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Rheology of high-performance cement pastes: effect of calcined kaolin

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Abstract. The search for a quality of concrete is a major concern in Algeria especially after the 2003 earthquake (East- Algeria). So it's necessary to improve the properties of concrete using fine particles such as mineral additions as a solution. These are currently used in the concrete to develop its performance and reduce consumption of clinker. This reduction will contribute to economic and easy way to solve problems related to the environment. In this work, an experimental rheological investigation was conducted to evaluate the performances of Algerian metakaolin MK on cement pastes. The latter is obtained from calcined natural kaolin found in large amounts in eastern Algeria (Tamazert- Milia). Several rheological tests were carried out by using the stress controlled rheometer AR2000, on the fresh cement pastes incorporating 0%, 5%, 10%, 15% and 20% of MK. The effects of metakaolin on the rheological behaviour of pastes were discussed. The parameters such as shear stress, viscosity, compliance, loss and storage shear modulus were evaluated by means of rheological techniques of both flow test, oscillatory and creep dynamic tests. The study in dynamic mode 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 the metakaolin improves the flowability and exhibits viscous rheological behaviour of cement pastes compared to the elastic behaviour of control paste (0%MK). Moreover, the creep test has shown that MK exhibits a viscoelastic liquid behaviour of cement pastes compared to a viscoelastic solid behaviour of control paste. In addition, it seems that the replacement rate of 10% of MK is an optimum for better rheological behavior of cement pastes. The rheological tests give promising results that encourage the use of metakaolin as component for a high performance concrete designated for industry.

1 Introduction

In recent years, there has been a growing interest in the use of metakaolin (MK) for producing high-performance concrete. It is a thermally activated alulimino-silicate material produced from kaolinite clay through a calcining process within the temperature range of 700-850 °C [1]. It contains typically 50-55% S_iO_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 [2] 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 [3]. In this work, the mineral admixture used is the metakaolin MK obtained from calcined natural kaolin found in large amounts 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. Effect of MK varying of 0%, 5%, 10%, 15% and 20%, on the rheological behaviour of cement pastes was analyzed.

The rheological parameters (shear stress, viscosity, compliance, loss and storage moduli) have been evaluated by means of the flow test (static mode) and the oscillatory and creep tests (dynamic mode).The dynamic tests are carried out for studying the viscoelastic behaviour of MK cement pastes.

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 [4] (elastic solid, viscoelastic solid, viscoelastic liquid and viscous liquid) (figure 1).

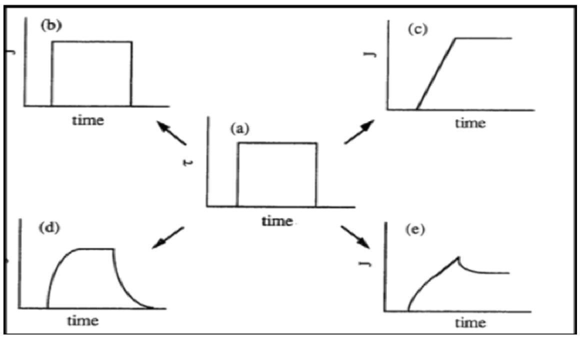

Fig. 1. General creep/recovery behaviour of (b) elastic solid, (c) viscous liquid, (d) viscoelastic solid and (e) viscoelastic liquid under shear stress (a) [4].

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:

$$G^* = \frac{\tau}{\gamma} = G' + iG'' \quad (1)$$

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

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

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. δ is the phase lag between shear stress and strain. τ is the shear stress, η is the material viscosity, γ is the strain and ω is the frequency.

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 [5] (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.

2.4 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.

3 Experimental programs

3.1. Materials

Metakaolin (MK) and cement were used as binder components. As superplasticizer (SP), a commercial high water reducer based on a polycarboxylate and a modified phosfonate, was used during the mix. The cement is a CEM I 52, 5 according to european standart EN 197-1.

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.

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 [6].

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 [7].

The physical properties and the chemical compositions of used materials are given in table1 and table 2 respectively.

Table 1. Physical Properties of materials.

Materials	Cement	MK
Specific Surface (cm^3/g)	4200	8722
Density	3.12	2.54
Mineral activity mgCa(OH)/g	-	137.5

Table 2. Chemical Composition of materials.

Wt%	Cement	MK
SiO_2	19,85	7,235
Al_2O_3	4.80	35,36
Fe_2O_3	2,75	1,18
CaO	63,60	1,33
MgO	1,45	0,21
SO_3	3,45	0,31
K_2O	0,90	1,13
Na_2O	0,15	0,15
PF	2,20	2,01

3.2 Preparing cement pastes and testing

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. 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. In the flow test, cement paste was sheared by applying a sweep stress from 0 to 200pa within 2 min to produce the curve of the flow test. During the oscillatory testing, the stress-control mode was used. A constant stress of 0.03 Pa was applied, after determining the limits of linear viscoelastic region by means of stress sweep experiments from 0.01 to 20pa of stress at a 1 Hz constant frequency. Moreover, 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).

4 Results and discussion

4.1 Flow test

Figure 2 shows that for all pastes containing MK, the shear stresses increase with increasing of the shear rate and are lower than those the paste control (0%MK). So the MK improves the cement pastes flowability, especially the rate of 10%MK and 15%MK.

Figure 3 represents the evolution of the cement paste viscosity. All pastes containing MK, present an initial shear thinning behaviour because of decreasing of the viscosity. After, the viscosity increases with increasing of the 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 [8]. The replacement of 10%MK and 15%MK of cement exhibit the best paste flowability. This is explained by the fact that the MK has the highest specific surface area.

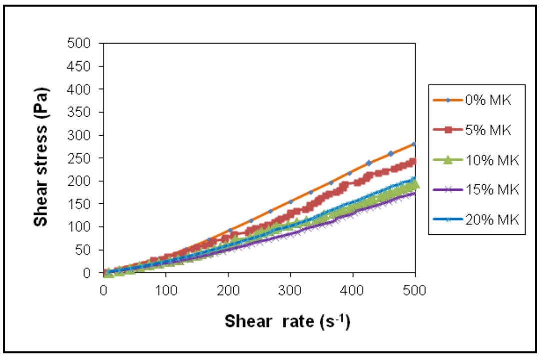

Fig.2. Flow curves of cement pastes for different proportion of MK.

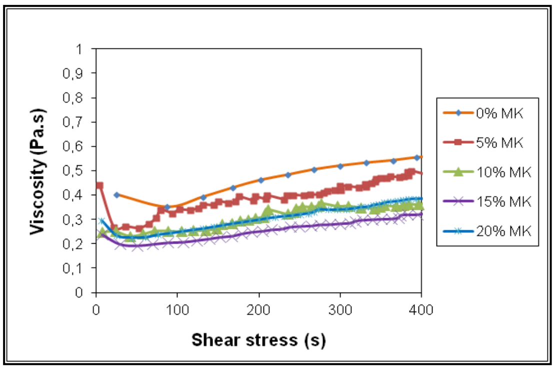

Fig.3. Evolution of viscosity of cement pastes for different proportion of MK.

4.2 Oscillatory test

Oscillatory test provides 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 4). 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 there is a predominance of viscous behaviour compared to elastic behaviour of control cement paste (G' < G"). So the addition of MK improves the cement paste behaviour. It has significant effect when the replacement takes 10%MK and 15%MK.

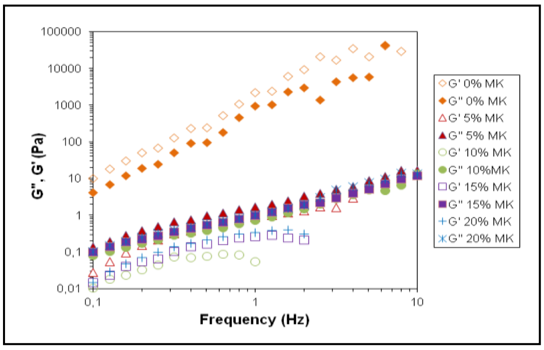

Fig.4. Storage and loss modulus as function as frequency of cement pastes for different proportion of MK

4.3 Creep/recovery test

Figure 5 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 viscoelatic behavior whose character decreases with increasing of the replacement rate of MK. Moreover, deformations (compliances) undergone by MK paste increase with the replacement rate of MK. The increase of deformation is characteristic of weak interactions shown in the microstructure compared to the low deformation undergone by the control paste where the interparticle bonds are strong [9].

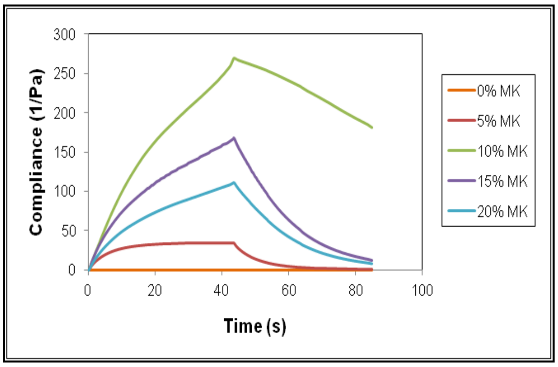

Fig.5 Evolution of compliance as function as time.

Thus MK improves the paste rheological behaviour. These results confirm those obtained from the flow and oscillatory tests.

5 Conclusions

The rheological tests have been carried out to study the effect of metakaolin, varying the dosage, on the rheological behaviour of the cement pastes. The conclusions of this study are as follows:

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

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

The creep test has shown that the substitution of the part of cement by MK exhibits behaviour typical of a viscoelastic whose character decreases with increasing of the replacement rate of MK. The behavior of cement paste is improved with 10% MK.

Rheometric tests led us promising results that encourage the use of cement with admixture such as the metakaolin component of concrete designated for industry since the metakaolin improves the rheological behavior of cement paste in fresh state.

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