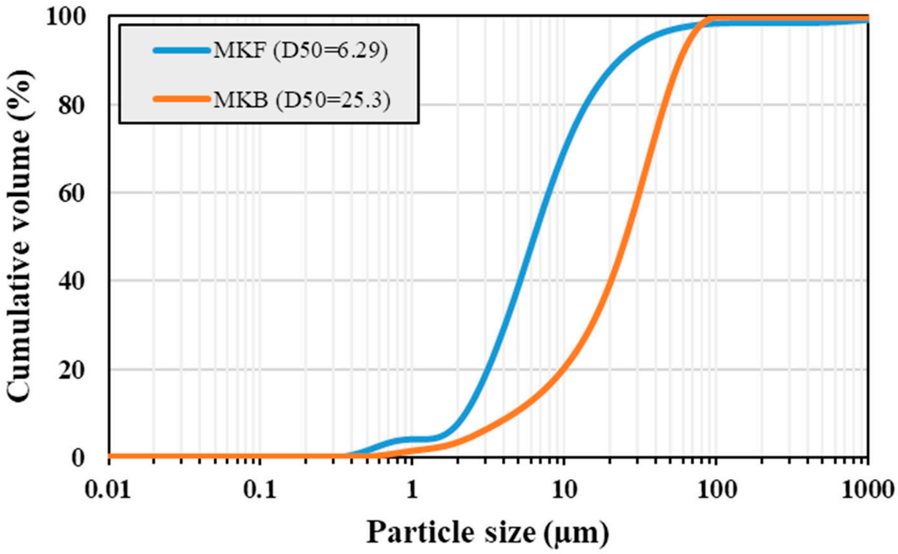


Figure 4. Cumulative particle size distributions (PSDs) of metakaolin samples MKB and MKF.

The Si and Al solubility results are shown in Figure 5. It can be seen that the Al solubility of MKB was significantly lower compared to MKF, which could be a result of its large quartz content and the lower kaolinite content. Furthermore, the Si solubility was higher for MKB than MKF, which indicates that some of the quartz in MKB dissolves as well. As a crystalline material, quartz is not easily dissolvable. But, it has been found that quartz may partly dissolve at high hydroxide concentrations [33], which potentially explains the Si solubility numbers for MKB as this sample contains considerable amounts of quartz.

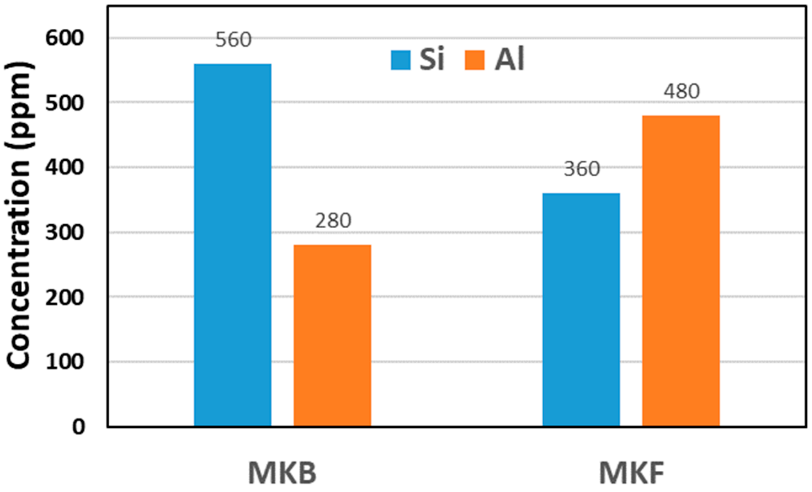


Figure 5. Solubility of Si and Al for metakaolin samples MKB and MKF after 18 h dissolution in 5 M KOH.

3.2. Slurry Properties and Setting Time

During the initial experiments, MKB was found to have a low reactivity towards alkali activation, i.e., the samples did not set within a reasonable time at room temperature when activators were added to MKB as the sole precursor. This low reactivity could be due to the relatively low Al solubility (Figure 5), as sufficient amounts of dissolved Al and Si are required for geopolymerization reactions to occur [5,34]. It has been found for other low-reactive aluminosilicate precursors, such as mine tailings, that the reactivity can be improved by the addition of minor amounts of another, more reactive aluminosilicate precursor that acts as a "co-binder" in the slurry [27,28]. In other words, the co-binder helps to start the geopolymerization reaction, thereby enabling the low-reactive precursor to react as well. Consequently, another metakaolin sample (MKF) was included in the mixture as a co-binder to ensure the proper setting of the cement slurry. The MKF sample was expected to be considerably more reactive than MKB, due to its lower particle size (Figure 4) and higher Al solubility (Figure 5).

Figure 6 shows the setting times of the metakaolin-based cement samples with varying amounts of MKF as a co-binder, and where the KOH concentration was 6.5 M. While it was observed that neat MKB samples set after about a week, the setting time decreased significantly with increasing amounts of MKF as a co-binder. Indeed, the addition of at least 6% MKF was needed to ensure a setting time below 24 h, which is required in order to ensure proper cement placement [7]. However, although the addition of MKF led to a shorter setting time, the fineness of the MKF particles (Figure 4) also generated a considerable increase in slurry viscosity. Figure 7 shows the rheology flow curves (shear rate vs. shear stress) for MKB-based slurries with varying amounts of MKF, and where the KOH concentration was 6.5 M. (Regarding the shear stress values in Figure 7, it should be noted that the viscometer had an upper, inherent limitation of 170 Pa, and therefore, all data points with actual shear stress values above this limit were discarded).

It is beyond the scope of the present paper to perform a thorough rheological analysis of these slurries; however, a simplified, qualitative assessment can be performed. From the shapes of the flow curves, it can be assumed that the slurries follow a Bingham rheology model, where the flow curve is a straight line and the intersection between the flow curve and the y-axis determines the yield stress of the slurry [7]. Consequently, the viscosity of the slurry is determined by slope of the flow curve, where steeper slopes mean higher viscosity. Therefore, it can be seen from Figure 7 that increasing amounts of MKF in the slurry led to steeper curves and thereby a higher viscosity, which may result in slurry pumpability problems. Nonetheless, at 10% MKF and below, the viscosity was at its lowest for this mix design. Therefore, combined with its sufficiently low setting time (Figure 6), 10% MKF was added as a co-binder in the subsequent strength development tests.

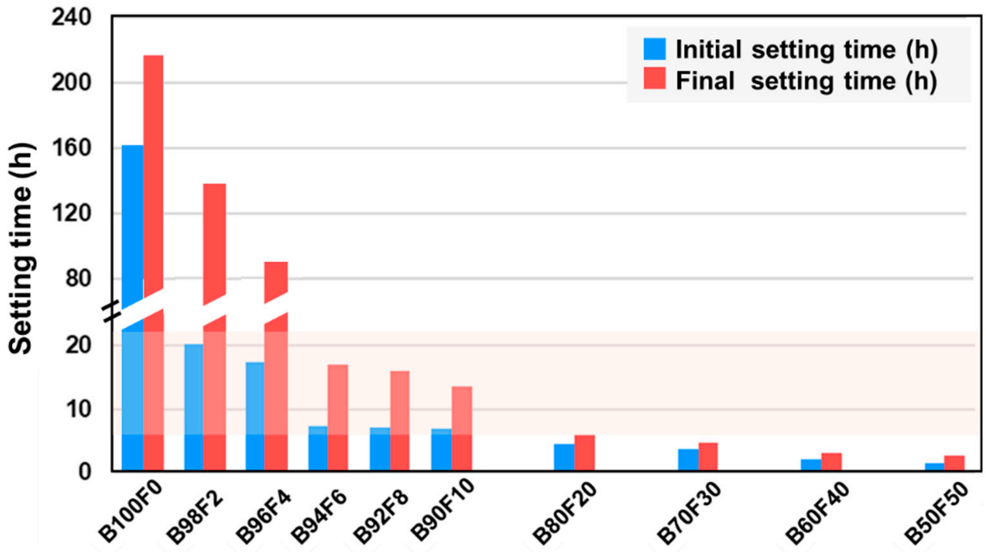


Figure 6. Setting time of MKB-based cement samples with varying amounts of MKF as co-binder.

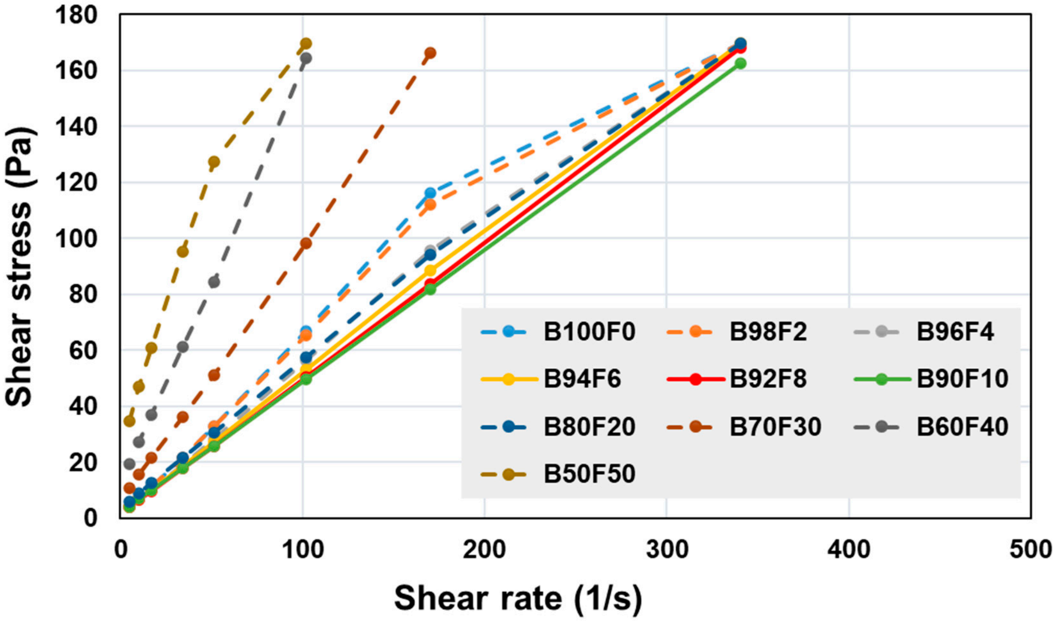


Figure 7. Rheology flow curves for MKB-based slurries with varying amounts of MKF as co-binder.

3.3. Strength Development with MKF as Co-Binder

Strength development is perhaps the most important property of cementitious materials, both for well cementing applications and within civil engineering. For geopolymer cements, the strength development of the aluminosilicate gel binder is dependent upon the Si/Al ratio in the mixture [35–37], where a Si/Al ratio of about 2 is optimal with respect to the obtained compressive strength. As noted above, all samples were based upon MKB as the main precursor, with MKF as a co-binder. The intention of using the more reactive MKF as the co-binder was that it would dissolve quickly and react with the activator to form an initial K-A-S-H gel in the slurry, thereby ensuring setting and sufficient early strength. Furthermore, this initially precipitated K-A-S-H gel should act as nucleation sites for subsequent K-A-S-H gel formation when the less reactive MKB precursor also dissolves. It should be noted that it was not verified experimentally in this study that the precipitated binder phase was indeed K-A-S-H, but due to the low Ca content of the MK precursors this is a credible assumption.

Figure 8 shows the obtained compressive strength after 1, 7, and 28 days curing time for the metakaolin-based cement samples with 10% MKF (B90F10) and varying Si/Al ratios in the mix design (the KOH concentration was 6.5 M). It can be seen from the figure that although the early strength (1 day) was relatively low, there was a significant increase in strength from 1 day to 7 days, and also from 7 days to 28 days for most of the samples. The early strength is probably caused by K-A-S-H gel precipitation from the co-binder MKF, whereas the delayed strength increase strongly indicates that MKB also reacted and participated in the strength development. For example, for the sample with a Si/Al ratio of 1.4, there was an observed strength increase from about 8 MPa at 7 days to about 17 MPa at 28 days, which is more than a doubling of compressive strength. Such a significant increase strongly indicates that the low reactive MKB has dissolved and been successfully alkali-activated, and that the initial K-A-S-H gel from the MKF acts as nucleation sites for the subsequent geopolymerization of the less reactive MKB precursor.

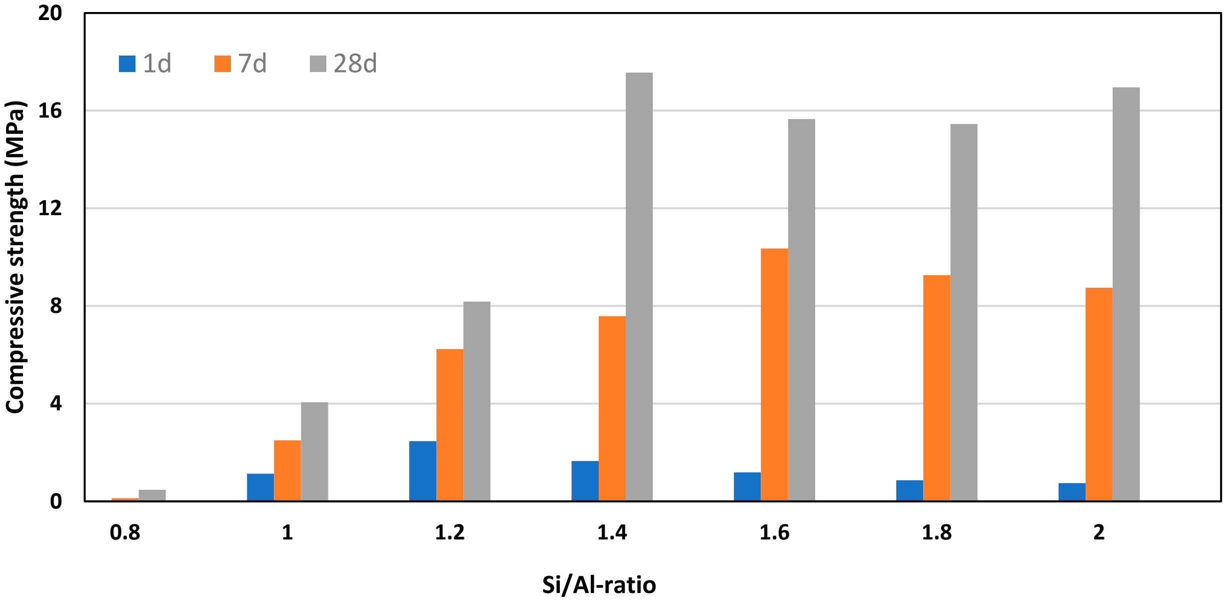


Figure 8. Compressive strength of MKB-based cement samples with 10% MKF at varying Si/Al ratios.

Moreover, the measured compressive strengths were significantly dependent upon the Si/Al ratio in the slurry. The highest strengths are obtained at Si/Al ratios of 1.4 and above, which is considerably lower than the predicted optimum of 2. However, it should be noted that the calculated Si/Al ratios of the mixtures were based upon the assumption that only the kaolinite parts of the metakaolin samples dissolved, and that the quartz parts remained inert. However, the Si solubility results for MKB (Figure 5) indicate that this assumption is at least partly incorrect. It is likely that the high quartz content in MKB dissolves at least partially over time, thereby increasing the actual Si/Al ratio in the slurry above the simplified, calculated ratios. The actual Si/Al ratio of the samples may therefore be closer to 2 than their denoted values, which would potentially explain the high compressive strengths found for the samples with Si/Al ratios below 2.

In addition to the Si/Al ratio, the activator concentration is also important in influencing the strength development of aluminosilicate cements [6,34]. Figure 9 shows the obtained compressive strength after 1, 7, and 28 days curing time for B90F10 cement samples with varying KOH concentrations and Si/Al ratios of both 1.2 and 1.6. The resulting compressive strength was heavily dependent upon the KOH concentration of the activator, where concentrations above 5–6 M led to lower compressive strengths, possibly due to an increased solubility of the K-A-S-H gel.

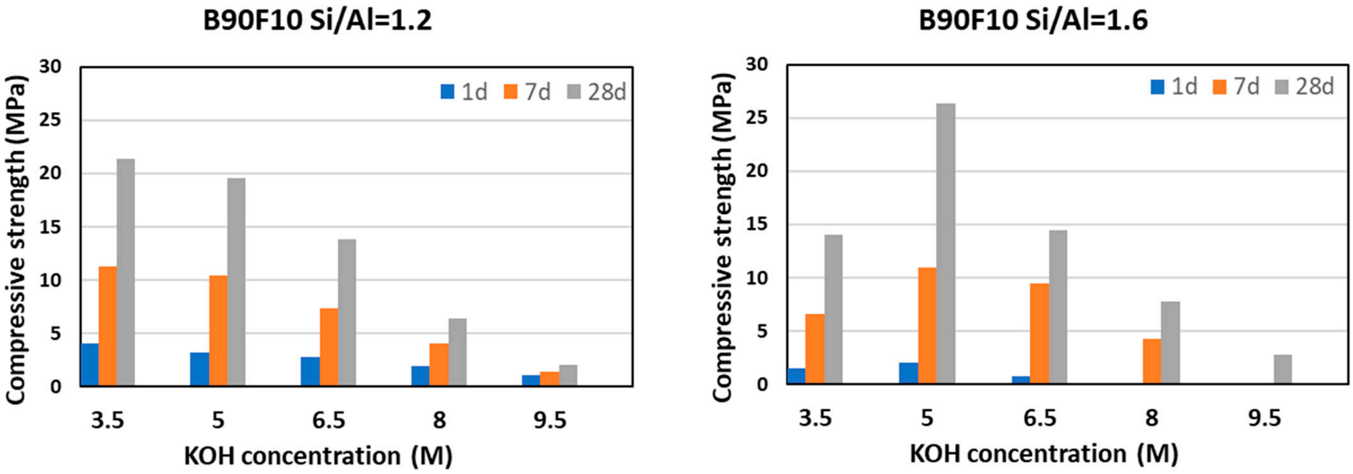


Figure 9. Compressive strength of MKB-based cement samples with 10% MKF and varying KOH concentrations. Si/Al ratio = 1.2 (**left**) and Si/Al ratio = 1.6 (**right**) in the initial mix design.

Therefore, from these findings, it can be concluded that the obtained compressive strength is dependent upon both the Si/Al ratio and the KOH concentration, which leaves considerable room for slurry composition optimization to achieve the targeted strength.

3.4. Strength Development with BFS as Co-Binder

For comparison, some samples were also prepared with 10% GGBFS as a co-binder instead of MKF using otherwise the exact same slurry compositions. Several studies with low-reactive fly ash as a precursor during alkali activation have shown that the addition of increasing amounts of BFS as a co-binder can both decrease setting time and increase compressive strength [38–40]. BFS is a high-calcium aluminosilicate precursor that forms a C-A-S-H gel during alkali activation [5,6], and it has been shown that this initial C-A-S-H gel can act as nucleation sites for subsequent N-A-S-H gel formation [39,40]. Consequently, BFS should function as a co-binder for the low-reactive MKB as well.

Figure 10 shows the obtained compressive strength after 1, 7, and 28 days curing time for MKB-based cement samples with 10% GGBFS of varying KOH concentrations and Si/Al ratios of 1.2 and 1.6. The same significant strength increases from 1 day to 7 days to 28 days curing time was seen as that observed when MKF was used as the co-binder (Figures 8 and 9). Consequently, GGBFS also acted well as a co-binder providing some early strength within 1 day, probably due to C-A-S-H gel formation, which led to significant subsequent strength increases due to potential K-A-S-H gel formation by the later MKB dissolution. It should be noted that it was not verified experimentally in this study that this precipitated initial binder phase was indeed C-A-S-H, but due to the high Ca content of the BFS precursors, this is a credible assumption.

Moreover, although the highest obtained strength with GGBFS as a co-binder was similar to what was observed with MKF as a co-binder, a general trend of somewhat higher compressive strengths at 28 days with BFS as the co-binder was seen for most of the samples. This slightly increased strength may be caused by the presence of Ca^{2+} ions in the slurry, as it has been shown that Ca^{2+} ions in solution can improve the dissolution of quartz [33], thereby increasing the amount of dissolved Si from MKB that can contribute to the C-A-S-H or K-A-S-H formation. Consequently, the addition of BFS as a co-binder resulted in both early strength development and increased later strength development.

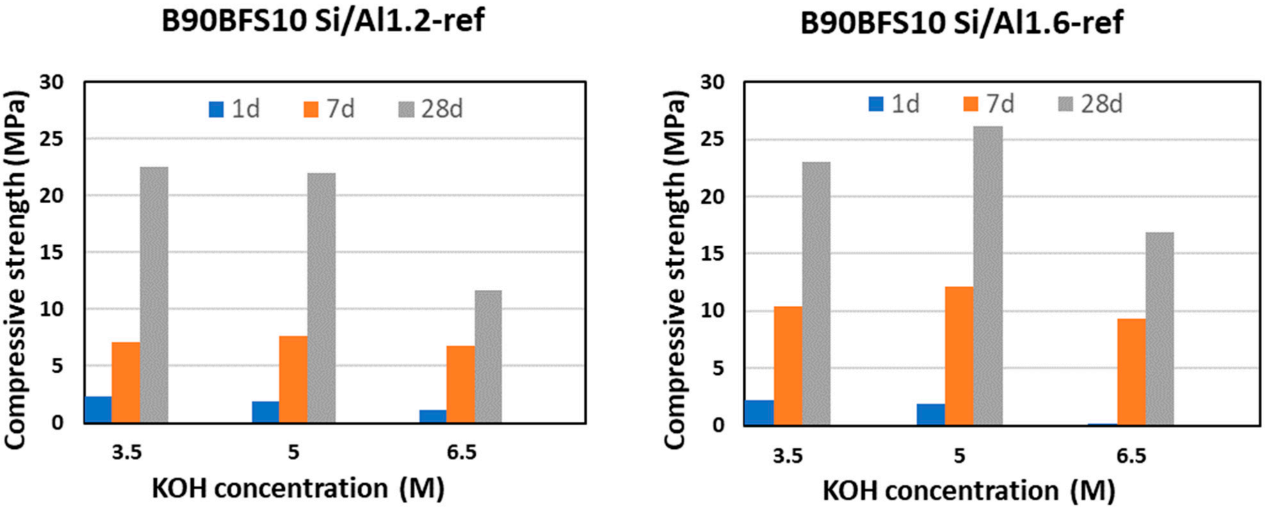


Figure 10. Compressive strength of MKB-based cement samples with 10% GGBFS with varying KOH concentrations. Si/Al ratio = 1.2 (**left**) and Si/Al ratio = 1.6 (**right**) in the initial mix design.

4. Conclusions

Metakaolin is a commonly used precursor for alkali-activated cements due to its amorphous nature and high reactivity. In this study, however, a metakaolin sample of relatively poor reactivity was used as the main precursor, and there was a need to use more reactive co-binders to improve the final reactivity and resulting strength development.

The following conclusions can be drawn:

- The compressive strength of metakaolin-based geopolymer cement depends upon both the Si/Al ratio of the mix design as well as the activator concentration. By varying both of these parameters in a systematic way, it would be possible to optimize the obtained strength.
- When an initially low reactive metakaolin material is used as precursor, the use of co-binders such as a more reactive metakaolin and BFS should be added to the mix design.
- The co-binders ensure early strength development via precipitation of K-A-S-H and C-A-S-H gels, and also by enabling subsequent strength development due to improved dissolution of the low-reactive metakaolin. Significant increases in compressive strength, in fact, a doubling in some cases, were observed from 7 days to 28 days of curing, which indicated that the poorly reactive metakaolin did dissolve and contribute to the final strength.
- Similar strength development trends were found for both co-binders, but overall, somewhat higher strengths were observed for BFS as a co-binder than metakaolin.

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Conflicts of Interest: Baowen Lou and Torbjørn Vrålstad were employed by the company Saferock AS. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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