Impact of particle packing on the rheological properties of cementitious pastes dispersed with polycarboxylate

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ABSTRACT

Concretes with low binder content have been an alternative for reducing the environmental impact of the cement production chain. For this, the use of superplasticizers to reduce the water demand, and the implementation of particle packing concepts, are essential tools. While the optimization of packing results in lower need of water to fill the space between the particles, the steric stabilization promoted by the superplasticizer is responsible for improving the workability over time. However, the effects of particle packing, associated with dispersion on the rheological/chemical reactions are still poorly understood, deserving deeper investigations. So, the main purpose of this work was to evaluate the impact of packing on particle mobility during the flow (using an interference model) and the chemical reaction of compositions formulated with Portland cement and limestone filler. The binder content was kept constant and the superplasticizer optimized. Chemical reaction was monitored by isothermal conduction calorimetry and the rheological properties by rotational and oscillatory rheometry. The results show the reduction of yield stress and viscosity with improvements of particle packing and changes on the consistency gain over time and chemical reaction.

INTRODUCTION

In the modern society, concrete is the most produced material in the world, with an estimated production higher than 10 km^3 per year[1]. Basically, concrete is a mix of aggregates, water and binder, This last constituent has a production of more than 4 billion tons/year, with expected growth in the coming years[2].

At the same time, the United Nations (UN, www.un.org) estimates that up to 2050 the world population will be around 9,6 billion people, increasing in relation to the current 7 billion.

So, this indicates that there is a clear need to improve the urban infrastructure to attend the population needs.

This scenario, which is independent of economic crises, elevates the society's challenge for more sustainable growth in an era where natural resources are headed for depletion, if the exploitation, consumption and waste generation patterns are maintained [www.wealthydebates.com].

Thus, it is necessary to employ more advanced technological solutions in the buildings, resulting in more efficient and less labour-intensive productive processes. This should also be considered for the future of construction materials.

Independent of that, the great challenge is: *how to increase the production of the most important building materials to meet the demands of growth and urbanization, without increasing the impact of the enormous produced volumes?*

So, the modern society can not tolerate that the environmental impact increases at the same pace as the growth of cementitious materials consumption.

It is in this context that this work is inserted, looking for development of concrete compositions using lower binder content, leading to reductions of CO_2 emissions, while the performance and durability of the products are maintained.

This development can be done using different alternative materials, substituting part of the clinker during the cement production or in the compositions of concretes[3,4,5,6]. The use of superplasticizer is another way, which makes possible the reduction of water demand, improving thus some hardened properties[7,8,9].

This substitution is not trivial because: i. the reduction of cement changes the fresh and hardened properties of products, often in an undesirable manner; and ii. there are many kinds of raw material that can be used, presenting very distinct physicochemical properties.

So, to correctly understand the performance of materials in use, it is first necessary to understand the behaviour during the transition from fluid to hardened state[10,11].

EXPERIMENTAL
Materials

The work was carried out using a Brazilian Portland cement, named according national standard as CPIIE, and two kind of limestone fillers, named as LF1 and LF5, respectively used for improve the performance (due to the high amount of finer particles) and for substitution (due to the particle size distribution similar of the binder).

A polycarboxylate superplasticizer was used to reduce the water contend. According to the manufacturer, this superplasticizer is not recommended to maintain the workability for long time.

Figure 1 and Table 1 presents the physical characterization of raw materials used, indicating the particle size distribution (obtained by laser granulometry, Helos – Sympatec), real density (gas He pycnometry, Quantachrome), and specific surface area (BET method, Belsorpmax – Bel Japan).
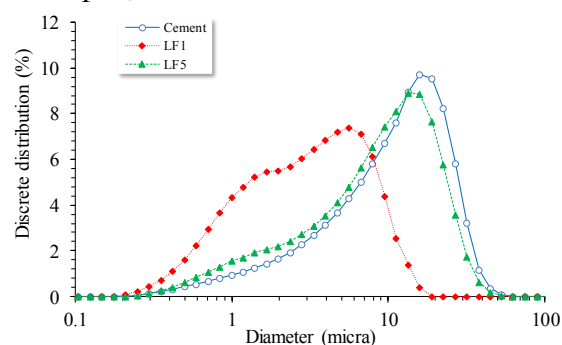

Figure 1. Particle size distribution. Fillers: LF1 = performance, LF5 = substitution.

Table 1. Real density, specific surface area and characteristic diameter of 10, 50 and 90% of particle

Raw material	Cement	LF1	LF5
Real density (g/cm³)	3.08	2.78	2.78
Specific surface area (m²/g)	1.87	3.73	1.16
d_{10} (micra)	2.10	0.74	1.50
d_{50} (micra)	10.5	2.8	8.7
d_{90} (micra)	22.5	7.6	20.5

Particle size distribution d_{50} is known as the median diameter, an important parameter for characterizing particle size. It is the value of the particle diameter at 50% in the cumulative volume distribution. For example, in the cement, d_{50}=10.5 μm, then this represents that 50% of the volume of the particles are smaller than this size, while for LF1 the d_{50} is smaller than 2.8 μm, indicating a high amount of finer particle. So, this kind of filler was used to improve the filler effect and packing of particles.

The chemical compositions of cement and limestone fillers, obtained by X-ray fluorescence, are presented in Table 2.

As expected, it was quantified more calcium and silicon content in the clinker, indicating the predominance of silicate phases. It is important to say that, according to the Brazilian standard, this kind of cement can have up to 10% of calcium carbonate, and it was quantified, by thermal analysis, around 8.5% of calcite. All the

other chemical elements are in conformity with the Brazilian standards.

Table 2. Cement chemical composition

Tests	Cement	LF1	LF5
Loss on ignition	3.36	42.6	29.6
SiO_2	21.1	1.66	3.68
Al_2O_3	5.01	0.10	0.10
Fe_2O_3	2.64	0.30	0.04
CaO	60.1	47.8	60.7
MgO	2.63	7.90	5.76
SO_3	2.86	0.01	0.02
Na_2O	0.33	< 0.01	< 0.01
K_2O	0.85	< 0.01	< 0.01

Limestone fillers have predominance of calcium, but it was quantified almost 8% of magnesium (by LF1) and around 5.8% for LF5, indicating the presence of dolomite and calcite.

Methods
Rotational and oscillatory rheometry

The fresh state properties evaluation were divided in 3 steps:

i. admixture optimization (for each raw material);
ii. evaluation of flow properties (using blended suspensions); and
iii. consolidation monitoring in time.

In the steps i and ii the rheological parameters were evaluated using *stepped flow test* as represented in Figure 2a, consisting in shear rate changes from 0 to $400s^{-1}$ and then returned to 0, in 4 minutes.

During the admixture optimization, each raw material was mixed at a constant weight water-to-solid ratio of 0.3 and increasing the superplasticizer contend from 0 to 1.2% (increments of 0.1%).

After the determination of the admixture contends for each material, new pastes were formulated with different proportions of cement and limestone fillers.

These compositions were used in steps ii and iii. to evaluate the impact of packing and dispersion during flow and consolidation. In stage iii., the time sweep test was used maintaining the strain and frequency constant at 10^{-4} and 1Hz,

respectively, according to Figure 2b, during 4 hours at 23°C.
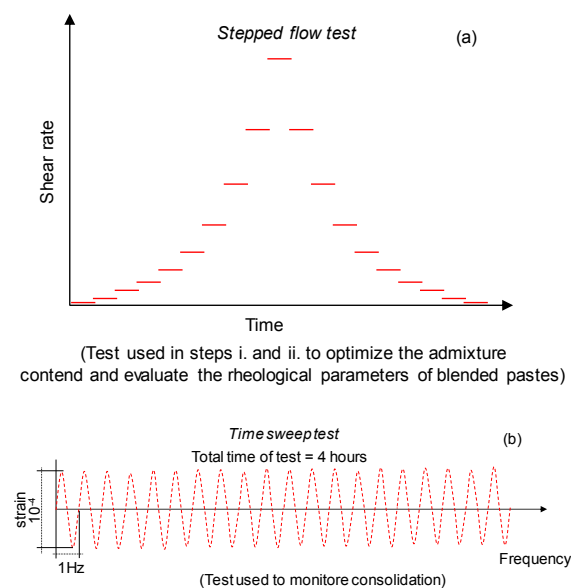

Figure 2. Procedures used during the rotational (a) and oscillatory (b) rheometry

The tests were performed in an AR550 rheometer (TA Instruments), with parallel plate geometry of 40 mm of diameter and distance between the plates of 1000 μm. All rheological tests started 4 minutes after the start of mixture.

Isothermal calorimetry

The heat release during the chemical reaction was monitored in an TAM Air isothermal calorimeter (TA Instruments), with sensibility of ± 20 μW. Tests were carried out at 23°C for 48 hours. Around 20mL of suspension was added into an ampoule which was sealed and inserted into the equipment. As in the rheology tests, calorimetry also started 4 minutes after the start of mixture.

Mix conditions

All pastes were mixed in a high shear energy mixer (adapted from a Tupia *'wood shaper'*, Makita), using a cowles propeller. All dry material was added into a container and then the water was added, waiting 30 seconds for wetting. The mixing was carried

out at 10000 rpm for 1.5 minutes to homogenize and disperse the suspension.

RESULTS AND DISCUSSION
Admixture optimization (pure raw material)

Rotational rheometry results ordinarily correlate shear stress (or viscosity) with shear rate, but, to find the optimum admixture contend in this work, the apparent viscosity, yield stress and thixotropy were evaluated as a function of admixture addition.

These parameters can be estimated applying rheological models to the data. This needs to be done very carefully, because in many cases they do not fit correctly the experimental data, presenting a high modelling error, mainly in the extreme shear conditions (very low or very high shear rates).

Instead of model parameters, in this work data obtained directly from the experiments were used (Figure 3): apparent viscosity (η_{ap}) at the highest shear rate (400 s^{-1}); yield stress (σ_0), considered to be the shear stress at the lowest shear rate in the deceleration period; and thixotropy (calculated area between the curves of increase and decrease of shear rate).
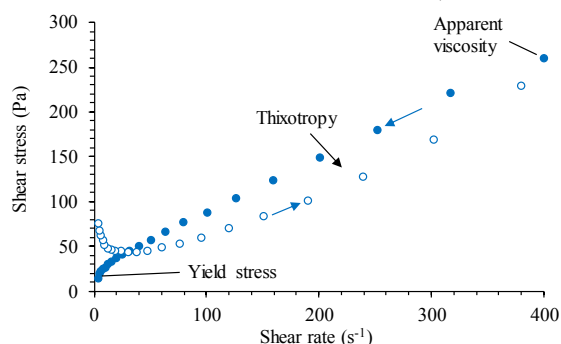

Figure 3. Illustration of graphical method used to estimate yield stress, apparent viscosity and thixotropy.

Changes on the rheological behaviour observed during the acceleration period may occur when particle agglomerates are broken, releasing the water trapped inside the agglomerates, which increases the

separation distance of the particles. So, this results are not stables, obtained in a non-dispersed system.

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

The thixotropy needs to me calculated carefully: when the tests are performed using logarithmic control, there is a clear reversal of curves when the solicitation is at low shear; so, two hysteresis areas can be calculated and used for comparison of admixture content. However, in this work it was used just the area calculated from 25s^{-1} to 400s^{-1}.

A good dispersion results in low values of yield stress and apparent viscosity, and thixotropy around 0 (zero). Positive thixotropy indicates that the agglomerates, broken during the acceleration period, are re-agglomerating slower during the deceleration. In the contrary, rheopexy is observed (negative thixotropy).

Figure 4 shows how the parameters yield stress (a), apparent viscosity (b) or thixotropy (c) evolve with the increase of the admixture content.

With Increasing superplasticizer content a reduction in the values of all rheological parameters was observed

Usually, the optimized superplasticiser content is adopted as the content above which yield stress or apparent viscosity are no longer affected. In this work, thixotropy was also considered , because it indicates the power of agglomerates. It is common to observe low σ_0 and η_{app}, but high thixotropy, indicating that even with good flow capacity the material is yet agglomerated.

Thus, to continue the work and evaluate the blended pastes, the values of 1.0%, 0.5% and 0.3% were adopted as optimized for cement, LF1 and LF5, according to Figure 4.
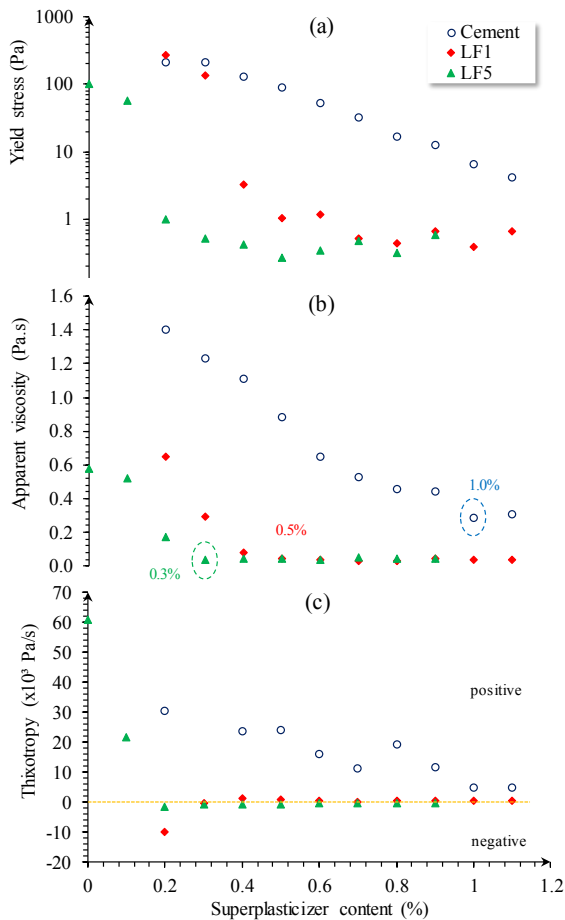
Figure 4. Yield stress (a), apparent viscosity (b) and thixotropy (c) as function of admixture content.

Rheological properties of blended pastes

Table 3 presents the compositions of the tested blended pastes. The values of SP (superplasticizer) presented are a weighted average of optimized values for each material. Weighted water-to-solid ratio was kept constant at 0.3. As the SP has 50% of solid content, the extra water added with the admixture was discounted from the water added during the mixture.

Particle size distribution of each paste are presented in Figure 5 and packing porosity and mobility parameters are presented in Table 4. The packing porosity was calculated using the *Westman* and *Hugill* model, according reported by *Funk and Dinger*[12] and IPS – interparticle size separation according defined by *Oliveira et al.*[13].

Increasing the amount of LF1 there is reduction of packing porosity, even maintaining the particle size extension.

However, these changes were observed significantly just up to 30% of performance filler LF1. This means that further increments of performance filler do not impact considerably in the packing.

Table 3. Amount (% weight) of each raw material used in the compositions. The numbers indicated in the labels refer to volumetric proportions.

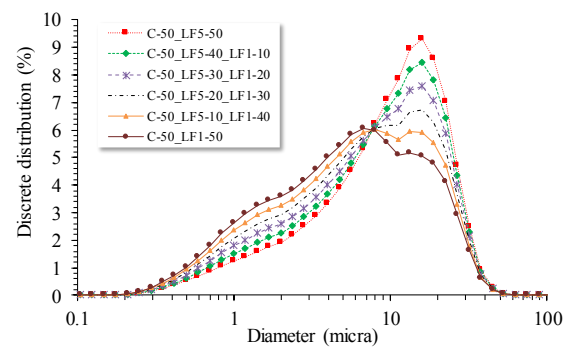| Reference	Cement	LF5	LF1	SP
C-50_LF5-50	52.6	47.4	-	1.02
C-50_LF5-40_LF1-10	52.6	37.9	9.5	1.04
C-50_LF5-30_LF1-20	52.6	28.4	19.0	1.06
C-50_LF5-20_LF1-30	52.6	19.0	28.4	1.08
C-50_LF5-10_LF1-40	52.6	9.5	37.9	1.10
C-50_LF1-50	52.6	-	47.4	1.12

Figure 5. Particle size distribution of blended pastes

Table 4. Packing porosity and mobility parameters of each formulation

Reference	PP (%)	VSA (m²/cm³)	SSA (m²/g)	IPS (micra)
C-50_LF5-50	17.4	4.49	1.53	0.29
C-50_LF5-40_LF1-10	15.4	5.20	1.78	0.26
C-50_LF5-30_LF1-20	12.9	5.92	2.02	0.24
C-50_LF5-20_LF1-30	12.0	6.63	2.25	0.22
C-50_LF5-10_LF1-40	11.7	7.34	2.51	0.20
C-50_LF1-50	11.6	8.06	2.75	0.18

PP: packing porosity, VSA: volumetric surface area, SSA: Specific surface area, IPS: interparticle size separation

On the other hand, the mean interparticle size separation distance (IPS), reduced in function of the changes in filler proportion. In theory, the higher the packing porosity, the lower is the water demand to recover and separate the particles, but this can lead to difficulties in the mobility due to the

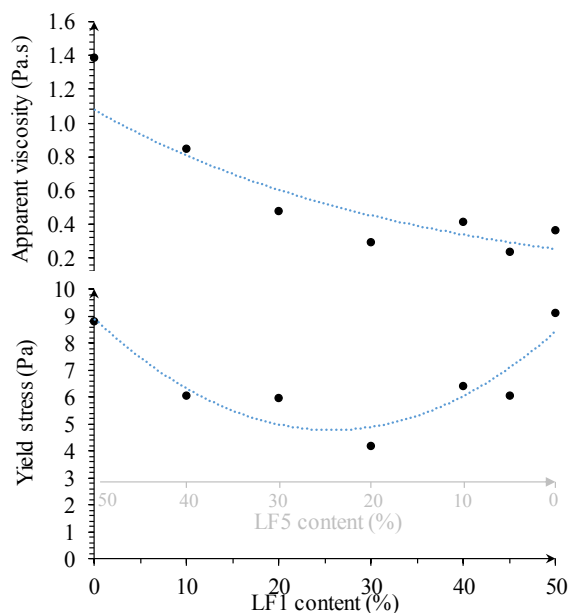higher probability of contact between them[13].

Figure 6. Yield stress (above) and apparent viscosity (below) versus LF1 content (performance filler).
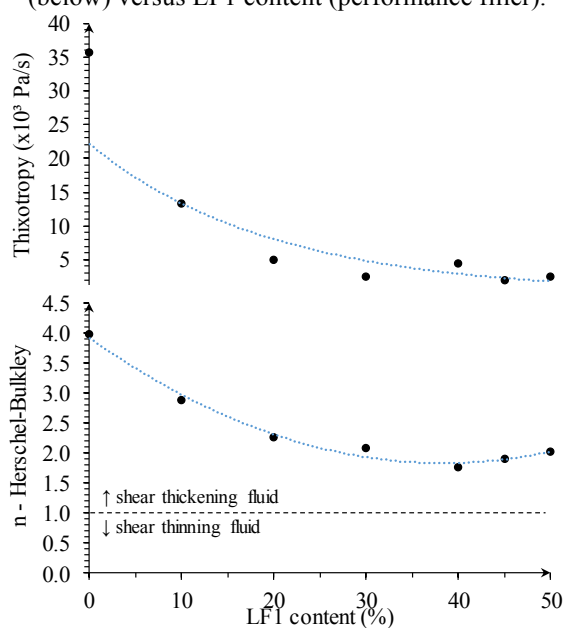

Figure 7. Thixotropy level (above) and n-Herschel-Bulkley (below), indicating the rheological behaviour, as function of LF1 content (performance filler).

As the SSA of LF1 is higher than the other materials, the higher the amount of this product the higher the impact in the surface area. This is an important information because it represents a higher demand of water to maintain the consistency.

As higher the amount of performance limestone filler (LF1), reducing the packing particle and IPS, lower the viscosity of suspension is. However, there is an optimized proportion of limestone filler that results in a minimum value of yield stress.

It was observed a thixotropic and shear thickening behaviour (n>1) for all evaluated suspension, independently of LF1 content.

Consolidation

Figure 8 presents the monitoring of consistency gain up to 300 minutes (5 hours), represented by the storage modulus – G'.
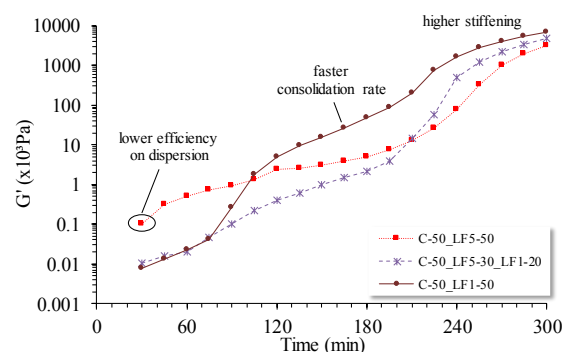

Figure 8. Impact of packing in the changes of storage modulus over time.

At the beginning of test, the G' value of the suspension without performance filler (C-50_LF5-50) was higher than the other suspensions. This indicates that the initial stage is influenced by the dispersion efficiency shown previously.

On the other hand, in the composition only with performance filler (C-50_LF1-50) there is a clear intensification of consistency gain from 70 to 100 minutes, indicated by the faster consolidation rate. This indicates that the use of this finer particles results in better dispersed suspensions (which allows lower water-to-solid content and improvement of some hardened properties) and faster stiffening (which is recommended to speed up the building process).

An intermediate behaviour was observed for the composition C-50_LF5-30_LF1-20,

showing the possibility of proportion optimization using substitution and performance limestone filler, to adequate the rheological behaviour to the application settings.

Chemical reaction

Figure 9 presents the heat release due to the chemical reaction, over time, as a function of packing porosity. The cumulative heat in the first 5 hours of hydration (period of rheological evaluations) is shown in the detail of Figure 9,. The cumulative heat presented was calculated eliminating the pre-induction period because the used procedure results in imprecision in this stage of hydration.
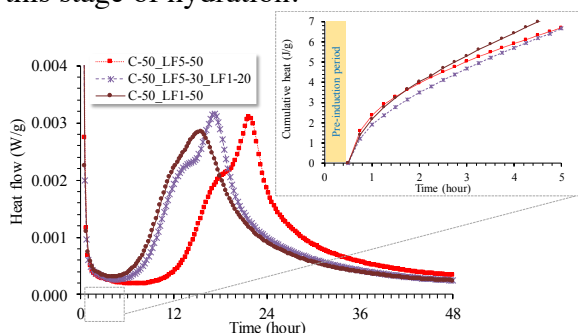

Figure 9. Impact of packing in the chemical reaction. The cumulative heat in the first 5 hours of hydration (period of rheological evaluations) is shown in the detail The pre-induction period was eliminated from the calculation.

The cement reaction is frequently described in stages of heat release. Table 5 presents the results of the main stages.

Table 5. Detail of main stages during the hydration reaction

	C-50_LF5-50	C-50_LF5-30_LF1-20	C-50_LF1-10
Beginning of induction period (h:min)	00:30	00:30	00:30
Cumulative heat up to 5 hours (J/g)	6.69	6.67	7.55
Time of induction period (h:min)	12:30	07:50	07:10
Reaction rate (mW.g/h)	0.36	0.42	0.42
End of acceleration period (h:min)	21:30	17:10	15:20
Cumulative heat up to 48 hours (J/g)	151.25	157.84	155.81

The induction period starts 30 minutes after mixing and after 5 hours the total heat released depends on the fineness of the limestone filler. For the performance filler (LF1) 13% more heat was released in this period, possibly due to the nucleation promoted by the smaller particles. Also the duration of the induction period was affected and was very lower for this composition (7:10 hours) than for the composition with LF5 (12:30 hours). At the same time, the intensification on the pits of nucleation improve the reaction rate of the compositions with performance filler, reducing the time to finish the acceleration period.

Combined evaluation

The hardening of reactive suspensions depends on the chemical and physical changes of the particles. While the first phenomenon is governed by the cement hydration reaction, the physical contribution accentuates the power of particle agglomeration.

Thus, it is important to evaluate the transition from fluid to solid behaviour combining both kind of contribution, as presented in Figure 10.
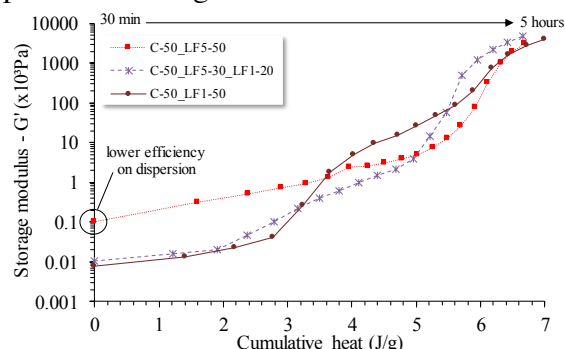

Figure 10. Combined evaluation of hardening.

For the suspensions evaluated in this work, the physical contribution was more intense than the chemical changes to the hardening process, mainly due to the changes in the beginning of consolidation.

In the beginning of hardening the dispersion governs the stiffening of the microstructure, but changes were observed over time due to formulation parameters: the higher the amount of fine particles, the more intense are the physicochemical changes.

So, the use of LF1 speeds up the cement chemical reaction, intensifies the particle

agglomeration forces and accentuates the hardening.

CONCLUSIONS

The optimized superplasticizer content was not governed by the specific surface area of raw materials, because cement and limestone filler has different specific particle charge, which affect the adsorption of admixture.

Each composition was mixed using the weighted average of optimized superplasticizer content for each material and the results observed during the flow, consolidation or chemical reaction occurred due to changes in the formulation parameters.

The higher the amount of performance limestone filler (filler finer than cement), improving the particle packing, the lower is the viscosity of the suspensions. However, there is an optimized proportion of limestone filler that results in a minimum value of yield stress. Independently of that, it was observed an expressive delay in the chemical reaction using the substitution filler (filler with granulometry close to cement).

In summary, the use of performance limestone filler speeds up the cement chemical reaction, intensifies the power of particle agglomeration and accentuates the hardening.

ACKNOWLEDGMENTS

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