Thermal behaviour of inorganic aluminosilicate polymer based on cement kiln dust

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Abstract. Alkali activated materials have shown potential for use in high temperature applications. This paper deals with thermal behaviour of various inorganic polymer formulations, which were prepared by mixing metakaolin, blast furnace slag, fly ash and cement kiln dust as alkaline activator. The cement kiln dust was added in the amount of 10 wt.%. The influence of thermal treatment ranging from 30 to 1000°C on the following characteristics was evaluated: compressive strength, thermal expansion, weight loss, melting point, morphology changes and dehydration. The thermal behaviour was studied by TG-DTA analysis, dilatometry and heating microscope, XRD analysis was used to examine phase changes. All measurements were conducted on samples after 28 days of curing time.

1. Introduction

Attempts to reduce the energy cost and environmental effect of Portland cement production have led to the development and application of alternative materials such as alkali-activated binders. The principle of alkaline activation is the reaction of aluminosilicates (blast furnace slag, fly ash, siliceous sediments, metakaolin, etc.) with an alkaline activator, most often in the form of solutions of hydroxides in combination with water glass. The most common activator is sodium hydroxide solution and sodium silicate, preferably with a higher silicate module in water glass [1]. Due to high cost of alkaline activators such as hydroxides and water glass, an effort is made to replace them with waste materials. Cement kiln dust (CKD) is a suitable alternative material due to high content of alkali and negligible price.

CKD is a by-product of Portland cement manufacture. It is generated during the calcining process in the kiln. CKD is a fine cementitious powder, particulate material, readily entrained in the combustion gases moving through the kiln. It is composed primarily of variable mixtures of calcined feed materials, fine cement clinker, fuel combustion by-products, and condensed alkali compounds [2–4]. Due to high alkali content and large amount of free lime, CKD can be used as an activator for pozzolanic materials. CKD was used as an activator for blast furnace slag, fly ash and metakaolin [5]. Addition of CKD reduces the required amount of NaOH. Another research investigated the effects of CKD content on the compressive strength, water absorption, durability etc. [6]. Effects of curing temperature and NaOH addition on hydration and strength development CKD-fly ash (FA) binders were investigated [7]. The results showed significant improvement of comprehensive strength and durability when CKD was used. Bílek et al. [8] studied effects of the CKD and fly ash on workability, mechanical properties, and shrinkage of alkali-activated slag-based composites. Proper dosage of CKD improved the workability
but did not affect the shrinkage reduction. The possibility of utilizing CKD as an activator for blast furnace slag (BFS) was investigated by Konsta-Gdoutos and Shah [2]. Kiln dust – slag concrete, with good overall performance regarding setting time, temperature rise, and mechanical properties was successfully produced.

Investigation of thermal properties of alkali-activated materials has explored some of the basic material properties after exposure to high temperature. The key characteristics of thermal stability assessment are thermal expansion, thermal conductivity, spalling, melting point, phase stability, morphology changes etc. [9]. These properties are dependent on various factors like physical and chemical properties of raw materials, alkali sources, curing regime, ratio of sodium silicate to sodium hydroxide and many more.

The objective of this work was to investigate the effect of temperature on the properties of alkali-activated materials containing 10% of CKD and possibility of using as refractory material. The properties and phase changes of pastes after exposure to temperatures up to 1000°C are reported.

2. Experimental

2.1. Materials

Cement kiln dust with high calcium content obtained from cement plant Mokrá (Czech Republic) was used as alkali activator for alkali-activated material preparation. Metakaolin (MK), blast furnace slag and fly ash were used as main starting materials. MK Mefisto K05 was supplied by České lupkové závody, a.s. (Czech Republic), finely ground BFS was from Trinec (Czech Republic) and FA was from combined heat and power plant in Skawina (Poland).

Chemical analysis of used materials is given in Table 1. Characteristic particle diameters $D_{10}$, $D_{50}$ and $D_{90}$ are summarized in Table 2.

| Table 1. Chemical composition of materials used in mixtures (%) |
| SiO$_2$ | Al$_2$O$_3$ | CaO | Na$_2$O | K$_2$O | MgO | Fe$_2$O$_3$ | TiO$_2$ | LOI |
|--------|------------|-----|--------|--------|-----|-------------|--------|-----|
| MK     | 57.14      | 38.16 | 0.39  | 0.033  | 0.81 | 0.45        | 0.64   | 0.42 | 1.67 |
| BFS    | 37.42      | 7.80  | 40.04 | 0.047  | 0.47 | 8.67        | 0.46   | 0.35 | 0.70 |
| FA     | 49.36      | 25.71 | 3.52  | 1.77   | 2.90 | 2.39        | 6.84   | -   | 5.46 |
| CKD    | 8.66       | 1.65  | 32.81 | 0.38   | 23.99| 0.53        | 0.93   | 0.62 | 20.17|

| Table 2. Particle diameters of materials (µm). |
| D10 | D50 | D90 | Mean diameter |
|-----|-----|-----|---------------|
| MK  | 1.71| 6.10| 10.63        | 6.17 |
| BFS | 1.33| 9.91| 30.45        | 13.62|
| FA  | 2.30| 15.12| 44.48      | 20.15|
| CKD | 1.20| 17.69| 56.83       | 24.56|

The XRD analysis of these raw materials was performed. MK contained quartz (SiO$_2$), kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), illite (KAl$_2$(AlSi$_3$O$_10_9$(OH)$_2$), rutile (TiO$_2$) and significant amount of amorphous phase. BFS contained calcite (CaCO$_3$), merwinite (Ca$_3$MgSi$_2$O$_8$) and melilite (Ca$_4$Al$_2$MgSi$_3$O$_{14}$). In addition, quartz (SiO$_2$) and significant amount of the amorphous phase was present. The majority phase in FA was quartz (SiO$_2$), then mullite (Al$_2$Si$_2$O$_{13}$), hematite (Fe$_2$O$_3$), maghemite (Fe$_3$O$_4$), anhydrite.
(CaSO$_4$) and amorphous phase. Sylvite (KCl) was the main component of CKD, lime (CaO), larnite (Ca$_2$SiO$_4$), arkanite (K$_2$SO$_4$), quartz (SiO$_2$) and wollastonite (CaSiO$_3$) were also identified.

2.2. Methods

The composition of raw materials and final products was determined by X-ray powder diffraction. The X-ray diffraction analysis was conducted using Bruker D8 Advance apparatus with Cu anode ($\lambda$K$_\alpha$ = 1.54184 Å) and variable divergence slits at Θ-Θ Bragg-Brentano reflective geometry.

Dilatometric measurements were made under air, by means of a contact horizontal dilatometer (Netzsch 402 E/3) on bulk samples ($7 \times 7 \times 50$ mm) up to 1000°C. Heating rate was 5 °C·min$^{-1}$.

Combined TGA/DTA data were obtained using STA 449 F3 Jupiter (by Netzsch). The samples were tested in Pt crucibles, temperature gradient was 10 °C·min$^{-1}$ from 35 to 1100°C. Measurement atmosphere was synthetic air (50 ml·min$^{-1}$, N$_2$/O$_2$ ratio was 80/20).

Material behavior during sintering and melting was investigated by horizontal type heating microscope EM 201 (Leitz). All samples were grinded to powder and then pressed into a cylindrical testing body 3 mm high and 2 mm in diameter. The sample was heated under the heating rate 5 °C·min$^{-1}$ up to 1350°C or up to the sample melting point. The picture recorded by CCD camera with 25°C step was used to determine the temperatures of standard points which are defined for heating microscopy and from which the point of sintering (SP), deformation (DP), hemisphere (HP) and flowing (FP) were identified.

Determination of total porosity of prepared material was performed on the apparatus Carlo Erba Strumentazione model 200; measuring range: 3.75–10000 nm. Various levels of pressure were applied onto a sample immersed in mercury.

2.3. Sample preparation

Paste were prepared by mixing solid materials including CKD, MK, BFS or FA with an activating solution in defined ratios. The solid materials were premixed for a few minutes. Subsequently, a 4M NaOH solution was added. The amount of additional water was adjusted to obtain a similar consistency of pastes. Detailed composition of mixtures is given in Table 3. The paste was casted into moulds sized $40 \times 40 \times 160$ mm and $7 \times 7 \times 50$ mm for dilatometric analysis. The samples were then wrapped with plastic foil to avoid moisture evaporation. After 24 h, hardened specimens were demoulded and stored in plastic bags under laboratory conditions for 28 days. The prepared samples were heated in furnace to temperatures 600, 800 and 1000°C for 2 h at a constant heating rate of 5 °C·min$^{-1}$.

| Table 3. Mix proportion of paste (wt. %). |
|------------------------------------------|
| C1 | C2 | C3 |
| CKD | 10 | 10 | 10 |
| BFS | 64.5 | 38 | 43 |
| MK | - | 20 | - |
| FA | - | - | 21 |
| 4M NaOH | 23 | 29 | 26 |
| Water | 2.5 | 3 | - |
3. Result and discussion

3.1. XRD

The structure analysis of prepared samples was carried out by XRD. Figure 1 presents XRD traces of prepared sample before and after thermal treatment to 1000°C.

The XRD patterns of all samples had a broad hump, characteristic of an amorphous content. The main crystalline phases of all samples were quartz (SiO$_2$), calcite (CaCO$_3$), larnite (β-Ca$_2$SiO$_4$), merwinite (Ca$_3$MgSi$_2$O$_6$), åkermanite (Ca$_2$MgSiO$_4$), hydroxylacte (Mg$_6$Al$_2$CO$_3$(OH)$_{16}$·4H$_2$O) and aphthitalite (K$_3$Na$_2$SiO$_5$). The CaO that was present in the CKD completely disappeared after polycondensation and formation of calcium carbonate. The calcite is the main Ca-based product. Hydroxylacte has been identified as one of the main hydration products in alkali-activated blast-furnace slag in earlier works and reflections corresponding to hydroxylacte are present at 7.8° 2θ [10]. The C1 and C3 samples show reflections at 7° 2θ and 49.7° 2θ, which can be attributed to C-S-H (I) [10]. The effect of Ca$^{2+}$ presence and formation of C-S-H gel as a co-product of Ca-added alkali-activated system was discussed in many papers. The reason why C-S-H was not formed in the C2 sample may be due to Ca$^{2+}$ content in the matrix and the difference in the kinetics of dissolution Si and Ca due to different matrix composition [6]. The level of dissolved silicate in the activating solution plays a significant role in determining the effects of calcium on the final reaction product. The formation of calcium silicate hydrates could remove a proportion of the excess silicate from solution [11]. In addition, sylvite (KCl) is present in samples C1 and C3. Mullite (Al$_6$Si$_2$O$_{13}$) whose source is fly ash was identified in sample C3.

Thermal treatment of samples at 1000°C has induced some significant changes in samples composition. Samples treated at 400°C were mainly amorphous. Comparing the composition, there was no significant difference between samples treated at room temperature. The peaks of hydroxylacte, aphthitalite, C-S-H (I) were not identified. These phases were decomposed to 400°C. From 600°C to 800°C the amount of the amorphous phase decreased and at 1000°C the amorphous phase was no longer present.

Figure 1. XRD traces of alkali activated material by CKD before and after thermal treatment to 1000°C: H = hydroxylacte, Q = quartz, C = calcite, MII = mullite, K = sylvite, A = aphthitalite, Mer = merwinite, G = gehlenite, N = nepheline, An = andradite, M = maghemite, Akr = åkermanite, Lr = larnite.
recognizable. At 800°C, the first new phase formation was identified: gehlenite (Ca$_2$Al$_2$SiO$_7$), nepheline (NaAlSiO$_4$), maghemite (Fe$_2$O$_3$), and andradite (Ca$_3$Fe$_2$(Si$_3$O$_{12}$)). All samples contained gehlenite. Gehlenite is produced by the decomposition of C-S-H phases at around 800°C in samples containing lime [12]. Peaks of maghemite were found in sample C1. Nepheline [13–15] was identified in sample C3. Nepheline structure is based on a tridymite-like structure [16]. Andradite [13, 17] was found in C2 and C3 samples. Peaks of lazurite [13] (Na$_3$Ca(Al$_3$Si$_3$O$_{12}$)S) were identified in sample C1 at 1000°C.

The peak intensity of mullite (Al$_6$Si$_2$O$_{13}$) in sample C3 decreased due to reaction of mullite with surrounding matrix [13, 18]. All these changes are consistent with the data presented in the literature.

3.2. Heat microscope
The high-temperature characteristics: deformation, sphere, hemisphere and flow temperatures were determined by heat microscope. Measurement shows that the sample C1 shrunk in temperature range from 650°C to 770°C. It represented an area loss about 17%. This could be related to softening or recrystallization of some products. The sintering of the sample started at 1100°C and at 1250°C occurred deformation of the sample followed by melting, formation of hemisphere and final spread over the alumina sample holder. Total shrinkage of sample was over 73%.

Sample C2 started to sinter at 950°C and no other changes were measured up to the final temperature 1300°C. Shrinkage caused by sintering was quantified as 43% area loss of sample. For sample C3 sintering started at 1030°C and caused 40% area loss of sample. Above 1260°C deformation of the sample started followed by melting, formation of hemisphere and final spread over the alumina sample holder. Total shrinkage of the sample volume is over 77%.

3.3. Dilatometry
Thermal expansion/shrinkage of prepared materials was measured in-situ through dilatometry. Shrinkage or expansion during heating caused both internal and external stresses, which weakened or damaged the structure. The effect of the water/solid ratio, alkali type or source material on the thermal expansion has been observed in previous works [9, 14, 19–21].

Figure 2 presents results of dilatometric analysis of prepared samples. All samples exhibited less thermal stability due to the shrinkage up to 13% that occurred during heating. All samples showed small expansion between 50–175°C as free water is released [22]. Shrinkage between 150–450°C was caused by dehydration of free water and dehydroxylation confirmed by TG as evidenced by the TG/DTG. Slow expansion occurred at 450°C. Another slight shrinkage occurred in sample C1 between 680–750°C likely due to densification and consequently expansion occurs which may be due to recrystallization [14]. Thermal expansion during heating of sodium silicate-fly ash alkali-activated materials has been discussed in the literature [18, 20]. Sharp shrinkage between 450°C and 850°C is probably due to viscous flow in aluminosilicate material causing sintering and subsequent densification of samples [18]. C3 sample has a similar trend of the dilatometric curve, with a difference in the temperature range of 20–150°C resulting in more pronounced expansion due to water excess. Slow expansion started at 450°C. Slight shrinkage due to the densification of the sample is not identified around 700°C as in the case of the sample C1.
The derivative of dilatometric data is shown in figure 2b, which gives a clear overview of the changes in the rate of axial shrinkage and the onset temperatures. Onset temperature of dehydration of free water is higher for C1 sample than C2 and C3. The rate of shrinkage of this process is lower for C1 than for C2 and C3. The peak around 700°C indicates shrinkage due to densification in sample C1.

3.4. Thermogravimetric analysis

Figure 3a presents results of TG/DTA analysis of prepared materials using CKD activator. The same effects can be observed for all three samples. There was a continuous loss of weight up to 1000°C with the total weight loss around 13%.

The thermogravimetric analysis shows (Figure 3) a major weight loss (around 6%) from room temperature to 220°C due to evaporation of free and physically bounded water [17]. Between 150°C and 250°C, the rate of weight loss for all samples starts to slow down as the physical free water is already evaporated and the interstitial water starts to decompose. The gradual weight loss between approximately 250–400°C is attributed to the dehydroxylation. The weight loss (around 2.5%) between 200°C and 400°C is associated with dehydroxylation and decarboxylation of hydrotalcite [10, 23]. The presence of hydrotalcite was confirmed on the X-ray diffraction pattern. Thermal decomposition of portlandite occurs at about 450°C, the amount of portlandite is around 9.9% in C1, 2.5% in C2 and 7.8% in C3, however, this process is influenced by other simultaneous processes, therefore, the amounts are only approximate. The other small mass loss (around 1.5%) occurs between 550–650°C in samples C2.
and C3 and it could be related to the sintering process. Recrystallization appears to cause mass loss between 650°C and 800°C in all samples [17]. The decrease in the amorphous phase in the range of 600°C to 800°C was recorded by XRD. The thermogravimetry data are consistent with the dilatometry analysis.

3.5. Compressive strength
Compressive strength of prepared samples was tested before and after exposure to high temperature in order to assess their strength retention. Figure 4 presents compressive strength of specimens cured at temperature range up to 1000°C. Initial compressive strengths ranged from 40 MPa (C2) to 25 MPa (C3). Samples produced with CKD showed moderate strength. Thermal exposure affected the mechanical strength of tested materials. The changes in mechanical strength occurred due to changes in structure and phase composition. Structural changes include sintering, densification, melting, cracking or pore size changes [14].

In the case of sample C1, the compressive strength decreased under 10 MPa with increasing temperature. Higher susceptibility to strength degradation of sample may be due to a higher content of C-S-H gel which is more vulnerable to dehydroxylation and decarbonation [17]. Sample C2 did not show any decrease in the strength value due to temperature rise, but at 800°C the sample disintegrated as a result of cracking. The cracking is due to migration and evaporation of water in the samples during thermal exposure. Higher strengths are probably due to the content of finer metakaolin particles in the original matrix. The compressive strength of sample C3 gradually increased up to 400°C then it also dropped sharply to 3 MPa. This is mainly attributed to the formation of additional binder gel or sintering un-reacted fly ash particles [9, 17].

![Figure 4. Compressive strength before and after heating to 1000 °C of alkali activated materials with CKD.](image)

3.6. Porosity
The results of total porosity of prepared samples are shown in Figure 5. At higher temperatures, multiple factors influence the size and distribution of the pores. Pore structure that changes during thermal exposure has a mixed effect on the mechanical strength [9].
The total porosity of C2 sample is 50% lower than the other samples, which is probably due to the finer particles of metakaolin in the original matrix. A larger number of open pores in samples C2 and C3 can be assumed from the water adsorption results. Sample C1 has most pores in the range of 10–20 nm, while sample C2 had most pores between 20–40 nm and sample C3 between 40–100 nm.

The total porosity of sample C1 decreases with increasing temperature and the number of pores in the region below 100 nm increases to 600°C. Reduction of total porosity during dehydroxylation and sintering resulted in densification. After heating to 1000°C, small pores in the range of 10–20 nm are not longer detectable and the number of larger pores in the 250–350 nm range increased.

An increase in the number pore size in the 40 nm region occurs with a temperature rise of up to 600°C for sample C2. At higher temperatures, macro cracks and sample destruction occurred. Development of large pores is possibly connected to the decomposition of material due to heating. A number of pores could be the predominant factor related to strength decrease.

For sample C3, the total porosity with the temperature rises and from 600°C the total porosity does not change, only the pores size changes. It was confirmed [9] that fly ash alkali-activated binders have large numbers of interconnected pores which simplify the permeation of water to surface, causing smaller damage to the structure. In general, alkali-activated materials based on metakaolin do not exhibit as great increase in pore volume after heating as fly ash geopolymer.

4. Conclusions

Physical characteristic of alkali-activated materials based on cement kiln dust before and after heating to 1000°C have been observed. The thermal stability of all observed samples was rather low due the shrinkage during thermal treatment. The material shrinkage was closely related to volume changes of aluminosilicate caused by dehydration between 25 and 400°C. Based on XRD analysis, it was proved that the prepared materials were amorphous, still containing the crystalline phases initially presented in raw material. New phases formation was identified after heating to 800°C: gehlenite, nepheline and andradite.

Alkali-activated material with MK (C2) showed better mechanical properties compared to material based on FA (C3) and BFS (C1) after 28 days under laboratory conditions. After heating, compressive strength was affected by the varying influence of phase changes, increase of total porosity and damages due to dehydration. The MK sample (C2) exhibited the best compressive strength up to 600°C, but then macro cracks and sample destruction occurred. The compressive strength of sample C3 gradually increased up to 400°C due to formation of additional gel binder.

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