

Improvement of Rheological behaviour of Cement Pastes by Incorporating Metakaolin

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Abstract

An experimental rheological investigation was conducted to evaluate the performance of Algerian metakaolin MK on cement pastes. In the present work, several rheological tests were carried out at 20°C, by using the stress controlled rheometer AR2000, on the fresh cement pastes incorporating 0%, 5%, 10%, 15% and 20% of MK. Effect of metakaolin on the rheological behaviour of cement pastes were discussed. Rheological parameters such as viscosity, compliance, loss and storage shear modulus are evaluated by means of rheological techniques of both flow and creep/recovery tests (static mode) and oscillatory test (dynamic mode). Shear moduli allow to give information on the evolution of the paste structure related to practically interesting problems such as workability. The results obtained have shown that MK improves the flowability and exhibits viscous rheological behaviour of cement pastes over elastic behaviour of control paste (0%MK). Moreover, the creep/recovery test show that the addition of MK exhibits a behaviour of viscoelastic liquid of cement pastes compared to a viscoelastic solid behaviour of control paste. The MK acts as filler and controls rheology.

Keywords: Rheology, Dynamic mode, Creep, Oscillation, Behaviour, Cement paste, Metakaolin

1. Introduction

The advances of concrete technology show that the use of mineral admixtures such as silica fume (SF), fly ash (FA) and blast furnace slag (BFS) is necessary and essential for producing high-performance concrete. In recent years, there has been a growing interest in the use of metakaolin (MK) for this purpose. It is a thermally activated aluminosilicate material produced from kaolinite clay through a calcining process within the temperature range of 700-850°C [Badogiannis, 2005]. It contains typically 50-55% SiO_2 and 40-45% Al_2O_3 and is highly reactive.

The rheological behaviour of fresh cement paste and concrete is a topic of considerable interest. Fresh concrete is a fluid material and its rheological behaviour affects or even limits the way it can be processed, therefore, measurement and control of rheological parameters are very important in the production of quality concrete. Much research [Park et al, 2004] has been conducted for improving rheology and mechanical properties using various fine particles and reported that the admixtures could contribute to increase workability in the fresh state, densify the microstructure and develop higher mechanical properties due to their latent hydraulic properties and pozzolanic reaction, respectively [Ferraris et al, 2001].

Predicting flowability by testing concrete is not always practical. Extensive concrete testing requires a large amount of materials and labour, which is expensive. Recently, the quantitative fundamental methodology, which was developed to assess the rheology of fluid state, has been used for analyzing cement paste.

Builders in Algeria are not familiar with the practice of using mineral additives, as cement substitutes, in cast-in-place and in ready-mix concretes. It thus seemed important to study and evaluate the impact of these additives, as cement substitutes, on the properties of the fresh cement pastes. The mineral additive used is metakaolin which is obtained from calcined natural kaolin found in large quantities in eastern Algeria (Tamazert- Milia). It could replace a significant part of the cement at the manufacture of concrete, and then a substantial saving could be achieved especially for an importer of cement such as Algeria.

In this work, cement pastes containing 0%, 5%, 10%, 15% and 20% MK were prepared from deionised water and 2% of superplasticizer. These pastes were investigated rheologically in order to analyze rheological parameters (stress, viscosity, compliance, loss and storage moduli). In addition, effect of MK on the pastes behaviour was discussed. These rheological parameters have been evaluated by means of the flow, creep/recovery and oscillatory tests.

Dynamic tests are carried out for studying the viscoelastic behaviour of MK cement pastes. The technique which was used to monitor the viscoelastic properties of cement pastes is called oscillating rheometric method. In this method [Sun et al, 2006], the storage and loss shear moduli of the cement paste can directly be measured by applying oscillating shear stress according to a sine function and measuring the corresponding shear strain. By controlling the value of oscillatory shear stress and the frequency within the linear viscoelastic region of the material, the microstructure of the cement paste will not be destroyed during the dynamic tests, and the evolution of the material properties during the time can be observed.

2. Rheological Measurements

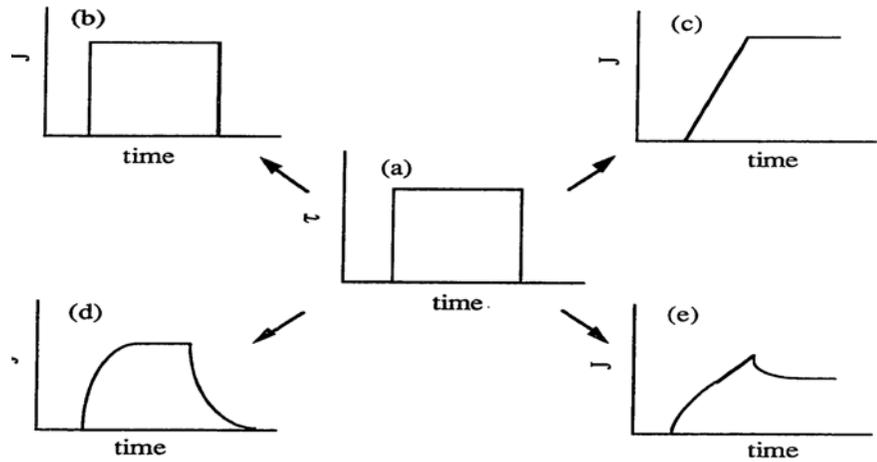
A key development in recent years in rheology has been the development of dynamic techniques for characterization of viscoelastic materials. Such techniques measure the behaviour when there is a change in strain or shear stress. The key dynamic techniques used for suspensions are low-amplitude oscillatory shear and creep/recovery.

2.1. Creep/Recovery Technique

The creep /recovery technique measures strain when stress is applied (creep) or removed (recovery), from this, is determined the compliance (strain divided by stress). Furthermore, this dynamic technique

provides information for the full range of material behaviour [Struble et Schultz, 1993] (elastic solid, viscoelastic solid, viscoelastic liquid and viscous liquid) (figure 1).

Figure 1: General creep/recovery behaviour of (b) elastic solid, (c) viscous liquid, (d) viscoelastic solid, (e) viscoelastic liquid under shear stress (a).



2.2. Oscillatory Shear Technique

Understanding the viscoelastic properties of Portland cement paste can be helpful to better understand the behaviour of concrete. In this context, dynamic methods can help to distinguish between the elastic and viscous properties of the material. When a linear viscoelastic body is subjected to stress varying sinusoidally with time at a certain frequency, the corresponding strain is not in the same phase as applied stress, which results in a phase lag between strain and stress. According to the decomposed stress components, the relationship between stress and strain of a viscoelastic material can be established by using the modulus of rigidity in a complex format. The shear modulus can be expressed as follows:

$$G^* = \frac{\tau}{\gamma} = G' + iG'' \tag{1}$$

$$G' = \frac{\tau_0}{\gamma_0} \cos(\delta) \tag{2}$$

$$G'' = \frac{\tau_0}{\gamma_0} \sin(\delta) = \omega \eta' \tag{3}$$

Where G^* is the complex shear modulus, G' is the storage shear modulus, which represents the elastic behaviour or the energy storage of the material, and G'' is the loss shear modulus, which represents the viscous behaviour or energy dissipation of the material.

2.3. Linear Viscoelastic Region (LVER)

Generally speaking, the elastic moduli of a viscoelastic material are time dependent. However, there is a specific region, called linear viscoelastic region (LVER), under which the elastic moduli of such a viscoelastic material are independent of time, amplitude of the oscillating strain or stress, and applied oscillating frequency. To define the LVER of a certain material, two aspects need to be considered. First, a critical maximum value of the stress needs to be found [Sun et al, 2006]. There is a linear part of the stress– strain curve, where the shear modulus is independent of the applied stress (or strain). And the loading and unloading paths within this linear region are identical. The critical stress, which marks

the ending of the linear stress–strain relation, is defined as the limit stress of LVER. Beyond this region, loading and unloading paths are different, which means that there will be a residual strain in the cement particles during the oscillation test. Second, a critical frequency of the applied oscillating stress needs to be found in order to define the LVER. The structure of the material requires sufficient time to relax and release residual energy during oscillating, so that particles in the microstructure can elastically recover to their equilibrium status. This requires the applied frequency to be lower than a certain level so that there will not be any residual strain or energy from the previous oscillation during the whole period of testing.

3. Rheological Models

Various rheological models were used to characterise the flow curves of cement pastes and to determine the rheological properties, using Rheological data analysis software which estimate the models standard error. It is used as a scale for measuring the relative level of accuracy of the different models. We cite:

Bingham model

$$\tau = \tau_0 + \eta_{pl} \cdot \dot{\gamma} \quad (\tau > \tau_0) \text{ (Pa)} \quad (4)$$

Herschel- Bulkley model

$$\tau = \tau_0 + \eta_{app} \cdot \dot{\gamma}^n \quad (\tau > \tau_0) \text{ (Pa)} \quad (5)$$

Power-law mode

$$\tau = \eta_{app} \cdot \dot{\gamma}^n \quad (6)$$

In these models the parameters τ_0 , η_{app} , η_{pl} , $\dot{\gamma}$ and n are considered as the shear stress, shear rate, plastic viscosity, apparent viscosity, rate index respectively.

4. Apparatus

In this study, the rheometer AR2000 with vane geometry was used to characterize the rheology of cement pastes. The radius of the vane rotor is 14 mm. The vane rotates inside a fixed hollow 15- mm-radius cylinder. The gap between outer cylinder and vane is 1 mm. The movable test accessories were attached to the driving motor spindle of the rheometer which is able to plot the continuous rheological curve of paste from the relationship between shear rate and shear stress at physically defined condition.

5. Experimental Program

5.1. Materials

Metakaolin (MK) and ordinary cement were used as binder components. As superplasticizer (SP) a commercial high water reducer based on a polycarboxylate and a modified phosphonate, was used during the mix. The cement is composed by clinker and 5% of gypsum. The MK was chosen because it is well recognized as a highly pozzolanic material. In this study, MK was obtained by calcination of Algerian kaolin at 700° for 7h. In this region, kaolin sample is composed of grains kaolinized feldspar, quartz, flakes of muscovite and traces of rutile. Kaolins are found at the location of their training, mixed with rock debris that gave birth [Merabet D., and H. Belkacemi, 2003]. The silica and alumina contained in the metakaolin are active and react with calcium hydroxide obtained during the hydration of cement with water to form calcium silicates and aluminosilicates of calcium hydrated stable possessing binding properties, which can greatly improve the strength and durability of concrete [Sabir et al, 2001]. The physical properties and the chemical compositions of used materials are given in

table1 and table2 respectively. In addition, materials morphology given by the scanning electron microscope SEM in GSED mode is shown in figure 2 and figure 3. The sized curve (laser granulometer) of metakaolin is represented in figure 4.

Figure 2: Morphology of metakaolin (SEM, GSE mode)

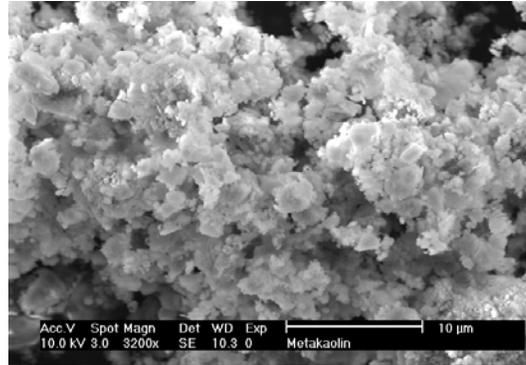


Figure 3: Morphology of cement (SEM, GSE mode)

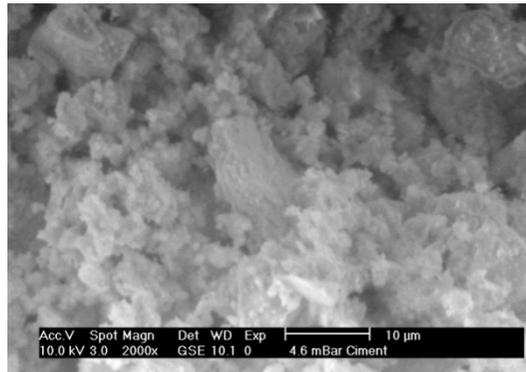


Figure 4: Particle size distribution of metakaolin

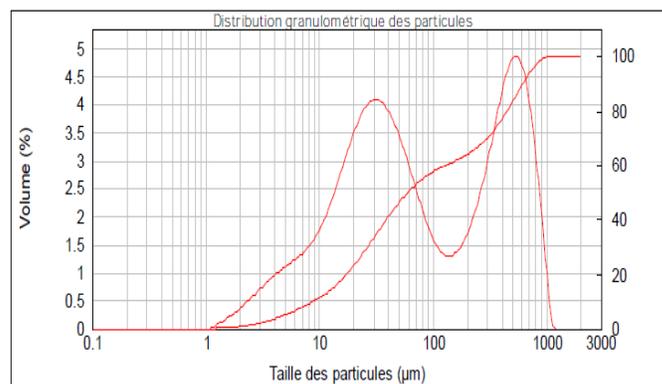


Tableau 1: Physical Properties of materials

Materials	Cement	MK
Specific Surface (cm ³ /g)	4200	22177
Density	3.12	2.54
Mineral Activity mg Ca(OH) ₂ /g	-	137.5
Superplasticizer		
Density	1.07	
Chlorine content	< 1%	
pH	6±1	
Solids (%)	30.5±1	

Tableau 2: Chemical Composition of cement and metakaolin. Bogue Composition of cement

Wt %	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	PF
Cement	19,85	4.80	2,75	63,60	1,45	3,45	0,90	0,15	2,20
MK	7,235	35,36	1,18	1,33	0,21	0,31	1,13	0,15	2,01
Bogue Composition of cement	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Gypsum				
	62.0	10.2	8.1	8.4	5.0				

5.2. Mixing and Preparing Cement Pastes

The cement paste was prepared with deionised water (the ratio of water to binder w/c corresponds at paste standard consistency determined by the Vicat apparatus in accordance with EN 196-3) and with 2% SP. For The mixing water blended with the superplasticizer was poured into the mixer. Subsequently, cement blended was added into the mixer over 1min of mixing at low speed. The mixing was continued for another minute at high speed. Then, the mixer was stopped for 1.5 min. During this time, the sidewall of the mixing container was scrapped with a rubber spatula to recover the material sticking to the container's wall. Mixing resumed for an additional minute at high speed. The cement paste was then kept at rest for 30 s. The sample of cement paste was poured thereafter into the rheometer. A preshearing of 500s⁻¹ was applied for 60s, and was allowed to rest for 60 s to let the particles achieve their structural equilibrium and by this to reach the same strain status before the test. The preshearing was found to take the paste through the irreversible structural breakdown [Wei-Guo, 1990].

5.3. Flow Test

After the preshearing of 500s⁻¹, the cement paste was sheared by applying a sweep stress from 0 to 200 Pa within 2 min to produce the curve of the flow test.

5.4. Strain Sweep and Frequency Sweep Rheometric Methods

In order to define the LVER of the cement pastes, a two-step procedure was applied. First, a stress sweep was used to determine the magnitude of the critical stress. During the stress sweep test, a small frequency at the level of 1 Hz was used. Shear stress was swept from 0.01pa, to 20pa. The shear moduli were measured during the stress sweep tests and the critical stress values were determined using the value at which the shear moduli began to decrease. Second, critical value of applied frequency was determined by frequency sweep. During the frequency sweep, cement paste is subjected to an oscillatory stress with constant amplitude at a value smaller than the critical strain determined by step one. Frequency was swept from 0.1 Hz to 10 Hz for all pastes. Critical value of applied frequency is defined as the frequency at which measured shear modulus begins to decrease.

5.5. Oscillatory Rheometric Method (OR-Method)

During the oscillatory testing, the stress-control mode was used. A 0.1 to 100 Hz frequency sweep with 0.03 Pa of constant stress was applied, after determining the limits of linear viscoelastic region [Sun et al, 2006] by means of stress sweep experiments from 0.01 to 20pa of stress at a 1 Hz constant frequency. All oscillatory experiments started 1 min after paste taking paste in the rheometer. The temperature of the specimens was maintained at 20°C by controlling the circulating water in the water cup in which the outer cylinder is embedded.

5.6. Creep/Recovery Test

After a preshearing of $500s^{-1}$ applied for 240s, allowed to equilibrium for 60s, the rheological tests were begun. This procedure was followed before each creep measurement. The preshearing was found to take the paste through the irreversible structural breakdown [Tattersall, 2003]. In measuring creep and recovery, an imposed constant stress of 0.03pa was applied while strain was measured for 40s (creep), then the stress was removed and strain measured for another 40s (recovery).

6. Results and Discussion

6.1. Microstructure of Materials

Figure 2 and Figure 3 show the morphology of materials used in the cement pastes, and reveal that the metakaolin possesses a dense matrix with irregular particles over cement. In addition, figure 4 shows the very fine particle size of MK which leads to a large number of particles.

Effectively, the large diameter of their particles is lower than that of cement particles (table 3). This fact shows the micro filler effect of MK which has exhibited best cement pastes flowability.

Table 3: Geometrical characteristics of materials

Diameter (μm)	Cement	MK
Large diameter d_{20}	76.7	7.07
Mean diameter d_{50}	39.0	3.32
Little diameter d_{90}	7.1	0.54

6.2. Rheological Model

Flow curves were not linear and thus the pastes were not plastic in their behaviour since they often exhibited shear thinning or shear thickening behaviour. However, these materials are not Bingham. All flow curves have been modelled by Herschel-Bulkley equation for describing the rheological behaviour of different cement pastes.

6.3. Influence of Mineral Admixtures

6.3.1. Flow Test

For shear stress as function of shear rates, the samples show very similar shapes each other, and for all pastes, shear stresses increase with the increasing of shear rates and are lower than those the paste control (0%MK) (figure 5). So the MK improves the cement pastes flowability, especially the rate of 10%MK and 15%MK.

Figure 6 represents the evolution of the cement paste viscosity for different proportions of MK as function as shear rate. All pastes, present an initial shear thinning behaviour till a certain limit of shear rate because of the viscosity decreasing. After, the viscosity increases with increasing of shear rate (shear thickening), but stays lower than that the control paste (0% MK). This increasing could also be linked to the presence of superplasticizer as a physical component of the paste. It is possible that the

increase of shear rate enhances the disorder, not only between the particles of cement, but within the polymeric chains of the superplasticizer Barnes [Cyr and al, 2000]. The replacement of 10%MK and 15%MK of cement exhibit the best paste flowability. This is explained by the fact that MK has the highest specific surface area and the dense microstructure with the fines particles which fill into the spaces made by larger particles of cement [Schultz and Struble, 1993] and decrease friction forces of MK cement paste. In addition, the replacement of cement by MK, decrease hydration activity of the paste which contains little amount of cement, and higher absorbance of SP, as much as replacement of MK resulting in contributing to high flowability of this system.

Figure 5: Flow curves of cement pastes for different proportion of MK.

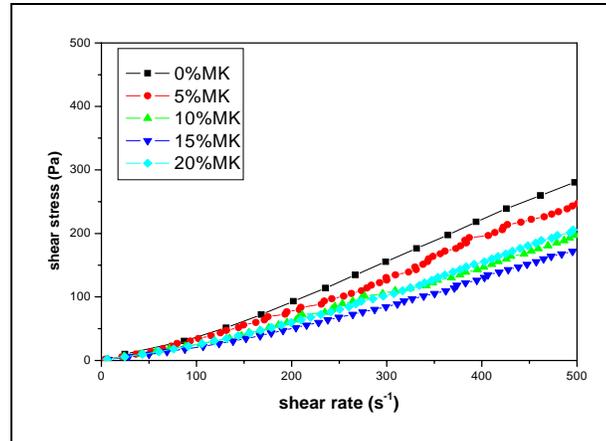
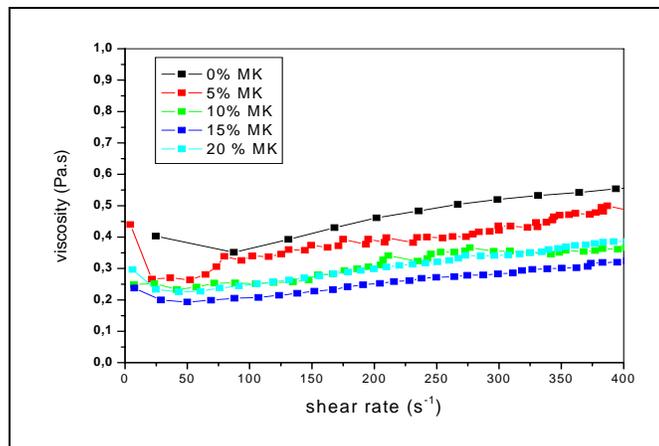


Figure 6: Evolution of viscosity of cement pastes for different proportion of MK.

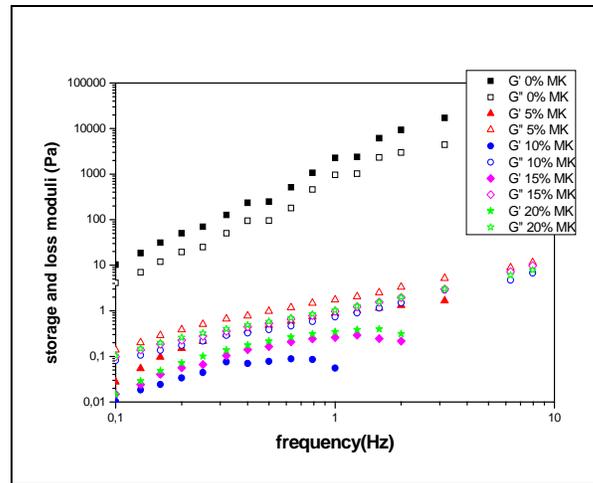


6.3.2. Oscillatory Test

Oscillatory tests provide information about the structure of the cement paste through its mechanical properties. Rheometric measurements show a parallel evolution of the storage (elastic) modulus G' and the loss (viscous) modulus G'' of cement pastes as function as frequency, after both become independent of frequency (figure 7). This is evidences the fact that the sample is undergoing a structural change, from rather dispersed state to structured state. G'' is always higher than G' for all MK pastes, that is there is a predominance of viscous behaviour. On the other side, G' was smaller than G'' for cement paste control (elastic behaviour). On the other side, G' was smaller than G'' for control cement paste (elastic behaviour). Evolution of the structure of the paste is occurring during the first minutes after the end of mixing. Here, the only evolution is the increase in moduli. Thus, it seems that there is no major change in the structure of the cement pastes during this period. Moreover, the fines metakaolin particles retards the hydration of cement and the C-S-H formation coming cover C_3S

and increasing less modulus over storage modulus. These results show that the MK addition improves the flowability of cement paste and their behaviour in oscillation. It has significant effect when the replacement takes 10%MK and 15%MK.

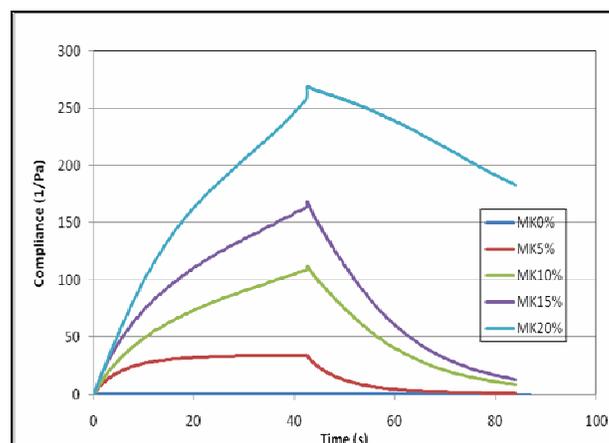
Figure 7: Storage and loss modulus as function as frequency of cement pastes for different proportion of MK



6.3.3. Creep/Recovery Test

For complete the study of the behaviour of cement pastes containing metakaolin, several measurements in creep have been carried out. Figure 8 represents the evolution of compliance as function as time. It shows the effect of metakaolin on the viscoelastic behaviour of cement paste. It is shown that the behavior of all cement pastes is typical of a viscoelastic behavior whose character decreases with increasing of the replacement rate of MK. Moreover, deformations (compliances) undergone by MK paste increase with increasing of the replacement rate of MK. The increase of deformation is characteristic of weak interactions shown in the microstructure compared to the low deformations undergone by the paste control where the interparticle bonds are strong [Zhang, 2000]. A residual strain in pastes is observed for each replacement rate of metakaolin: 0.0021, 0.0365, 0.3358, 0.5037 and 5.7462 corresponding to 0% MK, 5% MK, 10% MK, 15% MK and 20% MK respectively. So these particles in the microstructure don't elastically recover to their equilibrium status. Thus MK improves the paste rheological behaviour. These results confirm those obtained from the flow and oscillatory tests which have shown an improvement of cement pastes behaviour.

Figure 8: Creep /Recovery curves of MK cement pastes.



7. Conclusions

Some products like mineral additives are now inevitable when designing a concrete. These products can give unexpected rheological behaviour of pastes as the main phase affecting the rheology of concrete. The rheological tests have been carried out to study the effect of metakaolin, varying the dosage, on the rheological behaviour of the cement pastes containing 2%SP. The conclusions of this study are as follows:

All the flow curves of cement pastes are modelled with the Herschel-Bulkley model.

The MK exhibit better rheological parameters (viscosity, shear stress) and improve the cement paste flowability, especially the replacement rate of 10%MK and 15%MK.

The MK acts as filler and controls rheology. The dense microstructure, the micro filler and pozzolanic effects of the metakaolin provide the positive effect on the cement pastes flow behaviour.

The dynamic tests have shown two types of behaviour: Viscous behaviour for the cement pastes containing MK and elastic behaviour for the control cement paste (0%MK). So, addition of MK improves the cement paste behaviour. It has significant effect when the replacement takes 10%MK and 15%MK.

The creep /recovery test show that the addition of MK in cement exhibit behaviour typical of a viscoelastic whose character decreases with increasing of the replacement rate of MK. It improves cement paste behavior in creep.

Rheometric tests show promising results witch encourage the use of cement with additions such as the metakaolin component of concrete designated for industry in Algeria since the metakaolin improves the rheological behavior of cement paste in the fresh state.

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