Alkali-Activated Metakaolin and Fly Ash as Unfired Ceramic Bonding Systems

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Abstract: Metakaolin (MK) prepared by the calcination of kaolin at 550 °C and fly ash (FA) from the combustion of black coal in a granulating boiler were used to prepare unfired ceramic bonding systems via the alkali activation process. A long-term stability of the mechanical properties of the prepared samples similar to the unfired ceramic systems was observed. The optimal metakaolin and fly ash ratio, the type of the activator (NaOH or water glass) and its concentration were evaluated after the hydration in: a) laboratory conditions; b) hydration box; and c) under the hydrothermal activation. Raw materials and the samples prepared by alkali activation process were characterized by XRD, XRF, TG/DTA, and FTIR methods. The mechanical properties of the prepared samples were tested using a compressive strength test after 2, 28 and 56 days of hydration. The compressive strengths of 16 and 24 MPa after 28 days of hydration were reached for FA samples activated with water glass. The alkali activation of MK was successful in the NaOH solution of the molar concentration above 5 M. The compressive strength values of metakaolin, activated hydrothermally and hydrated at laboratory conditions, reached 11.2 and 5.5 MPa, respectively, for 5 M activator of NaOH.

Keywords: metakaolin; fly ash; alkali activation; binder; hydration process

1. Introduction

With increasing demand, research activities in building and ceramic materials are being focused on the development of new environmentally friendly materials. These materials are also called “eco-friendly materials”, since the priority the saving of primary natural resources. The area of alkali-activated materials (AAMs), geopolymers, zeolites and waste has been a long-term focus of many researchers, who are looking to find the materials that are both environmentally friendly and low-cost [1].

AAMs have the properties similar to the ceramic materials. Their advantage is that lower temperature is necessary during their preparation in comparison to the traditional fired ceramics. AAMs are based on the activation of the materials with latent hydraulic properties (typically the materials with a high content of amorphous phase) by suitable activators. The resulting product of the alkali activation process is the system in which the bonds between the chemical species are not the result of the high temperatures typical for the preparation of fired ceramics and with respect to this fact they are called unfired ceramic bonding systems. If the pH of the alkali-activated mixture is high, the amorphous structures based on aluminosilicate (A–S) components are disrupted and new amorphous phases are formed. After heating for a long time, or simply in the course of time, their structure turns to crystalline [2]. The most frequently used raw materials with latent hydraulic properties are
either natural (andalusite, illite, kaolin clay, volcanic ash, risk husk, red mud) or synthetic (metakaolin, slag, fly ash or other industry residues) [3–5]. A comprehensive review of the alkali activation (AA) processes is provided in the article published by Chao et al. [6]. The most famous group of AAMs are the geopolymers introduced by Davidovits [7]. Geopolymers are formed by the activation of Al–Si raw materials with alkaline solutions of different concentrations. Theoretically, materials containing Si and Al can be AA by solutions consisting of the Na+ or K+ cations. The formed geopolymer’s structure depends on many factors, for example on the temperature, where: (1) amorphous structures are produced at temperatures of up to 90 °C or (2) crystalline structures are produced at higher temperatures, forming zeolite crystalline phases [8,9]. Roy [10] proposed the sub-division of AA binding systems into two Me2O–MeO–Me2O3–SiO2–H2O and Me2O–Me2O3–SiO2–H2O groups, where Me is alkaline metal. Palomo et al. [11] and Davidovits [12] defined the AA binding systems based on the presence of: (i) blast furnace slag, which the AA process leads to the origination of C–S–H phase as the main reaction product and (ii) the metakaolin or fly ash which the AA process leads to the formation of polymers based mainly on the zeolite structures as the main reaction products. Differences between the hydration process of AA systems and the hydration of Portland clinker are reflected in the different final reaction products and their properties. The hydration of Portland cement in the water environment results in the formation of C–S–H gels and Ca(OH)2. The alkali activation of granulated blast furnace slag (GBFS) belonging to the AAM group forms also primarily C–S–H gels and small quantities of zeolitic phases, but the formation of Ca(OH)2 is significantly suppressed. Products from the AAs of metakaolin and fly ash contain mainly zeolitic phases (Na, Kn=[(Si–O)2–Al–O]n·wH2O). In general, calcined clay minerals react better than pristine clay minerals and the calcination process is important for the production of highly reactive pozzolanic materials [13–16].

Metakaolin is widely used in the industry. It can be used especially in the construction industry as a filler in plasters, stucco and concrete mixtures, fireproof coatings, it is used in the production of paints or refractory materials. Several works dealing with the metakaolin AA process can be found, for example, Rakhimova et al. published the comprehensive review about the products of metakaolin alkali activation and their properties [17], similarly Rashad [18] provided the review regarding to alkali-activated metakaolin covering the hydration, the effect of the curing conditions and other important topics. Great emphasis is placed on the temperature regime of kaolinite to metakaolin transformation as evident for example from the paper published by Gasparini et al. [19]. The heat treatment process can be intensified by microwave heating as shown, for example, by Youssef et al. [20]. Most of the works do not mention the need for a controlled atmosphere of clay heat treatment. The patent “Treatment of metakaolin” [21] discloses the secondary calcination of metakaolin in a reducing atmosphere in order to change the color of the products. The work [22] deals with the acid and alkaline activation of metakaolin. The resulting material can be used in the field of alternative pigments, as an adsorbent or catalyst support. A special application of metakaolin is their alkaline activation, which uses its latent hydraulicity.

The process of the kaolinite dehydroxylation depends on several parameters such as the kaolinite structure, granulometry and conditions during the thermal treatment. For example, Varga [23] mentioned the temperature of 420 °C as the initial temperature of kaolinite dehydroxylation during the isothermal firing conditions. Derkowski et al. [24] studied the weight changes of kaolinite using thermogravimetry and reported the temperatures for a maximum rate of dehydroxylation as 492 and 512 °C. Kaolinite thermally treated in the temperature range of 550–800 °C is transformed into a metakaolin (Al2O3·2SiO2), according to the following scheme: Al2O3·2SiO2·2H2O → Al2O3·2SiO2 + 2H2O [25]. The continuation of the metakaolin calcination to 925 °C leads to its transformation to the silicon–spinel phase, and further calcination leads to the mullite formation [26]. If metakaolin is alkali activated without the additives, the main hydration products of its AA process are zeolites with the ratio Si/Al = 1. The formation of the hydration products of AA metakaolin can be influenced by the increasing of the Si/Al ratio which can be achieved with the addition of
the different forms of silica [27,28]. The alkali activator used for the AA process is usually liquid in a form of concentrated alkali solutions and concentrated solutions of NaOH, KOH, Na₂SiO₃ or K₂SiO₃ are the most often used activators for the AA process. The authors [29,30] studied the effect of the type of hydroxide activator on the activation of A–S materials and found that A–S materials have a higher dissolution ratio in NaOH than in KOH. The reaction mechanism of the alkali activation of A–S materials involves the dissolution of Si and Al ions resulting in the formation of Si(OH)₄ units and its oligomers [31]. The dissolution of metakaolin is activated with NaOH, KOH or Ca(OH)₂ solutions, and also depends on other parameters such as temperature, pH, composition and the solid-to-liquid (s/L) ratio. Several researchers studied the curing process at different temperatures applied to facilitate the geopolymerization process [32,33].

Next to widely studied metakaolin for AA processes, the fly ash represents raw material with good latent hydraulic properties resulting in high reactivity during AA processes. Fly ash reactivity depends on the content of the glass phase. The grinding (mechanical activation) of fly ash particles leads to the decrease in particle size and changes in morphology, whereas both of these parameters are important for a higher dissolution rate of the fly ash particles in its alkali-activated systems. It is known that the mechanical activation of fly ash leads to an increase in the compressive strength of the geopolymers obtained by AA process compared to those values obtained for non-activated fly ash-based geopolymers. The compressive strength of the geopolymers depends on the strength of the formed gel phase, the amount of undissolved Al–Si particles, etc. The mechanical activation of fly ash is also a suitable procedure to achieve the curing of forming geopolymers at ambient temperatures [34–37]. The hydrothermal treatment of fly ash leads to the formation of zeolite phases as reported, for example, by Kotova et al. [38].

The unfired ceramic bonding systems as the products of the alkali activation of the latent hydraulic materials represent a promising alternative to the fired ceramics and the materials based on Portland cement. In comparison with both, fired ceramics and Portland cement-based products, the production of the alkali-activated materials is characterized by lower energy requirements. It is generally known that the fly ash can be directly alkali activated, the production of metakaolin requires temperature below 800 °C, while the production of fired ceramics and Portland cement needs the temperatures above 1000 °C. The aim of this research was to evaluate the optimum conditions for the AA of metakaolin, fly ash and their mixtures. For this purpose, the effect of the type and amount of the activator on the development of the compressive strength of the alkali-activated metakaolin and fly ash was tested in the initial stage of the experiments. The effect of the conditions during the hydration (humidity and temperature) and the possible synergy effect of both metakaolin and fly ash in their mixtures on the strength parameters were also studied. The stability of the products of the AA against the water environment was evaluated.

2. Materials and Methods

2.1. Materials

Kaolin (KA) (Sedlec, Czech Republic) was used as received. Metakaolin (MK) was prepared by the 2 h-long calcination of KA at 550 °C. Fly ash (FA) was the product of the combustion of hard coal (Ostrava–Karviná coal district) and collected in a granulation boiler. The aqueous solution of sodium silicate (WG) was obtained from Kittfort Praha, s.r.o. (Czech Republic). The chemical composition of WG was defined by the content of SiO₂ (26.88 wt.%) and Na₂O (8.15 wt.%), and the density of WG was 1355 kg·m⁻³. Sodium hydroxide (NaOH) of analytical grade purity was obtained from Penta s.r.o., Prague, Czech Republic. The solutions of NaOH with different molar concentrations (1, 2, 3 to 8 and 16 M) were prepared.

2.2. Sample Preparation

The experimental section was conveniently sub-divided into 3 parts based on the prepared samples and the process of their hydration.
2.2.1. Part I

In this part, MK and FA were activated using aqueous solutions of WG and NaOH. The hydration process was conducted at laboratory temperature in the hydration box. The following samples were prepared:

- 100 wt.% MK + WG (dosage Na₂O 4.5 wt.% against the amount of metakaolin) sample labelled as MK_WG4.5;
- 100 wt.% MK + NaOH with molar concentrations of 1, 2, 3, 4, 5, 6, 7, 8 and 16 M samples labelled as MK_NX, where X represents the NaOH molar concentration;
- 100 wt.% FA + WG (dosage Na₂O 4.5 wt.% against the amount of fly ash) sample labelled as FA_WG4.5;
- 100 wt.% FA + NaOH with molar concentrations of 2, 5, 8 and 16 M samples labelled as FA_NX, where X represents the NaOH molar concentration.

Compressive strength of the samples was determined after 2 and 28 days of the given hydration procedure and after the next 28 days of storage in a water environment.

2.2.2. Part II

In this part, MK was activated using aqueous solutions of NaOH and the hydration process of alkali-activated MK was conducted under the hydrothermal conditions (65 and 85 °C). The following samples were prepared:

- 100 wt.% MK + NaOH with molar concentration of 5 and 8 M samples labelled as (MK_N5, MK_N8).

The compressive strength of the samples was determined after 2 and 28 days of the given hydration procedure and after the next 28 days of storage in a water environment.

2.2.3. Part III

In this part, the mixtures of MK + FA were activated using aqueous solutions of WG and NaOH and the hydration process of the activated mixtures was simply conducted at laboratory conditions outside the hydration box. The following samples were prepared:

- 5, 10, 30 and 50 wt.% FA + 95, 90, 70 and 50 wt.% MK + WG (dosage Na₂O 4.5 wt.% against the amount of FA and MK) samples were labelled as FAX_MKY_WGZ, where X represents the content of MK, Y is the content of MK and Z is the dosage of Na₂O;
- 5, 10, 30 and 50 wt.% FA + 95, 90, 70 and 50 wt.% MK + NaOH with a molar concentration of 5 and 8 M samples were labelled as FAX_MKY_NZ, where X represents the content of MK, Y is the content of MK and Z is the molar concentration of NaOH.

The compressive strength of the samples was determined after 2 and 28 days of a given hydration procedure and after the next 28 days of storage in a water environment.

The composition of all the reaction mixtures for the AA process resulting in the formation of the respective samples is given in Table 1.

In the alkali activation process, dried raw materials were homogenized in a mixer with forced circulation for 2 min. In the next step, the solution of the selected alkali activator (WG or NaOH) was added. The amount of water glass was chosen as 27 mL per 100 g of dried compound(-s), which ensured the addition of 4.5 wt.% Na₂O (this amount of Na₂O was previously tuned for GBFS [39]). The addition of NaOH solution of a given concentration was 80 mL per 100 g of dried compound(-s). Finally, the resulting mixtures were homogenized for 3 min. Prepared paste was filled into the disassemblable metal molds with cavities of the dimensions 20 mm × 20 mm × 20 mm. The molded samples were vibrated for 2 min to eliminate air bubbles and further subjected to a selected hydration process. After 24 h of hydration, the samples were taken out of the molds. As already mentioned, the process of subsequent hydration was conducted in three various environments:

1. Hydration in hydration box (HB)—relative humidity 99%, laboratory temperature (approximately 20 °C);
2. Hydration in laboratory conditions (LC)—storage at laboratory conditions, temperature approximately 20 °C, not controlled humidity;
3. Hydrothermal hydration (HT)—the molds with the pastes after the vibration were tightly covered by stretch foil and thermally treated in a dryer at 65 or 85 °C for 20 h.

Table 1. The identification of the prepared samples and the composition of mixtures for an alkali activation (AA) process.

| Samples          | Experimental Part No. | Metakaolin | Fly Ash | Water Glass Dosage of N₂O * | NaOH Concentration |
|------------------|-----------------------|------------|---------|----------------------------|-------------------|
|                  | I        | II       | III     | (wt.%)               | (M)               |
| MK_WG4.5         | ✓        | -        | -       | 100                  | -                 |
| MK_N1            | ✓        | -        | -       | 100                  | -                 |
| MK_N2            | ✓        | -        | -       | 100                  | -                 |
| MK_N3            | ✓        | -        | -       | 100                  | -                 |
| MK_N4            | ✓        | -        | -       | 100                  | -                 |
| MK_N5            | ✓        | ✓        | -       | 100                  | -                 |
| MK_N6            | ✓        | -        | -       | 100                  | -                 |
| MK_N7            | ✓        | -        | -       | 100                  | -                 |
| MK_N8            | ✓        | ✓        | -       | 100                  | -                 |
| MK_N16           | ✓        | -        | -       | 100                  | -                 |
| FA_WG4.5         | ✓        | -        | -       | -                   | -                 |
| FA_N2            | ✓        | -        | -       | 100                  | -                 |
| FA_N5            | ✓        | -        | -       | 100                  | -                 |
| FA_N8            | ✓        | -        | -       | 100                  | -                 |
| FA_N16           | ✓        | -        | -       | 100                  | -                 |
| FA5_MK95_WG4.5   | -        | -        | ✓       | 95                   | 5                 |
| FA10_MK90_WG4.5  | -        | -        | ✓       | 90                   | 10                |
| FA30_MK70_WG4.5  | -        | -        | ✓       | 70                   | 30                |
| FA50_MK50_WG4.5  | -        | -        | ✓       | 50                   | 50                |
| FA5_MK95_N5      | -        | -        | ✓       | 95                   | 5                 |
| FA10_MK90_N5     | -        | -        | ✓       | 90                   | 10                |
| FA30_MK70_N5     | -        | -        | ✓       | 70                   | 30                |
| FA50_MK50_N5     | -        | -        | ✓       | 50                   | 50                |
| FA5_MK95_N8      | -        | -        | ✓       | 95                   | 5                 |
| FA10_MK90_N8     | -        | -        | ✓       | 90                   | 10                |
| FA30_MK70_N8     | -        | -        | ✓       | 70                   | 30                |
| FA50_MK50_N8     | -        | -        | ✓       | 50                   | 50                |

* The dose of Na₂O expresses the amount of sodium oxide, which is expressed against the amount of activated components (metakaolin (MK), fly ash (FA) and MK + FA mixtures). The symbol "✓" indicates that the sample was prepared in the given experimental part.

Selected samples after their 28-day-long hydration in a given environment were subjected to the tests of their stability in the water environment. In this test, the samples were stored in distilled water for the next 28 days. After this period, the samples were dried at 30 °C and subjected to a compressive strength test.

2.3. Characterization Methods

The characterization methods common in the field of silicate materials were chosen for the description of the initial state of the raw materials KA and FA and for the description of kaolinite dehydroxylation. The chemical composition of the starting materials FA and KA was determined by XRF spectroscopy, and the phase composition of KA, MK and FA was investigated by XRD method. The behavior of KA during the heating was studied with TG/DTA methods. The MK sample was further studied by FTIR spectroscopy to reveal the extent of the dehydroxylation of the original KA. The mechanical resistance of the hydrated samples was assessed by determining the compressive strength of the hydrated samples.
2.3.1. XRF

The chemical composition of the raw materials was determined by a method of energy dispersive X-ray fluorescence spectroscopy (ED-XRF) on the SPECTRO XEPOS (Spectro Analytical Instruments, Kleve, Germany). Powdered samples were shaped/pressed into tablets for the measurement.

2.3.2. XRD

Mineralogical composition of samples was evaluated using X-Ray diffraction analysis on the X-Ray diffractometer MiniFlex 600 (Rigaku, Tokyo, Japan) equipped with a Co tube and D/teX Ultra 250 detector. The XRD patterns were recorded in a 5–90° 2θ range with a scanning rate of 5°·min⁻¹.

2.3.3. FTIR

The FTIR spectra of the tested materials were measured by a Thermo Scientific Nicolet iS10 FTIR (Nicolet, Madison, WI, USA) Spectrometer. The measurements were carried out in the range of 500–4000 cm⁻¹ with a resolution of 2 cm⁻¹ using ATR mode. Each spectrum represents the average of 64 scans. Before each measurement, the background was collected to eliminate the apparatus and environmental effects. Each sample spectrum was rationed.

2.3.4. DTA/TG

A simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) of the KA sample was performed using the STA 504 instrument (TA instrument, New Castle, DE, USA) in an air atmosphere (5 L·h⁻¹) at a heating rate of 10 K·min⁻¹ between 25 and to 1200 °C.

2.3.5. Compressive Strength

A compressive strength (CS) test was performed on an LLB1 hydraulic press (Brio Hranice s.r.o., Hranice, Czech Republic) according to the standard ČSN EN 1402-5. The samples after 2 and 28 days of hydration were tested. The selected samples were tested after the following 28 days of storage in distilled water. CS values are the mean of three measurements.

3. Results and Discussion

3.1. Characterization of the Raw Materials

The chemical analysis and loss of ignition (LOI) of original materials (KA and FA) used in the experiments are shown in Table 2. The amount of Al₂O₃ is close to the theoretical amount (39.5 wt.%) in kaolinite. The ED-XRF analysis of FA revealed the presence of the dominant components—SiO₂, Al₂O₃ and Fe₂O₃. Other important component of FA is CaO and the used sample consists of 2.82 wt.% of this oxide. Based on the CaO amount, FA is sorted: CaO > 10 wt.% (FA with pozzolanic cementitious properties) and CaO < 10 wt.% (FA with pozzolanic properties). According to the classification, the tested FA sample is categorized as type F: (SiO₂ + Al₂O₃ + Fe₂O₃) > 70 wt.% [40,41]. The analyzed amount of CaO is typical for FA obtained by coal combustion without the addition of limestone. The loss of ignition of FA was low.

| Table 2. Chemical composition of original kaolin (KA) and original fly ash (FA) in weight%. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Chemical Composition wt.% | Oxides | MgO | Al₂O₃ | SiO₂ | CaO | TiO₂ | MnO | Fe₂O₃ | P₂O₅ | Na₂O | K₂O | SO₃ | LOI * |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| KA              | 0.32            | 36.20           | 47.70           | 0.31            | 0.20            | 0.01            | 1.10            | 0.10            | -               | -               | -               | 12.9            |                 |
| FA              | 2.05            | 26.42           | 52.20           | 2.82            | 1.31            | 0.10            | 7.39            | 0.91            | 0.82            | 3.25            | 0.86            | 0.40            |                 |

* LOI: loss on ignition.
Thermal analysis was used to study the thermal stability of KA and the obtained TG and DTA curves are shown in Figure 1.

The dominant weight loss of the KA sample started at the temperature slightly above 400 °C and reached the maximum rate at 506 °C as evidenced by the DTG curve. The observed weight loss of 13% of the KA sample in the temperature range of 400–680 °C (Figure 1) is connected to the dehydroxylation process characterized by the loss of hydroxyl groups. The dehydroxylation of kaolinite is an endothermic process as evidenced by the shape of the corresponding peak on the DTA curve showing the minima at 506 °C. An additional exothermic peak at 1000 °C observed on the DTA curve at 1000 °C is connected to the formation of the mullite phase [42,43]. Based on the results of the TG/DTA analysis, the temperature of the KA calcination 550 °C was deliberately chosen to be slightly higher for the KA treatment to ensure the quantitative dehydroxylation of kaolinite in the whole volume of the sample.

The FTIR analysis was performed for the KA and MK samples and the respective FTIR spectra are shown in Figure 2. As shown in Figure 2a, the FTIR spectrum of the KA sample exhibits numerous absorption peaks corresponding to the kaolinite mineral in the kaolin clay [44]. The vibration at 521 cm\(^{-1}\) is caused by Al–O bond, and bands with maxima at 749 and 789 cm\(^{-1}\) confirm the presence of Si–O and Al–O bonds, respectively. Bands occurring at 996, 1024 and 1114 cm\(^{-1}\) indicate an Si–O bond. Vibration at 909 cm\(^{-1}\) belongs to Al–OH groups. The occurrence of hydroxyl groups (O–H) is confirmed by the bands in the region of 3619–3686 cm\(^{-1}\) [16,45,46]. The FTIR spectrum of MK is shown in Figure 2b and documents the process of KA dehydroxylation. This process is confirmed by the absence the bands in the range of 3619–3686 cm\(^{-1}\) and the band at 909 cm\(^{-1}\). The calcination also caused the other structural changes documented by the bands in the range of 500–1250 cm\(^{-1}\). The change in the octahedral coordination of Al to its tetrahedral coordination is verified with the band
at 794 cm$^{-1}$, and the presence of amorphous SiO$_2$—typically indicated by the bands at 1100 and 1200 cm$^{-1}$ [46]—is not obvious.

The XRD pattern of KA (Figure 3a) revealed the presence of kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$, PDF-2 card no. 00-058-2004), muscovite (K,H$_3$O)Al$_3$Si$_3$O$_10$(OH)$_2$, PDF-2 card no. 01-076-2579), and next identified phases are quartz (SiO$_2$, PDF-2 card no. 00-005-0490). The XRD pattern of MK is presented in Figure 3a and shows the presence of the residue of a non-transformed kaolinite phase. The XRD pattern of MK also demonstrates the presence of a diffusion peak which is typical for the amorphous phase. The diffraction pattern for FA (Figure 3b) shows the presence of mullite (Al$_6$Si$_3$O$_{13}$, PDF-2 card no. 01-076-2579), and next identified phases are quartz (SiO$_2$, PDF-2 card no. 01-089-1961) and magnetite (Fe$_3$O$_4$, PDF-2 card no.00-084-2728). The presence of a diffusion peak in the range of 10–40 2$\theta$ observed on the diffraction pattern of FA indicates the presence of an amorphous phase.
3.2. Selection of the Activator for KA and FA Alkali Activation (Part 1)

Experiments included in Part I were focused on a choice of alkali activator of latent hydraulicity for FA and MK. Two alkali activators were tested: (i) sodium water glass with \( w(\text{Na}_2\text{O}) = 4.5 \text{ wt.\%} \) and (ii) the solution of NaOH prepared in various concentrations. Within the experiments in Part 1, the effect of the hydration conditions (LC and HB) for the activation of MK and FA samples was also studied. It was observed that the hydration conditions at elevated humidity and laboratory temperature (HB) were not suitable for the MK sample. The samples obtained by the MK activation with WG and NaOH (MK_WG_4.5, MK_N1 to MK_N16) further hydrated in HB conditions did not reach even manipulation strength. On the contrary, the FA samples activated at HB conditions showed increased compressive strength values. Namely, the sample FA_WG4.5 exhibited a compressive strength (CS) value of 3 MPa after 28 days of hydration under HB conditions.

Due to the fact that the environment with higher humidity was not suitable for the hydration of alkali-activated MK samples, the tests with the hydration of MK samples in LC conditions (simply outside the box, but keeping the laboratory temperature) were conducted. The same tests (hydration in LC) were done for the activation of FA samples and achieved the CS values shown in Table 3. Under LC conditions of hydration, the sample FA_WG4.5 achieved the compressive strength 16 MPa after 28 days of hydration. A compressive strength of FA activated by 2 and 5 M NaOH solution after 28 days of hydration (samples FA_N2 and FA_N5) reached considerably lower CS values (Table 3). Further increase in the concentration of NaOH solution (samples FA_N8 and FA_N16) had a positive effect on the CS of activated products. In the case of FA, the activation with 8 M NaOH solution secured the CS values of hydrated samples (28 days hydration at LC conditions, sample FA_N8) similar to those values obtained for the hydrated sample of FA activated by WG—sample FA_WG4.5 (Table 3). For both raw materials, MK and FA, the CS values increased after 28 days of hydration with the increasing NaOH concentration (Table 3). The maximum values of compressive strength were achieved for MK_N16 (15 MPa) and FA_N16 (24 MPa). These values did not reach the parameters typical for conventional hydraulic binders. For example, the compressive strength of a body prepared by the hydration of Portland cement (CEM I 42.5R) typically reaches values of more than 75 MPa after 28 days of hydration [39]. On the other hand, the achieved mechanical parameters allow the utilization of these materials, for example, for the components not exposed to structural loads.

Table 3. Compressive strength (MPa) of the tested samples activated by NaOH and aqueous solution of sodium silicate (WG) solution after 2 and 28 days of hydration (CS 2 and CS 28, respectively) and after 28 days of storage in distilled water (CS 28 + 28).

| Samples    | CS 2 Standard Deviation | CS 28 Standard Deviation | CS 28 + 28 Standard Deviation |
|------------|-------------------------|--------------------------|-------------------------------|
| MK_WG4.5  | -                       | -                        | -                             |
| MK_N1     | 0.28                    | 0                        | 0.36                          |
| MK_N2     | 0.33                    | 0.02                     | 0.43                          |
| MK_N3     | 0.47                    | 0.06                     | 0.72                          |
| MK_N4     | 0.65                    | 0.03                     | 0.93                          |
| MK_N5     | 1.50                    | 0.09                     | 2.19                          |
| MK_N6     | 1.59                    | 0.10                     | 2.36                          |
| MK_N7     | 1.86                    | 0.02                     | 3.40                          |
| MK_N8     | 2.31                    | 0.02                     | 5.51                          |
| MK_N16    | 0.62                    | 0.04                     | 15.40                         |
| FA_WG4.5  | 4.73                    | 0.01                     | 15.95                         |
| FA_N2     | 0.86                    | 0.12                     | 1.94                          |
| FA_N5     | 0.97                    | 0.10                     | 9.44                          |
| FA_N8     | 1.43                    | 0.03                     | 15.44                         |
| FA_N16    | 0.76                    | 0.01                     | 23.60                         |
From the point of view of short-term strength (two days of hydration), water glass is more suitable for FA alkali activation as evident from CS values in Table 3. Raising the concentration of NaOH increased the initial strength, whereas the maximum CS value was achieved for sample FA_N8, then the increase in NaOH concentration (sample FA_N16) caused a decrease in the initial strength as shown in Table 3. This phenomenon was also confirmed for the alkali-activated MK samples. The CS values obtained for the samples after 2 days of hydration gradually increased with the NaOH concentrations MK_N1 to MK_N8. Further increase in NaOH (16 M) allowed to decrease the initial CS on the level of the MK sample activated with 4 M NaOH (Table 3). The described effect of NaOH concentration is only valid in the case of short-term strength (after 2 days of hydration).

In general, FA samples activated by water glass (dose of 4.5 wt.% of Na₂O) achieved higher strength values than the samples activated by the NaOH solutions of molar concentrations of 2, 5 and 8 M. The development of 2- and 28-day values of CS obtained for activated the FA and MK in dependency on NaOH concentration up to 8 M is illustrated in Figure 4.

The stability of the samples hydrated in LC was tested by their immersion in distilled water. The products of alkali-activated systems hydrated on the air can further solidify in the water environment and they are water resistant [47]. The CS values of the samples after their 28-day-long exposure to distilled water are shown in Table 3. In sum, the duration of the hydration process of such tested samples was 56 days (28 days hydration in LC and 28 days stayed in distilled water). The samples of metakaolin activated by NaOH solution with a molar concentration from 1 to 4 M spontaneously decomposed in water and their CS values after exposure in the water environment were only possible to measure for the samples activated by NaOH solution with molar concentrations of 5 M and above. Only the samples FA_N8 and FA_N16 (activated by NaOH solution) exhibited 17% and 55% increases in CS values after their exposure to distilled water. CS values for other tested samples decreased between 2% and 10% in comparison to CS values for the samples hydrated for 28 days at LC.

The jump increase in compressive strength was observed for the MK samples activated by NaOH at the concentration of 5 M and hydrated for 2 and 28 days (Figure 4). The stability of the samples stored in a water expressed using the compressive strength values CS 28 + 8 in Table 3 indicated the samples MK_N1–MK_N4 (the MK samples activated by NaOH of the concentration up to 4M) as unstable. Both, the jump in compressive strength values and stability of the samples activated with NaOH of the concentration 5M and
higher is connected with the phase composition of hydrated materials. The characterization of the hydration products was not performed in this study, however, for example, Prasanphan et al. [48] found that the formation of the geopolymers product depends on the molar concentration of the NaOH activator. The growing NaOH concentration caused the higher dissolution of Si\(^{4+}\) and Al\(^{3+}\), which subsequently resulted in a higher degree of geopolymerization and grew the compressive strength values which is aligned with our results. The raw material used in their studies was reach on the metakaolin, other components were quartz, muscovite, mica and halloysite. Using the XRD technique, the authors observed that the presence of the mentioned admixtures was clearly detectable in activated systems. Recently, Qian et al. [49] reported the positive effect of the addition of mechanically activated quartz on the mechanical properties of the alkali-activated mixture quartz and metakaolin (20 wt.% of quartz), on the other hand the effect of the non-mechanically treated quartz on the strength parameters was almost negligible in comparison to the sample prepared without the quartz addition. Similarly, Chen et al. [50] proved that the quartz in the admixture of metakaolin did not participate in the metakaolin alkali activation process. From this point of view, the possible effect of the quartz content variation on the mechanical properties of the resulting samples could be considered a minor. Palomo et al. [11] researched the alkali activation process of CaO low content fly ash and confirmed the existence of crystalline phases (mullite, quartz and maghemite) in the hydrated samples regardless of the time and temperature of curing as well as the concentration of NaOH. Based on the information from these papers, it can be supposed that these admixtures did not negatively influence the hydration process of metakaolin and fly ash.

3.3. Hydrothermal Treatment of MK Samples Activated with NaOH (Part 2)

In this part of the experiments, we studied the of course of MK samples activated with NaOH and stored under HT conditions. The aim of the hydrothermal treatment of MK samples was to achieve higher strength, which was three times lower for the LC condition and given a concentration of activator in comparison to FA samples (Table 3).

The hydration of alkali-activated MK at increased temperature was already recommended by authors [51–53] who performed the hydrothermal treatment of MK in the temperature range of 40–80 °C. In these experiments, freshly molded pastes prepared by the mixing of MK with given NaOH solution (5 and 8 M) were tightly covered by stretch foil (whole mold with pastes) and exposed to 65 and 85 °C for 20 h in a laboratory oven. The values of CS achieved for the samples hydrated at HT conditions are shown in Table 4.

**Table 4.** Compressive strength (MPa) of the samples after 2 and 28 days of hydration (CS 2 and CS 28) under different conditions of temperature preparation and after their storage in distilled water (CS 28 + 28).

| Temperature | Samples | CS 2 | Standard Deviation | CS 28 | Standard Deviation | CS 28 + 28 | Standard Deviation |
|-------------|---------|------|--------------------|-------|--------------------|------------|--------------------|
| 65 °C       | MK_N5  | 1.59 | 0.05               | 2.20  | 0.08               | 1.91       | 0.02               |
|             | MK_N8  | 6.18 | 0.33               | 9.11  | 0.01               | 8.92       | 0.03               |
| 85 °C       | MK_N5  | 2.31 | 0.09               | 3.36  | 0.13               | 3.20       | 0.05               |
|             | MK_N8  | 6.37 | 0.19               | 11.18 | 0.01               | 10.17      | 0.05               |

Figure 5 graphically presents the values of compressive strength after 2 and 28 days of hydration at the temperatures of 20, 65 and 85 °C. It is obvious from the data that the HT treatment of samples at 85 °C had a positive effect on the increase in the mechanical properties of activated samples. The experiment also revealed the fact that the effect of the temperature is higher for the samples activated by NaOH solution of higher molar concentration. For MK_N8 sample, the increase in compressive strength is well observable, even at a temperature of 65 °C. Our results are in good agreement with the results published by Mo et al. [54], who observed the positive effect of the curing temperature on the
compressive strength of alkali-activated metakaolin and explained this fact by the increased dissolution rate of Al and Si from an amorphous phase.

![Graph](image)

**Figure 5.** Compressive strength after 2 (plot a) and 28 (plot b) days of hydration with the different temperatures of the activated samples.

It was confirmed that the samples prepared by HT way were water resistant (Table 4). Although the compressive strength values of the samples placed in the distilled water environment decreased by about 2-6% in comparison to the samples after 28 days of hydration in HT conditions, the samples could be considered water resistant.

### 3.4. Alkali Activation of MK + FA Mixtures Using NaOH and WG (Part 3)

In this part of the experimental section, the effect of the NaOH (5 and 8 M) or WG activator on the CS values of MK + FA mixtures (ratios of 95:5, 90:10, 70:30 and 50:50) was studied to test if the addition of FA to the MK sample would have a positive effect on mechanical strength. Obtained CS values after 2 and 28 days of hydration are shown in Table 5.

**Table 5.** Compressive strength (MPa) of tested samples with a variable amount of 5, 10, 30 and 50 wt.% of FA and MK after 2 and 28 days of hydration (CS 2 and CS 28) in LC and compressive strength (MPa) of the samples stored 28 days in distilled water (CS 28 + 28).

| Samples       | CS 2 | Standard Deviation | CS 28 | Standard Deviation | CS 28 + 28 | Standard Deviation |
|---------------|------|--------------------|-------|--------------------|------------|--------------------|
| FA5_MK95_WG4.5 | 0.67 | 0.02               | 2.87  | 0.27               | 1.98       | 0.05               |
| FA5_MK95_N5    | 0.52 | 0.01               | 3.63  | 0.02               | 2.87       | 0.02               |
| FA5_MK95_N8    | 0.84 | 0.05               | 7.77  | 0.16               | 7.02       | 0.32               |
| FA10_MK90_WG4.5| 0.79 | 0.06               | 3.49  | 0.29               | 3.01       | 0.01               |
| FA10_MK90_N5   | 0.93 | 0.09               | 4.10  | 0.63               | 3.87       | 0.05               |
| FA10_MK90_N8   | 1.13 | 0.01               | 8.38  | 0.39               | 7.56       | 0.04               |
| FA30_MK70_WG4.5| 0.87 | 0.05               | 4.75  | 0.06               | 3.79       | 0.10               |
| FA30_MK70_N5   | 0.78 | 0.03               | 4.33  | 0.10               | 3.86       | 0.10               |
| FA30_MK70_N8   | 0.86 | 0.01               | 8.32  | 0.04               | 8.10       | 0.13               |
| FA50_MK50_WG4.5| 1.4  | 0.05               | 6.16  | 0.23               | 5.91       | 0.05               |
| FA50_MK50_N5   | 0.71 | 0.02               | 3.96  | 0.24               | 3.10       | 0.04               |
| FA50_MK50_N8   | 0.74 | 0.01               | 6.49  | 0.21               | 5.79       | 0.11               |

The compressive strength after 2 days of hydration was the highest for pure FA activated with WG and for MK activated with NaOH (Figure 6a). FA addition to MK did not improve short-term mechanical properties as evident from Figure 6a. Zhang et al. [55] stud-
ied the effect of the presence of fly ash on geopolymerization of metakaolin and observed the decrease in the reaction rate in the initial stage of hydration. On the other hand the positive effect of FA addition to the long-term strength (after 28 days of hydration) of MK was confirmed as evident from Figure 6b. As already discussed in Section 3.2, the samples prepared by the activation of MK with WG did not reach even manipulation strength. For example, the CS value after 28 days of hydration of samples FA5_MK95_WG4.5 and FA50_MK_50_4.5WG was 3 and 6 MPa, respectively. A higher portion of FA in the mixture with MK ensured higher mechanical parameters in the case of activation by WG. The same trend was not observed for the NaOH activator. A maximum strength was achieved for the sample containing 90% MK (FA10_MK90_N8).

![Figure 6. Compressive strength after 2 (plot a) and 28 (plot b) days of mixtures with different amount of metakaolin (MK) and fly ash (FA).](image)

Higher CS values of the MK and FA hydrated mixtures were achieved by their activation with an NaOH of concentration 8 M. Maximum CS values after the 28 days of hydration 8 MPa was achieved for the sample with 10 wt.% of FA (FA10_MK90_N8) and a further increase in FA content decreased the CS values. The similar trend was also observed for the mixtures activated with an NaOH activator of concentration 5 M.

By comparison of the CS 28 and CS 28 + 28 values obtained for MK + FA mixtures presented in Table 5 it is evident that the samples withstand the influence of the distilled water and the average decrease in CS values was 9.5%.

4. Conclusions

It was observed that the compressive strength values of the prepared samples are strongly influenced by the method used for their preparation. FA originated during the combustion of black coal in the granulating boiler can be activated by water glass, in opposition to MK, which did not reach the measurable values of compressive strength if activated with this activator. NaOH solution was tested as an alternative to the water glass activator for FA and MK. The compressive strength values of alkali-activated MK as well as FA increased with NaOH concentration, whereas the samples prepared from FA exhibited obviously higher values. The compressive strength of metakaolin activated with NaOH can be further improved by the hydrothermal treatment of freshly prepared mixes and the strength values increased with the temperature. MK samples activated with NaOH and hydrothermally treated at a temperature of 85 °C exhibited the increase in the compressive strength values by tenths of percent in comparison to the MK samples hydrated at laboratory conditions. All of the samples showed acceptable resistance to the distilled water environment except the MK samples activated with NaOH of a maximum
concentration of 4 M. The studied FA and MK alkali-activated systems represent unfired bonding systems and could also be good alternatives to fired ceramics, whereas their preparation did not require the treatment at high temperatures.

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