Mechanical properties and compositional heterogeneities of fresh geopolymer pastes

A. Favier [a], G. Habert [a,b,*], J.B. d'Espinose de Lacaillerie [c,d], N. Roussel [a]

[a] Univ Paris-Est, IFSTTAR, Materials department, 58 bd Lefebvre, 75732 Paris cedex 15, France
[b] Institute for construction and infrastructure management, ETH Zürich, 8092 Zürich, Switzerland
[c] ESPCI ParisTech, Soft Matter Sciences and Engineering laboratory SIMM, UMR 7615 ESPCI-CNRS-UPMC, 10 rue Vauquelin, 75005 Paris, France
[d] Institute for building materials, ETH Zurich, 8092 Zürich, Switzerland

ABSTRACT

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.

© 2013 Elsevier Ltd. All rights reserved.

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

* Corresponding author at: ETH Zürich, IBI, HIL F 27-3, Wolfgang Pauli Str. 15, 8092 Zürich, Switzerland. Tel.: +41 44 633 05 60; fax: +41 44 633 10 88.
E-mail address: habertg@ethz.ch (G. Habert).

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
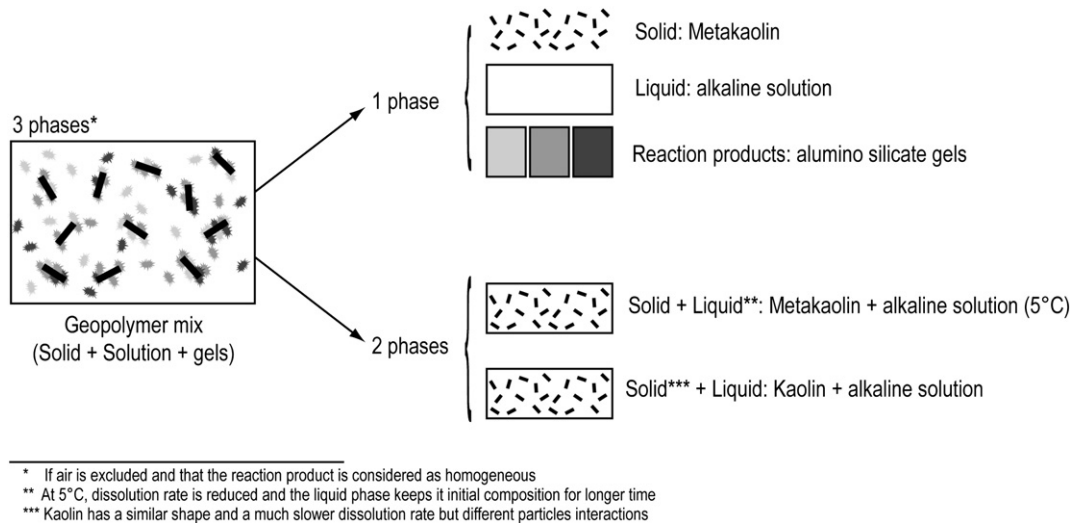
* If air is excluded and that the reaction product is considered as homogeneous
** At 5°C, dissolution rate is reduced and the liquid phase keeps it initial composition for longer time
*** Kaolin has a similar shape and a much slower dissolution rate but different particles interactions

Fig. 1. General framework of the experiments conducted in the study.

NMR measurements have a better resolution for lower solid volume fractions. These variations in the solid volume fraction modify the Na_2O/Al_2O_3 and SiO_2/Al_2O_3 ratios. In this study, we assumed that these two ratios although pregnant with the properties of the final solid products do not play a strong role on the early stages of geopolymerisation, which are much more controlled by the dissolution and polymerisation rates. Those latter mechanisms are instead deeply related to a molar ratio associated with alkaline solution (H_2O/Na_2O; SiO_2/Na_2O).

2.2.2. Synthesis of aluminosilicate gels

Aluminosilicate gels were prepared by mixing with a magnetic stirrer an alkaline solution of silica with an alkaline aluminate solution until the formation of a homogeneous gel. Both solutions were prepared 24 h before testing and allowed to cool. Silicate solutions were prepared from silica gel (Merck KGaA, Germany), sodium hydroxide pellets and distilled water. Aluminate solutions were prepared from sodium aluminate (Sigma-Aldrich, France), hydroxide pellets and distilled water. The chemical compositions of the gels are given in Table 1. All gels were prepared by varying only the concentration of aluminium in the system, which meant that the final solution always had similar H_2O/Na_2O and SiO_2/Na_2O ratios in order to keep the same silicon speciation in solution for all mixtures [45].

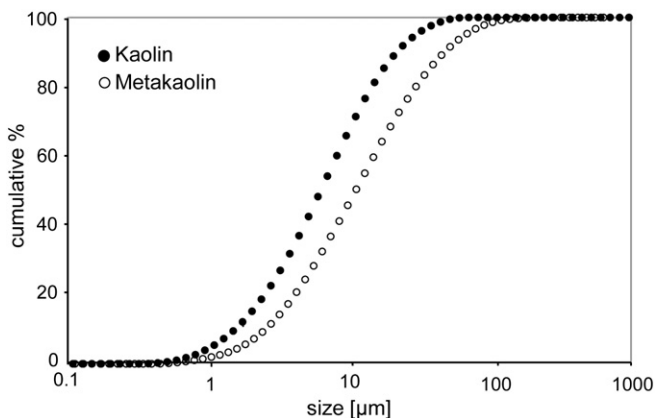Furthermore, these ratios were similar to the ratio used to prepare the alkaline solution for geopolymer mixes.

2.3. Experimental procedures

2.3.1. ^{27}Al NMR measurements

Nuclear Magnetic Resonance static (NMR) ^{27}Al experiments were performed on a Bruker Avance500 spectrometer at 11.74 T. The geopolymer paste was placed in a 5 mm PTFE tube. The one-pulse spectra were measured at different time intervals with a pulse width of 5 μs ($\pi/2$), 40 scans and a recycle delay of 1 s. ^{27}Al chemical shifts were referenced to an $AlCl_3$ 100 mM aqueous solution. The same solution was used to normalise the NMR signal intensities.

2.3.2. Rheological measurements

The rheological measurements were carried out with a C-VOR Bohlin® rheometer equipped with a vane geometry for geopolymer mixes [60]. The Vane geometry was chosen to minimise the disturbance of the material during the introduction of the geometry as well as to avoid wall slip [61]. For synthetic gels, the available quantities were insufficient for the Vane geometry, so a parallel plate geometry was used instead. This latter geometry is particularly adapted for liquid measurements [60].

For the test on geopolymer mixes, the paste was mixed with a mechanical stirrer for 5 min before immediate transfer into the rheometer's cup. An initial preshear at 100 s^{-1} during 60 s was applied prior to each test to ensure that all samples were in the same reference state of stress and strain.

The critical strain of the system marking the end of the linear elastic regime was assessed by applying strain oscillations of increasing amplitude at an oscillation frequency of 1 Hz. The storage modulus of the geopolymer mixes was then measured by applying strain oscillations of amplitudes lower than the critical strain of the network. As a consequence, the measurements were continuous, non destructive and gave data on the linear elastic behaviour of the system. Our data showed that the system deforms irreversibly above a critical strain of 0.1% (Fig. 3). It can be noted that this value was close to the one reported by Poulesquen et al. [38] and slightly higher than the 0.05% value obtained for traditional OPC pastes [62]. Consequently, the elastic modulus measurements were performed with a strain amplitude of 5×10^{-4} and a frequency of 1 Hz.

Fig. 2. Cumulative particle size distributions for the kaolin and metakaolin used in this study.

Table 1
Chemical composition of aluminosilicate gels expressed in mole percent.

Si/Al ratio	100	50	20	10	5	4.5	4.25	4	3.5	3
H_2O	83.90	83.85	83.71	83.48	83.02	82.92	82.86	82.79	82.63	82.42
Na	10.49	10.48	10.46	10.44	10.38	10.37	10.36	10.35	10.33	10.30
Si	5.56	5.56	5.55	5.53	5.50	5.49	5.49	5.49	5.47	5.46
Al	0.06	0.11	0.28	0.55	1.10	1.22	1.29	1.37	1.56	1.82

3. Results

3.1. Evolution of elastic modulus of geopolymer

While following the evolution of the viscoelastic properties (G' and G'') of a geopolymer mix through strain oscillations on the rheometer, a fast increase of viscous and elastic modulus was observed during the first several hundreds of seconds after the pre-shearing phase. This fast initial increase was followed by a slow linear increase of the modulus. Then, after a couple of hours, another sharp increase of the modulus was observed (Fig. 4). From a practical point of view, this second increase can be considered as the material's setting. Note that the above rheological evolution was exalted in the sample represented in Fig. 4 by using high volume fractions. The same trend was nevertheless observed for a more realistic lower MK content but with the modulus increases occurring at different times.

In this study, we focussed on the first part of the reaction, even if an explanation for the sharp increase of the modulus after 4 h will be discussed briefly at the end of the paper. A reasonable assumption is to consider the first strong increase of the elastic modulus as the macroscopic manifestation of the formation of a percolating network of interacting elements at the mesoscopic scale. At least two interaction modes could be at the origin of this network and of the associated observed elastic behaviour.

First, MK grains could interact directly via non-contact colloidal interactions such as van der Waals and electrostatic forces similarly to what happens in fresh cement suspensions [63,64]. It is well established that these elastic forces are at the origin of the coagulation of clay suspensions [65,66] but the system studied here was significantly different from traditional clay suspensions as MK is a dehydroxylated clay. Indeed, dehydroxylation is known to reduce the van der Waals interactions between kaolinite particles [67]. Moreover, the anionic silicate oligomers present in the alkaline solution are known to be very efficient clay deflocculants [68,69], acting probably by increasing the electrostatic repulsion between particles and thus counteracting attractive forces. In fresh geopolymer pastes, the formation of an elastic network by direct colloidal interactions between aluminosilicate solid precursors is thus a priori unlikely.

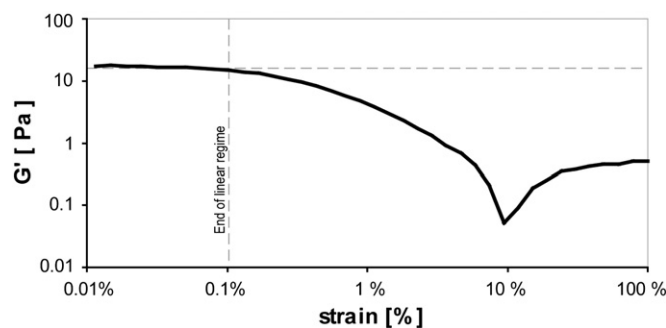Second, MK grains could interact indirectly through a mechanical solicitation (squeezing or shearing) of the interstitial fluid that separates them. It remains that in order to create a macroscopic elastic behaviour, the interstitial fluid must itself be elastic. As the original alkaline silicate solution has an almost purely viscous behaviour [50], this interpretation necessarily implies the formation of aluminosilicate reaction products within the interstitial fluid in order to modify the mechanical properties of the paste. This formation can either be homogeneous or heterogeneous as long as the resulting rheological behaviour of the interstitial fluid located between MK grains is predominantly elastic. In order to get a better understanding of the relative contributions of this possible indirect mode of interaction on the observed elastic modulus, we studied the rheological properties of synthetic aluminosilicate gels.

3.2. Elastic modulus of synthetic aluminosilicate gel

No significative elastic modulus was measured for the aluminosilicate gels with a molar ratio Si/Al higher than 4.5. In contrast, for those which have been prepared with lower Si/Al ratio, a linear elastic regime was observed until at least 1% of strain (Fig. 5). The following decrease in elastic modulus thus defined a critical strain always higher than 1%, a value which is one order of magnitude higher than the critical strain of the geopolymer mixes tested in Section 2.3.2 (i.e. 0.1%). Furthermore, the elastic modulus values for gels with Si/Al molar ratio lower than 4.25 are also one order of magnitude lower than the elastic modulus of the geopolymer mix and the elastic modulus for the gel with a Si/Al molar ratio of 4.5 is higher by a factor 2.

At this stage, it is useful to analyse these results through an elementary scaling law approach. If as a first approximation, the geopolymer mix can be considered as a homogeneous gel phase in which MK grains are suspended and since the gel phase has obviously a lower elastic modulus than the rigid MK grains, any given macroscopic deformation will concentrate in this soft interstitial gel phase. The interstitial gel has therefore to accommodate a higher local strain $\gamma_{interstitial}$ than the macroscopic strain $\gamma_{macroscopic}$. This local strain can be estimated from the macroscopic strain following:

$$\gamma_{interstitial} \cong \gamma_{macroscopic} \cdot \frac{d}{h} \qquad (1)$$

Fig. 3. Shear elastic modulus (G') as a function of shear strain for a typical metakaolin geopolymer formulation (volume fraction $\Phi = 0.22$, $H_2O/Na_2O = 16$). The oscillation frequency is 1 Hz.
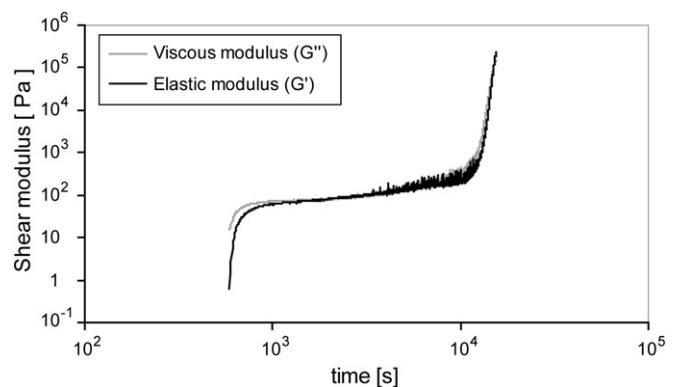

Fig. 4. Evolution of viscoelastic parameters during geopolymer setting (T = 26 °C) on a metakaolin geopolymer mix designed to exalt the rheological behaviour (volume fraction $\Phi = 0.3$ and $H_2O/Na_2O = 10$). The oscillation frequency is 1 Hz and the shear strain is 5.10^{-4}.
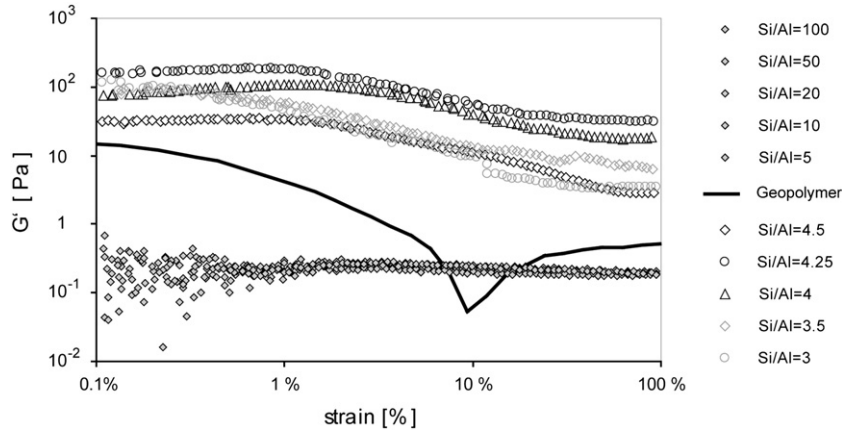
Fig. 5. Shear elastic modulus as a function of strain for different materials: one geopolymer (volume fraction $\Phi = 0.22$, $H_2O/Na_2O = 16$) and synthetic gels prepared with different Si/Al ratios. The oscillation frequency is 1 Hz.

where d is the particle diameter and h the inter-particle distance. The above relation assumes that the system is isotropic, homogeneous and not flocculated. For the systems considered here, d is of the order of 10 μm. Considering the solid fraction, the average inter-particle distance could be estimated as being one order of magnitude lower. In such a configuration, the local strain shall be around ten times higher than the macroscopic strain. The observed critical macroscopic strain in the order of 0.1% for the geopolymer mix was therefore compatible with a critical local strain in the order of 1% for the interstitial gel phase.

Similarly, concerning the stress that the network can resist to, the local elastic modulus has to be higher than the macroscopic elastic modulus. Roussel et al. [62] estimated that, for the particles of diameter d, separated by elastic cylinders of diameter D and of elastic modulus G'_{local}, the macroscopic elastic modulus of the suspension is of the order of

$$G'_{macro} \cong G'_{local} \cdot \frac{D^2}{d.h} \qquad (2)$$

where h is the inter-particle distance. Applying this relation to the particle studied here suggests a factor 5 between the macroscopic and local moduli. If this is the case, then the gel separating the MK grains shall have an elastic modulus close to the one observed in the synthetic gels with Si/Al ratio equal to 4.5 or 4. Reciprocally, this strongly suggests, first that a gel forms between the MK grains, and second, that this gel has a Si/Al ratio of about 4.5 or above.

All these observations are thus in accordance with an attribution of the macroscopic elastic modulus to the mechanical solicitation of reaction products formed between the MK particles. However, a contribution of direct colloidal interaction between MK grains still could not be strictly ruled out. To do so, the behaviour of a system involving non reacting rigid particles in an alkaline silicate solution was studied in order to evaluate the potential contribution of direct particles interactions.

3.3. Elastic modulus and grain interactions

3.3.1. Rheological properties of kaolin based mixture

The time evolution of the elastic modulus was compared for suspensions prepared with either kaolin or MK grains in two different alkaline solutions which have different alkalinities ($H_2O/Na_2O = 10$ and $H_2O/Na_2O = 20$) but a similar modulus ($SiO_2/Na_2O = 1.06$). As the elastic modulus of kaolin based suspension is considerably higher than the one of MK based suspensions, the values were normalised by the value reached after the initial increase in elastic modulus. The results are shown in Fig. 6 and highlight the fact that the elastic

modulus evolution of kaolin based suspensions is not influenced by a modification of the alkaline solution composition contrarily to MK based suspensions. This confirmed a-posteriori that kaolinite could be considered as chemically inert in the sodium silicate solution. Hence, the time evolution of the elastic modulus of the kaolin suspension was solely due to physical coagulation or flocculation. These physical processes are dictated by the competition between Brownian motion that tends to bring the particles into contact and viscous effects, which dissipate the particle kinetic energy and slow the coagulation or flocculation process down. These processes thus only slightly depend on the alkaline solution composition through the viscosity. On the contrary, the time evolution of the elastic modulus of MK based suspensions is strongly dependent on the alkaline solution composition, which suggests that the kinetics of dissolution and diffusion of Al, which both strongly depend on the alkaline solution composition are at the origin of the measured elasticity.

3.3.2. Rheological properties at 5 °C

To further confirm the conclusions of the previous section, the time evolutions of the modulus at different temperatures were compared. At low temperature, due to a decrease of the dissolution rate of aluminium, the geopolymerisation reaction is quenched for a sufficient time and a rheological characterization of the pastes is possible. Indeed, a comparison of the elastic modulus evolutions of a geopolymer mix at 5 °C and 20 °C showed that although the final measured values were similar, the initial fast increase observed at 293 K was already considerably slowed down at 278 K (Fig. 7). In Fig. 7, the characteristic times, which can be evaluated, for instance, as the time at which the elastic modulus reaches 80% of its final
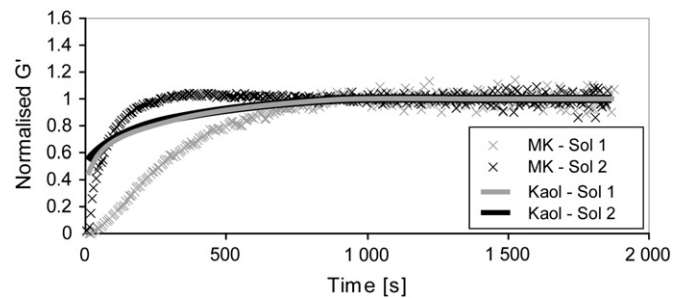

Fig. 6. Time evolution of the elastic modulus of suspensions made with kaolin (volume fraction $\Phi = 0.3$) or MK (volume fraction $\Phi = 0.22$) in alkaline solutions with two different H_2O/Na_2O molar ratios. Solution 1: $H_2O/Na_2O = 10$; solution 2: $H_2O/Na_2O = 20$. Elastic modulus is normalised to the plateau value of each curve.
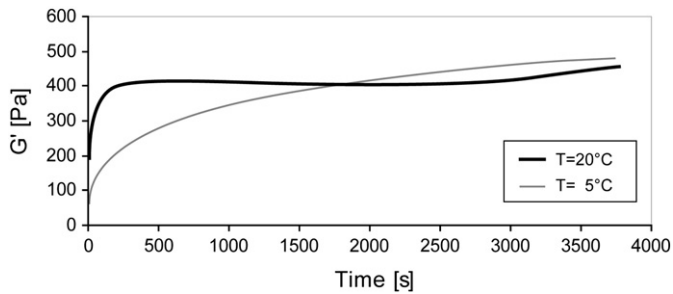
Fig. 7. Elastic modulus as a function of time for a geopolymer paste at two different temperatures with volume fraction $\Phi = 0.3$; $H_2O/Na_2O = 20$ and $SiO_2/Na_2O = 1.06$. The oscillation frequency is 1 Hz and the shear strain is 5.10^{-4}.

Fig. 8. Evolution of aluminium content measured in static NMR for various solid volume fractions of MK in an alkaline solution with $H_2O/Na_2O = 16$.

value, are changing by a factor of 15, from 100 s at 293 K to 1500 s at 278 K.

To associate the retardation of the development of the elastic modulus at a low temperature to a quenching of the geopolymerisation reaction, it is necessary to first rule out a slowdown of the Brownian motion at a low temperature that could reduce coagulation and flocculation of MK grains.

For particles of diameter d in a suspension of viscosity η, the temperature dependence of the time t that a particle needs to cover a distance h can be estimated in the case of Brownian motion by:

$$t = \frac{h^2}{D} \text{ with } D \propto \frac{k_B T}{6\pi \eta d} \tag{3}$$

and consequently one can expect that

$$t \propto \frac{1}{T}.$$

A change in temperature from 293 K to 278 K would thus result in a change in the characteristic time by a factor of only 1.05 (considering that the viscosity of the carrying fluid remains around 3 Pa·s in this temperature range). The observed change by a factor of 15 is thus considerably higher than what would be expected if only colloidal interactions between rigid particles were involved. It could thus be safely concluded that the increase of the elastic modulus during the first time of the reaction was a result of the dissolution/polymerisation reaction and not of the colloidal interaction between MK grains.

To conclude, at this stage, it was evidenced that colloidal interactions between metakaolin grains are not the main drivers for the very early age mechanical properties of geopolymer mixes but that a geopolymeric gel located at the grain boundaries is responsible for the elastic modulus of the geopolymer mixture.

3.4. Determination of Al content in the liquid phase

The amount of Al in the liquid phase was determined by static NMR measurements throughout the entire reaction. The measured Al is expressed relatively to the total amount of Al that can be released by the MK introduced in the mix. During the first couple of hours, the same percentage of Al was dissolved no matter the initial solid volume fraction of MK (Fig. 8). This fact suggested that, during this time, the dominant mechanism was the dissolution of Al which is expected to be directly proportional to the available surface of MK exposed in contact to the alkaline solution, which in turn is related to the amount of available MK. The linear increase in Al content observed from the very first point less than 10 min after the end of mixing up to the first couple of hours suggested that dissolution stayed the dominant mechanism. The existence of a peak in the percentage of Al content as shown in Fig. 8 showed that at a later time, a second mechanism involved the Al extracted from the MK. This
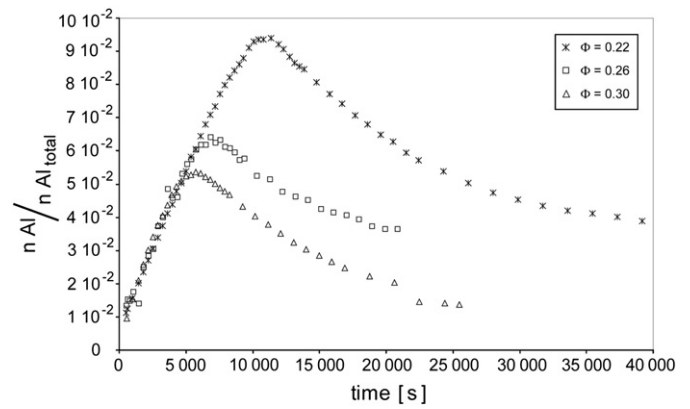
mechanism was either negligible at shorter times or needed a certain amount of aluminium dissolved in the solution to occur. The occurrence of this peak was correlated with the time at which the second sharp increase in elastic modulus was observed (Fig. 4). This correlation certainly needs further experiments to be fully understood but it is probably rich in significance and will thus be discussed albeit briefly at the end of the present paper.

NMR measurements showed that at 300 s after mixing, which is when the first elastic modulus developed, no more than 1% of the total Al was present in the liquid. If an homogeneous repartition of Al is supposed, this corresponded to a lower bound for the Si/Al molar ratio equal to 50 in the liquid phase for a geopolymeric mixture made with $H_2O/Na_2O = 16$ and a volume fraction of 0.22. However, our experiments on synthetic aluminosilicate gels clearly demonstrated that for such ratios no elastic modulus can be observed; Si/Al ratios lower than 4.5 were needed to record an elastic modulus commensurate to the one measured in the geopolymer mixes. As a consequence, since, as we have previously established, the elastic modulus of the geopolymer paste was controlled by the presence of an aluminosilicate gel, it is necessary to consider that the Al dissolved from the MK was not homogeneously distributed in the solution but was rather concentrated in the gel at the grain boundaries.

4. Discussion and suggested phenomenology

From the rheological studies, it was concluded that the development of an elastic modulus in fresh geopolymer pastes could only be due to the formation of an aluminosilicate gel between the MK aluminosilicate solid precursors. The measured modulus corresponded to the ones of gels with a much lower Si/Al ratio than the one measured in-situ in the interstitial phase by static ^{27}Al NMR. From these considerations, it was further concluded that the interstitial gel phase is highly heterogeneous. Interestingly from a methodological perspective, the macroscopic mechanical measurements and the bulk NMR measurement were thus able to reveal heterogeneities at the colloidal scale, the rheology of the fresh paste being both a signature and a consequence of mesoscale heterogeneities.

To rely on the formation of a heterogeneous gel to explain the development of an elastic modulus (and reciprocally), is very similar to what has been done in ordinary cementitious materials [62]. The heterogeneous character of this gel is also in accordance with the fact that it is not possible to produce gel with every possible Si/Al molar ratio. Only the molar ratio comprised between 1 and 5 has been actually reported to produce gels [55,70]. Finally, it is also in line with early observation on solidified geopolymers that highlighted the presence of an Al-rich gel phase [42,71].

Our study would therefore confirm the existence of an Al-rich gel. Furthermore, it highlights the fact that this Al-rich gel exists at the

very early stage of the reaction. Less than 15 min after the beginning of the mixing, this gel was able to be at the origin of an elastic modulus for the geopolymer suspension. This is coherent with the previous NMR studies of MK dissolution in sodium hydroxides that showed that monomeric silica species remain undetected thus suggesting a rapid condensation of silica with $[Al(OH)_4]^-$ to generate aluminosilicate species [72]. However, it was not possible with the experiments performed in this study to identify the exact molar ratio of the Al-rich gel. NMR studies done by Fernández-Jiménez et al. [42] suggest the presence of gels with very low Si/Al ratio (1.4) which is somehow too low to be in accordance with our experimental results. Actually a gel with a Si/Al ratio equal to 1.4 would have an elastic modulus higher than 1000 Pa in contradiction with the low elastic modulus value recorded for the geopolymer mix in Fig. 4. A higher ratio closer to 3 to 4 would be more in agreement, but as the gel forms at the scale of dozens to hundreds of nanometres, it is altogether possible that different Al-rich gels coexist as a distribution of solid solutions between Si/Al = 1 to Si/Al = 4.5.

Furthermore, the linear evolution that we observed after the first rapid elastic modulus increase (Fig. 3) was correlated with the linear increase in Al content observed on NMR measurement (Fig. 8). It would thus suggest a continuous phenomenon where a progressive thickening of the bridges is created between MK particles by the Al-rich gel(s). Finally, after a few hours, the geopolymer hardens with a second rapid increase of the elastic modulus. This fast increase can be seen as typical of the multiplication of percolation paths and it was probably significant that it occurred at the maximum Al concentration seen by NMR, indicating that a new chemistry is taking over. This aspect would need further questions as different hypotheses are possible. One of them would be the precipitation of a new geopolymeric phase, which could have a higher Si/Al ratio and could be correlated with the Si-rich gels that have been identified on previous studies on solidified geopolymers [42].

5. Conclusions

This study shows that the colloidal interactions between metakaolin grains are not the main drivers for the early age mechanical properties of geopolymer mixes and that a gel with Si/Al < 4.5 (Al-rich gel) located at the grain boundaries is responsible of the elastic modulus of the geopolymer mixture. This aluminosilicate gel is formed at the very early stage of the reaction (less than 15 min after the beginning of mixing). The measurement of the Al content in the solution evidences that such a high Al concentration can only be explained by a heterogeneity of the solution. This Al-rich gel is formed at the grain boundaries while the rest of the solution is still mainly composed of silicate oligomers. Finally, as a word of caution before generalizing the results of the present study, it is important to note that the mechanisms governing the formation of an aluminosilicate gel at an early age are strongly dependent on the chemical composition of the mixture and therefore the precursor selected. The presence of Ca in the solid precursors, as would typically be the case when fly ashes and slags are used, could dramatically change the chemistry of the system and enhance the colloidal interactions between grains as well.

References

[1] P. Capros, N. Kouvaritakis, L. Mantzos, Economic evaluation of sectoral emission reduction objectives for climate change: top-down analysis of greenhouse gas emission possibilities in the EU, Contribution to a Study for DG Environment, European commission, 2001.
[2] H.G. Van Oss, A.C. Padovani, Cement manufacture and the environment, part II: environmental challenges and opportunities, J. Ind. Ecol. 7 (2003) 93–127.
[3] D.N. Huntzinger, T.D. Eatmon, A life-cycle assessment of Portland cement manufacturing: comparing the traditional process with alternative technologies, J. Clean Prod. 17 (2009) 668–675.
[4] F. Liu, M. Ross, S. Wang, Energy efficiency of China's cement industry, Energy 20 (1995) 669–681.
[5] L. Szabo, I. Hidalgo, J.C. Cisar, A. Soria, CO_2 emission trading within the European union and annex b countries: the cement industry case, Energy Policy 34 (2006) 72–87.
[6] M. Taylor, C. Tam, D. Gielen, Energy efficiency and CO_2 emissions from the global cement industry, in: International Energy Agency (Ed.), Energy Efficiency and CO_2 Emission Reduction Potentials and Policies in the Cement Industry, Paris, 2006.
[7] E. Worrell, N. Martin, L. Price, Potentials for energy efficiency improvement in the US cement industry, Energy 25 (2000) 1189–1214.
[8] G. Habert, C. Billard, P. Rossi, C. Chen, N. Roussel, Cement production technology improvement compared to factor 4 objectives, Cem. Concr. Res. 40 (2010) 820–826.
[9] C. Shi, A. Fernández Jiménez, A. Palomo, New cements for the 21st century: the pursuit of an alternative to Portland cement, Cem. Concr. Res. 41 (2011) 750–763.
[10] E.M. Gartner, D.E. Macphee, A physico-chemical basis for novel cementitious binders, Cem. Concr. Res. 41 (2011) 736–749.
[11] R.J. Flatt, N. Roussel, C.R. Cheeseman, Concrete: an eco material that needs to be improved, J. Eur. Ceram. Soc. 32 (2012) 2787–2798.
[12] M. Jackson, D. Deocampo, F. Marra, B. Scheetz, Mid-pleistocene pozzolanic volcanic ash in ancient roman concretes, Geoarcheology. 25 (2010) 36–74.
[13] A.O. Purdon, The action of alkali on blast furnace slags (in French), J. Soc. Ind. Chim. 59 (1940) 191–202.
[14] V.D. Glukhovsky, Soil silicates, their properties, technology and manufacturing and fiels of application, PhD thesis. Civil engineering institute, Kiev, Ukraine (former USSR), 1965.
[15] J. Davidovits, Solid phase synthesis of a mineral blockpolymer by low temperature polycondensation of aluminosilicate polymers, IUPAC International Symposium on Macromolecules, Stockholm, Sept 1976.
[16] J. Davidovits, Geopolymers: inorganic polymeric new materials, J. Therm. Anal. 37 (1991) 1633–1656.
[17] J.G.S. Van Jaarsveld, J.S.J. Van Deventer, A. Schwartzman, The potential use of geopolymeric materials to immobilise toxic metals: part II. Material and leaching characteristics, Miner. Eng. 12 (1999) 75–91.
[18] A. Palomo, M.W. Grutzeck, M.T. Blanco, Alkali-activated fly ashes: a cement for the future, Cem. Concr. Res. 29 (1999) 1323–1329.
[19] P. De Silva, K. Sagoe-Crentsil, V. Sirivivatnanon, Kinetics of geopolymerization: role of Al_2O_3 and SiO_2, Cem. Concr. Res. 37 (2007) 512–518.
[20] P. Duxson, J.L. Provis, G.C. Lukey, Jannie S.J. van Deventer, The role of inorganic polymer technology in the development of 'green concrete', Cem. Concr. Res. 37 (2007) 1590–1597.
[21] M.C.G. Juenger, F. Winnefeld, J.L. Provis, J.H. Ideker, Advances in alternative cementitious binders, Cem. Concr. Res. 41 (2011) 1232–1243.
[22] G. Habert, J.B. d'Espinose de Lacaillerie, N. Roussel, An environmental evaluation of geopolymer based concrete production: reviewing current research trends, J. Clean Prod. 19 (2011) 1229–1238.
[23] J.L. Provis, P. Duxson, J.S.J. van Deventer, The role of particle technology in developing sustainable construction materials, Adv. Powder Technol. 21 (2010) 2–7.
[24] S. Alonso, A. Palomo, Calorimetric study of alkaline activation of calcium hydroxide–metakaolin solid mixtures, Cem. Concr. Res. 31 (2001) 25–30.
[25] H. Rahier, J.F. Denayer, B. van Mele, Low-temperature synthesized aluminosilicate glasses. Part IV. Modulated DSC study on the effect of particle size of metakaolinite on the production of inorganic polymer glasses, J. Mater. Sci. 38 (2003) 3131–3136.
[26] R.R. Lloyd, J.L. Provis, J.S.J. van Deventer, Microscopy and microanalysis of inorganic polymer cements: the gel binder, J. Mater. Sci. 44 (2009) 620–631.
[27] M. Stevenson, K. Sagoe-Crentsil, Relationships between composition, structure and strength of inorganic polymers. Part I: metakaolin-derived inorganic polymers, J. Mater. Sci. 40 (2005) 2023–2036.
[28] J. Davidovits, Structural characterization of geopolymeric materials with X-Ray Diffractometry and MAS-NMR spectroscopy, Geopolymer '88 Proceedings, 1988, pp. 149–166.
[29] M. Criado, A. Fernández-Jiménez, A.G. de la Torre, M.A.G. Aranda, A. Palomo, An XRD study of the effect of the SiO_2/Na_2O ratio on the alkali activation of fly ash, Cem. Concr. Res. 37 (2007) 671–679.
[30] P. De silva, K. Sagoe-Crentsil, Medium-term phase stability of $Na_2O–Al_2O_3–SiO_2–H_2O$ geopolymer systems, Cem. Concr. Res. 38 (2008) 870–876.
[31] W.K.W. Lee, J.S.J. Van Deventer, Use if Infrared Spectroscopy to study geopolymerisation of heterogeneous amorphous aluminosilicates, Langmuir 19 (2003) 8726–8734.
[32] C.A. Rees, J.L. Provis, G.C. Lukey, J.S.J. van Deventer, ATR–FTIR analysis of fly ash geopolymer gel ageing, Langmuir 23 (2007) 8170–8179.
[33] J.L. Provis, J.S.J. Van Deventer, Direct measurement of kinetics of geopolymerisation by in-situ energy dispersive X-ray diffractometry, J. Mater. Sci. 42 (2007) 2974–2981.
[34] P. Duxson, J.L. Provis, G.C. Lukey, F. Separovic, J.S.J. Van Deventer, ^{29}Si NMR study of structural ordering in aluminosilicate geopolymer gels, Langmuir 21 (2005) 3028–3036.
[35] M.R. Rowles, J.V. Hanna, K.J. Pike, M.E. Smith, B.H. O'Connor, Si-29, Al-27, H-1 and Na-23 MAS NMR study of the bonding character in aluminosilicate inorganic polymers, Appl. Magn. Reson. 32 (2007) 663–689.
[36] F. Zibouche, H. Kerdjoudj, J.B. d'Espinose de Lacaillerie, H. Van Damme, Geopolymers from Algerian metakaolin. Influence of secondary minerals, Appl. Clay Sci. 43 (2009) 453–458.
[37] M. Criado, A. Palomo, A. Fernández-Jiménez, P.F.G. Banfill, Alkali activated fly ash: effect of admixtures on paste rheology, Rheol. Acta 48 (2009) 447–455.
[38] A. Poulesquen, F. Frizon, D. Lambertin, Rheological behavior of alkali-activated metakaolin during geopolymerization, J. Non-Cryst. Solids 357 (2011) 3565–3571.
[39] C.E. White, J.L. Provis, A. Llobet, T. Proffen, J.S.J. Van Deventer, Evolution of local structure in geopolymer gels: an in situ neutron pair distribution function analysis, J. Am. Ceram. Soc. 94 (2011) 3532–3539.

[40] A. Hajimohammadi, J.L. Provis, J.S.J. van Deventer, The effect of silica availability on the mechanism of geopolymerisation, Cem. Concr. Res. 41 (2011) 210–216.

[41] A. Hajimohammadi, J.L. Provis, J.S.J. van Deventer, The effect of alumina release rate on the mechanism of geopolymer gel formation, Chem. Mater. 22 (2010) 5199–5208.

[42] A. Fernandez-Jimenez, A. Palomo, I. Sobrados, J. Sanz, The role played by the reactive alumina content in the alkaline activation of fly ashes, Microporous Mesoporous Mater. 91 (2006) 111–119.

[43] C. Li, H. Sun, L. Li, A review: the comparison between alkali-activated slag (Si + Ca) and metakaolin (Si + Al) cements, Cem. Concr. Res. 40 (2010) 1341–1349.

[44] J.E. Oh, P.J.M. Monteiro, S.S. Jun, S. Choi, S.M. Clark, The evolution of strength and crystalline phases for alkali-activated ground blast furnace slag and fly ash-based geopolymers, Cem. Concr. Res. 40 (2010) 189–196.

[45] H. Maekawa, T. Maekawa, K. Kawamura, T. Yokokawa, The structural groups of alkali silicate glasses determined from ^{29}Si MAS-NMR, J. Non-Cryst. Solids 127 (1991) 53–64.

[46] T.W. Swaddle, Silicate complexes of Aluminium (III) in aqueous systems, Coord. Chem. Rev. 219 (2001) 665–686.

[47] R. Engler, Loesliche Silikate, Woellner-Werke, 1-15; offprint of a series of publications in Seifen, Oele, Fette, Wachse 7, 8, 11, and 12, 1974. (pp. 165, 207, 269, 298).

[48] T.H. Gerber, B. Himmel, C. Hubert, WAXS and SAXS investigation of structure formation of gels from sodium water glass, J. Non-Cryst. Solids 175 (1994) 160–168.

[49] X. Yang, W. Zhu, Q. Yang, The viscosity properties of sodium silicate solutions, J. Solut. Chem. 37 (2008) 73–83.

[50] A. Bourlon, Physico-chimie et rhéologie de géopolymères frais pour la cimentation des puits pétroliers. PhD thesis, Université Paris VI, 2010.

[51] J.L. Bell, P. Sarin, P.E. Driemeyer, R.P. Haggerty, P.J. Chupas, W.M. Kriven, X-ray pair distribution function analysis of a metakaolin-based, KAlSi$_2$O$_6$·5.5H$_2$O inorganic polymer (geopolymer), J. Mater. Chem. 18 (2008) 5974.

[52] C. Meral, C.J. Benmore, P.J.M. Monteiro, The study of disorder and nanocrystallinity in C–S–H, supplementary cementitious materials and geopolymers using pair distribution function analysis, Cem. Concr. Res. 41 (2011) 696–710.

[53] P. Duxson, J.L. Provis, G.C. Lukey, S.W. Mallicoat, W.M. Kriven, J.S.J. van Deventer, Understanding the relationship between geopolymer composition, microstructure and mechanical properties, Colloids Surf. A 269 (2005) 47–58.

[54] I. Krznarić, T. Antonić, B. Subotić, Physical chemistry of aluminosilicate gels. Part 1. Influence of batch concentration on chemical composition of the gels, Zeolites 19 (1997) 29–40.

[55] A. Buchwald, H.D. Zellmann, C.H. Kaps, Condensation of aluminosilicate gels—model system for geopolymer binders, J. Non-Cryst. Solids 357 (2011) 1376–1382.

[56] I. Garcia-Lodeiro, A. Palomo, A. Fernández-Jiménez, D.E. Macphee, Compatibility studies between N-A-S-H and C-A-S-H gels. Study in the ternary diagram Na$_2$O–CaO–Al$_2$O$_3$–SiO$_2$–H$_2$O, Cem. Concr. Res. 41 (2011) 923–931.

[57] J.W. Phair, J.D. Smith, J.S.J. Van Deventer, Characteristics of aluminosilicate hydrogels related to commercial "Geopolymers", Mater. Lett. 57 (2003) 4356–4367.

[58] L. Heller-Kallai, I. Lapides, Reactions of kaolinites and metakaolinites with NaOH—comparison of different samples (part 1), Appl. Clay Sci. 35 (2007) 99–107.

[59] M. Rowles, B. O'Connor, Chemical optimisation of the compressive strength of aluminosilicate geopolymers synthesised by sodium silicate activation of metakaolinite, J. Mater. Chem. 13 (2003) 1161–1165.

[60] P. Coussot, Rheometry of Pastes, Suspensions, and Granular Materials, Wiley-Interscience, Hoboken (N.J.), 2005.

[61] A.W. Saak, H.M. Jennings, S.P. Shah, The influence of wall slip on yield stress and viscoelastic measurements of cement paste, Cem. Concr. Res. 31 (2001) 205–212.

[62] N. Roussel, G. Ovarlez, S. Garrault, C. Brumaud, The origins of thixotropy of fresh cement pastes, Cem. Concr. Res. 42 (2012) 148–157.

[63] R. Flatt, Towards a prediction of superplasticized concrete rheology, Mater. Struct. 27 (2004) 289–300.

[64] N. Roussel, A. Lemaître, R.J. Flatt, P. Coussot, Steady state flow of cement suspensions: a micromechanical state of the art, Cem. Concr. Res. 40 (2010) 77–84.

[65] B. Rand, I.E. Melton, Particle interactions in aqueous kaolinite suspensions I. Effect of pH and electrolyte upon the mode of particle interaction in homoionic sodium kaolinite suspensions, J. Colloid Interface Sci. 60 (1977) 308–320.

[66] D. Penner, G. Lagaly, Influence of anions on the rheological properties of clay mineral dispersions, Appl. Clay Sci. 19 (2001) 131–142.

[67] L.T. Drzal, P. Rynd, T. Fort Jr., Effect of calcination on the surface properties of kaolinite, J. Colloid Interface Sci. 93 (1983) 126–138.

[68] M. Romagnoli, F. Andreola, Mixture of deflocculants: a systematic approach, J. Eur. Ceram. Soc. 27 (2007) 1871–1874.

[69] N. Yildiz, M. Erol, B. Baran, Y. Sarikaya, A. Çalimili, Modification of rheology and permeability of turkish ceramic clays using sodium silicate, Appl. Clay Sci. 13 (1998) 65–77.

[70] I. Krznarić, T. Antonić, B. Subotić, Physical chemistry of aluminosilicate gels. Part 2. Influence of the batch molar ratio SiO$_2$/Al$_2$O$_3$ on chemical composition of the gels, Microporous Mesoporous Mater. 20 (1998) 161–175.

[71] A. Fernández-Jiménez, A. Palomo, M. Criado, Microstructure development of alkali-activated fly ash cement: a descriptive model, Cem. Concr. Res. 35 (2005) 1204–1209.

[72] L. Weng, K. Sagoe-Crentsil, Dissolution process, hydrolysis and condensation reactions during geopolymer synthesis: part I—low Si/Al ratio systems, J. Mater. Sci. 42 (2007) 2997–3006.