Utilization of flue dust arising from metakaolin production for alkali-activated materials preparation

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Abstract. This paper assesses the feasibility of using flue dust, which is a residue from metakaolin manufacturing in a rotary kiln as a raw material for production of alkali-activated materials. This material contains besides metakaolin also residues of clays, and mullite. Metakaolin and blast furnace slag were used as initial materials. Flue dust was used for the replacement of initial materials up to 100%. Mortars were prepared for the determination of compressive strength by adding sand at the weight ratio of 1:1. As an alkaline activator was used potassium water glass and s/w ratio was 1.25. The prepared samples were tested for physical-mechanical properties after 28, 56, 90 and 180 days. Setting time and leaching characteristic were also evaluated.

1. Introduction

Geopolymer binders are based on aluminosilicate materials and possess good mechanical properties. Thanks to these properties, geopolymers can be considered as an alternative binder compared to Portland cement. In earlier studies, metakaolin was used as the main aluminosilicate raw materials, due its high reactivity and the formation of homogenous reaction product [1]. Most of the waste materials such as fly ash, blast furnace slag and various mining waste can be used for the alkaline reaction. The type and nature of initial materials used directly affect the final properties of geopolymer prepared from these materials [2]. Many industrial wastes have been tested to reduce the cost of geopolymers. The type and nature of the initial materials used directly affect the final physical and chemical properties of geopolymer prepared from waste materials.

In the previous work [3] there were studied properties of geopolymers synthesized from the clay calcined in a rotary kiln. The clay contained 30–70% of kaolinite which was transformed by calcination at 750°C to metakaolinite.

The thermally treated kaolin mining wastes formed mainly kaolinite were tested [4]. Kaolinite-based clays require a thermal activation and therefore it raises cost of these materials [5]. It has been proved that calcined materials which are mostly amorphous, usually display a higher reactivity during geopolimerization compared to non-calcined materials [6].

The use of raw kaolin itself in geopolymer has not been studied in detail. Heah et al [7] investigated kaolin-based geopolymers in sodium alkaline-activator and confirmed good volume stability of these materials. Various combinations of kaolinite, albite and fly ash have been tested for the preparation of geopolymers. The results showed that the compressive strength was greatly increased when these three minerals undergo geopolymerization together [8].
The aim of this work was to prove the possibility of using flue dust in its original state without sufficient thermal activation. This material has already undergone a calcination process in a rotary kiln, and it contains besides metakaolin also residues of kaolinite. Physical observation, workability and leachability test of alkali-activated materials are reported in this paper.

2. Experimental part

2.1. Materials

Metakaolin (MK) and blast furnace slag (BFS) were used as main initial materials. MK Mefisto L05 was supplied by České lupkové závody, a.s. (Czech Republic), finely ground BFS originated from Třinec (Czech Republic). Rotary kiln flue dust (RON) is a by-product of metakaolin production. Chemical composition of all raw materials was determined by XRF analysis (PANalytical Axios PW4400/30) (See table 1). Characteristic particle diameters D10, D50 and D90 are summarized in table 2. Potassium water glass was used as alkaline-activator (Ms = 1.78).

| Table 1. Chemical composition of materials used in mixtures (%) |
|-------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| SiO2 | Al2O3 | CaO | Na2O | K2O | MgO | Fe2O3 | TiO2 | SO3 | LOI |
| MK   | 53.21 | 42.94 | 0.20 | 0   | 0.78 | 0.28 | 0.92 | 1.56 | 0.05 | 2.10 |
| BFS  | 39.99 | 8.99  | 38.70 | 0.47 | 0.48 | 8.71 | 0.49 | 0.34 | 1.84 | 0.71 |
| RON  | 52.06 | 39.98 | 1.16 | 0.28 | 0.88 | 0.71 | 2.19 | 2.04 | 0.58 | 5.55 |

| Table 2. Particle diameters of used materials (µm) |
|-------------------|----------------|----------------|----------------|----------------|
|                  | D10 | D50 | D90 | Mean diameter |
| MK    | 1.21 | 4.65 | 11.00 | 5.52 |
| BFS   | 1.66 | 10.73 | 28.63 | 13.38 |
| RON   | 2.06 | 16.31 | 58.23 | 24.08 |

The XRD analysis of these raw materials was performed. The amorphous phase was a main component of MK. MK contained 83% of amorphous phase, quartz (SiO2), kaolinite (Al2Si2O5(OH)4), illite (KA12(AlSi3O10)(OH)2), anatase (TiO2) and mullite (Al6Si2O13). BFS contained amorphous phase (78%), calcite (CaCO3), than merwinitie (CaMgSi2O6), akermanite (Ca2MgSi2O7) and larnite (Ca2SiO4). RON contained 64% of amorphous phase, 17% of kaolinite, also quartz (SiO2), anatase (TiO2), illite (KA12(AlSi3O10)(OH)2) and mullite (Al6Si2O13).

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

2.2. Sample preparation

Metakaolin and blast furnace slag were used as the primary aluminosilicate raw material. Ratio SiO2/Na2O was 6.9 and ratio SiO2/Al2O3 was 4.28. MK and BFS was partially replaced by RON at 0–100 wt. %. After homogenization, the solid materials were mixed with alkaline-activator in ratio S/L 1.25. Shale (0-0.4 mm) was used as a filler in a weight ratio of 1:1. The mortars were casted into moulds sized 40 × 40 × 160 mm. The samples were then wrapped with a plastic foil to avoid moisture evaporation. After 24 h, hardened specimens were demoulded and stored in plastic bags under laboratory conditions for 180 days.
2.3. Testing methods
The consistency of prepared mortars was determined according to EN 12350-5 using the flow table test, where the mean diameter of a test sample was measured. Initial setting time of geopolymer pastes was determined using the Vicat needle method according to EN 196-3:2016.

The flexural strength of a hardened mortar was determined by three point loading of a prism specimen, subsequently to the failure and breakage of this specimen the compressive strength was determined on each half of the prism 160 × 40 × 40 mm. The samples were tested in several terms up to 180 days.

The leachability test was performed after 28 days at 20°C. The samples were soaked in water up to 7 days. The volume of water was determined by calculated surface of the tested prism at the volume ratio of 1:5. Once a day the leachate was stirred. The resulting leachate was analysed by ICP-OES method (ICP IRIS Intrepid II XSP Duo) and K+, Na+, Ca2+, and SO42-, NO3-, Cl- were determined.

3. Results and discussion
3.1. Workability and setting time
In the first phase, the effect of the amount of RON in the mixture on the consistency and initial setting time was studied. Figure 1a and figure 1b show the consistency and setting times of the pastes as a function of the RON content.

A small amount of the raw material RON results in an increase in the mortar diameter, then decreases up to 140 mm for the 100RON sample. It is clearly illustrated that the setting times were prolonged of various degrees by adding RON. The setting time was slowly affected by RON up to 40%. At higher dosages, the onset of setting time significantly prolonged. The reference sample (0RON) has a setting time of about 115 min, while 100RON over 2,100 min.

One of the factors that fundamentally affect the workability in particle size of starting materials. RON has a higher ratio of coarser particles than metakaolin and slag (See table 2). Setting time of geopolymer mixtures depends on the specific surface area. The lower specific surface area leads to higher setting time of geopolymer mixtures [9, 10]. Simultaneously, the kaolin particles should decrease workability due to the plate-like structure [7]. The kaolinite content in RON results in lower reactivity of mixtures due to kaolinite slower dissolution in alkaline solution [11].
3.2. Compressive and flexural strength

The compressive strength and flexural strength of geopolymer mortars at the ages of 28, 56, 90 and 180 days are depicted in figure 2. The strengths decreased as the amount of RON in the mixture increased. The compressive strength of the reference sample (0RON) was 54 MPa and flexural strength was 7 MPa after 28 days. The 100RON sample had much lower compressive and flexural strength after 28 days, i.e. 20 MPa and 3.8 MPa, respectively. Overall results showed that strengths increased with the ageing time. The most significant increase in strength was recorded within 90 days. After 180 days the strength increases slightly especially in samples containing RON. After 180 days the reference sample had 72 MPa and 8.8 MPa, respectively, and 100RON sample had 41.6 MPa and 6.5 MPa, respectively.

Strengths were strongly affected by the composition of samples. The kaolinite from RON required more time for reaction and became hard solid. Because of the low reactivity of kaolinite, a weak structure was formed resulting in the decrease of strength [7, 8]. In addition to composition of the raw materials, strengths can also be affected by particle size. Coarser particles could harder fill the spaces leading to less dense structure [12].

Heah [7] was involved in the preparation of kaolin-based geopolymer with sodium alkaline-activator with various solid-to-liquid ratios. Compressive strengths exceeding 5 MPa were measured for the prepared samples. In another work [8], geopolymers were prepared from fly ash, which was partially replaced by kaolinite. In this case, a compressive strength of about 30 MPa was achieved, using a sodium alkaline activator. Using kaolinite as the source of aluminium definitely had a negative effect on the compressive strength as compared to that of the matrices where metakaolinite was used.

![Figure 1. Results of consistency determination (a) and initial setting time (b) depending on the RON content in the mixtures.](image)
Figure 2. Development of compressive strength (a) and flexural strength (b) in time.

3.3. XRD measurement
The structure analysis of prepared pastes after 28, 90 and 180 days was carried out by XRD method. The XRD patterns of all samples had a broad hump, characteristic for an amorphous phase. In the case of reference sample without RON addition, the main crystalline phases were calcite (CaCO$_3$), quartz (SiO$_2$), anatase (TiO$_2$), muscovite (KAl$_3$Si$_4$O$_{10}$H$_2$), mullite (Al$_6$Si$_2$O$_{13}$), merwinite (Ca$_3$MgSi$_2$O$_8$) and akermanite (Ca$_2$MgSi$_2$O$_7$). Kaolinite characteristic peaks (7.19 Å; 1.48 Å; 3.58 Å) were identified in all samples containing RON (See figure 3a). Kaolinite is unable to be incorporated into the polymer structure due to fact, that the dissolution of kaolinite in alkaline solution is extremely slow [6, 7]. The intensity of kaolinite peak increased with the amount of RON in the matrix and decreased with ageing days. After 180 days, kaolinite peaks were still identified in the XRD pattern of all samples where the raw materials have been replaced with RON. Calcite-related peaks (3.03 Å) from slag were not identified in the 100RON sample (See figure 3b).

RON content in the matrix influenced the formation of precipitate on the surface of the samples. This was especially evident in the samples 75RON and 100RON after 90 and 180 days. These precipitates were identified as aragonite (CaCO$_3$) by X-ray diffraction.
3.4. Leaching test

After 28 days of maturation, leaching tests were carried out and ions that could potentially contribute to efflorescence were analyzed. Using ICP-OES method K⁺, Na⁺, Ca²⁺ and SO₄²⁻, NO₃⁻, Cl⁻ were determined. The use of potassium water glass should reduce the possibility of efflorescence. The development of determined ions in leachate is shown in figure 4a and 4b.

The content of chlorides and nitrates in the extract was very low as well as the content of sodium and calcium ions. Conversely, the content of sulfate and potassium ions in the leachate increased very intensively with the amount of RON in the matrix. The results suggest that potassium ions are released into the solution because there is no appropriate structure of the geopolymer. The work by Jaarsveld [2] confirmed that the inclusion of kaolinite serves to provide structure-forming species to the overall geopolymerization process, but a large amount of added kaolinite may not take part in the synthesis reaction at all. The samples 75RON, 100RON were disintegrated after 7 days of soaking. This is probably due to the very weak structure as shown by the very low compressive strength.

An increasing concentration of sulfate ions could probably cause aragonite to precipitate on the sample surface. Previous work [13] has confirmed that a pH below 11 is suitable for crystallization of aragonite. Aragonite can be formed from sodium carbonate and calcium sulfate. Aragonite formation is promoted by the addition of sodium sulfate due to a decrease in supersaturation and sulfate ion adsorption.
Figure 4. Development of concentration of cations (a) and anions (b) in leachate in dependence on RON content in the geopolymer matrix.

4. Conclusions
For the preparation of geopolymer materials, the flue dust of 0-100% was used as a substitute in blast-furnace slag and metakaolin matrix. It was found that this material can also be used successfully for the preparation of geopolymers, but due to the content of kaolinite, which dissolves very slowly in the alkaline environment, such a high-quality and appropriate aluminate-silicate structure is not formed. The addition of the flue dust results in reduced compressive and flexural strengths, prolongation of setting time and affects the flowability of the mixtures.

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