Study of Rheological Parameters of Lime-Metakaolin Paste Made of Kaolin Wastes and Lime paste

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Abstract. Metakaolin has been presented as a very good pozzolanic material for using in lime mortars and cement mortars. Several studies also have shown that wastes, coming from the kaolin production, can produce good quality pozzolans. In Brazil, industries that produce kaolin, generate a lot of wastes. These wastes have not been placed in adequate sites or reused. Many studies have discussed about the microstructural characteristics of lime-metakaolin pastes and hardened properties of lime-metakaolin mortars. However few works have been carried out about rheological properties of this kind of paste and mortars. In this work, rheological properties of lime and lime-metakaolin (L-MK) pastes were assessed in their fresh state. The metakaolin used here came from the kaolin production wastes. Static and dynamic rheological parameters like yield stress, viscosity (static rheology test), viscous and elastic modulus, creep and recovery (dynamic rheology tests) behavior were studied in these pastes. The results showed that the curves of pastes presented as a non-Newtonian fluid following a Herschel Bulkely moldel. When the metakaolin was added to lime paste the yield stress and the viscosity was lower. From the dynamic tests it was obtained that the L-MK pastes were less rigid than lime paste. And according to the creep and recovery tests these pastes presented a curve model as a viscoeslastic liquid.

Introduction

Lime-pozzolan pastes and mortars have been studied extensively in order to restore historical buildings. Many works have been focus on the perfomance of lime or lime-pozzolan mortars [1], [2],[3],[4]. As pozzolanic material, metakaolin (MK) have showed better performance than other pozzolanic materials for using in this kind of mortars [1].

In Brazil, there are industries that produce kaolin, and they generate a lot of amount of wastes. These wastes are not used and so they are threw away in not adequate sites and this fact is an environmental problem for landfill near the plant. Nóbrega [5] and Azeredo et. al. [6] has showed that the kaolin production waste can become a good pozzolan, if it is treated (sieved and calcined). Other studies also showed that kaolin wastes as pozzolan presents good perforamnce in concretes and mortars [7],[8], [9],[10],[11].

The performance of lime and lime-metakaolin pastes and mortars has been investigated in many works. Most of these studies have focused on the mechanical properties of these mortars [12], [1],[13],[2],[14]. The results of these works show that mortars containing lime-MK as binder can reach up to 16 MPa compressive strength at 90 days. Others have studied the hydrated products in lime-metakaolin system (paste) [15], [3],[16],[17], [18], [19], [20]. But few authors have studied the rheological properties of this kind of pastes and mortars. And most of them have investigated only viscosity and yield stress (Bingham model) – static shear behavior (flow curves). Studies involving dynamic rheology (oscillatory shear and creep and recovery measurements) in lime or lime-pozzolan pastes and mortars are not found in research sources.
Nowadays there are a new class of rheometers which shear stress is controlled and strain rate is measured. These rheometers are used to measure static shear behavior (flow curves), and they offer improved accuracy at very low strain rate levels. Alternatively, the controlled stress rheometers may be used to measure dynamic behavior.

Creep and recovery measurements using controlled stress is a useful rheological technique for studying the behavior of viscoelastic materials, either solids or liquids ([21]Struble and Shultz, 1993). Colloidal suspensions (ex. Cement pastes) are often viscoelastic in their behavior, and creep/recovery measurements may be used to characterize aspects of their flow behavior ([22]Struble and Shultz, 1993a). This is a transient technique, in that a single abrupt change in stress is imposed and the resulting strain is measured as a function of time. From these results and the solution of some equations you be able characterize a material as an elastic solid, a viscous liquid, or a viscoelastic solid or liquid ([21]Struble and Shultz, 1993). Concern to oscillatory shear, according to Shultz and Struble [22] (1993b), it is a dynamic method, in which strain is oscillated according to a sine function. The measured output, therefore, includes both the level of stress and the extent to which the stress is in phase with the applied strain. By limiting the strain to small amplitudes (i.e., < 1%), the particles stay in close contact with one another and are able to recover elastically, so the microstructure is not disturbed and the paste behaves as a solid. At larger amplitudes the particles are separated and the paste becomes liquid in its behavior. Thus oscillatory shear provides information concerning the viscoelastic properties of suspensions. The parameters that can be obtained from oscillatory shear are G’ (storage modulus) and G” (loss modulus). G’ represents the elastic component of stress and G” represents the liquid component of stress. When G’ > G” the material is a solid-like and the vice-versa is a liquid-like.

Most of the studies of rheology of construction materials are about Portland cement pastes or Portland cement+pozzolan pastes using static rheology. [23]Banfill e Frías (2007), [24]Banfill et al. (2009), [25]Janotka et al. (2009), [26]Mansour et al. (2010) and Safi et al. (2011) studied the rheology of cement paste containing pozzolanic addition and all pastes presented a Herschel Bulkley curve model. Azeiteiro et al. [28] (2013) studied the rheological parameters (viscosity and yield stress) according to Bingham model of lime mortars. In his work it was shown that the viscosity and yield stress in mortars decreased as the superplastisizer content increased.

However very few works have investigated the rheology of cement pastes using the dynamic rheology techniques. Mansour et al.[26] (2010) studied pastes containing Portland cement and metakaolin (MK) and only Portland cement. All pastes presented similar behavior. G’ was higher than G” when the oscillatory shear reach up the critical stress (yield stress). This fact means that the pastes presented a behavior as a solid. When the oscillatory stress was higher than the yield stress, G’ was lower than G” which indicates that the paste became more liquid-like. In the same work, the creep and recovery tests were analyzed as well. All pastes presented as viscoelastic fluid and when the MK content increased the strain was higher.

In the current work both static and dynamic rheology were used to study the rheological properties of lime and lime-metakaolin pastes in order to understand better the influence of the metakaolin on the workability of lime mortars for restoration.

Materials and Experimental procedure

Materials
The materials used in this research were hydrated lime, a local commercial product, and metakaolin (MK) produced from kaolin production wastes (K PW), which was generated during the production of kaolin at the Caulisa S. A. plant located in Juazeirinho, Paraíba-Brazil. In order to produce the pozzolan this waste was first sieved to remove material coarser than 75-μm. To produce the metakaolin, the finer fraction was calcined at 700°C for 2 hours following the procedure used by others ([15]Pera and Amrouz 1998; [29]Kakali et al. 2001; [30]Oliveira 2004).

All materials were characterized using x-ray diffraction (XRD), x-ray fluorescence (XRF) and laser granulometry. The XRD analysis used a Siemens Bruker D5000 diffractometer with Cu Kα
radiation, at 40 kV and 30 mA, and scan speed of 10/min. For the XRF analysis the samples were dried in an oven at 110 °C, pressed into tablets, and analyzed using a Rigaku RX 3000 X-ray spectrometer. For laser granulometry the specimens were dispersed for 20 min in 250 ml of distilled water using a mechanical mixer, after which 15 ml of the suspension were dispersed in an ultrasonic bath and then analyzed using a CILAS 1064 granulometer. The XRD patterns are shown in Fig. 1. Chemical compositions from XRF are given in the table 1.

The hydrated lime contains portlandite (P) as the main phase and calcite (C) as a minor phase. The kaolin production waste is largely kaolinite but also contains microcline and perhaps another feldspar, plus quartz and illite (or mica). After calcination all peaks of kaolinite disappeared and the other phases remained. In the calcined kaolin XRD pattern there is a broad hump centered around 23°, which is a characteristic of amorphous metakaolin.

According to the x-ray fluorescence analysis the hydrated lime contains mainly CaO and some MgO. The kaolin production waste contains mainly SiO₂ and Al₂O₃. In Fig. 2 is shown the particle size distribution curves obtained using a laser granulometer for the lime, kaolin production waste and metakaolin. According to this data the lime is finer than KPW and MK. Most of its grains are smaller than 20 μm. The KPW and MK have almost the same particle size, both finer than 100 μm as they had both previously been passed through a 75-μm sieve.

Fig. 1 XRD of hydrated lime, KW and MK.

<table>
<thead>
<tr>
<th>Materials</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>1.25</td>
<td>0.47</td>
<td>0.35</td>
<td>93.10</td>
<td>4.57</td>
<td>0.06</td>
<td>0.03</td>
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<tr>
<td>KPW</td>
<td>61.66</td>
<td>33.66</td>
<td>0.48</td>
<td>0.12</td>
<td>0.25</td>
<td>3.6</td>
<td>-</td>
</tr>
<tr>
<td>MK</td>
<td>54.44</td>
<td>41.82</td>
<td>0.43</td>
<td>0.06</td>
<td>0.21</td>
<td>2.95</td>
<td>-</td>
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</table>
Experimental Procedure
Two kinds of pastes were studied: one containing only hydrated lime (LP) and the other one lime and MK (LMK). The lime-MK ratio was 1:1 and the water/materials ratio was 1.0 for all pastes. In all pastes it was used 10g of materials and the water was added slowly. The pastes were mixed gently by hand up then transferred into the rheometer. The rheometer used was a C-VOR Bholin instrument. The tests were measured using coaxial cylinders (cup and bob – Fig. 3).

Before each measurement a 50 Pa shear stress was applied during 45s in order to eliminate any residual strain and stress from the sample. After that, the paste rested for 10 min. And then the measurements started. These conditions for the tests measure were fixed based on works of literature ([21],[22]. All samples were covered to avoid the water evaporation during the test.

To obtain yield stress and viscosity data of the pastes a shear stress range from 1.5 to 510s\(^{-1}\) was applied during 5.5 min and also a shear stress constant at 5s\(^{-1}\) during 20 min. The same conditions were studied by Izaguirre et al. [31]. For the dynamic tests this work based on the studies carried out by others [21], [31], [20].

G’ and G’’ parameters were obtained when the range of oscillatory shear was 10\(^{-4}\) and 1 hertz frequency as function of time. For creep and recovery measurements a 0.5 Pa shear stress were applied during 30 min. (creep) and after that, the stress was removed, then the strain was measured.
for 30 min. also (recovery). The shear stress of 0.5 Pa was chosen based on the flow curves obtained from the static shear behaviour. The other parameters were chosen based on the works carried out by [21],[22].

**Results and Discussion**

**Viscosity and yield stress (flow curves – static rheology)**

The flow curves of the pastes presented behavior as a Non-Newtonian fluid, i.e., the strain/shear stress ratio is not constant. The yield stress of LP paste was around 2 Pa and for LMK paste was near 1 Pa. So when the metakaolin was added to the lime paste the yield stress decreased. This fact is due to the metakaolin particle shape, which is lamellar. Its shape contributes to the lime and metakaolin particles can slide more easily between them Vlack, 1970 apud [33]. The results are shown in Fig. 4.

![Flow curves of LP and LMK pastes](image)

Fig. 4 Flow curves of LP and LMK pastes

LP paste presented a higher initial viscosity than MK paste. The viscosity decreased with high shear rates for both pastes. i.e., the pastes become more fluid with high shear rate. The diminution of viscosity can be related to the volume fraction of the particles in the solution [34], [35], [36],[37]. Thus in LMK paste, as the MK particle is bigger than LP one, the amount of particles was lower and so contributing to the decreasing of viscosity in this paste. The viscosity decreased with time for both pastes. The results are shown in Fig. 5 and Fig. 6.

When a lower value shear stress (5.5 s⁻¹) was applied during 20 minutes, the viscosity of both pastes increased with time. LP paste viscosity increased slightly while for LMK paste the increasing was stronger (from 0.3 Pa.s to 0.5 Pa.s). During the time test the viscosity the curve of LMK paste was always below the LP curve. The result is shown in Fig. 7.
Fig. 5 Viscosity $\times$ shear rate data of LP and LMK pastes

Fig. 6 Viscosity $\times$ time curves of LP and LMK pastes

Fig. 7 Viscosity $\times$ time curves of LP and LMK pastes for 5.5 s$^{-1}$ shear stress
In general way, according to the literature, cement Portland pastes, mortars and concrete behave as Non-Newtonian fluid. They can be as a Bingham model curve or Herschel-Bukley (HB) model curve. Ferraris et al. [38] showed in his work that HB model curve is the best model that represents the self-compact concrete flow curve behaviour. In Fig. 6 is shown the flow curve of paste studied in this work and a mathematical curve model obtained from the non-linear model from the computational software Origin 8.0. The result show that the LP and LMK pastes behave very well as a HB model. Banfill and Frias [23] showed in their work that curves of Portland cement+metakaolin (from paper sludge) pastes containing superplatisizer presented a HB model curve behaviour. Also the same behaviour occurred in the pastes studied by Janotka et al. [25]. The pastes studied for him were made of Portland cement and mekaolin (from kaolinitic sand).

In the equations for both curves (Fig. 8) the label c represents the fluid behaviour index: when it is higher than 1 the fluid is dilatant, if it is between 0 and 1 the fluid is pseudoplastic, and when it is equal 1, the fluid is Newtonian. In the present work all pastes have this index value between 0 and 1, which implies that all pastes like is pseudoplastic fluid.

**Creep and recovery (dynamic rheology)**

In the creep and recovery measurements the results are obtained from the compliance (J) as a function of time. The compliance is the measured strain divided by the imposed stress, which is constant throughout the experiment (Struble and Schultz, 1993). The results allows characterizing a material as an elastic solid, a viscous liquid, or a viscoelastic solid or liquid. In Fig. 9 the results of the pastes studied here are shown. The ascendant part of the curve represents the creep behavior and the descendent part represents the recovery behavior.
Both pastes presented a viscouselastic liquid behavior curve, according to Struble and Shultz [22] (1993). For this kind of mix when a stress is applied a viscous strain happens. And after the stress is removed there is a instantaneous recovery and late elastic stress, but not all strain is recovered. Comparing the LP and LMK paste it is observed that LMK paste presented a less elastic behavior than the LP paste.

Storage and loss modulus (G’ and G” - dynamic rheology)

In all pastes when the oscillatory stress was below the yield stress, both G’ and G” curves followed a plateau. When the stress increased the G’ and G” modulus decreased. This fact means that from this stress the mix started flow. The part of curve where is a plateau the value of G’ and G” for LP was higher than LMK (around 500 Pa-LP and 200 Pa-LMK). The results are shown in Fig. 10. When MK was added to lime paste, the LMK paste became less rigid, because LMK mix turned more dispersed. Azeredo et al. [20] (2012) mention in his study that the MK surface area is higher than Portland cement surface area, allowing to fill the spaces between cement particles and thereby mitigate friction and reduce stiffness of the paste. In the current work the lime surface area is higher than MK surface area, so in this case the lime fill the spaces between MK particles.

Concern to the behavior of G’ and G” curve it can observed that for both paste the value of G” was always lower than G’ value. This fact indicated that an elastic behavior was dominant.
Conclusions

From the results of this paper it was observed that:

The yield stress of LMK paste was lower than LP paste. The LMK pastes were less viscous than LP paste. The lower concentration of particles in the solution (mix) was the main reason to the decreasing of yield stress and viscosity of LMK paste.

Both lime (LP) and lime-metakaolin (LMK) pastes presented flow curves that can be adjust very well to the Hercshel-Bulkley model.

From the dynamic data it can be drawn the following:

The result from creep and recovery measurements showed that both pastes had a viscouselastic liquid behavior. The LMK pastes behaved more elastic than LP paste.

When the MK was added to lime paste, the LMK paste were less rigid. Both pastes presented a dominant elastic behavior, where the loss modulus (G") was higher than storage modulus (G').

In general view, the addition of MK in lime paste strongly influenced the rheological behavior of this paste. The reasons for this fact are: the shape of the MK particle, surface area and particles volume fraction of mix. So, we can say that the workability of lime paste was better when the MK was added to. This work showed the behavior of lime and LMK pastes using rheological techniques which have been used for understanding better the rheological properties of Portland cement paste containing or not any addition. Further the current work have brought to the scientific community a few understanding about the rheological properties of lime and LMK pastes).

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References


