ABSTRACT

Metakaolin based geopolymers are presented in many studies as an alternative to normal Portland cement. Previous studies have focused on their chemical and mechanical properties, their microstructures and their potential uses, but very few on their rheological behaviour.

Our work highlights the main differences that exist between geopolymer and Portland cement. These materials behave as Newtonian fluids as the colloidal interactions between particles are dominated by the hydrodynamic effects, which are mainly controlled by the high viscosity of the alkaline silicate solution and not by the contribution of direct contacts between Metakaolin grains.

Keywords: geopolymer; metakaolin; rheological behaviour; sodium silicate solution; Portland cement
INTRODUCTION

Geopolymers are based on the chemistry of alkali activated inorganic binders and are considered as a highly potential solution to reduce CO$_2$ emissions[1,2] in the field of construction materials. In the 1970’s, Davidovits [3] coined the term “geopolymer” and developed the idea of an inorganic polymer with highly cross-linked amorphous network, which resulted from the hydroxylation and polycondensation reaction of thermally activated kaolin (metakaolin) in an alkaline solution.

In the last 15 years, an intensive academic research on these binders has considerably extended the understanding of the geopolymerization reaction and led to an intense development of both research and applications. However, few studies have been carried out about rheological behaviour. Furthermore, most of theses studies are carried out on fly ashes or slags based geopolymers [4–8] and not on simpler model systems such as metakaolin based geopolymer.

In this study, we focus on the rheology of metakaolin based geopolymer paste. We highlight the difference that exist between these geopolymer mixtures and cement pastes.

EXPERIMENTAL PROCEDURE

Materials and rheological measurements

The metakaolin (MK) used as starting material for this research was Argical M-1000 from AGS minéraux (France). The alkaline solutions were prepared from 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 solution was then allowed to cool for 24h. The standard system for geopolymer is defined to obtain sufficient mechanical properties. The mass of MK is then adjusted relatively to the alkaline solution in order to provide suitable SiO$_2$/Al$_2$O$_3$ and Na$_2$O/Al$_2$O$_3$ ratio (i.e. around 4 and 1 respectively) [9,10]. In this range of chemical composition, MK geopolymer pastes present the same rheological behaviour. The typical cement paste is made with cement CEMI (pure Portland cement) with a water/cement ratio (W/C) between 0.35 and 0.5. This system is selected as a reference because it is stable under the effect of gravity. It can flow and allows manufacturing a structural concrete.

The rheological measurements were carried out with a C-VOR Bohlin® rheometer equipped with Vane geometry for geopolymer mixes and parallel plate geometry for solutions. For the test on geopolymer mixtures, the paste was mixed with a
Mechanical stirrer for 5 min and immediately transferred into the rheometer’s cup. An initial pre-shear at 100s\(^{-1}\) was applied prior to each test to ensure that all samples were in the same reference state of stress and strain.

**MACROSCOPIC FLOW CURVES**

Fresh geopolymer pastes, as cement pastes, can be viewed as suspensions of particles (MK) in a continuous fluid (sodium silicate solution). Cement suspensions display in steady state flow, either Newtonian (constant apparent viscosity), shear thinning (decreasing apparent viscosity with shear rate) or shear thickening behaviour (increasing apparent viscosity with shear rate). These three behaviours are controlled by colloidal interactions which are due to electrostatic and Van der Waals forces, viscous interactions controlled by hydrodynamic forces and inertial interaction generated by contact forces between particles [11, 12].

Due to these interactions, cement suspensions can handle a stress that can be described by a Bingham model:

\[ \tau = \tau_0 + \eta \gamma \]  

(1)

With \( \tau_0 \) is the yield stress, \( \eta \) the apparent viscosity and \( \gamma \) the shear rate.

*Figure 1 Apparent viscosity as function of shear rate for cement pastes (SP= superplasticizer) relative to different applications.*

Figure 1 shows the different range of viscosities which can be obtained by modifying the water to cement ratio (W/C) and by adding organic admixtures in cement paste. In this study, we refer to typical cement paste with an intermediate rheological behaviour named standard cement paste. The objective of the study is to evaluate the relative contribution of these different interactions for MK-based geopolymer.
Figure 2 shows the viscosity of typical MK geopolymer in comparison with the viscosity of cement paste. We observe that the geopolymer’s viscosity in an intermediate range of shear rate is lower than the cement’s one. Furthermore, the viscosity seems dominated by a viscous contribution and not by a colloidal contribution as in cement paste. In a first part, we will then evaluate the viscous behaviour of the mixture. Then we will evaluate the contribution of yield stress.

**EVALUATION OF THE VISCOSITY**

Suspensions present a viscosity, which can be described by empirical expressions such as the Krieger-Dougherty relation [13]. The general form of this relation can be written as:

\[ \eta = \eta_0 \times (1 - \frac{\phi}{\phi_{\text{max}}})^n \]

With \( \eta_0 \) is the solution viscosity, \( \phi \) packing fraction, \( \phi_{\text{max}} \) dense packing fraction. In this work, we study separately the two contributions: the one of the liquid and the one of the grains.

**Evaluation of the liquid contribution**

*Figure 3 Viscosity as function of shear rate for different silicate solutions at 20°C*
In our study, the liquid phase is a sodium silicate solution. The viscosities of the different studied solutions are presented in Figure 3. This figure shows that sodium silicate solutions are Newtonian fluids but with a viscosity which is 10 to 100 times higher than the viscosity of water.

As a consequence, for a specific $\phi/\phi_{\text{max}}$, the viscous dissipation is 10 to 100 times higher than the one in standard cement paste. However, the $\phi$ in geopolymer is lower than in cement paste and this aspect will be discuss in the next section.

**Evaluation of solid fraction contribution**

*Figure 4* The relative viscosity as function of the solid fraction for a geopolymer paste ($\text{H}_2\text{O}/\text{Na}_2\text{O} = 15$) and a deflocculated cement paste with 0.5% superplasticizer (SP).

The relative viscosity measured in Figure 4 is the ratio between the effective viscosity of geopolymer or cement and the viscosity of the silicate solution or water respectively. The contribution of the solution viscosity is then removed and allows focusing exclusively on the solid fraction contribution as shown in equation (2). Figure 4 shows that for a solid volume fraction $\phi$ near 0.45, the relative viscosity diverges. The exact value of this maximum packing fraction is difficult to measure and no appropriate procedure have been developed [14]. MK based geopolymers present a lower $\phi_{\text{max}}$ (around 0.55) in comparison to deflocculated cement suspension (around 0.8). This was expected as MK grains have a plate shape which is very deleterious for flow and for packing properties [15]. As a consequence, the volume fraction of a geopolymer can not reach a value as high as that of a cement paste.

However, it is interesting to note that when chemical ratios of $\text{Al}_2\text{O}_3/\text{SiO}_2$; $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ are respected, the volume fraction of MK introduced in the sodium silicate solution is actually quite small (around 0.25) compared to the one used in typical cement paste (>0.4). As a consequence, even if MK’s $\phi_{\text{max}}$ is small, the limited volume of solid grains in the suspension prevents any contact between grains as it is evidenced in the Figure 5 where the ratio between normal and shear stress in
geopolymer is one hundred times lower than the one commonly measured in cement paste. Therefore, the viscosity of a geopolymer is nearly exclusively controlled by the viscosity of interstitial fluid $\eta_0$.

*Figure 5 Ratio between normal stress and shear stress as function of time for geopolymer paste ($H_2O/Na_2O=15$, $\phi=0.3$) and for a standard cement paste at room temperature at 100 s$^{-1}$*

EVALUATION OF YIELD STRESS

Once the viscous behaviour of equation (1) has been explained, we focused on the first term related to the colloidal interactions.

*Figure 6 Shear stress as a function of shear rate for geopolymer ($H_2O/Na_2O=15$), cement paste ($W/C=0.35$) and the geopolymer suspending fluid (silicate solution)*

We can observe in Figure 6 the shear stress of geopolymer, cement paste and silicate solution (considered as Newtonian fluid). We can estimate by extrapolation the yield stress $\tau_0$. We notice that the yield stress of geopolymer is far lower than the one of typical cement paste. Roussel et al. [12] show that the yield stress in cement paste is due to a network of attractive forces such as Van der Waals forces. These forces increase with the volume packing fraction and can be controlled by adding organic
mixtures which modify the inter-particles interactions. Favier et al. [16] already show that the origin of elastic modulus in MK based geopolymer and therefore of the weak yield stress is due to the formation of a gel at very early age and not due to colloidal interactions between grains.

As a consequence, geopolymer pastes can flow under their own weight until a stable state depending on the viscosity as water or oil.

CONCLUSIONS AND PERSPECTIVES

Based on the results of this experimental investigation, the following conclusions can be drawn. On a macroscopic point of view, geopolymer is a viscous fluid. It is nearly Newtonian as very low yield stress is measured and highly viscous as the liquid is 10 to 100 times more viscous than water.

This work allows us to find some new ways of research. In fact, we identified specificity of MK-based geopolymer mixture that is different from common cementitious materials. Actually, most of rheological improvement in cementitious materials have been done with the help of plasticisers and super-plasticisers which mainly act of the yield stress [11]. This is not useful for MK-based geopolymers as they have a nearly purely viscous behaviour. Today, MK based geopolymer does not seem therefore suitable as a binder in mortar applications where you need a high yield stress or in applications requiring fast flow as pumping because of its high viscosity. Applications where it could be substituted for cement are self compacting or self levelling applications as floor screed.

Finally, as a word of caution before generalizing the results of the present study, it is important to note that the parameters governing the rheology of a MK based geopolymer can be different from the one involved when other precursors such as fly ashes or slags are used to obtain geopolymers. Actually, with these precursors, even if the flow behaviour can still be described by a Bingham model [7], the presence of Ca ions in the solution will change the interaction forces between particle surfaces. In respect of the DLVO theory, the presence of divalent cations can produce attractive ion correlation forces such as the one present between C-S-H particles [17] whereas monovalent cations only induce repulsive forces [18]. We might then expect an increasing in colloidal interactions which will have a direct consequence on yield stress. In that case, using plasticizers would have a certain interest as soon as the conformation stability of the organic plasticizer can be assured in those alkaline solutions [19].