Production of refractory chamotte particle-reinforced geopolymer composite

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Abstract. Geopolymer resins are obtained by alkaline activation of aluminosilicate sources where raw calcined clays are one of the suitable potentialities. Besides the fact that chemical composition has an essential effect on final properties of the geopolymer binder, the type of filler strongly affected resulting properties of such granular composite. However, very few comparative studies have been done on detail description of composite systems: binder – granular filler, in relation to aggregate gradation design and rheology properties of the mixture. The aim of this work is to develop and describe granular composite concerning workability of the mixture and kinetics of geopolymerization/polycondensation through flow behaviour. The rheological measurements indicated that initial viscosities of the mixtures and their evolution are different for various proportions of the filler. Moreover, it was demonstrated that increase in complex viscosity responds to the creation of chemical bonds and the formation of structural network. Finally, a correlation of the mechanism of geopolymer formation was carried out by differential scanning calorimetry (DSC).

1. Introduction

Geopolymer binders can be considered as a class of inorganic polymers having predominantly amorphous structure consisting of tetrahedrons SiO4 and AlO4 mutually bonded by oxygen bridges [1]. Thus, the complex structure of polymer network is formed based on Si-O-Al chains. The negative charge in the aluminosilicate network is balanced by alkali cations (mostly Na+, K+, Ca2+) in the cavities of framework [2,3]. Geopolymers are generally prepared via alkaline solutions by mixing of an aluminosilicate raw material in form of powder derived from natural minerals (calcined clays, natural pozzolans) or industrial products (fly ash, blast-furnace slag, silica rich waste sludge) [4-6]. The mechanism for geopolymer formation involves a reaction between aluminosilicates and alkali metal hydroxides/silicates [7]. The first disaggregation process entails the severance of the Me–O (where Me is Na+ or K+), Si–O–Si, Al–O–Al and Al–O–Si bonds on the surface of solid particles. Dissolution of the solid aluminosilicate source by alkaline hydrolysis produces aluminate and silicate species [8]. Also, the effect of hydroxy groups on the Al-O-Si and Si-O-Si bonds results in disaggregation/dissolution of alumimates-silicates and formation of hydroxylated complexes such as Si(OH)4 −, Al(OH)4 − or Al(OH)3−6 [9]. Once, the species and complexes are released and incorporated in aqueous phase by dissolution, the accumulation enhances contact among the disaggregated products and coagulated structure is formed [10]. This results, in concentrated solutions, into the gel precipitation through oligomers networking in aqueous phase by condensation process.
The geopolymer binders with a cured rigid structure are represented by good resistance to high temperatures, acid resistance and mechanical properties [11,12]. Hence, it is an attractive alternative to standard Portland cement where advanced technical properties of binders are requested. The physical properties of geopolymer mixtures are strongly dependent on the type and chemical composition of raw materials, Si/Al molar ratio of prepared slurry and cured conditions [13-15]. The processing properties of geopolymer binders also depend on the rate of water add to the mixture, proportion of raw materials and stirring conditions. Also, plate/lamellar-like particle shape of clay minerals affects rheological properties of the fresh paste, such as thixotropic behaviour with a relatively high yield stress [16]. The rheology of fresh geopolymer pastes is highly complex process because of the mutual interactions such as surface forces during dissolution including chemical and mineralogical factors, contact forces between particles, ratio of water, mixing conditions as well as proportion and type of filler [17].

The aim of the present study was to investigate the effect of granular filler of ceramic grog on the rheological properties of variously filled geopolymer paste based on potassium silicate solution. Differential scanning calorimetry (DSC) was used to study the curing process at elevated temperature through reactions of heat change.

2. Experimental and methods

The geopolymer paste was synthesized as a two component system consists of alkaline potassium silicate solution with silica modulus 1.6 and reactive schistous clay residues as a main source of solid silica and alumina as presented in Table 1 with particle size distribution details as follows: d50 at 3.98 μm, d90 at 6.87 μm and BET surface area 12.99 m2 g⁻¹. The mixture was formulated by molar ratios: SiO₂/Al₂O₃ = 2.5, SiO₂/K₂O = 6.80, Al₂O₃/K₂O = 2.80, H₂O/K₂O = 19.00. The ceramic grog as granular filler was used with maximum grain size 1 mm and specific aggregates gradation design as presented in Figure 1.

| Table 1. Main chemical composition of solid and liquid components (mass %) |
|-----------------|-----|-----|-----|-----|-----|-----|-----|
| Clay residues   | SiO₂| Al₂O₃| CaO | MgO | TiO₂| K₂O | Fe₂O₃|
|                 | 50.20| 45.10| 0.12| 0.15| 1.45| 0.62| 1.00|
| Silicate solution| 17.57| -    | -   | -   | -   | 17.10| -    |

The geopolymer paste was prepared in the mass ratio 1/0.8 (solid/liquid). The materials were proportioned by weight ratio for optimum workability and the mixing was conducted in a laboratory automatic blender for 6 min (1000 rpm). After that the batch of A111 filler was added and the final mixture was blended for an additional 5 min.

The filler gradation design was applied with various proportion of ceramic grog to clay residues expressed as mass% in the range 260 – 320 mass%.

Dynamic rheological measurements were performed using a rotary rheometer (Ares G2, TA Instruments) operated in oscillation mode with small amplitude. Time sweep experiments were performed at an angular frequency 10 rad/sec (1.59 Hz) and strain rate 0.01% in plain-plain geometry as presented in Figure 1, detail (a, b). The curing kinetic at 30, 60 and 80°C was evaluated by differential scanning calorimetry (DSC Q200, TA Instruments) using Tzero hermetic alodined aluminum pans/lids. The purge gas was nitrogen at flow rate 50 mL min⁻¹.

3. Results and Discussion

3.1. Rheology

As shown in Figure 2, the rheological time sweep measurements indicate the increasing of viscosity in time for all filled mixtures. The time zero is taken as a + 15 min in virtue of preparation of the mixture for each measurement at 30 °C ± 0.1°C. The higher proportion of granular filler increased viscosity rapidly in comparison with the other states, as presented in the Figure 2 (4). This evolution
corresponds to the creation of chemical bonds within the reactive mixture [18] and evidently to the rapid desiccation of the gel infilled by fine particles of ceramic grog. As presented in Figure 2 (0), the unfilled paste indicates minimal viscosity change in setting time (8000 s). Whereas, the filled mixtures started notable increasing their viscosities after 2000 s. The geopolymer mixture filled of 260 mass% reached its viscosity value to 5 GPa.s at 8000 s. Trend indicates that the increasing of proportion of the filler led to increasing of viscosity value and shorter setting time. As presented in Figure 2 (4), the highly filled paste increased its ultimate viscosity value to 7.5 GPa.s during 5000 s. The mixture was spontaneously detached plain-plain geometry after viscosity value reached its maximum.

**Figure 1.** Gradation curve for ceramic grog with a detail of plain-plain geometry (a, b) for dynamic rheological measurements

**Figure 2.** Viscosity curves in function of time of filled mixtures (1) 260 mass %, (2) 280 mass %, (3) 300 mass %, (4) 320 mass % and (0) unfilled paste
3.2. Curing kinetics
The geopolymer paste based on potassium silicate solution was measured by differential scanning calorimetry and started at a time + 10 min in virtue of stirring and moulding/setting the DSC run. The obtained thermographs indicate curing reactions as a heat evolution under isothermal conditions at 30, 60 and 80°C. The exothermic peaks appeared immediately after starting the measurements indicating the process of partial dissolution/disaggregation of solid particles in the strong alkaline aqueous solution as presented in Figure 3 (A1, B1, C1) [19]. Further, the formation of alumina/silica-hydroxy species and consolidation of larger network started as showed in Figure 3 (B2, C2) [20].

It is evident that the elevated temperature affects the mixture to release more heat within the increasing temperature. Also, the reaction rate in Figure 3 (C1) at 80°C is higher than that of A1 at 30°C implying that dissolution of raw material is accelerated by elevated temperature. This indicates that elevated temperature 60-80°C speed up curing time to ~ 20 min and both mechanism disaggregation and reorganization proceeds in short time period.

Figure 3. The effects of heat evolution under isothermal conditions at (A) 30 °C, (B) 60 °C, (C) 80°C

4. Conclusion
In this investigation, the influences of the proportion of granular filler to geopolymer paste were studied. Therefore, the ceramic grog with specific aggregate gradation design was applied in various proportions. It was showed, that increasing of proportion of the filler led to increasing of viscosity value and shorter setting time. Moreover, it was demonstrated that increasing of complex viscosity indicates the formation of structural network and gradual desiccation of the gel.

The curing kinetic of experimental mixture was described by effects of heat evolution at normal and elevated temperatures under isothermal conditions. The exothermic effects indicating acceleration of structural changes by elevated temperature in the range 60-80°C.
Acknowledgements
The result was developed within the CENTEM project, reg. no. CZ.1.05/2.1.00/03.0088, cofunded by the ERDF as part of the Ministry of Education, Youth and Sports OP RDI programme and, in the followup sustainability stage, supported through CENTEM PLUS (LO1402) by financial means from the Ministry of Education, Youth and Sports under the National Sustainability Programme I.

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