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Rheological characterization of fly ash-based suspensions

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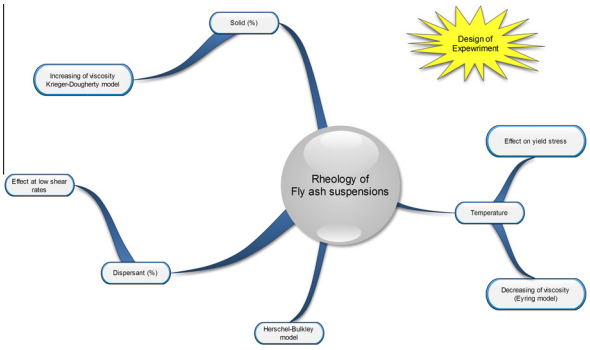
HIGHLIGHTS

- The yield stress is mainly influenced by temperature.
- The type of dispersant used have only a moderate influence on the rheology.
- Solid content is the most influential parameter on apparent viscosity.
- The apparent viscosity was found to decrease with temperature.
- Design of experiment is a valid support in the study of the geopolymer rheology.

GRAPHICAL ABSTRACT



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ABSTRACT

The importance of flow properties in most handling techniques requires specific characterizations of geopolymer rheology in the fresh state. In this work, a Design of Experiment (DOE) approach was used to evaluate the influence of solid load, temperature and dispersant on apparent viscosity and yield stress of fly ash-based geopolymers. The solid load was found to be the most influential variable on viscosity. An increase in solid load led to an increase in apparent viscosity but also of yield stress. Apparent viscosity was found to have an Arrhenius type relationship with temperature. The influence of dispersant on yield stress and viscosity appeared to be minor.

1. Introduction

Geopolymers form a class of inorganic polymers, largely X-ray amorphous, generally synthesized by reaction of aluminosilicate powder with a concentrated alkali hydroxide solution, and if necessary a silicate solution. Their typical structures consist of tetrahedral $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ connected by oxygen corners [1,2]. Geopolymers exhibit interesting physical and mechanical properties, and can potentially be used in a wide range of applications, such as concrete pavements and products, immobilization of toxic, hazardous and radioactive wastes, fire resistant composite and refractory ceramics [3]. Even though the exact synthesis mechanism of geopolymers is not yet fully understood [4,5], the following step mechanisms are generally accepted [2,4].

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(a) Dissolution of the aluminosilicate source in highly alkaline aqueous solution, including breaking of the covalent Si–O–Si and Al–O–Si bonds. At high pH, the dissolution of aluminosilicate occurs quickly, releasing (probably monomeric) aluminates or silicates.
(b) Condensation, in which the monomers react via both addition and autocatalytic polymerization, leading to a tridimensional structure mainly composed of aluminosilicate monomers and oligomers, with the consistence of a gel.
(c) Polymerization, in which the gel continues to rearrange and the connectivity of the polymeric chains increases, resulting in a solid tridimensional aluminosilicate network.

The major driving force for the extensive research and development of geopolymeric materials is their potential as substitutes for Portland cement. In fact, the possibility to use metakaolin, which is obtained from the calcination at 450–800 °C of kaolinites [6] rather than 1400–1500 °C of clinker, or secondary raw materials, obtained as waste from other productive processes, will lead to economic and environmental benefits, e.g. a drastic reduction of CO_2 emission per ton of cement [7]. Most of the research carried out during last decades has dealt with metakaolinite and coal fly ash as raw materials. However, other aluminosilicate sources, such as blast furnace slag or red mud can also be used [8–10].

The workability of geopolymers is determined by using empirical methods established for Portland cement based materials, such as mini slump test [11].

Since typical handling techniques for concrete products, like casting, molding, pumping and spreading, are strongly dependent on rheological properties of materials [10], as demonstrated by the large number of works present in literature on the subject for Portland based cements [12–16], it is rather surprising that only a few studies have been conducted about the rheology of geopolymers at the early stage, prior to setting/hardening. In addition, often rheology measurements were used as an indirect method to better understand geopolymeric reaction kinetics and setting behavior, rather than focusing on identifying rheological behavior. For instance, Rahier et al. used dynamic mechanical analysis (DMA) to monitor the hardening process in metakaolin-based geopolymers [17]. Phair et al. evaluated the possibility to use rheology to investigate early age properties of geopolymers, and found that the technique is sensitive to compositional variations [18]. Palomo et al. use rheological measurements to study the rate of reaction in fly ash-based geopolymers, and found that there is an Arrhenius-type relationship between setting rate and temperature [19]. Rheological behavior of fly ash-based geopolymer mortar with fine and coarse aggregates was studied by Bhattacharjee and Laskar [20]. Poulesquen et al. used dynamic rheology to investigate the evolution of viscoelastic parameters during geopolymerization in metakaolin-based geopolymers [21]. Romagnoli et al. used a DOE approach to evaluate the influence of solid load, curing temperature, curing time and dispersant content on apparent viscosity and yield stress both for fresh and aged metakaolin-based geopolymers [22]. Solid load and temperature were found to be the most influential variables on both analyzed responses. The authors observed that an increase in solid load lead to an increase in viscosity and yield stress. These observations were explained by higher interaction forces among particles in the suspension when the solid load was increased. Viscosity and yield stress were also found to increase with temperature for both fresh and aged samples. This was attributed to a speedup in geopolymerization reactions, leading to a faster formation of geopolymeric structures.

The DOE technique is an approach used to minimize the number of experiments necessary to obtain statistically valid relationship between response and factors within an experimental field. Regression methods are used to analyze the data and the validity of the results can be evaluated using statistics such as goodness of fit (adjusted-R^2), goodness of prediction, analysis of variance (ANOVA) and normal probability plots [23]. In addition, synergic and competitive effects eventually present among factors can be revealed.

Since the final properties of geopolymers are strongly influenced by raw material characteristics [24] it is logical to expect differences also in rheological behavior. Hence, the aim of this work is to contribute to a full understanding of geopolymer rheology, focusing on fly ash-based geopolymer. For the first time in this work, a methodic approach as design of experiment was used to study the rheology of fresh fly ash-based geopolymer pastes. The influence of solid load, curing temperature and dispersant additive concentration on basic rheological parameters were investigated.

2. Experimental

2.1. Materials

Industrial grade of sodium silicate (Crystall 79°, PQ corp. Liverpool, UK) having a SiO_2/Na_2O mean molar ratio of 3.41, a mean density of 1.40 g/cm^3 and a viscosity of 2.5–5.0 mPa s at 20 °C was used together with sodium hydroxide (Purity ⩾ 99.0%, PQ corp. Liverpool, UK), distilled water, sodium polyacrylate and class F fly ash [25] to prepare the geopolymeric suspensions used for rheological characterizations. The fly ash, derived from combustion of coal for energy production. X-ray fluorescence (XRF) was used to determine the chemical composition. The mineralogical composition, including both crystalline phases and the amorphous fraction, was determined using X-ray diffraction (XRD, Philips PW3710, Bragg–Brentano geometry, Cu-anode and gas proportional detector) and the combined Rietveld-RIR method [26]. Rietveld refinements were performed using the GSAS package [27] and its graphical interface EXPGUI [28]. As required by the adopted method, 10 wt.% of an internal standard (corundum NIST 676a) was added to the dry sample (105 °C for 24 h). The mixture was grinded by hand in an agate mortar and subsequently side-loaded in an aluminum sample holder and analyzed.

Laser particle size distribution analysis (Malvern mastersize 2000) was used to determine the fly ash particle size distribution (PSD). A sodium polyacrylate, (water solution with 50 wt.% sodium polyacrylate, molecular weight 2000, supplied by Lamberti S.p.A) was used as dispersant. The samples were prepared according to the following procedure:

(1) A 20 M aqueous solution of sodium hydroxide was prepared and consequently stored in a polypropylene bottle.
(2) The activating solution was prepared by mixing distilled water, sodium silicate solution, sodium hydroxide solution (20 M) and sodium polyacrylate in a polyethylene container.
(3) The fly ash was slowly added to the activating solution and hand stirred for five minutes.

2.2. Rheological measurements

A coaxial cylinder rheometer model Haake RS1 was used to perform rheological measurements.

Wall slippage phenomenon was avoided by using serrated measurement surfaces [13]. The rheometer was equipped with a thermocryostat, allowing precise control of the sample temperature during measurement.

The chosen procedure for measurements is represented in Fig. 1. The first step consisted in a pre-shear at 100 s^{-1} for 60 s followed by a rest period of 60 s, and was performed to reduce memory effects. In the second step, a shear stress ramp from 0 to 400 Pa was performed in steady state mode. A total number of 100 measurement points were acquired during the tests. The acquisition was carried out in logarithmical mode, in order to have a higher resolution at low shear rates so improving the data-fitting for the identification of yield stress.

To prevent evaporation during measurements, a thin film of silicon oil was applied over the air-exposed sample surface to isolate it from direct contact with the air.

2.3. Experimental design

The experiments were performed according to a Box–Wilson design, also called Central Composite Design (CCD) [23]. The studied variables and their variation ranges are reported in Table 1. The Box Wilson design is a full factorial design with added central points, which are positioned at the medium value of each variable, and faced points, that correspond to the medium value of one variable and the extreme values of the remained variables. The full experimental design is reported in first four columns on the left in Table 2. The silica/alumina molar ratio