Mechanical properties and compositional heterogeneities of fresh geopolymer pastes

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A B S T R A C T

This work explains the elastic properties of the reactive suspensions of metakaolin in sodium silicate solutions immediately after mixing. The flow properties of the interstitial fluid were obtained by mimicking it with synthetic aluminosilicate gels of different Si/Al molar ratios. By comparing these results with the rheological properties of fresh geopolymer pastes and with the ones of unreactive suspensions, we showed that the early age mechanical properties of geopolymer mixes cannot be explained by the colloidal interactions between metakaolin grains but rather by the formation of a gel with a molar ratio Si/Al<4.5. In addition, we measured the evolution of the total concentration of tetrahedral Al in the interstitial liquid by static NMR. It was thus evidenced that the afore-mentioned aluminosilicate gel is formed at a very early stage of the geopolymerisation reaction resulting in a heterogeneous suspension with an Al-rich gel formed at the grain boundaries.

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1. Introduction

Concrete is the most commonly used construction material. Its use by the communities across the globe is second only to water. Customarily, concrete is produced by using Ordinary Portland Cement (OPC) as the binder but OPC's production is highly energy intensive and releases massive amounts of carbon dioxide (CO_2). Due to a world-wide increase in the demand for OPC [1], cement production could represent nearly 10% of the total anthropogenic CO_2 emissions in the close future. As a result, numerous studies have dealt with mitigation perspectives in the cement industry [2–7]. A recent one showed that it is possible to halve, based on the 1990 levels, the CO_2 emissions due to cement production in developed countries by improving current technologies [8]. However without a technological turn around, the goals recommended by the Intergovernmental Panel Group for Climate Change (IPCC), that is a reduction by a factor 4 of CO_2 emissions, will not be reached [8]. New low-CO_2 binders are therefore needed to meet the demand for concrete and still reach the CO_2 reduction goals. Among these new binders, it is commonly accepted that sulfo-aluminate clinkers and geopolymers have high potentials [9–11].

Geopolymers are based on the chemistry of alkali activated inorganic binders. This chemistry is involved in antique binders [12] and has been accidentally rediscovered by Purdon in the contemporary era [13]. In fact, geopolymers have already been used in the 1950's as a cement replacement binder in many buildings that are still in service today [14]. These binders were made with alkali and slags. In the 1970's, Davidovits coined the term "geopolymer" and developed a binder which resulted from the hydroxylation and polycondensation reaction of thermally activated kaolin (metakaolin) in an alkaline solution [15,16]. In the last 15 years, an intensive academic research on these binders has considerably extended the understanding of the geopolymerisation [e.g. 17–19] and led to an intense development of both research and applications.

Geopolymer can be categorized as a "low-carbon" binder, as the CO_2 emitted during its production can be as low as 10% of the CO_2 remitted during OPC production [20,21]. However, the use of water glass leads to significant environmental impacts such as surface water acidification which can reduce the environmental benefit of producing and using geopolymers as a substitute to OPC [22]. A better mix design is therefore needed. Actually, recent research in cement technology has shown that a detailed understanding of the physics and chemistry of setting allows the development of tailored mixes with a reduced binder content but that still fulfils the mechanical requirements of the industry for the paste (setting time, yield stress during casting, compressive strength after 24 h) [23]. Along the same line, it can be expected that a better understanding and control of the setting behaviour of geopolymers would permit a significant reduction of their environmental impacts when used as binders. In that respect, previous studies have applied a variety of techniques in the analysis of the early stage of geopolymerisation. In particular

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calorimetry [24,25], scanning electron microscopy (SEM) [26,27], X-ray diffraction (XRD) [28–30], Fourier transform infrared spectroscopy (FTIR) [31,32], in-situ energy dispersive synchrotron diffractometry [33], nuclear magnetic resonance (NMR) [28,34–36] and rheology [37,38] have been used to progress the understanding of the kinetics of geopolymerisation. Also, synchrotron radiation-based infrared microscopy and in-situ neutron pair distribution function (PDF) analysis have been able to provide details on the local gel structure [39], which is largely responsible of the macroscale properties of the material. However none of those techniques are able to be simultaneously spatially time resolved with a sufficient resolution during the early stage of the geopolymerisation, that is before setting.

There is actually a dilemma. Either the local organisation is clearly observed but on solid end-products (e.g. SEM or spatially resolved FTIR), or the reaction is followed in time but with tools that probe a mean organisation and are thus insensitive to local heterogeneities (e.g. calorimetry, XRD, NMR, FTIR or neutron PDF analysis). This might be of importance because the characterization of solid end-products has evidenced that geopolymer gels are highly heterogeneous and that this heterogeneity depends on the availability of Al and Si species in the liquid phase [40,41]. Likewise, in the fresh paste, changes in the gel microstructure have been evidenced with a transition from a first Al-rich geopolymer structure to a more stable and resistant Si-rich gel but it has not been possible yet to localize those gels [42].

The objective of this study is thus to solve this experimental dilemma by relating the mechanical properties of the geopolymer paste at different stages of reaction to eventual compositional heterogeneities. NMR was used as an indicator of bulk chemical modifications while rheology allowed to follow the mechanical consequences of the chemical reactions and to infer details of the interactions at grain boundaries. Furthermore, the contributions of the different constituents of the paste have been disentangled by comparing the behaviour of the geopolymer mix to the one of the model mixes with synthetic aluminosilicate gels or inert solid fractions (kaolinite). In this manner, we showed that the early age mechanical properties of geopolymer mixes can be explained by the formation of a gel at the grain boundaries with local compositions differing from the bulk.

2. Methodological approach

2.1. General framework for the study

If air bubbles are not considered, a geopolymer mix at an early stage of the reaction can be seen as a three phase material.

The first phase is the aluminosilicate precursor which is added as a solid phase. Due to the chemical and mineralogical complexities of slags and fly ashes, metakaolin was chosen here as a simple precursor, reducing therefore the number of possible competing mechanisms [43].

The second phase is the alkaline solution which contains alkali and pre-existing silicate oligomers. Actually, it is known that a pure hydroxide solution leads, at least partially, to the formation of crystalline zeolitic products[44], and that consequently a solution of sodium silicate is needed to produce amorphous geopolymers. This sodium silicate alkaline solution has been widely studied from a chemical and a rheological point of view [45–47]. Recent results suggest that sodium silicate solution can be considered as concentrated newtonian solutions of interacting silicate oligomers with an effective average size in the nanometre range [48–50]. Moreover, sodium silicate solution viscosity was shown to be partly predicted by the Mark–Houwink equation used for electrolyte and organic polymer solutions [49].

The third and last phase is the reaction product between the two previous ones, namely here the metakaolin and the alkaline silicate solution. This product is certainly the most complex phase present in the paste and is probably not homogeneous even when the initial reactants are homogeneous and well mixed [51,52]. This phase is essential as it is the one that will ultimately be responsible for the mechanical properties of the geopolymer mix [53]. Previous authors have already studied these geopolymer gels alone by synthetizing them in the absence of solid aluminosilicate precursors through the mixing of silicate and aluminate solutions [54–56] and have emphasised the dependency of their mechanical properties on the Si/Al ratio. They have also established that these hydrogels constitute good analogues to the geopolymer mixes [55,57].

The fundamental consideration of the present study is that what prevents the assessment of the mechanisms at the origin of the rheological properties of a geopolymer mix is the fact that, in the fresh state, the above three main phases are hardly distinguishable with most existing and standard experimental tools. We therefore choose to observe them separately and, through basic upscaling approaches, conclude on the underlying physics and chemistry of the geopolymer paste.

In a first step, we therefore measured the rheological behaviour of the geopolymer mix (i.e. the three phases). In a second step, we measured the behaviour of a non reacting geopolymer mix (i.e. a mix of the liquid and solid phases without the reaction product) along with the behaviour of the alkaline solution. In a third and final step, we measured the behaviour of a synthetic geopolymer gel (i.e. the reaction product alone).

Fig. 1 schematises this general framework. For the first step, metakaolin and alkaline solution were mixed together and observed at 20 °C (Figs. 1, 3 phases).

For the second step, metakaolin and alkaline solution were mixed together under a temperature of 5 °C, which considerably slowed down the mechanisms necessary for the geopolymerisation reaction (i.e. dissolution and diffusion) and therefore allowed for the study of the properties of the two phases without having to consider their reaction products (Figs. 1, 2 phases). Similarly, mixing kaolin with alkaline solution allowed for the study of a model system containing non reacting solid particles with size and shapes similar to the reactive metakaolin in the true geopolymer mix. At an early age, indeed, the kaolin dissolution rate is considerably lower than the one of metakaolin [58] (Figs. 1, 2 phases).

Finally, in the third step, synthetic aluminosilicate gels were produced by mixing a silicate solution with an aluminate solution. This allowed for the study of homogeneous gels separately from the reaction mixture (Fig. 1, 1 phase).

2.2. Materials

2.2.1. Preparation of geopolymer paste

The metakaolin (MK) used as a starting material for this research was Argical M-1000 from AGS minéraux (France). The kaolin was provided by Merck. Both products have a d50 around 10 μm but kaolin has a smaller grain size than MK as shown in Fig. 2. The BET specific surface areas are equal to 20 m²/g for kaolin and 17 m²/g for MK.

The alkaline solutions were prepared from a commercial sodium silicate solution (VWR International, France), sodium hydroxide pellets (Merck KGaA, Germany) and distilled water. They were prepared by mixing solid NaOH and liquids (sodium silicate and distilled water) in a closed plastic bottle to prevent evaporation. The solutions were then allowed to cool for 24 h. Three solutions were prepared with H_2O/Na_2O molar ratio of 10, 16 or 20 but with a constant SiO_2/Na_2O molar ratio of 1.06.

MK and alkaline solution were mechanically mixed with a stirrer during 5 min. The mass of MK was adjusted relatively to the alkaline solution in order to provide suitable SiO_2/Al_2O_3 and Na_2O/Al_2O_3 ratios (i.e. around 4 and 1 respectively) [59]. The mass of MK was also adjusted according to the experimental device of interest in order to provide the best measurement conditions. Indeed, better rheological measurements are obtained for high solid volume fractions while