

Use of rheological models for the evaluation of cement pastes with air-entraining agent in different temperatures

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ABSTRACT

Despite the air-incorporation improve the workability and productivity of cementitious materials, making them more sustainable, it can become very sensitive to extrinsic factors, like processing and environmental conditions. Therefore, the correct evaluation of the rheological properties is extremely important for an understanding of the main causes of use of air-entraining agents (AEA) in these compositions. Tests with variation in the shear rate are commonly used, and the results are often evaluated applying rheological models to quantify both the yield stress and the plastic viscosity of these products. The most commons are Herschel-Bulkley, Casson or Bingham, but in many cases the models applied do not correctly represent the results obtained, do not fitting to a reality observed in everyday life. So, in this work the rheological properties of cement pastes with air-entraining agents were quantified at different temperatures, and applied rheological models to evaluate the relationship between the results that was measured and modelled. The main conclusions were that the use of AEA and the temperature affected the rheological properties, the temperature affected in the air-incorporation and, the application of rheological models does not well represent that have been measured, mainly in extreme shear rates.

INTRODUCTION

Air entrainment is the process whereby many small air bubbles are incorporated into fresh cementitious materials to become part of the matrix that binds the aggregate together after hardening. This technique is primarily used to improve the freeze-thaw resistance of a concrete, but is very important either to improve the workability and productivity, making them more sustainable. the intentional air-bubble incorporation.

However, the intentional air-bubble incorporation and the possibility of reduction of binder/m², can make these materials very sensitive to the process and environmental conditions [1-8].

Thus, the use of this technique has become a complex operational factor [8] because there is no precise control of the rheological properties, and the changes in the viscosity or yield stress may occur in an undesirable manner many cases. Consequently, the hardened properties are not controlled.

Type of cement, water-to-cement ratio, kind and content of admixture, and others, are some variables that affect the suspensions quality: i.e. changes on the type or content of air-entraining agent (AEA) promotes considerable alterations in the air-bubble volume, changing directly the air-incorporated in the suspensions and consequently, the air-void volume after hardening, decreasing the mechanical strength and elasticity modulus and increase the air-permeability [1,9].

So, the correct and complete comprehension of the main factors that affects the rheological properties can be considered the first step to become the cementitious systems less sensitive to extrinsic factors.

Generally, the quantification of fresh state changes has been carry out using rotational rheometry, changing the shear rate and quantifying the shear stress and viscosity. In the sequence, is common to apply rheological models to extrapolate the results obtained, mainly to determine yield stress and plastic viscosity [10-12].

However, it has been noticed that not always the applied models correctly represented the results obtained, do not fitting the real measurements.

At this way, the main purpose of this work was evaluating the rheological changes promoted using air-entraining agents in cementitious pastes evaluated in different temperatures, and the applicability of rheological models to quantify the interested parameters and fit the results obtained.

EXPERIMENTAL

The work was carry out using a Brazilian Portland cement, named according national standard by CPIIF, and two air-entraining agents with molecules based on sodium lauryl sulphate (SLS), commonly employed in formulations of industrialized rendering mortars. Both admixtures have the same foaming capacity and, in this work were designed by SLS-1 and SLS-2.

The chemical compositions of cement is presented in Table 1 and the particle size distribution in Figure 1.

As expected it was quantified more calcium and silicon content, indicating the predominance of silicate phases of clinker. It is important to say that this kind of cement should have up to 15% of calcium carbonate, but it was quantified, by thermal analysis, around 20% calcite. This means that the binder was not stored correctly, resulting in powder carbonation. Because of

this the loss on ignition was a little above that is established by the Brazilian standard (NBR 11578/91), but this is not a problem to the evaluations did in this work. All the other chemical elements are in conformity with the referred standard.

Table 1. Cement chemical composition

Tests	% in weight	Limits of NBR 11578/91 *
Loss on ignition	8.83	≤ 6.5%
SiO ₂	16.35	***
Al ₂ O ₃	3.50	***
Fe ₂ O ₃	4.25	***
CaO	55.60	***
MgO	5.98	≤ 6.5%
SO ₃	2.26	≤ 4.0%
Na ₂ O	0.08	***
K ₂ O	0.24	***
CO ₂	8.66	≤ 5.0%
Insoluble residue	2.32	≤ 2.5%
Free lime	1.58	***

* NBR – Brazilian standard methods

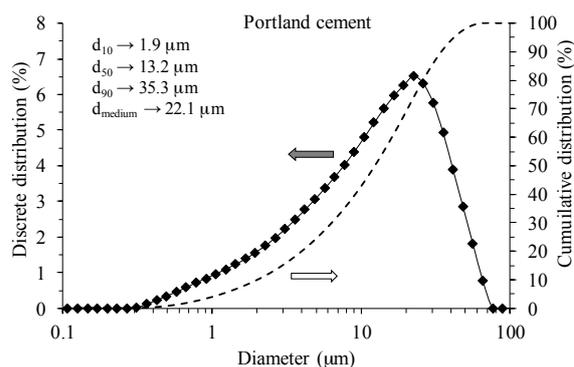


Figure 1. Particle size distribution of Portland cement

Table 2 presents the real density, obtained by gas He picnometry (Quantachrome), and the specific surface area (BET method, Belsorpmax – Bel Japan), by Portland cement and AEA.

Table 2. Real density ana specific surface area of Portland cement and air-entraining agents

Raw material	Real density (g/cm ³)	SSA* (m ² /g)
Portland cement	3.00 ± 0.10	1.75
SLS-1	1.06 ± 0.01	1.44
SLS-2	1.05 ± 0.01	0.71

* specific surface area

Mix conditions

Cement pastes were mixed using an equipment Labortechnik RW20, IKA,

maintaining the water-to-solid ratio at 0,4. All cement was put into a becker and the water was added following, waiting 30 seconds to wetting. Starts the mixing using rotational speed of 300 rpm by 2 minutes to homogenize the suspension, then the rotational speed was increased to 600 rpm for more 2 minutes. After this first homogenization, the particles were dispersed using a high shear energy mixer, Labortechnik T25 basic, IKA, for 5 minutes at 9500rpm.

After dispersion, the AEA was added in the paste (0,05%-weight) and starts the mixture for more 30 seconds at 600 rpm. To guarantee the same mix condition the reference paste (without AEA), was mixed following the same procedure.

All pastes were evaluated at 10, 25 and 40°C to simulate different environmental conditions.

Fresh properties

Characterizations used in this work consists in quantification of air-incorporation and rheological tests under flow conditions.

Air-incorporations: the air-volume was quantified using the gravimetric method following the Brazilian standard NBR 13278/02.

Rheological evaluations: tests were performed in an AR550 rheometer, TA Instruments, with parallel plate geometry of 40 mm and a gap of 1000 μm. A flow continuous method was used, changing the shear rate from 0 to 150s⁻¹ and return to 0, in 1 minute. All rheological tests starts 5 minutes after end the mixture.

Rheological Models

To establish a comparative criterion the rheological models of *Herschel-Bulkley*, *Casson* and *Bingham*, were applied to estimate the plastic viscosity and yield stress (σ₀), according eq.1 to 3 [11-12]:

Herschel-Bulkley $\sigma = \sigma_0 + \eta * \dot{\gamma}^n$ (1)

Casson $\sqrt{\sigma} = \sqrt{\sigma_0} + \sqrt{\eta} * \sqrt{\dot{\gamma}}$ (2)

Bingham $\sigma = \sigma_0 + \eta * \dot{\gamma}$ (3)

where σ is shear stress (Pa), η é the viscosity (Pa.s), γ̇ is the shear rate, n is a Herschel-Bulkley’s fluid index (n=1 Newtonian, n>1 shear thinning e n<1 shear thickening).

Thus, for each rheological model there is a global error, calculated in each point, according eq. 4:

$$Error = \frac{\sqrt{\frac{\sum(x_m - x_c)^2}{n' - 2}}}{Range} \cdot 1000$$
 (4)

where x_m is the measured value, x_c is the calculated value, n’ is the number of points and range in the maximum x_m value.

RESULTS AND DISCUSSION

Air-incorporation

Figure 2 show the results of air-volume incorporated in the reference and additived pastes.

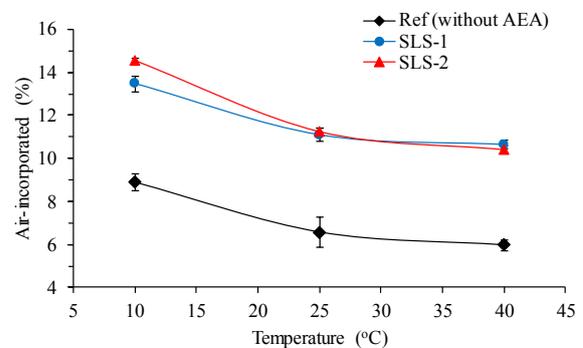


Figure 2. Effect of temperature and use of air-entraining agent on the air-incorporation

The higher the temperature, the lower the volume of air incorporated, because the temperature rise:

- results in reduction of liquid viscosity and the air-bubbles are easily collapsed: the amount of liquid in the interface is quickly reduced, changing the morphology of air-bubble (from spherical to polyhedral) and, according the Laplace’s law, pressure

gradients are generated which facilitates the air-bubble coalescence due to capillary suction [13,14].

- reduces the hydration of admixture hydrophilic groups and the water surface tension, and increase the brownian motion and cement particle collisions. This can to generate water molecules disorganization around the admixture polar group, increasing the disadjustment, disfavoring the micelle formation [14].
- directly impacts in the AEA foaming capacity and bubble stability, due to the reduction of thickness and strength of films that surround the air-bubbles, facilitating the coalescence [13].

The use of AEA was responsible for increasing the air volume compared to reference paste, as expected. However, no significant differences in air volume were observed as a function of the type of addition, showing that both have the same foaming ability. This is consistent because they have similar molecules, with anionic dissociation, but only with subtle difference in molecular chain length.

Subtracting the air volume incorporated in the pastes with AEA of reference pastes, the average of increase was $4,7\% \pm 0,4$, independent of temperature. So, this is the air-volume incorporated due to the action of AEA. The percentage reduction on the air-volume in function of temperature increase (from 10°C to 40°C), was around 33% to reference paste, 21% to SLS-1, and 28% to SLS-2.

Rheological characterization

The presentation of rheological results was divided in two steps of discussions:

- i. real data measured
- ii. application of models

Figure 3 presents the relation between shear stress and shear rate. From top to bottom are the results of reference pastes, SLS-1 and SLS-2, respectively. Arrows with

solid line indicates the period when the shear rate is rising, and the dashed arrows indicates the period of deceleration

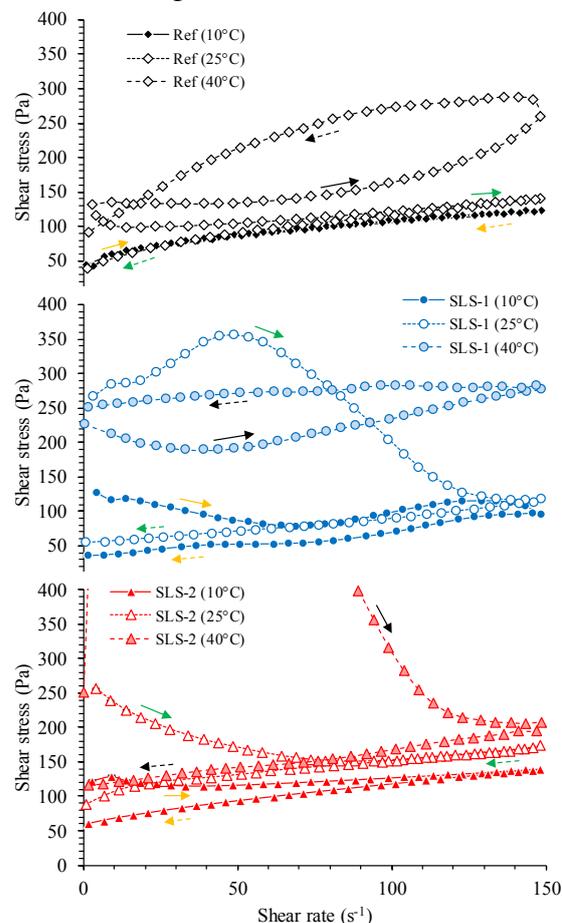


Figure 3. Shear stress vs shear rate. From top to bottom are the results of reference, SLS-1 and SLS-2, respectively. Arrows with solid line indicates the period of rising the shear rate, and the dashed arrows indicates the period of deceleration

Some points that deserves more attention are that the temperature rise increased the particle agglomeration and thixotropy, but all pastes followed the shear thickening fluid behaviour.

When systems presented thixotropy > 0 indicates that the particle de-agglomeration is faster than the re-agglomeration [10]. In the contrary, there is an indicative that the particle re-organization is faster than de-agglomeration; to the same shear rate, the shear stress in the second stage of test is higher than observed in the first one.

Changes on the rheological properties observed during the acceleration period are quantified when the particle agglomerates are being broken, releasing the water that was trapped inside the agglomerates for the separation of the particles. So, this results are not pure, obtained in a non-disperse system.

On the other hand, during the deceleration stage the particles are better dispersed in function of the rise of shear rate in the first stage, and the quantification of rheological properties are more reliable.

Application of rheological models

From the curves presented in Figure 3 were applied the rheological models to quantify yield stress and plastic viscosity. It is convenient to say that it was used the results obtained in the second stage of test, because there was better particle dispersion, according discussed before.

It was obtained either the apparent viscosity (η_{ap}) and yield stress from the real data: while the value of viscosity at 150 s^{-1} was used as η_{ap} , (because is this was the highest shear condition), the σ_0 was the value of shear stress at the lowest shear rate. These mode is described in this work as *graphical method*.

Statistically, among the rheological models applied, the values of yield stress and plastic viscosity were best fitted by the Herschel-Bulkley's, represented by the smaller average error obtained in all curves.

So, Figure 4 presented the relationship between yield stress and viscosity (plastic or apparent), estimated according Herschel-Bulkley model (on the left) or graphically (on the right).

As it can be seen, there are no coherence between the real data and modelling rheological parameters.

In the reference pastes the results of modelling pointed out to the rise of plastic viscosity and decrease of yield stress, in function of temperature rise. On the other

hand, in the pastes with AEA the presence of air-bubble resulted in the increment of both rheological parameters, but with poor R^2 .

Although the results obtained for the other rheological models are not being presented, it was not observed the same correlation of Herschel-Bulkley, indicating that there are not a convergence of results modelled.

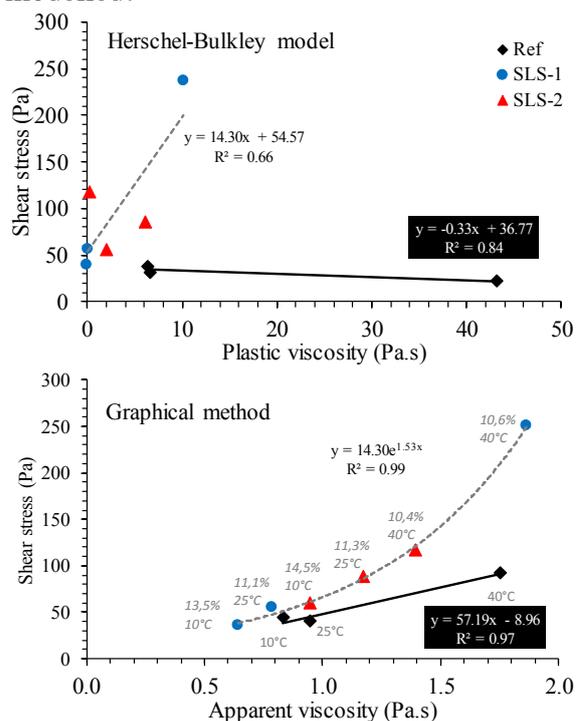


Figure 4. Relationship between yield stress and viscosity defined using the Herschel-Bulkley model (above) and graphical method (below).

Due to these incoherencies it can be said that these rheological models are not correctly describing the results measured in the pastes, with or without AEA.

This is a relevant information because, in case of evaluated pastes, there were not observed correlation between yield stress and viscosity in function of air-incorporation, independently of temperature. So, it can be said that the use of AEA, resulted in randomical alterations in rheological properties, because:

- it was produced a new phase in the suspension which can be disrupted in function of the shear;
- the stability of air-bubble, liquid viscosity, brownian motion and frequency of particle collisions, were affected by the temperature changes.

Assuming that a rheological model should describe a system as a whole, the presence of the AEA and the temperature variation are too complex to be described by these chosen models.

Using the graphical method to show the real data, on the other hand, the correlation of rheological parameters is more coherent: in this case, it was observed increases in both parameters, independently of temperature or use of AEA.

However, the reference paste presented a linear relationship between η and σ_0 , illustrating the effect of temperature variation, but in the pastes with AEA was observed an exponential relationship, emphasizing besides the increase in temperature, the contribution of the air bubbles to change the rheological properties.

Summarizing the results obtained using the graphical method, the tendencies observed are presented in Figure 5. It was presented just the real data because there was not observed coherency in the modelled results.

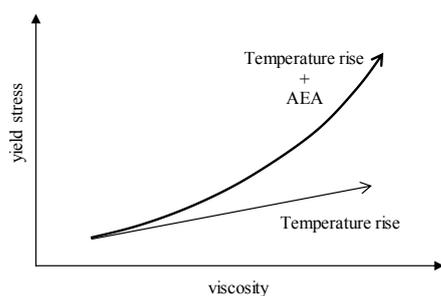


Figure 5. Effect of temperature rise and use of AEA in the changes of rheological parameters.

This complexity indicates that it is not possible to evaluate the systems as a whole, but rather as a function of a series of

variables that may interfere in the quality of the cement compounds, such as air-volume, temperature, water quantity, type of cement, admixture content, etc. (these last three do not presented in this work) 12.

Representativeness of rheological models

The characterization of rheological behaviour of pastes used in this work is intrinsically complex, because the cement chemical reaction, the particle agglomeration and the air-bubble volume and stability are affected by the changes in the temperature.

Because of these, the application of rheological models can generalize a lot what is occurring during the flow.

To show this affirmation are presented in Figure 6a a comparison between the real data quantified during the test and the modelled curves. In (b) are presented the relative difference between the real and modelled data. From top to bottom are the results for Herschel-Bulkley, Casson and Bingham, respectively.

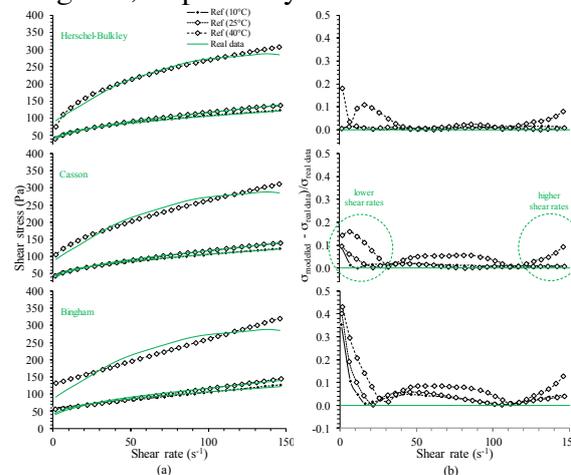


Figure 6. Comparison between the real data quantified during the test and the modelled curves. In (b) are presented the relative difference between the real and modelled data.

In the reference pastes the Herschel-Bulkley's model better fitted the results, mainly when the tests were carry out at 10 and 25°C. At 40°C there was considerable

differences in the extreme shear rates (lower than $40s^{-1}$ or higher than $120s^{-1}$).

Casson and Bingham models presented the same restrictions, but were independent of temperature, illustrating that they are inadequate to fit this kind of suspensions. Additionally, both presented higher deviation in extreme shear conditions than observed by Herschel-Bulkley (mainly Bingham).

So, as all models presented high deviation in the extreme shear conditions it is correct to say that they are not good tools to estimate yield stress or viscosity and cannot be used to fit these results.

At the same way, the evaluation was done for the pastes formulated with AEA and the results are presented in Figure 7. In (a) are the results of pastes with SLS-1 and in (B) SLS-2. In the sequence, are presented in Figure 8 the relative difference between the real and modelled data.

Despite of Herschel-Bulkley model represents the best fitting, as yet observed previously in the reference pastes, there is not any tendency. For instance, the composition SLS-1 ($10^{\circ}C$) presented higher deviation, independent of model used, while SLS-1 ($40^{\circ}C$) was better represented,

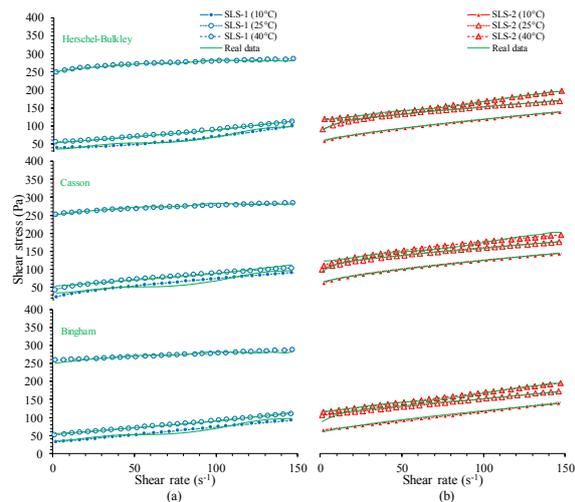


Figure 7. Comparison between the results measured and modelled for the pastes with AEA. (a) SLS-1 and (b) SLS-2

showing a divergence that was observed for the reference paste, where the temperature rise difficulted the modelling.

Pastes formulated with SLS-2 were better fitted by Herschel-Bulkley model and indicating the same higher deviation at extreme shear rates that was discussed before.

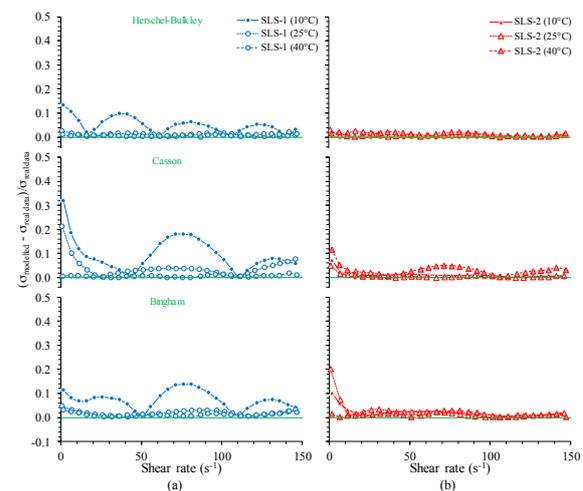


Figure 8. Relative difference between the real and modelled data. (a) SLS-1 and (b) SLS-2

So, as previously reported, in case of the pastes used in this work, the use of rheological models was not adequate tool to predict yield stress and viscosity. It is important to evaluate this results very carefully because cementitious pastes are very complex systems that depends on many variable, intrinsic or extrinsic, and any change can completely modify the flow condition.

CONCLUSIONS

Based on the results presented, it can be concluded that:

- temperature was the most impacting variable that affected the rheological changes;
- as higher the temperature, lower the air-volume is;
- even with similarity in the molecules, the SLS-2 affected less the rheological properties than SLS-1;

- the use of rheological models to fit the results did not well represent the real data obtained;
- comparing the real and modelled data, Herschel-Bulkley was the model with lower deviation, but even so, it was not adequate to represent yield stress and viscosity, because the main deviation was observed at the extreme shear rates. Using Casson and Bingham this problem was still higher;
- so, the modelled σ_0 and η are not consistent with reality. At this way, for the pastes evaluated in this work it was not indicated the use of the rheological models, because complex systems like these are suitable of changes in function of many other variables.
- the best way find to compare the results obtained in this work was the graphical method, which show that variations in the temperature and use of AEA resulted in a direct correlation between σ_0 and η , but the complexity indicates that it is not possible to evaluate the systems as a whole, but rather as a function of a series of variables that may interfere in the quality of the cement compounds.

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