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The influence of ambient pH on fly ash-based geopolymer

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ABSTRACT

This study reports the comprehensive observation of the influence of ambient pH on the changes of fly ash-based geopolymer in an aqueous solution at various time periods up to 720 days. The aim of the study was to find a relationship between ambient pH, the change of composition, the structural changes and mechanical properties. The results of XRF, NMR, XRD showed that, Na can still leach into solutions of pH $\leq$ 13. The percentage of Na_2O decreased over time in solutions of pH $\leq$ 13, and the decreasing rate of the Na_2O percentage increased at low pH. The structural changes still proceeded for specimens in water, the number of Al-O-Si bonds increased over time. The cleavage Si-O-Si stopped, when specimens were immersed in the solution of pH = 1(HCl) due to the fast leaching of Na to solution and neutralization. In a high pH environment (NaOH), the Al-O-Si bond was more consistent than the Si-O-Si bond. The phase change was recorded only in the solution of pH = 14 with the small amount of Na-P1 zeolite. Even though the chemical composition and structure of specimens changed over time, the mechanical properties of the geopolymer were quite stable even when specimens were immersed in solutions of extreme pH (pH = 1, 2 or up to pH = 14).

1. Introduction

The alkaline-activated fly ash-based geopolymer pastes, mortars or even concretes exposed to conditions with the alternation of wetting and drying accompanies efflorescence [1,2]. Na can leach easily as a free Na^+ ion in water that reacts in turn with CO_2 present in the air to make soluble Na_2CO_3. Consequently, the leachability of geopolymer in water was investigated to optimize the composition for the immobilization of components to reduce leaching [3]. In addition, acid corrosion of the hardened paste of the geopolymer cement in solutions of nitric acid and sulphuric acid has been discussed in previous publications [4–7]. Equally important is that this study investigated and compared the response of fly ash-based geopolymer in water and at extreme pH levels (e.g. pH 1, 2, 12, 13 and 14) using chloric acid and sodium hydroxide as examples of a strong mineral acid and base. In addition, this work focused on the long-term internal changes of the chemical composition, structure, and mechanical properties of the geopolymer and differs from previous studies that focused solely on the concentration of Na^+ or the pH change in ambient solutions [8].

2. Materials and methods

2.1. Material

The fly ash used in this work was obtained from the brown coal-classically fired power plant, in Opatovice, Czech Republic. The chemical composition of the fly ash was determined by X-ray fluorescence (XRF), and are shown in Table 1.

The mineral components of the fly ash were examined by X-ray diffraction (XRD). The result is shown in Fig. 1.

Pure silica sand was used for the mortar preparation with 3 types of grain sizes (d: diameter) with the fraction (1:1:1), (1. type: coarse-grained (d: 2 mm), 2. type: medium coarse-grained (d: 1 mm), 3. type: fine grain size (d: 0.5 mm).

2.2. Preparation

The alkaline-activation is characterized by three parameters. The first parameter is the percentage of sodium oxide (%Na_2O) in the alkaline activator. The second is the silicate modulus (Ms) Ms = SiO_2/Na_2O of the alkaline activator. The third is a water coefficient (w); this is the ratio of the fly ash weight to the total weight of water in the alkaline activator. Experiments were carried out by the alkaline activator containing %Na_2O = 7; Ms = 0.75, and w = 0.33. These optimized parameters were chosen from the

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Table 1
Composition of the Opatovice fly ash (percent by weight).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	P_2O_5	LOI
52.85	31.84	7.34	2.12	1.14	0.41	1.69	0.36	1.51	0.21	0.74

Table 2
Chemical composition of the water glass.

Oxide	SiO_2	Na_2O	H_2O
%	~25	~16	~57

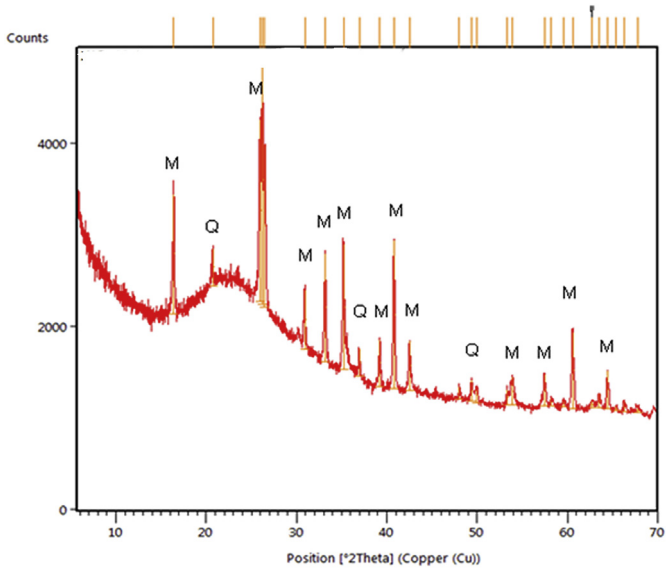

Fig. 1. XRD pattern of fly ash. Phases in fly ash: mullite - M, quartz – Q, Water glass is industrially produced by K. P. in Czech Republic. Table 2 lists the chemical compositions of the water glass.

previous dissertations in the same project [9–12].

The activator solutions include a NaOH solution (~77 g NaOH, ~185 g water, their weighs depended on the composition of water glass) and water glass (~231 g). The NaOH solution was prepared by dissolving NaOH pellets (purity of 99%) in water, and cooled to 70 °C. The activator was prepared by quickly mixing the water glass with NaOH solution and then it was immediately added to the Opatovice fly ash (~1100 g) to make a paste. After 4.5 min in the mixing step in an electric stand mixer, the mixture was poured into open steel moulds and cured in a laboratory dryer at 80 °C, ~25% measured relatively humidity (R.H.) for 12 h. Hardened paste specimens were then demoulded and left under the laboratory conditions of ~24 °C and ~50% R.H. for 7 days. Mortar specimens were also prepared similarly by adding 3-grain size fractions of the above pure sand to the mixing process. The mass ratio of fly ash to the sands was 1:1.5.

2.3. Testing and characterisation

After 7 days, all paste and mortar specimens were exposed to various solutions, they were fully immersed in the solutions of an amount about 50 dm^3 and in water about 1 m^3. The solutions were: HCl, NaOH, and water (at pH respectively equal to 1, 2 (HCl); 12, 13, and 14 (NaOH); and about 7 (water)). Every day, the solutions were continuously monitored to keep the pH levels constant by the addition of NaOH and HCl, then renewed by a new solution each 7 days.

2.3.1. Mortar specimens

After preparation, the strength of the mortar was determined without drying at 7, 28, 120, 360 days up to 720 days. The compressive and flexural strength were determined on specimens of ~40 mm (a: wide) × 40 mm (b: height) x 160 mm (c: length) in size. The specimens were also measured for mass (m) and dimension without drying in order to calculate the density (ρ) ($\rho = \frac{m}{V}$. V = a × b × c). The compressive strength was determined by using the 2 residues from the specimen used in the three points bending flexural test [13]. The resulting values of the flexural strength represent the arithmetic mean of the 6 measured values of mortar specimens (n = 6). The resulting values of the compressive strength represent the arithmetic mean of the 12 measured values of mortar specimens (n = 12). The average error incurred during the strength determination amounted to 10 relative percent.

2.3.2. Methods used for paste specimens

Paste specimens were milled, all powder from the specimens was stirred and divided into small parts for X-ray powder diffraction XRD, X-ray fluorescence XRF, ^{23}Na, ^{27}Al, ^{29}Si, MAS NMR. The specimens were analysed by X-ray powder diffraction XRD, using PANalytical X'Pert PRO Philips, operated at 30 mA and 40 kV, with a step size [°2Th.]: 0.0170, scan step time [s]: 20.32, scan types: continuous, and measurement temperature [°C]: 25.00, with Ni filter). X-ray fluorescence XRF was performed by spectrometer ARL 9400 XP with full automatic measurement, calculated as oxides, and X-ray path = vacuum, matrix (shape and ImpFC: 2 SiO_2), film type: 2 PP, 4 mikr., Eff. Diam. = 25 mm, eff. area = 490 mm^2). Solid-state one-dimensional of nuclear magnetic resonance spectroscopy (^{23}Na, ^{27}Al, ^{29}Si, MAS NMR) experiments were carried out by the Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic. They were measured at 11.7 T using a Bruker Avance 500 WB/US NMR spectrometer with double-resonance 4-mm probe-head at spinning frequency of 11 kHz. All spectra were acquired at TPPM15 decoupling sequence. To compensate for frictional heating of the spinning samples, all NMR experiments were measured under active cooling. The sample temperature was maintained at 308 K, and the temperature calibration was performed on $Pb(NO_3)_2$ using a calibration procedure described in the literature [14]. ^{23}Na MAS NMR spectra at 132.31 MHz were acquired, excitation $\pi/2$ pulse width was 3.2 μs; recycle delay 2 s ^{27}Al MAS NMR spectra at 130.33 MHz were gained, excitation $\pi/2$ pulse width was 1.2 μs; recycle delay 2 s and ^{29}Si MAS NMR spectra at 99.33 MHz were obtained with 90° pulse width was 4 μs and recycle delay 2 s. The spectra were calibrated at NaCl at −7.2 ppm, $Al(NO_3)_3$ at 0.0. ppm and M_8Q_8 at −109.8 ppm. The data was recorded after various periods of time. The XRD, XRF analyses were performed after 7, 28, 56, 90, 120, 360, 540 and 720 days. The scanning electron microscope [15] and Energy-dispersive X-ray spectroscopy (SEM-EDX) (30 keV) were performed by using Hitachi S4700 for a surface analysis. The SEM-EDX analysis was used to study the distribution of Na in paste specimens. The specimens immersed in solutions were cleaved into two equal portions, and the new surface formed after cleavage was analysed. From the centre of the outer edge towards the centre of the surface, the average element percentages in mass were successively measured with the small spot on the surface. The areas of the analysed spots were about 0.16–0.45 mm^2. Concentration profiles of Na were created from the data of the analysed spots. The resulting values of NMR and XRF method represent an arithmetic mean (n = 3). The average error incurred to XRF method about 0.2 relative percent, and to NMR about 3%.